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J. Org. Chem., **Just Accepted Manuscript** • Publication Date (Web): 03 Oct 2012

Palladium-Catalyzed Synthesis of Benzimidazoles and Quinazolinones from Common Precursors

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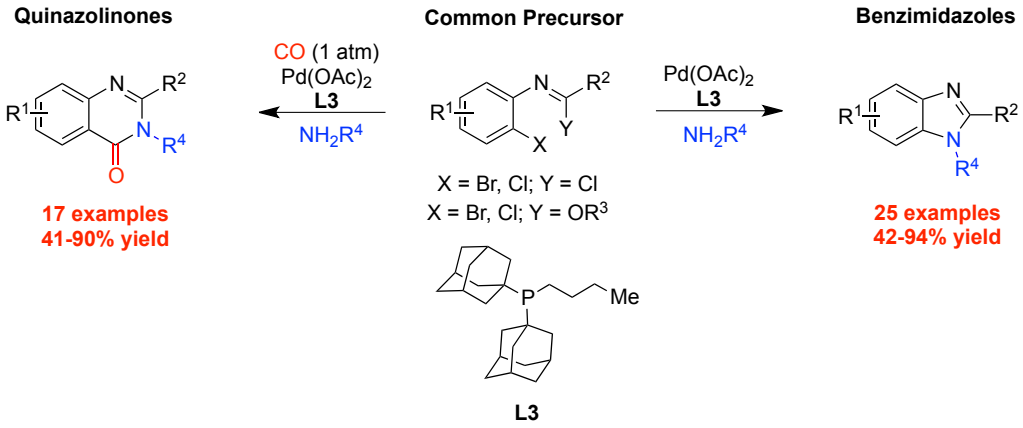
Graphical Abstract



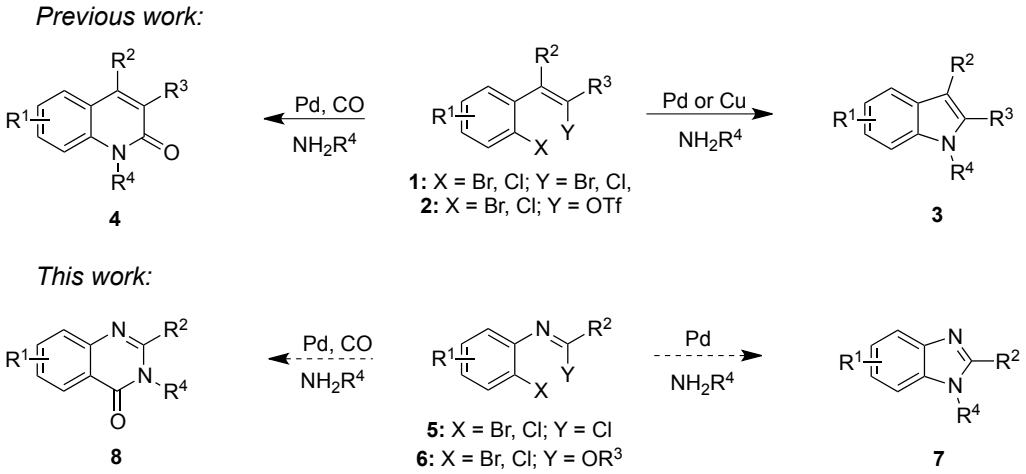
Abstract

N-(*o*-halophenyl)imidoyl chlorides and the corresponding imidates are easily prepared and can be utilised as complementary substrates for the synthesis of important heterocycles. The synthesis of *N*-substituted benzimidazoles was possible from the palladium-catalyzed reaction of both class of substrate with a variety of *N*-nucleophiles. The use of the imidate precursor for the synthesis of *N*-substituted quinazolinones by incorporation of a palladium-catalyzed aminocarbonylation reaction has also been demonstrated. Both processes tolerate a wide range of functional groups.

Introduction

Nitrogen-containing heterocycles such as benzimidazoles[1] and quinazolinones[2] display a wide range of pharmacological activities. Palladium catalysis has had a significant impact on the synthesis of these important molecules as it provides notable advantages over classical syntheses.[3,4,5] For example, readily available starting materials can be utilised under mild reaction conditions to afford complex scaffolds. However, there is a continuing need to develop ever more efficient ways of preparing these molecules. One attractive strategy is the use of a single class of precursor to synthesise a variety of heterocyclic motifs.[6] Towards this end, we have developed substrates which when subjected to palladium or copper-catalyzed reactions with appropriate nucleophiles undergo tandem processes to form a number of different heterocycles. For example, 2-(2-haloalkenyl)-aryl halides **1** (Scheme 1) or the corresponding alkenyl triflates **2** have been efficiently used to construct indoles **3** as a result of tandem C-N bond forming reactions[7] with *N*-nucleophiles.[8,9] The use of these substrates for the construction of 2-quinolones **4** was also possible by inclusion of a palladium-catalyzed alkenyl aminocarbonylation[10] to the reaction sequence.[11] We envisaged that the use of structurally similar *N-(o*-halophenyl)imidoyl chlorides **5** or imidates **6** could be used to synthesise benzimidazoles **7** and quinazolinones **8**. This could occur *via* a palladium-catalyzed coupling at the aryl halide, followed by a condensation/cyclisation or by nucleophilic substitution at the imidoyl moiety then an intramolecular palladium-catalyzed ring closing reaction. This reactivity difference would be determined by the susceptibility of the imidoyl unit to undergo nucleophilic attack.

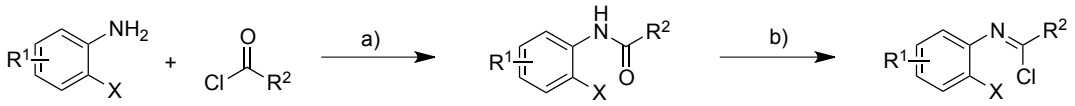
Scheme 1. Synthesis of heterocycles from Common Precursors



Results and Discussion

Initial investigations focused on the viability of *N*-(*o*-halophenyl)imidoyl chlorides **5** as substrates for benzimidazoles.[12] These substrates were prepared in a two-step process, namely by synthesis of amides **9** and then conversion of these to imidoyl chlorides **5** using phosphorous pentachloride (Scheme 2).[13] Although not stable towards purification by column chromatography, these substrates were obtained in excellent conversions and were employed directly in the heterocycle forming transformation (see experimental section and supporting information for ^{1}H and ^{13}C NMR spectra). It was found that use of $SOCl_2$[14] or oxalyl chloride and 2,6-lutidine,[15] were both less efficient methods.

Scheme 2. Synthesis of imidoyl chlorides 5 from amides 9[a]



9a: R^1 = H; R^2 = Ph; X = Cl
9b: R^1 = 5-OMe; R^2 = Ph; X = Cl
9c: R^1 = 4-Me; R^2 = Ph; X = Cl
9d: R^1 = 6-Me; R^2 = Ph; X = Cl
9e: R^1 = 4-CN; R^2 = Ph; X = Cl
9f: R^1 = 5-COMe; R^2 = Ph; X = Cl
9g: R^1 = Py; R^2 = Ph; X = Cl
9h: R^1 = 4-F; R^2 = Ph; X = Cl
9i: R^1 = 4-Cl; R^2 = Ph; X = Br
9j: R^1 = H; R^2 = 2-Fu; X = Cl
9k: R^1 = H; R^2 = 4-Py; X = Cl
9l: R^1 = H; R^2 = ^{t}Bu; X = Cl

5a: R^1 = H; R^2 = Ph; X = Cl
5b: R^1 = 5-OMe; R^2 = Ph; X = Cl
5c: R^1 = 4-Me; R^2 = Ph; X = Cl
5d: R^1 = 6-Me; R^2 = Ph; X = Cl
5e: R^1 = 4-CN; R^2 = Ph; X = Cl
5f: R^1 = 5-COMe; R^2 = Ph; X = Cl
5g: R^1 = Py; R^2 = Ph; X = Cl
5h: R^1 = 4-F; R^2 = Ph; X = Cl
5i: R^1 = 4-Cl; R^2 = Ph; X = Br
5j: R^1 = H; R^2 = 2-Fu; X = Cl
5k: R^1 = H; R^2 = 4-Py; X = Cl
5l: R^1 = H; R^2 = ^{t}Bu; X = Cl

[a]Reaction Conditions: a) 2-haloaniline (1.0 equiv), acid chloride (1.2 equiv), triethylamine (1.1 equiv), THF, 0 °C, 3 h; b) PCl_5 (1.1 equiv), DCM, reflux, 24 h.

Reaction of imidoyl chloride **5a** with benzylamine (**10a**) in the presence of a catalyst derived from $Pd_2(dba)_3$ and SPhos (**L1**)[16] (see Figure 1) along with sodium *tert*-butoxide and toluene at 100 °C afforded a low yield of benzimidazole **7a** (entry 1). Changing the ligand to DavePhos (**L2**)[17] increased the yield (entry 2), however, use of cesium carbonate as the base gave only a trace amount of product (entry 3). The use of an alternative palladium source, namely $Pd(OAc)_2$ gave an excellent yield (entry 4). Unfortunately, when this system was applied to the more challenging electron-rich imidoyl chloride **5b**, a poor yield of benzimidazole **7b** was obtained, even at an elevated reaction temperature (entry 5). When an alternative ligand was utilised, cata*C*Xium® A (**L3**),[18] an increase in yield was observed (entry 6). This reaction was then subjected to microwave irradiation[19] with benzotrifluoride as the solvent, which has previously been used as a toluene substitute in similar microwave reactions.[20] This gave only a small increase in yield (entry 7). However, increasing the temperature to 135 °C afforded a high yield (entry 8).

Figure 1. Structures of Ligands L1-L6.

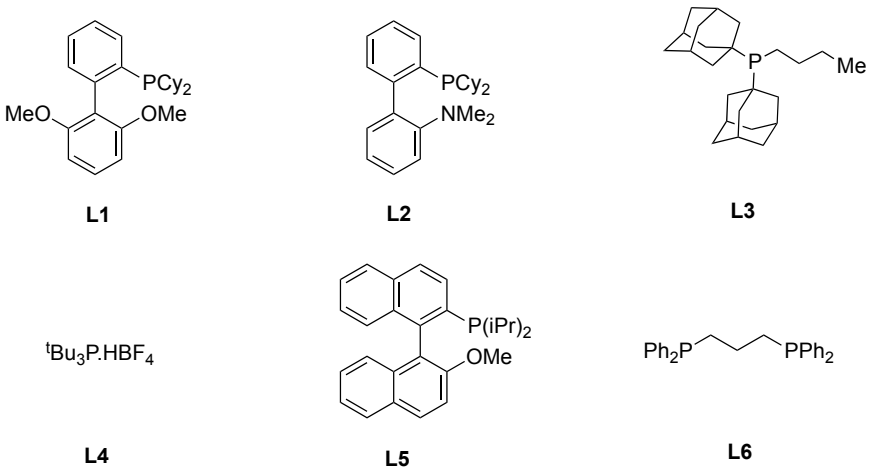
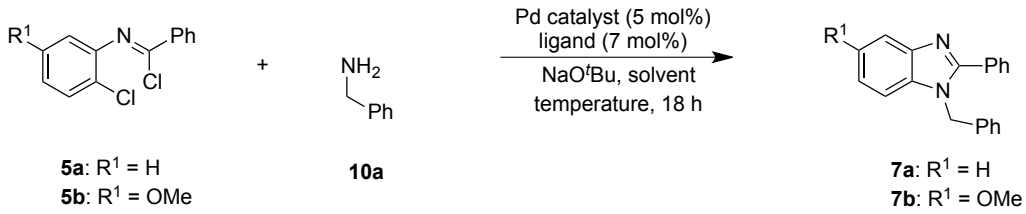


Table 1. Optimisation of Reaction Conditions using imidoyl chlorides 5a and 5b[a]



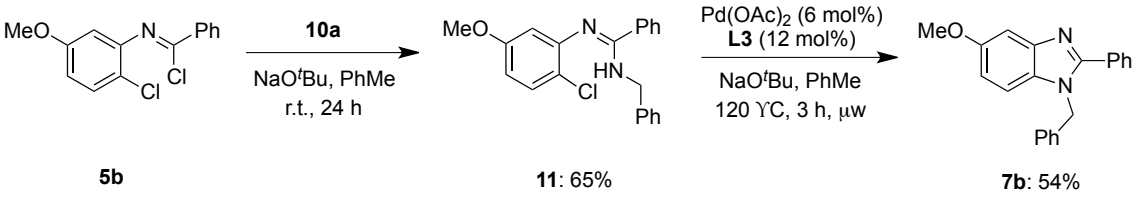
Entry	Imidoyl chloride	Catalyst	Ligand	Temperature (°C)	Solvent	Product	Yield (%)
1	**5a**	$Pd_2(dba)_3$	**L1**	100	PhMe	**7a**	23
2	**5a**	$Pd_2(dba)_3$	**L2**	100	PhMe	**7a**	63
3[b]	**5a**	$Pd_2(dba)_3$	**L2**	100	PhMe	**7a**	trace
4	**5a**	$Pd(OAc)_2$	**L2**	100	PhMe	**7a**	98
5	**5b**	$Pd(OAc)_2$	**L2**	120	PhMe	**7b**	18
6	**5b**	$Pd(OAc)_2$	**L3**	120	PhMe	**7b**	30
7[c]	**5b**	$Pd(OAc)_2$	**L3**	120	BTF[d]	**7b**	38
8[c,e]	**5b**	$Pd(OAc)_2$	**L3**	135	BTF[d]	**7b**	80

[a]Reaction Conditions: *N*-(*o*-chlorophenyl)imidoyl chloride **5** (1.0 equiv), **10a** (1.5 equiv), Pd catalyst (5.0 mol%), Ligand (7.0 mol%), base (3.0 eq), solvent, 18 h. [b]Cs_2CO_3 used as base.

[c]Reaction conducted with microwave irradiation for 2 h. [d]BTF = Benzotrifluoride. [e]2.2 equiv of base used.

Small amounts of amidine **11** had been isolated during the reaction optimisation, and so in order to probe the reaction mechanism, and establish if amidine **11** was an intermediate, imidoyl chloride **5b** was reacted with amine **10a** in the absence of a palladium catalyst (Scheme 3). This afforded amidine **11** in a 65% yield. Exposure of amidine **11** to the optimised reaction conditions led to the formation of benzimidazole **7b** (together with 41% of recovered amidine **11**). Therefore, we postulate that the reaction mechanism involves initial nucleophilic substitution by the amine at the imidoyl chloride to afford an amidine intermediate, followed by intramolecular palladium-catalyzed amination.

Scheme 3. Synthesis of benzimidazole 7b from imidoyl chloride 5b via amidine 11

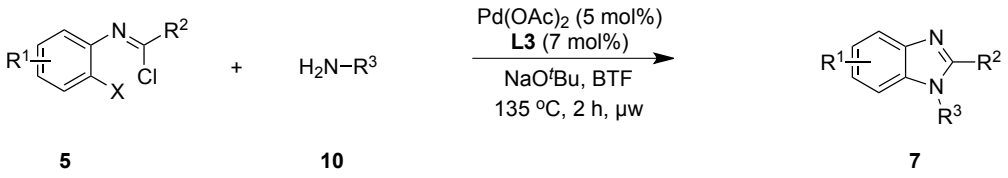


5b **11**: 65% **7b**: 54%

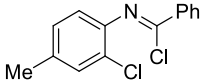
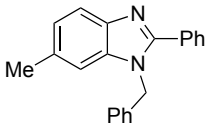
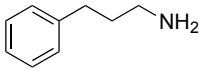
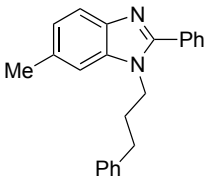
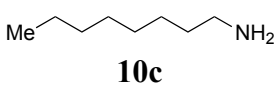
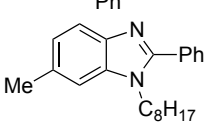
With these optimised conditions in hand, we then explored the variety of *N*-nucleophiles (**10**) and imidoyl chloride substrates (**5**) which could be utilised in this reaction (Table 2). Entries 1-5 illustrate the effectiveness of primary amines as coupling partners in this reaction, as generally high yields of *N*-alkyl benzimidazoles **7c**-**7g** were obtained. Unfortunately, the reactivity of anilines proved to be less successful with only moderate yields of *N*-aryl benzimidazoles **7i**-**7j** obtained (entries 6-8). Similarly, hydrazine **10i** gave poor yield (entry 9). Entries 10 and 11 demonstrate the successful incorporation of electron-donating substituents on the imidoyl chloride substrate. Electron-withdrawing moieties were also

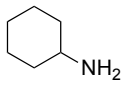
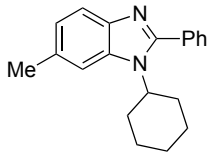
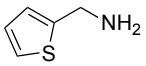
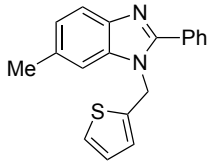
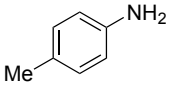
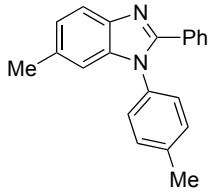
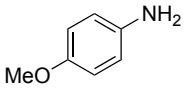
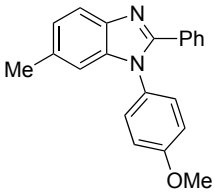
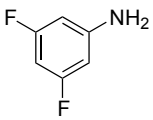
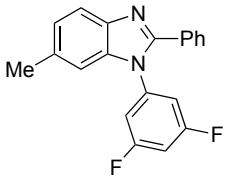
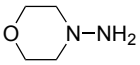
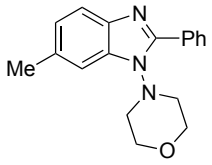
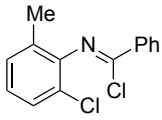
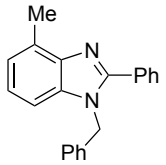
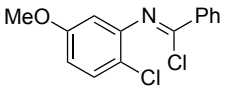
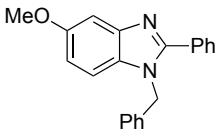
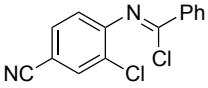
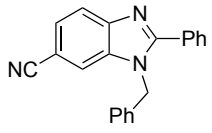
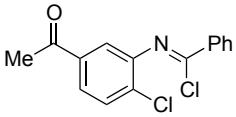
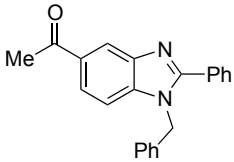
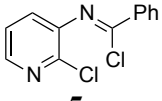
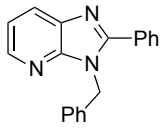
tolerated as shown in entries 12 and 13. Entry 14 demonstrates the application of these reactions conditions for the successful synthesis of aza-benzimidazole **7o**. A fluorine atom was tolerated affording halogenated heterocycle **7p** in a high 75% yield (entry 15). Use of *N*-(2-bromo-4-chlorophenyl)imidoyl chloride **5i** successfully afforded chloro-substituted benzimidazole **7q** in a good 67% yield (entry 16). This is a useful substituent as it allows a handle for further functionalization.[8e] Both furan and pyridine substituents could be incorporated successfully at the 2-position of the benzimidazole product (entries 17 and 18). The latter, however, required a higher catalyst loading and a prolonged reaction time in order to obtain a good conversion of the intermediate imidamide to the heterocycle. A sterically demanding *tert*-butyl group afforded the corresponding 2-alkyl benzimidazole **7t** in an excellent yield (entry 19).

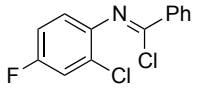
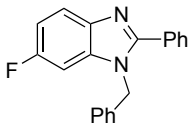
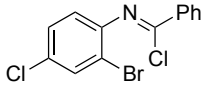
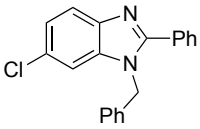
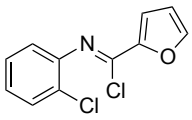
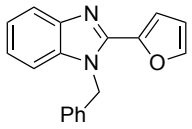
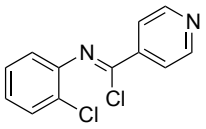
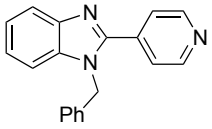
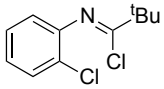
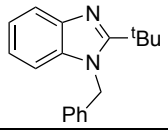
Table 2. Palladium-catalyzed preparation of benzimidazoles from *N*-(*o*-halophenyl)imidoyl chlorides 5[a]



5 **10** **7**

Entry	Imidoyl chloride	*N*-nucleophile	Product		Yield (%)
1	 **5c**	**10a**		**7c**	69
2	**5c**	 **10b**		**7d**	75
3	**5c**	 **10c**		**7e**	73

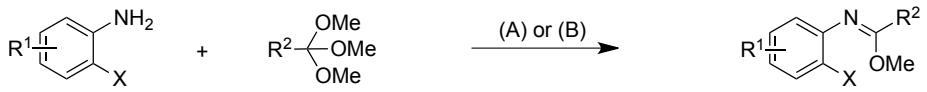
4[b]	**5c**	 **10d**		**7f**	94
5[b]	**5c**	 **10e**		**7g**	48
6[b]	**5c**	 **10f**		**7h**	53
7[b]	**5c**	 **10g**		**7i**	46
8[b]	**5c**	 **10h**		**7j**	45
9[b]	**5c**	 **10i**		**7k**	47
10[b]	 **5d**	**10a**		**7l**	91
11	 **5b**	**10a**		**7b**	80
12[b]	 **5e**	**10a**		**7m**	46
13[b]	 **5f**	**10a**		**7n**	71
14[b]	 **5g**	**10a**		**7o**	50

15[b]	 **5h**	**10a**		**7p**	75
16[c]	 **5i**	**10a**		**7q**	67
17	 **5j**	**10a**		**7r**	80
18[d]	 **5k**	**10a**		**7s**	72
19[b]	 **5l**	**10a**		**7t**	84

[a]Conditions: *N*-(*o*-halophenyl)imidoyl chloride 5 (1.0 equiv), *N*-nucleophile 10 (1.5 equiv), $Pd(OAc)_2$ (5.0 mol%), L3 (7.0 mol%), NaO^{t}Bu (2.2 equiv), BTF, 135 °C, 2 h, μw. [b]Reaction carried out at 50 °C, 0.5 h, μw then 135 °C, 2 h, μw. [c]Reaction carried out at 50 °C, 0.5 h, μw then 120 °C, 2 h, μw. [d]Reaction carried out with $Pd(OAc)_2$ (10 mol%), L3 (14 mol%) at 50 °C, 0.5 h, μw then 135 °C, 4 h, μw.

We next turned our attention to the use of *N*-(*o*-halophenyl)imidates **6** in this process. These substrates were readily synthesised either by the acid-catalyzed reaction of 2-haloanilines with *ortho*-esters following literature precedent (*p*-TSA, PhMe, reflux,Condition A),[21] or by heating 2-haloanilines with an excess of *ortho*-esters to 90-110 °C (Condition B) (Scheme 4).[22]

Scheme 4. Synthesis of imidates 6[a]

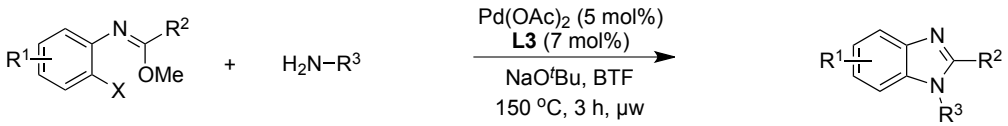


6a: R^1 = 4-Me; R^2 = Ph; X = Cl
6b: R^1 = 5-OMe; R^2 = Ph; X = Cl
6c: R^1 = Py; R^2 = Ph; X = Cl
6d: R^1 = 4-F; R^2 = Ph; X = Cl
6e: R^1 = H; R^2 = ^{n}Bu; X = Cl
6f: R^1 = H; R^2 = Bn; X = Cl
6g: R^1 = H; R^2 = Ph; X = Br
6h: R^1 = 4,6-di-Me; R^2 = Ph; X = Br
6i: R^1 = 5-OMe; R^2 = Ph; X = Br
6j: R^1 = 4-CO_2Me; R^2 = Ph; X = Br
6k: R^1 = Py; R^2 = Ph; X = Br
6l: R^1 = 4-F; R^2 = Ph; X = Br
6m: R^1 = 4-Cl; R^2 = Ph; X = Br
6n: R^1 = H; R^2 = ^{n}Bu; X = Br
6o: R^1 = H; R^2 = Bn; X = Br

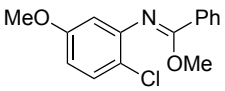
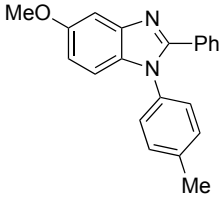
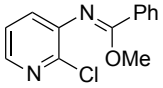
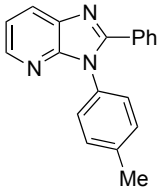
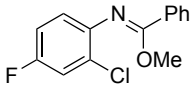
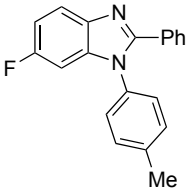
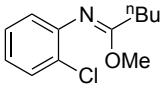
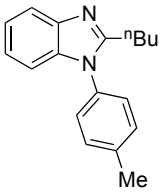
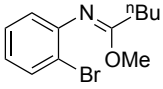
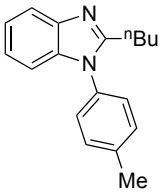
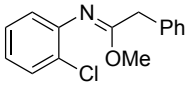
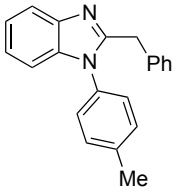
[a]Reaction Conditions: (A) 2-haloaniline (1.0 equiv), *ortho*-ester (1.1-2.0 equiv), *p*-TSA (cat.), PhMe, reflux, 3 h. or (B) 2-haloaniline (1.0 equiv), *ortho*-ester (1.1-2.0 equiv), 90-110 °C, 19-53 h.

Exploratory palladium-catalyzed reactions revealed that under similar reaction conditions to those used for the imidoyl chloride substrates, these precursors gave high yields of the desired heterocycle only when an aniline nucleophile was employed, demonstrating complementary reactivity to the corresponding imidoyl chloride substrates. The scope of both the *N*-nucleophile (**10**) and imidate substrate (**6**) were explored (Table 3). The use of electron-rich anilines gave excellent yields of *N*-aryl benzimidazoles **7h** and **7i** (entries 1 and 2). However, moderate yields were obtained for electron-poor aniline **10h** (entry 3) and hydrazine **10i** (entry 4). Entries 5-10 show that a variety of functional groups (methoxy, pyridyl, fluoro, alkyl and benzyl) can be tolerated on the substrate back-bone. In addition, comparison of entries 8 and 9 demonstrates the increased reactivity of aryl bromide substrates relative to aryl chlorides, as an excellent yield of benzimidazole **7x** was obtained in a shorter reaction time and at a lower reaction temperature when the bromide substrate was employed.

Table 3. Palladium-catalyzed preparation of benzimidazoles from *N*-(*o*-halophenyl) imidates 6[a]



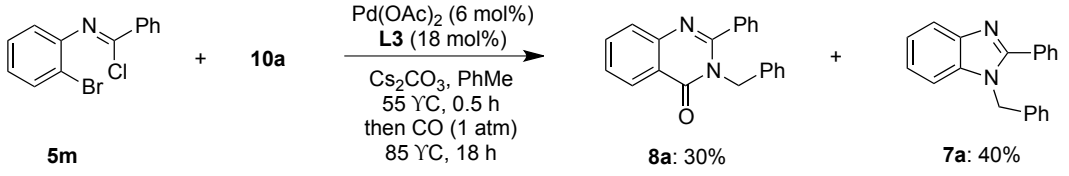
6 **10** **7**

Entry	Imidate	*N*-nucleophile	Product		Yield (%)
1	**6a**	**10f**	**7h**		87
2	**6a**	**10g**	**7i**		86
3	**6a**	**10h**	**7j**		42
4	**6a**	**10i**	**7k**		43
5	 **6b**	**10f**		**7u**	42
6	 **6c**	**10f**		**7v**	80
7	 **6d**	**10f**		**7w**	80
8	 **6e**	**10f**		**7x**	64
9[b]	 **6n**	**10f**		**7x**	94
10	 **6f**	**10f**		**7y**	76

[a]Conditions: *N*-(*o*-halophenyl)imidate **6** (1.0 equiv), *N*-nucleophile **10** (1.5 equiv), $Pd(OAc)_2$ (5.0 mol%), **L3** (7.0 mol%), NaO^tBu (2.2 equiv), BTF, 150 °C, 3 h, μw. [b]Reaction carried out at 135 °C, 2 h, μw.

Having demonstrated the use of both substrate classes in the palladium-catalyzed synthesis of benzimidazoles, we then focused on their use in quinazolinone synthesis. Investigations began with the reaction of *N*-(*o*-bromophenyl)imidoyl chloride **5m** with benzylamine (**10a**) utilising the catalyst system developed for benzimidazole synthesis in a two-step process (Scheme 5). The reaction was initially carried out at 55 °C for 0.5 h to allow formation of an amidine intermediate, which was then subjected to a balloon atmosphere of carbon monoxide. The desired quinazolinone heterocycle **8a** was obtained in a 30% yield as a result of a palladium-catalyzed aminocarbonylation reaction; however, benzimidazole **7a** was also isolated. Evaluation of a variety of reaction parameters did not result the identification of a selective set of conditions for the preparation of quinazolinones from the imidoyl chloride precursors.

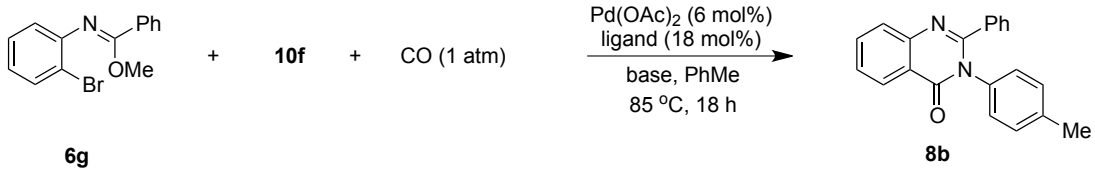
Scheme 5. Palladium-catalyzed synthesis of quinazolinone 8a from imidoyl chloride 5m



We postulated that the use of the imidate precursor should provide a more effective route to quinazolinones. An initial palladium-catalyzed aminocarbonylation reaction should occur at the aryl halide, forming an amide intermediate,[23] which could then undergo base induced cyclisation. Additionally, a two-step one-pot process should no longer be required. In order to

test this we investigated the coupling of imidate **6g** with aniline **10f** under a balloon atmosphere of carbon monoxide (Table 4). The use of NaO^{t}Bu, K_2CO_3 or Cs_2CO_3 (entries 1-3) as the base revealed Cs_2CO_3 to be the most successful, as quinazolinone **8b** was obtained in 75% yield. Reduction of the catalysts and ligand loadings gave a lower conversion (entry 4), as did the use of ligands which have been successfully used in our earlier quinolone synthesis (entries 5-7).[11]

Table 4. Optimisation of reaction conditions using imidate 6g[a]



6g **8b**

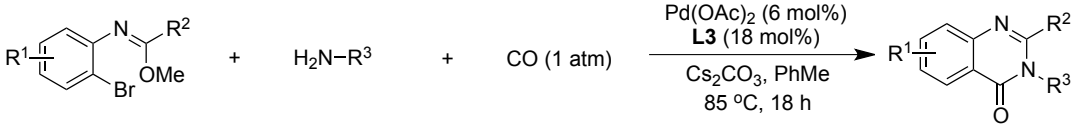
Entry	Ligand	Base	Yield (%)
1	**L3**	NaO^{t}Bu	65
2	**L3**	K_2CO_3	62
3	**L3**	Cs_2CO_3	75
4[b]	**L3**	Cs_2CO_3	37[c]
5	**L4**	Cs_2CO_3	33[c]
6	**L5**	Cs_2CO_3	46
7	**L6**	Cs_2CO_3	18[c]

[a]Reaction conditions: **6g** (1.0 equiv), **10f** (1.5 equiv), $Pd(OAc)_2$ (6.0 mol%), ligand (18 mol%), CO (1 atm), base (3.0 equiv), PhMe, 85 °C, 18 h. [b]$Pd(OAc)_2$ (4.0 mol%), **L3** (12 mol%) used. [c]Conversion determined from ^{1}H NMR spectrum of crude reaction mixture.

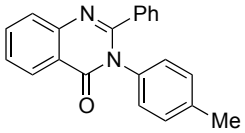
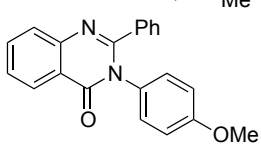
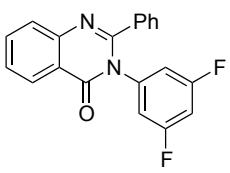
We then explored the variety of *N*-nucleophiles (**10**) and imidates (**6**) that could be incorporated in this process (Table 5). The use of aniline nucleophiles bearing a range of substituents delivered quinazolinones in high yields (entries 1-4). When alkyl amines were

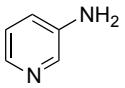
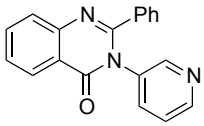
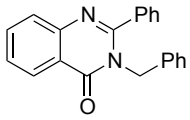
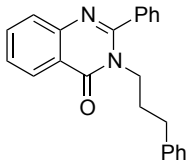
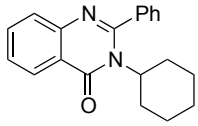
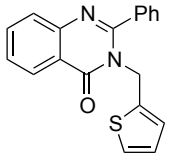
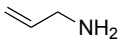
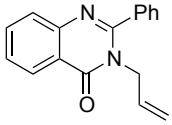
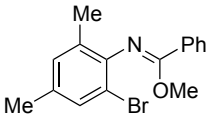
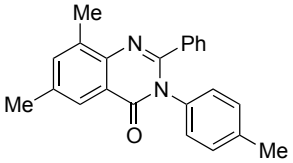
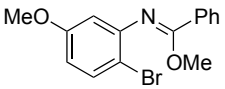
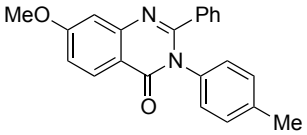
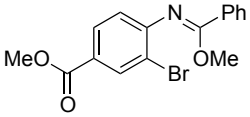
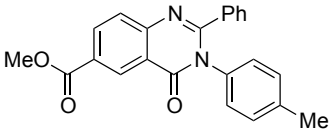
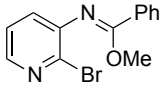
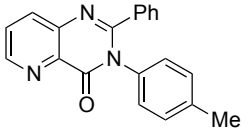
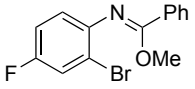
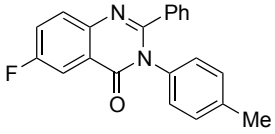
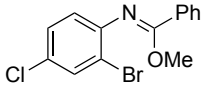
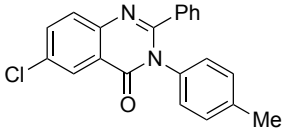
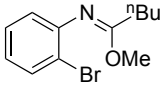
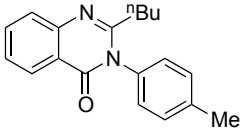
employed, it was found that greater yields of *N*-alkyl quinazolinones **8a** and **8e-h**, were observed when the reaction temperature was raised and more of equivalents of amine (3 equiv) used (entries 5-8). Allyl amine **10k** afforded the expected product in only a moderate yield under the standard reaction conditions (entry 9). Both electron-donating (entries 10 and 11) and electron-withdrawing substituents (entry 12) on the aryl ring of the substrate were successfully incorporated. Entry 13 demonstrates the use of a pyridyl substrate to synthesise pyrimidinone **8m** in an excellent yield. Fluoro- and chloro-substituted quinazolinones **8n** and **8o** were also prepared in good yields from corresponding imidates **6l** and **6m**, respectively (entries 14 and 15). 2-Alkyl substituted quinazolinones can also be prepared using this method (entries 16 and 17). Finally, entry 18 highlights the difficulties associated with using unactivated aryl chlorides in aminocarbonylation reactions.

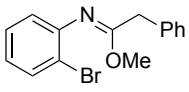
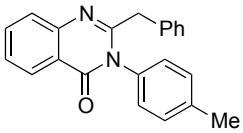
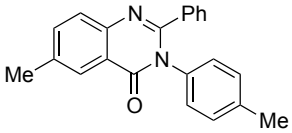
Table 5. Palladium-catalyzed preparation of quinazolinones from *N*-(*o*-halophenyl) imidates 6[a]



6 **10** **8**

Entry	Imidate	*N*-nucleophile	Product		Yield (%)
1	**6g**	**10f**		**8b**	75
2	**6g**	**10g**		**8c**	65
3	**6g**	**10h**		**8d**	89

4[b]	**6g**	 **10j**		**8e**	76
5[c]	**6g**	**10a**		**8a**	59
6[c]	**6g**	**10b**		**8f**	72
7[c]	**6g**	**10d**		**8g**	54
8[c]	**6g**	**10e**		**8h**	67
9	**6g**	 **10k**		**8i**	41
10[d]	 **6h**	**10f**		**8j**	81
11[d]	 **6i**	**10f**		**8k**	71
12	 **6j**	**10f**		**8l**	76
13	 **6k**	**10f**		**8m**	90
14	 **6l**	**10f**		**8n**	58
15	 **6m**	**10f**		**8o**	74
16	 **6n**	**10f**		**8p**	71

17	 **6o**	**10f**		**8q**	67
18[e]	**6a**	**10f**			0

[a]Conditions: *N*-(*o*-halophenyl)imidate **6** (1.0 equiv), *N*-nucleophile **10** (1.5 equiv), $Pd(OAc)_2$ (6.0 mol%), **L3** (18 mol%), Cs_2CO_3 (3.0 equiv), CO (1 atm), PhMe, 85 °C, 18 h. [b]Reaction carried out at 90 °C. [c]Reaction carried out using **10** (3.0 equiv) and at 95 °C. [d]Reaction carried out at 90 °C. [e]Reaction carried out at 120 °C.

Conclusion

In summary, we have demonstrated the use of *N*-*(o*-halophenyl)imidoyl chlorides and the corresponding imidates as useful precursors for the synthesis of *N*-heterocycles by palladium-catalyzed reactions with a variety of *N*-nucleophiles. Significant variation of the substrates allowed for the preparation of structurally diverse benzimidazole and quinazolinone products. Identification of a single catalyst system has proved to be general for the synthesis of both heterocycles from either precursor. Finally, the ease of the synthesis of these precursors from readily available starting materials makes them attractive building blocks for heterocycle preparation.

Experimental Section

General Experimental Methods All reactions were conducted under a positive pressure of dry argon in glassware that had been oven-dried prior to use. Microwave reactions were carried out in a CEM Discover® S microwave using 10 mL CEM microwave tubes. The reaction temperatures were measured by infrared detector during microwave heating. All

reagents and solvents were purchased and used without further purification or drying. Thin layer chromatography (TLC) was performed using pre-coated silica gel plates. Flash column chromatography was performed with silica gel. Infrared spectra were recorded on a Fourier Transform spectrometer. ^{1}H and ^{13}C nuclear magnetic resonance spectra (NMR) were recorded in the order: chemical shift, integration, multiplicity in ppm (δ) downfield of TMS ($\delta = 0$) in $CDCl_3$. Signal splitting patterns were described as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quin), sextet (sex), broad (br), or multiplet (m), with coupling constants (J) in hertz and are rounded to the nearest 0.1 Hz. High resolution mass spectra (HRMS) were performed on an electron spray injection (ESI) TOF mass spectrometer.

General procedure A for the Synthesis of Amides 9 (Scheme 2). To a solution of 2-haloaniline (1.0 equiv) and triethylamine (1.1 equiv) in anhydrous THF (0.3 M) at 0 °C was added drop wise acid chloride (1.2 equiv). The solution was stirred at this temperature for 3 h then quenched with brine and the aqueous phase extracted with diethyl ether. The combined organic phases were dried ($MgSO_4$) and concentrated *in vacuo*. Purification was conducted by column chromatography or recrystallization.

***N*-(2-Chlorophenyl)benzamide 9a.** General procedure A was followed using 2-chloroaniline (10.0 g, 78.0 mmol) and benzoyl chloride (11.0 mL, 94.0 mmol). Recrystallization from dichloromethane afforded **9a** as a white crystalline solid (15.4 g, 85 %). Spectral data are consistent with those in the literature.[24]

***N*-(2-Chloro-5-methoxyphenyl)benzamide 9b.** General procedure A was followed using 2-chloro-5-methoxyaniline (2.0 g, 13.0 mmol) and benzoyl chloride (1.8 mL, 15.0 mmol). Column chromatography (petrol/diethyl ether 4:1) afforded **9b** as a white crystalline solid (2.6 g, 78%); mp: 82-83 °C; IR: (KBr, ν_{max}/cm^{-1}) 3223, 3012, 2956, 2835, 1776, 1636, 1600, 1579, 1519, 1481; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.48 (1H, br. s), 8.32-8.29 (1H, m), 7.95-7.91 (2H, m), 7.63-7.57 (1H, m), 7.56-7.50 (2H, m), 7.32-7.26 (1H, m), 6.69-6.64 (1H, m),

3.88-3.85 (3H, m); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 165.3, 159.1, 135.4, 134.6, 132.3, 129.2, 129.0, 127.0, 114.1, 111.4, 106.2, 55.7; HRMS: (ESI) found *m/z* 284.0447 $[M+Na]^+$, $C_{14}H_{12}{}^{35}ClNNaO_2$ requires 284.0449.

***N*-(2-Chloro-4-methylphenyl)benzamide 9c**. General procedure A was followed using 2-chloro-4-methylaniline (5.0 g, 35.0 mmol) and benzoyl chloride (4.9 mL, 42.0 mmol). Recrystallization from ethanol afforded **9c** as a white crystalline solid (7.5 g, 87%). Spectral data are consistent with those in the literature.[25]

***N*-(2-Chloro-6-methylphenyl)benzamide 9d.** General procedure A was followed using 2-chloro-6-methylaniline (0.5 g, 3.5 mmol) and benzoyl chloride (0.5 mL, 4.2 mmol). Column chromatography (petrol/diethyl ether 3:1) afforded **9d** as a white solid (0.7 g, 86%). Spectral data are consistent with those in the literature.[26]

***N*-(2-Chloro-4-cyanophenyl)benzamide 9e**. General procedure A was followed using methyl 4-amino-3-chlorobenzonitrile (3.0 g, 20.0 mmol) and benzoyl chloride (2.7 mL, 24.0 mmol). Recrystallization from ethanol afforded **9e** as an orange crystalline solid (2.6 g, 51%). mp: 136-137 °C; IR: (neat, ν_{max}/cm^{-1}) 3429, 3412, 3065, 2224, 1686, 1596, 1578, 1508, 1494, 1464; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.81 (1H, d, *J* 8.7 Hz), 8.64 (1H, br. s), 7.95-7.91 (2H, m), 7.74 (1H, d, *J* 1.8 Hz), 7.67-7.61 (2H, m), 7.59-7.53 (2H, m); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 165.3, 138.9, 133.7, 132.9, 132.5, 132.1, 129.2, 127.2, 122.8, 121.0, 117.5, 107.7; HRMS: (ESI) found *m/z* 257.0481 $[M+H]^+$, $C_{14}H_{10}{}^{35}ClN_2O$ requires 257.0476.

***N*-(5-Acetyl-2-chlorophenyl)benzamide 9f.** General procedure A was followed using methyl 1-(3-amino-4-chlorophenyl)ethanone (1.0 g, 6.0 mmol) and benzoyl chloride (0.8 mL, 7.0 mmol). Recrystallization from ethanol afforded **9f** as a light yellow crystalline solid (0.4 g, 26%); mp: 114-116 °C; IR: (neat, ν_{max}/cm^{-1}) 3282, 1681, 1655, 1574, 1524, 1491, 1450, 1408, 1355; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 9.20 (1H, d, *J* 2.1 Hz), 8.51 (1H, br. s), 7.97-7.92 (2H, m), 7.71 (1H, dd, *J* 8.4 Hz, *J* 2.1 Hz), 7.64-7.60 (1H, m), 7.58-7.50 (3H, m), 2.66 (3H,

s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 197.1, 165.4, 136.6, 135.0, 134.1, 132.5, 129.3, 129.1, 127.6, 127.1, 124.0, 121.7, 26.7; HRMS: (ESI) found *m/z* 296.0447 $[M+Na]^+$, $C_{15}H_{12}{}^{35}ClNNaO_2$ requires 296.0449.

***N*-(2-Chloropyridin-3-yl)benzamide 9g.** General procedure A was followed using 3-amino-2-chloropyridine (3.0 g, 23.0 mmol) and benzoyl chloride (3.3 mL, 28.0 mmol). Recrystallization from ethanol afforded **9g** as a light pink crystalline solid (3.4 g, 63%). Spectral data are consistent with those in the literature.[27]

***N*-(2-Chloro-4-fluorophenyl)benzamide 9h.** General procedure A was followed using 2-chloro-4-fluoroaniline (2.0 g, 14.0 mmol) and benzoyl chloride (1.9 mL, 17.0 mmol). Recrystallization from dichloromethane afforded **9h** as a light pink crystalline solid (3.1 g, 90%); mp: 110-112 °C; IR: (KBr, ν_{max}/cm^{-1}) 3201, 3095, 2833, 2678, 1988, 1818, 1778, 1647, 1595, 1579, 1519, 1493, 1390; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.47 (1H, dd, *J* 9.1 Hz, *J* 5.7 Hz), 8.33 (1H, br. s), 7.91 (2H, d, *J* 7.5 Hz), 7.60-7.56 (1H, m), 7.52-7.49 (2H, m), 7.16 (1H, dd, *J* 8.0 Hz, *J* 2.8 Hz), 7.07-7.02 (1H, m); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 165.3, 158.5 (d, *J* 247.3 Hz), 134.3, 132.3, 131.2 (d, *J* 3.3 Hz), 128.9, 127.1, 123.9 (d, *J* 10.3 Hz), 122.9 (d, *J* 8.2 Hz), 116.3 (d, *J* 25.9 Hz), 114.7 (d, *J* 21.7 Hz); ^{19}F NMR: (376 MHz, $CDCl_3$) δ −116.0 (1F, s); HRMS: (ESI) found *m/z* 272.0249, $[M+Na]^+$, $C_{13}H_9{}^{35}ClFNNaO$ requires 272.0249.

***N*-(2-Bromo-4-chlorophenyl)benzamide 9i.** General procedure A was followed using 2-bromo-6-chloroaniline (2.5 g, 12.0 mmol) and benzoyl chloride (1.7 mL, 14.0 mmol). Recrystallization from ethanol afforded **9i** as a white crystalline solid (3.1 g, 84%). Spectral data are consistent with those in the literature.[28]

***N*-(2-Chlorophenyl)furan-2-carboxamide 9j.** General procedure A was followed using 2-chloroaniline (2.0 g, 15.7 mmol) and 2-furoyl chloride (1.9 mL, 19.0 mmol).

Recrystallization from ethanol afforded **9j** as a white crystalline solid (1.4 g, 41%). Spectral data are consistent with those in the literature.[29]

***N*-(2-Chlorophenyl)isonicotinamide 9k.** General procedure A was followed using 2-chloroaniline (2.4 g, 19.0 mmol) and isonicotinoyl chloride hydrochloride (4.0 g, 22.0 mmol). Recrystallization from ethanol afforded **9k** as a yellow crystalline solid (0.6 g, 11%). Spectral data are consistent with those in the literature.[30]

***N*-(2-Chlorophenyl)pivalamide 9l.** General procedure A was followed using 2-chloroaniline (3.0 g, 24.0 mmol) and pivaloyl chloride (3.6 mL, 29.0 mmol). Recrystallization from ethanol afforded **9l** as a white crystalline solid (5.0 g, 99%). Spectral data are consistent with those in the literature.[31]

General procedure B for the Synthesis of Imidoyl Chlorides 5 from Amides 9 (Scheme 2). To amide **9** (1.0 equiv), in anhydrous DCM (0.2 M) was added PCl_5 (1.1 equiv). The reaction was refluxed for 24 h before cooling to room temperature. The resulting solution was stirred and heated at 50 °C under reduced pressure until ^{31}P NMR confirmed the complete removal of all phosphoryl trichloride. No further purification was carried out and % conversions are given. Full characterisation data was unattainable due to low stability of these molecules.[13, 15]

(*Z*)-*N*-(2-Chlorophenyl)benzimidoyl chloride 5a. General procedure B was followed using amide **9a** (5.0 g, 21.5 mmol), affording **5a** as a pale green liquid (99% conversion); ^1H NMR: (400 MHz, $CDCl_3$) δ 8.24 (2H, d, *J* 7.8 Hz), 7.58-7.62 (1H, m), 7.48-7.54 (3H, m), 7.33 (1H, dd, *J* 7.8, *J* 1.4 Hz), 7.16 (1H, dd, *J* 7.8, *J* 1.4 Hz), 7.00 (1H, dd, *J* 8.0, *J* 1.4 Hz); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 146.2, 145.3, 135.0, 132.5, 129.8, 129.6, 128.5, 127.2, 125.8, 124.8, 121.1.

(*Z*)-*N*-(2-Chloro-5-methoxyphenyl)benzimidoyl chloride 5b. General procedure B was followed using amide **9b** (0.6 g, 3.8 mmol), affording **5b** as a yellow oil (98% conversion);

^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.21 (2H, d, *J* 7.6 Hz), 7.61-7.55 (1H, m), 7.54-7.48 (2H, m), 7.35 (1H, d, *J* 8.8 Hz), 6.71 (1H, dd, *J* 8.8 Hz, *J* 2.9 Hz), 6.53 (1H, d, *J* 2.9 Hz), 3.82 (3H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 158.7, 146.5, 145.9, 134.9, 132.5, 130.2, 129.6, 128.5, 116.1, 111.6, 106.6, 55.6.

(*Z*)-*N*-(2-Chloro-4-methylphenyl)benzimidoyl chloride 5c. General procedure B was followed using amide **9c** (1.0 g, 4.1 mmol), affording **5c** as an amorphous yellow solid (100% conversion); ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.21 (2H, d, *J* 7.7 Hz), 7.59-7.56 (1H, m), 7.52-7.48 (2H, m), 7.29 (1H, s), 7.12 (1H, d, *J* 8.0 Hz), 6.90 (1H, d, *J* 8.0 Hz), 2.37 (3H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 145.8, 142.6, 135.9, 135.1, 132.3, 130.2, 129.6, 128.5, 127.9, 124.6, 120.9, 20.8.

(*Z*)-*N*-(2-Chloro-6-methylphenyl)benzimidoyl chloride 5d. General procedure B was followed using amide **9d** (0.4 g, 1.4 mmol), affording **5d** as an amorphous yellow solid (100% conversion); ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.95-7.90 (2H, m), 7.59-7.52 (1H, m), 7.49-7.43 (2H, m), 7.29 (1H, dd, *J* 6.7 Hz, *J* 2.0 Hz), 7.18-7.13 (2H, m), 2.29 (3H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 138.2, 133.9, 132.8, 132.0, 131.5, 129.3, 128.7, 127.9, 127.5, 127.5, 127.0, 19.0.

(*Z*)-*N*-(2-Chloro-4-cyanophenyl)benzimidoyl chloride 5e. General procedure B was followed using amide **9e** (2.0 g, 3.3 mmol), affording **5e** as a colourless oil (100% conversion); ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.20 (2H, d, *J* 7.8 Hz), 7.78-7.76 (1H, m), 7.65-7.58 (2H, m), 7.53 (2H, t, *J* 7.7 Hz), 7.06 (1H, d, *J* 8.2 Hz); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 149.4, 148.2, 134.4, 133.5, 133.2, 131.2, 129.7, 128.7, 125.8, 121.9, 117.7, 109.4.

(*Z*)-*N*-(5-Acetyl-2-chlorophenyl)benzimidoyl chloride 5f. General procedure B was followed using amide **9f** (0.4 g, 1.5 mmol), affording **5f** as an orange oil (98% conversion); ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.21 (2H, d, *J* 7.6 Hz), 7.74 (1H, dd, *J* 8.3 Hz, *J* 1.8 Hz),

7.63-7.48 (5H, m), 2.61 (3H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 196.6, 147.5, 145.6, 136.2, 134.6, 132.8, 130.2, 130.1, 129.6, 128.6, 125.5, 121.1, 26.7.

(*Z*)-*N*-(2-Chloropyridin-3-yl)benzimidoyl chloride 5g. General procedure B was followed using amide **9g** (1.0 g, 4.3 mmol), affording **5g** as an amorphous yellow oil (98% conversion); ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.27 (1H, dd, *J* 4.5 Hz, *J* 1.9 Hz), 8.22 (2H, d, *J* 7.9 Hz), 7.64-7.59 (1H, m), 7.56-7.48 (2H, m), 7.37-7.29 (2H, m); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 148.4, 145.5, 142.3, 141.9, 134.5, 132.9, 129.7, 129.5, 128.7, 122.7.

(*Z*)-*N*-(2-Chloro-4-fluorophenyl)benzimidoyl chloride 5h. General procedure B was followed using amide **9h** (1.0 g, 4.0 mmol), affording **5h** as an amorphous white solid (98% conversion); ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.22-8.20 (2H, m), 7.61-7.58 (1H, m), 7.53-7.49 (2H, m), 7.28-7.22 (1H, m), 7.08-7.03 (1H, m), 7.00-6.96 (1H, m); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 159.7 (d, *J* 247.0 Hz), 146.8, 141.6 (d, *J* 3.3 Hz), 134.9, 132.6, 129.6, 128.6, 125.8 (d, *J* 10.3 Hz), 122.0 (d, *J* 8.7 Hz), 117.1 (d, *J* 25.6 Hz), 114.4 (d, *J* 22.4 Hz); ^{19}F NMR: (376 MHz, $CDCl_3$) δ −116.5 (1F, s).

(*Z*)-*N*-(2-Bromo-4-chlorophenyl)benzimidoyl chloride 5i. General procedure B was followed using amide **9i** (1.0 g, 3.4 mmol), affording **5i** as an amorphous yellow solid (99% conversion); ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.21 (2H, d, *J* 7.2 Hz), 7.66 (1H, d, *J* 2.0 Hz), 7.62-7.57 (1H, m), 7.54-7.48 (2H, m), 7.34 (1H, dd, *J* 8.5 Hz, *J* 2.0 Hz), 6.93 (1H, d, *J* 8.5 Hz); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 146.7, 145.3, 134.8, 132.7, 132.4, 130.7, 129.6, 128.6, 128.1, 121.9, 115.3.

(*Z*)-*N*-(2-Chlorophenyl)furan-2-carbimidoyl chloride 5j. General procedure B was followed using amide **9j** (1.0 g, 4.5 mmol), affording **5j** as a brown oil (100% conversion); ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.68 (1H, s), 7.46 (1H, d, *J* 8.0 Hz), 7.33-7.25 (2H, m), 7.17-7.12 (1H, t, *J* 7.7 Hz), 6.99 (1H, d, *J* 7.9 Hz), 6.56 (1H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 148.0, 147.2, 144.5, 134.9, 129.8, 127.2, 126.1, 125.2, 121.5, 119.0, 112.5.

(*Z*)-*N*-(2-Chlorophenyl)isonicotinimidoyl chloride 5k. General procedure B was followed using amide **9k** (0.5 g, 4.3 mmol), affording **5k** as an amorphous yellow solid (100% conversion); ^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.95 (2H, d, *J* 6.5 Hz), 8.49 (2H, d, *J* 6.5 Hz), 7.53 (1H, dd, *J* 8.1 Hz, *J* 1.3 Hz), 7.38 (1H, td, *J* 7.8 Hz, *J* 1.3 Hz), 7.30-7.24 (1H, m), 7.06 (1H, dd, *J* 7.9 Hz, *J* 1.5 Hz); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 146.7, 144.4, 143.5, 141.8, 130.2, 127.6, 127.4, 125.3, 125.2, 120.5.

(*Z*)-*N*-(2-Chlorophenyl)pivalimidoyl chloride 5l. General procedure B was followed using amide **9l** (2.0 g, 9.5 mmol), affording **5l** as a yellow oil (98% conversion); ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.40 (1H, d, *J* 8.0 Hz), 7.26-7.22 (1H, m), 7.08 (1H, td, *J* 7.7 Hz, *J* 1.2 Hz), 6.82 (1H, dd, *J* 7.9 Hz, *J* 1.2 Hz), 1.42 (9H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 158.3, 145.1, 129.7, 127.1, 125.7, 124.2, 120.9, 44.0, 28.3.

(*Z*)-*N*-Benzyl-*N*'-(2-chloro-5-methoxyphenyl)benzimidamide 11 (Scheme 3). To a 5 mL microwave vial was added (*Z*)-*N*-(2-chloro-5-methoxyphenyl)benzimidoyl chloride **5b** (150 mg, 0.5 mmol) and sodium *t*-butoxide (77 mg, 0.9 mmol). This was capped and purged with N_2 three times and then toluene (1.5 mL) and benzylamine **10a** (90 μL, 0.9 mmol) were added. The reaction mixture was heated at room temperature for 24 h. The reaction mixture was then diluted with diethyl ether (2 mL) and filtered through a Celite pad, washing with diethyl ether (40 mL) and concentrated *in vacuo*. Column chromatography (petrol/diethyl ether 3:1) afforded **11** as yellow crystalline solid (123 mg, 65%); mp: 88-91 °C; ν_{max} (neat/cm^{-1}) 3423, 1625, 1586, 1513, 1471, 1289, 1130; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.55-7.49 (2H, m), 7.45-7.28 (8H, m), 7.15 (1H, d, *J* 8.7 Hz), 6.42-6.36 (1H, m), 6.23-6.16 (1H, m), 5.18 (1H, br. s), 4.75 (2H, br. s), 3.63 (3H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 158.4, 157.9, 138.7, 135.0, 129.5, 129.0, 128.7 (2C), 128.3, 128.1, 127.9, 127.4, 118.8, 109.4, 108.7, 55.3, 46.1; HRMS (ESI) found *m/z* 351.1252 $[M+H]^+$, $C_{21}H_{20}{}^{35}ClN_2O$ requires 351.1259.

1-Benzyl-5-methoxy-2-phenyl-1*H*-benzo[*d*]imidazole 7b (Scheme 3). To a 5 mL microwave vial was added amidine **11** (100 mg, 0.3 mmol), palladium (II) acetate (3.8 mg, 0.02 mmol), **L3** (12.0 mg, 0.03 mmol) and sodium *t*-butoxide (86 mg, 0.9 mmol). This was capped and purged with N_2 three times and anhydrous toluene (1.0 mL) and benzylamine **10a** (45 μL, 0.5 mmol) were then added. This was heated in a microwave for 3 h at 120 °C. After cooling to room temperature the reaction mixture was diluted with diethyl ether (5 mL) and filtered through a Celite pad, washing with diethyl ether (40 mL). This was then concentrated *in vacuo*. Column chromatography (petrol/diethyl ether 1:3) afforded **7b** as a pale yellow crystalline solid (60 mg, 54%). Spectral data are consistent with those in the literature.[32] Amidine **11** (41mg, 41%) was also recovered. Data as reported previously.

General procedure D for the synthesis of Imidates 6 (Scheme 4) (Condition A). A mixture of 2-haloaniline (1.0 equiv), *ortho*-ester (1.1-2.0 equiv) and *p*-toluenesulfonic acid (cat.) in anhydrous toluene (0.3 M) was heated under reflux for 3 h with the aid of Dean-Stark apparatus. The mixture was cooled and concentrated *in vacuo*. The residue was re-dissolved in diethyl ether, washed with a saturated aqueous solution of sodium bicarbonate and then brine. This was then dried ($MgSO_4$) and concentrated *in vacuo*. Purification was conducted by column chromatography.

General procedure E for the synthesis of Imidates 6 (Scheme 4) (Condition B). A mixture of 2-haloaniline (1,0 equiv) and *ortho*-ester (1.1-2.0 equiv) was heated at 90-110 °C for 9-53 h with the aid of Dean-Stark apparatus. Purification was conducted by column chromatography.

(*Z*)-Methyl *N*-2-chloro-4-methylphenylbenzimidate 6a. General procedure E was followed using 2-chloro-4-methylaniline (1.6 mL, 13.0 mmol) and trimethyl orthobenzoate (4.7 mL, 27.0 mmol) and heated at 90 °C for 53 h. Column chromatography (petrol/diethyl ether 12:1) afforded **6a** as a yellow oil and as a single isomer (3.1 g, 93%); IR: (neat, ν_{max}/cm^{-1}) 3026,

2985, 1667, 1609, 1493, 1435, 1285; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.35-7.29 (3H, m), 7.25-7.22 (2H, m), 7.14-7.12 (1H, m), 6.84 (1H, dd, *J* 8.0 Hz, *J* 1.1 Hz), 6.54 (1H, d, *J* 8.0 Hz), 4.03 (3H, s), 2.25 (3H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 160.2, 143.1, 133.3, 131.6, 130.0, 130.0, 128.6, 128.0, 128.0, 125.3, 122.4, 54.3, 20.5; HRMS: (ESI) found *m/z* 282.0652 $[M+Na]^+$, $C_{15}H_{14}{}^{35}ClNNaO$ requires 282.0656.

(*Z*)-Methyl *N*-2-chloro-5-methoxyphenylbenzimidate 6b. General procedure D was followed using 2-chloro-5-methoxyaniline (1.0 g, 6.3 mmol) and trimethyl orthobenzoate (2.3 mL, 13.0 mmol). Column chromatography (petrol/diethyl ether 12:1) afforded **6b** as a crystalline colourless solid as a single isomer (1.0 g, 59 %); mp: 67-69 °C; IR: (neat, ν_{max}/cm^{-1}) 3006, 2950, 1666, 1593, 1573, 1493, 1479, 1461, 1445, 1434, 1399, 1317; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.39-7.31 (3H, m), 7.28-7.22 (2H, m), 7.18 (1H, d, *J* 8.8 Hz), 6.48 (1H, dd, *J* 8.8 Hz, *J* 2.9 Hz), 6.27 (1H, d, *J* 2.9 Hz), 4.03 (3H, s), 3.67 (3H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 160.2, 158.7, 146.5, 131.4, 130.3, 130.0, 128.5, 128.0, 117.3, 109.6, 108.0, 55.4, 54.4; HRMS: (ESI) found *m/z* 276.0795 $[M+H]^+$, $C_{15}H_{15}{}^{35}ClNO_2$ requires 276.0786.

(*Z*)-Methyl *N*-2-chloropyridin-3-ylbenzimidate 6c. General procedure D was followed using 3-amino-2-chloropyridine (2.0 g, 16.0 mmol) and trimethyl orthobenzoate (2.9 mL, 17.0 mmol). Column chromatography (petrol/ethyl acetate 10:1) afforded **6c** as an orange oil and as a single isomer (1.2 g, 31%); IR: (neat, ν_{max}/cm^{-1}) 3057, 2946, 1721, 1656, 1601, 1580, 1554, 1493, 1443, 1396; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.02 (1H, dd, *J* 4.7 Hz, *J* 1.8 Hz), 7.37-7.22 (5H, m), 7.03 (1H, dd, *J* 7.8 Hz, *J* 4.7 Hz), 6.95 (1H, dd, *J* 7.8 Hz, *J* 1.8 Hz), 4.05 (3H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 161.6, 143.6, 143.3, 142.6, 130.8, 130.6, 130.3, 128.5, 128.3, 122.8, 54.7; HRMS: (ESI) found *m/z* 247.0633 $[M+H]^+$, $C_{13}H_{12}{}^{35}ClN_2O$ requires 247.0633.

(*Z*)-Methyl *N*-2-chloro-4-fluorophenylbenzimidate 6d. General procedure D was followed using 2-chloro-4-fluoroaniline (2.0 g, 14.0 mmol) and trimethyl orthobenzoate (2.6 mL, 15.0

mmol). Column chromatography (petrol/ethyl acetate 20:1) afforded **6d** as a yellow oil and as a single isomer (1.2 g, 32%); IR: (neat, ν_{max}/cm^{-1}) 2989, 2946, 1737, 1662, 1661, 1579, 1518, 1485, 1458, 1447, 1434; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.36-7.31 (3H, m), 7.29-7.24 (2H, m), 7.10 (1H, dd, *J* 8.4 Hz, *J* 2.8 Hz), 6.82-6.76 (1H, m), 6.62 (1H, dd, *J* 8.8 Hz, *J* 5.6 Hz), 4.05 (3H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 160.2 (d, *J* 155.8 Hz), 157.0, 142.3 (d, *J* 3.2 Hz), 131.3, 130.3, 128.6, 128.1, 126.1 (d, *J* 10.4 Hz), 123.2 (d, *J* 8.3 Hz), 116.7 (d, *J* 25.3 Hz), 114.3 (d, *J* 22.1 Hz), 54.4; ^{19}F NMR: (376 MHz, $CDCl_3$) δ −119.7 (1F, s); HRMS: (ESI) found *m/z* 264.0591 $[M+H]^+$, $C_{14}H_{12}{}^{35}ClFNO$ requires 264.0586.

(*Z*)-Methyl *N*-2-chlorophenylpentanimidate 6e. General procedure D was followed using 2-chloroaniline (1.0 g, 7.8 mmol) and trimethyl orthovalerate (1.4 mL, 8.6 mmol). Column chromatography (petrol/ethyl acetate 20:1) afforded **6e** as colourless oil and as a single isomer (1.5 g, 83%); IR: (neat, ν_{max}/cm^{-1}) 2962, 1713, 1670, 1589, 1437, 1360, 1267, 1220; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.37 (1H, dd, *J* 8.0 Hz, *J* 1.3 Hz), 7.18 (1H, td, *J* 7.6 Hz, *J* 1.3 Hz), 6.97 (1H, td, *J* 7.8 Hz, *J* 1.5 Hz), 6.80 (1H, dd, *J* 7.8 Hz, *J* 1.5 Hz), 3.85 (3H, s), 2.12 (2H, t, *J* 7.7 Hz), 1.51 (2H, quin, *J* 7.6 Hz), 1.24 (2H, sex, *J* 7.4 Hz), 0.83 (3H, t, *J* 7.3 Hz); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 165.4, 145.9, 129.7, 127.2, 125.6, 123.7, 122.6, 53.5, 30.0, 27.9, 22.3, 13.7; HRMS: (ESI) found *m/z* 226.0992 $[M+H]^+$, $C_{12}H_{17}{}^{35}ClNO$ requires 226.0993.

(*Z*)-Methyl *N*-2-chlorophenyl-2-phenylacetimidate 6f. General procedure E was followed using 2-chloroaniline (0.3 g mL, 1.7 mmol) and (2,2,2-trimethoxyethyl)benzene (0.7 g, 3.3 mmol) and was heated at 90 °C for 22 h. Column chromatography (petrol/diethyl ether 18:1) afforded **6f** as a colourless oil and as a single isomer (0.62 g, 73%); IR: (neat, ν_{max}/cm^{-1}) 3063, 3029, 2986, 2945, 2842, 1651, 1603, 1588, 1495, 1474, 1455; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.42 (1H, d, *J* 8.0 Hz), 7.32-7.19 (4H, m), 7.14 (2H, d, *J* 7.3 Hz), 7.05-7.00 (1H, m), 6.84 (1H, dd, *J* 7.8 Hz, *J* 1.4 Hz), 3.89 (3H, s), 3.50 (2H, s); ^{13}C NMR: (100 MHz,

$CDCl_3$) δ 163.0, 145.6, 135.2, 129.8, 129.1, 128.4, 127.3, 126.7, 125.7, 124.1, 122.9, 54.0, 36.8; HRMS: (ESI) found *m/z* 260.0841 $[M+H]^+$, $C_{15}H_{15}{}^{35}ClNO$ requires 260.0837.

(*Z*)-Methyl *N*-2-bromophenylbenzimidate 6g. General procedure D was followed using 2-bromoaniline (2.0 g, 12.0 mmol) and trimethyl orthobenzoate (2.3 mL, 13.0 mmol). Column chromatography (petrol/ethyl acetate 25:1) afforded **6g** as colourless oil and as a single isomer (3.0 g, 89%); IR: (neat, ν_{max}/cm^{-1}) 3055, 2986, 2947, 1721, 1667, 1602, 1584, 1493, 1469, 1447; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.53 (1H, dd, *J* 8.0 Hz, *J* 1.4 Hz), 7.36-7.30 (3H, m), 7.28-7.22 (2H, m), 7.09 (1H, td, *J* 7.7 Hz, *J* 1.4 Hz), 6.83 (1H, td, *J* 7.7 Hz, *J* 1.5 Hz), 6.64 (1H, dd, *J* 7.9 Hz, *J* 1.5 Hz), 4.05 (3H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 159.9, 147.1, 132.7, 131.3, 130.2, 128.7, 128.0, 127.9, 123.8, 122.5, 116.3, 54.4; HRMS: (ESI) found *m/z* 311.9996 $[M+Na]^+$, $C_{14}H_{12}{}^{79}BrNNaO$ requires 311.9994.

(*Z*)-Methyl *N*-2-bromo-4,6-dimethylphenylbenzimidate 6h. General procedure D was followed using 2-bromo-4,6-dimethylaniline (2.0 g, 10.0 mmol) and trimethyl orthobenzoate (1.9 mL, 11.0 mmol). Column chromatography (petrol/ethyl acetate 50:1) afforded **6h** as a colourless oil and as a single isomer (2.6 g, 81%); mp: 39-42 °C; IR: (neat, ν_{max}/cm^{-1}) 3052, 2941, 1663, 1601, 1493, 1438, 1317, 1298, 1264; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.39-7.31 (3H, m), 7.27-7.22 (2H, m), 7.18 (1H, s), 6.84 (1H, s), 4.05 (3H, s), 2.23 (3H, s), 2.02 (3H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 159.0, 142.8, 133.0, 132.1, 130.7, 130.3, 130.3, 129.2, 128.0, 128.0, 115.2, 54.3, 20.4, 18.9; HRMS: (ESI) found *m/z* 318.0491 $[M+H]^+$, $C_{16}H_{17}{}^{79}BrNO$ requires 318.0488.

(*Z*)-Methyl *N*-2-bromo-5-methoxyphenylbenzimidate 6i. General procedure D was followed using 2-bromo-5-methoxyaniline (0.8 g, 4.0 mmol) and trimethyl orthobenzoate (1.3 mL, 7.5 mmol). Column chromatography (petrol/ethyl acetate 18:1) afforded **6i** as white crystalline solid and as a single isomer (1.0 g, 70%); mp: 76-78 °C; IR: (neat, ν_{max}/cm^{-1}) 3025, 3006, 2966, 2835, 1662, 1585, 1570, 1492, 1476, 1443; ^1H NMR: (400 MHz, $CDCl_3$) δ

7.39-7.31 (4H, m), 7.28-7.23 (2H, m), 6.43 (1H, dd, *J* 8.8 Hz, *J* 2.9 Hz), 6.23 (1H, d, *J* 2.9 Hz), 4.03 (3H, s), 3.65 (3H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 159.9, 159.4, 147.9, 133.0, 131.3, 130.2, 128.6, 128.0, 110.1, 107.9, 107.0, 55.4, 54.4; HRMS: (ESI) found *m/z* 320.0280 $[M+H]^+$, $C_{15}H_{15}{}^{79}BrNO_2$ requires 320.0281.

(*Z*)-Methyl 3-bromo-4-(methoxy(phenyl)methyleneamino)benzoate 6j. General procedure D was followed using methyl 4-amino-3-bromobenzoate (0.4 g, 1.7 mmol) and trimethyl orthobenzoate (0.3 mL, 1.9 mmol). Column chromatography (petrol/ethyl acetate 18:1) afforded **6j** as a thick colourless oil and as a single isomer (0.4 g, 70%); IR: (neat, ν_{max}/cm^{-1}) 3062, 2991, 2948, 2842, 1718, 1659, 1591, 1548, 1494, 1433, 1391; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.22 (1H, d, *J* 1.8 Hz), 7.77 (1H, dd, *J* 8.3 Hz, *J* 1.8 Hz), 7.37-7.30 (3H, m), 7.27-7.22 (2H, m), 6.66 (1H, d, *J* 8.3 Hz), 4.05 (3H, s), 3.87 (3H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 165.9, 159.9, 151.7, 134.3, 130.8, 130.6, 129.5, 128.6, 128.2, 125.5, 122.0, 116.0, 54.7, 52.1; HRMS: (ESI) found *m/z* 370.0044 $[M+Na]^+$, $C_{16}H_{14}{}^{79}BrNNaO_3$ requires 370.0049.

(*Z*)-Methyl *N*-2-bromopyridin-3-ylbenzimidate 6k. General procedure D was followed using 3-amino-2-bromopyridine (0.6 g, 3.5 mmol) and trimethyl orthobenzoate (0.7 mL, 3.8 mmol). Column chromatography (petrol/ethyl acetate 10:1) afforded **6k** as an orange oil and as a single isomer (0.6 g, 61%); IR: (neat, ν_{max}/cm^{-1}) 3460, 3322, 3187, 2947, 1720, 1653, 1601, 1580, 1549, 1493; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.99 (1H, dd, *J* 4.6 Hz, *J* 1.6 Hz), 7.37-7.22 (5H, m), 7.03 (1H, dd, *J* 7.8 Hz, *J* 4.6 Hz), 6.86 (1H, dd, *J* 7.8 Hz, *J* 1.6 Hz), 4.05 (3H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 161.5, 144.5, 143.7, 136.8, 130.7, 130.6, 129.6, 128.6, 128.3, 123.1, 54.7; HRMS: (ESI) found *m/z* 312.9939 $[M+Na]^+$, $C_{13}H_{11}{}^{79}BrN_2NaO$ requires 312.9947.

(*Z*)-Methyl *N*-2-bromo-4-fluorophenylbenzimidate 6l. General procedure E was followed using 2-bromo-4-fluoroaniline (0.6 mL, 5.0 mmol) and trimethyl orthobenzoate (1.8 mL, 10.0 mmol) and was heated at 100 °C for 19 h. Column chromatography (petrol/diethyl ether 30:1)

afforded **6l** as a colourless oil and as a single isomer (1.2 g, 79%); IR: (neat, ν_{max}/cm^{-1}) 3065, 2981, 2945, 2840, 1723, 1658, 1599, 1580, 1493, 1447; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.37-7.24 (6H, m), 6.85-6.79 (1H, m), 6.56 (1H, dd, *J* 8.8 Hz, *J* 5.5 Hz), 4.04 (3H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 160.1 (d, *J* 138.7 Hz), 156.9, 143.6 (d, *J* 3.2 Hz), 131.2, 130.3, 128.6, 128.1, 122.8 (d, *J* 8.1 Hz), 119.6 (d, *J* 25.2 Hz), 116.1 (d, *J* 21.9 Hz), 114.9 (d, *J* 21.9 Hz), 54.5; ^{19}F NMR: (376 MHz, $CDCl_3$) δ −119.9 (1F, s); HRMS: (ESI) found *m/z* 308.0083 $[M+H]^+$, $C_{14}H_{12}{}^{79}BrFNO$ requires 308.0081.

(*Z*)-Methyl *N*-2-bromo-4-chlorophenylbenzimidate 6m. General procedure E was followed using 2-bromo-4-chloroaniline (1.0 g mL, 4.8 mmol) and trimethyl orthobenzoate (1.7 mL, 9.6 mmol) and was heated at 110 °C for 24 h. Column chromatography (petrol/diethyl ether 30:1) afforded **6m** as an orange oil and as a single isomer (0.9 g, 57%); IR: (neat, ν_{max}/cm^{-1}) 3055, 2944, 1654, 1601, 1580, 1493, 1433, 1381, 1283; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.53 (1H, d, *J* 2.2 Hz), 7.38-7.24 (5H, m), 7.06 (1H, dd, *J* 8.5 Hz, *J* 2.2 Hz), 6.54 (1H, d, *J* 8.5 Hz), 4.04 (3H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 160.5, 146.0, 132.2, 131.0, 130.4, 128.6, 128.2, 128.1, 128.0, 123.1, 116.7, 54.6; HRMS: (ESI) found *m/z* 323.9790 $[M+H]^+$, $C_{14}H_{12}{}^{79}Br^{35}ClNO$ requires 323.9785.

(*Z*)-Methyl *N*-2-bromophenylpentanimidate 6n. General procedure D was followed using 2-bromoaniline (2.0 g, 11.6 mmol) and trimethyl orthovalerate (2.2 mL, 13.0 mmol). Column chromatography (petrol/ethyl acetate 20:1) afforded **6n** as a yellow oil and as a single isomer (2.5 g, 78%); IR: (neat, ν_{max}/cm^{-1}) 2960, 2872, 1715, 1668, 1586, 1466, 1435, 1357, 1313, 1267; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.55 (1H, dd, *J* 8.0 Hz, *J* 1.1 Hz), 7.23 (1H, td, *J* 7.6 Hz, *J* 1.1 Hz), 6.90 (1H, td, *J* 7.7 Hz, *J* 1.5 Hz), 6.78 (1H, dd, *J* 7.8 Hz, *J* 1.5 Hz), 3.86 (3H, s), 2.11 (2H, t, *J* 7.7 Hz), 1.51 (2H, quin, *J* 7.6 Hz), 1.24 (2H, sex, *J* 7.6 Hz), 0.83 (3H, t, *J* 7.3 Hz); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 165.2, 147.2, 132.7, 127.9, 123.9, 122.3, 116.1,

53.6, 30.0, 27.9, 22.4, 13.7; HRMS: (ESI) found *m/z* 270.0494 $[M+H]^+$, $C_{12}H_{17}{}^{79}BrNO$ requires 270.0488.

(*Z*)-Methyl *N*-2-bromophenyl-2-phenylacetimidate 6o. General procedure E was followed using 2-bromoaniline (0.4 g, 2.6 mmol) and (2,2,2-trimethoxyethyl)benzene (1.0 g, 5.0 mmol) and was heated at 90 °C for 20 h. Column chromatography (petrol/diethyl ether 18:1) afforded **6o** as a colourless oil and as a single isomer (0.76 g, 96%); IR: (neat, ν_{max}/cm^{-1}) 3062, 3029, 2944, 2841, 1650, 1602, 1585, 1495, 1468, 1455; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.60 (1H, d, *J* 8.0 Hz), 7.32-7.23 (4H, m), 7.14 (2H, d, *J* 7.1 Hz), 6.95 (1H, t, *J* 8.1 Hz), 6.82 (1H, d, *J* 7.8 Hz), 3.89 (3H, s), 3.49 (2H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 162.9, 146.9, 135.1, 132.9, 129.1, 128.4, 128.0, 126.7, 124.3, 122.7, 116.2, 54.1, 36.8; HRMS: (ESI) found *m/z* 304.0335 $[M+H]^+$, $C_{15}H_{15}{}^{79}BrNO$ requires 304.0332.

1-Benzyl-2-phenyl-1H-benzo[*d*]imidazole 7a. **(Table 1, entry 4)** To a 5 mL microwave vial was added imidoyl chloride **5a** (100 mg, 0.4 mmol), palladium (II) acetate (4.5 mg, 0.02 mmol), **L2** (11.0 mg, 0.03 mmol) and sodium *t*-butoxide (115.9 mg, 1.21 mmol). This was capped and purged with N_2 three times and toluene (1.0 mL) and benzylamine **10a** (64.3 mg, 0.07 mL, 0.06 mmol) were then added. This was heated for 18 h at 100 °C. After cooling to room temperature the reaction mixture was diluted with diethyl ether and filtered through a Celite pad, eluting with diethyl ether and concentrated *in vacuo*. Column chromatography (petrol/ether 17:3 then DCM/ether 1:1) and recrystallization from DCM afforded **7a** as a white crystalline solid (113 mg, 98 %). Spectral data are consistent with those in the literature.[32]

General procedure F for the Synthesis of Benzimidazoles 7 from Imidoyl Chlorides 5 and *N*-nucleophiles 10 (Table 2). To a 5 mL microwave vial was added imidoyl chloride **5** (1.0 equiv), palladium (II) acetate (5 mol%), **L3** (7 mol%) and sodium *t*-butoxide (2.2 equiv). This was capped and purged with N_2 three times and anhydrous BTF (0.4 M) and *N*-

nucleophile **10** (1.5 equiv) were then added. This was heated in a microwave for 2 h at 135 °C (unless otherwise stated). After cooling to room temperature the reaction mixture was diluted with diethyl ether and filtered through a Celite pad, washing with diethyl ether. This was then concentrated *in vacuo*. Purification was conducted by column chromatography.

1-Benzyl-5-methoxy-2-phenyl-1*H*-benzo[*d*]imidazole 7b. General procedure F was followed using imidoyl chloride **5b** (100 mg, 0.4 mmol) and benzylamine **10a** (60 μL, 0.6 mmol). Column chromatography (petrol/diethyl ether 1:3) afforded **7b** as a pale yellow crystalline solid (89 mg, 80%). Spectral data are consistent with those in the literature.[33]

1-Benzyl-6-methyl-2-phenyl-1*H*-benzo[*d*]imidazole 7c. General procedure E was followed using imidoyl chloride **5c** (100 mg, 0.4 mmol) and benzylamine **10a** (60 μL, 0.6 mmol). Column chromatography (petrol/diethyl ether 2:1) afforded **7c** as a colourless solid (79 mg, 69%). Spectral data are consistent with those in the literature.[34]

6-Methyl-2-phenyl-1-(3-phenylpropyl)-1*H*-benzo[*d*]imidazole 7d. General procedure F was followed using imidoyl chloride **5c** (100 mg, 0.4 mmol) and 3-phenyl-1-propylamine **10b** (80 μL, 0.6 mmol). Column chromatography (petrol/diethyl ether 2:1) afforded **7d** as a yellow crystalline solid (93 mg, 75%); mp: 80-82 °C; IR: (neat, ν_{max}/cm^{-1}) 3030, 2980, 2910, 2850, 1650, 1621, 1604, 1585, 1543, 1497, 1479; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.74 (1H, d, *J* 8.2 Hz), 7.69-7.64 (2H, m), 7.50-7.44 (3H, m), 7.32-7.26 (2H, m), 7.25-7.20 (1H, m), 7.14 (1H, d, *J* 8.2 Hz), 7.12-7.07 (3H, m), 4.20 (2H, t, *J* 7.7 Hz), 2.61 (2H, t, *J* 7.4 Hz), 2.53 (3H, s), 2.16 (2H, quin, *J* 7.6 Hz); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 153.1, 141.3, 140.4, 135.9, 132.7, 130.7, 129.5, 129.2, 128.7, 128.6, 128.3, 126.3, 124.0, 119.5, 110.0, 43.9, 32.8, 31.0, 21.9; HRMS: (ESI) found *m/z* 327.1855 $[M+H]^+$, $C_{23}H_{23}N_2$ requires 327.1856.

6-Methyl-1-octyl-2-phenyl-1*H*-benzo[*d*]imidazole 7e. General procedure F was followed using imidoyl chloride **5c** (100 mg, 0.4 mmol) and octylamine **10c** (90 μL, 0.6 mmol). Column chromatography (petrol/diethyl ether 3:1) afforded **7e** as a colourless oil (88 mg,

73%); IR: (neat, ν_{max}/cm^{-1}) 3423, 2927, 2856, 1652, 1486, 1393, 1331, 1277; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.72- 7.69 (3H, m), 7.54-7.49 (3H, m), 7.20 (1H, s), 7.13 (1H, d, *J* 8.2 Hz), 4.20-4.16 (2H, m), 2.54 (3H, s), 1.82-1.77 (2H, m), 1.29-1.17 (10H, m), 0.87 (3H, t, *J* 7.0 Hz); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 153.3, 141.2, 135.8, 132.6, 130.9, 129.5, 129.3, 128.6, 123.9, 119.4, 110.9, 44.6, 31.7, 29.7, 29.1, 28.9, 26.6, 22.6, 21.9, 14.1; HRMS: (ESI) found *m/z* 321.2328 $[M+H]^+$, $C_{22}H_{29}N_2$ requires 321.2325.

1-Cyclohexyl-6-methyl-2-phenyl-1*H*-benzo[*d*]imidazole 7f. General procedure F was followed using imidoyl chloride **5c** (100 mg, 0.4 mmol) and cyclohexylamine **10d** (70 μL, 0.6 mmol) and heated in the microwave for 30 min at 50 °C then 2 h at 135 °C. Column chromatography (petrol/diethyl ether 2:1) afforded **7f** as an orange oil (103 mg, 94%); IR: (neat, ν_{max}/cm^{-1}) 3061, 3031, 2930, 2856, 1609, 1580, 1526, 1495, 1467, 1449; ^1H NMR: (400 MHz, $CDCl_3$); δ 7.70 (1H, d, *J* 8.2 Hz), 7.65-7.61 (2H, m), 7.54-7.49 (3H, m), 7.45 (1H, s), 7.11 (1H, d, *J* 8.2 Hz), 4.34 (1H, tt, *J* 12.4 Hz, *J* 3.8 Hz,), 2.54 (3H, s), 2.41-2.28 (2H, m), 2.01-1.88 (4H, m), 1.80-1.73 (1H, m), 1.39-1.29 (3H, m); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 153.3, 141.8, 134.2, 131.9, 131.3, 129.5, 129.4, 128.6, 123.5, 119.7, 112.5, 56.9, 31.4, 25.9, 25.3, 22.0; HRMS: (ESI) found *m/z* 291.1852 $[M+H]^+$, $C_{20}H_{23}N_2$ requires 291.1856.

6-Methyl-2-phenyl-1-(thiophen-2-ylmethyl)-1*H*-benzo[*d*]imidazole 7g. General procedure F was followed using imidoyl chloride **5c** (200 mg, 0.8 mmol) and 2-thiophenemethylamine **10e** (0.1 mL, 1.2 mmol) and heated in the microwave for 30 min at 50 °C then for 2 h at 135 °C. Column chromatography (petrol/diethyl ether 2:1) afforded **7g** as a brown crystalline solid (111 mg, 48%); mp: 170-172 °C; IR: (neat, ν_{max}/cm^{-1}) 3227, 3066, 3031, 2929, 2857, 1714, 1646, 1620, 1580, 1531, 1480; ^1H NMR: (400 MHz, $CDCl_3$); δ 7.78-7.72 (3H, m), 7.52-7.47 (3H, m), 7.24 (1H, dd, *J* 5.1 Hz, *J* 0.9 Hz), 7.18-7.13 (2H, m), 6.95 (1H, dd, *J* 5.1 Hz, *J* 3.5 Hz), 6.85 (1H, dd, *J* 3.5 Hz, *J* 0.9 Hz), 5.53 (2H, s), 2.49 (3H, s); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 153.3, 141.3, 139.4, 136.0, 133.1, 130.1, 129.9, 129.3, 128.8, 127.1, 125.4,

125.3, 124.4, 119.6, 110.2, 44.1, 21.9; HRMS: (ESI) found *m/z* 305.1098 $[M+H]^+$, $C_{19}H_{17}N_2S$ requires 305.1107.

6-Methyl-2-phenyl-1-*p*-tolyl-1*H*-benzo[*d*]imidazole 7h. General procedure F was followed using imidoyl chloride **5c** (100 mg, 0.4 mmol) and *p*-toluidine **10f** (61 mg, 0.6 mmol) and heated in the microwave for 30 min at 50 °C then for 2 h at 135 °C. Column chromatography (petrol/ethyl acetate 6:1) and recrystallization from diethyl ether afforded **7h** as a pale pink crystalline solid (60 mg, 53%). Spectral data are consistent with those in the literature.[35]

1-(4-Methoxyphenyl)-6-methyl-2-phenyl-1*H*-benzo[*d*]imidazole 7i. General procedure F was followed using imidoyl chloride **5c** (100 mg, 0.4 mmol) and *p*-anisidine **10g** (70 mg, 0.6 mmol) and heated in the microwave for 30 min at 50 °C then for 2 h at 135 °C. Column chromatography (petrol/diethyl ether 1:2) and recrystallization from diethyl ether afforded **7i** as a pink crystalline solid (55 mg, 46%); mp: 140-141 °C; IR: (neat, ν_{max}/cm^{-1}) 3042, 2918, 2850, 1609, 1582, 1511, 1471, 1451, 1389, 1332, 1310; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.77 (1H, d, *J* 8.1 Hz), 7.61-7.58 (2H, m), 7.34-7.27 (3H, m), 7.25-7.20 (2H, m), 7.16 (1H, d, *J* 8.1 Hz), 7.03-6.98 (3H, m) 3.87 (3H, s), 2.45 (3H, s); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 159.4, 152.0, 141.0, 137.9, 133.3, 130.2, 129.8, 129.3, 129.2, 128.6, 128.2, 124.4, 119.3, 115.0, 110.3, 55.5, 21.8; HRMS: (ESI) found *m/z* 315.1491 $[M+H]^+$, $C_{21}H_{19}N_2O$ requires 315.1492.

1-(3,5-Difluorophenyl)-6-methyl-2-phenyl-1*H*-benzo[*d*]imidazole 7j. General procedure F was followed using imidoyl chloride **5c** (200 mg, 0.8 mmol) and 3,5-difluoroaniline **10h** (146 mg, 1.1 mmol) and heated in the microwave for 30 min at 50 °C then for 2 h at 135 °C. Column chromatography (petrol/diethyl ether 2:1) and recrystallization from diethyl ether afforded **7j** as pale pink crystalline solid (115 mg, 45%); mp: 164-167 °C; IR: (neat, ν_{max}/cm^{-1}) 3055, 1712, 1615, 1603, 1480, 1445, 1362, 1338, 1309; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.77 (1H, d, *J* 8.2 Hz), 7.56 (2H, d, *J* 7.2 Hz), 7.43-7.33 (3H, m), 7.19 (1H, d, *J* 8.2 Hz), 7.08 (1H, s), 6.94 (1H, td, *J* 8.7 Hz, *J* 2.0 Hz), 6.90-6.84 (2H, m), 2.49 (3H, s); ^{13}C NMR: (125

MHz, $CDCl_3$) δ 163.3 (dd, *J* 251.4 Hz, *J* 14.1 Hz), 151.7, 141.1, 139.3 (t, *J* 12.2 Hz), 136.7, 134.0, 129.7, 129.5, 129.3, 128.5, 125.0, 119.7, 111.1 (dd, *J* 27.4 Hz, *J* 11.5 Hz), 109.9, 104.3 (*J* 25.3 Hz), 21.8; ^{19}F NMR: (376 MHz, $CDCl_3$) δ −106.7 (2F, s); HRMS: (ESI) found *m/z* 321.1195 $[M+H]^+$, $C_{20}H_{15}F_2N_2$ requires 321.1198.

4-(6-Methyl-2-phenyl-1*H*-benzo[*d*]imidazol-1-yl)morpholine 7k. General procedure F was followed using imidoyl chloride **5c** (100 mg, 0.4 mmol) and 4-aminomorpholine **10i** (60 µL, 0.6 mmol) and heated in the microwave for 30 min at 50 °C then for 2 h at 135 °C. Column chromatography (petrol/diethyl ether 1:1) and recrystallization from diethyl ether afforded **7k** as a white crystalline solid (52 mg, 47%); mp: 169-170 °C; IR: (neat, ν_{max}/cm^{-1}) 3024, 2961, 2899, 2859, 1602, 1580, 1521, 1473, 1456, 1445; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.12-8.07 (2H, m), 7.70 (1H, d, *J* 8.2 Hz), 7.53-7.43 (4H, m), 7.12 (1H, d, *J* 8.2 Hz), 4.07-3.96 (4H, m), 3.86-3.73 (2H, m), 3.14-3.07 (2H, m), 2.53 (3H, s); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 151.2, 139.8, 133.0, 132.7, 129.9, 129.6, 129.4, 128.1, 124.1, 120.4, 111.6, 67.0, 52.8, 21.9; HRMS: (ESI) found *m/z* 294.1603 $[M+H]^+$, $C_{18}H_{20}N_3O$ requires 294.1601.

1-Benzyl-4-methyl-2-phenyl-1*H*-benzo[*d*]imidazole 7l. General procedure F was followed using imidoyl chloride **5d** (200 mg, 0.8 mmol) and benzylamine **10a** (0.1 mL, 1.1 mmol) and heated in the microwave for 30 min at 50 °C then for 2 h at 135 °C. Column chromatography (petrol/diethyl ether 3:1) afforded **7l** as a yellow solid (205 mg, 91%). Spectral data are consistent with those in the literature.[30]

1-Benzyl-2-phenyl-1*H*-benzo[*d*]imidazole-6-carbonitrile 7m. General procedure F was followed using imidoyl chloride **5e** (200 mg, 0.7 mmol) and benzylamine **10a** (0.1 mL, 1.1 mmol) and heated in the microwave for 30 min at 50 °C then 2 h at 135 °C. Column chromatography (petrol/diethyl ether 2:1) afforded **7m** as a yellow crystalline solid (105 mg, 47%). mp: 161-163 °C; IR: (neat, ν_{max}/cm^{-1}) 3020, 2226, 1606, 1579, 1517, 1497, 1461; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.88 (1H, d, *J* 8.3 Hz), 7.70 (2H, d, *J* 7.5 Hz), 7.56-7.44 (5H, m),

7.30-7.30 (3H, m), 7.07 (2H, d, *J* 7.1 Hz), 5.48 (2H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 157.4, 146.1, 135.6, 135.2, 130.7, 129.3, 129.3, 129.0, 129.0, 128.3, 126.2, 125.9, 120.9, 119.8, 115.4, 105.7, 48.7; HRMS: (ESI) found *m/z* 310.1329 $[M+H]^+$, $C_{21}H_{16}N_3$ requires 310.1339.

1-(1-Benzyl-2-phenyl-1*H*-benzo[*d*]imidazol-5-yl)ethanone 7n. General procedure F was followed using imidoyl chloride **5f** (100 mg, 0.3 mmol) and benzylamine **10a** (0.06 mL, 0.5 mmol) and heated in the microwave for 30 min at 50 °C then 2 h at 135 °C. Column chromatography (petrol/ethyl acetate 6:1) afforded **7n** as a thick orange oil (80 mg, 71%); IR: (neat, ν_{max}/cm^{-1}) 3054, 1676, 1614, 1475, 1451, 1432, 1382, 1357, 1333; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.47 (1H, d, *J* 1.2 Hz), 7.93 (1H, dd, *J* 8.5 Hz, *J* 1.2 Hz), 7.71-7.67 (2H, m), 7.51-7.44 (3H, m), 7.36-7.29 (3H, m), 7.24 (1H, d, *J* 8.5 Hz), 7.09-7.04 (2H, m), 5.48 (2H, s), 2.67 (3H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 197.9, 156.0, 142.8, 139.3, 135.8, 132.5, 130.3, 129.5, 129.2, 129.2, 128.9, 128.0, 125.9, 123.3, 121.5, 110.5, 48.5, 26.7; HRMS: (ESI) found *m/z* 327.1495 $[M+H]^+$, $C_{22}H_{19}N_2O$ requires 327.1492.

3-Benzyl-2-phenyl-3*H*-imidazo[4,5-*b*]pyridine 7o. General procedure F was followed using imidoyl chloride **5g** (100 mg, 0.4 mmol) and benzylamine **10a** (0.07 mL, 0.6 mmol) and heated in the microwave for 30 min at 50 °C then 2 h at 135 °C. Column chromatography (petrol/diethyl ether 1:1) afforded **7o** as a brown crystalline solid (57 mg, 50%); mp: 117-119 °C; IR: (neat, ν_{max}/cm^{-1}) 2923, 1597, 1470, 1451, 1418, 1381, 1296; ^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.49 (1H, d, *J* 4.6 Hz), 8.24 (1H, d, *J* 8.0 Hz), 7.73 (2H, d, *J* 7.5 Hz), 7.58-7.47 (3H, m), 7.37 (1H, dd, *J* 8.0 Hz, *J* 4.6 Hz), 7.33-7.25 (3H, m), 7.10 (2H, d, *J* 7.0 Hz) 5.66 (2H, s); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 154.1, 148.0, 145.1, 136.2, 131.1, 129.4, 129.0, 129.0, 128.8, 128.2, 127.9, 126.9, 126.5, 119.6, 47.0; HRMS: (ESI) found *m/z* 308.1161 $[M+Na]^+$, $C_{19}H_{15}N_3Na$ requires 308.1158.

1-Benzyl-6-fluoro-2-phenyl-1*H*-benzo[*d*]imidazole 7p. General procedure F was followed using imidoyl chloride **5h** (100 mg, 0.4 mmol) and benzylamine **10a** (70.0 µL, 0.6 mmol) and heated in the microwave for 30 min at 50 °C then for 2 h at 135 °C. Column chromatography (petrol/diethyl ether 3:1) afforded **7p** as pale pink crystalline solid (85 mg, 75%); mp: 132-135 °C; IR: (neat, ν_{max}/cm^{-1}) 3423, 1620, 1439, 1391, 1143, 1106; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.79 (1H, dd, *J* 8.8 Hz, *J* 4.8 Hz) 7.70-7.66 (2H, m), 7.51-7.41 (3H, m), 7.38-7.29 (3H, m), 7.12-7.02 (3H, m), 6.88 (1H, dd, *J* 8.6 Hz, *J* 2.4 Hz), 5.41 (2H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 159.7 (d, *J* 240.1 Hz), 154.9 (d, *J* 2.9 Hz), 139.6, 136.2 (d, *J* 13.0 Hz), 135.8, 130.0, 129.8, 129.2, 129.2, 128.8, 128.0, 125.9, 120.7 (d, *J* 10.0 Hz), 111.0 (d, *J* 25.2 Hz), 97.3 (d, *J* 27.5 Hz), 48.5; ^{19}F NMR: (376 MHz, $CDCl_3$) δ −118.1 (1F, s); HRMS: (ESI) found *m/z* 325.1112 $[M+Na]^+$, $C_{20}H_{15}FN_2Na$ requires 325.1111.

1-Benzyl-6-chloro-2-phenyl-1*H*-benzo[*d*]imidazole 7q. General procedure F was followed using imidoyl chloride **5i** (100 mg, 0.5 mmol) and benzylamine **10a** (70 µL, 0.6 mmol) and heated in the microwave for 30 min at 50 °C then 2 h at 100 °C. Column chromatography (petrol/ethyl acetate 7:1) afforded **7q** as a colourless crystalline solid (98 mg, 67%). mp: 159-161 °C; IR: (neat, ν_{max}/cm^{-1}) 3066, 1611, 1525, 1497, 1461, 1442, 1386, 1358, 1327; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.77 (1H, d, *J* 8.6 Hz), 7.70-7.65 (2H, m), 7.50-7.42 (3H, m), 7.38-7.31 (3H, m), 7.28 (1H, dd, *J* 8.6 Hz, *J* 1.8 Hz), 7.20 (1H, d, *J* 1.8 Hz), 7.09 (2H, d, *J* 6.8 Hz), 5.42 (2H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 155.0, 141.8, 136.7, 135.8, 130.2, 129.6, 129.2, 129.2, 128.8, 128.7, 128.0, 125.9, 123.4, 120.8, 110.6, 48.5; HRMS: (ESI) found *m/z* 319.1000 $[M+H]^+$, $C_{20}H_{16}{}^{35}ClN_2$ requires 319.0997.

1-Benzyl-2-(furan-2-yl)-1*H*-benzo[*d*]imidazole 7r. General procedure F was followed using imidoyl chloride **5j** (100 mg, 0.4 mmol) and benzylamine **10a** (70 µL, 0.6 mmol) and heated in the microwave for 30 min at 50 °C then for 2 h at 135 °C. Column chromatography

(petrol/diethyl ether 2:1) afforded **7r** as a yellow solid (88 mg, 80%). Spectral data are consistent with those in the literature.[30]

1-Benzyl-6-methyl-2-(pyridin-4-yl)-1*H*-benzo[*d*]imidazole 7s. General procedure F was followed using imidoyl chloride **5k** (200 mg, 0.8 mmol), palladium (II) acetate (18 mg, 0.08 mmol), **L3** (40 mg, 0.1 mmol) and benzylamine **10a** (0.1 mL, 1.6 mmol) and heated in the microwave at 50 °C for 30 min then 135 °C for 4 h. Column chromatography (petrol/ethyl acetate 1:3) afforded **7s** as a thick orange oil (163 mg, 72%); IR: (neat, ν_{max}/cm^{-1}) 3050, 2979, 2928, 1605, 1554, 1518, 1497, 1476, 1453, 1415; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.72 (2H, d, *J* 5.7 Hz), 7.91 (1H, d, *J* 7.9 Hz), 7.61 (2H, dd, *J* 4.5 Hz, *J* 1.5 Hz), 7.39-7.28 (6H, m), 7.10 (2H, d, *J* 7.1 Hz), 5.50 (2H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 151.1, 150.4, 143.1, 137.7, 136.3, 135.8, 129.3, 128.1, 125.8, 124.0, 123.2, 123.2, 120.5, 110.6, 48.4; HRMS: (ESI) found *m/z* 286.1336 $[M+H]^+$, $C_{19}H_{16}N_3$ requires 286.1339.

1-Benzyl-2-*tert*-butyl-1*H*-benzo[*d*]imidazole 7t. General procedure F was followed using imidoyl chloride **5l** (200 mg, 0.9 mmol) and benzylamine **10a** (0.2 mL, 1.4 mmol) and heated in the microwave for 30 min at 50 °C then for 2 h at 135 °C. Column chromatography (petrol/diethyl ether 2:1) afforded **7t** as a yellow crystalline solid (200 mg, 84%). mp: 161-163 °C; IR: (neat, ν_{max}/cm^{-1}) 3056, 3026, 2992, 2964, 2925, 2867, 1646, 1612, 1590, 1494, 1452; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.82 (1H, d, *J* 8.0 Hz), 7.32-7.20 (4H, m), 7.13 (1H, t, *J* 7.5 Hz), 7.01 (1H, d, *J* 8.1 Hz), 6.97 (2H, d, *J* 7.1 Hz), 5.62 (2H, s), 1.54 (9H, s); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 161.2, 141.8, 136.7, 136.3, 128.8, 127.5, 125.7, 122.4, 121.9, 119.5, 109.9, 48.7, 34.1, 29.8; HRMS: (ESI) found *m/z* 265.1698 $[M+H]^+$, $C_{18}H_{21}N_2$ requires 265.1699.

6-Methyl-2-phenyl-1-*p*-tolyl-1*H*-benzo[*d*]imidazole 7h and (*Z*)-methyl *N*-*p*-tolylbenzimidate 12 (Scheme 5). To a 5 mL microwave vial was added imidate **6a** (100 mg, 0.4 mmol), palladium (II) acetate (4.0 mg, 0.02 mmol), **L3** (10 mg, 0.03 mmol), *p*-toluidine

10f (62 mg, 0.6 mmol) and sodium *t*-butoxide (82 mg, 0.9 mmol). This was capped and purged with N_2 three times and BTF (1.0 mL) was then added. This was heated in a microwave for 3 h at 150 °C. After cooling to room temperature the reaction mixture was diluted with diethyl ether (2 mL) and filtered through a Celite pad, washing with diethyl ether (40 mL) and then concentrated *in vacuo*. Column chromatography (petrol/ethyl acetate 8:1) afforded benzimidazole **7h** as a pale pink crystalline solid (100 mg, 87%) (data as reported previously) and imidate **12** as a yellow oil (16 mg, 13%); ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.35-7.20 (5H, m), 6.99 (2H, d, *J* 8.0 Hz), 6.63 (2H, d, *J* 8.0 Hz), 3.98 (3H, s), 2.27 (3H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 159.1, 145.7, 131.9, 131.6, 129.7, 129.5, 129.3, 127.9, 121.5, 53.9, 20.8; LRMS (ESI) *m/z* 226.1 (100%, $[M+H]^+$).

General procedure G for the Synthesis of Benzimidazoles 7 from Imidates 6 and *N*-nucleophiles 10 (Table 3). To a 5 mL microwave vial was added imidate **6** (1.0 equiv), palladium (II) acetate (5 mol%), **L3** (7 mol%), *N*-nucleophile (1.5 equiv) and sodium *t*-butoxide (2.2 equiv). This was capped and purged with N_2 three times and anhydrous BTF (0.4 M) was then added. This was heated in a microwave for 3 h at 150 °C (unless otherwise stated). After cooling to room temperature the reaction mixture was diluted with diethyl ether and filtered through a Celite pad, washing with diethyl ether and then concentrated *in vacuo*. Purification was conducted by column chromatography.

1-(4-Methoxyphenyl)-6-methyl-2-phenyl-1*H*-benzo[*d*]imidazole 7i. General procedure G was followed using imidate **6a** (100 mg, 0.4 mmol) and *p*-anisidine **10g** (70 mg, 0.6 mmol). Column chromatography (petrol/ethyl acetate 8:1) afforded **7i** as a pink crystalline solid (104 mg, 86%). Data as reported previously.

1-(3,5-Difluorophenyl)-6-methyl-2-phenyl-1*H*-benzo[*d*]imidazole 7j. General procedure G was followed using imidate **6a** (100 mg, 0.4 mmol) and 3,5-difluoroaniline **10h** (75 mg, 0.6

mmol). Column chromatography (petrol/ethyl acetate 8:1) afforded **7j** as a pale pink crystalline solid (52 mg, 42%). Data as reported previously.

4-(6-Methyl-2-phenyl-1*H*-benzo[*d*]imidazol-1-yl)morpholine 7k. General procedure G was followed using imidate **6a** (100 mg, 0.4 mmol) and 4-aminomorpholine **10i** (60 μL, 0.6 mmol). Column chromatography (petrol/ethyl acetate 7:1) afforded **7k** as a white crystalline solid (62 mg, 56%). Data as reported previously.

5-Methoxy-2-phenyl-1-*p*-tolyl-1*H*-benzo[*d*]imidazole 7u. General procedure G was followed using imidate **6b** (100 mg, 0.4 mmol) and *p*-toluidine **10f** (58 mg, 0.6 mmol). Column chromatography (petrol/ethyl acetate 8:1) afforded **7u** as a pale yellow solid (48 mg, 42%); mp: 118-120 °C; IR: (neat, ν_{max}/cm^{-1}) 2961, 2923, 2853, 1617, 1594, 1581, 1485, 1470, 1450, 1429; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.58 (2H, d, *J* 7.2 Hz), 7.38 (1H, d, *J* 2.2 Hz), 7.35-7.26 (5H, m), 7.18 (2H, d, *J* 8.1 Hz), 7.11 (1H, d, *J* 8.8 Hz), 6.90 (1H, dd, *J* 8.8 Hz, *J* 2.2 Hz), 3.90 (3H, s), 2.44 (3H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 156.7, 152.6, 143.6, 138.5, 134.4, 132.1, 130.4, 130.1, 129.3, 129.2, 128.2, 127.0, 113.3, 110.9, 101.8, 55.8, 21.2; HRMS: (ESI) found *m/z* 315.1488 $[M+H]^+$, $C_{21}H_{19}N_2O$ requires 315.1492.

2-Phenyl-3-*p*-tolyl-3*H*-imidazo[4,5-*b*]pyridine 7v. General procedure G was followed using imidate **6c** (100 mg, 0.4 mmol) and *p*-toluidine **10f** (65 mg, 0.6 mmol). Column chromatography (petrol/ethyl acetate 8:1) afforded **7v** as a pale yellow solid (114 mg, 80%); mp: 156-158 °C; IR: (neat, ν_{max}/cm^{-1}) 3044, 1595, 1517, 1472, 1444, 1424, 1378, 1341, 1292, 1244; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.37 (1H, dd, *J* 4.8 Hz, *J* 1.4 Hz), 8.14 (1H, dd, *J* 8.0 Hz, *J* 1.4 Hz), 7.64-7.61 (2H, m), 7.38-7.23 (8H, m), 2.42 (3H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 153.4, 149.7, 144.6, 138.8, 135.2, 132.9, 130.3, 129.9, 129.7, 129.4, 128.4, 127.5, 127.3, 119.1, 21.3; HRMS: (ESI) found 286.1338 $[M+H]^+$, $C_{19}H_{16}N_3$ requires 286.1339.

6-Fluoro-2-phenyl-1-*p*-tolyl-1*H*-benzo[*d*]imidazole 7w. General procedure G was followed using imidate **6d** (100 mg, 0.4 mmol) and *p*-toluidine **10f** (61 mg, 0.6 mmol). Column

chromatography (petrol/ethyl acetate 8:1) afforded **7w** as a dark red solid (96 mg, 83%); mp: 121-123 °C; IR: (neat, ν_{max}/cm^{-1}) 3051, 1620, 1515, 1484, 1474, 1454, 1441, 1384, 1264; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.79 (1H, dd, *J* 8.8 Hz, *J* 4.8 Hz), 7.57 (2H, d, *J* 6.8 Hz), 7.36-7.28 (5H, m), 7.17 (2H, d, *J* 8.2 Hz), 7.07 (1H, td, *J* 9.2 Hz, *J* 2.4 Hz), 6.92 (1H, dd, *J* 8.7 Hz, *J* 2.4 Hz), 2.45 (3H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 160.0 (d, *J* 240.2 Hz), 153.1 (d, *J* 3.0 Hz), 139.3, 138.9, 137.5 (d, *J* 13 Hz), 134.0, 130.6, 129.8, 129.5, 129.3, 128.3, 126.9, 120.5 (d, *J* 9.9 Hz), 111.2 (d, *J* 25.2 Hz), 97.2 (d, *J* 28.0 Hz), 21.2; ^{19}F NMR: (376 MHz, $CDCl_3$) δ −118.1 (1F, s); HRMS: (ESI) found *m/z* 303.1298 $[M+H]^+$, $C_{20}H_{16}FN_2$ requires 303.1292.

2-Butyl-1-p-tolyl-1*H*-benzo[*d*]imidazole 7x. General procedure G was followed using imidate **6e** (100 mg, 0.4 mmol) and *p*-toluidine **10f** (71 mg, 0.7 mmol). Column chromatography (petrol/ethyl acetate 8:1) afforded **7x** as a white solid (75 mg, 64%); mp: 96-98 °C; IR: (neat, ν_{max}/cm^{-1}) 3057, 3038, 2948, 2925, 2864, 1614, 1584, 1519, 1511, 1476; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.80-7.76 (1H, m), 7.40-7.35 (2H, m), 7.29-7.15 (4H, m), 7.11-7.06 (1H, m), 2.78 (2H, t, *J* 7.8 Hz), 2.49 (3H, s), 1.77 (2H, quin, *J* 7.7 Hz), 1.35 (2H, sex, *J* 7.4 Hz), 0.88 (3H, t, *J* 7.3 Hz); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 155.5, 142.5, 138.9, 136.6, 133.4, 130.5, 127.1, 122.4, 122.2, 119.0, 109.9, 29.9, 27.4, 22.4, 21.2, 13.7; HRMS: (ESI) found *m/z* 265.1702 $[M+H]^+$, $C_{18}H_{21}N_2$ requires 265.1699.

2-Butyl-1-p-tolyl-1*H*-benzo[*d*]imidazole 7x. General procedure G was followed using imidate **6n** (100 mg, 0.4 mmol) and *p*-toluidine **10f** (60 mg, 0.6 mmol) and heated in the microwave for 2 h at 135 °C. Column chromatography (petrol/ethyl acetate 8:1) afforded **7x** as a white solid (110 mg, 94%). Data as reported previously.

2-Benzyl-1-*p*-tolyl-1*H*-benzo[*d*]imidazole 7y. General procedure G was followed using imidate **6f** (100 mg, 0.4 mmol) and *p*-toluidine **10f** (62 mg, 0.6 mmol). Column chromatography (petrol/ethyl acetate 8:1) afforded **7y** as an orange solid (114 mg, 80%); mp: 116-118 °C; IR: (neat, ν_{max}/cm^{-1}) 3055, 3031, 2907, 1673, 1602, 1514, 1494, 1475, 1455,

1421; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.85 (1H, d, *J* 8.0 Hz), 7.32-7.26 (3H, m), 7.24-7.15 (4H, m), 7.12-7.04 (5H, m), 4.20 (2H, s), 2.47 (3H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 153.5, 142.6, 139.0, 136.9, 136.7, 133.1, 130.3, 128.7, 128.4, 127.4, 126.6, 122.7, 122.3, 119.4, 110.2, 34.2, 21.3; HRMS: (ESI) found *m/z* 299.1543 $[M+H]^+$, $C_{21}H_{19}N_2$ requires 299.1543.

3-Benzyl-2-phenylquinazolin-4(3*H*)-one 8a and 1-Benzyl-2-phenyl-1H-benzo[*d*]imidazole 7a. **(Scheme 6)**. To a 50 mL Schlenk tube was added palladium (II) acetate (4.6 mg, 0.02 mmol), **L3** (22 mg, 0.06 mmol), cesium carbonate (326 mg, 1.0 mmol) and benzylamine **10a** (55.0 mg, 0.06 mL, 0.05 mmol) under N_2. A solution of imidoyl chloride **5m** (100 mg, 0.3 mmol) in anhydrous toluene (0.65 mL) was then added. A balloon fitted with a glass tap attachment was filled with N_2 and evacuated three times. The balloon was then filled with carbon monoxide from a lecture bottle or cylinder and attached to the top of the Schlenk tube. The inert atmosphere was then exchanged for carbon monoxide by briefly exposing the reaction vessel to vacuum (1-2 seconds) through the side arm of the Schlenk tube and filling the vessel with carbon monoxide *via* the balloon. This was performed three times. The reaction was then left under an atmosphere of carbon monoxide and stirred vigorously, heating at 85 °C for 18 h. The reaction was then allowed to cool to room temperature and the carbon monoxide balloon removed. The reaction mixture was diluted with ethyl acetate and filtered through a Celite pad, washing with ethyl acetate and DCM and then concentrated *in vacuo*. Column chromatography (petrol/ethyl acetate 8:1) afforded benzimidazole **7a** (40 mg, 40%) (data as reported previously) and **8a** as a yellow crystalline solid (33 mg, 30%); mp: 131-133 °C; IR: (neat, ν_{max}/cm^{-1}) 3281, 3033, 1675, 1603, 1584, 1567, 1521, 1494, 1474, 1433; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.41-8.37 (1H, m), 7.80-7.77 (2H, m), 7.56-7.51 (1H, m), 7.50-7.45 (1H, m), 7.44-7.33 (4H, m), 7.24-7.19 (3H, m), 6.97-6.91 (2H, m), 5.29 (2H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 162.5, 156.4, 147.3, 136.6,

135.3, 134.6, 129.9, 128.6, 128.5, 128.0, 127.6, 127.4, 127.2, 127.1, 127.0, 120.9, 48.8; HRMS: (ESI) found *m/z* 335.1148 $[M+Na]^+$, $C_{21}H_{16}N_2NaO$ requires 335.1155.

General procedure H for the Synthesis of Quinazolinones 8 from Imidates 6 and *N*-nucleophiles 10 (Table 5). To a 50 mL Schlenk tube was added palladium (II) acetate (6 mol%), **L3** (18 mol%), cesium carbonate (3.0 equiv) and *N*-nucleophile **10** (1.5-3.0 equiv) under N_2. A solution of imidate **6** (1.0 equiv) in anhydrous toluene (0.5 M) was then added. A balloon fitted with a glass tap attachment was filled with N_2 and evacuated three times. The balloon was then filled with carbon monoxide from a lecture bottle or cylinder and attached to the top of the Schlenk tube. The inert atmosphere was then exchanged for carbon monoxide by briefly exposing the reaction vessel to vacuum (1-2 seconds) through the side arm of the Schlenk tube and filling the vessel with carbon monoxide *via* the balloon. This was performed three times. The reaction was then left under an atmosphere of carbon monoxide and stirred vigorously, heating at 85 °C (unless otherwise stated) for 18 h. The reaction was then allowed to cool to room temperature and the carbon monoxide balloon removed. The reaction mixture was diluted with ethyl acetate and filtered through a Celite pad, washing with ethyl acetate and DCM and then concentrated *in vacuo*. Purification was conducted by column chromatography.

3-Benzyl-2-phenylquinazolin-4(3*H*)-one 8a. General procedure H was followed using imidate **6g** (100 mg, 0.3 mmol) and benzylamine **10a** (0.1 mL, 1.0 mmol) at 95 °C. Column chromatography (petrol/ethyl acetate 8:1) afforded **8a** as a yellow crystalline solid (63 mg, 59%). Data as reported previously.

2-Phenyl-3-*p*-tolylquinazolin-4(3*H*)-one 8b. General procedure H was followed using imidate **6g** (100 mg, 0.4 mmol) and *p*-toluidine **10f** (55 mg, 0.5 mmol). Column chromatography (petrol/diethyl ether 3:1) afforded **8b** as a white crystalline solid (88 mg, 73%). Spectral data are consistent with those in the literature.[5b]

3-(4-Methoxyphenyl)-2-phenylquinazolin-4(3*H*)-one 8c. General procedure H was followed using imidate **6g** (100 mg, 0.3 mmol) and *p*-anisidine **10g** (64 mg, 0.5 mmol). Column chromatography (petrol/ethyl acetate 8:1) afforded **8c** as a pale yellow crystalline solid (72 mg, 65%). Spectral data are consistent with those in the literature.[5b]

3-(3,5-Difluorophenyl)-2-phenylquinazolin-4(3*H*)-one 8d. General procedure H was followed using imidate **6g** (100 mg, 0.3 mmol) and 3,5-difluoroaniline **10h** (67 mg, 0.5 mmol). Column chromatography (petrol/ethyl acetate 10:1) afforded **8d** as a white crystalline solid (101 mg, 89%); mp: 227-228 °C; IR: (neat, ν_{max}/cm^{-1}) 3068, 1675, 1606, 1587, 1574, 1561, 1494, 1460, 1446, 1357; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.37-8.34 (1H, m), 7.86-7.83 (2H, m), 7.59-7.55 (1H, m), 7.39-7.28 (5H, m), 7.80-6.74 (3H, m); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 162.7 (dd, *J* 250.8 Hz, *J* 13.6 Hz), 161.8, 154.2, 147.2, 139.7 (t, *J* 12.4 Hz), 135.1, 134.7, 129.9, 128.7, 128.4, 127.9, 127.7, 127.2, 120.6, 113.2 (dd, *J* 27.7 Hz, *J* 14.1 Hz), 104.5 (t, *J* 25.2 Hz); ^{19}F NMR: (376 MHz, $CDCl_3$) δ −108.3 (2F, s); HRMS: (ESI) found *m/z* 357.0809 $[M+Na]^+$, $C_{20}H_{12}F_2N_2NaO$ requires 357.0810.

2-Phenyl-3-(pyridin-3-yl)quinazolin-4(3*H*)-one 8e. General procedure H was followed using imidate **6g** (100 mg, 0.3 mmol) and 3-aminopyridine **10j** (48 mg, 0.5 mmol) at 90 °C. Column chromatography (SiO_2, petrol/ethyl acetate 4:1) afforded **8e** as a pale yellow crystalline solid (101 mg, 89%); mp: 174-176 °C; IR: (neat, ν_{max}/cm^{-1}) 3062, 1681, 1604, 1593, 1580, 1565, 1495, 1472, 1445, 1425; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.50 (1H, br. s), 8.39 (1H, br. s), 8.33 (1H, d, *J* 8.0 Hz), 7.83 (2H, d, *J* 4.0 Hz), 7.58-7.52 (2H, m), 7.33-7.20 (6H, m); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 162.1, 154.5, 149.7, 149.2, 147.3, 136.6, 135.1, 134.7, 129.8, 129.1, 129.1, 128.4, 127.9, 127.6, 127.2, 123.5, 120.6; HRMS: (ESI) found *m/z* 322.0949 $[M+Na]^+$, $C_{19}H_{13}N_3NaO$ requires 322.0951.

2-Phenyl-3-(3-phenylpropyl)quinazolin-4(3*H*)-one 8f. General procedure H was followed using imidate **6g** (100 mg, 0.3 mmol) and 3-phenylpropylamine **10b** (0.1 mL, 1.0 mmol) at

95 °C. Column chromatography (petrol/ethyl acetate 8:1) afforded **8f** as a yellow crystalline solid (83 mg, 72%); mp: 120-123 °C; IR: (neat, ν_{max}/cm^{-1}) 3062, 3027, 2933, 1673, 1605, 1587, 1566, 1496, 1472; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.35 (1H, d, *J* 8.5 Hz), 7.79-7.72 (2H, m), 7.54-7.47 (6H, m), 7.22-7.11 (3H, m), 7.01-6.97 (2H, m), 4.04-3.99 (2H, m), 2.52 (2H, t, *J* 7.6 Hz), 1.96 (2H, quin, *J* 7.8 Hz); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 162.1, 156.1, 147.2, 140.5, 135.4, 134.3, 129.8, 128.8, 128.4, 128.0, 127.7, 127.5, 127.0, 126.8, 125.9, 120.9, 45.5, 32.9, 29.7; HRMS: (ESI) found *m/z* 341.1646 $[M+H]^+$, $C_{23}H_{21}N_2O$ requires 341.1648.

3-Cyclohexyl-2-phenylquinazolin-4(3*H*)-one 8g. General procedure H was followed using imidate **6g** (100 mg, 0.3 mmol) and cyclohexylamine **10d** (0.1 mL, 1.0 mmol) at 95 °C. Column chromatography (petrol/ethyl acetate 8:1) afforded **8g** as a pale yellow crystalline solid (56 mg, 54%). mp: 133-135 °C; IR: (neat, ν_{max}/cm^{-1}) 3033, 2935, 2857, 1672, 1605, 1586, 1567, 1497, 1474, 1454; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.29 (1H, dd, *J* 7.8 Hz, *J* 2.6 Hz), 7.74-7.66 (2H, m), 7.53-7.43 (6H, m), 3.91-3.80 (1H, m), 2.73 (2H, q, *J* 12.4 Hz), 1.82-1.64 (4H, m), 1.57-1.48 (1H, m), 1.23-1.15 (1H, m), 0.96 (2H, qd, *J* 13.0 Hz, *J* 3.2 Hz); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 162.6, 156.9, 146.8, 136.5, 134.1, 129.7, 128.9, 127.2, 127.1, 126.8, 126.5, 122.2, 62.6, 28.8, 26.2, 24.9; HRMS: (ESI) found *m/z* 327.1470 $[M+Na]^+$, $C_{20}H_{20}N_2NaO$ requires 327.1468.

2-Phenyl-3-(thiophen-2-ylmethyl)quinazolin-4(3*H*)-one 8h. General procedure H was followed using imidate **6g** (100 mg, 0.3 mmol) and 2-thiophenemethylamine **10e** (0.1 mL, 1.0 mmol) at 95 °C. Column chromatography (petrol/ethyl acetate 8:1) afforded **8h** as a pale yellow crystalline solid (73 mg, 67%); mp: 130-132 °C; IR: (neat, ν_{max}/cm^{-1}) 3064, 1671, 1605, 1586, 1566, 1496, 1472, 1445, 1426, 1378; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.39 (1H, d, *J* 8.0 Hz), 7.79-7.72 (2H, m), 7.56-7.47 (6H, m), 7.17 (1H, dd, *J* 5.1 Hz, *J* 1.0 Hz), 6.84 (1H, m), 6.61 (1H, d, *J* 3.1 Hz), 5.38 (2H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 162.2, 155.7, 147.1,

138.2, 135.0, 134.6, 130.1, 128.8, 128.3, 127.6, 127.3, 127.2, 127.0, 126.3, 126.0, 120.9, 44.1; HRMS: (ESI) found *m/z* 341.0716 $[M+Na]^+$, $C_{19}H_{14}N_2NaOS$ requires 341.0719.

3-Allyl-2-phenylquinazolin-4(3*H*)-one 8i. General procedure H was followed using imidate **6g** (100 mg, 0.3 mmol) and allylamine **10k** (40 μL, 0.5 mmol). Column chromatography (petrol/ethyl acetate 7:1) afforded **8i** as a yellow crystalline solid (36 mg, 41%); mp: 79-81 °C; IR: (neat, ν_{max}/cm^{-1}) 3059, 2927, 1679, 1603, 1583, 1566, 1495, 1472, 1445, 1425; ^1H NMR: (400 MHz, $CDCl_3$) δ 8.35 (1H, d, *J* 7.9 Hz), 7.79-7.74 (2H, m), 7.57-7.46 (6H, m), 5.93-5.82 (1H, m), 5.17 (1H, dd, *J* 10.4 Hz, *J* 1.0 Hz), 4.94 (1H, dd, *J* 17.2 Hz, *J* 0.9 Hz), 4.63-4.58 (2H, m); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 162.0, 156.3, 147.2, 135.2, 134.4, 132.2, 130.0, 128.6, 128.0, 127.5, 127.1, 126.9, 120.8, 117.5, 48.2; HRMS: (ESI) found *m/z* 285.1000 $[M+Na]^+$, $C_{17}H_{14}N_2NaO$ requires 285.0998.

6,8-Dimethyl-2-phenyl-3-*p*-tolylquinazolin-4(3*H*)-one 8j. General procedure H was followed using imidate **6h** (100 mg, 0.3 mmol) and *p*-toluidine **10f** (51 mg, 1.0 mmol) at 95 °C. Column chromatography (petrol/ethyl acetate 8:1) afforded **8j** as a white crystalline solid (78 mg, 81%); mp: 207-209 °C; IR: (neat, ν_{max}/cm^{-1}) 3054, 1676, 1616, 1590, 1564, 1512, 1494, 1475, 1446, 1379; ^1H NMR: (400 MHz, $CDCl_3$) δ 8.01 (1H, s), 7.49 (1H, s), 7.40 (2H, d, *J* 7.4 Hz), 7.29-7.19 (3H, m), 7.13 (2H, d, *J* 8.1 Hz), 7.05 (2H, d, *J* 8.1 Hz), 2.66 (3H, s), 2.49 (3H, s), 2.33 (3H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 162.9, 152.8, 144.1, 138.1, 136.8, 136.7, 136.0, 135.4, 129.6, 129.4, 129.4 129.0, 128.8, 127.7, 124.2, 120.6, 21.4, 21.2, 17.3; HRMS: (ESI) found *m/z* 341.1646 $[M+H]^+$, $C_{23}H_{21}N_2O$ requires 341.1648.

7-Methoxy-2-phenyl-3-*p*-tolylquinazolin-4(3*H*)-one 8k. General procedure H was followed using imidate **6i** (100 mg, 0.3 mmol) and *p*-toluidine **10f** (50 mg, 0.5 mmol) at 90 °C. Column chromatography (petrol/ethyl acetate 8:1) afforded **8k** as a pale pink crystalline solid (76 mg, 71%); mp: 217-219 °C; IR: (neat, ν_{max}/cm^{-1}) 3060, 3037, 2921, 1674, 1613, 1591, 1561, 1513, 1484, 1445; ^1H NMR: (400 MHz, $CDCl_3$) δ 8.24 (1H, d, *J* 8.8 Hz), 7.37-7.33

(2H, m), 7.28-7.19 (4H, m), 7.12-7.07 (3H, m), 7.05-7.00 (2H, m), 3.93 (3H, s), 2.30 (3H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 164.8, 161.9, 156.1, 149.7, 138.2, 135.7, 135.0, 129.6, 129.2, 128.9, 128.8, 128.8, 128.0, 117.3, 114.4, 108.3, 55.7, 21.1; HRMS: (ESI) found *m/z* 343.1440 $[M+H]^+$, $C_{22}H_{19}N_2O_2$ requires 343.1441.

Methyl 4-oxo-2-phenyl-3-*p*-tolyl-3,4-dihydroquinazoline-6-carboxylate 8l. General procedure H was followed using imidate **6j** (100 mg, 0.3 mmol) and *p*-toluidine **10f** (46 mg, 0.4 mmol). Column chromatography (petrol/ethyl acetate 8:1) afforded **8l** as a pale pink crystalline solid (82 mg, 76%); mp: 229-232 °C; IR: (neat, ν_{max}/cm^{-1}) 3035, 2952, 1721, 1688, 1605, 1587, 1554, 1512, 1495, 1436; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 9.00 (1H, d, *J* 1.9 Hz), 8.40 (1H, dd, *J* 8.5 Hz, *J* 1.9 Hz), 7.83 (1H, d, *J* 8.5 Hz), 7.38-7.34 (2H, m), 7.28-7.20 (3H, m), 7.12 (2H, d, *J* 8.2 Hz), 7.03 (2H, d, *J* 8.2 Hz), 3.96 (3H, s), 2.31 (3H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 166.0, 161.9, 157.3, 150.5, 138.6, 135.2, 134.9, 134.7, 129.7, 129.7, 129.6, 129.0, 128.6, 128.6, 128.0, 128.0, 120.7, 52.4, 21.2; HRMS: (ESI) found *m/z* 371.1389 $[M+H]^+$, $C_{23}H_{19}N_2O_3$ requires 371.1390.

2-Phenyl-3-*p*-tolylpyrido[3,2-*d*]pyrimidin-4(3*H*)-one 8m. General procedure H was followed using imidate **6k** (100 mg, 0.3 mmol) and *p*-toluidine **10f** (55 mg, 0.5 mmol). Column chromatography (petrol/ethyl acetate 4:1) afforded **8m** as a brown solid (95 mg, 90%); mp: 219-221 °C; IR: (neat, ν_{max}/cm^{-1}) 3060, 2922, 1705, 1640, 1606, 1573, 1555, 1511, 1495, 1495; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.93 (1H, dd, *J* 4.3 Hz, *J* 1.4 Hz), 8.16 (1H, dd, *J* 8.3 Hz, *J* 1.5 Hz), 7.73 (1H, dd, *J* 8.3 Hz, *J* 4.3 Hz), 7.31-7.22 (5H, m), 7.15-7.11 (2H, m), 7.07-7.03 (2H, m), 2.32 (3H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 160.9, 156.4, 150.1, 144.2, 138.7, 137.8, 136.0, 135.1, 134.6, 129.8, 129.5, 128.9, 128.7, 128.6, 128.0, 21.2; HRMS: (ESI) found *m/z* 336.1101 $[M+Na]^+$, $C_{20}H_{15}N_3NaO$ requires 336.1107.

6-Fluoro-2-phenyl-3-*p*-tolylquinazolin-4(3*H*)-one 8n. General procedure H was followed using imidate **6l** (100 mg, 0.3 mmol) and *p*-toluidine **10f** (52 mg, 0.5 mmol). Column

chromatography (petrol/ethyl acetate 8:1) afforded **8n** as a pale pink crystalline solid (60 mg, 58%); mp: 207-209 °C; IR: (neat, ν_{max}/cm^{-1}) 3054, 1693, 1679, 1622, 1590, 1565, 1512, 1485, 1446, 1346; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.98 (1H, dd, *J* 8.4 Hz, *J* 3.0 Hz), 7.83 (1H, dd, *J* 8.9 Hz, *J* 4.8 Hz), 7.55-7.50 (1H, m), 7.37-7.32 (2H, m), 7.29-7.20 (3H, m), 7.14-7.10 (2H, m), 7.05-7.01 (2H, m), 2.31 (3H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 161.7 (d, *J* 3.4 Hz), 161.1 (d, *J* 248.7 Hz), 154.7 (d, *J* 2.2 Hz), 144.2, 138.5, 135.3, 134.8, 130.1 (d, *J* 8.4 Hz), 129.7, 129.3, 129.0, 128.6, 128.0, 123.2 (d, *J* 24.2 Hz), 122.3 (d, *J* 8.8 Hz), 112.0 (d, *J* 23.8 Hz), 21.2; ^{19}F NMR: (376 MHz, $CDCl_3$) δ −112.1 (1F, s); HRMS: (ESI) found *m/z* 331.1237 $[M+H]^+$, $C_{21}H_{16}FN_2O$ requires 331.1241.

6-Chloro-2-phenyl-3-*p*-tolylquinazolin-4(3*H*)-one 8o. General procedure H was followed using imidate **6m** (100 mg, 0.3 mmol) and *p*-toluidine **10f** (50 mg, 0.5 mmol). Column chromatography (petrol/ethyl acetate 9:1) afforded **8o** as a pale pink crystalline solid (82 mg, 74%); mp: 234-236 °C; IR: (neat, ν_{max}/cm^{-1}) 3326, 2962, 2920, 1685, 1599, 1586, 1549, 1511, 1491, 1471; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.31 (1H, d, *J* 2.2 Hz), 7.78-7.70 (2H, m), 7.37-7.32 (2H, m), 7.29-7.20 (3H, m), 7.12 (2H, d, *J* 8.2 Hz), 7.02 (2H, d, *J* 8.2 Hz), 2.31 (3H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 161.4, 155.6, 146.0, 138.6, 135.3, 135.1, 134.7, 132.9, 129.7, 129.4, 129.4, 129.0, 128.6, 128.0, 126.5, 122.0, 21.2; HRMS: (ESI) found *m/z* 347.0949 $[M+H]^+$, $C_{21}H_{16}{}^{35}ClN_2O$ requires 347.0946.

2-Butyl-3-*p*-tolylquinazolin-4(3*H*)-one 8p. General procedure H was followed using (*Z*)-methyl imidate **6m** (100 mg, 0.4 mmol) and *p*-toluidine **10f** (60 mg, 0.6 mmol). Column chromatography (petrol/ethyl acetate 9:1) afforded **8p** as a pink crystalline solid (80 mg, 71%); mp: 112-113 °C; IR: (neat, ν_{max}/cm^{-1}) 3053, 2961, 2873, 1680, 1593, 1570, 1511, 1473, 1421, 1380; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.27 (1H, d, *J* 7.9 Hz), 7.77-7.68 (2H, m), 7.46-7.41 (1H, m), 7.34 (2H, d, *J* 8.2 Hz), 7.14 (2H, d, *J* 8.2 Hz), 2.47-2.42 (5H, m), 1.68 (2H, quin, *J* 7.7 Hz), 1.26 (2H, sex, *J* 7.5 Hz), 0.82 (3H, t, *J* 7.4 Hz); ^{13}C NMR: (100 MHz,

$CDCl_3$) δ 162.6, 157.4, 147.6, 139.2, 134.7, 134.4, 130.5, 128.0, 127.0, 127.0, 126.4, 120.7, 35.5, 29.3, 22.3, 21.3, 13.7; HRMS: (ESI) found 293.1643 $[M+H]^+$, $C_{19}H_{21}N_2O$ requires 293.1648.

2-Benzyl-3-*p*-tolylquinazolin-4(3*H*)-one 8q. General procedure H was followed using imidate **6o** (100 mg, 0.3 mmol) and *p*-toluidine **10f** (53 mg, 0.5 mmol). Column chromatography (petrol/ethyl acetate 9:1) afforded **8q** as a yellow crystalline solid (72 mg, 67%); mp: 204-208 °C; IR: (neat, ν_{max}/cm^{-1}) 3304, 3031, 2922, 1685, 1608, 1592, 1568, 1510, 1496, 1472; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.29 (1H, d, *J* 7.9 Hz), 7.81-7.78 (2H, m), 7.52-7.47 (1H, m), 7.22-7.14 (5H, m), 6.94-6.89 (2H, m), 6.85 (2H, d, *J* 8.2 Hz), 3.93 (2H, s), 2.42 (3H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 162.7, 155.6, 147.4, 139.2, 135.5, 134.5, 134.2, 130.0, 128.6, 128.3, 128.3 127.3, 127.1, 126.9, 126.8, 120.9, 42.6, 21.3; HRMS: (ESI) found *m/z* 327.1491 $[M+H]^+$, $C_{22}H_{19}N_2O$ requires 327.1492.

Acknowledgements

We thank the EPSRC and Pfizer for support of this study.

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra for all compounds obtained. This material is available free of charge via the Internet at http://pubs.acs.org.

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