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General Access to *ortho*- and *meta*-Alkylanilines for the Synthesis of Polyanilines and Poly(Anilines-co-Substituted Anilines)

Aurélie Falcou,[a] Didier Marsacq,[b] Patrick Hourquebie[b] and Alain Duchêne[a,*]

[a]*Laboratoire de Physicochimie des Interfaces et des Milieux Réactionnels, Faculté des Sciences de Tours, Parc de Grandmont, 37200 Tours, France*

[b]*CEA/Le Ripault, Département Matériaux, BP 16, 37260 Monts, France*

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Abstract—*Ortho* (or *meta*)-alkylanilines are obtained in good yields by the cross-coupling reaction of *ortho*(*meta*)-haloanilines with vinyltins in the presence of palladium catalysts.

Over the last ten years, new polymers containing such groups as a thiophene or an aniline unit[1] have retained the attention of a number of organic chemists; the numerous potential industrial applications of these polymers, such as sensors,[2] EMI (electromagnetic interference) shielding agents,[3] corrosion inhibitors,[4] and micro-electronic devices,[5] explain the great interest in the synthesis of the monomers which are precursors of these polymers, among which polyanilines are important conducting polymers[6] because of the unique combination of electrical properties in the doped state and environmental stability.[7] Like most conductive polymers, the commercial applications of the conductive form of polyaniline are limited due to its poor solubility in common organic solvents and poor processability in the melted state. A common technique to increase solubility and lower the melting point of the stiff chain is the attachment of a flexible side-chain to the polymer backbone.[8] In the field of conductive polymers, this concept has been successfully applied to polythiophenes. Indeed solubility and processability can be significantly enhanced by introducing a flexible alkyl side chain to the thiophene monomer.[9] However, neither the conductivity of the doped state nor the thermal stability of poly(3-alkylthiophene)[10] remain stable and these polymers do not satisfy all the requirements for the various possible applications. In order to obtain a material which combines the conductivity and chemical stability of polyanilines and the processability of poly(3-alkylthiophenes), polyaniline derivatives have been synthesised from commercially available substituted anilines (methyl, ethyl, propyl).[11] Nevertheless, the resulting polymers were insoluble in common organic solvents and their conductivity and processability were not significant. We therefore decided to prepare new polymers with aniline with substituents in the *ortho* or *meta* position or copolymers composed of aniline and substituted aniline (Fig. 1). We developed a simple procedure for the synthesis of such monomers allowing the introduction of a wide range of substituents in the *ortho* or *meta* position. Large scale (5–7 g) synthesis of monomers was required for the polymerisation reaction in order to test their physical properties.

We report here a general synthesis of some new *ortho* and *meta* substituted anilines, offering a choice of substituents and based on the low price of starting materials. The preparation of 2-substituted alkylanilines has previously been reported and is based on different methods such as nitration of alkylbenzene[12] and the addition of Grignard reagents to cyanoaniline.[13,14] However the latter procedure provided a high yield only for the introduction of the propyl group and required the use of 9 equiv. of Grignard reagents (three examples). Wittig reactions on nitrobenzaldehyde[13] were also performed but no yield was given (two examples). Palladium catalysed cross-coupling between haloanilines and vinyl or ethynyl metal reagents has subsequently been proved to be efficient in the synthesis of indole derivatives.[15]

An interesting procedure has recently been described involving direct alkylation of 4-haloanilines with Grignard reagents without a protection–deprotection sequence[16] under palladium salt catalysis (Scheme 1).

We therefore decided to apply this promising procedure to the synthesis of 2- or 3-alkylanilines. Unfortunately, the yields obtained and the purity of the coupling products were disappointing and forced us to examine other organometallic reagents.

Keywords: alkylation; anilides; coupling reactions; tin and compounds.

* Corresponding author. Tel.: +33-2-47-36-69-59; fax: +33-2-47-36-70-40; e-mail: duchene@delphi.phys.univ-tours.fr

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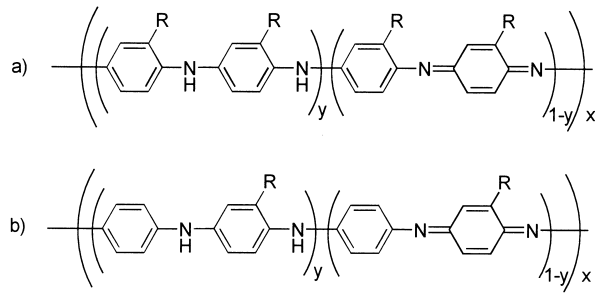
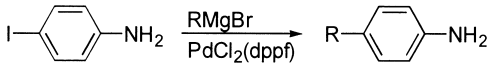
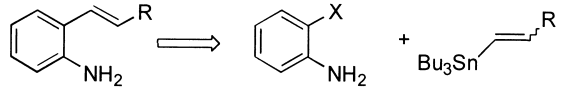


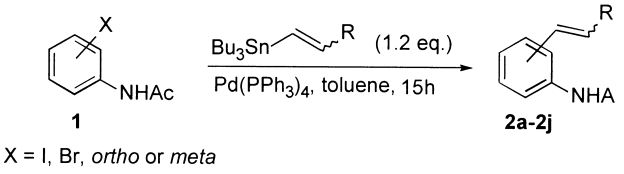
Figure 1. (a) Substituted aniline homopolymer; (b) copolymer composed of aniline and substituted aniline.



Scheme 1.



Scheme 2.



Scheme 3.

For the synthesis of these monomers, the retrosynthetic scheme used is based on coupling between 2- (or 3-) haloanilines and vinyltins through a Stille cross-coupling reaction (Scheme 2).

After some unsuccessful attempts of direct cross-coupling between haloanilines and various vinyltins without any protection of the amino group, we selected acetic anhydride from the wide choice of protective methods for the amino group offered in the literature.[17] After testing all the reactions on a small scale, i.e. protection, cross-coupling, hydrogenation and deprotection, the overall yield was satisfactory and provided clean products.

After protecting the *ortho*- and *meta*-haloanilines with acetic anhydride, the cross-coupling reaction[18] in the presence of a catalytic amount (2 mol%) of tetrakistriphenylphosphine palladium(0) with various vinyltins (readily obtained by hydrostannation of the corresponding alkynes) gave the compounds **2a**–**2j** in fair to good yields as shown in Scheme 3.

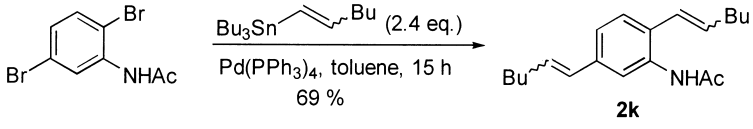
Table 1. Cross-coupling reactions of vinyltins with halogenoanilines

Entry	X	Bu_3Sn–CH=CH–R	No.	Yield (%)
1	*o*-Br	R=*n*-C_4H_9	**2a**	85
2	*m*-Br	R=*n*-C_4H_9	**2b**	71
3	*o*-Br	R=*n*-C_7H_{15}	**2c**	67
4	*m*-Br	R=*n*-C_7H_{15}	**2d**	75
5	*o*-Br	R=*n*-C_9H_{19}	**2e**	61
6	*o*-Br	R=$SiMe_3$	**2f**	67
7	*m*-Br	R=$SiMe_3$	**2g**	71
8	*o*-Br	R=$-CH_2-CH(OEt)_2$	**2h**	74
9	*m*-Br	R=$-CH_2-CH(OEt)_2$	**2i**	95
10	*o*-Br	R=$SnBu_3$	**2j**	62
11	2,5-diBr	R=*n*-C_4H_9	**2k**	69

As shown by the results reported in Table 1, the substitution reaction appeared to have a mild and general character leading to substituted *ortho*- and *meta*-anilines. Only the (*E*)-isomer (except entries 8 and 9) was reactive under our experimental conditions. The scale of the products necessary for subsequent polymerisation was reached without difficulty and no cyclisation occurred during the process (no by-product). The introduction of a tributylstannylvinyl unit through (*E*)-bis(tributylstannyl)ethylene is reported for the first time on bromoacetanilide (entry 10) (the synthetic potential offered by this new compound **2j** will not be studied here).[19] The introduction of two vinyl units was possible from dibromoacetanilide using 2.4 equiv. of vinyltin reagent (entry 11) and providing an interesting new monomer (Scheme 4).

The unsaturated compounds **3a** and **3c** (from **2a** and **2c**) were then tested for polymerisation after deprotection of the aniline function but the unsatisfactory results obtained led to abandoning this route. Hydrogenation of compounds **2a**–**2g** was quantitative using the system H_2/palladium 5 wt% on activated carbon,[20] but was very dependent on the presence of impurities (presence of some tin by-products), even in very small amounts, and consequently hydrogenation times were increased from one hour to three days.

We therefore preferred to use the couple $NaBH_4/Ni(OAc)_2$ in absolute ethanol[21] which provided almost the same results but in a shorter time (3 h). The yields of the saturated acetanilides **4a**–**4g** are reported in Table 2. Finally the regeneration of the aniline function with concentrated hydrochloric acid in ethanol yielded the desired *ortho*- and *meta*-alkylanilines **5a**–**5g**.



Scheme 4.

Table 2. Hydrogenation and deprotection of compounds **2a**–**2g**

No.		No.	Yield (%)	No.	Yield[a] (%)
2a	(R=*n*-C_4H_9)	**4a**	82[b]	**5a**	90
2b	(R=*n*-C_4H_9)	**4b**	98[c]	**5b**	82
2c	(R=*n*-C_7H_{15})	**4c**	80[b]	**5c**	71
2d	(R=*n*-C_7H_{15})	**4d**	99[c]	**5d**	88
2e	(R=*n*-C_9H_{19})	**4e**	78[b]	**5e**	75
2f	(R=$SiMe_3$)	**4f**	85[b]	**5f**	78
2g	(R=$SiMe_3$)	**4g**	99[c]	**5g**	76

[a] Yield after deprotection and purification.
[b] Hydrogenation using the couple $NaBH_4$/Ni(OAc)$_2$ in absolute ethanol.
[c] Hydrogenation over H_2/Pd 5 wt% on activated carbon.

In conclusion, we describe a new procedure allowing the synthesis of *ortho*- and *meta*-alkylanilines, substituted with a wide range of substituents, performed on a large scale (8–10 g) with an overall yield of about 30% from the commercially available starting haloanilines. The potential of certain intermediates such as compounds **2j** or **2k** were not exploited in this work.

Some of them (**5a**–**5g**) are currently being tested for polymerisation or copolymerisation and are providing promising results in terms of solubility, conductivity and processability. The polymerisation process and characterisation of these polymers are currently underway and will be reported in due course.[22]

Experimental

All reactions were carried out under inert atmosphere (Ar or N_2). THF, ether and toluene were freshly distilled over sodium/benzophenone ketyl and CH_2Cl_2 over calcium hydride. Flash chromatographies were performed on silica gel 230–400 mesh. GLC analyses were performed on a Perkin–Elmer instrument (FID detector, fitted with a 25 m×0.32 mm SE 52 capillary column). ^{1}H NMR spectra were recorded on a Bruker AC 200. Data, reported using the residual solvent proton resonance of $CDCl_3$ (δ_H=7.25 ppm) as the internal reference, are as follows in the order: chemical shift (δ in ppm relative to Me_4Si), multiplicity (s, d, t, q, m, b for singlet, doublet, triplet, quartet, multiplet and broad, respectively), coupling constants (J in Hz). ^{13}C NMR were recorded at 50 MHz on the same instrument, using the $CDCl_3$ solvent peak at δ_C=77.0 ppm as the reference. Mass spectra were obtained on a Hewlett Packard apparatus (engine 5989A) in GC/MS mode (70 eV). IR spectra were recorded on a Nicolet 250 FT-IR spectrophotometer.

(*E*)-1-Trimethylsilyl-2-*n*-tributylstannylethylene was prepared according to Ref. 23, (*E*)-1,2-bis(tributylstannyl)-ethylene was prepared according to Ref. 24, other vinyltin reagents were prepared by hydrostannation of the corresponding terminal alkynes under radicalar conditions (AIBN) and used as a thermodynamic mixture of (*E*) and (*Z*)-isomers.[25] All new compounds gave satisfactory microanalysis (C, H±0.5) performed by the 'Service Central d'Analyse' of the CNRS in Vernaison.

Coupling reactions with vinyltins

General procedure: 30 g (0.14 mol) of 2-bromo- or 3-bromoacetanilide, 0.17 mol of vinyltin and 2 g (1 mol%) of tetrakis(triphenylphosphine)palladium diluted in 250 mL of toluene are stirred overnight at 100°C and then cooled to room temperature. After evaporation of the solvent, 100 mL of a 1 M solution of potassium fluoride and 100 mL of ethyl acetate are added to precipitate the tributyltin bromide formed. After vigorously stirring for 2 h, the reaction mixture is filtered over Celite and extracted with diethylether (3×100 mL). After usual work-up, the crude products **2a**–**2g** are purified by crystallisation (hexane) or by chromatography using hexane/dichloromethane (elution gradient).

2-[Hex-1′-enyl]acetanilide 2a. IR (cm^{-1}): 3289, 3040, 1654, 1532.

^{1}H NMR (200 MHz): 0.97 (3H, t, $^3J_{2H}$=6.9 Hz), 1.30–1.60 (4H, m), 2.15–2.40 (2H, m), 2.24 (3H, s), 6.14 (1H, dt, $^3J_{1H}$=15.8 Hz, $^3J_{2H}$=7.0 Hz), 6.45 (1H, d, $^3J_{1H}$=15.8 Hz), 7.10–7.27 (2H, m), 7.38 (1H, d, $^3J_{1H}$=7.1 Hz), 7.88 (1H, d, $^3J_{1H}$=7.8 Hz).

^{13}C NMR (50 MHz): 14.5, 22.8, 24.8, 32.0, 33.6, 123.9, 125.2, 125.7, 127.7, 128.2, 131.3, 134.7, 136.4, 168.8.

MS: *m*/*z*=217 (M$^{\cdot}$, 18), 175 (14), 174 (100), 146 (13), 132 (70), 131 (11), 130 (27), 119 (13), 118 (74), 117 (35), 115 (17), 106 (31), 91 (13), 77 (18), 43 (59), 41 (14), 39 (10).

3-[Hex-1′-enyl]acetanilide 2b. IR (cm^{-1}): 3295, 1668, 1557.

^{1}H NMR (200 MHz): 0.96 (3H, t, $^3J_{2H}$=6.7 Hz), 1.34–1.60 (4H, m), 2.15–2.30 (2H, m), 2.21 (3H, s), 6.17–6.42 (2H, m), 7.12 (1H, d, $^3J_{1H}$=7.3 Hz), 7.21–7.38 (2H, m), 7.54 (1H, s).

^{13}C NMR (50 MHz): 14.5, 22.8, 24.9, 32.0, 33.2, 118.3, 119.2, 122.5, 129.5, 129.9, 132.3, 138.9, 139.4, 169.7.

MS: *m*/*z*=217 (M$^{\cdot}$, 52), 188 (14), 175 (28), 174 (23), 161 (17), 149 (15), 146 (41), 133 (27), 132 (100), 120 (12), 119 (40), 118 (10), 117 (28), 115 (27), 107 (29), 106 (17), 103 (12), 93 (10), 91 (17), 77 (19), 65 (12), 43 (74), 41 (16), 39 (13).

2-[Non-1′-enyl]acetanilide 2c. IR (cm^{-1}): 3289, 3035, 1656, 1532.

^{1}H NMR (200 MHz): 0.93 (3H, t, $^3J_{2H}$=6.6 Hz), 1.22–1.62 (10H, m), 2.15–2.40 (2H, m), 2.24 (3H, s), 6.15 (1H, dt, $^3J_{1H}$=15.7 Hz, $^3J_{2H}$=6.8 Hz), 6.45 (1H, d, $^3J_{1H}$ = 15.7 Hz), 7.10–7.27 (2H, m), 7.39 (1H, d, $^3J_{1H}$=6.8 Hz), 7.87 (1H, d, $^3J_{1H}$=7.8 Hz).

^{13}C NMR (50 MHz): 14.7, 23.2, 24.7, 29.7, 29.8, 29.9, 32.4, 33.9, 124.4, 125.2, 125.8, 127.5, 128.1, 130.6, 134.7, 135.9, 169.1.

MS: *m*/*z*=259 (M$^{\cdot}$, 15), 217 (18), 216 (100), 146 (18), 144

(13), 133 (10), 132 (78), 131 (15), 130 (36), 119 (17), 118 (80), 117 (39), 115 (18), 107 (12), 106 (51), 91 (11), 77 (13), 57 (29), 43 (76), 41 (23).

Anal. Calcd for $C_{17}H_{27}NO$: C, 78.09; H, 10.42; N, 5.36. Found: C, 78.21; H, 10.39; N, 5.37.

3-[Non-1′-enyl]acetanilide 2d. IR (cm^{-1}): 3302, 1666, 1556.

^{1}H NMR (200 MHz): 0.93 (3H, t, $^3J_{2H}$=7.2 Hz), 1.20–1.70 (10H, m), 2.15–2.30 (2H, m), 2.21 (3H, s), 6.10–6.42 (2H, m), 7.12 (1H, d, $^3J_{1H}$=7.4 Hz), 7.23–7.34 (2H, m), 7.54 (1H, s).

^{13}C NMR (50 MHz): 14.6, 23.2, 25.1, 29.7, 29.9, 32.4, 33.6, 117.9, 118.9, 122.5, 129.6, 129.9, 132.5, 138.7, 139.5, 168.9.

MS: *m*/*z*=259 (M$^{\cdot}$, 67), 217 (15), 202 (10), 188 (19), 175 (11), 174 (40), 162 (20), 161 (53), 149 (63), 146 (34), 144 (12), 133 (28), 132 (100), 120 (15), 119 (62), 118 (10), 117 (26), 115 (24), 107 (50), 106 (22), 91 (13), 77 (12), 43 (74), 41 (26), 39 (10).

2-[Undec-1′-enyl]acetanilide 2e. IR (film, cm^{-1}): 3287, 3034, 1656, 1532.

^{1}H NMR (200 MHz): 0.92 (3H, t, $^3J_{2H}$=6.4 Hz), 1.20–1.64 (14H, m), 2.15–2.40 (2H, m), 2.23 (3H, m), 6.14 (1H, dt, $^3J_{1H}$=15.7 Hz, $^3J_{2H}$=6.8 Hz), 6.45 (1H, d, $^3J_{1H}$=15.7 Hz), 7.10–7.30 (2H, m), 7.39 (1H, d, $^3J_{1H}$=6.8 Hz), 7.89 (1H, d, $^3J_{1H}$=8.0 Hz).

^{13}C NMR (50 MHz): 14.7, 23.2, 24.6, 29.8, 29.9, 30.1, 30.2, 32.4, 33.9, 124.0, 125.1, 125.7, 127.7, 128.2, 130.9, 134.7, 136.4, 169.1.

MS: *m*/*z*=287 (M$^{\cdot}$, 13), 245 (19), 244 (100), 148 (10), 146 (117), 144 (13), 133 (10), 132 (66), 131 (11), 130 (29), 119 (15), 118 (78), 117 (31), 115 (13), 107 (15), 106 (61), 77 (10), 57 (18), 55 (10), 43 (98), 41 (30).

Anal. Calcd for $C_{19}H_{31}NO$: C, 78.83; H, 10.80; N, 4.84. Found: C, 78.91; H, 10.76; N, 4.86.

2-[2′-Trimethylsilylethenyl]acetanilide 2f. IR (cm^{-1}): 3225, 1660, 1538,1481, 838.

^{1}H NMR (200 MHz): 0.21 (9H, s), 2.25 (3H, s), 6.45 (1H, d, $^3J_{1H}$=19.0 Hz), 6.97 (1H, d, $^3J_{1H}$=19 Hz), 7.10–7.37 (2H, m), 7.49 (1H, d, $^3J_{1H}$=7.1 Hz), 7.83 (1H, d, $^3J_{1H}$=8.1 Hz).

^{13}C NMR (50 MHz): −0.71, 24.8, 124.9, 126.1, 127.2, 128.9, 132.4, 134.7, 134.9, 139.2, 169.2.

MS: *m*/*z*=233 (M$^{\cdot}$, 5), 190 (41), 160 (13), 144 (65), 118 (11), 75 (11), 73 (100), 45 (12), 43 (30).

Anal. Calcd for $C_{13}H_{19}NOSi$: C, 66.92; H, 8.21; N, 6.00. Found: C, 67.01; H, 8.19; N, 6.03.

3-[2′-Trimethylsilylethenyl]acetanilide 2g. IR (cm^{-1}): 3222, 1665, 1538,1483, 828.

^{1}H NMR (200 MHz): 0.16 (9H, s), 2.18 (3H, s), 6.49 (1H, d, $^3J_{1H}$=19.1 Hz), 6.85 (1H, d, $^3J_{1H}$=19.1 Hz), 7.16–7.30 (2H, m), 7.40 (1H, d, $^3J_{1H}$=8.1 Hz), 7.74 (1H, m), 8.53 (1H, bs).

^{13}C NMR (50 MHz): −1.38, 24.8, 117.9, 119.5, 122.3, 128.9, 130.1, 138.2, 139.1, 143.0, 169.

MS: *m*/*z*=233 (M$^{\cdot}$, 29), 218 (45), 203 (17), 202 (100), 176 (14), 161 (12), 160 (17), 116 (37), 73 (15), 59 (27), 45 (12), 43 (36).

2-[4′,4′-Diethoxybut-1′-enyl]acetanilide 2h. IR (cm^{-1}): 3401, 1660, 1546.

Z isomer: ^{1}H NMR (200 MHz): 1.21 (6H, t, $^3J_{2H}$=7.0 Hz), 2.18 (3H, s), 2.42 (2H, dd, $^3J_{1H}$=7.2 Hz, $^3J_{1H}$=5.4 Hz), 3.41–3.70 (4H, m), 4.56 (1H, t, $^3J_{2H}$=5.4 Hz), 5.98 (1H, dt, $^3J_{1H}$=11.1 Hz, $^3J_{2H}$=7.2 Hz), 6.48 (1H, d, $^3J_{1H}$= 11.1 Hz), 7.09–7.29 (3H, m), 7.42 (1H, bs), 8.14 (1H, d, $^3J_{1H}$=7.7 Hz).

E isomer: ^{1}H NMR (200 MHz): 1.26 (6H, t, $^3J_{2H}$=7.7 Hz), 2.21 (3H, s), 2.59 (2H, dd, $^3J_{1H}$=7.2 Hz, $^3J_{1H}$=5.3 Hz), 3.49–3.79 (4H, m), 4.62 (1H, t, $^3J_{2H}$=5.3 Hz), 6.10 (1H, dt, $^3J_{1H}$=15.6 Hz, $^3J_{2H}$=7.2 Hz), 6.54 (1H, d, $^3J_{1H}$= 15.6 Hz), 7.09–7.39 (3H, m), 7.53 (1H, bs), 7.84 (1H, d, $^3J_{1H}$=7.7 Hz).

^{13}C NMR (50 MHz): 15.2, 24.1, 37.8, 61.4, 102.1, 123.5, 125.0, 126.9, 127.4, 127.7, 129.4, 130.7, 132.4, 168.6.

MS: *m*/*z*=277 (M$^{\cdot}$, 1), 144 (12), 132 (21), 118 (13), 117 (19), 115 (11), 103 (94), 77 (11), 75 (82), 47 (100), 43 (60).

Anal. Calcd for $C_{16}H_{23}NO_3$: C, 69.27; H, 8.36; N, 5.05. Found: C, 69.32; H, 8.32; N, 5.02.

3-[4′,4′-Diethoxybut-1′-enyl]acetanilide 2i. IR (film, cm^{-1}): 3309, 1669, 1553.

Z isomer: ^{1}H NMR (200 MHz): 1.18 (6H, t, $^3J_{2H}$=8.8 Hz), 2.13 (3H, s), 2.68 (2H, dd, $^3J_{1H}$=7.1 Hz, $^3J_{1H}$=5.7 Hz), 3.53–3.77 (4H, m), 4.60 (1H, t, $^3J_{2H}$=5.7 Hz), 5.72 (1H, dt, $^3J_{1H}$=11.8 Hz, $^3J_{2H}$=7.1 Hz), 6.48 (1H, d, $^3J_{1H}$= 11.8 Hz), 7.03–7.44 (4H, m).

E isomer: ^{1}H NMR (200 MHz): 1.26 (6H, t, $^3J_{2H}$=8.8 Hz), 2.20 (3H, s), 2.57 (2H, dd, $^3J_{1H}$=6.9 Hz, $^3J_{1H}$=5.7 Hz), 3.53–3.77 (4H, m), 4.58 (1H, t, $^3J_{2H}$=5.7 Hz), 6.23 (1H, dt, $^3J_{1H}$=15.8 Hz, $^3J_{2H}$=6.9 Hz), 6.46 (1H, d, $^3J_{1H}$= 15.8 Hz), 7.11–7.53 (4H, m).

^{13}C NMR (50 MHz): 15.2, 24.3, 37.7, 61.4, 102.4, 117.6, 118.7, 121.8, 125.6, 128.8, 131.9, 138.1, 138.2, 168.9.

MS: *m*/*z*=277 (M$^{\cdot}$, 1), 144 (19), 143 (13), 132 (26), 130 (13), 117 (11), 103 (100), 75 (80), 47 (92), 43 (52).

2-[2′-Tributylstannylethenyl]acetanilide 2j. IR (cm^{-1}): 3274, 3042, 1652, 1531.

^{1}H NMR (200 MHz): 0.80–1.20 (15H, m), 1.22–1.80 (12H,

m), 2.19 (1H, s), 6.79 (1H, d, $^3J_{1H}$=19.4 Hz, $^3J_{Sn\text{-}H}$=66.6 Hz), 6.99 (1H, d, $^3J_{1H}$=19.4 Hz, $^2J_{Sn\text{-}H}$= 61.2 Hz), 7.21 (2H, m), 7.43 (1H, d, $^3J_{1H}$=6.0 Hz), 7.80 (1H, d, $^3J_{1H}$ = 7.7 Hz).

^{13}C NMR (50 MHz): 9.59 ($^1J_{Sn\text{-}C}$=345–330 Hz), 13.6, 24.2, 27.2 ($^3J_{Sn\text{-}C}$=42–54 Hz), 29.0 ($^2J_{Sn\text{-}C}$=20.5 Hz), 125.0, 126.0, 127.1, 128.4, 133.4, 134.5, 134.8, 142.2, 169.2.

MS: *m*/*z*=394 (M$^{\cdot}$−57, 95), 338 (13), 282 (9), 254 (18), 252 (15), 177 (12), 144 (100), 118 (39), 43 (45).

2-5-Di[hex-1′-en-1-yl]acetanilide 2k. IR (cm^{-1}): 3263, 3021, 1664.

^{1}H NMR (200 MHz): 0.95 (6H, t, $^3J_{2H}$=6.9 Hz), 1.42 (8H, m), 2.15–2.30 (4H, m), 2.24 (3H, m), 6.08 (1H, dt, $^3J_{1H}$=15.9 Hz, $^3J_{2H}$=7.0 Hz), 6.20–6.44 (3H, m), 7.11 (1H, d,$^3J_{1H}$=8.7 Hz), 7.35 (1H, d, $^3J_{1H}$=8.7 Hz), 7.77 (1H, s).

^{13}C NMR (50 MHz): 14.5, 22.8, 24.5, 32.0, 33.3, 33.6, 122.5, 125.2, 129.8, 123.6, 127.1, 130.2, 134.7, 131.8, 134.6, 137.9, 168.8.

MS: *m*/*z*=299 (M$^{\cdot}$, 23), 256 (100), 230 (11), 214 (16), 200 (14), 186 (47), 174 (31), 170 (12), 168 (12), 158 (13), 156 (25), 145 (10), 144 (61), 143 (20), 132 (20), 131 (14), 130 (38), 129 (14), 128 (14), 117 (10), 115 (15), 55 (41), 43 (80), 41 (38), 39 (10).

Anal. Calcd for $C_{20}H_{29}NO$: C, 80.21; H, 9.77; N, 4.68. Found: C, 80.33; H, 9.73; N, 5.67.

Hydrogenation of the double bond[20,21]

General procedure: To 0.10 mol of compound **2** dissolved in 250 mL of absolute ethanol were added 5 g (20 mmol) of nickel(II) acetate tetrahydrate then the solution was gently warmed until the solution was homogenous. The mixture was cooled to 0°C and 1.9 g (0.05 mol) of sodium borohydride dissolved in 50 mL of ethanol were added dropwise with stirring. After completion of the reaction, the solution was hydrolysed with 100 mL of a saturated solution of ammonium chloride, filtered over Celite and extracted with dichloromethane (3×300 mL). After usual work-up, the crude products were clean enough and could be used without further purification.

2-Hexylacetanilide 4a. IR (cm^{-1}): 3278, 3039, 1654, 1534.

^{1}H NMR (200 MHz): 0.92 (3H, t, $^3J_{2H}$=6.3 Hz), 1.35 (6H, m), 1.60 (2H, m), 2.20 (3H, s), 2.58 (2H, t, $^3J_{2H}$=7.6 Hz), 7.19–7.41 (3H, m), 7.67 (1H, d, $^3J_{1H}$=7.4 Hz)

^{13}C NMR (50 MHz): 14.7, 23.2, 23.9, 29.7, 30.4, 31.8, 32.2, 126.5, 126.6, 129.8, 135.8, 137.2, 170.4.

MS: *m*/*z*=219 (M$^{\cdot}$, 9), 176 (14), 120 (12), 107 (21), 106 (100), 77 (11), 43 (30).

3-Hexylacetanilide 4b. IR (cm^{-1}): 3290, 1665, 1557.

^{1}H NMR (200 MHz): 0.91 (3H, t, $^3J_{2H}$=6.3 Hz), 1.32 (6H, m), 1.63 (2H, m), 2.19 (3H, s), 2.61 (2H, t, $^3J_{2H}$=7.6 Hz), 6.96 (1H, d, $^3J_{1H}$=7.3 Hz), 7.21–7.44 (3H, m).

^{13}C NMR (50 MHz): 14.6, 23.1, 24.9, 29.5, 31.9, 32.3, 36.5, 117.9, 120.6, 124.9, 129.3, 138.6, 144.5, 169.3.

MS: *m*/*z*=219 (M$^{\cdot}$, 20), 177 (19), 149 (24), 120 (12), 107 (100), 106 (28), 79 (10), 77 (11), 43 (37), 41 (11).

2-Nonylacetanilide 4c. IR (film, cm^{-1}): 3275, 3039, 1654, 1536.

^{1}H NMR (200 MHz): 0.92 (3H, t, $^3J_{2H}$=6.5 Hz), 1.30 (12H, m), 1.61 (2H, m), 2.21 (3H, s), 2.60 (2H, t, $^3J_{2H}$=7.5 Hz), 7.10–7.30 (3H, m), 7.71 (1H, d, $^3J_{1H}$= 7.4 Hz).

^{13}C NMR (50 MHz): 14.6, 23.2, 24.9, 29.8, 30.1 (3C), 30.4, 31.9, 32.4, 127.3 (3C), 130.0, 134.6, 135.7, 168.4.

MS: *m*/*z*=261 (M$^{\cdot}$, 7), 218 (15), 162 (10), 149 (10), 120 (12), 107 (23), 106 (100), 43 (41), 41 (18).

2-Undecylacetanilide 4e. IR (cm^{-1}): 3270, 3040, 1652, 1537.

^{1}H NMR (200 MHz): 0.92 (3H, t, $^3J_{2H}$=6.4 Hz), 1.30 (16H, m), 1.61 (2H, m), 2.23 (3H, s), 2.60 (2H, t, $^3J_{2H}$=7.6 Hz), 7.10–7.30 (2H, m), 7.51 (1H, d, $^3J_{1H}$=7.6 Hz), 7.63 (1H, d, $^3J_{1H}$=7.4 Hz).

^{13}C NMR (50 MHz): 14.0, 22.6, 24.2, 29.2, 29.4 (3C), 29.5 (2C), 29.7, 31.2, 31.8, 124.1, 125.4, 126.5, 129.3, 133.9, 134.8, 168.4.

MS: *m*/*z*=289 (M$^{\cdot}$, 10), 246 (18), 162 (11), 149 (10), 120 (12), 107 (23), 106 (100), 43 (53), 41 (26).

2-[2′-Trimethylsilylethyl]acetanilide 4f. IR (cm^{-1}): 3258, 1653, 1533, 1462, 832.

^{1}H NMR (200 MHz): 0.08 (9H, s), 0.82 (2H, m), 2.21 (3H, s), 2.58 (2H, m), 7.09–7.30 (3H, m), 7.68 (1H, d, $^3J_{1H}$=6.4 Hz).

^{13}C NMR (50 MHz): −1.2, 17.9, 24.8, 26.3, 125.0, 126.3, 127.1, 129.4, 135.3, 137.4, 169.0.

MS: *m*/*z*=235 (M$^{\cdot}$, 9), 220 (26), 192 (17), 178 (27), 162 (17), 146 (14), 144 (11), 120 (19), 106 (14), 75 (13), 74 (10), 73 (100), 59 (11), 45 (25), 43 (53).

3-[2′-Trimethylsilylethyl]acetanilide 4g. IR (cm^{-1}): 3321, 1667, 1557, 1483, 830.

^{1}H NMR (200 MHz): 0.05 (9H, s), 0.89 (2H, m), 2.20 (3H, s), 2.64 (2H, m), 6.99 (1H, d, $^3J_{1H}$=6.97 Hz), 7.21–7.33 (3H, m), 7.43 (1H, s large).

^{13}C NMR (50 MHz): −1.85, 18.4, 24.4, 29.9, 117.3, 119.3, 123.7, 128.9, 137.8, 146.2, 168.6.

MS: *m*/*z*=235 ($M^{\cdot}$, 45), 234 (26), 220 (28), 205 (12), 204 (71), 192 (14), 144 (12), 116 (26), 75 (11), 74 (12), 73 (100), 59 (24), 45 (25), 43 (37).

Regeneration of the amino group[26]

General procedure: 0.10 mol of acetanilide **4** in 50 mL of ethanol and 150 mL of concentrated hydrochloric acid were refluxed for 10 h. After cooling, the mixture was treated with a 5% solution of sodium hydroxide, extracted with diethylether (2×200 mL) and dried over $MgSO_4$. The obtained alkylaniline **5** was then purified by column chromatography (petroleum ether/diethylether: 80/20).

2-Hexylaniline 5a. IR (cm^{-1}): 3467, 3378, 1621, 1498, 1457.

^{1}H NMR (200 MHz): 0.96 (3H, t, $^3J_{2H}$=6.4 Hz), 1.39 (6H, m), 1.67 (2H, m), 2.54 (2H, t, $^3J_{2H}$=7.7 Hz), 3.65 (2H, bs), 6.71–6.83 (2H, m), 7.08 (2H, m).

^{13}C NMR (50 MHz): 14.9, 23.5, 29.5, 30.2, 31.2, 32.6, 116.3, 119.4, 127.6, 130.1, 145.0.

MS: *m*/*z*=177 ($M^{\cdot}$, 16), 107 (15), 106 (100), 77 (15), 41 (10).

3-Hexylaniline 5b. IR (cm^{-1}): 3434, 3351, 1621, 1462.

^{1}H NMR (200 MHz): 0.92 (3H, t, $^3J_{2H}$=6.4 Hz), 1.35 (6H, m), 1.59 (2H, m), 2.55 (2H, t, $^3J_{2H}$=7.7 Hz), 3.3 (2H, bs), 6.54–5.65 (3H, m), 7.11 (1H, m).

^{13}C NMR (50 MHz): 14.7, 23.3, 29.7, 32.0, 32.4, 36.7, 113.2, 115.9, 119.5, 129.7, 144.8, 147.0.

MS: *m*/*z*=177 ($M^{\cdot}$, 10), 120 (11), 107 (100), 106 (40), 79 (10), 77 (13).

2-Nonylaniline 5c. IR (cm^{-1}): 3468, 3378, 1621, 1498, 1457.

^{1}H NMR (200 MHz): 0.92 (3H, t, $^3J_{2H}$=6.3 Hz), 1.20–1.47 (12H, m), 1.66 (2H, m), 2.52 (2H, t, $^3J_{2H}$=7.7 Hz), 3.67 (2H, bs), 6.70–6.81 (2H, m), 7.07 (2H, m).

^{13}C NMR (50 MHz): 14.7, 23.2, 29.4, 29.9, 30.1 (2C), 30.3, 31.9, 32.5, 116.2, 119.4, 127.4, 127.7, 130.0, 144.4.

MS: *m*/*z*=219 ($M^{\cdot}$, 10), 107 (17), 106 (100).

Anal. Calcd for $C_{15}H_{25}N$: C, 82.12; H, 11.49; N, 6.39. Found: C, 82.22; H, 11.48; N, 6.38.

3-Nonylaniline 5d. IR (cm^{-1}): 3457, 3371, 1619, 1462.

^{1}H NMR (200 MHz): 0.93 (3H, t, $^3J_{2H}$=6.4 Hz), 1.32 (12H, m), 1.63 (2H, m), 2.56 (2H, t, $^3J_{2H}$=7.7 Hz), 3.3 (2H, bs), 6.54–6.65 (3H, m), 7.11 (1H, m).

^{13}C NMR (50 MHz): 14.7, 23.3, 29.9, 30.0, 32.2 (2C), 31.9, 32.5, 36.6, 113.1, 115.9, 119.5, 129.7, 144.8, 146.9.

MS: *m*/*z*=219 ($M^{\cdot}$, 12), 120 (13), 107 (100), 106 (31), 41(10).

2-Undecylaniline 5e. IR (cm^{-1}): 3471, 3379, 1621, 1498, 1458.

^{1}H NMR (200 MHz): 0.95 (3H, t, $^3J_{2H}$=6.3 Hz), 1.25–1.39 (16H, m), 1.68 (2H, m), 2.54 (2H, t, $^3J_{2H}$=7.7 Hz), 3.67 (2H, bs), 6.56–6.83 (2H, m), 7.09 (2H, m).

^{13}C NMR (50 MHz): 14.2, 22.7, 28.8, 29.5, 29.6, 29.7, 29.8 (2C), 29.9, 31.3, 32.0, 115.5, 118.7, 126.8, 126.9, 129.4, 144.0.

MS: *m*/*z*=247 ($M^{\cdot}$, 20), 107 (16), 106 (100), 41 (13).

Anal. Calcd for $C_{17}H_{29}N$: C, 82.51; H, 11.82; N, 5.66. Found: C, 82.50; H, 11.84; N, 5.65.

2-[2′-Trimethylsilylethyl]aniline 5f. IR (film, cm^{-1}): 3466, 3376, 1621, 1496, 1248, 835.

^{1}H NMR (200 MHz): 0.09 (9H, s), 0.91 (2H, m), 2.53 (2H, m), 3.70 (2H, bs), 6.71–6.83 (2H, m), 7.04–7.16 (2H, m).

^{13}C NMR (50 MHz): −1.1, 16.2, 25.9, 116.1, 119.5, 127.3, 129.8 (2C), 144.4.

MS: *m*/*z*=193 ($M^{\cdot}$, 42), 179 (14), 178 (89), 161 (32), 150 (28), 134 (13), 120 (21), 119 (13), 106 (99), 91 (10), 77(19), 74 (16), 73 (100), 59 (34), 45 (33), 44 (11), 43 (12).

3-[2′-Trimethylsilylethyl]aniline 5g. IR (cm^{-1}): 3471, 3371, 1614, 1248.

^{1}H NMR (200 MHz): 0.09 (9H, s), 0.91 (2H, m), 2.60 (2H, m), 3.49 (2H, bs), 6.55–6.71 (3H, m), 7.17 (1H, t, $^3J_{1H}$=7.64 Hz).

^{13}C NMR (50 MHz): −1.81, 18.4, 29.9, 112.5, 114.6, 118.1, 129.2, 146.2, 146.5.

MS: *m*/*z*=193 ($M^{\cdot}$, 60), 179 (10), 178 (60), 150 (50), 120 (13), 119 (15), 74 (22), 73 (100), 59 (42), 45 (22), 43 (10).

Anal. Calcd for $C_{11}H_{19}NSi$: C, 68.35; H, 9.91; N, 7.25. Found: C, 68.29; H, 9.89; N, 7.25.

2-[Hex-1′-enyl]aniline 3a. IR (cm^{-1}): 3456, 3374, 1618, 1456.

^{1}H NMR (200 MHz): 0.97 (3H, t, $^3J_{2H}$=7.0 Hz), 1.47 (4H, m), 2.27 (2H, dt, $^3J_{2H}$=6.7 Hz, $^3J_{1H}$=6.7 Hz), 3.68 (2H, bs), 6.12 (1H, dt, $^3J_{1H}$=15.6 Hz, $^3J_{2H}$=6.8 Hz), 6.45 (1H, d, $^3J_{1H}$=15.6 Hz), 6.70–6.83 (2H, m), 7.09 (1H, dt, $^3J_{1H}$=7.7 Hz, $^4J_{1H}$=1.5 Hz), 7.27 (1H, dd, $^3J_{1H}$=7.7 Hz, $^4J_{1H}$=1.5 Hz).

^{13}C NMR (50 MHz): 14.7, 23.0, 32.4, 33.8, 116.7, 119.6, 125.1, 126.1, 128.0, 128.5, 133.8, 144.1.

MS: *m*/*z*=217 ($M^{\cdot}$, 35), 133 (12), 132 (100), 119 (15), 118 (65), 117 (26), 115 (14), 107 (13), 106 (90), 93 (12), 41 (10).

2-[Nona-1′-enyl]aniline 3c. IR (cm^{-1}): 3456, 3377, 1618, 1456.

^1H NMR (200 MHz): 1.20 (3H, t, $^3J_{2H}$=6.7 Hz), 1.59 (10H, m), 2.48 (2H, dt, $^3J_{2H}$=6.7 Hz, $^3J_{1H}$=6.7 Hz), 3.90 (2H, bs), 6.34 (1H, dt, $^3J_{1H}$=15.7 Hz, $^3J_{2H}$=6.8 Hz), 6.64 (1H, d, $^3J_{1H}$=15.7 Hz), 6.81 (1H, d, $^3J_{1H}$=7.9 Hz), 6.99 (1H, dt, $^3J_{1H}$=7.4 Hz), 7.27 (1H, dd, $^3J_{1H}$=7.5 Hz, $^4J_{1H}$=1.5 Hz), 7.49 (1H, d, $^3J_{1H}$=7.6 Hz).

^{13}C NMR (50 MHz): 14.3, 22.9, 29.4 (2C), 29.7, 32.0, 33.6, 116.1, 118.9, 124.5, 125.6, 127.4, 127.9, 133.0, 143.4.

MS: *m*/*z*=217 ($M^{\cdot}$, 35), 133 (12), 132 (100), 119 (15), 118 (65), 117 (26), 115 (14), 107 (13), 106 (90), 93 (12), 41 (10).

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