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Hypervalent Iodine(III)-Mediated Oxidative Dearomatizing Cyclization of Arylamines

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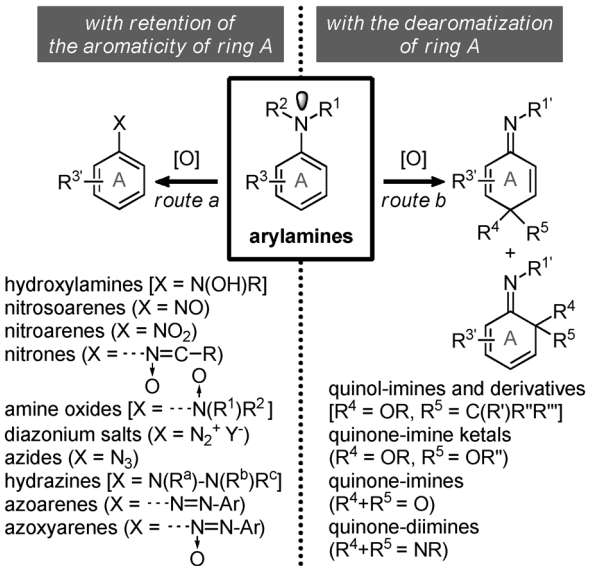
Abstract: An oxidative dearomatizing cyclization of arylamines promoted by iodobenzene bis(trifluoroacetate) [$PhI(CF_3CO_2)_2$] has been explored, leading to a novel synthetic approach to functionalized spirocyclic building blocks containing the structurally unique dieniminium moiety. This unprecedented methodology, featuring oxidative dearomatization and carbon-carbon bond-forming cyclization, to some extent, not only expands the synthetic potential of hypervalent iodine chemistry, but also enriches the oxidation chemistry of arylamines.

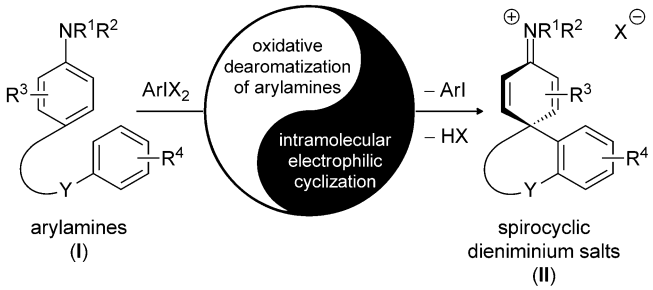
Keywords: amines; C–C coupling; dearomatization; iodine; oxidation; spiro compounds



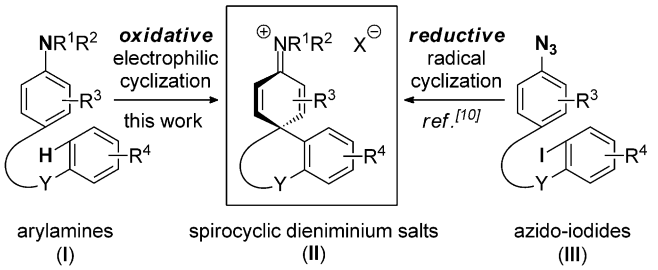
Scheme 1. Selected functional group transformations in the oxidation of arylamines.

Arylamines (aromatic amines) are one of the most important classes of nitrogen functional compounds in organic chemistry and biochemistry.[1,2] Stimulated by the intrinsic chemical properties of arylamines, various oxidation reactions involving the amino group have been extensively explored to install a series of synthetically versatile nitrogen-rich functional groups.[1,3,4] Among these chemical conversions, the oxidative substitution and/or addition occurring at the nitrogen center (route a, Scheme 1) using metallic and non-metallic oxidants typically constitutes the main reaction patterns, providing a variety of synthetically useful nitrogen-containing building blocks and precursors (e.g., hydroxylamines, nitrosoarenes, nitroarenes, nitrones, amine oxides, diazonium salts, azides, hydrazines, azoarenes, and azoxyarenes).[1,3,4] Except for the above transformations with retention of the aromaticity of the parent ring A (route a), the reactions involving the oxidative dearomatization of arylamines (route b) are also documented for the synthesis of quinoids (e.g., quinol-imines and derivatives,[5] quinone-imine ketals,[6] quinone-imines,[7d–j] and quinone-diimines[7a–c,e]). Compared with the vast majority of literature reports on the classical oxidation of the arylamino moiety (route a),[1,3,4] however, less attention has been paid to the development of methodologies based on the selective oxidative dearomatization of arylamines, especially those involving a new carbon-carbon bond-forming sequence.

With our interest in the dearomatization chemistry[8] as well as inspiration from the previous exploration of the phenolic oxidative coupling reaction,[9] recently we have disclosed a novel hypervalent iodine(III)-mediated oxidative dearomatizing cyclization of arylamines **I** (Scheme 2) and, interestingly, one class of structurally unique spirocyclic dieniminium salts **II** could be unprecedentedly accessed by an *oxidative dearomatization strategy*. Notably, to the best of our



Scheme 2. Hypervalent iodine(III)-mediated intramolecular oxidative dearomatizing cyclization of arylamines.

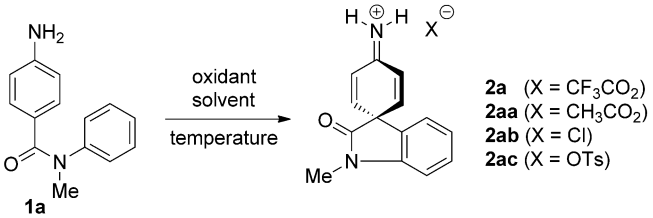


Scheme 3. The synthesis of spirocyclic dieniminium salts with a dearomatization strategy.

knowledge, the previous efforts on the synthesis of such type of spirocyclic dieniminium salts were only realized on the basis of a *reductive dearomatization strategy* (Scheme 3), in which a reductive radical cyclization of azido-iodides **III** was elegantly demonstrated for this transformation by Minozzi, Nanni and Spagnolo.[10] Compared with previous mainstream reports on the oxidation of arylamines in organic synthesis,[1,3,4] importantly, our current methodology features a novel oxidative dearomatization of arylamines and a subsequent intramolecular carbon-carbon bond-forming cyclization, strategically enabling a straightforward approach to functionalized spirocyclic building blocks with the iminium moiety. Herein, we present our preliminary results on this aspect.

As a model to explore the titled iodine(III)-mediated oxidative dearomatizing cyclization, as shown in Table 1, the arylamine **1a**, which could be readily prepared by amidation and nitro-reduction using *N*-methylaniline and 4-nitrobenzoic acid,[11] was initially selected to evaluate the reaction conditions. On the basis of substantial progress in hypervalent iodine chemistry,[12] iodobenzene diacetate [$PhI(OAc)_2$] was firstly examined using CF_3CH_2OH as a solvent at room temperature, and pleasingly the desired spirocyclic dieniminium salt **2aa** could be obtained albeit in a modest yield of 16% (entry 1). When employing iodobenzene bis(trifluoroacetate) [$PhI(CF_3CO_2)_2$], the oxidative dearomatization/cyclization reaction proceeded smoothly, giving the related spirocyclic product **2a** in a highly increased yield of 62% (entry 2). The structural elucidation of **2a** was confirmed unambiguously by X-ray crystallographic analysis (Figure 1).[13] In order to probe the electronic effect of the aryl substituent in the analogues of $PhI(CF_3CO_2)_2$, the fully fluorinated iodine(III) reagent – $C_6F_5I(CF_3CO_2)_2$ – was then tested (entry 3), but a negative influence on the reaction yield was observed in this case. Besides, two other iodine(III) oxidants, $PhICl_2$ (entry 4) and Koser's reagent [PhI(OTs)OH] (entry 5), were also used in this model, but no expected dieniminium salt **2ab** or **2ac** was isolated in the control experiments. In addition to the above preliminary screening of hypervalent iodine(III) oxidants, the solvent effect on this transformation was subsequently investigated (entries 6–14). Among a series of

Table 1. Optimization of reaction conditions.[a]



Entry	Oxidant	Solvent	*T* [°C]	Product	Yield [%][b]
1	$PhI(OAc)_2$	TFE	25	**2aa**	16
2	$PhI(CF_3CO_2)_2$	TFE	25	**2a**	62
3	$C_6F_5I(CF_3CO_2)_2$	TFE	25	**2a**	11[c]
4	$PhICl_2$	TFE	25	**2ab**	–[d]
5	PhI(OH)OTs	TFE	25	**2ac**	–[d]
6	$PhI(CF_3CO_2)_2$	HFIP	25	**2a**	46
7	$PhI(CF_3CO_2)_2$	EtOH	25	**2a**	19[c]
8	$PhI(CF_3CO_2)_2$	MeCN	25	**2a**	46
9	$PhI(CF_3CO_2)_2$	$MeNO_2$	25	**2a**	63
10	$PhI(CF_3CO_2)_2$	acetone	25	**2a**	42
11	$PhI(CF_3CO_2)_2$	AcOEt	25	**2a**	15[c]
12	$PhI(CF_3CO_2)_2$	THF	25	**2a**	8[c]
13	$PhI(CF_3CO_2)_2$	$PhCH_3$	25	**2a**	–[d]
14	$PhI(CF_3CO_2)_2$	CH_2Cl_2	25	**2a**	22[c]
15	$PhI(CF_3CO_2)_2$	TFE	−40[f]	**2a**	27[c,e]
16	$PhI(CF_3CO_2)_2$	$MeNO_2$	−20[f]	**2a**	33[c,e]

[a] To a solution of **1a** (1.0 mmol) in solvent (6.6 mL) at the indicated temperature was added the oxidant (1.1 mmol). For details, see the Supporting Information.
[b] Yield of isolated product.
[c] The starting material disappeared completely, and several unidentified by-products were observed.
[d] No desired product was isolated from the complex reaction mixture.
[e] The reaction proceeded in 3 h.
[f] Melting points of CF_3CH_2OH and $MeNO_2$ are −44 °C and −29 °C, respectively. TFE = CF_3CH_2OH, HFIP = $(CF_3)_2CHOH$.

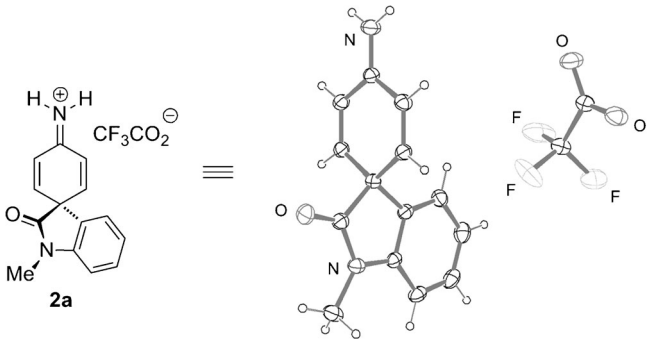
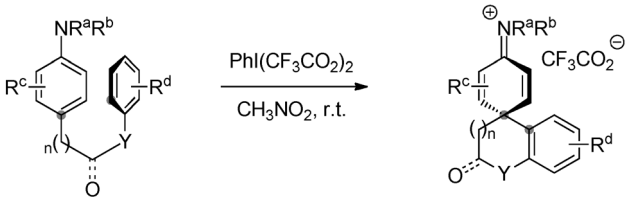


Figure 1. X-ray structure of **2a**.

protic and non-protic polar media tested, it was generally found that 2,2,2-trifluoroethanol (TFE = CF_3CH_2OH; entry 2) or nitromethane ($MeNO_2$; entry 9) as a solvent could effectively promote this arylamine oxidation/cyclization reaction. Notably, decreasing the temperature did not improve the reaction yield (entries 15 and 16).

After the above optimization of the reaction conditions, we then sought to examine the scope and limitations of this methodology (Table 2). Firstly, a series of primary arylamines (**1a**–**1j**, entries 1–11) was employed in this iodine(III)-mediated oxidative dearomatization/cyclization, and the reactions proceeded quickly and were complete within one minute at room temperature, giving various dieniminium-containing spirocyclic products **2a**–**2j**. For example, when *N*-phenyl-*para*-aminobenzamide derivatives **1a**–**1c**

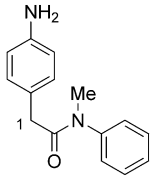
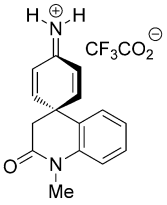
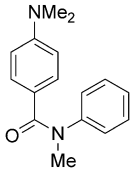
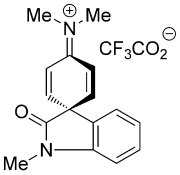
Table 2. Iodine(III)-mediated intramolecular oxidative dearomatization of arylamines.[a]



1 **2**

Entry	Substrate	Product	Yield [%][b]	Entry	Substrate	Product	Yield [%][b]
1	**1a** ($R^1=R^2=H$, $R^3=Me$)	**2a**	63	10	**1i**	**2i**	40 (53[d])
2	**1a″** ($R^1=R^2=R^3=H$)	**2a″**	–[c]				
3	**1b** ($R^1=Cl$, $R^2=H$, $R^3=Me$)	**2b**	69				
4	**1c** ($R^1=H$, $R^2=Cl$, $R^3=Me$)	**2c**	42				
5	**1d** ($R^4=R^5=H$)	**2d**	89	11	**1j**	**2j**	45
6	**1e** ($R^4=H$, $R^5=Br$)	**2e**	85				
7	**1f** ($R^4=R^5=Br$)	**2f**	63				

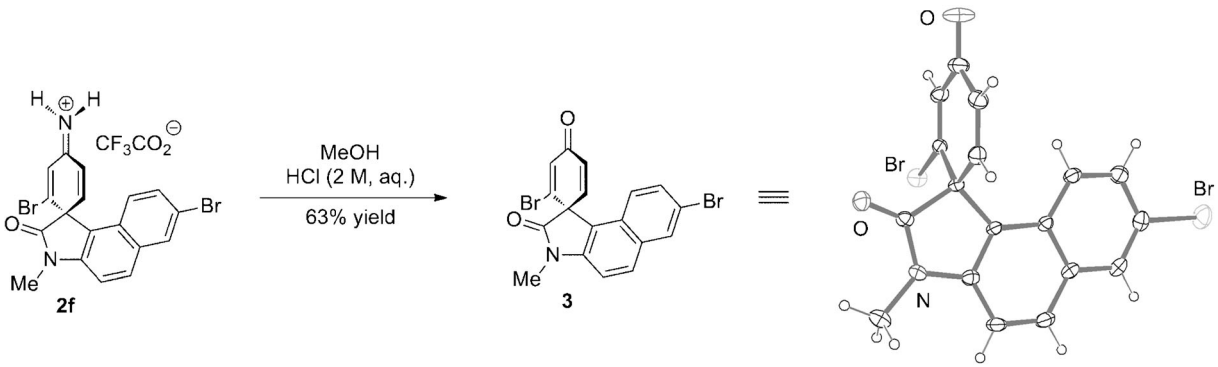
Table 2. (Continued)

Entry	Substrate	Product	Yield [%][b]	Entry	Substrate	Product	Yield [%][b]
8	**1g**	**2g**	91	12	**1k** (R^6 = Me)	**2k**	56
				13	**1l** (R^6 = Bn)	**2a** (R^6 = H)	28[c]
				14	**1m** (R^6 = Ph)	**2m**	–[c]
				15	**1n** (R^6 = CO_2Et)	**2n**	–[e]
							
9	**1h**	**2h**	24[c] (46[d])	16	**1o**	**2o**	–[f] (47[g])

[a] Unless otherwise noted, $PhI(CF_3CO_2)_2$ (1.1 mmol) as oxidant was added to a solution of arylamines **1** (1.0 mmol) in $MeNO_2$ (6.6 mL) as solvent at room temperature (for details, see the Supporting Information).
[b] Yield of isolated product.
[c] The starting material disappeared completely, and several unidentified by-products were observed.
[d] CF_3CH_2OH instead of $MeNO_2$ was used as the solvent in this case.
[e] No reaction and recovery of starting material.
[f] The starting material disappeared completely, and only trace amounts of product were observed in the resulting complex reaction mixture.
[g] The mixed solvent of CF_3CH_2OH/acetone (5:1 v/v) instead of $MeNO_2$ was used in this case, with 24% yield of the demethyl product **2k**, employing two equivalents of $PhI(CF_3CO_2)_2$.

($R^3 \neq H$) were used as substrates, the products **2a**–**2c** containing the 2-azaspiro[4.5]decane core could be obtained in moderate yields (entries 1, 3 and 4). For the case using **1c** (entry 4), the lower yield of 42% to some extent reflects the unfavorable influence of ring B having an electron-withdrawing substituent (R^2 = Cl) on the subsequent intramolecular electrophilic cyclization. However, in contrast to these positive results, employing the substrate **1a″** (R^3 = H, entry 2) with the secondary amide moiety did not give the desired oxidative coupling product.

To probe the regioselectivity of the carbon-carbon bond formation in this oxidative dearomatizing cyclization, *N*-naphthyl-*para*-aminobenzamide derivatives **1d**–**1f** (entries 5–7 of Table 2) were designed as substrates. Following the arylamine oxidative coupling, interestingly the regioselective products **2d**–**2f** were predominantly formed in good yields at the kinetically favorable α-position of the naphthyl unit (entries 5–7), wherein the regio-defined structure of chemically labile **2f** was clearly assigned by X-ray crystallographic analysis of its hydrolysis compound **3**[13] (Scheme 4). Notably compared with the example using **1d** (entry 5), the decreased yields in the cases of **1e** (entry 6) and **1f** (entry 7) analogously show the negative effect of ring B and ring A substituted by the electron-withdrawing groups (R^4 and R^5 = Br) on the current oxidative dearomatizing cyclization. Be-



Scheme 4. Structure determination of **2f** by X-ray crystallographic analysis of its hydrolysis compound **3**.

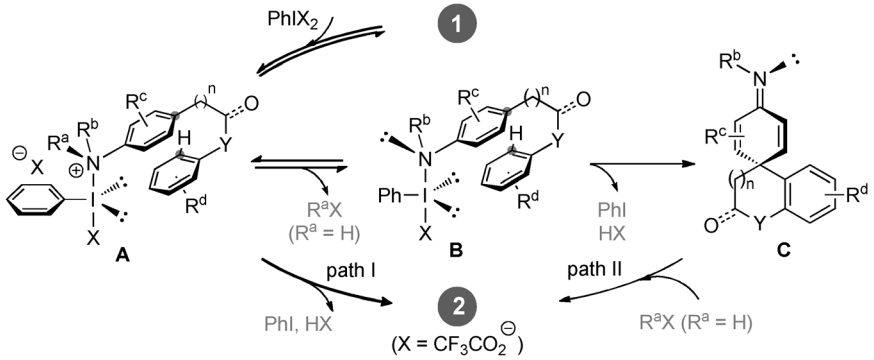
sides, one example using *N*-naphthyl-*para*-aminobenzamide derivative **1g** (entry 8) was also investigated, and the regioselective cyclization at the electron-enriched β-position of naphthyl unit afforded the expected product **2g** in 91% yield.[14]

As part of a continuing evaluation for the feasibility to access functionalized spirocycles,[15] two representative examples using *N*-aryl-*para*-aminophenylacetamides **1h** and **1i** (entries 9 and 10 of Table 2) were then examined under the standard conditions, and the titled iodine(III)-mediated reaction delivered the desired coupling products, **2h** and **2i**, with the 3-azaspiro[5.5]undecane core but in low isolated yields of 24% and 40%, respectively. Notably, the partially improved yields of 46% and 53% in these two cases (entries 9 and 10) could be realized by using the protic solvent CF_3CH_2OH, which was previously found to be an alternative medium to CH_3NO_2 (entries 2 and 9 of Table 1). In addition, the survey of *para*-aminobenzyl ether **1j** (entry 11) in this iodine(III)-mediated oxidation was also conducted, and the dieniminium-containing spirocyclic ether **2j** with the 2-oxaspiro[5.5]undecane core could be obtained in 45% yield. It should be noted that due to the presence of the C-1-methylene unit in the substrates **1h**–**1j** (entries 9–11), the undesired C-1-benzylic deprotonation to form the *para*-azaquinone methide (*para*-quinone methide imine) intermediates might competitively occur as one of side reactions, resulting in their lower yields.

With the aforementioned exploration for the reactivity of primary arylamines **1** ($R^a = R^b = H$, Table 2), the influence of the sp^3 and sp^2 carbon substituents at nitrogen center of arylamines **1** (R^a and/or $R^b \neq H$) was further investigated. For example, when the methyl-substituted secondary arylamine **1k** ($R^6 = Me$, entry 12 of Table 2) was subjected to the reaction conditions, the desired spirocyclic product **2k** could be afforded in 56% yield. Compared with this result, the iodine(III)-mediated oxidative reaction of the benzyl-substituted secondary arylamine **1l** ($R^6 = Bn$, entry 13) only gave the unexpected debenzylation product **2a** in a modest yield of 28%, possibly due to the undesired competitive cleavage of the *N*-benzyl group.[16] While using the phenyl-substituted secondary arylamine **1m** ($R^6 = Ph$, entry 14) as a substrate, surprisingly, the expected spirocyclic dieniminium salt **2m** was not observed after the rapid disappearance of starting material in the presence of hypervalent iodine(III) reagent, possibly arising from the unfavorable impact of the oxidatively more active sp^2-hybridized R^6 substituted at the arylamine nitrogen center. In contrast to the high reactivity described above, the secondary arylamine **1n** ($R^6 = CO_2Et$, entry 15) bearing an electron-withdrawing *N*-alkoxycarbonyl group did not undergo the expected transformation, showing the fact that the electronic deactivation of arylamines is primarily responsible for the total recovery of starting material in the present hypervalent iodine-promoted oxidation.

Furthermore, the tertiary arylamine as substrate was also investigated in this reaction. Compared with the observation of trace amounts of the desired product **2o** under the standard conditions (entry 16 of Table 2), *para*-(*N*,*N*-dimethylamino)-benzamide **1o** was subjected to the modified conditions using a mixed solvent of CF_3CH_2OH/acetone (5:1 v/v) and two equivalents of $PhI(CF_3CO_2)_2$, and the corresponding spirocyclic product **2o** with the dieniminium subunit could be obtained in 47% yield, together with the *N*-demethylation side-product **2k** which was also isolated in 24% yield.[17]

To account for the results obtained above, a potential rationale for two plausible pathways from arylamines **1** to spirocyclic dieniminium salts **2** is presented on the basis of the literature,[12] although the mechanistic details remain to be explored. As shown in Scheme 5, the hypervalent iodine(III) reagent $PhIX_2$ with a typical T-shaped geometry would firstly undergo a nucleophilic attack of the aromatic amino group of **1**, delivering an ammonium intermediate **A**; then a single two-electron or successive one-electron transfer redox process follows,[18,19] chemically initiated by a higher oxidation state of its iodine center in **A**, the iodine(III)-mediated oxidative cyclization of aryl-



Scheme 5. Plausible pathways from **1** to **2** in the presence of hypervalent iodine(III) reagent.

amines directly gives the dearomatizing coupling product **2** with the release of PhI and HX (path I). Meanwhile, the leaving tendency of the R^a group ($R^a = H$) in the cationic ammonium center of **A** might drive the *in-situ* generation of the neutral intermediate **B**, giving an equilibrium between **A** and **B**. Subsequently, the redox process in **B** would analogously result in the formation of spirocyclic imines **C**, which could alternatively afford the final iminium salt products **2** followed by the non-aqueous protonation in the presence of R^aX ($R^a = H$) (path II). According to this scenario, the oxidative coupling of primary, secondary and tertiary arylamines (**1a–1j**, **1k** and **1o** of Table 2) could be mechanistically unified through path I and/or path II, affording the corresponding iminium products **2a–2j**, **2k** and **2o**.

In conclusion, a novel oxidative dearomatization coupling of arylamines mediated by hypervalent iodine(III) reagents has been developed, in which a new carbon-carbon bond-forming sequence *via* an intramolecular electrophilic cyclization was combined. Interestingly, the synthetic potential of this methodology has been preliminarily explored in the construction of functionalized spirocyclic building blocks containing the structurally unique dieniminium moiety, which was directly assembled by an unprecedented oxidative electrophilic cyclization strategy using arylamines. The current oxidative dearomatizing cyclization reaction not only expands the application of hypervalent iodine chemistry, but also enriches the chemical transformation of arylamines in organic chemistry.

Experimental Section

General Procedure for the Hypervalent Iodine(III)-Mediated Oxidative Dearomatizing Cyclization of Arylamines in Table 2

Unless otherwise noted, the hypervalent iodine(III) reagent $PhI(CF_3CO_2)_2$ (1.1 mmol) was added to a solution of arylamines **1** (1.0 mmol) in $MeNO_2$ (6.6 mL) at room temperature. The reaction mixture was stirred until the starting material had disappeared by TLC inspection. Following evaporation of the solvent, the residue was directly purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH to afford the spirocyclic dieniminium salts **2**.

Procedures, spectral data, and copies of ^1H and ^{13}C NMR spectra are available in the Supporting Information.

Acknowledgements

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These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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