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Palladium catalysed aryl amination reactions in supercritical carbon dioxide

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Palladium catalysed C–N bond formation in supercritical carbon dioxide has been accomplished. Carbamic acid formation is avoided in part through the use of an *N*-silylamine as the coupling partner. Employing a catalyst system of Pd_2dba_3 (1 mol%) and 2-dicyclohexylphosphino-2′,4′,6′-triisopropyl-1,1′-biphenyl (X-Phos) (2 mol%) enabled the catalytic amination of aryl bromides and chlorides with *N*-silylanilines to be realised in excellent yield. Extension of the methodology to the *N*-arylation of *N*-silyldiarylamines, *N*-silylazoles and *N*-silylsulfonamides is reported.

Introduction

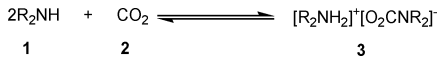
N-Arylamines have found extensive application as pharmaceutical targets,[1] as ligands for metal complexes[2,3] and in electronic and optical materials.[4] Common synthetic protocols for the preparation of arylamines include direct nucleophilic substitution and copper-catalysed Ullmann reactions.[5,6] More recently the palladium catalysed amination of aryl halides under relatively mild conditions has emerged as a powerful and general method for the construction of the *N*-aryl moiety.[7–9]

Aryl amination reactions have until now been confined to the use of volatile organic solvents as the reaction medium. In recent years, supercritical carbon dioxide ($scCO_2$) has emerged as an attractive solvent for a wide range of chemical processes;[10–15] $scCO_2$ is naturally abundant, inflammable and demonstrates low toxicity, making it a more environmentally friendly alternative to the traditional organic solvents currently in widespread use. In addition, $scCO_2$ offers downstream processing benefits such as simple product isolation and purification and the potential for integrated syntheses.[16,17]

Our studies[18–21] and those of others[22,23] have shown that palladium catalysed carbon–carbon bond forming processes (Heck, Suzuki, Stille, and Sonagashira) can be performed as efficiently (or better) in $scCO_2$ as in conventional solvents under both homogeneous and heterogeneous conditions. Recently, we published a preliminary communication describing an extension to the range of palladium catalysed reactions that can be accomplished in $scCO_2$ to include carbon–nitrogen bond formation.[24] We revealed that a series of diarylamines could be successfully synthesised *via* the palladium mediated coupling of aryl bromides and *N*-silylanilines. We report herein the expansion of the scope of our methodology to include the cross-coupling of aryl halides with a range of *N*-silylamines. The results of investigations into alternative palladium–ligand systems will also be discussed.

Results and discussion

Amines are known to exist in carbon dioxide in equilibrium with their carbamic acid ammonium salts (Scheme 1), dramatically affecting their solubility and reactivity.[25–27] This reactivity has been exploited by Fürstner *et al.* temporarily to protect an N–H group *in situ* whilst performing ring closing metathesis in carbon



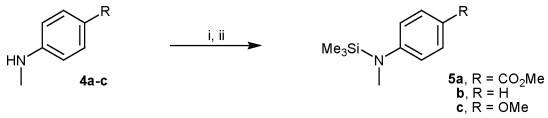
Scheme 1 Carbamic acid ammonium salt formation.

dioxide.[28] Evidently, the possibility of carbamic acid formation could present a major obstacle to our objective of realising C–N cross-coupling reactions in $scCO_2$. Carbamic acid formation may be prevented by employing sterically hindered amines,[26] but the consequences could also be that such amines are incapable of undergoing aryl amination. A possible solution to this problem would be to employ surrogates that could undergo oxidative addition to palladium faster than carbamic acid formation.

Early amination reactions were achieved by Migita and colleagues[29] with aminostannanes and not free amines. Transmetallation of the amino group from tin to the organopalladium complex was followed by reductive elimination furnishing the desired arylamine. Spurred on by this work, we have successfully developed an analogous cross-coupling reaction of less toxic silylamines with aryl halides in both conventional solvents and $scCO_2$. We believe this reaction proceeds *via* the transmetallation of the amino group from silicon to palladium, circumventing the use of free amines and avoiding in part the formation of carbamic acid.

Amination of aryl bromides and aryl chlorides with *N*-silylanilines in $scCO_2$

The *N*-silylanilines **5** were readily prepared from the free amine, base and trimethylsilyl chloride and isolated in pure form *via* vacuum distillation (Scheme 2).



Scheme 2 *Reagents and conditions*: (i) R = CO_2Me; a. *n*-BuLi, THF, −78 °C, 2 h, b. TMSCl, rt, 17 h, 71%; (ii) R = OMe or H; Et_3N, CH_2Cl_2, R = OMe 73%, R = H 65%.

Our initial work[24] focused on the catalyst system of palladium acetate (2.5 mol%) and the bulky, electron rich ligand di-*tert*-butylbiphenylphosphine (5 mol%) developed by Buchwald.[30]

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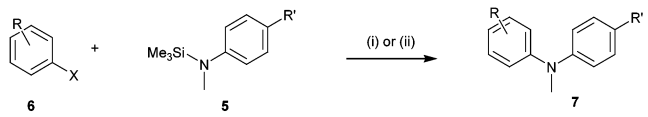
Table 1 Amination of aryl halides with *N*-silylanilines in $scCO_2$



6 5 7

					Conditions (i)		Conditions (ii)	
Entry	X	R	R′	Product **7**	Time/h	Yield (%)	Time/h	Yield (%)
1	Br	4-NO_2	CO_2Me	**a**	—	—	17	80
2	Br	4-NO_2	H	**b**	—	—	17	87
3	Cl	4-NO_2	H	**b**	—	—	24	75
4	Br	4-CO_2Me	CO_2Me	**c**	17	84[a]	17	89
5	Br	4-CO_2Me	H	**d**	48	76	17	90
6	Br	4-CO_2Me	OMe	**e**	48	77	17	71
7	Br	4-*t*Bu	H	**f**	—	—	17	74
8	Cl	4-Me	H	**g**	—	—	24	61
9	Br	H	CO_2Me	**d**	17	77	17	74
10	Br	H	H	**h**	48	55	17	76
11	Br	H	OMe	**i**	48	66	17	83
12	Br	4-OMe	CO_2Me	**e**	17	57	17	77
13	Br	4-OMe	H	**i**	48	25	17	73
14	Cl	4-OMe	H	**i**	—	—	24	73
15	Br	4-OMe	OMe	**j**	48	25	17	62
16	Cl	4-OMe	OMe	**j**	—	—	48	56
17	Cl	2-OMe	H	**k**	—	—	48	10

Reagents and conditions: (i) 2.5 mol% $Pd(OAc)_2$, 5 mol% P(*t*-Bu)$_2$(*o*-biphen), 1.4 equiv. Cs_2CO_3, $scCO_2$, 1800 psi, 100 °C unless otherwise indicated.[a] 3000 psi; (ii) 1 mol% Pd_2dba_3, 2 mol% 2-dicyclohexylphosphino-2′,4′,6′-triisopropyl-1,1′-biphenyl (X-Phos), 1.4 equiv. Cs_2CO_3, $scCO_2$, 1800 psi, 100 °C.

Using this catalyst system, good to excellent yields were obtained for the coupling of electron deficient and electron neutral aryl bromides [Table 1, conditions (i), entries 4–6, 9–11]. However, only poor yields were achieved with electron rich aryl bromides [Table 1, conditions (i), entries 12, 13 and 15].

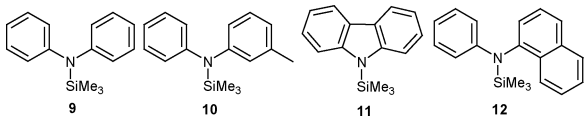
In order to improve the overall performance of our methodology, an extensive screening of palladium–ligand catalyst systems was undertaken. The catalyst system comprising Pd_2dba_3 (1 mol%) and 2-dicyclohexylphosphino-2′,4′,6′-triisopropyl-1,1′-biphenyl (X-Phos) (2 mol%) was observed to show the highest activity.[31] The cross-coupling of a range of both electron rich and electron poor aryl bromides with a variety of silylanilines was achieved in excellent yield. The most improved results were observed for the coupling of the electron-rich silylaniline (4-methoxyphenyl)-methyltrimethylsilylamine **5c** with electronically neutral and rich aryl bromides (Table 1, entries 11 and 15). For example, the reaction of (4-methoxyphenyl)-methyltrimethylsilylamine and bromoanisole using the Pd_2dba_3–X-Phos catalyst system afforded the required product in 62% yield [Table 1, conditions (ii), entry 15] after 17 h. Previously, only a 25% yield was achievable after 48 h [Table 1, conditions (i), entry 15].[24]

The use of aryl chlorides in cross-coupling chemistry has been actively pursued because of their low cost and ready availability.[32,33] Using our Pd_2dba_3–X-Phos catalyst system, we found that the coupling of aryl chlorides and *N*-silylanilines was indeed possible. Good yields were achieved with *para*-substituted aryl chlorides; however, longer reaction times than those required for the coupling of aryl bromides were necessary depending on the substrate involved [Table 1, conditions (ii), entries 2 *cf.* 3, 13 *cf.* 14, 15 *cf.* 16]. The amination of *ortho*-substituted chloroanisole with *N*-trimethylsilyl methylaniline was extremely sluggish, affording only a 10% yield after 48 h [Table 1, conditions (ii), entry 17].

Control amination reactions were carried out between methyl 4-bromobenzoate and the protio analogues of **5**, (*N*-methylaniline, the 4-OMe, and 4-CO_2Me derivatives). In all cases, the respective yields of products **7d**, **7e** and **7c** were considerably lower than those shown in Table 1. We conclude that the silicon substituent plays an important role in allowing efficient amination to take place in $scCO_2$.

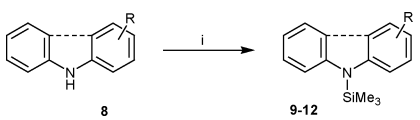
Amination of aryl bromides with *N*-silyldiarylamines in $scCO_2$

The triarylamine subunit is a fundamental structure that features in many biologically active compounds and novel materials, making them attractive targets.[4] We therefore turned our attention towards the extension of our methodology to the synthesis of triarylamines. *N*-Silyldiarylamines **9–12** (Fig. 1) were synthesised using a similar procedure to that used for anilines (Scheme 3). Deprotonation of the diamine with *n*-BuLi furnished the lithium amide which was readily trapped with chlorotrimethylsilane to yield the *N*-silyldiarylamine in good to excellent yield (53–91%).



9 10 11 12

Fig. 1 *N*-Trimethylsilyldiarylamines used in cross-couplings.



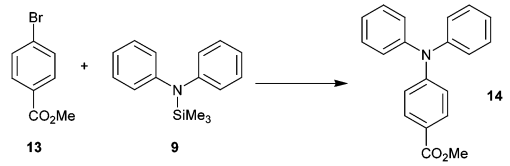
8 9-12

Scheme 3 *Reagents and conditions*: (i) a. *n*-BuLi, THF, −78 °C, 2 h, b. TMSCl, rt, 17 h.

A range of catalyst systems was screened, with the combination of Pd_2dba_3 and P(*t*-Bu)$_3$ demonstrating the most promise. Nonetheless, an unsatisfactory yield of only 28% was obtained after 48 h (Table 2, entry 1), and other additives were explored.

Whilst the transfer of carbon functionalities (alkenyl, allyl, alkynyl and aryl) from silicon to palladium is known, in most cases the addition of a fluoride source is required to facilitate this process.[34,35] A pentacoordinated silicon species is formed

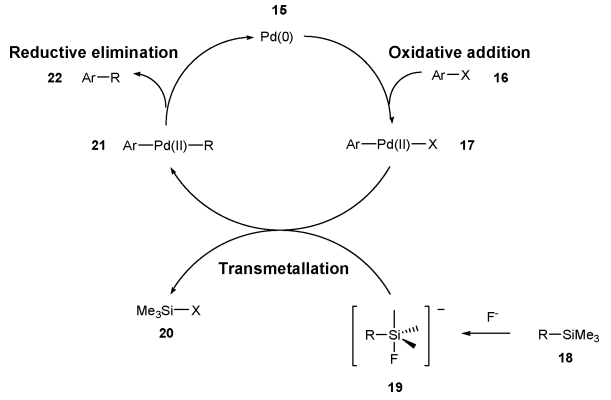
Table 2 Effect of fluoride additive on the amination of methyl 4-bromobenzoate **13** with *N*-silyldiphenylamine **9** in $scCO_2$



Entry	Additive	Yield[a] (%)
1	—	28
2	KF	50
3	CsF	89

Reagents and conditions: 2.5 mol% Pd_2dba_3, 5 mol% P(*t*-Bu)$_3$, 1.4 equiv. Cs_2CO_3, 2 equiv. additive, $scCO_2$, 1800 psi, 100 °C, 48 h.[a] Determined by gas chromatography.

which enhances the nucleofugacity of the sp^2 carbon atom and promotes transmetallation.[36] In the cross-coupling of *N*-silylanilines, we had ascribed the efficient transmetallation of nitrogen from silicon to palladium in the absence of fluoride to the enhanced nucleophilicity of nitrogen relative to carbon. Diarylamines are much less nucleophilic than their monoaryl analogues [pK_a $C_6H_5NH_3^+$ 4.6 *cf.* pK_a $(C_6H_5)_2NH_2^+$ 0.78]. Therefore we believed the addition of fluoride might enhance the transmetallation step according to the proposed mechanistic cycle shown in Scheme 4. On the addition of 2 equivalents of CsF to the reaction mixture containing **13** and **9** we were pleased to observe a dramatic increase in yield of **14** from 28% to 89% (Table 2, entry 3).



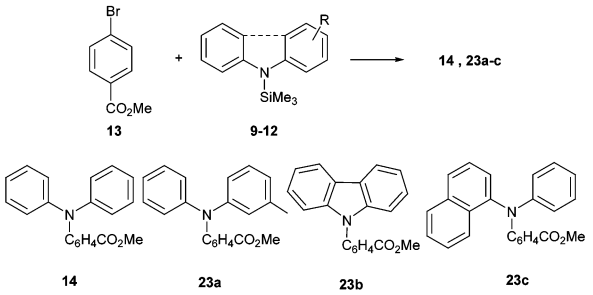
Scheme 4 Mechanistic cycle of palladium catalysed cross-coupling involving fluoride additive.

Extending the scope of triarylamines which could be synthesised efficiently *via* our methodology proved challenging. The reaction of *N*-silyldiarylamines **9–12** with methyl 4-bromobenzoate **13** proceeded in moderate to good yields although extended reaction times were required to drive the reactions to completion (Table 3).

The effect of electronic substituents on the aryl bromide was also investigated (Table 4). In all the cases studied, the yields were lower than those observed for methyl 4-bromobenzoate (Table 4, entry 1). No reaction was observed between *N*-silyldiphenylamine **9** and the electron rich 4-bromoanisole **24c** (Table 4, entry 4). We believe the superior behaviour demonstrated by the coupling partner methyl 4-bromobenzoate **13** may be attributed to the presence of the CO_2Me substituent. Oxygen-containing functional groups interact with CO_2 and are known to enhance the solubility of compounds in CO_2 dramatically.[37]

Our cross-coupling protocol was next applied to the synthesis of diaryl benzidines (Table 5) that have achieved prominence

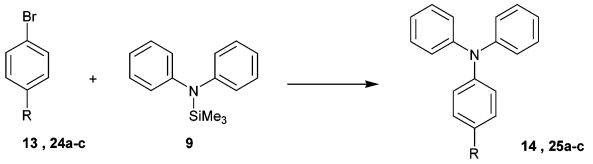
Table 3 Amination of methyl 4-bromobenzoate **13** with *N*-silyldiarylamines **9–12** in $scCO_2$



Entry	Amine	Product	Yield (%)
1	**9**	**14**	83
2	**10**	**23a**	53
3	**11**	**23b**	54
4	**12**	**23c**	70

Reagents and conditions: 2.5 mol% Pd_2dba_3, 5 mol% P(*t*-Bu)$_3$, 1.4 equiv. Cs_2CO_3, 2 equiv. CsF, $scCO_2$, 1800 psi, 100 °C, 48 h.

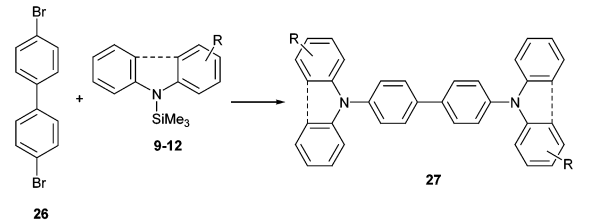
Table 4 Amination of aryl bromides **13**, **24** with *N*-silyldiphenylamine **9** in $scCO_2$



Entry	**13**, **24**	Product	Yield (%)
1	**13**, R = COOMe	**14**	83
2	**24a**, R = NO_2	**25a**	58
3	**24b**, R = F	**25b**	46
4	**24c**, R = OMe	**25c**	0

Reagents and conditions: 2.5 mol% Pd_2dba_3, 5 mol% P(*t*-Bu)$_3$, 1.4 equiv. Cs_2CO_3, 2 equiv. CsF, $scCO_2$, 1800 psi, 100 °C, 48 h.

Table 5 Amination of 4, 4′-dibromobiphenyl **26** with *N*-silyldiarylamines **9–12** in $scCO_2$



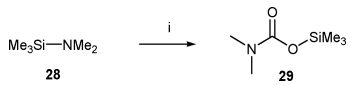
Entry	Amine	Product **27**	Yield (%)
1	**9**	**a**	58
2	**10**	**b**	38
3	**11**	**c**	47
4	**12**	**d**	35

Reagents and conditions: 5 mol% Pd_2dba_3, 10 mol% P(*t*-Bu)$_3$, 2.8 equiv. Cs_2CO_3, 4 equiv. CsF, $scCO_2$, 1800 psi, 100 °C, 48 h.

in xerography and other organic electronic applications. Disappointingly, the amination of 4, 4′-dibromobiphenyl **26** with a range of *N*-silyldiarylamines **9–12** did not occur cleanly, with monosubstituted product being detected in all cases examined. This may have been due to the poor solubility of the products in $scCO_2$.

N-Arylation of *N*-silylazoles

In our initial studies we had observed that aliphatic silylamines tended to form *O*-silylcarbamates *in situ* by CO_2 insertion into the N–Si bond (Scheme 5). However, aromatic silylamines were found to be sufficiently stable, presumably owing to their lower nucleophilicity (pK_a $C_6H_5NH_3^+$ 4.6 *cf.* pK_a $MeNH_3^+$ 10.65). With this in mind, we set out to explore amination reactions with aromatic silylamines whose conjugate acids exhibited pK_a values of approximately 5 or lower.

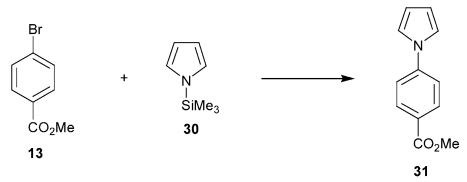


Scheme 5 *Reagents and conditions*: (i) $scCO_2$, 60 °C, 1800 psi.

N-Aryl azoles are important synthetic targets, show diverse activity in biological systems, and the precursor azoles conform to the pK_a requirement. Initial studies were carried out in toluene on a model cross-coupling of methyl 4-bromobenzoate **13** and *N*-trimethylsilylpyrrole **30** using a $Pd(OAc)_2$–P(*t*-Bu)$_2$(*o*-biphen) catalyst system. The addition of fluoride was again found to be crucial to the success of the reaction (Table 6); a dramatic increase in yield from 6% to 68% was observed on the addition of one equivalent of KF (with respect to *N*-silylpyrrole).

Transfer of the catalyst system to $scCO_2$ proved fairly successful. Employing 5 mol% $Pd(OAc)_2$, 10 mol% P(*t*-Bu)$_2$(*o*-biphen) and 1.2 equivalents KF, the reaction of *N*-silylpyrrole **30** with an electron-poor aryl bromide furnished the coupled product in a moderate yield (59%) (Table 7, entry 1, ligand **35**). The coupling of less activated aryl bromides was found to be poor. Of note was the difference in ability between silylpyrrole **30** and silylindole **32** to undergo cross-coupling with bromobenzene **24d** (Table 7, entry 2 *cf.* entry 5, ligand **35**). Contrasting results were obtained with a poor 11% yield for the reaction with silylpyrrole **30** and an acceptable 68% yield for the reaction with silylindole **32**. We believe this disparity in reactivity could be attributed to the steric bulk of the indole species, promoting more efficient reductive elimination. We postulated that using more hindered ligands would increase the crowding around the transition metal and act in a similar manner to improve reactivity. Thus a systematic study of the effect of increasingly bulky ligands was undertaken (Table 7). It is clear from the results that the structure of the ligand is important and that a balance must be found between hindered and non-hindered. For example, 1-(di-*tert*-butylphosphino)-1′-(isopropyl)biphenyl **36** effected the desired cross-coupling transformation between silylpyrrole **30** and bromobenzene **24d** more effectively than both the more hindered ligand 2-dicyclohexylphosphino-2′,4′,6′-triisopropyl-1,1′-biphenyl **38** and the less hindered di-*tert*-butylbiphenylphosphine **35** (Table 7, entry 2). Overall, ligand **36** demonstrated the best cross-coupling yields with the full range of aryl bromides.

Table 6 Effect of fluoride additive on the amination of methyl 4-bromobenzoate **13** with *N*-silylpyrrole **30** in toluene



Entry	Additive	Yield (%)
1	None	6
2	TBAF	0
3	TBAF + 4 Å MS	0
4	CsF	<5
5	KF	68

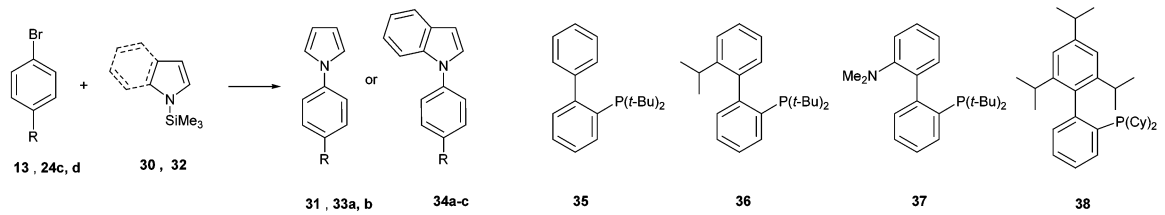
Reagents and conditions: 5 mol% $Pd(OAc)_2$, 10 mol% P(*t*-Bu)$_2$(*o*-biphen), 1.2 equiv. additive, 1.4 equiv. Cs_2CO_3, toluene, 100 °C, 17 h.

In an attempt to improve the coupling of electron-neutral and electron-rich coupling partners we employed silacyclobutanes as the silyl protecting group. Silacyclobutanes have been shown by Denmark and Sweis to exhibit enhanced Lewis acidity compared with acyclic silanes and have been used with great effect in organosilicon chemistry.[34,35] The greater Lewis acidity of silacyclobutanes can promote the formation of the activated pentacoordinate silicon species. In order to investigate this hypothesis, 1-methyl-1-azolyl-silacyclobutanes **40** and **42** were synthesised and their reactivity was studied.

Dropwise addition of an excess of 1-chloro-1-methylsilacyclobutane to a solution of the azole anion at −78 °C in THF followed by stirring at room temperature overnight and purification by vacuum distillation afforded the 1-methyl-1-azolyl-silacyclobutanes **40** and **42** in excellent yield (Scheme 6).

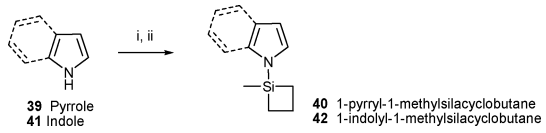
The reactivity of the silacyclobutanes **40** and **42** towards palladium-catalysed *N*-arylation in $scCO_2$ was first investigated under the optimised conditions developed for the trimethylsilyl analogues [1 equiv. aryl bromide, 1.2 equiv. silacyclobutane, 1.4 equiv. Cs_2CO_3, 1.2 equiv. KF, 5 mol% $Pd(OAc)_2$ and 10 mol%

Table 7 Effect of ligand **35–38** on the amination of aryl bromides with *N*-silylarylazoles in $scCO_2$



Entry	Substrate	**13**, **24**	Product	Effect of ligand **35–38** on yield (%) **35**	**36**	**37**	**38**
1	**30**	**13**, R = CO_2Me	**31**	59	75	79	—
2	**30**	**24d**, R = H	**33a**	11	46	24	4
3	**30**	**24c**, R = OMe	**33b**	7	30	21	0
4	**32**	**13**, R = CO_2Me	**34a**	70	88	—	—
5	**32**	**24d**, R = H	**34b**	68	70	—	—
6	**32**	**24c**, R = OMe	**34c**	25	50	—	—

Reagents and conditions: 5 mol% $Pd(OAc)_2$, 10 mol% ligand, 1.2 equiv. KF, 1.4 equiv. Cs_2CO_3, $scCO_2$, 1800 psi, 100 °C, 17 h.

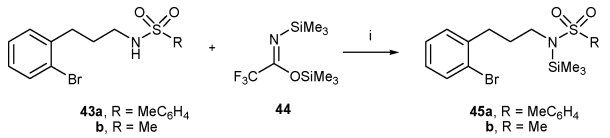


Scheme 6 *Reagents and conditions*: (i) *n*-BuLi, THF, −78 °C; (ii) 1.2 equiv. $Me(C_3H_6)SiCl$, −78 °C → rt. **40**, 70%; **42**, 79%. Note that use of one equivalent of 1-chloro-1-methylsilacyclobutane resulted in decomposition of material on attempted distillation.

P(*t*-Bu)$_2$(i-Pr-biphen)]. The results in Table 8 are illustrated for the pyrrole derivative **40**. Reactions conducted at 75 °C were higher yielding for the silacyclobutane derivatives, although no significant improvement was observed at 100 °C (Table 8). Arylation with bromobenzene **24d** showed an increase from 39% to 50% (Table 8, entry 2 *cf.* entry 5) and with bromoanisole **24c** from 25% to 38% (Table 8, entries 3, 6) at 75 °C. Lowering the reaction temperature further to 50 °C resulted in poor conversion. Analogous results were obtained with the indole derivative **42** (see experimental).

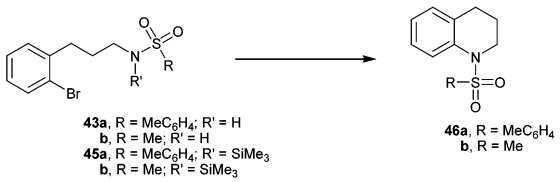
Extending the scope of C–N bond formation

The results so far have been limited to examples of palladium-catalysed amination with aromatic or heteroaromatic amines. Aliphatic amines were unreactive and formed silylcarbamates. We therefore sought functionality that could be attached to the aliphatic amine to tune its reactivity and be readily removed once coupling was complete. Free amides showed no reactivity in $scCO_2$ and the *N*-silylated analogues could not be synthesised owing to preferred *O*-silylation. Sulfonamides having a pK_a of *ca.* 10 and the capability of conversion back to the free amine[38] were an attractive option. Following the precedent of Buchwald *et al.*[39] the intramolecular coupling of *N*-silylsulfonamides **45** was investigated. Synthesis of *N*-silylsulfonamides was best achieved using the method of Iley, Bassindale and Patel.[40] Heating a solution of the sulfonamide **43** in acetonitrile with an excess of bis(trimethylsilyl)-trifluoroacetamide (BSTFA) **44** at reflux followed by purification *via* vacuum distillation furnished the product *N*-silylated sulfonamides **45** in excellent yield (Scheme 7).



Scheme 7 *Reagents and conditions*: (i) MeCN, reflux, 3 h, R = MeC_6H_4, 95%; R = Me, 76%.

Table 9 Intramolecular arylation of sulfonamides in $scCO_2$



Entry	Substrate	Additive	Time/h	Product **46**	Yield (%)
1	**43a**	—	17	**a**	20
2	**45a**	—	41	**a**	61
3	**45a**	KF	41	**a**	57
4	**43b**	—	17	**b**	22
5	**45b**	—	41	**b**	55
6	**45b**	KF	41	**b**	72

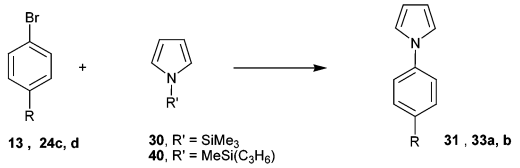
Reagents and conditions: 2.5 mol% $Pd(OAc)_2$, 5 mol% P(*t*-Bu)$_2$(*o*-biphen), 1.2 equiv. additive, 1.4 equiv. Cs_2CO_3, $scCO_2$, 1800 psi, 100 °C, 17 h.

Cyclisation of the *N*-tosyl and the *N*-methanesulfonamides **43a** and **43b** and their *N*-silylated equivalents **45a** and **45b** was investigated in $scCO_2$ using a catalyst system of 2.5 mol% $Pd(OAc)_2$ and 5 mol% P(*t*-Bu)$_2$(*o*-biphen) and Cs_2CO_3 as base (Table 9). The use of the silylamine as a surrogate for the free amine was essential for good conversion in both systems. Longer reaction times were required to complete the cyclisation of the more bulky tosyl derivatives. Interestingly, the effect of the addition of KF increased the reaction yield for methanesulfonamide **45b** but decreased the yield for the tosyl analogue **45a**. We have no explanation for this observation.

Conclusion

In summary, an efficient method for C–N bond formation in supercritical carbon dioxide has been achieved using an *N*-silylated amine as a surrogate for the free amine. *N*-Arylation of anilines with aryl bromides and aryl chlorides has been accomplished in excellent yield. The methodology has been extended to realise the *N*-arylation of azoles and the intramolecular arylation of sulfonamides in good to excellent yield. Expansion of the palladium mediated C–N bond formation methodology to $scCO_2$ as a solvent provides potential for the processing and environmental benefits of this reaction medium to be exploited.

Table 8 Amination of aryl bromides with 1-pyrryl-1-methylsilacyclobutane **40** in $scCO_2$



Entry	**13**, **24**	Substrate	Product	Yield (%) 100 °C	75 °C	50 °C
1	**13**, R = CO_2Me	**30**	**31**	75	61	—
2	**24d**, R = H	**30**	**33a**	46	39	—
3	**24c**, R = OMe	**30**	**33b**	30	25	—
4	**13**, R = CO_2Me	**40**	**31**	46	48	24
5	**24d**, R = H	**40**	**33a**	49	50	3
6	**24c**, R = OMe	**40**	**33b**	37	38	4

Reagents and conditions: 5 mol% $Pd(OAc)_2$, 10 mol% P(*t*-Bu)$_2$(i-Pr-biphen), 1.2 equiv. KF, 1.4 equiv. Cs_2CO_3, $scCO_2$, 1800 psi, 100 °C, 17 h.

Experimental

General

^{1}H-NMR spectra were recorded on Bruker DRX-400 (400 MHz) and Bruker DRX-500 (500 MHz) instruments using an internal deuterium lock. The chemical shift data for each signal is given in units δ relative to tetramethylsilane (TMS) where δ(TMS) = 0.00 ppm and referenced to the residual solvent. The multiplicity of the signal is indicated as: s-singlet, d-doublet, t-triplet, q-quartet, qu-quintet, br-broad, m-multiplet, dd-doublet of doublets, dt-doublet of triplets *etc.* Coupling constants (J) are quoted in Hz and are recorded to the nearest 0.5 Hz.

^{13}C-NMR spectra were recorded on Bruker DRX-400 (100 MHz) and Bruker DRX-500 (125 MHz) instruments using an internal deuterium lock with proton decoupling. The chemical shift data for each signal is given in units of δ relative to tetramethylsilane (TMS) where δ(TMS) = 0.00 ppm. The multiplicity of the signal was determined by APT (Attached Proton Test) experiments and is indicated as C (s), CH (d), CH_2 (t) and CH_3 (q) groups where determined.

Infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrometer. The sample was prepared as a thin liquid film or as a solution in the solvent indicated. Relative intensities are indicated as s-strong, m-medium, w-weak and br-broad.

Mass spectra were recorded by the Mass Spectrometry Service of the University of Swansea. In Swansea, Electron Impact (EI) and Chemical Ionisation (CI) low resolution spectra were carried out on a VG model 12–253 under ACE conditions and a Quattro II low resolution triple quadrupole MS. Accurate mass measurements for EI and CI were performed on a +VG ZAB–E instrument and Finnigan MAT 900 XLT instruments. All CI measurements were performed with NH_3 as the carrier gas.

Melting points were determined using a Köfler block melting point apparatus and are uncorrected.

Kugelrohr bulb-to-bulb distillations were carried out using a Büchi GKR-51 machine. Boiling points are the actual oven temperatures.

Flash chromatography[41] was carried out on silica gel [Merck 9385 Kieselgel 60 (230–400 ASTM)]. TLC was performed on 0.25 mm thick plates precoated with Merck Kieselgel 60 F_{254} silica gel.

Non-aqueous reactions were carried out under an atmosphere of dry nitrogen or argon unless indicated to the contrary.

Dry THF was distilled from sodium in a recycling still using benzophenone ketyl as indicator. Other solvents were purified by standard techniques.[42] Ether refers to diethyl ether. Brine refers to a saturated solution of sodium chloride in water.

Reactions in supercritical carbon dioxide were conducted in a 10 cm^3 stainless steel cell. Carbon dioxide (Messer 99.9995%-further purified over an Oxisorb® catalyst) was delivered to the reaction using a NWA Pickel PM101 air driven pump at the desired pressure. Heating of the cell was achieved by the use of a heating tape. The system pressure was measured by a pressure transducer (A105, RDP Electronics) and displayed on a digital display (E308, RDP Electronics). The internal temperature was monitored by an Industrial Mineral Insulated thermocouple (Type K, RS Electronics) and displayed on a temperature indicator (T200, RS Electronics).

4-[Methyl(trimethylsilyl)amino]benzoic acid methyl ester, 5a. To a solution of 4-(methylamino)benzoic acid methyl ester (2.0 cm^3, 29 mmol) dissolved in dry THF (50 cm^3) under nitrogen and cooled to −78 °C was added *n*-BuLi (1.59 M in hexanes; 18.1 cm^3, 29 mmol, 1 eq). The solution was stirred at −78 °C for 2 h. Chlorotrimethylsilane (4.4 cm^3, 45 mmol, 1.2 eq) was added dropwise and the resultant mixture allowed to warm to room temperature and stirred overnight during which time LiCl precipitated out.

The stirring was stopped and the clear solution separated *via* cannula. The filtrant was concentrated under atmospheric pressure under nitrogen and the residue was purified by vacuum distillation through a short Vigreux column to furnish 4-[methyl(trimethylsilyl)amino]benzoic acid methyl ester **5a** (bp 138–142 °C, 2 mmHg) (2.84 g, 71%) as a colourless oil. δ_H(400 MHz; distilled $CDCl_3$) 7.89 (2H, dd, J 9.0 and 2.5, Ar*H*), 6.85 (2H, dd, J 9.0 and 2.5, Ar*H*), 3.86 (3H, s, OCH_3), 2.92 (3H, s, NCH_3) and 0.33 [9H, s, Si(CH_3)$_3$]; δ_C(100 MHz; distilled $CDCl_3$) 167.3 (s), 155.2 (s), 130.6 (s), 119.0 (d), 115.6 (d), 51.5 (q), 34.8 (q) and 0.8 (q).

***N*-Methyl trimethylsilylaniline, 5b.** To a solution of chlorotrimethylsilane (8.78 cm^3, 70 mmol, 1.5 eq) in dry dichloromethane (40 cm^3) cooled to 0 °C under nitrogen was added triethylamine (6.43 cm^3, 46 mmol, 1 eq). *N*-Methylaniline (5.0 cm^3, 46 mmol) was added dropwise over 0.5 h and the reaction mixture was allowed to warm to room temperature and stirred for 48 h.

The dichloromethane and excess unreacted chlorotrimethylsilane were removed under nitrogen *via* distillation. Dry pentane (60 cm^3) was added to the residue and the mixture stirred for a further 1 h in order to ensure complete precipitation of the amine salts. The salts were allowed to settle and the clear solution removed through a cannula. The salts were washed with further portions of pentane (2 × 20 cm^3) and the process repeated.

The combined pentane washes were purified by distillation under nitrogen. The filtrant was concentrated under atmospheric pressure and the residue purified by vacuum distillation through a Vigreux column (10 cm) to furnish the pure silylamine **5b** (bp 110–112 °C, 53 mmHg) (5.36 g, 65%) as a colourless oil. δ_H(400 MHz; distilled $CDCl_3$) 7.29 (2H, dd, J 8.5 and 8.0, Ar*H*), 6.97 (2H, d, J 8.5, Ar*H*), 6.87 (1H, t, J 8.0, Ar*H*), 2.98 (3H, s, NCH_3) and 0.36 [9H, s, Si(CH_3)$_3$]; δ_C(100 MHz; distilled $CDCl_3$) 151.0 (s), 128.7 (s), 118.4 (d), 117.7 (d), 35.2 (q) and 0.8 (q).

(4-Methoxyphenyl)-methyl-trimethylsilylamine, 5c. To a solution of chlorotrimethylsilane (2.93 cm^3, 23 mmol, 1.5 eq) in dry dichloromethane (15 cm^3) cooled to 0 °C under nitrogen was added triethylamine (2.14 cm^3, 15.4 mmol, 1 eq). A solution of *N*-methyl-4-anisidine (2.1 g, 15 mmol) in dichloromethane (5 cm^3) was added dropwise over 0.5 h and the reaction mixture was allowed to warm to room temperature and stirred for 17 h.

The dichloromethane and excess unreacted chlorotrimethylsilane were removed under nitrogen *via* distillation. Dry pentane (20 cm^3) was added to the residue and the mixture stirred for a further 1 h in order to ensure complete precipitation of the amine salts. The salts were allowed to settle and the clear solution removed through a cannula. The salts were washed with further portions of pentane (2 × 10 cm^3) and the process repeated.

The combined pentane washes were purified by distillation under nitrogen. The filtrant was concentrated under atmospheric pressure and the residue purified by vacuum distillation through a Vigreux column (10 cm) to furnish the pure silylamine **5c** (bp 88–90 °C, 2 mmHg) (2.33 g, 73%) as a colourless oil. δ_H(400 MHz; distilled $CDCl_3$) 6.85 (2H, d, J 8.0, Ar*H*), 6.82 (2H, d, J 8.0, Ar*H*), 3.79 (3H, s, OCH_3), 2.91 (3H, s, NCH_3) and 0.24 [9H, s, Si(CH_3)$_3$]; δ_C(100 MHz; distilled $CDCl_3$) 153.2 (s), 144.8 (s), 120.9 (d), 114.1 (d), 55.6 (q), 36.2 (q) and 0.4 (q).

The catalytic amination of aryl halides with silylamines in $scCO_2$ (general procedure A) [conditions (i)]. A 10 cm^3 stainless steel high pressure cell equipped with a PTFE stirrer bar was charged with caesium carbonate (228 mg, 0.7 mmol, 1.4 eq), $Pd(OAc)_2$ (2.8 mg, 0.012 mmol, 2.5 mol%), di-*tert*-butyl biphenylphosphine (7.5 mg, 0.025 mmol, 5 mol%) and aryl halide (0.5 mmol, 1 eq) and then sealed. The cell was evacuated and refilled with nitrogen (3 cycles). The silylamine (0.6 mmol, 1.2 eq) was injected through the inlet port into the cell and the cell connected to the CO_2 manifold. It was then filled with liquid CO_2 to approximately 800 psi (volume of CO_2 *ca.* 1 cm^3) and the cell heated to 100 °C. The pressure was adjusted to *ca.* 1800 psi by the addition of further CO_2. The reaction mixture was then

stirred at this temperature and pressure for the required time. After the reaction mixture was cooled to room temperature, the contents of the cell were vented into ethyl acetate (20 cm^3). The cell was opened and rinsed with further portions of ethyl acetate (3×10 cm^3) and the washing solutions combined with the vented solution. The organic solution was filtered, concentrated *in vacuo* to give the crude material which was purified by flash column chromatography.

The catalytic amination of aryl halides with silylamines in $scCO_2$ (general procedure B) [conditions (ii)]. A 10 cm^3 stainless steel high pressure cell equipped with a PTFE stirrer bar was charged with caesium carbonate (228 mg, 0.7 mmol, 1.4 eq), Pd_2dba_3 (4.6 mg, 0.005 mmol, 1.0 mol%), X-Phos (4.8 mg, 0.01 mmol, 2.0 mol%) and aryl halide (0.5 mmol, 1.0 eq) and then sealed. The cell was evacuated and refilled with nitrogen (3 cycles). The silylamine (0.6 mmol, 1.2 eq) was injected through the inlet port into the cell and the cell connected to the CO_2 manifold. It was then filled with liquid CO_2 to approximately 800 psi (volume of CO_2 *ca.* 1 cm^3) and the cell heated to 100 °C. The pressure was adjusted to *ca.* 1800 psi by the addition of further CO_2. The reaction mixture was then stirred at this temperature and pressure for the required time. After the reaction mixture was cooled to room temperature, the contents of the cell were vented into ethyl acetate (20 cm^3). The cell was opened and rinsed with further portions of ethyl acetate (3×10 cm^3) and the washing solutions combined with the vented solution. The organic solution was filtered, concentrated *in vacuo* to give the crude material which was purified by flash column chromatography.

4-[Methyl(4-nitrophenyl)amino]benzoic acid methyl ester [7a, Table 1, entry 1, conditions (ii)]. General procedure B using 1-bromo-4-nitrobenzene (101 mg, 0.5 mmol, 1.0 eq) and 4-[methyl(trimethylsilyl)amino]benzoic acid methyl ester **5a** (142 mg, 0.6 mmol, 1.2 eq) gave the title compound **7a** (114 mg, 80%) as a yellow solid after 17 h. R_f 0.30 (1 : 3 ethyl acetate–hexane); mp 149-151 °C (from ethyl acetate–hexane); found: C, 62.9; H, 4.9; N, 9.7%. $C_{15}H_{14}N_2O_4$ requires C, 62.9; H, 4.9; N, 9.8%; ν_{max} (nujol)/cm^{-1} 2970 s, 2943 s, 2885 s, 2841 s, 2359 m, 1724 m, 1587 m, 1460 s and 1377 s; δ_H(500 MHz; $CDCl_3$) 8.12 (2H, d, *J* 9.5, Ar*H*), 8.07 (2H, d, *J* 9.0, Ar*H*), 7.25 (2H, d, *J* 9.0, Ar*H*), 6.90 (2H, d, *J* 9.5, Ar*H*), 3.93 (3H, s, OCH_3) and 3.46 (3H, s, NCH_3); δ_C(125 MHz; $CDCl_3$) 166.3 (s), 152.9 (s), 150.6 (s), 139.8 (s), 131.4 (d), 126.6 (s), 125.6 (d), 124.0 (d), 115.4 (d), 52.2 (q) and 40.3 (q); *m*/*z* (ES) 287.1027 [(M + H)$^+$. $C_{15}H_{15}O_4N_2$ requires M, 287.1026]. *m*/*z* (EI) 286 (M^+, 90%).

Methyl(4-nitrophenyl)phenylamine[43] [7b, Table 1, entry 2, conditions (ii)]. General procedure B using 1-bromo-4-nitrobenzene (101 mg, 0.5 mmol, 1.0 eq) and *N*-methyl-trimethylsilylaniline **5b** (107 mg, 0.6 mmol, 1.2 eq) gave the title compound **7b** (99 mg, 87%) as a bright yellow oil after 17 h. R_f 0.18 (1 : 9 ethyl acetate–hexane); δ_H(500 MHz; $CDCl_3$) 8.06 (2H, d, *J* 9.5, Ar*H*), 7.46 (2H, dd, *J* 9.0 and 7.5, Ar*H*), 7.31 (1H, t, *J* 7.5, Ar*H*), 7.23 (2H, d, *J* 9.5, Ar*H*), 6.67 (2H, d, *J* 9.0, Ar*H*) and 3.41 (3H, s, OCH_3). Spectroscopic data identical to literature values.

Methyl(4-nitrophenyl)phenylamine[43] [7b, Table 1, entry 3, conditions (ii)]. General procedure B using 1-chloro-4-nitrobenzene (79 mg, 0.5 mmol, 1.0 eq) and *N*-methyl-trimethylsilylaniline **5b** (107 mg, 0.6 mmol, 1.2 eq) gave the title compound **7b** (86 mg, 75%) as a bright yellow oil after 24 h.

Bis-(4-methoxycarbonylphenyl)methylamine [7c, Table 1, entry 4, conditions (i)]. General procedure A using methyl 4-bromobenzoate (108 mg, 0.5 mmol, 1.0 eq) and 4-[methyl(trimethylsilyl)amino]benzoic acid methyl ester **5a** (142 mg, 0.6 mmol, 1.2 eq) gave the title compound **7c** (127 mg, 84%) as a white crystalline solid after heating at 100 °C, *ca.* 3000 psi for 17 h. R_f 0.19 (4 : 1 hexane–ethyl acetate); mp 89–91 °C (from hexane–ethyl acetate); ν_{max} ($CHCl_3$)/cm^{-1} 2954 w, 2899 w, 1710 s, 1613 w, 1592 s, 1509 m, 1433 m and 1281 s; δ_H(400 MHz; $CDCl_3$) 7.96 (4H, d, *J* 7.0, Ar*H*), 7.08 (4H, d, *J* 7.0, Ar*H*), 3.89 (6H, s, COOCH_3 × 2) and 3.42 (3H, s, NCH_3); δ_C(100 MHz, APT; $CDCl_3$) 166.7 (s), 151.5 (s), 131.1 (d), 123.2 (s), 119.7 (d), 51.9 (q) and 40.0 (q); *m*/*z* (ES) 300.1235 [(M + H)$^+$. $C_{17}H_{18}NO_4$ requires M, 300.1230]; *m*/*z* (EI) 299 (M^+, 100%) and 268 [(M–OMe)$^+$, 59].

Bis-(4-methoxycarbonylphenyl)methylamine [7c, Table 1, entry 4, conditions (ii)]. General procedure B using methyl 4-bromobenzoate (108 mg, 0.5 mmol, 1.0 eq) and 4-[methyl(trimethylsilyl)amino]benzoic acid methyl ester **5a** (142 mg, 0.6 mmol, 1.2 eq) gave the title compound **7c** (133 mg, 89%) as a white crystalline solid after 17 h.

4-(Methylphenylamino)benzoic acid methyl ester [7d, Table 1, entry 5, conditions (i)]. General procedure A using methyl 4-bromobenzoate (108 mg, 0.5 mmol, 1.0 eq) and *N*-methyl trimethylsilylaniline **5b** (107 mg, 0.6 mmol, 1.2 eq) gave the title compound **7d** (104 mg, 76%) as a colourless oil after heating at 100 °C, *ca.* 1800 psi for 48 h. R_f 0.36 (4 : 1 hexane–ethyl acetate); found: C, 74.3; H, 6.2; N, 5.8%. $C_{15}H_{15}NO_2$ requires C, 74.7; H, 6.3; N, 5.8%; ν_{max} ($CHCl_3$)/cm^{-1} 2947 w, 1703 s, 1606 m, 1585 m, 1516 m, 1496 m, 1433 m, 1350 m, 1281 s and 1184 s; δ_H(400 MHz; $CDCl_3$) 7.87 (2H, dq, *J* 7.0 and 1.5, Ar*H*), 7.38 (2H, dd, *J* 7.5 and 7.5, Ar*H*), 7.23–7.20 (3H, m, Ar*H*), 6.77 (2H, dq, *J* 7.0 and 1.5, Ar*H*), 3.86 (3H, s, COOCH_3) and 3.36 (3H, s, NCH_3); δ_C(125 MHz, APT; $CDCl_3$) 167.2 (s), 152.5 (s), 147.5 (s), 131.0 (d), 129.8 (d), 125.9 (d), 125.3 (d), 119.1 (s), 113.7 (d), 51.6 (q) and 40.2 (q); *m*/*z* (ES) 242.1180 [(M + H)$^+$. $C_{15}H_{16}NO_2$ requires M, 242.1176]; *m*/*z* (EI) 241 (M^+, 65%), 227 (60), 210 [(M–OMe)$^+$, 43], 196 (41) and 167 (100).

4-(Methylphenylamino)benzoic acid methyl ester [7d, Table 1, entry 5, conditions (ii)]. General procedure B using methyl 4-bromobenzoate (108 mg, 0.5 mmol, 1.0 eq) and *N*-methyl-trimethylsilylaniline **5b** (107 mg, 0.6 mmol, 1.2 eq) gave the title compound **7d** (109 mg, 90%) as a colourless oil after 17 h.

4-[(4-Methoxyphenyl)methylamino]benzoic acid methyl ester [7e, Table 1, entry 6, conditions (i)]. General procedure A using methyl 4-bromobenzoate (108 mg, 0.5 mmol, 1.0 eq) and (4-methoxyphenyl)-methyl-trimethylsilylamine **5c** (126 mg, 0.6 mmol, 1.2 eq) gave the title compound **7e** (104 mg, 77%) as a pale yellow crystalline solid after heating at 100 °C and *ca.* 1800 psi for 48 h. R_f 0.19 (4 : 1 hexane–ethyl acetate); mp 91–92 °C (from hexane–ethyl acetate); found: C, 70.7; H, 6.3; N, 5.0%. $C_{16}H_{17}NO_3$ requires C, 70.8; H, 6.3; N, 5.2%; ν_{max} ($CHCl_3$)/cm^{-1} 3017 w, 2948 w, 2906 w, 2838 w, 1703 s, 1613 m, 1599 m, 1509 s and 1433 m; δ_H(400 MHz; $CDCl_3$) 7.84 [2H, d, *J* 90, *m*-Ar(COOMe)], 7.13 [2H, d, *J* 9.0, *m*-Ar(OMe)], 6.94 [2H, d, *J* 9.0, *o*-Ar(OMe)], 6.64 [2H, d, *J* 9.0, *o*-Ar(COOMe)], 3.85 (3H, s, OCH_3 or COOCH_3), 3.84 (3H, s, OCH_3 or COOCH_3) and 3.31 (3H, s, NCH_3); δ_C(125 MHz, APT; $CDCl_3$) 167.3 (s), 157.6 (s), 153.0 (s), 140.3 (s), 131.0 (d), 128.1 (d), 118.1 (s), 115.1 (d), 112.4 (d), 55.5 (q), 51.5 (q) and 40.4 (q); *m*/*z* (ES) 272.1279 [(M + H)$^+$. $C_{16}H_{18}NO_3$ requires M, 272.1281]; *m*/*z* (EI) 271 (M^+, 97%) and 256 [(M–Me)$^+$, 100].

4-[(4-Methoxyphenyl)methylamino]benzoic acid methyl ester [7e, Table 1, entry 6, conditions (ii)]. General procedure B using methyl 4-bromobenzoate (108 mg, 0.5 mmol, 1.0 eq) and (4-methoxyphenyl)-methyl-trimethylsilylamine **5c** (126 mg, 0.6 mmol, 1.2 eq) gave the title compound **7e** (96 mg, 71%) as a pale yellow crystalline solid after 17 h.

(4-*tert*-Butylphenyl)methylphenylamine[44] [7f, Table 1, entry 7, conditions (ii)]. General procedure B using 1-bromo-4-*tert*-butylbenzene (87 μL, 0.5 mmol, 1.0 eq) and *N*-methyl-trimethylsilylaniline **5b** (107 mg, 0.6 mmol, 1.2 eq) gave the title compound **7f** (88 mg, 74%) as a yellow oil after 17 h. R_f 0.61 (1 : 9 ethyl acetate–hexane); δ_H(500 MHz; $CDCl_3$) 7.35 (2H, d,

J 8.5, Ar*H*), 7.29 (2H, dd, *J* 8.0 and 7.5, Ar*H*), 7.05 (2H, d, *J* 8.5, Ar*H*), 7.02 (2H, d, *J* 8.0, Ar*H*), 6.94 (1H, t, *J* 7.5, Ar*H*), 3.34 (3H, s, NCH_3) and 1.36 [9H, s, C(CH_3)$_3$]. Spectroscopic data identical to literature values.

***N*-Methyl-*N*-phenyl-*para*-toluidine[43] [7g, Table 1, entry 8, conditions (ii)].** General procedure B using *p*-chlorotoluene (59 μL, 0.5 mmol, 1.0 eq) and *N*-methyl-trimethylsilylaniline **5b** (107 mg, 0.6 mmol, 1.2 eq) gave the title compound **7g** (60 mg, 61%) as a yellow oil after 24 h. R_f 0.44 (1 : 19 ethyl acetate–hexane); δ_H(500 MHz; $CDCl_3$) 7.23 (2H, dd, *J* 8.5 and 7.5, Ar*H*), 7.11 (2H, d, *J* 8.0, Ar*H*), 7.00 (2H, d, *J* 8.5, Ar*H*), 6.92 (2H, d, *J* 8.0, Ar*H*), 6.87 (1H, t, *J* 7.5, Ar*H*), 3.28 (1H, s, NCH_3) and 2.32 (1H, s, ArCH_3). Spectroscopic data identical to literature values.

4-(Methylphenylamino)benzoic acid methyl ester [7d, Table 1, entry 9, conditions (i)]. General procedure A using 4-bromobenzene (53 μL, 0.5 mmol, 1.0 eq) and 4-[methyl-(trimethylsilyl)amino]benzoic acid methyl ester **5a** (142 mg, 0.6 mmol, 1.2 eq) gave the title compound **7d** (93 mg, 77%) as a colourless oil after heating at 100 °C and *ca.* 1800 psi for 17 h.

4-(Methylphenylamino)benzoic acid methyl ester [7d, Table 1, entry 9, conditions (ii)]. General procedure B using 4-bromobenzene (53 μL, 0.5 mmol, 1.0 eq) and 4-[methyl-(trimethylsilyl)amino]benzoic acid methyl ester **5a** (142 mg, 0.6 mmol, 1.2 eq) gave the title compound **7d** (90 mg, 74%) as a colourless oil after 17 h.

Methyldiphenylamine[43] [7h, Table 1, entry 10, conditions (i)]. General procedure A using 4-bromobenzene (53 μL, 0.5 mmol, 1.0 eq) and *N*-methyl trimethylsilylaniline **5b** (107 mg, 0.6 mmol, 1.2 eq) gave the title compound **7h** (50 mg, 55%) as a colourless oil after heating at 100 °C and *ca.* 1800 psi for 48 h. R_f 0.58 (1 : 19 ethyl acetate–hexane); δ_H(500 MHz; $CDCl_3$) 7.32 (4H, dd, *J* 8.5 and 7.0 Ar*H*), 7.07 (4H, dd, *J* 7.0 and 1.0, Ar*H*), 6.99 (2H, tt, *J* 7.0 and 1.0, Ar*H*) and 3.36 (3H, s, NCH_3). Spectroscopic data identical to literature values.

Methyldiphenylamine[43] [7h, Table 1, entry 10, conditions (ii)]. General procedure B using 4-bromobenzene (53 μL, 0.5 mmol, 1.0 eq) and *N*-methyl trimethylsilylaniline **5b** (107 mg, 0.6 mmol, 1.2 eq) gave the title compound **7h** (70 mg, 76%) as a colourless oil after 17 h.

***N*-Methyl-*N*-phenyl-*para*-anisidine[43] [7i, Table 1, entry 11, conditions (i)].** General procedure A using 4-bromobenzene (53 μL, 0.5 mmol, 1.0 eq) and (4-methoxyphenyl)-methyl-trimethylsilylamine **5c** (126 mg, 0.6 mmol, 1.2 eq) gave the title compound **7i** (70 mg, 66%) as a pale yellow oil after heating at 100 °C and *ca.* 1800 psi for 48 h. R_f 0.49 (1 : 19 ethyl acetate–hexane); δ_H(400 MHz; $CDCl_3$) 7.26 (2H, dddd, *J* 8.5, 7.0, 5.0 and 5.0, Ar*H*), 7.14 (2H, ddd, *J* 6.5, 2.0 and 2.0, Ar*H*), 6.95 (2H, ddd, *J* 6.5, 2.0 and 2.0, Ar*H*), 6.86 (3H, m, Ar*H*), 3.86 (3H, s, OCH_3) and 3.31 (3H, s, NCH_3). Spectroscopic data identical to literature values.

***N*-Methyl-*N*-phenyl-*para*-anisidine[43] [7i, Table 1, entry 11, conditions (ii)].** General procedure B using 4-bromobenzene (53 μL, 0.5 mmol, 1.0 eq) and (4-methoxyphenyl)-methyl-trimethylsilylamine **5c** (126 mg, 0.6 mmol, 1.2 eq) gave the title compound **7i** (89 mg, 83%) as a pale yellow oil after 17 h.

4-[(4-Methoxyphenyl)methylamino]benzoic acid methyl ester [7e, Table 1, entry 12, conditions (i)]. General procedure A using 4-bromoanisole (63 μL, 0.5 mmol, 1.0 eq) and 4-[methyl(trimethylsilyl)amino]benzoic acid methyl ester **5a** (142 mg, 0.6 mmol, 1.2 eq) gave the title compound **7e** (78 mg, 57%) as a pale yellow crystalline solid after heating at 100 °C and *ca.* 1800 psi for 17 h.

4-[(4-Methoxyphenyl)methylamino]benzoic acid methyl ester [7e, Table 1, entry 12, conditions (ii)]. General procedure B using 4-bromoanisole (63 μL, 0.5 mmol, 1.0 eq) and 4-[methyl(trimethylsilyl)amino]benzoic acid methyl ester **5a** (142 mg, 0.6 mmol, 1.2 eq) gave the title compound **7e** (104 mg, 77%) as a pale yellow crystalline solid after 17 h.

***N*-Methyl-*N*-phenyl-*para*-anisidine[43] [7i, Table 1, entry 13, conditions (i)].** General procedure A using 4-bromoanisole (63 μL, 0.5 mmol, 1.0 eq) and *N*-methyl-trimethylsilylaniline **5b** (107 mg, 0.6 mmol, 1.2 eq) gave the title compound **7i** (27 mg, 25%) as a pale yellow oil after heating at 100 °C and *ca.* 1800 psi for 48 h.

***N*-Methyl-*N*-phenyl-*para*-anisidine[43] [7i, Table 1, entry 13, conditions (ii)].** General procedure B using 4-bromoanisole (63 μL, 0.5 mmol, 1.0 eq) and *N*-methyl-trimethylsilylaniline **5b** (107 mg, 0.6 mmol, 1.2 eq) gave the title compound **7i** (79 mg, 73%) as a pale yellow oil after 17 h.

***N*-Methyl-*N*-phenyl-*para*-anisidine[43] [7i, Table 1, entry 14, conditions (ii)].** General procedure B using 4-chloroanisole (61 μL, 0.5 mmol, 1.0 eq) and *N*-methyl-trimethylsilylaniline **5b** (107 mg, 0.6 mmol, 1.2 eq) gave the title compound **7i** (79 mg, 73%) as a pale yellow oil after 24 h.

Bis-(4-methoxyphenyl)methylamine[45] [7j, Table 1, entry 15, conditions (i)]. General procedure A using 4-bromoanisole (63 μL, 0.5 mmol, 1.0 eq) and (4-methoxyphenyl)-methyl-trimethylsilylamine **5c** (126 mg, 0.6 mmol, 1.2 eq) gave the title compound **7j** (30 mg, 25%) as a white crystalline solid after heating at 100 °C and *ca.* 1800 psi for 48 h. R_f 0.49 (1 : 4 ethyl acetate–hexane); mp 92–93 °C (from hexane–ethyl acetate) [lit.[46] 89 °C]; δ_H(500 MHz; $CDCl_3$) 6.92 (4H, d, *J* 9.0, Ar*H*), 6.83 (4H, d, *J* 9.0, Ar*H*), 3.78 (6H, s, OCH_3 × 2) and 3.22 (3H, s, NCH_3). Spectroscopic data identical to literature values.

Bis-(4-methoxyphenyl)methylamine[45] [7j, Table 1, entry 15, conditions (ii)]. General procedure B using 4-bromoanisole (63 μL, 0.5 mmol, 1.0 eq) and (4-methoxyphenyl)-methyl-trimethylsilylamine **5c** (126 mg, 0.6 mmol, 1.2 eq) gave the title compound **7j** (75 mg, 62%) as a white crystalline solid after 17 h.

Bis-(4-methoxyphenyl)methylamine[45] [7j, Table 1, entry 16, conditions (ii)]. General procedure B using 4-chloroanisole (61 μL, 0.5 mmol, 1.0 eq) and (4-methoxyphenyl)-methyl-trimethylsilylamine **5c** (126 mg, 0.6 mmol, 1.2 eq) gave the title compound **7j** (68 mg, 56%) as a white crystalline solid after 48 h.

(2-Methoxyphenyl)methylphenylamine[47] [7k, Table 1, entry 17, conditions (ii)]. General procedure B using 1-chloro-2-methoxybenzene (59 μL, 0.5 mmol, 1.0 eq) and *N*-methyl trimethylsilylaniline **5b** (107 mg, 0.6 mmol, 1.2 eq) gave the title compound **7k** (11 mg, 10%) as a colourless oil after 48 h. R_f 0.22 (1 : 4 dichloromethane–hexane); δ_H(500 MHz; $CDCl_3$) 7.24–7.15 (4H, m, Ar*H*), 7.02–6.95 (2H, m, Ar*H*), 6.72 (1H, t, *J* 7.5, Ar*H*), 6.65 (2H, d, *J* 8.5, Ar*H*), 3.77 (3H, s, OCH_3) and 3.22 (3H, s, NCH_3). Spectroscopic data identical to literature values.

4-(Methylphenylamino)benzoic acid methyl ester, 7d. A 10 cm^3 stainless steel high pressure cell equipped with a PTFE stirrer bar was charged with caesium carbonate (228 mg, 0.7 mmol, 1.4 eq), $Pd(OAc)_2$ (2.8 mg, 0.012 mmol, 2.5 mol%), di-*tert*-butyl-biphenylphosphine (7.5 mg, 0.025 mmol, 5 mol%) and methyl 4-bromobenzoate (108 mg, 0.5 mmol, 1.0 eq) and then sealed. The cell was evacuated and refilled with nitrogen (3 cycles). *N*-Methylaniline (0.6 mmol, 1.2 eq) was injected through the inlet port into the cell and the cell connected to the CO_2 manifold. It was then filled with liquid CO_2 to approximately 800 psi (volume of CO_2 *ca.* 1 cm^3) and the cell heated to 100 °C. The pressure was adjusted to *ca.* 1800 psi by the addition of further CO_2. The reaction mixture was then stirred at this temperature and pressure for 48 h. After the reaction mixture was cooled to room temperature, the contents of the cell were

vented into ethyl acetate (20 cm^3). The cell was opened and rinsed with further portions of ethyl acetate (3 × 10 cm^3) and the washing solutions combined with the vented solution. The organic solution was filtered and concentrated *in vacuo* to give the crude material. Purification by flash column chromatography gave the title compound **7d** (32 mg, 34%) as a colourless oil.

4-[(4-Methoxyphenyl)methylamino]benzoic acid methyl ester, 7e. A 10 cm^3 stainless steel high pressure cell equipped with a PTFE stirrer bar was charged with caesium carbonate (228 mg, 0.7 mmol, 1.4 eq), $Pd(OAc)_2$ (2.8 mg, 0.012 mmol, 2.5 mol%), di-*tert*-butyl-biphenylphosphine (7.5 mg, 0.025 mmol, 5 mol%) and methyl 4-bromobenzoate (108 mg, 0.5 mmol, 1.0 eq) and then sealed. The cell was evacuated and refilled with nitrogen (3 cycles). *N*-Methyl-4-anisidine (0.6 mmol, 1.2 eq) was injected through the inlet port into the cell and the cell connected to the CO_2 manifold. It was then filled with liquid CO_2 to approximately 800 psi (volume of CO_2 *ca.* 1 cm^3) and the cell heated to 100 °C. The pressure was adjusted to *ca.* 1800 psi by the addition of further CO_2. The reaction mixture was then stirred at this temperature and pressure for 48 h. After the reaction mixture was cooled to room temperature, the contents of the cell were vented into ethyl acetate (20 cm^3). The cell was opened and rinsed with further portions of ethyl acetate (3 × 10 cm^3) and the washing solutions combined with the vented solution. The organic solution was filtered and concentrated *in vacuo* to give the crude material. Purification by flash column chromatography gave the title compound **7e** (75 mg, 55%) as a pale yellow crystalline solid.

Bis-(4-methoxycarbonylphenyl)methylamine, 7c. A 10 cm^3 stainless steel high pressure cell equipped with a PTFE stirrer bar was charged with caesium carbonate (228 mg, 0.7 mmol, 1.4 eq), $Pd(OAc)_2$ (2.8 mg, 0.012 mmol, 2.5 mol%), di-*tert*-butyl-biphenylphosphine (7.5 mg, 0.025 mmol, 5 mol%) and methyl 4-bromobenzoate (108 mg, 0.5 mmol, 1.0 eq) and then sealed. The cell was evacuated and refilled with nitrogen (3 cycles). 4-(Methylamino)benzoic acid methyl ester (0.6 mmol, 1.2 eq) was injected through the inlet port into the cell and the cell connected to the CO_2 manifold. It was then filled with liquid CO_2 to approximately 800 psi (volume of CO_2 *ca.* 1 cm^3) and the cell heated to 100 °C. The pressure was adjusted to *ca.* 1800 psi by the addition of further CO_2. The reaction mixture was then stirred at this temperature and pressure for 17 h. After the reaction mixture was cooled to room temperature, the contents of the cell were vented into ethyl acetate (20 cm^3). The cell was opened and rinsed with further portions of ethyl acetate (3 × 10 cm^3) and the washing solutions combined with the vented solution. The organic solution was filtered and concentrated *in vacuo* to give the crude material. Purification by flash column chromatography gave the title compound **7c** (52 mg, 35%) as a white crystalline solid.

Synthesis of *N*-silyldiarylamines 9–12 (general procedure C). To a solution of the diarylamine (15 mmol, 1.0 eq) in dry tetrahydrofuran (5 cm^3) cooled to 0 °C under nitrogen was added *n*-butyllithium (1.6 M solution in hexanes; 10.32 cm^3, 16.5 mmol, 1.1 eq). A solution of chlorotrimethylsilane (2.93 cm^3, 23 mmol, 1.5 eq) in dry tetrahydrofuran (10 cm^3) was added dropwise over 0.5 h and the reaction mixture allowed to warm to room temperature and then stirred for 18 h. The tetrahydrofuran, hexane and excess unreacted chlorotrimethylsilane were removed under nitrogen *via* distillation. Dry pentane (20 cm^3) was added to the residue and the mixture stirred for a further 0.5 h at −30 °C to −40 °C to ensure complete precipitation of the salts. The salts were allowed to settle and the clear solution removed through a cannula. Further portions of pentane (2 × 10 cm^3) were used to wash the salts and the extraction process repeated. The combined pentane washes were purified by distillation under nitrogen. The filtrate was concentrated under atmospheric pressure and the residue purified by vacuum distillation to yield the pure diarylsilylamine.

***N*-Trimethylsilyldiphenylamine,[48] 9.** General procedure C using diphenylamine (2.54 g, 15 mmol, 1.0 eq) gave the title compound **9** (3.28 g, 91%) as a colourless oil. (Bp 112 °C, 4 mmHg); δ_H(400 MHz; distilled $CDCl_3$) 7.28 (4H, dd, *J* 8.0 and 7.5, Ar*H*), 7.03 (2H, t, *J* 7.5, Ar*H*), 6.92 (4H, d, *J* 8.0, Ar*H*) and 0.28 [9H, s, $Si(CH_3)_3$]. Spectroscopic data identical to literature values.

Phenyl-*meta*-tolyltrimethylsilylamine, 10. General procedure C using 3-methyldiphenylamine (2.58 cm^3, 15 mmol, 1.0 eq) gave the title compound **10** (3.08 g, 80%) as a colourless oil. Bp 127 °C, 2 mmHg; ν_{max} (neat)/cm^{-1} 2956 w, 1594 m, 1486 s, 1277 s, 1253 s, 1163 m, 970 m, 840 s, 754 m and 700 m; δ_H(400 MHz; distilled $CDCl_3$) 7.30 (2H, dd, *J* 8.5 and 7.5, Ar*H*), 7.20 (1H, dd, *J* 7.5 and 7.5, Ar*H*), 7.03 (1H, t, Ar*H*), 6.94 (2H, d, *J* 8.5, Ar*H*), 6.89 (1H, *J* 7.5, Ar*H*), 6.78 (1H, d, *J* 7.5, Ar*H*), 6.77 (1H, s, Ar*H*), 2.34 (3H, s, $ArCH_3$) and 0.31 [9H, s, $Si(CH_3)_3$]; δ_C (100 MHz; distilled $CDCl_3$) 148.6 (s), 148.2 (s), 138.8 (s), 129.0 (d), 128.8 (d), 125.4 (d), 123.9 (d), 123.1 (d), 121.8 (d), 121.7 (d), 21.5 (q) and 1.1 (q).

9-Trimethylsilyl-9*H*-carbazole,[49] 11. General procedure C using carbazole (2.51 g, 15 mmol, 1.0 eq) gave the title compound **11** (2.04 g, 53%) as a yellow crystalline solid. Bp 150 °C, 0.5 mmHg; δ_H(400 MHz; distilled $CDCl_3$) 8.10 (2H, d, Ar*H*), 7.64 (2H, d, Ar*H*), 7.40 (2H, m, Ar*H*), 7.26 (2H, m, Ar*H*) and 0.73 [9H, s, $Si(CH_3)_3$]. Spectroscopic data identical to literature values.

Naphthalen-1-yl-phenyl-trimethylsilylamine, 12. General procedure C using *N*-phenyl-1-naphthylamine (3.29 g, 15 mmol, 1.0 eq) gave the title compound **12** (2.30 g, 53%) as a yellow crystalline solid. Bp 190 °C, 1.5 mmHg; ν_{max} (neat)/cm^{-1} 2956 w, 1598 m, 1494 s, 1390 m, 1273 s, 1252 s, 1095 w, 952 m, 840 s, 777 s, 754 s and 693 m; δ_H(400 MHz; distilled $CDCl_3$) 7.99 (1H, d, *J* 8.5, Ar*H*), 7.93 (1H, d, *J* 7.5, Ar*H*), 7.83 (1H, d, *J* 8.5, Ar*H*), 7.55–7.44 (3H, m, Ar*H*), 7.31 (1H, d, *J* 7.5, Ar*H*), 7.15 (2H, dd, *J* 9.0 and 7.0, Ar*H*), 6.78 (1H, t, *J* 7.0, Ar*H*), 6.71 (2H, d, *J* 9.0, Ar*H*) and 0.31 [9H, s, $Si(CH_3)_3$]; δ_C(100 MHz; distilled $CDCl_3$) 150.3 (s), 142.5 (s), 134.9 (s), 133.3 (s), 128.8 (d), 128.3 (d), 127.8 (d), 126.6 (d), 126.3 (d), 126.2 (d), 126.0 (d), 124.2 (d), 118.0 (d), 116.9 (d) and 0.9 (q).

The catalytic amination of methyl 4-bromobenzoate with diphenylsilylamine with a fluoride additive in $scCO_2$ (general procedure D). A 10 cm^3 stainless steel high pressure cell equipped with a PTFE stirrer bar was charged with caesium carbonate (228 mg, 0.7 mmol, 1.4 eq), fluoride additive (1 mmol, 2 eq), Pd_2dba_3 (11 mg, 0.013 mmol, 2.5 mol%), P(*t*-Bu)$_3$ (75 μL; 10 wt% in hexane, 0.025 mmol, 5 mol%) and methyl 4-bromobenzoate (108 mg, 0.5 mmol, 1.0 eq) and then sealed. The cell was evacuated and refilled with nitrogen (3 cycles). The diphenylsilylamine (145 mg, 0.6 mmol, 1.2 eq) was injected through the inlet port into the cell and the cell was connected to the CO_2 manifold. It was then filled with liquid CO_2 to approximately 800 psi (volume of CO_2 *ca.* 1 cm^3) and the cell heated to 100 °C. The pressure was adjusted to *ca.* 1800 psi by the addition of further CO_2. The reaction mixture was then stirred at this temperature and pressure for 48 h. After the reaction mixture was cooled to room temperature, the contents of the cell were vented into ethyl acetate (20 cm^3). The cell was opened and rinsed with further portions of ethyl acetate (3 × 10 cm^3) and the washing solutions combined with the vented solution. The organic solution was filtered, concentrated *in vacuo* to give the crude material which was analysed by gas chromatography.

4-(Diphenylamino) benzoic acid methyl ester[50,51] (14, Table 2, entry 1). General procedure D using no fluoride additive gave the title compound **14** (43 mg, 28%) as a white crystalline solid. R_f 0.24 (1 : 1 dichloromethane–hexane); mp 88–89 °C

(dichloromethane–hexane) [lit.[51] 89 °C]; δ_H(400 MHz; $CDCl_3$) 7.86 (2H, d, *J* 9.0, Ar*H*), 7.31 (4H, dd, *J* 8.5 and 6.5 Ar*H*), 7.15–7.12 (6H, m, Ar*H*), 6.98 (2H, d, *J* 9.0, Ar*H*) and 3.88 (3H, s, OCH_3). Spectroscopic data identical to literature values.

4-(Diphenylamino) benzoic acid methyl ester[50,51] (14, Table 2, entry 2). General procedure D using potassium fluoride (58.1 mg, 1 mmol, 2 eq) gave the title compound **14** (76 mg, 50%).

4-(Diphenylamino) benzoic acid methyl ester,[50,51] 14 (Table 2, entry 3). General procedure D using caesium fluoride (152 mg, 1 mmol, 2 eq) gave the title compound **14** (135 mg, 89%).

The catalytic amination of aryl bromides with diarylsilylamines 9–12 in scCO$_2$ (general procedure E). A 10 cm^3 stainless steel high pressure cell equipped with a PTFE stirrer bar was charged with caesium carbonate (228 mg, 0.7 mmol, 1.4 eq), caesium fluoride (152 mg, 1 mmol, 2 eq), Pd_2dba_3 (11 mg, 0.013 mmol, 2.5 mol%), P(*t*-Bu)$_3$ (75 μL; 10 wt% in hexane, 0.025 mmol, 5 mol%) and aryl bromide (0.5 mmol, 1.0 eq) and then sealed. The cell was evacuated and refilled with nitrogen (3 cycles). The diarylsilylamine (0.6 mmol, 1.2 eq) was injected through the inlet port into the cell and the cell was connected to the CO_2 manifold. It was then filled with liquid CO_2 to approximately 800 psi (volume of CO_2 *ca.* 1 cm^3) and the cell heated to 100 °C. The pressure was adjusted to *ca.* 1800 psi by the addition of further CO_2. The reaction mixture was then stirred at this temperature and pressure for 48 h. After the reaction mixture was cooled to room temperature, the contents of the cell were vented into ethyl acetate (20 cm^3). The cell was opened and rinsed with further portions of ethyl acetate (3 × 10 cm^3) and the washing solutions combined with the vented solution. The organic solution was filtered and concentrated *in vacuo* to give the crude material which was purified by flash column chromatography.

4-(Diphenylamino) benzoic acid methyl ester[50,51] (14, Table 3, entry 1). General procedure E using methyl 4-bromobenzoate (108 mg, 0.5 mmol, 1.0 eq) and diphenylsilylamine **9** (145 mg, 0.6 mmol, 1.2 eq) gave the title compound **14** (126 mg, 83%) as a white crystalline solid.

4-(Phenyl-*meta*-tolylamino) benzoic acid methyl ester (23a, Table 3, entry 2). General procedure E using methyl 4-bromobenzoate (108 mg, 0.5 mmol, 1.0 eq) and phenyl-*meta*-tolyltrimethylsilylamine **10** (153 mg, 0.6 mmol, 1.2 eq) gave the title compound **23a** (84 mg, 53%) as a colourless oil. R_f 0.24 (1 : 1 dichloromethane–hexane); found: C, 79.5; H, 6.1; N, 4.4%. $C_{21}H_{19}NO_2$ requires C, 79.5; H, 6.0; N, 4.4%; ν_{max}(neat)/cm^{-1} 1714 s, 1589 s, 1488 m, 1434 m, 1315 m, 1273 s, 1175 m, 1107 m, 768 m and 697 m; δ_H(400 MHz; $CDCl_3$) 7.86 (2H, d, *J* 8.5, Ar*H*), 7.31 (2H, dd, *J* 7.5 and 8.5, Ar*H*), 7.20 (1H, dd, *J* 7.5 and 7.5, Ar*H*), 7.15 (2H, d, *J* 8.5, Ar*H*), 7.12 (1H, t, *J* 7.5, Ar*H*), 7.00–6.95 (5H, m, Ar*H*), 3.88 (3H, s, OCH_3) and 2.30 (3H, s, $ArCH_3$); δ_C(100 MHz; distilled $CDCl_3$) 166.9 (s), 152.1 (s), 146.6 (s), 139.5 (s), 130.8 (s), 129.5 (d), 129.3 (d), 126.6 (d), 125.7 (CH), 125.3 (d), 124.2 (d), 123.0 (d), 121.9 (s), 119.9 (d), 51.7 (q) and 21.3 (q); *m/z* (ES) 318.1493 [(M + H)$^+$. $C_{21}H_{20}O_2N$ requires M, 318.1489]; *m/z* (EI) 317 (M^+, 97%).

4-Carbazol-9-yl benzoic acid methyl ester[52] (23b, Table 3, entry 3). General procedure E using methyl 4-bromobenzoate (108 mg, 0.5 mmol, 1.0 eq) and 9-trimethylsilyl-9*H*-carbazole **11** (144 mg, 0.6 mmol, 1.2 eq) gave the title compound **23b** (80 mg, 54%) as a white solid. R_f 0.22 (2 : 3 dichloromethane–hexane); δ_H(400 MHz; $CDCl_3$) 8.29 (2H, d, *J* 8.5, Ar*H*), 8.15 (2H, d, *J* 7.5, Ar*H*), 7.69 (2H, d, *J* 8.5, Ar*H*), 7.45 (4H, m, Ar*H*, Ar*H*), 7.32 (2H, dd, *J* 7.5 and 1.0, Ar*H*) and 4.00 (3H, s, OCH_3). Spectroscopic data identical to literature values.

4-(Naphthalen-1-yl-phenylamino) benzoic acid methyl ester (23c, Table 3, entry 4). General procedure E using methyl 4-bromobenzoate (108 mg, 0.5 mmol, 1.0 eq) and naphthalen-1-yl-phenyl trimethylsilylamine **12** (153 mg, 0.6 mmol, 1.2 eq) gave the title compound **23c** (84 mg, 53%) as a colourless oil. R_f 0.22 (1 : 1 dichloromethane–hexane); found: C, 81.6; H, 5.5; N, 4.0%. $C_{24}H_{19}NO_2$ requires C, 81.6; H, 5.4; N, 4.0%; ν_{max}(neat)/cm^{-1} 1710 m, 1590 m, 1492 w, 1434 w, 1392 w, 1275 s, 1176 m, 1109 w, 1024 s, 1001 s, 823 m, 762 s and 696 w; δ_H(400 MHz; distilled $CDCl_3$) 7.98 (1H, d, *J* 8.0, Ar*H*), 7.91 (1H, d, *J* 8.0, Ar*H*), 7.81 (1H, d, *J* 8.5, Ar*H*), 7.71 (2H, d, *J* 8.5, Ar*H*), 7.53 (1H, dd, *J* 8.5 and 8.5, Ar*H*), 7.48 (1H, dd, *J* 8.0 and 8.5, Ar*H*), 7.41–7.38 (2H, m, Ar*H*), 7.27 (2H, dd, *J* 8.0 and 8.5, Ar*H*), 7.15 (2H, d, *J* 8.5, Ar*H*), 7.06 (1H, t, *J* 8.0, Ar*H*), 6.73 (2H, d, *J* 8.5, Ar*H*) and 3.73 (3H, s, OC*H*3); δ_C(100 MHz; distilled $CDCl_3$) 165.9 (s), 152.1 (s), 146.0 (s), 141.6 (s), 135.0 (s), 130.8 (d), 130.5 (s), 129.7 (d), 128.7 (d), 127.7 (d), 127.6 (d), 127.0 (d), 126.7 (d), 126.5 (d), 124.4 (d), 124.3 (d), 123.2 (d), 120.5 (s), 117.2 (d) and 51.6 (q); *m/z* (ES) 354.1487 [(M + H)$^+$. $C_{24}H_{20}O_2N$ requires M, 354.1489]; *m/z* (EI) 353 (M^+, 54%).

4-(Diphenylamino) benzoic acid methyl ester[50,51] (14, Table 4, entry 1). General procedure E using methyl 4-bromobenzoate (108 mg, 0.5 mmol, 1.0 eq) and diphenylsilylamine **9** (145 mg, 0.6 mmol, 1.2 eq) gave the title compound **14** (126 mg, 83%) as a white crystalline solid.

(4-Nitrophenyl)diphenylamine[53,54] (25a, Table 4, entry 2). General procedure E using 1-bromo-4-nitrobenzene (101 mg, 0.5 mmol, 1.0 eq) and diphenylsilylamine **9** (145 mg, 0.6 mmol, 1.2 eq) gave the title compound **25a** (84 mg, 58%) as a yellow crystalline solid. R_f 0.24 (1 : 1 dichloromethane–hexane); mp 143 °C (from dichloromethane–hexane) [lit.[54] 142–143 °C]; δ_H(400 MHz; $CDCl_3$) 8.04 (2H, d, *J* 9.0, Ar*H*), 7.37 (4H, dd, *J* 7.0 and 8.5, Ar*H*), 7.21 (2H, t, *J* 7.0, Ar*H*), 7.18 (4H, d, *J* 8.5, Ar*H*) and 6.92 (2H, d, *J* 9.0, Ar*H*). Spectroscopic data identical to literature values.

(4-Fluorophenyl)diphenylamine[55] (25b, Table 4, entry 3). General procedure D using 1-bromo-4-fluorobenzene (88 mg, 0.5 mmol, 1.0 eq) and diphenylsilylamine **9** (145 mg, 0.6 mmol, 1.2 eq) gave the title compound **25b** (61 mg, 46%) as a pale yellow crystalline solid. R_f 0.35 (1 : 4 dichloromethane–hexane); mp 96 °C (lit.[55] 98–98.5 °C from ethanol); δ_H(500 MHz; $CDCl_3$) 7.24 (4H, dd, *J* 8.0 and 7.5, Ar*H*), 7.09–7.04 (2H, m, Ar*H*), 7.05 (4H, d, *J* 7.5, Ar*H*) and 7.01–6.95 (4H, m, Ar*H*). Spectroscopic data identical to literature values.

The catalytic amination of 4, 4′-dibromobiphenyl with diarylsilylamines 9–12 in scCO$_2$ (general procedure F). A 10 cm^3 stainless steel high pressure cell equipped with a PTFE stirrer bar was charged with caesium carbonate (456 mg, 1.4 mmol, 2.8 eq), caesium fluoride (304 mg, 2 mmol, 4 eq), Pd_2dba_3 (22 mg, 0.025 mmol, 5 mol%), P(*t*-Bu)$_3$ (150 μL; 10 wt% in hexane, 0.05 mmol, 10 mol%) and 4, 4′-dibromobiphenyl (156 mg, 0.5 mmol, 1.0 eq) and then sealed. The cell was evacuated and refilled with nitrogen (3 cycles). The diarylsilylamine (1.2 mmol, 2.4 eq) was injected through the inlet port into the cell and the cell connected to the CO_2 manifold. It was then filled with liquid CO_2 to approximately 800 psi (volume of CO_2 *ca.* 1 cm^3) and the cell heated to 100 °C. The pressure was adjusted to *ca.* 1800 psi by the addition of further CO_2. The reaction mixture was then stirred at this temperature and pressure for 48 h. After the reaction mixture was cooled to room temperature, the contents of the cell were vented into ethyl acetate (20 cm^3). The cell was opened and rinsed with further portions of ethyl acetate (3 × 10 cm^3) and the washing solutions combined with the vented solution. The organic solution was filtered, concentrated *in vacuo* to give the crude material which was purified by flash column chromatography.

***N′*,*N′*,*N′*,*N′*-Tetraphenylbenzidine[56] (27a, Table 5, entry 1).** General procedure F using *N*-trimethylsilyldiphenylamine **9** (290 mg, 1.2 mmol, 2.4 eq) gave the title compound **27a** (128 mg, 58%) as a white solid. R_f 0.27 (1 : 20 diethyl ether–hexane v/v);

mp 224–225 °C (lit.[56] 224–225 °C); δ_H(400 MHz; distilled $CDCl_3$) 7.47 (4H, d, *J* 8.5, Ar*H*), 7.28 (8H, dd, *J* 8.0 and 7.5, Ar*H*), 7.16-7.14 (12H, m, Ar*H*) and 7.05 (4H, t, *J* 7.5, Ar*H*).

N^4,$N^{4\prime}$-Diphenyl-N^4,$N^{4\prime}$-di-*m*-tolyl-biphenyl-4,4′-diamine[57,58] (27b, Table 5, entry 2). General procedure F using phenyl-*meta*-tolyl trimethylsilylamine **10** (307 mg, 1.2 mmol, 2.4 eq) gave the title compound **27b** (98 mg, 38%) as a white solid. R_f 0.38 (1 : 20 diethyl ether–hexane v/v); mp 166–167 °C (lit.[58] 167 °C); δ_H(400 MHz; $CDCl_3$) 7.49 (4H, d, *J* 9.0, Ar*H*), 7.29 (4H, dd, *J* 7.5 and 7.5, Ar*H*), 7.19 (2H, dd, *J* 8.0 and 8.0, Ar*H*), 7.17–6.84 (16, m, Ar*H*) and 2.31 (6H, s, ArCH_3).

9, 9′-Biphenyl-4, 4′-diyl-bis-carbazole[53,59] (27c, Table 5, entry 3). General procedure F using 9-trimethylsilyl-9*H*-carbazole **11** (288 mg, 1.2 mmol, 2.4 eq) gave the title compound **27c** (114 mg, 47%) as a white solid. R_f 0.30 (1 : 10 diethyl ether–hexane v/v); mp 280 °C (lit.[59] 282.5–284 °C); δ_H(400 MHz; distilled $CDCl_3$) 8.19 (4H, d, *J* 8.0, Ar*H*), 7.93 (4H, d, *J* 8.0, Ar*H*), 7.72 (4H, d, *J* 8.0, Ar*H*), 7.53 (4H, d, *J* 8.0, Ar*H*), 7.46 (4H, dd, *J* 8.0 and 8.0, Ar*H*) and 7.33 (4H, dd, *J* 8.0 and 8.0, Ar*H*).

***N*,*N*′-Di-1-naphthalenyl-*N*,*N*′-diphenyl-1,1′-biphenyl-4,4′-diamine[60] (27d, Table 5, entry 4).** General procedure F using naphthalen-1-yl-phenyltrimethylsilylamine **12** (350 mg, 1.2 mmol, 2.4 eq) gave the title compound **27d** (103 mg, 35%) as a white solid. R_f 0.38 (1 : 19 diethyl ether–hexane v/v); mp 274 °C; δ_H(400 MHz; $CDCl_3$) 7.95 (2H, d, *J* 8.5, Ar*H*), 7.88 (2H, d, *J* 8.0, Ar*H*), 7.77 (2H, d, *J* 8.0, Ar*H*), 7.49–7.44 (4H, m, Ar*H*), 7.38 (8H, m, Ar*H*), 7.20 (4H, t, *J* 8.0, Ar*H*), 7.05 (8H, t, *J* 8.5, Ar*H*) and 6.93 (2H, t, *J* 7.5, Ar*H*).

***N*,*N*-Dimethyl-*O*-trimethylsilylcarbamate, 29.** A 10 cm^3 stainless steel cell was charged with trimethylsilyldimethylamine (0.5 cm^3) and the cell flushed with nitrogen and sealed. The cell was connected to the CO_2 line and charged with CO_2 (99.9995%-further purified over an Oxisorb® catalyst) to approximately 800 psi (volume *ca.* 1 cm^3 liquid carbon dioxide). The cell was heated to 60 °C and the pressure adjusted to *ca.* 1800 psi by the addition of further CO_2. The reagents were maintained at this temperature and pressure for 17 h before the cell was allowed to cool to room temperature. The content of the cell was diluted with distilled $CDCl_3$ and submitted directly to spectroscopic analysis; $\nu_{max}(CDCl_3)/cm^{-1}$ 1666 s; δ_H(400 MHz; distilled $CDCl_3$) 2.76 (6H, s, NMe_2) and 0.15 (9H, s, $SiMe_3$); δ_C(100 MHz; distilled $CDCl_3$) 155.4, 36.4, 35.8 and −0.21; *m*/*z* (EI) 161 (M^+, 47%), 147 (39) and 69 (100).

1-Trimethylsilyl pyrrole,[61] 30. To a solution of pyrrole (2.0 cm^3, 29 mmol) dissolved in dry THF (50 cm^3) under nitrogen and cooled to −78 °C was added *n*-BuLi (1.59 M in hexanes; 18.1 cm^3, 29 mmol, 1 eq). The solution was stirred at −78 °C for 2 h. Chlorotrimethylsilane (4.4 cm^3, 45 mmol, 1.2 eq) was added dropwise and the resultant mixture allowed to warm to room temperature and stirred overnight during which time LiCl precipitated out.

The stirring was stopped and the clear solution separated *via* cannula. The filtrant was concentrated under atmospheric pressure under nitrogen and the residue purified by vacuum distillation through a Vigreux column (10 cm) to furnish 1-trimethylsilyl pyrrole **30** (2.84 g, 71%) as a colourless oil. Bp 154–155 °C (lit.[61] 153 °C, 760 mmHg); δ_H(400 MHz; $CDCl_3$) 6.88 (2H, s, 2 × Ar*H*), 6.40 (2H, s, 2 × Ar*H*) and 0.40 [9H, s, $Si(CH_3)_3$]. Spectroscopic data identical to literature values.

The amination of methyl 4-bromobenzoate with 1-trimethylsilyl pyrrole with a fluoride additive in toluene (general procedure G). Flame dried caesium carbonate (228 mg, 0.7 mmol, 1.4 eq), methyl 4-bromobenzoate (108 mg, 0.5 mmol, 1 eq), $Pd(OAc)_2$ (5.6 mg, 0.026 mmol, 5 mol%), ligand (0.05 mmol, 10 mol%) and fluoride additive (0.6 mmol, 1.2 eq) were added to a dry schlenk tube. The tube was evacuated and refilled with nitrogen (three cycles). Dry toluene (2 cm^3) and 1-trimethylsilyl pyrrole **30** (84 mg, 0.6 mmol) were then consecutively injected into the schlenk tube. The reaction mixture was heated to 100 °C for 17 h before it was allowed to cool to room temperature. The reaction mixture was filtered, washed with ethyl acetate (50 cm^3) and then concentrated *in vacuo* to furnish the crude material which was purified by flash column chromatography.

4-Pyrrol-1-ylbenzoic acid methyl ester[62] (31, Table 6, entry 1). Employing general procedure G on a 0.5 mmol scale with no additive furnished the title compound **31** (6 mg, 6%) as a white crystalline solid. R_f 0.13 (9 : 1 hexane–ethyl acetate); mp 125–127 °C; δ_H(500 MHz; $CDCl_3$) 8.12 (2H, d, *J* 7.0, Ar*H*), 7.46 (2H, d, *J* 7.0, Ar*H*), 7.18 (2H, dd, *J* 2.0 and 2.0, Ar*H*), 6.41 (2H, dd, *J* 2.0 and 2.0, Ar*H*) and 3.95 (3H, s, OCH_3). Spectroscopic data identical to literature values.

Employing general procedure G on a 0.5 mmol scale with CsF (91 mg, 0.6 mmol, 1.2 eq) furnished the title compound **31** (5 mg, 5%) as a white crystalline solid.

Employing general procedure G on a 0.5 mmol scale with KF (35 mg, 0.6 mmol, 1.2 eq) furnished the title compound **31** (68 mg, 68%) as a white crystalline solid.

1-Trimethylsilyl indole,[63] 32. To a solution of indole (5.0 g, 43 mmol) dissolved in dry THF (75 cm^3) under nitrogen and cooled to −78 °C was added *n*-BuLi (1.59 M in hexanes; 27 cm^3, 43 mmol, 1 eq). The solution was stirred at −78 °C for 2 h. Chlorotrimethylsilane (6.5 cm^3, 51 mmol, 1.2 eq) was added dropwise and the resultant mixture was allowed to warm to room temperature and stirred overnight during which time LiCl precipitated out.

The stirring was stopped and the clear solution separated *via* cannula. The filtrant was concentrated under atmospheric pressure under nitrogen and the residue purified by vacuum distillation through a Vigreux column (10 cm) to furnish 1-trimethylsilyl indole **32** (6.85 g, 85%) as a colourless oil. Bp 100 °C, 2 mmHg (lit.[64] 68–70 °C, 0.06 mmHg); δ_H(500 MHz; $CDCl_3$) 7.59 (1H, d, *J* 7.5, Ar*H*), 7.59 (1H, d, *J* 8.0, Ar*H*), 7.29–7.20 (3H, m, Ar*H*), 6.69 (1H, d, *J* 3.0, Ar*H*) and 0.64 [9H, s, $Si(CH_3)_3$]. Spectroscopic data identical to literature values.

***N*-Arylation of *N*-silylazoles 30 and 32 in $scCO_2$ (general procedure H).** Flame dried caesium carbonate (228 mg, 0.7 mmol, 1.4 eq), aryl halide (0.5 mmol), $Pd(OAc)_2$ (5.6 mg, 0.026 mmol, 5 mol%), ligand (0.05 mmol, 10 mol%) and KF (35 mg, 1.2 eq) were placed in a 10 cm^3 stainless steel cell and the cell sealed. The cell was evacuated and refilled with nitrogen (three cycles). *N*-Silylazole (1.2 eq, 0.6 mmol) was injected through the inlet port and the cell connected to the CO_2 line and charged with CO_2 (99.9995%-further purified over an Oxisorb® catalyst) to approximately 800 psi (volume *ca.* 1 cm^3 liquid carbon dioxide). The cell was heated to 100 °C and the pressure adjusted to *ca.* 1800 psi by the addition of further CO_2. The reagents were maintained at this temperature and pressure for 17 h before the cell was allowed to cool to room temperature. The contents of the cell were vented into ethyl acetate (50 cm^3), and once atmospheric pressure had been reached, the cell was opened and washed with further ethyl acetate (3 × 10 cm^3). The combined organic fractions were filtered and concentrated *in vacuo* to furnish the crude material which was purified by flash column chromatography.

4-Pyrrol-1-ylbenzoic acid methyl ester[62] (31, Table 7, entry 1).

*With ligand **35**, P(t-Bu)$_2$(biphen).* Employing general procedure H on a 0.5 mmol scale with 1-trimethylsilyl pyrrole **30** (84 mg, 0.6 mmol) and P(*t*-Bu)$_2$(biphen) (15 mg, 10 mol%) furnished the title compound **31** (59 mg, 59%) as a white crystalline solid.

*With ligand **36**, P(t-Bu)$_2$(i-Pr-biphen).* Employing general procedure H on a 0.5 mmol scale with 1-trimethylsilyl pyrrole **30** (84 mg, 0.6 mmol) and P(*t*-Bu)$_2$(i-Pr-biphen) (17 mg, 10 mol%)

furnished the title compound **31** (75 mg, 75%) as a white crystalline solid.

*With ligand **37**, P(t-Bu)$_2$(Me$_2$N-biphen).* Employing general procedure H on a 0.5 mmol scale with 1-trimethylsilyl pyrrole **30** (84 mg, 0.6 mmol) and P(*t*-Bu)$_2$(Me$_2$N-biphen) (17 mg, 10 mol%) furnished the title compound **31** (79 mg, 79%) as a white crystalline solid.

1-Phenyl-1*H*-pyrrole[65] (33a, Table 7, entry 2)

*With ligand **35**, P(t-Bu)$_2$(biphen).* Employing general procedure H on a 0.5 mmol scale with 1-trimethylsilyl pyrrole **30** (84 mg, 0.6 mmol) and P(*t*-Bu)$_2$(biphen) (15 mg, 10 mol%) furnished the title compound **33a** (8 mg, 11%) as a white crystalline solid. R_f 0.54 (9 : 1 hexane–ethyl acetate); mp 61–62 °C (from hexane–ethyl acetate) [lit.[66] 60–62 °C]; δ_H(500 MHz; $CDCl_3$) 7.48–7.42 (4H, m, 4 × Ar*H*), 7.28 (1H, t, *J* 7.5 and 7.5, Ar*H*), 6.73 (2H, dd, *J* 3.0 and 3.0, Ar*H*) and 6.39 (2H, dd, *J* 3.0 and 3.0, Ar*H*). Spectroscopic data identical to literature values.

*With ligand **36**, P(t-Bu)$_2$(i-Pr-biphen).* Employing general procedure H on a 0.5 mmol scale with 1-trimethylsilyl pyrrole **30** (84 mg, 0.6 mmol) and P(*t*-Bu)$_2$(i-Pr-biphen) (17 mg, 10 mol%) furnished the title compound **33a** (27 mg, 46%) as a white crystalline solid.

*With ligand **37**, P(t-Bu)$_2$(Me$_2$N-biphen).* Employing general procedure H on a 0.5 mmol scale with 1-trimethylsilyl pyrrole **30** (84 mg, 0.6 mmol) and P(*t*-Bu)$_2$(Me$_2$N-biphen) (17 mg, 10 mol%) furnished the title compound **33a** (14 mg, 24%) as a white crystalline solid.

*With ligand **38**, P(Cy)$_2$(2′,4′,6′-triisopropylbiphen).* Employing general procedure H on a 0.5 mmol scale with 1-trimethylsilyl pyrrole **30** (84 mg, 0.6 mmol) and P(Cy)$_2$(2′,4′,6′-triisopropylbiphen (20 mg, 10 mol%) furnished the title compound **33a** (2 mg, 4%) as a white crystalline solid.

1-(4-Methoxyphenyl)pyrrole[67] (33b, Table 7, entry 3)

*With ligand **35**, P(t-Bu)$_2$(biphen).* Employing general procedure H on a 0.5 mmol scale with 1-trimethylsilyl pyrrole **30** (84 mg, 0.6 mmol) and P(*t*-Bu)$_2$(biphen) (15 mg, 10 mol%) furnished the title compound **33b** (6 mg, 7%) as a white crystalline solid. R_f 0.44 (6 : 1 hexane–ethyl acetate); mp 111–112 °C (from hexane–ethyl acetate) [lit.[67] 111–113 °C (from methanol)]; δ_H(500 MHz; $CDCl_3$) 7.33 (2H, d, *J* 7.0, Ar*H*), 7.02 (2H, dd, *J* 2.0 and 2.0, Ar*H*), 6.97 (2H, d, *J* 7.0, Ar*H*), 6.34 (2H, dd, *J* 2.0 and 2.0, Ar*H*) and 3.86 (3H, s, OCH_3). Spectroscopic data identical to literature values.

*With ligand **36**, P(t-Bu)$_2$(i-Pr-biphen).* Employing general procedure H on a 0.5 mmol scale with 1-trimethylsilyl pyrrole **30** (84 mg, 0.6 mmol) and P(*t*-Bu)$_2$(i-Pr-biphen) (17 mg, 10 mol%) furnished the title compound **33b** (26 mg, 30%) as a white crystalline solid.

*With ligand **37**, P(t-Bu)$_2$(Me$_2$N-biphen).* Employing general procedure H on a 0.5 mmol scale with 1-trimethylsilyl pyrrole **30** (84 mg, 0.6 mmol) and P(*t*-Bu)$_2$(Me$_2$N-biphen) (17 mg, 10 mol%) furnished the title compound **33b** (18 mg, 21%) as a white crystalline solid.

4-Indol-1-yl-benzoic acid methyl ester[68] (34a, Table 7, entry 4)

*With ligand **35**, P(t-Bu)$_2$(biphen).* Employing general procedure H on a 0.5 mmol scale with 1-trimethylsilyl indole **32** (114 mg, 0.6 mmol) and P(*t*-Bu)$_2$(biphen) (15 mg, 10 mol%) furnished the title compound **34a** (88 mg, 70%) as a colourless oil. R_f 0.30 (9 : 1 hexane–ethyl acetate); δ_H(400 MHz; $CDCl_3$) 8.20 (2H, d, *J* 8.5, Ar*H*), 7.70 (1H, d, *J* 7.5, Ar*H*), 7.64 (1H, d, *J* 7.5, Ar*H*), 7.61 (2H, d, *J* 8.5, Ar*H*), 7.37 (1H, d, *J* 3.5, Ar*H*), 7.27 (1H, dd, *J* 7.5 and 7.5, Ar*H*), 7.21 (1H, dd, *J* 7.5 and 7.5, Ar*H*), 6.73 (1H, d, *J* 3.5, Ar*H*) and 4.00 (3H, s, OCH_3). Spectroscopic data identical to literature values.

*With ligand **36**, P(t-Bu)$_2$(i-Pr-biphen).* Employing general procedure H on a 0.5 mmol scale with 1-trimethylsilyl indole **32** (114 mg, 0.6 mmol) and P(*t*-Bu)$_2$(i-Pr-biphen) (17 mg, 10 mol%) furnished the title compound **34a** (110 mg, 88%) as a colourless oil.

1-Phenyl-1*H*-indole[69] (34b, Table 7, entry 5)

*With ligand **35**, P(t-Bu)$_2$(biphen).* Employing general procedure H on a 0.5 mmol scale with 1-trimethylsilyl indole **32** (114 mg, 0.6 mmol) and P(*t*-Bu)$_2$(biphen) (15 mg, 10 mol%) furnished the title compound **34b** (66 mg, 68%) as a colourless oil. R_f 0.50 (9 : 1 hexane–ethyl acetate); δ_H(500 MHz; $CDCl_3$) 7.78 (1H, d, *J* 7.5, Ar*H*), 7.65 (1H, d, *J* 7.5, Ar*H*), 7.58 (4H, d, *J* 4.5, 4 × Ar*H*), 7.44–7.41 (2H, m, Ar*H*), 7.31 (1H, dd, *J* 7.5 and 7.0, Ar*H*), 7.26 (1H, dd, *J* 7.5 and 7.0, Ar*H*), and 6.77 (1H, d, *J* 3.5, Ar*H*). Spectroscopic data identical to literature values.

*With ligand **36**, P(t-Bu)$_2$(i-Pr-biphen).* Employing general procedure H on a 0.5 mmol scale with 1-trimethylsilyl indole **32** (114 mg, 0.6 mmol) and P(*t*-Bu)$_2$(i-Pr-biphen) (17 mg, 10 mol%) furnished the title compound **34b** (68 mg, 70%) as a colourless oil.

1-(4-Methoxyphenyl)-1*H*-indole[70] (34c, Table 7, entry 6)

*With ligand **35**, P(t-Bu)$_2$(biphen).* Employing general procedure H on a 0.5 mmol scale with 1-trimethylsilyl indole **32** (114 mg, 0.6 mmol) and P(*t*-Bu)$_2$(biphen) (15 mg, 10 mol%) furnished the title compound **34c** (28 mg, 25%) as a white crystalline solid. R_f 0.47 (9 : 1 hexane–ethyl acetate); mp 57–58 °C (lit.[71] 57–58 °C); δ_H(500 MHz; $CDCl_3$) 7.72 (1H, d, *J* 8.0, Ar*H*), 7.49 (1H, d, *J* 8.0, Ar*H*), 7.43 (2H, d, *J* 9.0, Ar*H*), 7.31 (1H, d, *J* 3.0, Ar*H*), 7.24 (1H, dd, *J* 8.0 and 8.0, Ar*H*), 7.19 (1H, dd, *J* 8.0 and 8.0, Ar*H*), 7.07 (2H, d, *J* 9.0, Ar*H*), 6.77 (1H, d, *J* 3.5, Ar*H*) and 3.91 (3H, s, OCH_3). Spectroscopic data identical to literature values.

*With ligand **36**, P(t-Bu)$_2$(i-Pr-biphen).* Employing general procedure H on a 0.5 mmol scale with 1-trimethylsilyl indole **32** (114 mg, 0.6 mmol) and P(*t*-Bu)$_2$(i-Pr-biphen) (17 mg, 10 mol%) furnished the title compound **34c** (56 mg, 50%) as a white crystalline solid.

1-Pyrrolyl-1-methylsilacyclobutane, 40. To a solution of pyrrole (0.48 cm^3, 6.9 mmol) dissolved in dry THF (11 cm^3) under nitrogen and cooled to −78 °C was added *n*-BuLi (1.59 M in hexanes; 4.34 cm^3, 6.9 mmol, 1 eq). The solution was stirred at −78 °C for 2 h. 1-Chloro-1-methylsilacyclobutane (1.0 g, 8.3 mmol, 1.2 eq) was added dropwise and the resultant mixture was allowed to warm to room temperature and stirred overnight during which time LiCl precipitated out.

The stirring was stopped and the clear solution separated *via* cannula. The filtrant was concentrated *via* distillation under atmospheric pressure under nitrogen and the residue purified by Kugelrohr distillation (bp *ca.* 195 °C) to furnish 1-pyrrolyl-1-methylsilacyclobutane **40** (0.73 g, 70%) as a colourless oil. δ_H(500 MHz; $CDCl_3$) 6.98 (2H, dd, *J* 2.0 and 2.0, Ar*H*), 6.44 (2H, dd, *J* 2.0 and 2.0, Ar*H*), 2.30–2.21 (1H, m, C*H*), 2.09–2.00 (1H, m, C*H*), 1.61–1.54 (2H, m, CH_2), 1.46–1.40 (2H, m, CH_2) and 0.75 (3H, s, CH_3); δ_C(125 MHz; $CDCl_3$) 123.2 (d), 111.4 (d), 17.8 (t), 15.6 (t) and −1.8 (q).

1-Indolyl-1-methylsilacyclobutane, 42. To a solution of indole (1.22 g, 10.4 mmol) dissolved in dry THF (19 cm^3) under nitrogen and cooled to −78 °C was added *n*-BuLi (2.5 M in hexanes; 4.16 cm^3, 10.4 mmol, 1 eq). The solution was stirred at −78 °C for 2 h. 1-Chloro-1-methylsilacyclobutane (1.50 g, 12.4 mmol, 1.2 eq) was added dropwise and the resultant mixture was allowed to warm to room temperature and stirred overnight during which time LiCl precipitated out.

The stirring was stopped and the clear solution separated *via* cannula. The filtrant was concentrated *via* distillation under atmospheric pressure under nitrogen and the residue purified by Kugelrohr distillation to furnish 1-indolyl-1-methylsilacyclobutane **42** (1.65 g, 79%) as a colourless oil. Bp *ca.* 240 °C, 4 mmHg; δ_H(400 MHz; $CDCl_3$) 7.70 (1H, d, *J* 8.0, Ar*H*), 7.57 (1H, d, *J* 8.0, Ar*H*), 7.29 (1H, d, *J* 3.0, Ar*H*), 7.26–7.19 (2H, m, Ar*H*), 6.69 (1H, dd, *J* 3.0 and 1.0,

Ar*H*), 2.40–2.26 (1H, m, C*H*), 2.21–2.08 (1H, m, C*H*), 1.78–1.69 (2H, m, CH_2), 1.52–1.44 (2H, m, CH_2) and 0.77 (3H, s, CH_3); δ_C(100 MHz; $CDCl_3$) 140.2 (s), 131.5 (d), 129.4 (s), 121.7 (d), 120.9 (d), 120.3 (d), 112.7 (d), 105.3 (d), 16.7 (t), 16.2 (t) and −0.4 (q).

***N*-Arylation of azoles in scCO$_2$ employing 1-azolyl-1-methylsilacyclobutane (general procedure I).** Flame dried caesium carbonate (228 mg, 0.7 mmol, 1.4 eq), KF (35 mg, 0.6 mmol, 1.2 eq), aryl halide (0.5 mmol), palladium acetate (5.6 mg, 0.025 mmol, 5 mol%) and P(*t*-Bu)$_2$(i-Pr-biphen) (0.05 mmol, 10 mol%) were placed in a 10 cm^3 stainless steel cell and the cell sealed. The cell was evacuated and refilled with nitrogen (three cycles). 1-Azolyl-1-methylsilacyclobutane (1.2 eq, 0.6 mmol) was injected through the inlet port and the cell connected to the CO_2 line and charged with CO_2 (99.9995%-further purified over an Oxisorb® catalyst) to approximately 800 psi (volume *ca.* 1 cm^3 liquid carbon dioxide). The cell was heated to the desired temperature and the pressure adjusted to *ca.* 1800 psi by the addition of further CO_2. The reagents were maintained at this temperature and pressure for 17 h before the cell was allowed to cool to room temperature. The contents of the cell were vented into ethyl acetate (50 cm^3), and once atmospheric pressure had been reached, the cell was opened and washed with further ethyl acetate (3 × 10 cm^3). The combined organic fractions were filtered and concentrated *in vacuo* to furnish the crude material which was purified by flash column chromatography.

4-Pyrrol-1-ylbenzoic acid methyl ester[62] (31, Table 8, entry 1)

At 100 °C. Employing general procedure I on a 0.5 mmol scale with 1-trimethylsilyl pyrrole **30** (84 mg, 0.6 mmol) furnished the title compound **31** as a white crystalline solid (75 mg, 75%).

At 75 °C. Employing general procedure I on a 0.5 mmol scale with 1-trimethylsilyl pyrrole **30** (84 mg, 0.6 mmol) furnished the title compound **31** as a white crystalline solid (61 mg, 61%).

1-Phenyl-1*H*-pyrrole[65] (33a, Table 8, entry 2)

At 100 °C. Employing general procedure I on a 0.5 mmol scale with 1-trimethylsilyl pyrrole **30** (84 mg, 0.6 mmol) furnished the title compound **33a** as a white crystalline solid (33 mg, 46%).

At 75 °C. Employing general procedure I on a 0.5 mmol scale with 1-trimethylsilyl pyrrole **30** (84 mg, 0.6 mmol) furnished the title compound **33a** as a white crystalline solid (28 mg, 39%).

1-(4-Methoxyphenyl)pyrrole[67] (33b, Table 8, entry 3)

At 100 °C. Employing general procedure I on a 0.5 mmol scale with 1-trimethylsilyl pyrrole **30** (84 mg, 0.6 mmol) furnished the title compound **33b** as a white crystalline solid (26 mg, 30%).

At 75 °C. Employing general procedure I on a 0.5 mmol scale with 1-trimethylsilyl pyrrole **30** (84 mg, 0.6 mmol) furnished the title compound **33b** as a white crystalline solid (22 mg, 25%).

4-Pyrrol-1-ylbenzoic acid methyl ester[62] (31, Table 8, entry 4)

At 100 °C. Employing general procedure I on a 0.5 mmol scale with 1-pyrrolyl-1-methylsilacyclobutane **40** (91 mg, 0.6 mmol) furnished the title compound **31** as a white crystalline solid (46 mg, 46%).

At 75 °C. Employing general procedure I on a 0.5 mmol scale with 1-pyrrolyl-1-methylsilacyclobutane **40** (91 mg, 0.6 mmol) furnished the title compound **31** as a white crystalline solid (48 mg, 48%).

At 50 °C. Employing general procedure I on a 0.5 mmol scale with 1-pyrrolyl-1-methylsilacyclobutane **40** (91 mg, 0.6 mmol) furnished the title compound **31** as a white crystalline solid (24 mg, 24%).

1-Phenyl-1*H*-pyrrole[65] (33a, Table 8, entry 5)

At 100 °C. Employing general procedure I on a 0.5 mmol scale with 1-pyrrolyl-1-methylsilacyclobutane **40** (91 mg, 0.6 mmol) furnished the title compound **33a** as a white crystalline solid (35 mg, 49%).

At 75 °C. Employing general procedure I on a 0.5 mmol scale with 1-pyrrolyl-1-methylsilacyclobutane **40** (91 mg, 0.6 mmol) furnished the title compound **33a** as a white crystalline solid (36 mg, 50%).

At 50 °C. Employing general procedure I on a 0.5 mmol scale with 1-pyrrolyl-1-methylsilacyclobutane **40** (91 mg, 0.6 mmol) furnished the title compound **33a** as a white crystalline solid (2 mg, 3%).

1-(4-Methoxyphenyl)pyrrole[67] (33b, Table 8, entry 6)

At 100 °C. Employing general procedure I on a 0.5 mmol scale with 1-pyrrolyl-1-methylsilacyclobutane **40** (91 mg, 0.6 mmol) furnished the title compound **33b** as a white crystalline solid (32 mg, 37%).

At 75 °C. Employing general procedure I on a 0.5 mmol scale with 1-pyrrolyl-1-methylsilacyclobutane **40** (91 mg, 0.6 mmol) furnished the title compound **33b** as a white crystalline solid (33 mg, 38%).

At 50 °C. Employing general procedure I on a 0.5 mmol scale with 1-pyrrolyl-1-methylsilacyclobutane **40** (91 mg, 0.6 mmol) furnished the title compound **33b** as a white crystalline solid (3 mg, 4%).

4-Indol-1-yl-benzoic acid methyl ester,[68] 34a

At 100 °C. Employing general procedure I on a 0.5 mmol scale with 1-indolyl-1-methylsilacyclobutane **42** (121 mg, 0.6 mmol) furnished the title compound **34a** as a colourless oil (78 mg, 62%).

At 75 °C. Employing general procedure I on a 0.5 mmol scale with 1-indolyl-1-methylsilacyclobutane **42** (121 mg, 0.6 mmol) furnished the title compound **34a** as a colourless oil (90 mg, 72%).

1-Phenyl-1*H*-indole,[69] 34b

At 100 °C. Employing general procedure I on a 0.5 mmol scale with 1-indolyl-1-methylsilacyclobutane **42** (121 mg, 0.6 mmol) furnished the title compound **34b** as a colourless oil (57 mg, 59%).

At 75 °C. Employing general procedure I on a 0.5 mmol scale with 1-indolyl-1-methylsilacyclobutane **42** (121 mg, 0.6 mmol) furnished the title compound **34b** as a colourless oil (63 mg, 65%).

1-(4-Methoxyphenyl)-1*H*-indole,[70] 34c

At 100 °C. Employing general procedure I on a 0.5 mmol scale with 1-indolyl-1-methylsilacyclobutane **42** (121 mg, 0.6 mmol) furnished the title compound **34c** as a colourless oil (55 mg, 49%).

At 75 °C. Employing general procedure I on a 0.5 mmol scale with 1-indolyl-1-methylsilacyclobutane **42** (121 mg, 0.6 mmol) furnished the title compound **34c** as a colourless oil (51 mg, 46%).

***N*-Trimethylsilyl-*N*-(*para*-toluenesulfonyl)-3-(*ortho*-bromophenyl)propylamine, 45a.** To a solution of the tosylamide **43a** (425 mg, 1.15 mmol) in dry acetonitrile (8 cm^3) under nitrogen was added BSTFA (0.46 cm^3, 1.73 mmol, 1.5 eq). The reaction mixture was heated at reflux for 5 h.

The acetonitrile was removed *via* distillation and the crude residue purified by vacuum distillation in a Kugelrohr oven to furnish the silylamide **45a** (481 mg, 95%) as a pale orange, viscous oil. Bp 250 °C, 4 mmHg; δ_H(500 MHz; $CDCl_3$) 7.70 (2H, d, *J* 8.0, Ar*H*), 7.52 (1H, dd, *J* 8.0 and 1.0, Ar*H*), 7.27 (2H, d, *J* 8.0, Ar*H*), 7.23 (1H, ddd, *J* 7.5, 7.5 and 1.0, Ar*H*), 7.15 (1H, dd, *J* 7.5 and 1.5, Ar*H*), 7.07 (1H, ddd, *J* 7.5, 7.5 and 1.5, Ar*H*), 3.03 (2H, m, CH_2), 2.62 (2H, t, *J* 7.5, CH_2), 2.43 (3H, s, CH_3), 1.84 (2H, tt, *J* 7.5 and 7.5, CH_2) and 0.37

[9H, s, Si(CH_3)$_3$]; δ_C(125 MHz, APT; $CDCl_3$) 142.8 (s), 140.3 (s), 138.4 (s), 132.8 (d), 130.3 (d), 129.5 (d), 127.8 (d), 127.4 (d), 127.2 (d), 124.3 (s), 45.8 (t), 33.4 (t), 31.2 (t), 21.5 (q) and 1.4 (q).

***N*-(Trimethylsilyl)-*N*-(methanesulfonyl)-3-(*ortho*-bromophenyl)-propylamine, 45b.** To a solution of the methanesulfonamide **43b** (460 mg, 1.6 mmol) in dry acetonitrile (8 cm^3) under nitrogen was added BSTFA (0.63 cm^3, 2.36 mmol, 1.5 eq). The reaction mixture was heated at reflux for 17 h.

The acetonitrile was removed *via* distillation and the crude residue purified by vacuum distillation in a Kugelrohr oven to furnish the silylamide **45b** (435 mg, 76%) as a pale yellow, viscous oil. Bp 250 °C, 2 mmHg; δ_H(400 MHz; $CDCl_3$) 7.52 (1H, d, *J* 7.5, Ar*H*), 7.26–7.22 (2H, m, Ar*H*), 7.07 (1H, ddd, *J* 6.5, 6.5 and 2.5, Ar*H*), 3.16 (1H, m, CH_2), 2.87 (3H, s, CH_3), 2.71 (2H, t, *J* 8.0, CH_2), 1.97 (2H, m, CH_2) and 0.30 [9H, s, Si(CH_3)$_3$]; δ_C(100 MHz; $CDCl_3$) 140.3 (s), 132.9 (d), 130.3 (d), 127.9 (d), 127.6 (d), 124.3 (s), 46.1 (t), 41.6 (q), 33.4 (t), 32.2 (t) and 1.0 (q).

Intramolecular amination of *N*-sulfonyl-(*o*-bromophenyl) propylamines (general procedure J). Amine (0.12 mmol), flame dried caesium carbonate (52.3 mg, 0.16 mmol, 1.4 eq), palladium acetate (0.6 mg, 3 μmol, 2.5 mol%) and di-*tert*-butylbiphenylphosphine (1.7 mg, 6 μmol, 5 mol%) were placed in a 10 cm^3 stainless steel cell in a glovebox and the cell sealed. The cell was removed from the glovebox and evacuated and refilled with nitrogen (three cycles). The cell was connected to the CO_2 line and charged with CO_2 (99.9995%-further purified over an Oxisorb® catalyst) to approximately 760 psi (volume *ca.* 1 cm^3 liquid carbon dioxide). The cell was heated to 100 °C and the pressure adjusted to *ca.* 1800 psi by the addition of further CO_2. The reagents were maintained at this temperature and pressure for the set time before the cell was allowed to cool to room temperature. The contents of the cell were vented into ethyl acetate (50 cm^3), and once atmospheric pressure had been reached, the cell was opened and washed with further ethyl acetate (3 × 10 cm^3). The combined organic fractions were filtered and concentrated *in vacuo* to furnish the crude material which was purified by flash column chromatography.

1-(Toluene-12-sulfonyl)-1,7,8,9-tetrahydroquinoline,[39] 46a

*From the free tosylamide **43a** (Table 9, entry 1).* Employing general procedure J with *N*-(*para*-toluenesulfonyl)-5-(*ortho*-bromophenyl)propylamine **43a** (50 mg, 0.14 mmol), $Pd(OAc)_2$ (0.7 mg, 2.5 mol%), P(*t*-Bu)$_2$(biphen) (2 mg, 5 mol%) and Cs_2CO_3 (63 mg, 0.19 mmol) furnished the title compound **46a** (8 mg, 20%) as a colourless solid. R_f 0.35 (4 : 1 hexane–ethyl acetate); mp 92–93 °C (lit.[72] 93–94 °C); δ_H(400 MHz; $CDCl_3$) 7.78 (1H, d, *J* 8.0, Ar*H*), 7.48 (2H, d, *J* 8.0, Ar*H*), 7.18 (3H, m, Ar*H*), 7.06 (1H, ddd, *J* 7.5, 7.5 and 1.0, Ar*H*), 6.99 (1H, d, *J* 7.5, Ar*H*), 3.80 (2H, m, CH_2), 2.44 (2H, t, *J* 6.5, CH_2), 2.38 (3H, s, CH_3) and 1.66 (2H, ddt, *J* 6.5, CH_2). Spectroscopic data identical to literature values.

*From N-trimethylsilyl-N-(p-toluenesulfonyl)-5-(o-bromophenyl) propylamine **45a** (Table 9, entry 2).* Employing general procedure J with *N*-trimethylsilyl-*N*-(*para*-toluenesulfonyl)-5-(*ortho*-bromophenyl)propylamine **45a** (50 mg, 0.11 mmol), $Pd(OAc)_2$ (0.6 mg, 2.5 mol%), P(*t*-Bu)$_2$(biphen) (1.7 mg, 5 mol%) and Cs_2CO_3 (52 mg, 0.16 mmol) furnished the title compound **46a** (20 mg, 61%) as a colourless oil after heating for 41 h.

From *N*-trimethylsilyl-*N*-(*para*-toluenesulfonyl)-5-(*ortho*-bromophenyl)propylamine **45a** with the addition of KF (Table 9, entry 3): employing general procedure J with *N*-trimethylsilyl-*N*-(*para*-toluenesulfonyl)-5-(*ortho*-bromophenyl)propylamine **45a** (100 mg, 0.23 mmol), $Pd(OAc)_2$ (1.3 mg, 2.5 mol%), P(*t*-Bu)$_2$(biphen) (3.4 mg, 5 mol%), Cs_2CO_3 (105 mg, 0.32 mmol) and KF (16 mg, 0.27 mmol) furnished the title compound **46a** (37 mg, 57%) as a colourless oil after heating for 41 h.

1-Methanesulfonyl-1,7,8,9-tetrahydroquinoline, 46b

*From the free methanesulfonamide **43b** (Table 9, entry 4).* Employing general procedure J with *N*-(methanesulfonyl)-5-(*ortho*-bromophenyl)propylamine **43b** (50 mg, 0.17 mmol), $Pd(OAc)_2$ (1 mg, 2.5 mol%), P(*t*-Bu)$_2$(biphen) (2.6 mg, 5 mol%) and Cs_2CO_3 (79 mg, 0.24 mmol) furnished the title compound **46b** (8 mg, 22%) as a white crystalline solid. R_f 0.25 (2 : 1 hexane–ethyl acetate); mp 58–59 °C; found: C, 57.1; H, 6.1; N, 6.4; $C_{10}H_{13}NO_2S$ requires C, 56.9; H, 6.2; N, 6.6%; ν_{max}(thin film)/cm^{-1} 3068 w, 3025 w, 2951 m, 2257 m, 1605 m, 1579 w, 1490 m, 1455 m, 1339 s and 1156 s; δ_H(400 MHz; $CDCl_3$) 7.70 (1H, d, *J* 8.5, Ar*H*), 7.17–7.07 (3H, m, Ar*H*), 3.82 (2H, m, CH_2), 2.89 (3H, s, CH_3), 2.85 (2H, t, *J* 6.5, CH_2) and 2.01 (2H, tt, *J* 6.5 and 6.0, CH_2); δ_C(100 MHz; $CDCl_3$) 137.0 (s), 129.7 (d), 129.1 (s), 126.9 (d), 124.6 (d), 122.7 (d), 46.5 (t), 38.7 (q), 27.1 (t) and 22.3 (t); *m*/*z* (ES) 229.1007 [M$^+$. $C_{10}H_{13}NO_2S$ requires M, 229.1005]; *m*/*z* (CI) 229 (M$^+$, 100%), 134 (21).

*From N-trimethylsilyl-N-methanesulfonyl-5-(o-bromophenyl) propylamine **45b** (Table 9, entry 5).* Employing general procedure J with *N*-trimethylsilyl-*N*-methanesulfonyl-5-(*ortho*-bromophenyl)propylamine **45b** (50 mg, 0.14 mmol), $Pd(OAc)_2$ (0.6 mg, 2.5 mol%), P(*t*-Bu)$_2$(biphen) (2 mg, 5 mol%) and Cs_2CO_3 (63 mg, 0.19 mmol) furnished the title compound **46b** (16 mg, 55%) as a white crystalline solid.

From *N*-trimethylsilyl-*N*-methanesulfonyl-5-(*ortho*-bromophenyl)propylamine **45b** with the addition of KF (Table 9, entry 6): employing general procedure J with *N*-trimethylsilyl-*N*-methanesulfonyl-5-(*ortho*-bromophenyl)propylamine **45b** (50 mg, 0.14 mmol), $Pd(OAc)_2$ (0.8 mg, 2.5 mol%), P(*t*-Bu)$_2$(biphen) (2 mg, 5 mol%), KF (9.6 mg, 0.16 mmol) and Cs_2CO_3 (63 mg, 0.19 mmol) furnished the title compound **46b** (21 mg, 72%) as a white crystalline solid.

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