Synthesis of *N,N,N',N'*-tetraalkylbenzidines through oxidative coupling of *N,N*-dialkylarylamines induced by $SbCl_5$

Paola Vitale,[a,b] * **Leonardo Di Nunno,**[a,b] **and Antonio Scilimati**[b]

[a] *C.I.N.M.P.I.S., Università degli Studi di Bari "A. Moro", Via Orabona 4, 70125 Bari, Italy*
[b] *Dipartimento di Farmacia, Università degli Studi di Bari "A. Moro", Via Orabona 4, 70125 Bari, Italy*
E-mail: paola.vitale@uniba.it

Abstract
The oxidative coupling to 4,4'-*N*,*N*,*N*',*N*'-tetraalkylbenzidines is the main reaction observed during a study on the reactivity of *N*,*N*-dialkylanilines with $SbCl_5$. A possible reaction mechanism is presented and discussed in comparison with the *N*,*N*-dialkylanilines oxidative coupling achieved with other Lewis acids.

Keywords: $SbCl_5$, oxidative coupling, *N*,*N*-dialkylanilines, *4*,*4*'-*N*,*N*,*N*',*N*'-tetraalkylbenzidines, photoconductors oLEDs

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Introduction

Antimony pentachloride reacts with monoalkylbenzenes or deactivated aromatic compounds, providing an aromatic chlorination by electrophilic aromatic substitution either as a direct chlorinating agent,[1-5] or as a catalyst of the chlorination with chlorine gas,[6] because of the combination of its Friedel-Crafts catalytic activity and its oxidation-reduction potential. Some hypotheses have been proposed to explain the higher aromatic *para*/*ortho*-chlorination ratio observed with $SbCl_5$, in comparison to the reactions with $Cl_2/SbCl_5$, a bulky electrophilic species ($SbCl_4^+/SbCl_6^+$) being postulated in the former case.[1,7-8]

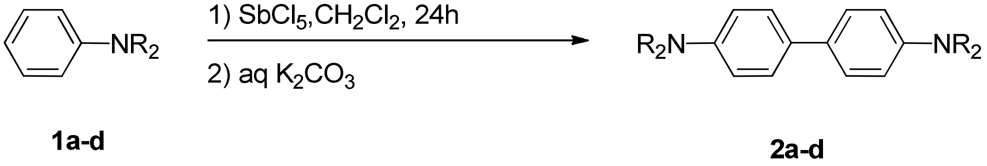
At variance with the above mentioned substrates, no studies on the reactivity of $SbCl_5$ with anilines or other arylamines were carried out. During the study of some *N*,*N*-disubstituted anilines,[9] we undertaken an investigation on the reactivity of a wide number of substituted benzenes in the presence of Lewis acids, and we found that after treatment of *N,N*-dialkylanilines with $SbCl_5$, followed by neutralization with a base, *N,N,N',N'*-tetralkylbenzidines can be isolated in fair to good yields from the reaction mixture.

Interestingly, in the used experimental conditions, $SbCl_5$ does not seem to react with anilines as a direct chlorinating agent, and *N,N,N',N'*-tetralkylbenzidines were the main reaction products.

Since substituted benzidines are interesting and useful compounds, for their application in the field of organic solar cells, photoconductors, oLED and other devices, we found interesting to investigate in detail such a new synthetic methodology to *N,N,N',N'*-tetraalkylbenzidines.

Results and Discussion

We found that the treatment of *N,N*-disubstituted anilines **1a-d** with $SbCl_5$, followed by neutralization with a base (aqueous KOH or K_2CO_3), afforded *N,N,N',N'*-tetralkylbenzidines **2a-d** in fair to good yields, together with little amounts of chlorinated products (Scheme 1 and Table 1). The formation of insoluble red-brown powders (named from now on, solids **3a-c**) was observed in the course of all reactions after $SbCl_5$ addition to the *N,N*-disubstituted aniline solution in CH_2Cl_2. However, some efforts aimed at the isolation of such intermediates in solid crystalline form, from the reaction mixture before the final basic treatment, failed.[10]



Scheme 1. Products of reaction of *N,N*-dialkylanilines **1a-d** with $SbCl_5$.

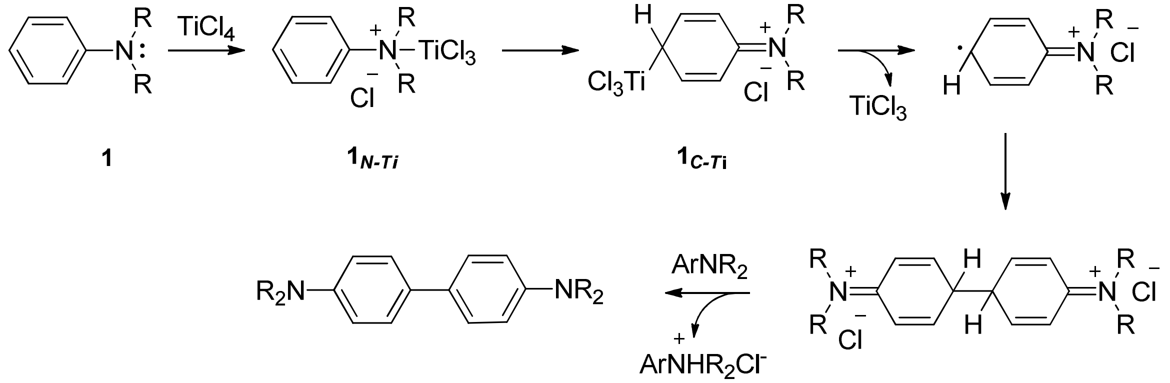
Table 1. Products of reaction of *N,N*-dialkylaniline (**1a-d**) with $SbCl_5/CH_2Cl_2$[a]

Entry	R	Yield **2** (%)
1a	Me	**2a** (81)
1b	Et	**2b** (84)
1c	*i*-Pr	**2c** (63)[b]
1d	$-(CH_2)_4-$	**2d** (38)

[a]Reaction conditions: $SbCl_5/C_6H_5NR_2$ (1:1 ratio) were stirred for 24 h under nitrogen atmosphere before treatment with K_2CO_3 (See Experimental). In this conditions $SbCl_5$ does not react with anilines as a direct chlorinating agent, and *N,N,N',N'*-tetralkylbenzidines were the main reaction products.

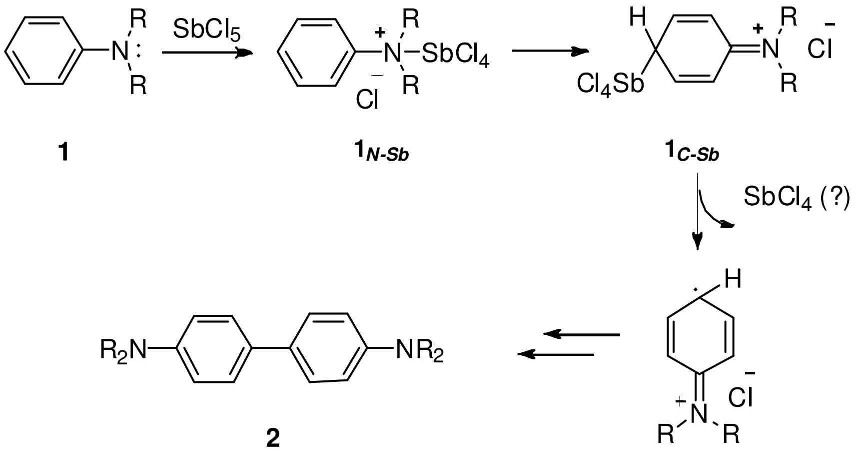
[b]The 3-chloro-$N^4,N^4,N^{4'},N^{4'}$-tetraisopropylbiphenyl-4,4'-diamine **2e** was also isolated in 35% yield.

Oxidative coupling of *N,N*-dialkylarylamines to benzidines is a known reaction,[7,8,11] and the formation of 4,4'-*N,N,N',N'*-tetraalkylbenzidines by reaction of *N,N*-dialkylanilines with some transition metals (CAN,[12] $TiCl_4$,[13] etc.) has also been reported.
In particular, to explain the oxidative coupling observed in the reaction of *N,N*-dialkylarylamines with $TiCl_4$,[13] a stepwise mechanism has been proposed, that involves the formation of two complexes with $TiCl_4$ (adduct $\mathbf{1}_{N\text{-}Ti}$ and $\mathbf{1}_{C\text{-}Ti}$), followed by the conversion of $\mathbf{1}_{C\text{-}Ti}$ into a radical cation intermediate (Scheme 2).



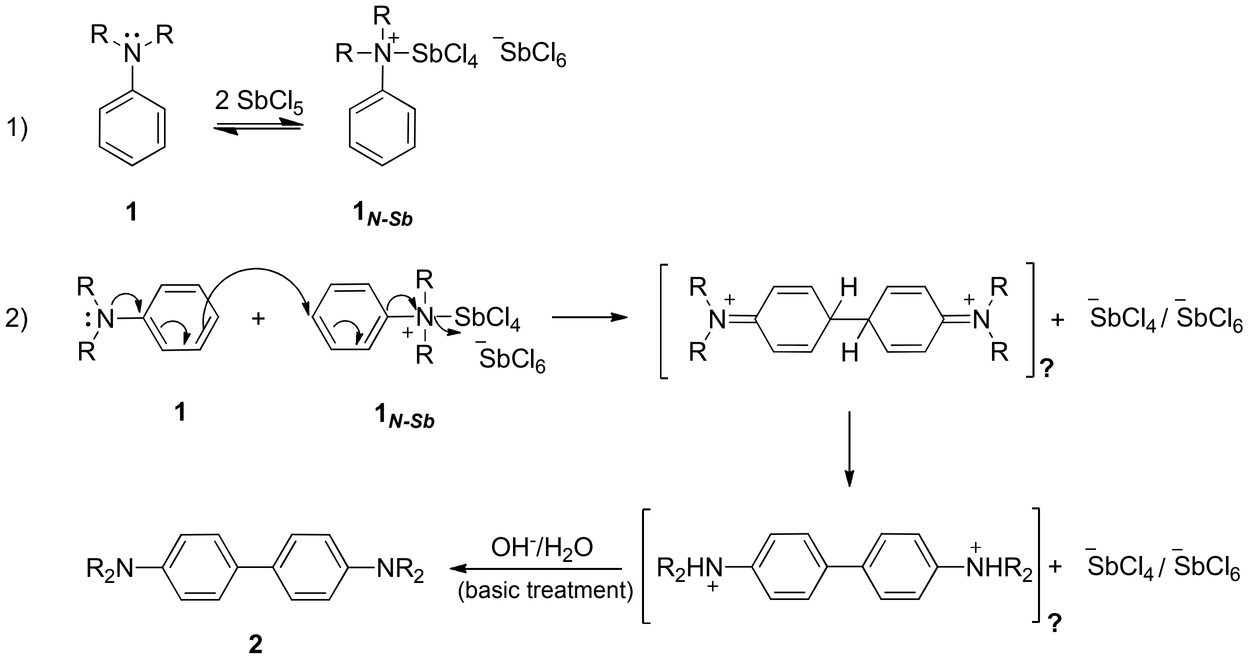
Scheme 2. Mechanistic hypothesis of 4,4'-*N,N,N',N'*-tetraalkylbenzidines formation by oxidative coupling of *N,N*-dialkylanilines in the presence of $TiCl_4$.

However, a similar mechanism could not to be proposed when $SbCl_5$ was used, since a very unusual oxidation number +4 should be required for the Sb species ($SbCl_4$) detachment in this case (Scheme 3).



Scheme 3. Mechanistic hypothesis of 4'-*N,N,N',N'*-tetraalkylbenzidines formation by radical oxidative coupling of *N,N*-dialkylanilines in the presence of $SbCl_5$.

So, we propose an alternative mechanistic hypothesis (Scheme 4), where the dimerization is just the result of a direct interaction between the starting *N*,*N*-dialkylaniline and the $\mathbf{1}_{\mathit{N}\text{-Sb}}$ adduct. Based on this hypothesis, the formation of the $\mathbf{1}_{\mathit{C}\text{-Sb}}$ intermediate depicted in Scheme 3 should be excluded.



Scheme 4. Mechanistic hypothesis of oxidative coupling of *N,N*-dialkylanilines in the presence of $SbCl_5$.

Since some spectroscopic and analytical data collected for the solid intermediates **3a-c** precipitated from the reaction mixture were consistent with the $N^4,N^4,N^{4'},N^{4'}$-tetraalkylbiphenyl-4,4'-diaminium structures (Scheme 4), we carried out some experiments to investigate the nature of that reaction intermediates and to deepen the synthetic applications of such reaction.

First, different experimental conditions have been explored, and the collected data showed that better yields of benzidines **2a-d** can be obtained in the presence of stoichiometric amounts of $SbCl_5$ (Table 2).

Subsequently, we performed some specific coupling experiments to clarify the nature of our reaction intermediates, aimed at definitively exclude the hypothesis of their "aniline" structure (e.g., adduct $\mathbf{1}_{\mathit{C\text{-}Sb}}$, Scheme 3) and/or confirming its "benzidinium" nature, as depicted in Scheme 4.

We isolated the two solid-intermediates **3a** and **3c** from the reaction of $SbCl_5$ with *N,N*-dimethylaniline **1a** and *N,N*-diisopropylaniline **1c**, respectively. Then, equimolecular amounts of **3a** and **3c** were mixed and heated under reflux in the presence of KOH (Scheme 5).

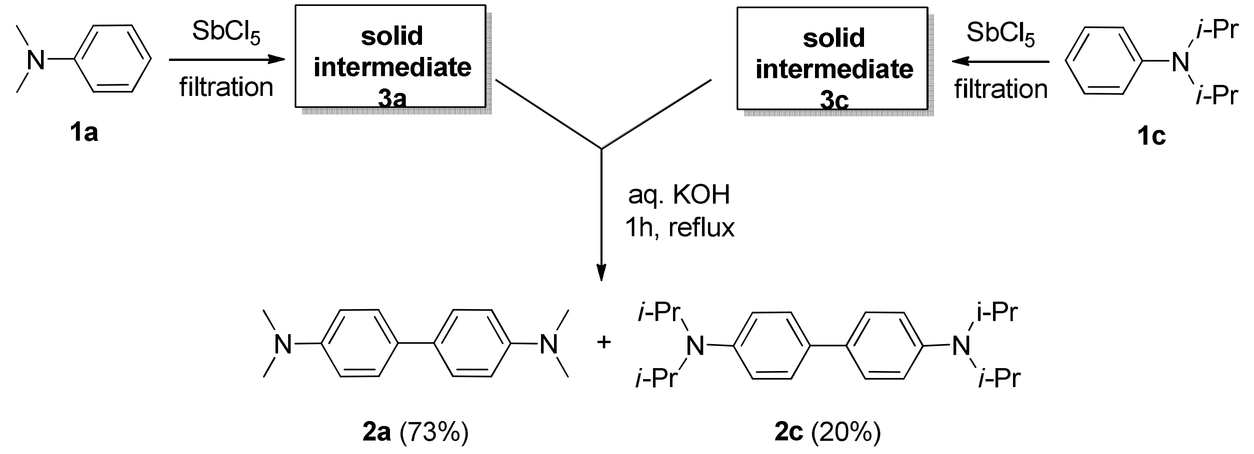
Table 2. Products and yields of the reaction of *N*,*N*-dialkylanilines (**1a-d**) with $SbCl_5/CH_2Cl_2$.[a]

Entry	R	$SbCl_5$/ $PhNR_2$	Conversion (%)	Yield 2a-d (%)
1	Me	1:1	100	**2a** (81)
2	Me	2:1	100	**2a** (80)
3	Me	5:1	100	**2a** (83)
4	Me	0.5:1	50	**2a** (50)
5	Me	0.2:1	30	**2a** (24)
6	Et	1:1	100	**2b** (84)
7	Et	0.5:1	50	**2b** (43)
8	$-(CH_2)_4-$	1:1	40	**2d** (38)
9	$-(CH_2)_4-$	2:1	70	**2d** (62)[b]

[a] The reaction mixtures were stirred for 24 h under nitrogen atmosphere after quenching with aq. K_2CO_3 (See Experimental).

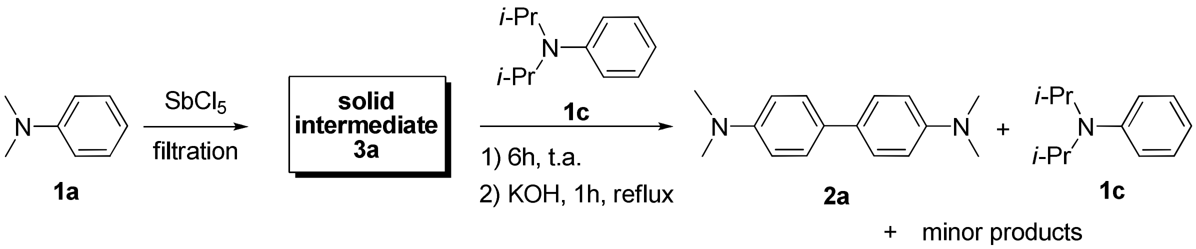
[b] 3% of chlorinated products were also observed.

As a result, only the symmetric benzidines **2a** and **2c** were obtained (Scheme 5), and no cross-coupling reactions were observed, as expected if the solids **3a** and **3c** had the adducts **1**$_{C\text{-}Sb}$ structures.



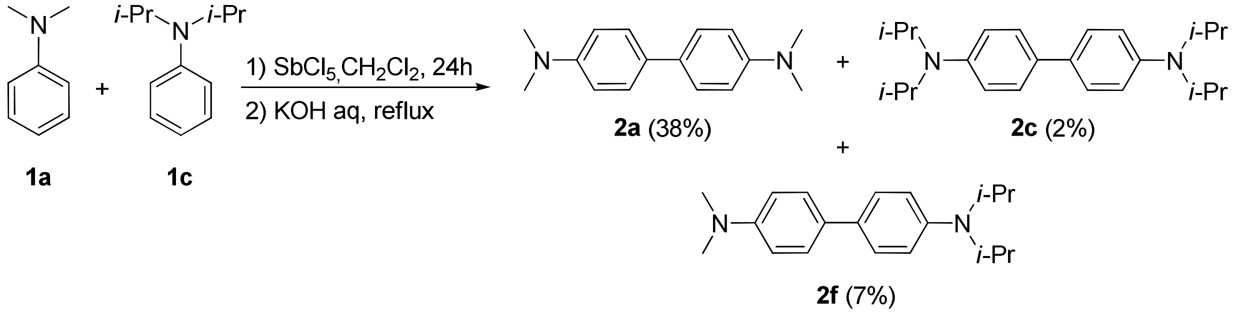
Scheme 5

Next, we studied the reaction between *N*,*N*-diisopropylamine **1c** and the solid **3a**: this experiment provided the symmetrical substituted benzidine **2a**, together with some starting unreacted aniline **1c** (Scheme 6).



Scheme 6

Conversely, little amounts of **2f** was detected in the reaction of an equimolecular mixture of the two anilines **1a** and **1c** with $SbCl_5$, followed by the basic treatment (aq. KOH) (Scheme 7). The different conversion of the two anilines could be due to the different rate of reaction of the starting materials.



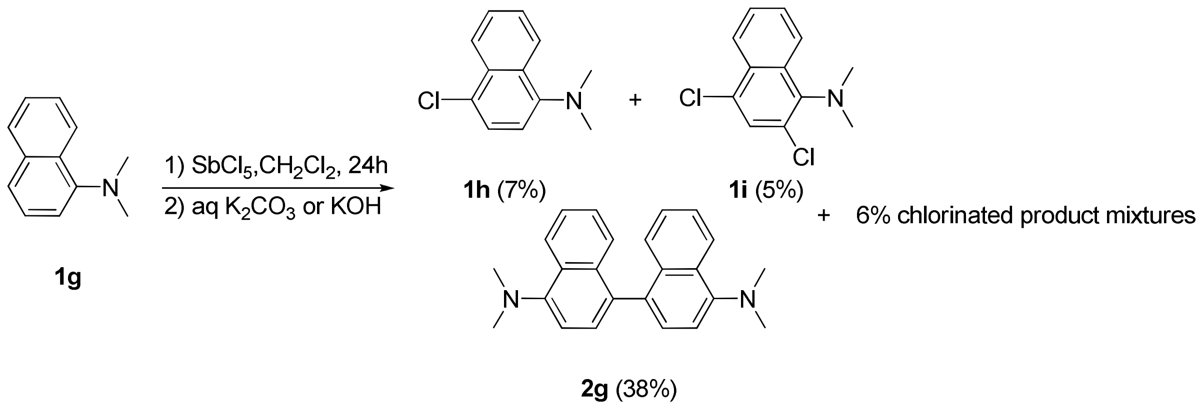
Scheme 7

All the results collected in the above described coupling experiments are consistent with the hypothesis that in the reaction with $SbCl_5$, the C-C formation between the two *N*,*N*-dialkylarylamines moieties plausibly takes place before the final basic treatment: consequently, the structure of adduct $\mathbf{1}_{C\text{-}Sb}$ (and the following radical intermediate of Scheme 3) are not consistent with the nature of the solid intermediates **3a-d**.

Based on the above results, we proposed that the benzidines formation could occur plausibly through a SE mechanism, as hypothesized in Scheme 4, where the dimerization could be explained as the result of a preliminary interaction of $SbCl_5$ with the arylamine nitrogen of one molecule, followed by the coupling of the $\mathbf{1}_{N\text{-}Sb}$ adduct with a second molecule of the starting aniline.

According to that hypothesis, the dimerization step should be rate determining, and a decrease of reactivity should be observed with sterically hindered substrates.

As expected, low reactivity was observed in the reaction of 1-*N,N*-dimethylnaphthylamine (**1g**) with $SbCl_5$ (Scheme 8), probably due to the involvement of two species (naphthylamine and ammonium adduct), both with a hindered α-position.



Scheme 8

However, since has been reported that $SbCl_5$ reacts through the formation of cation-radical intermediates in similar reaction conditions,[14] a radical mechanism hypothesis could not definitively be excluded. Further investigations are actually in progress on this point, aimed also to a full characterization of the reaction intermediates **3a-c** by X-ray crystallography.

Conclusions

In conclusion, in this investigation $SbCl_5$ was found to promote oxidative coupling of *N,N*-dialkylarylamines to benzidines. On the basis of specific coupling experiments, and the spectroscopic and analytical data collected for the solid intermediates **3a-c**, the benzidines formation could be explained as the result of a preliminary interaction of $SbCl_5$ with the nitrogen atom of one arylamine molecule, followed by the coupling of this *N*-adduct with a second molecule of the starting aniline. However, since $SbCl_5$ reacts through the formation of cation-radical intermediates,[14] a radical mechanism hypothesis could not definitively be excluded. Further investigations are in progress on this point, aimed to a full characterization of the reaction intermediates **3a-c** by X-ray crystallography. Other investigations are also in progress to optimize the yields of the formation of not-symmetrically substituted benzidines and/or other different coupling products.

The oxidative coupling of aniline derivatives here reported provides a new synthetic methodology to *N,N,N',N'*-tetraalkylbenzidines, that are actually interesting studied and used for their electric conductivity in the field of organic solar cells, photoconductors, oLED and other interesting devices.[15-18]

Experimental Section

General. Melting points taken on Electrothermal apparatus were uncorrected. ^{1}H NMR spectra were recorded on a VARIAN XL-200, a Varian-Mercury 300 MHz, a Varian-Inova-400 MHz, a

Bruker-Aspect 3000 console-500 MHz spectrometers and chemical shifts are reported in parts per million (δ). Absolute values of the coupling constant are reported. FT-IR spectra were recorded on a Perkin-Elmer 681 spectrometer. GC analyses were performed on a HP 6890 model, Series II by using a HP1 column (methyl siloxane; 30 m x 0.32 mm x 0.25 µm film thickness). Analytical thin-layer chromatography (TLC) was carried out on pre-coated 0.25 mm thick plates of Kieselgel 60 F_{254} visualisation was accomplished by UV light (254 nm) or by I_2 vapour. Column chromatography was conducted by using silica gel 60 with a particle size distribution 40-63 µm and 230-400 ASTM. Petroleum ether refers to the 40–60 °C boiling fraction. GC-MS analyses were performed on HP 5995C model and elemental analyses on an Elemental Analyzer 1106 Carlo Erba instrument. CH_2Cl_2 was distilled from CaH_2 under nitrogen; *N,N*-dialkylarylamines and all the other chemicals and solvents were commercial grade and used without further purification. Due to its toxicity, $SbCl_5$ (purchased from Aldrich Chemical Co.) must be handled with extreme caution and with dry utensils. All the operations must be done with care away from water and only in a functioning chemical fume hoods. *N,N,N',N'*-tetraalkylbenzidines **2** and the halogenated products of the reactions had analytical and spectroscopic data identical to those of commercially available compounds or previously reported in literature. The percentage of Cl for Elemental Analysis of solids **3a-c** was determined by Schöniger method.[19]

General Procedure for the synthesis of *N,N,N',N'*-tetraalkylbenzidines 2a-d, 2g by reaction of *N,N*-dialkylarylamines with $SbCl_5$ and final basic treatment. The amounts of *N,N*-dialkylarylamine indicated below refer to the reaction of *N,N*-diethylamine with $SbCl_5$. See Tables 1 and 2 for other substrate/base ratios and conditions.

To a solution of *N,N*-dialkylarylamine (**1a-g**) (0.960 mL, 5 mmol) in freshly distilled CH_2Cl_2 (5 mL) kept at room temperature, a solution of $SbCl_5$ (0.633 mL, 5 mmol) in CH_2Cl_2 (5 mL) was dropwise added, in a nitrogen-flushed three necked flask equipped with a magnetic stirrer, nitrogen inlet and two dropping funnels. The reaction mixture was stirred for 24 h at room temperature; then, to the formed red suspension, a solution of KOH 1M (10 mmol, 10 mL) was added. The obtained dark reaction mixture was refluxed for 1h at room temperature. The two phases were separated and the aqueous layer was extracted three times with $CHCl_3$. The combined organic extracts were dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. GC analysis or ^1H NMR spectra were recorded on reaction crudes for the determination of the substrate conversion percentages; column chromatography of the residue (alumina or silica gel, petroleum ether/ethyl acetate 19:1 to 7:3) afforded the products depicted in Tables 1-2 and Schemes 1, 5-8.

***N,N,N',N'*-Tetramethylbenzidine (2a).**[12,13,20] CAS: 366-29-0. 81% yield. Mp 196-197 °C. IR (ν_{max}, cm^{-1}): 2923, 2853, 2799, 1610, 1508, 1439, 1351, 1226, 1195, 1164, 1062, 943, 806, 510. ^1H NMR (500 MHz, $CDCl_3$): δ_H 7.50 (d, 4H, aromatic protons, *J* 8.8 Hz); 6.84 (d, 4H, aromatic protons, *J* 8.8 Hz); 3.00 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 149.5, 130.0, 127.2, 113.3, 41.0. MS, *m/z* (%) 240 (M^+, 100), 225 (30), 224 (12), 209 (5), 196 (4), 152 (7), 120 (11), 119

(17), 111 (5), 97 (3), 76 (1), 42 (1). In the reaction crude, 3% of **methylene bis (*N,N*-dimethylaniline)** was also revealed by GC-MS: MS, *m/z* (%) 254 (M$^+$, 23), 237 (3); 226 (100), 211 (39), 195 (5), 182 (4), 169 (3), 152 (5); 134 (5); 126 (6); 112 (20), 104 (5), 90 (2), 76 (2), 42 (1).

***N,N,N$'$,N$'$*-Tetraethylbenzidine (2b).**[12,13] 83% yield. IR (ν_{max}, cm^{-1}): 3038, 2968, 2929, 2876, 1609, 1505, 1392, 1373, 1355, 1262, 1197, 1155, 1074, 1007, 807, 513.^{1}H NMR (300 MHz, CDCl$_3$): δ_H 7.45 (d, 4H, aromatic protons, *J* 8.8 Hz); 6.76 (d, 4H, aromatic protons, *J* 8.8 Hz); 3.40 (q, 8H, *J* 6.9 Hz); 1.21 (t, 12H, *J* 6.9 Hz). ^{13}C NMR (75 MHz, CDCl$_3$): δ_C 146.1, 128.7, 126.9, 112.1, 44.3, 12.6. MS, *m/z* (%) 296 (M$^+$, 100), 282 (19), 281 (82), 252 (14), 251 (11), 238 (10), 237 (50), 209 (12), 208 (12), 196 (4), 152 (7), 120 (11), 119 (17), 111 (5), 97 (3), 76 (1), 42 (1).

***N,N,N$'$,N$'$*-Tetraisopropylbenzidine (2c).** 63% yield. IR (ν_{max}, cm^{-1}): 2969, 2930, 2872, 1609, 1524, 1484, 1380, 1363, 1330, 1288, 1239, 1187, 1155, 1119, 1052, 1019, 815. ^{1}H NMR (400 MHz, CDCl$_3$): δ_H 7.44 (d, 4H, aromatic protons, *J* 8.6 Hz); 6.96 (d, 4H, aromatic protons, *J* 8.6 Hz); 3.81 (m, 4H); 1.25 (d, 24H, *J* 6.8 Hz). MS, *m/z* (%) 352 (M$^+$, 70), 338 (28), 337(100), 295 (15), 279 (35), 251 (12), 237 (40), 194 (10), 152 (11), 119 (9), 111 (5), 43 (8). Anal. calcd for $C_{24}H_{36}N_2$: C, 81.76; H, 10.29; N, 7.95. Found: C, 81.45; H, 10.05; N, 7.90.

4,4'-Di(pyrrolidin-1-yl)biphenyl (2d). 38% yield. Dark solid. IR (ν_{max}, cm^{-1}): 3036, 2959, 2829, 1610, 1506, 1484, 1367, 1186, 959, 806. ^{1}H NMR (400 MHz, CDCl$_3$): δ_H 7.44 (d, 4H, aromatic protons, *J* 8.7 Hz), 6.62 (d, 4H, aromatic protons, *J* 8.7 Hz), 3.32-3.23 (m, 8H, C*H*$_2$), 2.05-1.95 (m, 8H, C*H*$_2$); ^{13}C NMR (100 MHz, CDCl$_3$): δ_C 146.7, 127.2, 112.2, 47.9, 25.7. MS, *m/z* (%) 292 (M$^+$, 100), 291 (33), 263 (6), 249 (4), 236 (4), 222 (3), 208 (4), 194 (3), 193 (3), 165 (4), 152 (7), 146 (9), 145 (9), 124 (3), 118 (6), 97 (5), 89 (3), 76 (3), 136 (5), 43 (8). Anal. calcd for $C_{20}H_{24}N_2$: C, 82.15; H, 8.27; N, 9.58 . Found: C, 82.19; H, 8.05; N, 9.95.

3-Chloro-*N^4,N^4,N$^{4'}$,N$^{4'}$*-tetraisopropylbiphenyl-4,4'-diamine (2e). 35% yield. IR (ν_{max}, cm^{-1}): 3031, 2969, 2931, 2872, 1609, 1524, 1484, 1414, 1380, 1366, 1330, 1288, 1239, 1189, 1155, 1120, 1052, 1020, 929, 880, 815, 676. ^{1}H NMR (400 MHz, CDCl$_3$): δ_H 7.62 (d, 1H, aromatic protons, *J* 2.2 Hz); 7.43 (d, 2H, aromatic protons, *J* 8.6 Hz); 7.38 (dd, 1H, aromatic protons, *J* 2.2, 8.3 Hz); 7.27 (d, 2H, aromatic protons, *J* 8.3 Hz); 6.92 (d, 1H, aromatic protons, *J* 2.2 Hz); 3.85 (septuplet, 2H, *J* 6.7 Hz); 3.54 (septuplet, 2H, *J* 6.4 Hz); 1.27 (d, 12H, *J* 6.7 Hz); 1.06 (d, 12H, *J* 6.4 Hz); ^{13}C NMR (125 MHz, CDCl$_3$): δ_C 147.6, 142.8, 139.1, 137.4, 131.3, 128.2, 127.2, 126.8, 123.9, 118.0, 50.0, 47.5, 21.2, 21.1. MS, *m/z* (%) 388 (M$^+$+2, 13), 386 (M$^+$, 70), 373 (35), 371 (100), 331 (10), 329 (30), 315 (7), 313 (19), 287 (4), 285 (9), 273 (12), 271 (33), 229 (3), 228 (3), 193 (4), 186 (4), 178 (4), 152 (4), 136 (5), 43 (8).

***N^4,N^4*-Diisopropyl-*N$^{4'}$,N$^{4'}$*-dimethylbiphenyl-4,4'-diamine (2f).** 7% yield. ^{1}H NMR (400 MHz, CDCl$_3$): δ_H 7.50-7.25 (m, 4H, aromatic protons); 6.72-6.63 (m, 4H, aromatic protons); 3.43 (m, 2H, *J* 6.8 Hz); 3.00 (s, 6H); 1.20 (d, 12H, *J* 6.8 Hz). MS, *m/z* (%) 296 (M$^+$, 71), 282 (25), 281 (100), 240 (18), 239 (61), 238 (71), 237 (23), 207 (12), 197 (12), 196 (10), 152 (16), 119 (13), 43(5).

N,N,N',N'-Tetramethylnaphthydine (2g).[12,13 21] 38% yield. Mp 132-134 °C. IR (ν_{max}, cm^{-1}): 3055, 2977, 2935, 2863, 2830, 2784, 1579, 1506, 1453, 1420, 1377, 1322, 1292, 1200, 1181, 1144, 1041, 1022, 940, 845, 772, 579. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.37 (d, 2H, *J* 8.4 Hz, aromatic protons); 7.47-7.51 (m, 2H, aromatic protons); 7.45 (d, 2H, *J* 8.4 Hz); 7.41 (d, 2H, *J* 7.6 Hz); 7.30-7.26 (m, 2H, aromatic protons); 7.19 (d, 2H, *J* 7.6 Hz); 3.00 (s, 12H);^{13}C NMR (100 MHz, $CDCl_3$): δ_C 150.5, 134.6, 133.4, 128.9, 128.1, 127.5, 125.9, 125.2, 124.4, 113.8, 45.6. MS, *m/z* (%) 340 (M$^+$, 100), 325 (17), 310 (6), 309 (5), 295 (4), 294 (4), 281 (6), 280 (9), 279 (4), 278 (5), 253 (5), 252 (9), 250 (4), 239 (4), 170 (6), 169 (4), 162 (4), 161 (3), 154 (4), 139 (4), 126 (3).

4-Chloro-*N,N*-dimethylnaphthalen-1-amine (1h). 7% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.37-8.33 (m, 1H, aromatic proton); 7.82 -7.78 (m, 1H, aromatic proton); 7.62-7.45 (m, 2H, aromatic protons); 7.38 (d, 2H, *J* 8.8 Hz); 3.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 145.5, 134.0, 133.4, 130.5, 128.7, 128.1, 126.7, 126.6, 126.2, 124.7, 43.0. MS, *m/z* (%) 207 (M$^+$+2, 36), 205 M$^+$, 100), 204 (51), 188 (14), 170 (35), 169 (66), 168 (55), 162 (12), 155 (13), 154 (27), 140 (8), 128 (8), 127 (20), 126 (21), 87 (3), 84 (7), 63 (5), 42 (7).

2,4-Dichloro-*N,N*-dimethylnaphthalen-1-amine (1i). 5% yield. IR (ν_{max}, cm^{-1}): 3072, 2925, 2861, 2794, 1570, 1561, 1478, 1444, 1380, 1298, 1246, 1209, 1165, 1146, 1055, 962, 894, 854, 782, 763, 722 685, 669, 614. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.41-8.35 (m, 1H, aromatic proton); 8.23-8.17 (m, 1H, aromatic proton); 7.61-7.57 (m, 2H, aromatic protons); 7.51 (s, 1H, aromatic proton); 2.99 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 145.5, 134.6, 130.6, 129.8, 129.4, 128.3, 127.5, 127.2, 125.2, 124.8, 43.0. MS, *m/z* (%) 243 (M$^+$+4, 13), 241 (M$^+$+2, 66), 239 (M$^+$, 100), 238 (49), 224 (10), 222 (13), 205 (22), 204 (29), 203 (59), 202 (42), 196 (12), 189 (11), 188 (22), 169 (31), 168 (34), 160 (14), 154 (10), 126 (14), 99 (5), 84 (10), 42 (5). A little amount of **3-chloro-$N^4,N^4,N^{4'},N^{4'}$-tetramethyl-1,1'-binaphthyl-4,4'-diamine** was also detected by MS, *m/z* (%) 376 (M$^+$+2, 37), 374 (M$^+$, 100), 359 (6), 307 (4), 294 (4), 293 (4), 292 (4), 279 (4), 278 (6), 252 (5), 250 (4), 187 (6), 172 (4), 161 (4), 154 (3), 139 (5), 125 (4), 126 (14), 99 (5), 84 (10), 42 (5).

General Procedure for the isolation of Sb-intermediates 3a-c by reaction of *N,N*-dialkylarylamines with $SbCl_5$ (Schemes 5-8). To a solution of *N,N*-dialkylarylamine (**1a-c**) (0.960 mL, 5 mmol) in freshly distilled CH_2Cl_2 (5 mL) kept at 0 °C, a solution of $SbCl_5$ (0.633 mL, 5 mmol) in CH_2Cl_2 (5 mL) was dropwise added, in a nitrogen-flushed three necked flask equipped with a magnetic stirrer, nitrogen inlet and two dropping funnels. The reaction mixture was stirred for 24 h at room temperature, and then the red-coloured solid intermediate precipitated during the reaction was filtered under *vacuum* and under nitrogen atmosphere, washed with anhydrous CH_2Cl_2, and the solvent residue evaporated under reduced pressure.

Sb-intermediate (3a). Mp 156-157 °C (dec. 154 °C). Red powder. IR (ν_{max}, cm^{-1}): 3447, 3072, 2964, 2689, 1619, 1570, 1389, 1221, 978, 829. ^{1}H NMR (200 MHz, CD_2Cl_2): δ_H 10.25 (bs, 2H, NH$^+$: exchange with D_2O), 7.69-7.59 (m, 8H, aromatic protons); 3.40 (d, 12H, *J* 4.0 Hz). Anal. calcd for $C_{16}H_{22}Cl_{10}N_2Sb_2$: C, 22.87; H, 2.64; Cl, 37.7, N, 3.33. Found: C, 22.54; H, 2.68; Cl, 37.28, N, 3.15. Analytical and spectroscopic data of intermediate (**3a**) are consistent with the *N*^{4},*N*^{4},*N*$^{4'}$,*N*$^{4'}$-tetramethylbiphenyl-4,4'-diaminium structure**.**

Sb-intermediate (3b). Mp (dec.) 160 °C, red powder. IR (ν_{max}, cm^{-1}): 3437, 2980, 1620, 1553, 1447, 1214, 1072, 828, 697, 551. ^{1}H NMR (300 MHz, DMSO-d$_6$): δ_H 12.30 (bs, 2H, NH$^+$: exchange with D$_2$O); 8.41-7.47 (m, 8H, aromatic protons); 3.39 (m, 8H); 1.01, (t, 6H, *J* 7.8 Hz); 0.96 (t, 6H, *J* 7.3 Hz); ^{13}C NMR (75 MHz, CDCl$_3$): δ_C 138.3, 130.9, 129.4, 124.2, 123.6, 53.1, 10.8. Anal. calcd for $C_{20}H_{30}Cl_{10}N_2Sb_2$: C, 26.79; H, 3.37; Cl, 39.55, N, 3.12. Found: C, 26.44; H, 3.68; Cl, 39.28, N, 3.15. Analytical and spectroscopic data of intermediate (**3b**) are consistent with *N*^{4},*N*^{4},*N*$^{4'}$,*N*$^{4'}$-tetraethylbiphenyl-4,4'-diaminium structure.

Sb-intermediate (3c). Mp. 230-233 °C (dec. 180 °C), red powder. IR (ν_{max}, cm^{-1}): 3431, 2974, 2685, 1619, 1536, 1450, 1378, 1365, 1162, 1118, 825, 673. ^{1}H NMR (300 MHz, DMSO-d$_6$): δ_H 11.95 (bs, 2H, NH$^+$: exchange with D$_2$O); 7.98-7.95 (d, 4H, aromatic protons); 7.82 -7.79 (d, 4H, aromatic protons); 4.22 (m, 4H); 1.26 (d, 6H, *J* 7.3 Hz); ^{13}C NMR (75 MHz, CDCl$_3$): δ_C 140.2, 133.3, 128.7, 126.1, 55.8, 19.3, 17.5. Anal. calcd for $C_{24}H_{38}Cl_{10}N_2Sb_2$: C, 30.26; H, 4.02; Cl, 37.22, N, 2.94. Found: C, 30.19; H, 4.05; N, 2.95. Analytical and spectroscopic data of intermediate (**3c**) are consistent with *N*^{4},*N*^{4},*N*$^{4'}$,*N*$^{4'}$-tetraisopropylbiphenyl-4,4'-diaminium structure**.**

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