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Intramolecular direct arylation in the synthesis of fluorinated carbazoles

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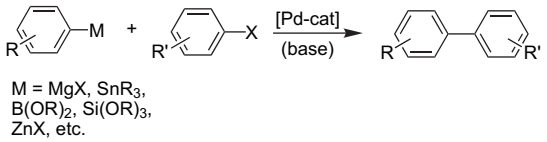
Abstract

The amination of 2-chloroanilines with aryl bromides and subsequent intramolecular direct arylation can be exploited in the synthesis of a range of fluorinated carbazoles, where the fluorine substituent can be introduced via the aniline, the aryl bromide or both substrates. Depending on substitution patterns, the two steps can either be performed in tandem in one-pot under microwave heating conditions or else require a two pot approach.

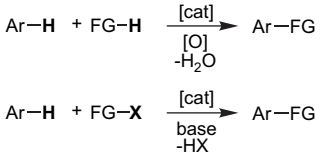
1. Introduction

Catalytic aromatic C–H activation is rapidly establishing itself as a viable alternative to classical, transition metal-catalysed cross-coupling reactions of the general type shown in Scheme 1.[1] This is not least because it obviates the need to introduce an organometallic group onto the nucleophilic substrate.



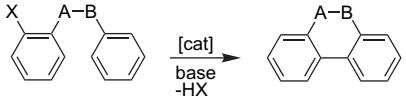
Scheme 1. Cross-coupling reactions.

Two general protocols are exploited in these processes; the first is to use oxidative coupling,[2,3] and the second relies on the oxidative addition of an organic halide (Scheme 2), the so called direct arylation reaction. The first class of reaction is obviously more atom-economical than the second—providing that the oxidant is oxygen—which renders the process more attractive from both environmental and commercial perspectives. However, this oxidative approach can lack the selectivity inherent in the second reaction type and often the use of more complex oxidants can detract from the atom economy of the process.



Scheme 2. Aromatic C–H functionalisation.

A well-developed class of reaction that proceeds via the second methodology outlined in Scheme 2 is the synthesis of heterocycles (and carbocycles) from 'tethered' biaryl substrates (Scheme 3); the intramolecular direct arylation reaction.



Scheme 3. Intramolecular direct arylation.

Scheme 4 shows a generalised reaction pathway for the annulation step; the crux of this is the formation of a palladacyclic intermediate via C–H activation. The mechanism of this step has been the subject of recent studies and current models favour a base-assisted deprotonation mechanism over the

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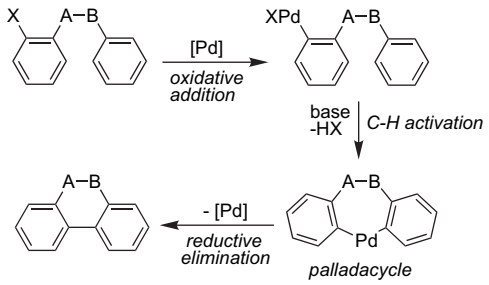
traditional extremes of C–H oxidative addition or electrophilic displacement.[4]



Scheme 4. Generalised reaction pathway for intramolecular direct arylation.

Over 20 years ago Ames and Opalko exploited this methodology in the synthesis of a range of five- and six-membered heterocycles such as dibenzofurans, carbazoles, quinolinones and pyranones.[5] This procedure was subsequently used in the synthesis of the benzylated forms of defucogilocarcins M and E, **1**;[6] and compounds **2** and **3**, intermediates in the syntheses of dioncophylline A and mastigophorene B, respectively (Fig. 1).[7,8]

More recently Sakamoto and co-workers employed a two-step method for the synthesis of carbolines from bromoaminopyridines and iodobenzene (Scheme 5) via sequential catalytic amination and arylation. Each step required different catalysts, bases and conditions.[9]

Maes and co-workers reported a related methodology for the synthesis of indoloquinolines possessing anti-malarial activity.[10] Microwave heating was used to facilitate the reaction

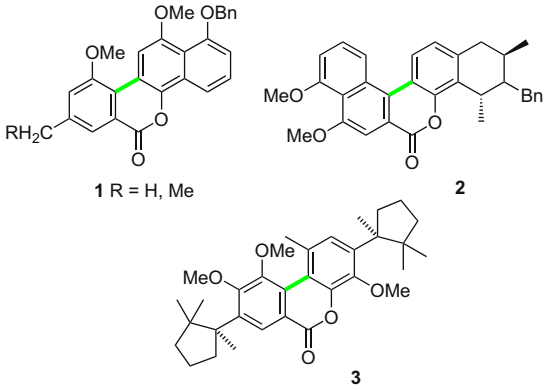
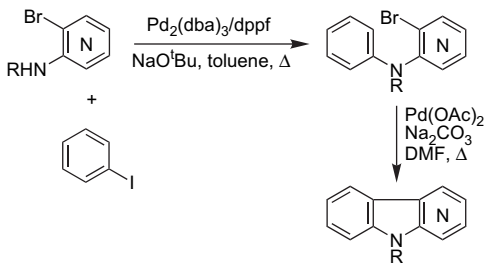
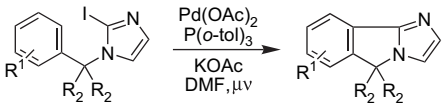


Figure 1. Natural products with pyranone structures formed by C–H activation; the bonds formed during the annulation are highlighted.



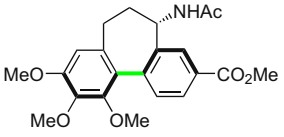
Scheme 5. Synthesis of carbolines via sequential amination and C–H activation.

but careful studies revealed no special 'microwave effect' rather that it is simply a more convenient way of performing higher temperature reactions. More recently Dubois and co-workers demonstrated that intramolecular arylation can be used to produce a wide range of imidazo[2,1-*a*]isoindoles from *N*-benzyl iodoimidazoles (Scheme 6) using microwave heating.[11]



Scheme 6. Microwave-assisted synthesis of imidazo[2,1-*a*]isoindoles.

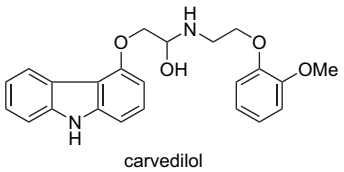
Whilst most of the syntheses via intramolecular direct arylation published to date produce five- or six-membered rings, Leblanc and Fagnou reported an elegant formal synthesis of allocochicine, **4**, in which the annulative step yields a seven-membered ring.[12] The formation of five- and six-membered rings proceeds via six- and seven-membered palladacyclic intermediates; presumably in this case a far less favourable eight-membered palladacycle is formed.



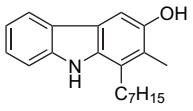
Allocolchicine, **4**, highlighted bond formed by C-H activation

All of the reactions described so far rely on soluble palladium-based pre-catalysts, however, Fagnou and co-workers showed that palladium hydroxide on carbon can be used to good effect in the intramolecular arylation of both bromide and iodide-containing substrates. They concluded that the reactions were not in fact catalysed by a heterogeneous catalyst, but rather by active homogeneous species formed in situ.[13]

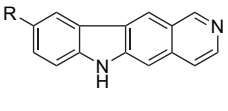
Carbazoles are important structural motifs found in pharmaceuticals, natural products, agrochemicals and dyes.[14,15] For instance, carvedilol is a beta-blocker used in the treatment of hypertension and angina whilst carazostatin is one of a family of carbazoles produced by bacteria that are potent free radical scavengers and act as anti-oxidants. Ellipticine and its derivatives, in particular 9-hydroxyellipticine, show potent anti-tumour activity.



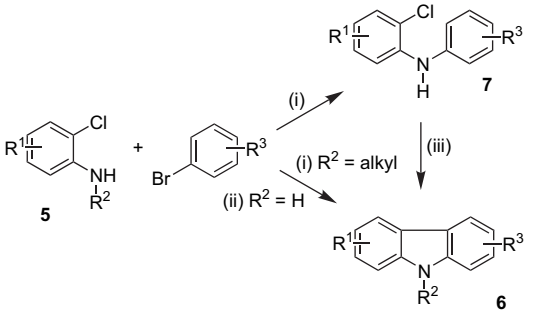
carvedilol



carazostatin



R = H, ellipticine;
R = OH, 9-hydroxyellipticine



Scheme 7. Pd-P^{t}Bu$_3$ catalysed formation of carbazoles by sequential amination; C–H activation reactions. Conditions: (i) reflux in toluene; (ii) microwave heating in toluene; (iii) reflux in 1,4-dioxane.

We have investigated producing carbazoles by exploiting sequential catalytic amination and annulation via C–H activation, using 2-chloroanilines and aryl bromides as starting materials. This choice of precursors reflects their lower costs and greater commercial availability compared with heavier congeners. Unfortunately, the aryl chloride substrates are electronically highly deactivated, due to the presence of an *ortho*-amine function, and represent a significant challenge.[16,17] We found that palladium catalysts with tri-*tert*-butylphosphine are sufficiently reactive to overcome this problem (Scheme 7). Where R^2 is a methyl or a benzyl group then the reaction proceeds in toluene at reflux temperature in one-pot.[18] By contrast the synthesis of 9-H carbazoles, that is to say when R^2=H, is more problematic and requires either significantly higher temperature, typically obtained using microwave heating, or the splitting of the reaction into two steps.[19] The first step is performed in toluene whilst the second requires dioxane as the solvent. The one-step, microwave heating processes appears to be more suited to aryl bromides with *ortho*-substituents.

The replacement of a hydrogen with a fluorine atom can have a profound influence on a molecule's physical, chemical and biological properties and this has been exploited in pharmaceutical, agrochemical and materials' production.[20,21] Accordingly we were interested to see whether our carbazole synthesis could be exploited for the synthesis of fluorinated examples and the results of this study are reported below.[22]

2. Results and discussion

2.1. One-step synthesis of fluorocarbazoles

Due to the more convenient nature of the one-step, microwave heating protocol outlined in Scheme 7, we first explored the potential of this route in the production of fluorocarbazoles from fluorinated 2-chloranilines; the results from this study are summarised in Table 1. The catalyst system and conditions employed are the same as those optimised previously.[19] The phosphonium salt [HP^{t}Bu$_3$][BF$_4$] was used in place of the free phosphine due to the latter's air-sensitivity.[23]

Examining entries 1–7 it can be seen that with 2-chloro-4-fluoroaniline as substrate reasonable yields of the desired carbazoles **6a–g** are obtained in one-step when 2-substituted aryl bromides are used as coupling partners. In most of these cases little or no aminated intermediate **7** is observed in the ^{1}H NMR spectra of the crude product mixtures obtained before isolation of the carbazole, with the exception of the reaction shown in entry 5 using 2,4-dimethoxy bromobenzene as substrate where nearly 30% of the product mixture is intermediate diarylamine **7e**. 3,5-Dimethoxy bromobenzene gives a reasonable amount of the carbazole **6h** (entry 8), despite the absence of *ortho*-substitution, but again ^{1}H NMR of the crude mixture reveals the presence of significant amounts of the non-cyclised intermediate, **7h**. The other *meta*-disubstituted aryl bromides investigated, 3,5-di-*tert*-butyl and 3,5-dimethyl bromobenzene, gave poor yields of the desired carbazole with the major component in the crude product mixtures being the aminated intermediates (entries 8 and 9).

Similarly a very low yield of the carbazole **6k** is obtained in the coupling of 3,5-dimethyl bromobenzene with 2-chloro-6-fluoroaniline (entry 11), although in this case ^{1}H NMR of the crude reaction mixture shows very little aminated intermediate either. Again *ortho*-substituted aryl bromides gave reasonable amounts of the carbazole product using this aniline (entries 12 and 13) as does 4-bromotoluene (entry 14). In these cases little or no aminated intermediate is obtained.

The use of 2-chloro-5-fluoroaniline typically leads to poor activity, even with *ortho*-functionalised aryl bromide substrates (entries 15–17), with the exception of 1-bromonaphthalene (entry 18), which gives a good yield of the carbazole. Interesting a small, but significant amount of a second isomer, **6p**, is seen in entry 15. This implies some palladium migration by an as yet unknown mechanism, after oxidative addition of the carbon–chlorine bond. We have observed a similar isomerisation previously.[19]

Using 1-bromonaphthalene with either 2-chloro-4-fluoro- or 2-chloro-6-fluoroaniline yields the desired carbazoles (**6g** and **6m**, entries 7 and 13, respectively), but the latter reaction also generates significant amounts of a second, incompletely characterised product **8** (ratio **6m/8**=5:1).[24] It is tempting to conclude on the limited data in hand that this second species is 8-fluoro-7*H*-benzo[*k*,*l*]acridine formed by competitive C–H activation in the 8-position of the naphthyl group.

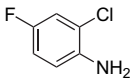
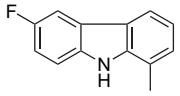
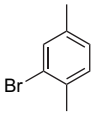
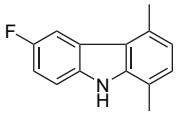
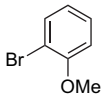
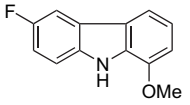
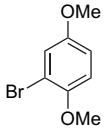
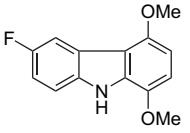
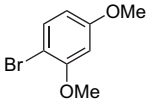
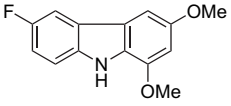
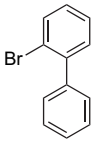
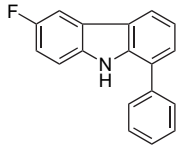
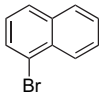
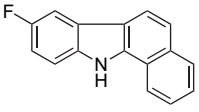
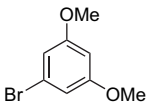
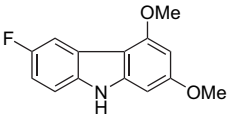
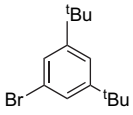
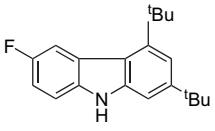
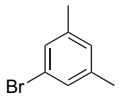
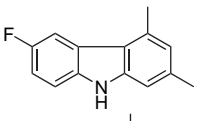
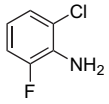
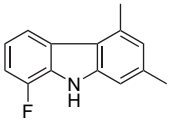
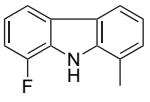
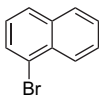
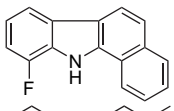
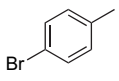
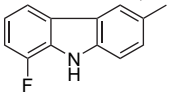
The one-pot methodology can also be used to introduce the fluorine atom via the aryl bromide. Thus 2-chloro-6-methylaniline reacts with 2-, 3- and 4-fluorobromobenzene to generate the desired carbazoles (entries 19–21). In the case of 3-fluorobromobenzene (entry 20) the two carbazoles **6o** and **6p** are formed in an approximately 1.4:1 ratio.

When all the data are taken together it is apparent that the one-step methodology works well for most *ortho*-substituted aryl bromides but can fail for other substitution patterns. This is particularly apparent when 3,5-dimethyl bromobenzene is used as a substrate. Therefore we next examined the application of a two-step methodology, where the aminated intermediate is isolated first and then subjected to ring-closing.

2.2. Two-step synthesis of fluorocarbazoles

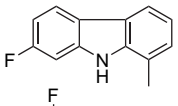
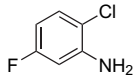
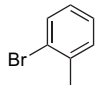
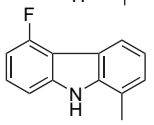
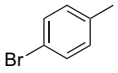
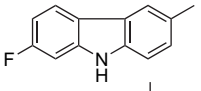
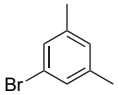
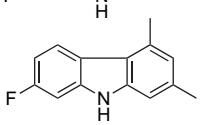
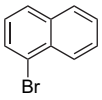
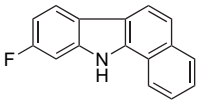
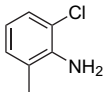
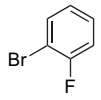
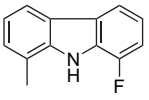
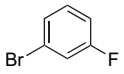
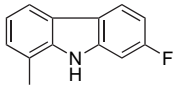
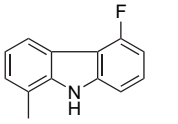
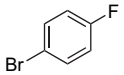
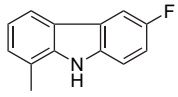
In the first instance we performed a brief optimisation study on the ring-closing of the intermediate **7u**, formed by the

Table 1
The one-pot synthesis of fluorinated carbazoles[a]

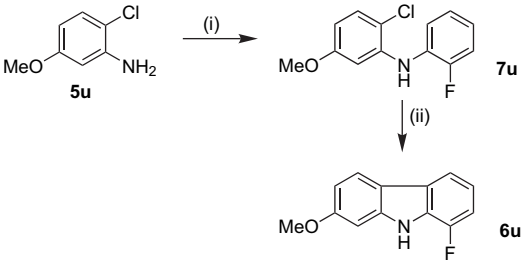
Entry	Chloroaniline	Aryl bromide	Product	Approx. ratio of product to aminated intermediates	Isolated yield of carbazole (%)
1			 **6a**	No intermediate observed	70
2			 **6b**	21:1	44
3			 **6c**	No intermediate observed	20 (65)[b]
4			 **6d**	12:1	64
5			 **6e**	2.5:1	62
6			 **6f**	9:1	44
7			 **6g**	12:1	61
8			 **6h**	5:2	53
9			 **6i**	1.5:2	21 (25)[b]
10			 **6j**	1:7	6
11			 **6k**		10
12			 **6l**	No intermediate observed	45
13			 **6m**	No intermediate observed Crude product contains second species **8** Ratio of **6m/8** in crude product=~5:1	56
14			 **6n**	7:1	23 (65)[b]

(*continued on next page*)

Table 1 (*continued*)

Entry	Chloroaniline	Aryl bromide	Product	Approx. ratio of product to aminated intermediates	Isolated yield of carbazole (%)
			 **6o**		
15			 **6p**	2:1 **6o/6p**=5:1	27 (30)[b]
16			 **6q**	1:4	24 (25)[b]
17			 **6r**	4:1	14 (24)[b]
18			 **6s**	No intermediate observed	77
19			 **6l**	No intermediate observed	37 (73)[b]
20			 **6o**  **6p**	No intermediate observed **6o/6p**=~1.4:1	62 **6o/6p**=~1.3:1
21			 **6t**	2.5:1	35 (65)[b]

[a] Conditions: fluoro-2-chloroaniline (0.5 mmol), aryl bromide (0.5 mmol), $Pd(OAc)_2$ (5 mol %), $[HP^tBu_3][BF_4]$, (7 mol %), NaO^tBu (2.5 mmol), μν, 160 °C, 3 h.
[b] Number in parentheses refers to spectroscopic yield in crude product mixture, determined by ^1H NMR (1,3,5-$MeO_3C_6H_3$ internal standard).



Scheme 8. Conditions: (i) **5u** (1 mmol), 2-FC_6H_4Br (1 mmol), NaO^tBu (5 mmol), $Pd(OAc)_2$ (5 mol %), $[HP^tBu_3][BF_4]$ (7 mol %), toluene, Δ, 18 h. (ii) **7u** (0.5 mmol), Pd complex (5 mol %), ligand (7 mol %), base (2.5 mmol), solvent (3 ml), Δ, 18 h—see Table 2 for catalysts, solvents and bases.

amination of 2-chloro-5-methoxyaniline with 2-fluorobromobenzene, according to Scheme 8. The results of the optimisation study are summarised in Table 2.

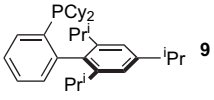
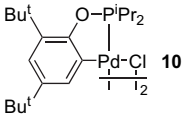
The aminated intermediate product **7u** contains an aryl chloride function, which is highly deactivated with respect to oxidative addition as it contains both an *ortho*-amino and *para*-methoxy function. Therefore it is not surprising that the best conversion to carbazole **6u** is only 61%, obtained with tri-*tert*-butylphosphine in 1,4-dioxane (entry 1). Comparing entries 1 and 2, it is interesting to note that the palladium source can have a profound influence on catalyst performance. The use of tricyclohexylphosphine, XPhos (**9**) or the palladacyclic catalyst **10** leads to a substantial diminution in catalyst activity as does changing the solvent or the base.

Having established the best catalyst and conditions, these were then used in the two-step couplings shown in Scheme 9. The structure of one example (**6w**) was determined by single crystal X-ray analysis and the molecule is shown in Figure 2. Interestingly there are no NH···F hydrogen bonding interactions apparent in the structure.

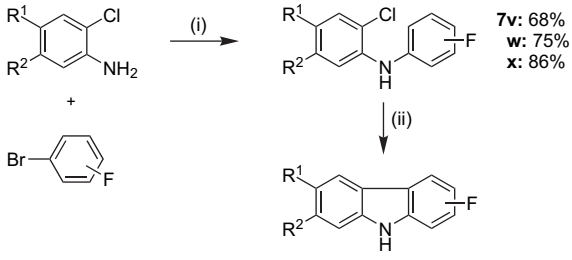
The methodology can be extended further to allow fluorine to be introduced both on the chloroaniline and aryl bromide substrates, as demonstrated by the synthesis of carbazole **6x** (Scheme 9). In this case we see very little aminated intermediate in the crude product mixture, but do observe substantial amounts of bis(4-fluorophenyl)amine (ratio of **6x**/diarylamine=1:1.1).

Next we examined the introduction of a single fluorine atom via the chloroaniline substrate. Firstly we investigated

Table 2
Optimisation of the annulation of **7u**

Entry	Pd source	Phosphine	Solvent	Base	Conversion[a] (%)
1	$Pd(OAc)_2$	$[HP^tBu_3][BF_4]$	1,4-Dioxane	NaO^tBu	61
2	$Pd_2(dba)_3$				12
3	$Pd(OAc)_2$	PCy_3			2
4		 **9**			12
5	 **10**	No ligand			9
6	$Pd(OAc)_2$	$[HP^tBu_3][BF_4]$	Toluene		20
7			DMF		0
8			1,4-Dioxane	Cs_2CO_3	22
9				K_3PO_4	3
10				NEt_3	2

[a] Determined by ^1H NMR spectroscopy (1,3,5-$MeOC_6H_3$ internal standard).



Scheme 9. Conditions: (i) **5** (1 mmol), ArBr (1 mmol), NaO^tBu (5 mmol), $Pd(OAc)_2$ (5 mol %), $[HP^tBu_3][BF_4]$ (7 mol %), toluene, Δ, 18 h. (ii) **7** (0.5 mmol), $Pd(OAc)_2$ (5 mol %), $[HP^tBu_3][BF_4]$ (7 mol %), NaO^tBu (2.5 mmol), 1,4-dioxane, Δ, 18 h.

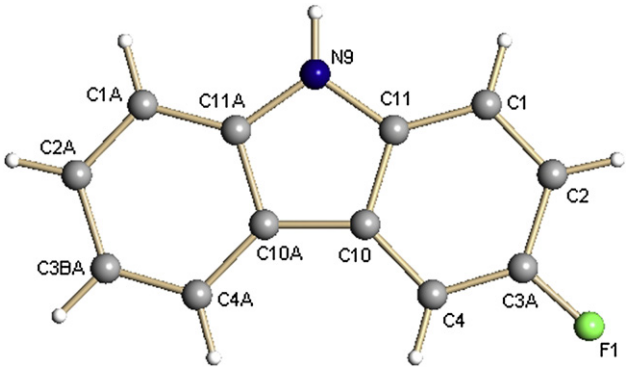
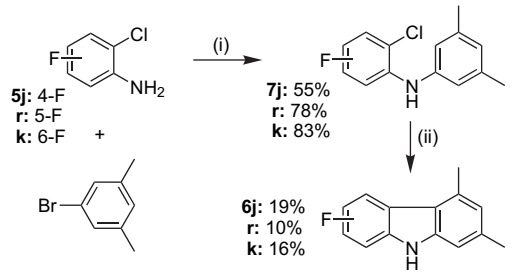


Figure 2. Crystal structure of carbazole **6w**, disorder not shown.

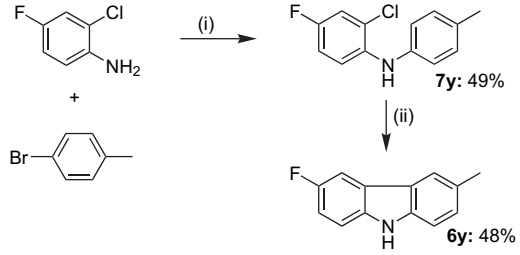
the coupling of 3,5-dimethyl bromobenzene with 4-, 5- and 6-fluoro-2-chloroanilines (Scheme 10) as these coupling partners led to very low yields of carbazoles in the one-pot method described above.

Unfortunately, whilst the aminated intermediates **7j**, **7k** and **7r** are isolated in reasonable to good yields, conversion to the carbazoles as determined by ^1H NMR remains poor. In all cases, the major material observed in the crude product



Scheme 10. Conditions: (i) **5** (1 mmol), ArBr (1 mmol), NaO^tBu (5 mmol), $Pd(OAc)_2$ (5 mol %), $[HP^tBu_3][BF_4]$ (7 mol %), toluene, Δ, 18 h. (ii) **7** (0.5 mmol), $Pd(OAc)_2$ (5 mol %), $[HP^tBu_3][BF_4]$ (7 mol %), NaO^tBu (2.5 mmol), 1,4-dioxane, Δ, 18 h.

mixture is the aminated intermediate **7**. Clearly the 1,3-disubstitution pattern can be deleterious to performance and it appears that in these cases the aryl chloride does not undergo oxidative addition. Better performance is obtained with 4-bromotoluene and 2-chloro-4-fluoroaniline in the production of carbazole **6y** (Scheme 11).



Scheme 11. Conditions: (i) **5** (1 mmol), ArBr (1 mmol), NaO^tBu (5 mmol), $Pd(OAc)_2$ (5 mol %), $[HP^tBu_3][BF_4]$ (7 mol %), toluene, Δ, 18 h. (ii) **7** (0.5 mmol), $Pd(OAc)_2$ (5 mol %), $[HP^tBu_3][BF_4]$ (7 mol %), NaO^tBu (2.5 mmol), 1,4-dioxane, Δ, 18 h.

In summary we find that intramolecular direct arylation is a viable synthetic route for the production of fluorinated carbazoles, typically in reasonable to good yields. Some

substitution patterns still prove problematic with the current methodology and strategies to address these shortcomings will be investigated further.

3. Experimental

3.1. General experimental conditions

All reactions and preparations were carried out under a dry nitrogen atmosphere, either in a glove box or using standard Schlenk techniques with anhydrous solvents. Microwave reactions were performed using a Biotage AB Initiator (300 W; software version 1.1) with autochanger (8 positions) using Biotage 5 ml sealed vials. XPhos (**9**) was purchased from Sigma–Aldrich and palladacycle **10** was prepared according to a literature procedure.[25]

3.2. General method for microwave-assisted, one-pot synthesis of fluorocarbazoles

NaO^tBu (0.240 g, 2.5 mmol), $Pd(OAc)_2$ (0.006 g, 0.025 mmol) and $[HP^tBu_3][BF_4]$ (0.010 g, 0.035 mmol) were suspended in toluene (3 ml) in a 5 ml microwave vial. The appropriate 2-chloroaniline (0.50 mmol) and aryl bromide (0.50 mmol) were then added and the vial sealed. The reaction was then heated in the microwave reactor at 160 °C for 3 h, allowed to cool and then quenched by addition of $HCl_{(aq)}$ (2 M, 3 ml). The organic phase was extracted with CH_2Cl_2 (2×20 ml), dried ($MgSO_4$), then filtered and the solvent removed under reduced pressure. The crude product mixture was then subjected to column chromatography (SiO_2).

3.2.1. 3-Fluoro-8-methyl-9H-carbazole, **6a** (Table 1, entry 1)

2-Chloro-4-fluoroaniline (0.06 ml, 0.50 mmol) and 2-bromotoluene (0.06 ml, 0.50 mmol) gave the product as a light grey powder: 70 mg (70%); R_f 0.88 ($CHCl_3$); mp 120.6–122.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.55 (s, 3H, Me), 7.15 (m, 2H, Ar H), 7.25 (d, J=8 Hz, 1H, Ar H), 7.37 (dd, J=8.6, 4.2 Hz, 1H, Ar H), 7.71 (dd, J=9.0, 2.4 Hz, 1H, Ar H), 7.87 (d, J=7.8 Hz, 1H, Ar H), 7.93 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.79 (s, CH_3), 106.06 (d, J=23.7 Hz, CH), 111.18 (d, J=9.2 Hz, CH), 113.42 (d, J=25.2 Hz, CH), 118.12 (s, CH), 119.59 (s, CH), 119.99 (s, C), 122.57 (s, CH), 124.37 (d, J=9.0 Hz, C), 135.65 (s, C), 139.91 (s, C), 157.50 (d, J=234.0 Hz, CF); ^{19}F NMR (282.65 MHz, $CDCl_3$) δ −124.35 (dt, J=9.1, 4.6 Hz); HRMS (EI) calcd for $C_{13}H_{10}FN$ [M^+]: 199.0797, found: 199.0792. Anal. Calcd for $C_{13}H_{10}FN$: C, 78.37; H, 5.06; N, 7.03. Found: C, 77.75; H, 5.40; N, 7.86.

3.2.2. 3-Fluoro-5,8-dimethyl-9H-carbazole, **6b** (Table 1, entry 2)

2-Chloro-4-fluoroaniline (0.06 ml, 0.50 mmol) and 2-bromo-*p*-xylene (0.07 ml, 0.50 mmol) gave the product as a dark brown powder: 47 mg (44%); R_f 0.86 ($CHCl_3$); mp 84.8–87.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.52 (s, 3H, Me), 2.81 (s, 3H, Me), 7.16 (m, 2H, Ar H), 7.38 (dd, J=8.8, 4.4 Hz, 1H, Ar H), 7.83 (dd, J=9.8, 2.7 Hz, 1H, Ar H), 7.94 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.63 (s, CH_3), 20.37 (s, CH_3), 108.28 (d, J=24.0 Hz, CH), 110.93 (d, J=9.0 Hz, CH), 112.77 (d, J=24.0 Hz, CH), 117.42 (s, C), 120.96 (s, CH), 121.33 (s, C), 124.92 (d, J=9.0 Hz, C), 126.80 (s, CH), 131.05 (s, C), 135.78 (s, C), 139.99 (s, C), 157.50 (d, J=232.0 Hz, CF); ^{19}F NMR (282.65 MHz, $CDCl_3$) δ −124.54 (dt, J=9.1, 4.5 Hz); HRMS (EI) calcd for $C_{14}H_{12}FN$ [M^+]: 213.0954, found: 231.0961. Anal. Calcd for $C_{14}H_{12}FN$: C, 78.85; H, 5.67; N, 6.57. Found: C, 78.95; H, 5.74; N, 7.10.

3.2.3. 3-Fluoro-8-methoxy-9H-carbazole, **6c** (Table 1, entry 3)

2-Chloro-4-fluoroaniline (0.06 ml, 0.50 mmol) and 2-bromotoluene (0.06 ml, 0.50 mmol) gave the product as a light brown powder: 22 mg (20%); R_f 0.78 ($CHCl_3$); mp 102.1–103.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.01 (s, 3H, OMe), 6.91 (d, J=7.8 Hz, 1H, Ar H), 7.36 (dd, J=8.8, 4.4 Hz, 1H, Ar H), 7.15 (m, 2H, Ar H), 7.62 (d, J=8.0 Hz, 1H, Ar H), 7.70 (dd, J=9.0, 2.7 Hz, 1H, Ar H), 8.22 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.50 (s, CH_3), 106.08 (s, C), 106.09 (d, J=23.3 Hz, CH), 111.43 (d, J=9.2 Hz, CH), 112.91 (s, CH), 113.53 (d, J=25.9 Hz, CH), 119.75 (s, CH), 123.95 (s, CH), 124.11 (d, J=9.0 Hz, C), 130.92 (s, C), 135.44 (s, C), 145.74 (s, C), 157.40 (d, J=234 Hz, CF); ^{19}F NMR (282.65 MHz, $CDCl_3$) δ −124.47 (dt, J=9.3, 3.7 Hz); HRMS (EI) calcd for $C_{13}H_{10}FNO$ [M^+]: 215.0746, found: 215.0751. Anal. Calcd for $C_{13}H_{10}FNO\cdot H_2O$: C, 66.94; H, 4.32; N, 6.00. Found: C, 67.86; H, 4.96; N, 5.97.[26]

3.2.4. 3-Fluoro-5,8-dimethoxy-9H-carbazole, **6d** (Table 1, entry 4)

2-Chloro-4-fluoroaniline (0.06 ml, 0.50 mmol) and 1-bromo-2,5-dimethoxybenzene (0.08 ml, 0.50 mmol) gave the product as a dark brown oil: 78 mg, (64%); R_f 0.73 ($CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.96 (s, 3H, OMe), 4.02 (s, 3H, OMe), 6.50 (d, J=8.3 Hz, 1H, Ar H), 6.79 (d, J=8.6 Hz, 1H, Ar H), 7.12 (dd, J=8.2, 2.6 Hz, 1H, Ar H), 7.31 (dd, J=8.8, 2.6 Hz, 1H, Ar H), 7.99 (dd, J=9.4, 2.6 Hz, 1H, Ar H), 8.25 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.70 (s, CH_3), 56.06 (s, CH_3), 99.03 (s, CH), 106.57 (s, CH), 108.63 (d, J=24.0 Hz, CH), 110.81 (d, J=9.0 Hz, CH), 112.84 (d, J=25.0 Hz, CH), 113.75 (s, C), 123.52 (d, J=10.0 Hz, C), 132.04 (s, C), 134.93 (s, C), 140.21 (s, C), 150.45 (s, C), 157.55 (d, J=233.0 Hz, CF); ^{19}F NMR (282.65 MHz, $CDCl_3$) δ −124.46 (dt, J=9.1, 4.5 Hz); HRMS (EI) calcd for $C_{14}H_{12}FNO_2$ [M^+]: 245.0852, found: 245.0847. Anal. Calcd for $C_{14}H_{12}FNO_2$: C, 68.56; H, 4.93; N, 5.71. Found: C, 68.33; H, 5.01; N, 5.91.

3.2.5. 3-Fluoro-6,8-dimethoxy-9H-carbazole, **6e** (Table 1, entry 5)

2-Chloro-4-fluoroaniline (0.06 ml, 0.50 mmol) and 1-bromo-2,4-dimethoxybenzene (0.07 ml, 0.50 mmol) gave the product as a dark brown oil: 76 mg (62%); R_f 0.80 ($CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.92 (s, 3H, OMe), 3.96

(s, 3H, OMe), 6.59 (d, J=2.1 Hz, 1H, Ar H), 7.03 (d, J=2.0 Hz, 1H, Ar H), 7.12 (dt, J=8.0, 2.0 Hz, 1H, Ar H), 7.33 (dd, J=8.0, 2.1 Hz, 1H, Ar H), 7.64 (dd, J=9.1, 2.5 Hz, 1H, Ar H), 8.06 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.68 (s, CH_3), 56.11 (s, CH_3), 93.91 (s, CH), 98.12 (s, CH), 105.87 (d, J=24.0 Hz, CH), 111.73 (d, J=9.0 Hz, CH), 113.55 (d, J=26.0 Hz, CH), 123.02 (s, C), 124.15 (d, J=9.0 Hz, C), 126.23 (s, C), 136.00 (s, C), 146.36 (s, C), 157.25 (d, J=230 Hz, CF); ^{19}F NMR (282.65 MHz, $CDCl_3$) δ −124.85 (dt, J=9.1, 4.5 Hz); HRMS (EI) calcd for $C_{14}H_{12}FNO_2$ [M^+]: 245.0852, found: 245.0845. Anal. Calcd for $C_{14}H_{12}FNO_2 \cdot 0.5H_2O$: C, 66.60; H, 4.79; N, 5.55. Found: C, 66.36; H, 4.95; N, 5.66.

3.2.6. 3-Fluoro-8-phenyl-9H-carbazole, ***6f*** *(Table 1, entry 6)*

2-Chloro-4-fluoroaniline (0.06 ml, 0.50 mmol) and 2-bromobiphenyl (0.09 ml, 0.50 mmol) gave the product as an orange oil: 58 mg (44%); R_f 0.75 (1:1 $CHCl_3$/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (dt, J=8.8, 2.4 Hz, 1H, Ar H), 7.33 (d, J=8.0 Hz, 2H, Ar H), 7.45 (m, 2H, Ar H), 7.56 (t, J=7.8 Hz, 2H, Ar H), 7.69 (d, J=8.0 Hz, 2H, Ar H), 7.75 (dd, J=8.9, 2.6 Hz, 2H, Ar H), 8.02 (d, J=7.8 Hz, 1H, Ar H), 8.26 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 106.21 (d, J=24.0 Hz, CH), 111.34 (d, J=9.0 Hz, CH), 113.90 (d, J=26.0 Hz, CH), 119.92 (d, J=24.0 Hz, CH), 123.52 (d, J=4.0 Hz, C), 124.18 (d, J=10.0 Hz, C), 125.42 (s, C), 126.37 (s, CH), 127.78 (s, CH), 128.43 (s, CH), 129.07 (s, CH), 129.41 (s, CH), 135.84 (s, C), 138.43 (s, C), 138.91 (s, C), 157.64 (d, J=234.0 Hz, CF); ^{19}F NMR (282.65 MHz, $CDCl_3$) δ −124.13 (dt, J=9.1, 4.5 Hz); HRMS (EI) calcd for $C_{18}H_{12}FN$ [M^+]: 261.0954, found: 261.0946. Anal. Calcd for $C_{18}H_{12}FN \cdot H_2O$: C, 77.40; H, 4.33; N, 5.01. Found: C, 77.34; H, 4.40; N, 5.87.

3.2.7. 3-Fluoro-11H-benzo(α)carbazole, ***6g*** *(Table 1, entry 7)*

2-Chloro-4-fluoroaniline (0.06 ml, 0.50 mmol) and 2-bromonaphthalene (0.07 ml, 0.50 mmol) gave the product as a dark brown powder: 72 mg (61%); R_f 0.85 ($CHCl_3$); mp 214.9−216.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (m, 1H, Ar H), 7.56 (m, 4H, Ar H), 7.75 (s, 1H, Ar H), 8.06 (m, 3H, Ar H), 8.71 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 105.45 (d, J=24.0 Hz, CH), 111.72 (d, J=9.0 Hz, CH), 112.89 (d, J=26.0 Hz, CH), 118.32 (s, C), 119.31 (s, CH), 120.39 (s, CH), 120.58 (s, CH), 121.22 (s, C), 124.76 (d, J=10.0 Hz, C), 125.68 (s, CH), 125.80 (s, CH), 129.17 (s, CH), 132.71 (s, C), 134.87 (s, C), 136.25 (s, C), 158.00 (d, J=235.0 Hz, CF); ^{19}F NMR (282.65 MHz, $CDCl_3$) δ −123.65 (dt, J=9.1, 3.7 Hz); HRMS (EI) calcd for $C_{16}H_{10}FN$ [M^+]: 235.0797, found: 235.0793. Anal. Calcd for $C_{16}H_{10}FN$: C, 81.69; H, 4.28; N, 5.95. Found: C, 80.85; H, 4.36; N, 6.33.[26]

3.2.8. 3-Fluoro-5,7-dimethoxy-9H-carbazole, ***6h*** *(Table 1, entry 8)*

2-Chloro-4-fluoroaniline (0.06 ml, 0.50 mmol) and 1-bromo-3,5-dimethoxybenzene (0.11 g, 0.50 mmol) gave the product as a black oil: 65 mg (53%); R_f 0.33 ($CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 3H, OMe), 4.01 (s, 3H, OMe), 6.29 (d, J=1.7 Hz, 1H, Ar H), 6.47 (d, J=1.7 Hz, 1H, Ar H), 7.00 (m, 1H, Ar H), 7.22 (dd, J=8.7, 4.0 Hz, 1H, Ar H), 7.84 (dd, J=9.5, 3.8 Hz, 1H, Ar H), 7.89 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.54 (s, CH_3), 55.74 (s, CH_3), 86.81 (s, CH), 91.17 (s, CH), 106.93 (s, C), 107.70 (d, J=25.0 Hz, CH), 110.02 (d, J=10.0 Hz, CH), 111.13 (d, J=25.0 Hz, CH), 123.50 (d, J=10.0 Hz, C), 134.94 (s, C), 142.63 (s, C), 156.73 (s, C), 157.76 (d, J=232.0 Hz, CF), 160.79 (s, C); ^{19}F NMR (282.65 MHz, $CDCl_3$) δ −124.52 (br s); HRMS (EI) calcd for $C_{14}H_{12}FNO_2$ [M^+]: 245.0852, found: 245.0854. Anal. Calcd for $C_{14}H_{12}FNO_2$: C, 68.56; H, 4.93; N, 5.71. Found: C, 68.43; H, 5.23; N, 6.19.

3.2.9. 3-Fluoro-5,7-di-tert-butyl-9H-carbazole, ***6i*** *(Table 1, entry 9)*

2-Chloro-4-fluoroaniline (0.06 ml, 0.50 mmol) and 1-bromo-3,5-di-*tert*-butylbenzene (0.14 g, 0.50 mmol) gave the product as a dark brown gum: 31 mg (21%); R_f 0.75 ($CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (s, 9H, Me), 1.66 (s, 9H, Me), 6.89 (s, 2H, Ar H), 7.09−7.15 (m, 1H, Ar H), 7.32−7.36 (m, 1H, Ar H), 7.99 (dd, J=11.6, 2.3 Hz, 1H), 8.11 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.54 (s, CH_3), 35.52 (s, C), 35.84 (s, C), 105.97 (s, CH), 110.75 (d, J=9 Hz, C), 111.86 (d, J=26 Hz, CH), 112.34 (s, CH), 115.00 (s, CH), 116.09 (d, J=23 Hz, CH), 119.70 (d, J=8 Hz, C), 122.99 (d, J=10 Hz, C), 136.39 (s, C), 142.41 (s, C), 146.39 (s, C), 157.01 (d, J=232 Hz, CF); ^{19}F NMR (282.65 MHz, $CDCl_3$) δ −124.56 (dt, J=8.2, 4.5 Hz); HRMS (EI) calcd for $C_{20}H_{24}FN$ [M^+]: 297.1893, found: 297.1894. Anal. Calcd for $C_{20}H_{24}FN \cdot 1.2H_2O$: C, 75.30; H, 7.58; N, 4.39. Found: C, 75.45; H, 8.17; N, 4.82.

3.2.10. 3-Fluoro-5,7-dimethyl-9H-carbazole, ***6j*** *(Table 1, entry 10)*

2-Chloro-4-fluoroaniline (0.06 ml, 0.50 mmol) and 5-bromo-*m*-xylene (0.07 ml, 0.50 mmol) gave the product as a yellow powder: 6 mg (6%); R_f 0.78 ($CHCl_3$); mp 110.5−112.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.48 (s, 3H, Me), 2.79 (s, 3H, Me), 6.84 (s, 1H, Ar H), 7.07 (s, 1H, Ar H), 7.11 (m, 1H, Ar H), 7.31 (dd, J=8.8, 4.3 Hz, 1H, Ar H), 7.77 (d, J=9.8, 2.4 Hz, 1H, Ar H), 7.94 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.66 (s, CH_3), 22.14 (s, CH_3), 98.16 (d, J=39 Hz, C), 108.16 (d, J=24 Hz, CH), 108.75 (s, CH), 110.81 (d, J=9 Hz, CH), 112.51 (d, J=26 Hz, CH), 118.11 (s, C), 122.92 (s, CH), 124.78 (s, C), 133.44 (s, C), 136.06 (s, C), 136.92 (s, C), 161.44 (d, J=241.2 Hz, CF); ^{19}F NMR (282.65 MHz, $CDCl_3$) δ −124.85 (dt, J=9.9, 4.5 Hz); HRMS (EI) calcd for $C_{14}H_{12}FN$ [M^+]: 213.0954, found: 213.0949. Anal. Calcd for $C_{14}H_{12}FN \cdot 0.4H_2O$: C, 76.27; H, 5.49; N, 6.35. Found: C, 75.91; H, 5.41; N, 6.49.

3.2.11. 1-Fluoro-5,7-dimethyl-9H-carbazole, ***6k*** *(Table 1, entry 11)*

2-Chloro-6-fluoroaniline (0.06 ml, 0.50 mmol) and 5-bromo-*m*-xylene (0.07 ml, 0.50 mmol) gave the product as

a grey powder: 11 mg (10%); R_f 0.59 (1:1 $CHCl_3$/hexane); mp 112.5–114.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.49 (s, 3H, Me), 2.81 (s, 3H, Me), 6.88 (s, 1H, Ar H), 7.13 (dd, J=8.0, 4.0 Hz, 1H, Ar H), 7.11 (d, J=4.0 Hz, 1H, Ar H), 7.13 (s, 1H, Ar H), 7.87 (m, 1H, Ar H), 8.10 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.61 (s, CH_3), 21.94 (s, CH_3), 100.00 (s, C), 108.74 (s, CH), 109.92 (s, C), 110.09 (d, J=18.1 Hz, CH), 117.88 (s, CH), 119.47 (d, J=3.1 Hz, CH), 123.16 (s, CH), 133.17 (s, C), 136.73 (s, C), 139.59 (s, C), 140.20 (s, C), 160.73 (d, J=220.0 Hz, CF); ^{19}F NMR (282.65 MHz, $CDCl_3$) δ −135.63 (dd, J=8.2, 8.0 Hz); HRMS (EI) calcd for $C_{14}H_{12}FN$ [M^+]: 213.0954, found: 213.0958. Anal. Calcd for $C_{14}H_{12}FN$: C, 78.85; H, 5.67; N, 6.57. Found: C, 79.30; H, 5.91; N, 6.98.

3.2.12. 1-Fluoro-8-methyl-9H-carbazole, **6l**. Method a (Table 1, entry 12)

2-Chloro-6-fluoroaniline (0.06 ml, 0.50 mmol) and 2-bromotoluene (0.06 ml, 0.50 mmol) gave the product as a brown powder: 45 mg (45%); R_f 0.93 ($CHCl_3$); mp 100.8–102.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.58 (s, 3H, Me), 7.12–7.26 (m, 3H, Ar H), 7.28 (d, J=8.0 Hz, 1H, Ar H), 7.83 (dd, J=8.0, 1.8 Hz, 1H, Ar H), 7.92 (d, J=7.8 Hz, 1H, Ar H), 8.09 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.94 (s, CH_3), 110.86 (d, J=12.1 Hz, CH), 116.22 (s, CH), 118.33 (s, CH), 119.79 (s, C), 120.24 (s, CH), 120.35 (d, J=12.0 Hz, CH), 122.86 (s, C), 127.16 (s, CH), 127.47 (d, J=3.1 Hz, C), 139.10 (s, C), 140.01 (s, C), 149.32 (d, J=241.0 Hz, CF); ^{19}F NMR (282.65 MHz, $CDCl_3$) δ −135.07 (dd, J=15.6, 6.5 Hz); HRMS (EI) calcd for $C_{13}H_{10}FN$ [M^+]: 199.0797, found: 199.0795. Anal. Calcd for $C_{13}H_{10}FN$: C, 78.37; H, 5.06; N, 7.03. Found: C, 78.03; H, 5.18; N, 7.28.

Method b (Table 1, entry 19): 2-chloro-6-methylaniline (0.06 ml, 0.50 mmol) and 1-bromo-2-fluorobenzene (0.06 ml, 0.50 mmol) gave product as a light cream powder: 37 mg (37%); data as above.

3.2.13. 1-Fluoro-11H-benzo(α)carbazole, **6m** (Table 1, entry 13)

2-Chloro-6-fluoroaniline (0.06 ml, 0.50 mmol) and 2-bromonaphthalene (0.07 ml, 0.50 mmol) gave the product as a dark green powder: 66 mg (56%); R_f 0.85 ($CHCl_3$); mp 143.8–145.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14–7.24 (m, 2H, Ar H), 7.54–7.63 (m, 2H, Ar H), 7.68 (d, J=8.5 Hz, 1H, Ar H), 7.87 (d, J=7.6 Hz, 1H, Ar H), 8.01 (d, J=7.6 Hz, 1H, Ar H), 8.10 (d, J=8.5 Hz, 1H, Ar H), 8.14 (d, J=8.1 Hz, 1H, Ar H), 8.90 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 109.91 (d, J=16.0 Hz, CH), 115.63 (d, J=3.0 Hz, CH), 118.53 (d, J=3.1 Hz, CH), 119.32 (s, CH), 120.26 (d, J=6.2 Hz, CH), 120.72 (d, J=21.8 Hz, CH), 121.18 (s, C), 125.68 (s, CH), 125.88 (s, CH), 126.72 (d, J=12.4 Hz, C), 127.99 (d, J=12.4 Hz, C), 129.08 (s, CH), 132.71 (s, C), 135.23 (s, C), 139.07 (s, C), 149.45 (d, J=243.0 Hz, CF); ^{19}F NMR (282.65 MHz, $CDCl_3$) δ −134.67 (dd, J=10.2, 4.8 Hz); HRMS (EI) calcd for $C_{16}H_{10}FN$ [M^+]: 235.0797, found: 235.0802. Anal. Calcd for $C_{16}H_{10}FN$: C, 81.69; H, 4.28; N, 5.95. Found: C, 81.40; H, 4.54; N, 6.51.[26]

3.2.14. 1-Fluoro-6-methyl-9H-carbazole, **6n** (Table 1, entry 14)

2-Chloro-6-fluoroaniline (0.06 ml, 0.50 mmol) and 4-bromotoluene (0.06 ml, 0.50 mmol) gave the product as a cream powder: 23 mg (23%); R_f 0.55 (1:1 $CHCl_3$/hexane); mp 165.5–167.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.53 (s, 3H, Me), 7.13 (m, 2H, Ar H), 7.28 (d, J=8.0 Hz, 1H, Ar H), 7.36 (d, J=8.0 Hz, 1H, Ar H), 7.80 (d, J=8.0 Hz, 1H, Ar H), 7.86 (s, 1H, Ar H), 8.08 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.51 (s, CH_3), 100.00 (s, C), 110.82 (d, J=12.1 Hz, CH), 110.92 (s, CH), 115.97 (d, J=3.0 Hz, CH), 119.51 (d, J=6.0 Hz, CH), 120.59 (s, CH), 123.52 (s, C), 126.82 (s, C), 127.99 (s, CH), 129.44 (s, C), 137.89 (s, C), 149.22 (d, J=241.0 Hz, CF); ^{19}F NMR (282.65 MHz, $CDCl_3$) δ −135.22 (dd, J=7.6, 7.4 Hz); HRMS (EI) calcd for $C_{13}H_{10}FN$ [M^+]: 199.0797, found: 199.0793. Anal. Calcd for $C_{13}H_{10}FN$: C, 78.37; H, 5.06; N, 7.03. Found: C, 78.76; H, 5.51; N, 7.56.[26]

3.2.15. 2-Fluoro-8-methyl-9H-carbazole, **6o** and 4-fluoro-8-methyl-9H-carbazole, **6p**. Method a (Table 1, entry 15)

2-Chloro-5-fluoroaniline (0.06 ml, 0.50 mmol) and 2-bromotoluene (0.06 ml, 0.50 mmol) gave the product as pink crystals: 27 mg (27%); R_f 0.75 ($CHCl_3$); mp 116.0–117.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.55 (s, 3H, Me), 6.96 (dt, J=8.0, 2.5 Hz, 1H, Ar H), 7.12 (dd, J=9.5, 2.3 Hz, 1H, Ar H), 7.18 (d, J=7.5 Hz, 1H, Ar H), 7.21 (d, J=8.0 Hz, 1H, Ar H), 7.87 (d, J=7.5 Hz, 1H, Ar H), 7.96 (dd, J=8.6, 5.4 Hz, 1H, Ar H), 7.99 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.92 (s, CH_3), 97.56 (d, J=26.0 Hz, CH), 107.79 (d, J=24.0 Hz, CH), 117.64 (s, CH), 119.84 (s, C), 120.13 (s, CH), 120.36 (s, C), 121.42 (d, J=10.0 Hz, CH), 122.54 (s, C), 126.20 (s, CH), 138.00 (s, C), 140.01 (s, C), 161.97 (d, J=240.0 Hz, CF); ^{19}F NMR (282.65 MHz, $CDCl_3$) δ −115.69 (dt, J=10.4, 5.5 Hz); HRMS (EI) calcd for $C_{13}H_{10}FN$ [M^+]: 199.0797, found: 199.0797. Anal. Calcd for $C_{13}H_{10}FN$: C, 78.37; H, 5.06; N, 7.03. Found: C, 77.96; H, 5.50; N, 7.48.[26] Data for **6p** are given below.

Method b (Table 1, entry 20): 2-chloro-6-methylaniline (0.06 ml, 0.50 mmol) and 1-bromo-3-fluorobenzene (0.06 ml, 0.50 mmol) gave a mixture of **6o** and **6p** (ratio 1.3:1) as a beige powder: 62 mg (62%); R_f 0.75 ($CHCl_3$); **6o** data as above; **6p**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.56 (s, 3H, Me), 6.91 (dd, J=9.1, 8.0 Hz, 1H, Ar H), 7.21 (m 1H, Ar H), 7.23 (d, J=8.1 Hz, 1H, Ar H), 7.28 (m, 1H, Ar H), 7.33 (dt, J=8.1, 3.2 Hz, 1H, Ar H), 8.03 (br s, 1H, NH), 8.06 (d, J=7.9 Hz, 1H, Ar H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 105.41 (d, J=19.2 Hz, CH), 106.60 (d, J=3.8 Hz, CH), 112.46 (d, J=20.8 Hz, C), 119.63 (s, C), 120.35 (s, CH), 120.64 (d, J=3.1 Hz, CH), 126.39 (d, J=8.5 Hz, CH), 126.74 (s, CH), 138.45 (s, C), 139.97 (d, J=12.3 Hz, C), 141.62 (d, J=10.8 Hz, CH), 158.69 (d, J=248.2 Hz, CH); ^{19}F NMR (282.65 MHz, $CDCl_3$) δ −119.40 (dd, J=9.4, 4.5 Hz);

HRMS (EI) calcd for $C_{13}H_{10}FN$ [M^+]: 199.0797, found: 199.0792. Anal. Calcd for $C_{13}H_{10}FN$: C, 78.37; H, 5.06; N, 7.03. Found: C, 78.77; H, 5.28; N, 7.56.

3.2.16. 2-Fluoro-6-methyl-9H-carbazole, **6q** (Table 1, entry 16)

2-Chloro-5-fluoroaniline (0.06 ml, 0.50 mmol) and 4-bromotoluene (0.06 ml, 0.50 mmol) gave the product as a silver powder: 24 mg (24%); R_f 0.74 ($CHCl_3$); mp 210.6–212.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.52 (s, 3H, Me), 6.94 (dd, J=8.0, 2.4 Hz, 1H, Ar H), 7.07 (dd, J=9.6, 2.3 Hz, 1H, Ar H), 7.21 (d, J=8.0 Hz, 1H, Ar H), 7.30 (d, J=8.0 Hz, 1H, Ar H), 7.81 (br s, 1H, Ar H), 7.93 (dd, J=8.5, 5.4 Hz, 1H, Ar H), 7.96 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.40 (s, CH_3), 97.44 (d, J=26.3 Hz, CH), 105.20 (d, J=18.1 Hz, C), 107.56 (d, J=24.0 Hz, CH), 110.14 (s, C), 110.36 (s, CH), 120.05 (s, CH), 121.22 (d, J=9.8 Hz, CH), 123.14 (d, J=20.3 Hz, C), 126.72 (d, J=32.4 Hz, C), 126.91 (s, CH), 129.54 (d, J=18.1 Hz, C), 162.12 (d, J=240.0 Hz, CF); ^{19}F NMR (282.65 MHz, $CDCl_3$) δ −115.78 (dt, J=10.2, 5.7 Hz); HRMS (EI) calcd for $C_{13}H_{10}FN$ [M^+]: 199.0797, found: 199.0793. Anal. Calcd for $C_{13}H_{10}FN$: C, 78.37; H, 5.06; N, 7.03. Found: C, 78.01; H, 5.10; N, 7.84.[26]

3.2.17. 2-Fluoro-5,7-dimethyl-9H-carbazole, **6r** (Table 1, entry 17)

2-Chloro-5-fluoroaniline (0.06 ml, 0.50 mmol) and 5-bromo-*m*-xylene (0.07 ml, 0.50 mmol) gave the product as a purple powder: 15 mg (14%); R_f 0.74 ($CHCl_3$); mp 111.7–114.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.48 (s, 3H, Me), 2.79 (s, 3H, Me), 6.85 (s, 1H, Ar H), 6.95 (dd, J=8.0, 2.5 Hz, 1H, Ar H), 7.06 (s, 1H, Ar H), 7.08 (dd, J=8.0, 4.0 Hz, 1H, Ar H), 7.97 (br s, 1H, NH), 8.00 (dd, J=8.7, 5.4 Hz, 1H, Ar H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.61 (s, CH_3), 21.88 (s, CH_3), 97.31 (d, J=26.4 Hz, CH), 103.77 (d, J=25.7 Hz, C), 107.48 (d, J=24.1 Hz, CH), 108.54 (s, CH), 117.11 (s, C), 123.10 (d, J=9.8 Hz, CH), 123.21 (s, CH), 124.24 (s, C), 130.72 (s, C), 132.70 (s, C), 135.84 (s, C), 161.56 (d, J=240.7 Hz, CF); ^{19}F NMR (282.65 MHz, $CDCl_3$) δ −117.03 (dd, J=13.6, 9.1 Hz); HRMS (EI) calcd for $C_{14}H_{12}FN$ [M^+]: 213.0954, found: 213.0946. Anal. Calcd for $C_{14}H_{12}FN$: C, 78.85; H, 5.67; N, 6.57. Found: C, 78.53; H, 6.03; N, 7.04.

3.2.18. 2-Fluoro-11H-benzo(α)carbazole, **6s** (Table 1, entry 18)

2-Chloro-5-fluoroaniline (0.06 ml, 0.50 mmol) and 2-bromonaphthalene (0.07 ml, 0.50 mmol) gave the product as a off-white powder: 90 mg (77%); R_f ($CHCl_3$); mp 223.6–225.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (dt, J=9.1, 2.3 Hz, 1H, Ar H), 7.28 (dd, J=9.0, 2.2 Hz, 1H, Ar H), 7.53 (dt, J=9.0, 2.1 Hz, 1H, Ar H), 7.60 (dt, J=7.5, 1.3 Hz, 1H, Ar H), 7.67 (d, J=8.5 Hz, 1H, Ar H), 8.01 (m 2H, Ar H), 8.09 (m, 2H, Ar H), 8.79 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 97.58 (d, J=26.9 Hz, CH), 108.24 (d, J=24.1 Hz, CH), 118.00 (s, CH), 118.77 (s, CH), 120.12 (s, CH), 120.54 (s, CH), 120.67 (s, C), 120.81 (s, C), 125.34 (d, J=40.0 Hz, CH), 128.94 (s, CH), 131.95 (s, C), 135.10 (d, J=3.1 Hz, C), 138.66 (d, J=12 Hz, C), 141.72 (s, C), 161.35 (d, J=240.1 Hz, CF); ^{19}F NMR (282.65 MHz, $CDCl_3$) δ −116.61 (dt, J=9.6, 5.7 Hz); HRMS (EI) calcd for $C_{16}H_{10}FN$ [M^+]: 235.0797, found: 235.0793. Anal. Calcd for $C_{16}H_{10}FN$: C, 81.69; H, 4.28; N, 5.95. Found: C, 81.57; H, 4.66; N, 6.35.

3.2.19. 3-Fluoro-8-methyl-9H-carbazole, **6t** (Table 1, entry 21)

2-Chloro-6-methylaniline (0.06 ml, 0.50 mmol) and 1-bromo-4-fluorobenzene (0.06 ml, 0.50 mmol) gave the product as a beige powder: 35 mg (35%); R_f 0.74 ($CHCl_3$); mp 98.0–102.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.56 (s, 3H, Me), 7.14 (dd, J=8.0, 4.0 Hz, 1H, Ar H), 7.17 (d, J=8.0 Hz, 1H, Ar H), 7.24 (d, J=8.0 Hz, 1H, Ar H), 7.37 (dd, J=8.8, 4.2 Hz, 1H, Ar H), 7.71 (dd, J=9.0, 2.6 Hz, 1H, Ar H), 7.87 (d, J=7.8 Hz, 1H, Ar H), 7.92 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.94 (s, CH_3), 106.19 (d, J=24.0 Hz, CH), 111.31 (d, J=9.0 Hz, CH), 113.55 (d, J=25.0 Hz, CH), 118.23 (s, CH), 119.70 (s, CH), 120.11 (s, C), 122.65 (s, C), 124.44 (s, C), 127.01 (s, CH), 135.77 (s, C), 140.03 (s, C), 157.61 (d, J=234.0 Hz, CF); ^{19}F NMR (282.65 MHz, $CDCl_3$) δ −124.35 (dt, J=10.2, 4.5 Hz); HRMS (EI) calcd for $C_{13}H_{10}FN$ [M^+]: 199.0797, found: 199.0789. Anal. Calcd for $C_{13}H_{10}FN$: C, 78.37; H, 5.06; N, 7.03. Found: C, 78.26; H, 5.38; N, 6.65.

3.3. General method for thermal synthesis of aminated intermediates

NaO^tBu (0.480 g, 5.0 mmol), $Pd(OAc)_2$ (0.012 g, 0.05 mmol) and $[HP^tBu_3][BF_4]$ (0.020 g, 0.070 mmol) were suspended in toluene (6 ml). The appropriate 2-chloroaniline (1.0 mmol) and the aryl bromide (1.0 mmol) were then added under nitrogen. The reaction was then heated at reflux for 18 h, allowed to cool and then quenched by addition of $HCl_{(aq)}$ (2 M, 3 ml). The organic phase was extracted with CH_2Cl_2 (2×40 ml), dried ($MgSO_4$), then filtered and the solvent removed under reduced pressure. The crude product mixture was then subjected to column chromatography (SiO_2).

3.3.1. (2-Chloro-5-methoxyphenyl)-(2-fluorophenyl)-amine, **7u**

2-Chloro-5-methoxyaniline hydrochloride (0.194 g, 1.0 mmol) and 1-bromo-2-fluorobenzene (0.12 ml, 1.0 mmol) gave the product as a brown oil: 214 mg (85%); R_f 0.85 ($CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.74 (s, 3H, OMe), 6.12 (br s, 1H, NH), 6.41 (dd, J=8.8, 2.8 Hz, 1H, Ar H), 6.79 (d, J=2.8 Hz, 1H, Ar H), 6.96–7.02 (m, 1H, Ar H), 7.08 (dd, J=8.0, 4.0 Hz, 1H, Ar H), 7.14 (dd, J=8.0, 4.0 Hz, 1H, Ar H), 7.27 (d, J=8.8 Hz, 1H, Ar H), 7.38 (dt, J=8.0, 2.0 Hz, 1H, Ar H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.54 (s, CH_3), 102.25 (s, CH), 106.33 (s, CH), 114.49 (s, C), 116.13 (d, J=19.3 Hz, CH), 120.69 (d, J=1.9 Hz, CH), 123.10 (d, J=7.5 Hz, CH), 124.55 (d, J=3.7 Hz, CH), 129.79 (d, J=11.8 Hz, C), 130.22 (s, CH), 140.32 (s, C),

154.61 (d, J=243.6 Hz, CF), 159.33 (s, C); ^{19}F NMR (282.65 MHz, $CDCl_3$) δ −128.90 (dt, J=12.4, 6.5 Hz); HRMS (EI) calcd for $C_{13}H_{11}ClFNO$ [M^+]: 251.0513, found: 251.0508.

3.3.2. (2-Chloro-5-methoxy-4-methylphenyl)-(2-fluorophenyl)amine, **7v**

2-Chloro-5-methoxy-4-methylaniline (0.12 ml, 1.0 mmol) and 2-bromofluorobenzene (0.12 ml, 1.0 mmol) gave the product as a brown oil: 181 mg (68%); R_f 0.80 ($CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.06 (s, 3H, Me), 3.64 (s, 3H, OMe), 5.90 (br s, 1H, NH), 6.69 (s, 1H, Ar H), 6.76–6.87 (m, 1H, Ar H), 6.96 (dt, J=8.0, 2.1 Hz, 1H, Ar H), 7.03 (m, 1H, Ar H), 7.04 (s, 1H, Ar H), 7.19 (dt, J=8.0, 1.8 Hz, 1H, Ar H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.26 (s, CH_3), 55.53 (s, CH_3), 100.78 (s, CH), 114.21 (s, C), 115.83 (d, J=19.3 Hz, CH), 118.40 (d, J=1.9 Hz, CH), 120.88 (s, C), 121.65 (d, J=7.5 Hz, CH), 124.36 (d, J=3.7 Hz, CH), 130.97 (d, J=11.3 Hz, CH), 130.98 (s, CH), 137.22 (s, C), 153.78 (d, J=242.4 Hz, CF), 156.95 (s, C); ^{19}F NMR (282.65 MHz, $CDCl_3$) δ −130.47 (m); HRMS (CI) calcd for $C_{14}H_{13}ClFNO$ [M^++H]: 266.0748, found: 266.0741.

3.3.3. (2-Chlorophenyl)-(3-fluorophenyl)amine, **7w**

2-Chloroaniline (0.11 ml, 1.0 mmol) and 4-bromofluorobenzene (0.11 ml, 1.0 mmol) gave the product as a brown oil: 166 mg (75%); R_f 0.90 ($CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82 (br s, 1H, NH), 6.96–7.26 (m, 3H, Ar H), 7.30 (d, J=8.5 Hz, 2H, Ar H), 7.38 (m, 1H, Ar H), 7.45 (d, J=8.0 Hz, 1H, Ar H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 114.83 (s, C), 116.21 (d, J=16.6 Hz, CH), 120.12 (s, CH), 123.38 (d, J=6.0 Hz, CH), 123.61 (s, C), 127.57 (s, CH), 129.78 (s, CH), 131.46 (s, CH), 141.27 (d, J=4.5 Hz, C), 154.33 (d, J=253.5 Hz, CF); ^{19}F NMR (282.65 MHz, $CDCl_3$) δ −130.47 (dt, J=9.1, 4.5 Hz); HRMS (EI) calcd for $C_{12}H_9ClFN$ [M^+]: 221.5962, found: 221.5957.

3.3.4. (2-Chloro-4-fluorophenyl)-(3-fluorophenyl)amine, **7x**

2-Chloro-4-fluoroaniline (0.12 ml, 1.0 mmol) and 4-bromofluorobenzene (0.11 ml, 1.0 mmol) gave the product as a dark green oil: 207 mg (86%); R_f 0.90 ($CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78 (br s, 1H, NH), 6.86 (dt, J=8.2, 3.0 Hz, 1H, Ar H), 6.98–7.08 (m, 5H, Ar H), 7.12 (dd, J=8.6, 2.9 Hz, 1H, Ar H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 114.48 (d, J=22.3 Hz, CH), 116.26 (d, J=22.3 Hz, CH), 116.46 (s, C), 116.91 (d, J=25.4 Hz, CH), 121.90 (d, J=10.8 Hz, C), 122.42 (d, J=7.7 Hz, CH), 123.30 (d, J=7.7 Hz, CH), 137.85 (d, J=36.9 Hz, C), 156.24 (d, J=241.3 Hz, CF), 158.98 (d, J=241.3 Hz, CF); ^{19}F NMR (282.65 MHz, $CDCl_3$) δ −120.05 (m), −122.63 (dt, J=8.0, 5.0 Hz); HRMS (CI) calcd for $C_{12}H_8ClF_2N$ [M^++H]: 240.0392, found: 240.0397.

3.3.5. (2-Chloro-4-fluorophenyl)-(3,5-dimethylphenyl)-amine, **7j**

2-Chloro-4-fluoroaniline (0.12 ml, 1.0 mmol) and 5-bromo-*m*-xylene (0.13 ml, 1.0 mmol) gave the product as a brown oil: 137 mg (55%); R_f ($CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 6H, Me), 5.78 (br s, 1H, NH), 6.66 (s, 1H, Ar H), 6.70 (s, 2H, Ar H), 6.88 (ddd, J=9.0, 8.0, 2.9 Hz, 1H, Ar H), 7.12 (dd, J=8.2, 2.9 Hz, 1H, Ar H), 7.22 (dd, J=9.1, 5.3 Hz, 1H, Ar H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.25 (s, CH_3), 114.35 (d, J=21.8 Hz, CH), 116.78 (d, J=25.5 Hz, CH), 117.00 (s, CH), 117.60 (d, J=8.1 Hz, CH), 122.43 (d, J=10.6 Hz, C), 124.16 (s, CH), 136.91 (d, J=3.1 Hz, C), 139.32 (s, C), 142.05 (s, C), 156.27 (d, J=241.7 Hz, CF); ^{19}F NMR (282.65 MHz, $CDCl_3$) δ −126.85 (dt, J=8.2, 5.5 Hz); HRMS (CI) calcd for $C_{14}H_{13}ClFN$ [M^++H]: 250.0799, found: 250.0803.

3.3.6. (2-Chloro-5-fluorophenyl)-(3,5-dimethylphenyl)-amine, **7r**

2-Chloro-5-fluoroaniline (0.12 ml, 1.0 mmol) and 5-bromo-*m*-xylene (0.13 ml, 1.0 mmol) gave the product as a brown oil: 195 mg (78%); R_f ($CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 6H, Me), 6.10 (br s, 1H, NH), 6.47 (ddd, J=8.7, 7.9, 2.9 Hz, 1H, Ar H), 6.76 (s, 1H, Ar H), 6.82 (s, 2H, Ar H), 6.93 (dd, J=11.1, 2.9 Hz, 1H, Ar H), 7.26 (dd, J=8.8, 5.7 Hz, 1H, Ar H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.33 (s, CH_3), 101.83 (d, J=28.0 Hz, CH), 106.32 (d, J=24.2 Hz, CH), 115.55 (d, J=3.1 Hz, C), 119.31 (s, CH), 125.76 (s, CH), 130.38 (d, J=10.6 Hz, CH), 139.56 (s, C), 140.42 (s, C), 142.36 (d, J=11.2 Hz, C), 162.37 (d, J=243.6 Hz, CF); ^{19}F NMR (282.65 MHz, $CDCl_3$) δ −113.26 (ddd, J=11.2, 7.5, 5.9 Hz); HRMS (CI) calcd for $C_{14}H_{13}ClFN$ [M^++H]: 250.0799, found: 250.0802.

3.3.7. (2-Chloro-6-fluorophenyl)-(3,5-dimethylphenyl)-amine, **7k**

2-Chloro-6-fluoroaniline (0.12 ml, 1.0 mmol) and 5-bromo-*m*-xylene (0.13 ml, 1.0 mmol) gave the product as a brown oil: 207 mg (83%); R_f ($CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.22 (s, 6H, Me), 5.60 (s, 1H, NH), 6.61 (s, 2H, Ar H), 6.63 (s, 1H, Ar H), 7.03 (ddd, J=9.0, 8.1, 2.9 Hz, 1H, Ar H), 7.22 (dd, J=9.1, 2.9 Hz, 1H, Ar H), 7.27 (dd, J=8.0, 5.5 Hz, 1H, Ar H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.31 (s, CH_3), 109.94 (d, J=16.2 Hz, CH), 115.55 (d, J=21.1 Hz, CH), 118.87 (s, CH), 123.05 (d, J=11.2 Hz, CH), 124.15 (s, CH), 127.78 (d, J=9.3 Hz, C), 136.24 (d, J=3.1 Hz, C), 138.66 (s, C), 146.17 (s, C), 161.47 (d, J=253.5 Hz, CF); ^{19}F NMR (282.65 MHz, $CDCl_3$) δ −120.60 (dd, J=9.1, 5.5 Hz); HRMS (CI) calcd for $C_{14}H_{13}ClFN$ [M^++H]: 250.0799, found: 250.0803.

3.3.8. (2-Chloro-4-fluorophenyl)-(4-methylphenyl)amine, **7y**

2-Chloro-4-fluoroaniline (0.12 ml, 1.0 mmol) and 4-bromotoluene (0.12 ml, 1.0 mmol) gave the product as a brown oil: 115 mg (49%); R_f 0.85 ($CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 3H, Me), 5.84 (br s, 1H, NH), 6.87 (dt, J=8.0, 4.0 Hz, 1H, Ar H), 7.04 (d, J=8.0 Hz, 2H, Ar H), 7.12–7.18 (m, 4H, Ar H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.84 (s, CH_3), 114.39 (d, J=22.3 Hz, CH), 116.35 (d, J=7.7 Hz, CH), 116.80 (d, J=26.1 Hz, CH), 120.50 (s, CH), 121.65 (d, J=10.0 Hz, C), 130.12 (s, CH), 132.47 (s, C), 137.58 (d, J=2.3 Hz, C), 139.30 (s, C), 155.98 (d,

J=241.1 Hz, CF); ^{19}F NMR (282.65 MHz, $CDCl_3$) δ −128.69 (dt, J=9.1, 5.0 Hz); HRMS (CI) calcd for $C_{13}H_{11}ClFN$ [M^++H]: 236.6856, found: 236.6860.

3.4. General method for thermal cyclisation of aminated product to fluorinated carbazole

NaO^tBu (0.240 g, 2.5 mmol), $Pd(OAc)_2$ (0.006 g, 0.025 mmol) and $[HP^tBu_3][BF_4]$ (0.010 g, 0.035 mmol) were suspended in 1,4-dioxane (3 ml). The appropriate aminated intermediate **7** (0.50 mmol) was then added. The reaction was then stirred at reflux temperature for 18 h, allowed to cool and then quenched by addition of $HCl_{(aq)}$ (2 M, 3 ml). The organic phase was extracted with CH_2Cl_2 (2×20 ml), dried ($MgSO_4$), then filtered and the solvent removed under reduced pressure. The crude product mixture was then subjected to column chromatography (SiO_2). Compounds **6j**, **6r** and **6k** prepared by this method where not isolated, rather the conversion to product was determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

3.4.1. 1-Fluoro-7-methoxy-9H-carbazole, *6u*

(2-Chloro-5-methoxyphenyl)-(2-fluorophenyl)amine (0.126 g, 0.50 mmol) gave the product as off-white powder: 61 mg, (57%); R_f 0.85 ($CHCl_3$); mp 149.2−151.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 (s, 3H, OMe), 6.87 (dd, J=8.6, 2.3 Hz, 1H, Ar H), 6.94 (d, J=2.2 Hz, 1H, Ar H), 7.03−7.14 (m, 2H, Ar H), 7.71 (d, J=8.0 Hz, 1H, Ar H), 7.91 (d, J=8.6 Hz, 1H, Ar H), 8.14 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.73 (s, CH_3), 95.01 (s, CH), 100.00 (s, C), 108.91 (s, CH), 109.02 (d, J=12.0 Hz, CH), 110.02 (s, C), 115.21 (s, CH), 119.93 (d, J=5.0 Hz, CH), 121.47 (s, CH), 131.05 (s, C), 150.22 (s, C), 159.63 (s, C), 165.23 (d, J=214.0 Hz, CF); ^{19}F NMR (282.65 MHz, $CDCl_3$) δ −135.49 (dd, J=10.2, 4.5 Hz); HRMS (EI) calcd for $C_{13}H_{10}FNO$ [M^+]: 215.0746, found: 215.0751. Anal. Calcd for $C_{13}H_{10}FNO$: C, 72.55; H, 4.68; N, 6.51. Found: C, 72.51; H, 4.77; N, 6.89.

3.4.2. 1-Fluoro-7-methoxy-6-methyl-9H-carbazole, *6v*

(2-Chloro-5-methoxy-4-methylphenyl)-(2-fluorophenyl)-amine (0.134 g, 0.50 mmol) gave the product as a brown powder: 59 mg (52%); R_f 0.90 ($CHCl_3$); mp 165.6−167.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 3H, Me), 3.84 (s, 3H, OMe), 6.82 (s, 1H, Ar H), 6.94−7.06 (m, 2H, Ar H), 7.62 (dd, J=8.0, 1.1 Hz, 1H, Ar H), 7.70 (s, 1H, Ar H), 7.98 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.92 (s, CH_3), 55.53 (s, CH_3), 92.83 (s, CH), 109.63 (d, J=16.2 Hz, CH), 115.24 (d, J=3.7 Hz, CH), 116.39 (d, J=3.0 Hz, C), 119.82 (d, J=6.2 Hz, CH), 121.97 (s, CH), 127.40 (s, C), 127.26 (d, J=3.7 Hz, C), 131.25 (s, C), 139.61 (s, C), 149.30 (d, J=241.7 Hz, CF), 158.24 (s, C); ^{19}F NMR (282.65 MHz, $CDCl_3$) δ −135.64 (dd, J=9.9, 5.6 Hz); HRMS (EI) calcd for $C_{14}H_{12}FNO$ [M^+]: 229.0903, found: 229.0904. Anal. Calcd for $C_{14}H_{12}FNO$: C, 73.35; H, 5.28; N, 6.11. Found: C, 73.92; H, 5.64; N, 6.22.

3.4.3. 3-Fluoro-9H-carbazole, *6w*

(2-Chlorophenyl)-(4-fluorophenyl)amine (0.111 g, 0.5 mmol) gave the product as white crystals: 59 mg (69%). Crystals of **6w** suitable for X-ray analysis were grown from a concentrated CH_2Cl_2 solution. R_f 0.70 (CH_2Cl_2); mp 201.1−203.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (dt, J=9.0, 2.6 Hz, 1H, Ar H), 7.23 (m, 1H, Ar H), 7.33 (dd, J=8.7, 4.2 Hz, 1H, Ar H), 7.43 (m, 2H, Ar H), 7.72 (dd, J=8.9, 2.6 Hz, 1H, Ar H), 7.98 (br s, 1H, NH), 8.01 (d, J=7.8 Hz, 1H, Ar H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 106.12 (d, J=10.1 Hz, CH), 110.85 (d, J=4.1 Hz, CH), 111.12 (s, CH), 113.58 (d, J=18.9 Hz, CH), 119.50 (s, CH), 120.55 (s, CH), 123.18 (s, C), 126.44 (s, CH), 135.98 (s, C), 141.35 (s, C), 157.68 (d, J=252.0 Hz, CF); ^{19}F NMR (282.65 MHz, $CDCl_3$) δ −124.36 (dt, J=9.0, 4.5 Hz); HRMS (CI) calcd for $C_{12}H_8FN$ [M^++H]: 186.0719, found: 186.0727. Anal. Calcd for $C_{12}H_8FN$: C, 77.82; H, 4.35; N, 7.56. Found: C, 78.25; H, 4.78; N, 7.65.

3.4.4. 3,6-Difluoro-9H-carbazole, *6x*

(2-Chloro-4-fluorophenyl)-(4-fluorophenyl)amine (0.120 g, 0.5 mmol) gave the product as a off-white powder: 43 mg (42%); R_f 0.70 ($CHCl_3$); mp 198.9−200.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (td, J=8.8, 2.6 Hz, 2H, Ar H), 7.35 (dd, J=8.8, 4.2 Hz, 2H, Ar H), 7.66 (dd, J=8.8, 2.6 Hz, 2H, Ar H), 7.98 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 106.14 (d, J=23.6 Hz, CH), 111.50 (d, J=8.7 Hz, CH), 114.41 (d, J=25.5 Hz, CH), 119.45 (d, J=7.6 Hz, C), 136.87 (s, C), 157.44 (d, J=236.1 Hz, CF); ^{19}F NMR (282.65 MHz, $CDCl_3$) δ −124.06 (dt, J=9.9, 6.2 Hz); HRMS (CI) calcd for $C_{16}H_{10}FN$ [M^++H]: 204.0625, found: 204.0616; Anal. Calcd for $C_{12}H_7F_2N$: C, 70.93; H, 3.47; N, 6.89. Found: C, 71.23; H, 3.42; N, 6.66.

3.4.5. 3-Fluoro-6-methyl-9H-carbazole, *6y*

(2-Chloro-4-fluorophenyl)-(4-methylphenyl)amine (0.118 g, 0.50 mmol) gave the product as a brown powder: 48 mg (48%); R_f 0.68 ($CHCl_3$); mp 153.1−155.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.52 (s, 3H, Me), 7.13 (dt, J=8.9, 2.5 Hz, 1H, Ar H), 7.26 (s, 1H, Ar H), 7.29 (d, J=8.0 Hz, 1H, Ar H), 7.31 (d, J=8.0 Hz, 1H, Ar H), 7.68 (dd, J=9.0, 2.5 Hz, 1H, Ar H), 7.81 (s, 1H, Ar H), 7.91 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.48 (s, CH_3), 105.95 (d, J=23.0 Hz, CH), 110.65 (s, CH), 111.11 (s, C), 113.50 (d, J=26.0 Hz, CH), 120.47 (s, CH), 123.77 (d, J=1.9 Hz, C), 127.92 (s, CH), 128.89 (s, CH), 130.01 (s, C), 136.18 (s, C), 138.86 (s, C), 157.48 (d, J=234.0 Hz, CF); ^{19}F NMR (282.65 MHz, $CDCl_3$) δ −124.70 (dt, J=8.2, 5.6 Hz); HRMS (EI) calcd for $C_{13}H_{10}FN$ [M^+]: 199.0797, found: 199.0793. Anal. Calcd for $C_{13}H_{10}FN$: C, 78.37; H, 5.06; N, 7.03. Found: C, 78.98; H, 5.24; N, 7.57.[26]

3.5. X-ray crystallographic analysis of carbazole *6w*

$C_{12}H_8FN$, M=185.19, orthorhombic, a=7.5282(4), b=19.5065(14), c=5.7432(3) Å, V=843.38(9) Å^3, T=120(2) K, space group *Pnma*, Z=4, μ=0.832 mm^{-1}, R_{int}=0.0442 (for

2271 measured reflections), R_1=0.0343 [for 339 unique reflections with $>2\sigma(I)$], wR_2=0.0756 (for all 753 unique reflections). A single crystal of **6w** was coated in high-vacuum grease and mounted on a glass fibre. X-ray measurements were made using an Oxford Diffraction Gemini R Ultra CCD area-detector diffractometer with Cu Kα radiation (λ=1.54178 Å).[27] Intensities were integrated[27] from several series of exposures, each exposure covering a narrow angle in ω or ϕ. Absorption corrections were applied, based on multiple and symmetry-equivalent measurements.[28] The structure was solved by direct methods and refined by least squares on weighted $F2$ values for all reflections.[29] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. All hydrogen atoms were constrained to ideal geometries and were assigned isotropic displacement parameters equal to 1.2 times that of their parent atom. Refinement proceeded smoothly to give the residuals above. Complex neutral-atom scattering factors were used.[30] The fluorine atom is disordered in exact 1:1 ratio over two sites, bonding to C3A and its crystallographic symmetry equivalent C3B. The other component of the disorder is a hydrogen atom similarly distributed over the two sites. Removing the mirror plane from the space group did not reduce this disorder. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 675115. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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