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N-Alkylation of Aniline and Its Derivatives by Alcohols in the Presence of Copper Compounds

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Abstract—*N*-Alkyl- and *N*,*N*-dialkyl-substituted anilines were obtained in the reaction of aniline and its derivatives with primary and secondary alcohols in the presence of catalysts $CuCl_2·2H_2O$, $CuBr_2$ and halomethanes as promoters.

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N-Alkyl- and *N*,*N*-dialkyl derivatives of aniline find wide practical applications. In particular, *N*-methylaniline is used as antidetonating additive to gasoline, and *N*,*N*-dimethylaniline finds application in the preparation of paints, explosives, and polyester resins [1]. *N*-Alkyl derivatives of aniline with functional groups are used in production of explosives, photography reagents, pesticides, stabilizers, paints, medications, and polymers [2].

N-Alkylation of derivatives of aniline is mainly performed with alkyl halides at high temperature. However this process has its disadvantages connected with low availability and toxicity of alkyl halides and the necessity of utilization of forming hydrogen halides [3]. Other important method of synthesis of *N*-alkyl derivatives is based on *N*-alkylation of aniline with alcohols in the presence of complexes of palladium, ruthenium, iridium, silver, gold, platinum, nickel, cobalt, rhodium, and osmium [4, 5]. Important benefit of alcohols application for *N*-alkylation of aniline is the generation of water as the side product of the reaction. Among the drawbacks of the mentioned metal complex catalysts is their expensiveness, the necessity to apply additional reagents (usually bases), and low activity with respect to secondary alcohols [6].

We developed a general method of synthesis of *N*-alkyl- and *N*,*N*-dialkyl-substituted products by the reaction of aniline and its derivatives with alcohols in the presence of copper compounds. Active catalysts of *N*-alkylation of aniline and its derivatives with alcohols are $CuBr_2$, $Cu(acac)_2$, $CuCl_2·2H_2O$, $Cu(CH_3COO)_2$, and $Cu(C_6H_5COO)_2$. The regularities of *N*-alkylation were investigated by an example of the reaction of aniline with methanol, optimal conditions of reaction were as follows: 180°C, 6 h at the molar ratio Cu–aniline–MeOH 10 : 100 : 200. The reaction occurs with the formation of *N*-methylaniline **1** and *N*,*N*-dimethylaniline **2**, whose yield and ratio depend of the catalyst nature (Scheme 1). The best ones in the series of investigated catalysts are $CuBr_2$ and $CuCl_2·2H_2O$, in the presence of which the conversion of aniline is 61 and 46% respectively. Without the catalyst the reaction does not occur.

Scheme 1.

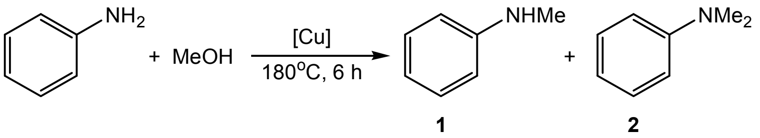


Table 1. Effect of promoter character on the yield of ***N*-methylaniline **1** and ***N*,*N*-dimethylaniline **2**[a]

Catalyst–promoter	Molar ratio $CuBr_2$–P–aniline–MeOH	Aniline conversion, %	Yield, %	
			1	**2**
$CuBr_2$	10 : 0 : 100 : 200	61	13	48
$CuBr_2$–CBr_4	10 : 5 : 100 : 200	94	32	62
$CuBr_2$–HCl	10 : 5 : 100 : 200	98	26	72
$CuBr_2$–$CHBr_3$	10 : 5 : 100 : 200	100	6	94
$CuBr_2$–HBr	10 : 5 : 100 : 200	93	33	60
$CuBr_2$–CCl_4	10: 5 : 100 : 200	100	0	99
	1 : 5 : 100 : 200	100	0	99
	0.1 : 5 : 100 : 200	100	0	99
	0.1 : 5 : 100 : 200[b]	60	44	16
	0.1 : 5 : 100 : 200[c]	77	42	35
	0.1 : 5 : 100 : 200[d]	100	0	0
	0.1 : 3 : 100 : 200	65	33	33
	0.1 : 1 : 100 : 200	45	21	24
$CuCl_2\cdot 2H_2O$	10 : 100 : 200	46	22	24
$CuCl_2\cdot 2H_2O$–CCl_4	0.1 : 5 : 100 : 200	100	0	99
$CuBr_2$–CCl_4	0.1 : 5 : 100 : 200[e]	100	2	98

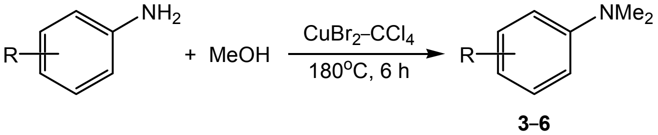
[a] Reaction conditions: 180°C, 6 h.
[b] 150°C.
[c] 170°C.
[d] 200°C (tarring).
[e] Reaction duration 5 h.

Aiming at improving the yield of *N*-methyl and *N*,*N* -dimethyl aniline derivatives we tested as promoters a series of compounds: CBr_4, CCl_4, $CHBr_3$, HBr, and HCl (Table 1).

The most effective catalytic systems were $CuBr_2$–CCl_4 and $CuCl_2\cdot 2H_2O$–CCl_4 at a molar ratio Cu–CCl_4–aniline–alcohol 0.1 : 5 : 100 : 200. Yield of *N*,*N*-dimethylaniline **2** was 99%.

In discovered optimal conditions in the presence of $CuBr_2$–CCl_4 3-chloroaniline, 4-chloroaniline, 2-methoxyaniline, 4-methoxyaniline reacted with methanol to afford the corresponding *N*,*N*-dimethyl derivatives in quantitative yields (Scheme 2).

Scheme 2.



3–6

R = 3-Cl (**3**), 4-Cl (**4**), 2-OMe (**5**), 4-OMe (**6**).

The reaction of *N*-alkylation of aniline in the presence of catalytic systems $CuCl_2\cdot 2H_2O$, $CuBr_2$ and CCl_4 proceeds as well with the other primary alcohols (EtOH, PrOH, BuOH, AmOH, HexOH). One of the benefits of copper compounds as catalysts is the possibility of introduction of secondary alcohols into the reaction of *N*-alkylation of aniline derivatives, in particular, of cyclopentanol, cyclohexanol, cycloheptanol, butan-2-ol and propan-2-ol (Table 2).

The reaction of aniline with butan-1,4-diol in the optimal conditions (180°C, 6 h, molar ratio Cu–CCl_4–aniline–alcohol 0.1 : 5 : 100 : 200) affords 1-phenylpyrrolidine **22** (yield 98%), a product of *N*-heterocyclization (Scheme 3).

Scheme 3.

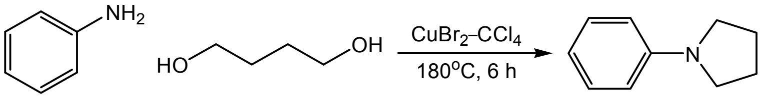


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Table 2. *N*-Alkylation of aniline with primary and secondary alcohols in the presence of the catalytic system $CuBr_2$–CCl_4

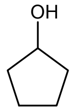
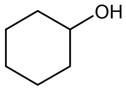
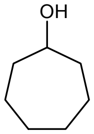
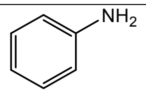
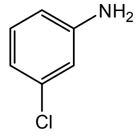
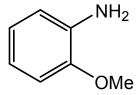
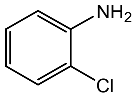
ROH	Aniline conversion, %	Yield of compounds **7–21**, %	
		C_6H_5NHR	$C_6H_5NR_2$
EtOH	91	78 (**7**)	13 (**17**)
PrOH	75	67 (**8**)	8 (**18**)
BuOH	75	65 (**9**)	10 (**19**)
AmOH	46	44 (**10**)	2 (**20**)
HexOH	44	42 (**11**)	2 (**21**)
	71	71 (**12**)	–
	33	33 (**13**)	–
	41	41 (**14**)	–
i-PrOH	53	53 (**15**)	–
s-BuOH	55	55 (**16**)	–

Table 3. *N*-Alkylation of aniline and its derivatives with benzyl alcohol at 180°C[a]

RNH_2	[Cu]–CCl_4	Amine conversion, %	Yield, %	
			RC_6H_4NHBn	$RC_6H_4NBn_2$
	$CuBr_2$–CCl_4	85	75 (**23**)	10 (**27**)
–//–	$CuBr_2$–CCl_4[b]	100	80 (**23**)	19 (**27**)
–//–	$CuCl_2 \cdot 2H_2O$–CCl_4[b]	100	79 (**23**)	20 (**27**)
–//–	$CuCl_2 \cdot 2H_2O$–CCl_4[c]	100	66 (**23**)	32 (**27**)
	$CuCl_2 \cdot 2H_2O$–CCl_4[b]	100	74 (**24**)	24 (**28**)
	$CuCl_2 \cdot 2H_2O$–CCl_4[b]	100	62 (**25**)	34 (**29**)
	$CuCl_2 \cdot 2H_2O$–CCl_4[b]	100	78 (**26**)	20 (**30**)

[a] Molar ratio [Cu]–CCl_4–amine–BnOH 0.1 : 5 : 100 : 100.

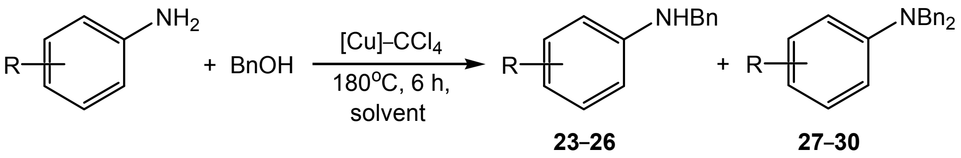
[b] The reaction was performed in benzene (0.5 mL).

[c] The reaction was performed in toluene (0.5 mL).

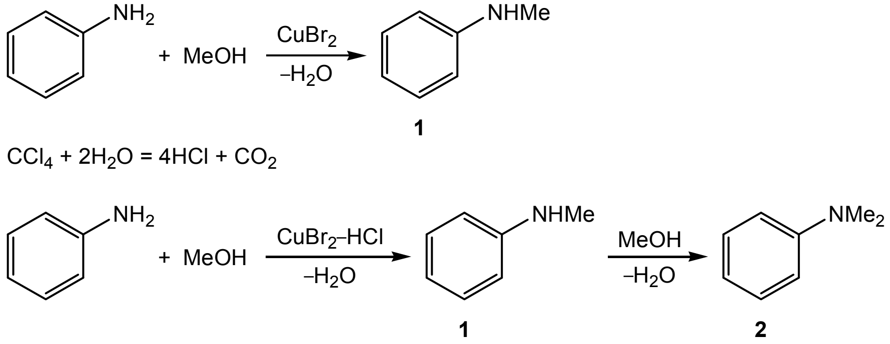
N-alkylation of aniline derivatives with benzyl alcohol was investigated in order to obtain *N*-benzyl and *N*,*N*-dibenzyl derivatives applicable to the synthesis of drugs, pesticides, antioxidants, and lubricants [7].

N-Alkylation of aniline and its substituted derivatives with benzyl alcohol to give *N*-benzyl (**23–26**) and *N*,*N*-dibenzyl (**27–30**) products is effectively catalyzed with $CuCl_2 \cdot 2H_2O$ and $CuBr_2$ in the presence

Scheme 4.



Scheme 5.



of promoter CCl_4. The reaction occurs in benzene and toluene at a molar ratio Cu–CCl_4–$C_6H_5NH_2$–$C_6H_5CH_2OH$ 0.1 : 5: 100 : 100, conversion of aniline is 100%, and yields of *N*-benzyl (**23–26**) and *N*,*N*-dibenzyl (**27–30**) derivatives are 64–80 and 20–36% respectively (Scheme 4). Without solvent the conversion of aniline in the reaction is not full (Table 3).

To find the explanation for the favorable effect of promoters on the course of the reaction an additional analysis of the reaction mass was performed. According to the analysis data, in the course of the reaction CCl_4 promoter undergoes hydrolysis and transforms into CO_2 and HCl. The presence of HCl in the reaction mixture was confirmed by the mercurimetric titration. The concentration of HCl was 48.72 (after 3 h), 44.16 (after 4 h), 42.46 (after 5 h), 41.4 mg/mL (after 6 h). The discovery of HCl in the reaction mixture allows a suggestion that HCl forms with copper salts Gustavson complexes [$CuBr_2$·HCl] and [$CuCl_2$·HCl] that catalyze *N*-alkylation of aniline with methanol to form *N*,*N*-dimethylaniline **2** (Scheme 5).

In all experiments water forms in concentration corresponding to the theoretical amount that is confirmed by Fischer titration.

Hence, $CuBr_2$ and $CuCl_2·2H_2O$ promoted by CCl_4 actively catalyze *N*-alkylation of aniline and its derivatives with primary and secondary alcohols providing *N*-alkyl and *N*,*N*-dialkyl derivatives.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were registered on a spectrometer Bruker Avance-400 (400.13 and 100.62 MHz respectively) in $CDCl_3$. Mass spectra were recorded on a chromato-mass-spectrometer Shimadzu GCMS-QP2010Plus (capillary column SPB-5 30 m × 0.25 mm, carrier gas helium, temperature programmed from 40 to 300°C at a rate 8 deg/min, evaporation temperature 280°C, temperature of ion source 200°C, ionization energy 70 eV). Chromatographic analysis was performed on a chromatograph Shimadzu GC-9A, GC-2014 [column 2 m × 3 mm, stationary phase silicone SE-30 (5%) on Chromaton N-AW-HMDS, ramp from 50 to 270°C, 8 deg/min, carrier gas helium (47 mL/min)].

Initial reagents were commercially available aniline, 3-chloroaniline, 4-chloroaniline, 2-methoxyaniline, 4-methoxyaniline, methanol, ethanol, propan-1 -ol, butan-1-ol, penthan-1-ol, hexan-1-ol, cyclopentanol, cyclohexanol, cycloheptanol, butan-2-ol, propan-2-ol, butan-1,4-diol, benzyl alcohol, CCl_4, CBr_4, and $CHBr_3$, and also catalysts $CuBr_2$, $CuCl_2·2H_2O$, $Cu(acac)_2$, Cu $(CH_3COO)_2$, $Cu(C_6H_5COO)_2$.

Alkylation of aniline derivatives. General method. Reactions were carried out in glass ampules (12 mL) placed into pressure microreactor of stainless steel of 17 mL capacity. Into the ampule in an argon flow was loaded 0.1 mmol of $CuBr_2$, 1 mmol (0.2 mL) of aniline, 2 mmol of primary or 1 mmol of secondary alcohol (0.18 mL of methanol, 0.26 mL of ethanol, 0.32 mL of propan-1-ol, 0.4 mL of butan-1-ol, 0.46 mL of penthan-1-ol, 0.54 mL of hexan-1-ol, 0.2 mL of cyclopentanol, 0.46 mL of cyclohexanol, 0.26 mL of cycloheptanol, 0.19 mL of butan-1,4-diol, 0.2 mL of butan-2-ol, 0.17 mL of propan-2-ol, 0.2 mL of benzyl alcohol), 5 mol (0.01 mL) of CCl_4, and 0.5 mL of benzene (toluene) as solvent. The sealed ampule was placed into the reactor, it was hermetically closed and heated during 6 h at 180°C at constant stirring, then the reactor was cooled to ~20°C, the ampule was opened, the reaction mixture was neutralized with 10% aqueous solution of Na_2CO_3, the reaction products were extracted with methylene chloride, the solvent was distilled off, the residue was distilled in a vacuum or subjected to column chromatography on silica gel, elution with a mixture petroleum ether-ethyl acetate, 1 : 1 (column 21 × 1.2 cm).

The structure of *N*-alkyl and *N*,*N*-dialkyl derivatives **1–30** was proved by NMR and mass spectra, as well as by comparison with authentic samples and published data. To identify compounds **1–30** we used samples obtained in 3–6 experiments.

***N*-Methylaniline (1).** Yield 44%, light-yellow liquid, bp 78–80°C (10 mmHg) {76–77°C (10 mmHg) [8]}.^{1}H NMR spectrum, δ, ppm: 3.00 s (3H, CH_3), 3.89 s (1H, NH), 6.66 d (2H, $C^{2,6}H$, *J* 8 Hz), 6.70–6.85 m (1H, C^4H), 7.15–7.35 m (2H, $C^{3,5}H$). ^{13}C NMR spectrum, δ, ppm: 30.90 (CH_3), 112.59 ($C^{2,6}$), 116.99 (C^4), 129.22 ($C^{3,5}$), 149.36 (C^1). Mass spectrum, *m/z* (I_{rel}, %): 107 (87) $[M]^+$, 106 (100), 93 (7), 77 (30), 65 (13).

***N*,*N*-Dimethyl-3-chloroaniline (3).** Yield 99%, light-yellow oily liquid, bp 105–106°C (10 mmHg) {231–232°C (740 mmHg) [9]}. ^{1}H NMR spectrum, δ, ppm: 3.00 s (6H, CH_3), 6.80 d (2H, $C^{2,6}H$, *J* 7.2 Hz), 6.80–6.82 m (1H, C^4H), 7.25–7.35 m (3H, $C^{3,5}H$). ^{13}C NMR spectrum, δ, ppm: 40.66 (CH_3), 112.70 ($C^{2,6}$), 116.66 (C^4), 129.11 ($C^{3,5}$), 150.70 (C^1). Mass spectrum, *m/z* (I_{rel}, %): 121 (90) $[M]^+$, 120 (100), 104 (15), 91 (8), 77 (25).

***N*,*N*-Dimethyl-3-chloroaniline (3).** Yield 99%, light-yellow oily liquid, bp 105–106°C (10 mmHg) {231–232°C (740 mmHg) [9]}. ^{1}H NMR spectrum, δ, ppm: 2.98 s (6H, CH_3), 6.80 d (1H, $C^{4,6}H$, *J* 7.4 Hz), 6.88 s (2H, C^2H), 7.19 t (1H, C^5H, *J* 7.8 Hz). ^{13}C NMR spectrum, δ, ppm: 41.52 (CH_3), 112.15 (C^6), 113.85 (C^2), 117.67 (C^4), 130.29 (C^5), 135.14 (C^3), 150.06 (C^1). Mass spectrum, *m/z* (I_{rel}, %): 155 (80) $[M]^+$, 139 (8), 118 (15), 111 (8), 77 (13).

***N*,*N*-Dimethyl-4-chloroaniline (4).** Yield 99%, light-yellow oily liquid, bp 120–121°C (20 mmHg) {233–236°C (740 mmHg) [9]}. ^{1}H NMR spectrum, δ, ppm: 2.91 s (6H, CH_3), 6.63 d (1H, $C^{2,6}H$, *J* 8 Hz), 7.16 d (1H, $C^{3,5}H$, *J* 12 Hz). ^{13}C NMR spectrum, δ, ppm: 40.42 (CH_3), 113.49 ($C^{2,6}$), 120.97 (C^4), 129.65 ($C^{3,5}$), 149.24 (C^1). Mass spectrum, *m/z* (I_{rel}, %): 155 (82) $[M]^+$, 154 (100), 139 (17), 118 (15), 111 (8), 77 (13).

***N*,*N*-Dimethyl-2-methoxyaniline (5).** Yield 99%, light-yellow oily liquid, bp 113°C (18 mmHg) {86–90°C (16 mmHg) [10]}. ^{1}H NMR spectrum, δ, ppm: 2.80 s (6H, CH_3), 3.90 s (3H, OCH_3), 6.88 d (1H, C^6H, *J* 8 Hz), 6.90–7.03 m (3H, $C^{3,4,5}H$). ^{13}C NMR spectrum, δ, ppm: 43.37 $[N(CH_3)_2]$, 55.27 (OCH_3), 110.90 (C^3), 118.16 (C^6), 120.76 (C^4), 122.48 (C^5), 142.43 (C^1), 152.40 (C^2). Mass spectrum, *m/z* (I_{rel}, %): 151 (100) $[M]^+$, 136 (66), 120 (24), 107 (20), 93 (10), 77 (12).

***N*,*N*-Dimethyl-4-methoxyaniline (6).** Yield 99%, light-yellow oily liquid, bp 124–125°C (20 mmHg) {70–75°C (5 mmHg) [11]}. ^{1}H NMR spectrum, δ, ppm: 2.87 s (6H, CH_3), 3.37 s (3H, OCH_3), 6.77 d (1H, $C^{2,6}H$, *J* 12 Hz), 6.85 d (1H, $C^{3,5}H$, *J* 8 Hz). ^{13}C NMR spectrum, δ, ppm: 41.82 $[N(CH_3)_2]$, 55.72 (OCH_3), 114.60 ($C^{3,5}$), 114.92 ($C^{2,6}$), 145.89 (C^1), 151.86 (C^4). Mass spectrum, *m/z* (I_{rel}, %): 151 (65) $[M]^+$, 136 (100), 120 (10), 108 (18), 92 (8), 77 (5).

***N*-Ethylaniline (7).** Yield 78%, light-yellow liquid, bp 85–87°C (12 mmHg) (204°C [12]). ^{1}H NMR spectrum, δ, ppm: 1.29 t (3H, C^8H_3, *J* 8 Hz), 3.20 q (2H, C^7H_2), 3.66 s (1H, NH), 6.65 d (2H, $C^{2,6}H$, *J* 8 Hz), 6.70–6.77 m (1H, C^4H), 7.72 t (2H, $C^{3,5}H$, *J* 8 Hz). ^{13}C NMR spectrum, δ, ppm: 14.91 (C^8), 38.47 (C^7), 112.76 ($C^{2,6}$), 117.22 (C^4), 129.24 ($C^{3,5}$), 148.48 (C^1). Mass spectrum, *m/z* (I_{rel}, %): 121 (33) $[M]^+$, 107 (8), 106 (100), 93 (5), 77 (18).

***N*,*N*-Diethylaniline (17).** Yield 13%, light-yellow liquid, bp 96–98°C (10 mmHg) (216°C [13]). ^{1}H NMR spectrum, δ, ppm: 1.20 t (3H, $C^{8,8'}H_3$, *J* 8 Hz), 3.39 q (2H, $C^{7,7'}H_2$, *J* 8 Hz), 6.55–6.57 m (2H, $C^{2,6}H$), 6.57–6.59 m (1H, C^4H), 7.05–7.15 m (2H, $C^{3,5}H$). ^{13}C NMR spectrum, δ, ppm: 12.58 ($C^{8,8'}$), 44.22 ($C^{7,7'}$), 113.73 ($C^{2,6}$), 115.12 (C^4), 129.05 ($C^{3,5}$), 148.33 (C^1). Mass spectrum, *m/z* (I_{rel}, %): 149 (35) $[M]^+$, 134 (100), 120 (5), 106 (45), 93 (5), 77 (20).

***N*-Propylaniline (8).** Yield 67%, light-yellow liquid, bp 112–114°C (20 mmHg) (222°C [12]). ^{1}H

NMR spectrum, δ, ppm: 1.09 t (3H, $C^{9}H_3$, J 8 Hz), 1.65–1.77 m (2H, $C^{8}H_2$), 3.16 t (2H, $C^{7}H_2$, J 8 Hz), 3.71 s (1H, NH), 6.69 d (2H, $C^{2,6}H$, J 8 Hz), 6.70–6.85 m (1H, $C^{4}H$), 7.22–7.35 m (2H, $C^{3,5}H$). ^{13}C NMR spectrum, δ, ppm: 11.74 (C^{9}), 22.79 (C^{8}), 45.85 (C^{7}), 112.78 ($C^{2,6}$), 117.12 (C^{4}), 129.30 ($C^{3,5}$), 148.63 (C^{1}). Mass spectrum, *m/z* (I_{rel}, %): 136 (5) $[M]^+$, 135 (30), 118 (5), 106 (100), 77 (18).

***N,N*-Dipropylaniline (18).** Yield 8%, light-yellow oily liquid, bp 112–114°C (10 mmHg) {62–66°C (0.23 mmHg) [14]}. ^{1}H NMR spectrum, δ, ppm: 1.02 t (3H, $C^{9,9'}H_3$, J 4 Hz), 1.80–1.92 m (2H, $C^{8,8'}H_2$), 3.30–3.35 m (2H, $C^{7,7'}H_2$), 6.58–6.64 m (2H, $C^{2,6}H$), 6.65–6.70 m (1H, $C^{4}H$), 7.05–7.20 m (2H, $C^{3,5}H$). ^{13}C NMR spectrum, δ, ppm: 11.55 ($C^{9,9'}$), 20.49 ($C^{8,8'}$), 52.94 ($C^{7,7'}$), 111.77 ($C^{2,6}$), 115.19 (C^{4}), 129.08 ($C^{3,5}$), 148.30 (C^{1}). Mass spectrum, *m/z* (I_{rel}, %): 177 (20) $[M]^+$, 162 (5), 148 (100), 120 (10), 106 (72), 77 (18).

***N*-Butylaniline (9).** Yield 65%, light-yellow oily liquid, bp 112–114°C (10 mmHg) {60–61°C (0.5 mmHg) [15]}. ^{1}H NMR spectrum, δ, ppm: 0.97 t (3H, $C^{10}H_3$, J 8 Hz), 1.40–1.50 m (2H, $C^{9}H_2$), 1.55–1.65 m (2H, $C^{8}H_2$), 3.11 t (2H, $C^{7}H_2$, J 4 Hz), 3.66 s (1H, NH), 6.61 d (2H, $C^{2,6}H$, J 8 Hz), 6.65–6.70 m (1H, $C^{4}H$), 7.15–7.20 m (2H, $C^{3,5}H$). ^{13}C NMR spectrum, δ, ppm: 13.89 (C^{10}), 19.30 (C^{9}), 31.65 (C^{8}), 43.65 (C^{7}), 112.64 ($C^{2,6}$), 116.99 (C^{4}), 129.18 ($C^{3,5}$), 148.56 (C^{1}). Mass spectrum, *m/z* (I_{rel}, %): 150 (5) $[M]^+$, 149 (20), 107 (10), 106 (100), 93 (3), 77 (10).

***N,N*-Dibutylaniline (19).** Yield 10%, light-yellow oily liquid, bp 146–148°C (15 mmHg) {82–84°C (0.23 mmHg) [14]}.^{1}H NMR spectrum, δ, ppm: 0.95–1.10 m (6H, $C^{10,10'}H_3$), 1.40–1.60 m (3H, $C^{9,9'}H_2$), 1.60–1.72 m (4H, $C^{8,8'}H_2$), 3.35 t (4H, $C^{7,7'}H_2$, J 8 Hz), 6.56–6.60 m (2H, $C^{2,6}H$), 6.61–6.65 m (1H, $C^{4}H$), 7.05–7.18 m (2H, $C^{3,5}H$). ^{13}C NMR spectrum, δ, ppm: 14.02 ($C^{10,10'}$), 20.40 ($C^{9,9'}$), 29.40 ($C^{8,8'}$), 50.84 ($C^{7,7'}$), 111.35 ($C^{2,6}$), 115.15 (C^{4}), 131.61 ($C^{3,5}$), 148.26 (C^{1}). Mass spectrum, *m/z* (I_{rel}, %): 205 (34) $[M]^+$, 162 (100), 120 (79), 106 (60), 93 (5), 77 (18).

***N*-Pentylaniline (10).** Yield 44%, light-yellow oily liquid, bp 148–150°C (20 mmHg) {130°C (11 mmHg) [16]}. ^{1}H NMR spectrum, δ, ppm: 0.96 t (3H, $C^{11}H_3$, J 4 Hz), 1.32–1.48 m (2H, $C^{10}H_2$), 1.32–1.48 m (2H, $C^{9}H_2$), 1.55–1.68 m (2H, $C^{8}H_2$), 3.62 t (2H, $C^{7}H_2$, J 4 Hz), 3.80 s (1H, NH), 6.62 d (2H, $C^{2,6}H$, J 8 Hz), 6.67–6.73 m (1H, $C^{4}H$), 7.12–7.22 m (2H, $C^{3,5}H$). ^{13}C NMR spectrum, δ, ppm: 14.08 (C^{11}), 22.56 (C^{10}), 28.02 (C^{9}), 32.44 (C^{8}), 44.05 (C^{7}), 112.86 ($C^{2,6}$), 117.14 (C^{4}), 129.25 ($C^{3,5}$), 148.63 (C^{1}). Mass spectrum, *m/z* (I_{rel}, %): 163 (20) $[M]^+$, 132 (3), 118 (5), 106 (100), 93 (7), 77 (14).

***N*-Hexylaniline (11).** Yield 42%, light-yellow oily liquid, bp 157–159°C (20 mmHg) {88–89°C (0.1 mmHg) [15]}. ^{1}H NMR spectrum, δ, ppm: 0.91 t (3H, $C^{12}H_3$, J 4 Hz), 1.25–1.45 m (6H, $C^{9,10,11}H_2$), 1.55–1.65 m (2H, $C^{8}H_2$), 3.62 t (2H, $C^{7}H_2$, J 4 Hz), 3.80 s (1H, NH), 6.62 d (2H, $C^{2,6}H$, J 8 Hz), 6.67–6.73 m (1H, $C^{4}H$), 7.12–7.22 m (2H, $C^{3,5}H$). ^{13}C NMR spectrum, δ, ppm: 14.03 (C^{12}), 22.65 (C^{11}), 25.47 (C^{10}), 26.87 (C^{9}), 29.53 (C^{8}), 44.04 (C^{7}), 112.76 ($C^{2,6}$), 117.10 (C^{4}), 129.20 ($C^{3,5}$), 148.56 (C^{1}). Mass spectrum, *m/z* (I_{rel}, %): 177 (18) $[M]^+$, 132 (3), 118 (3), 106 (100), 93 (5), 77 (10).

***N*-Cyclopentylaniline (12).** Yield 71%, light-yellow oily liquid, bp 140–142°C (15 mmHg) {137°C (12 mmHg) [17]}. ^{1}H NMR spectrum, δ, ppm: 1.45–1.55 m ($2H^{a}$, $C^{3',4'}H$), 1.60–1.70 m ($2H^{a}$, $C^{2',5'}H$), 1.70–1.80 m ($2H^{e}$, $C^{3',4'}H$), 2.00–2.10 m ($2H^{e}$, $C^{2',5'}H$), 3.67 br.s(1H, NH), 3.75–3.9 m (1H, $C^{1'}H$), 6.63 d (2H, $C^{2,6}H$, J 8 Hz), 6.71 t (1H, $C^{4}H$, J 8 Hz), 7.19 t (2H, $C^{3,5}H$, J 8 Hz). ^{13}C NMR spectrum, δ, ppm: 24.08 ($C^{3',4'}$), 33.61 ($C^{2',5'}$), 54.65 ($C^{1'}$), 113.16 ($C^{2,6}$), 116.89 (C^{4}), 129.19 ($C^{3,5}$), 148.06 (C^{1}). Mass spectrum, *m/z* (I_{rel}, %): 161 (50) $[M]^+$, 133 (13), 132 (100), 119 (30), 93 (18).

***N*-Cyclohexylaniline (13).** Yield 23%, light-yellow oily liquid, bp 140–142°C (10 mmHg) {92–96°C (2 mmHg) [11]}. ^{1}H NMR spectrum, δ, ppm: 1.20–1.50 m (2H, $C^{4'}H$), 1.50–1.70 m (4H, $C^{3',5'}H$), 2.00–2.20 m (4H, $C^{2',6'}H$), 3.31–3.37 m (1H, $C^{1'}H$), 3.37 s (1H, NH), 6.64 d (2H, $C^{2,6}H$, J 8 Hz), 6.75–6.85 m (2H, $C^{3,5}H$), 7.10–7.30 m (1H, $C^{4}H$). ^{13}C NMR spectrum, δ, ppm: 25.09 ($C^{3',5'}$), 25.99 ($C^{4'}$), 35.49 ($C^{2',6'}$), 51.72 ($C^{1'}$), 113.24 ($C^{2,6}$), 117.87 (C^{4}), 129.30 ($C^{3,5}$), 147.46 (C^{1}). Mass spectrum, *m/z* (I_{rel}, %): 175 (30) $[M]^+$, 146 (5), 132 (100), 106 (15), 93 (17).

***N*-Cycloheptylaniline (14).** Yield 41%, light-yellow oily liquid, bp 126–128°C (5 mmHg) {156°C (11 mmHg) [17]}. ^{1}H NMR spectrum, δ, ppm: 1.20–1.80 m (8H, $C^{3'-6'}H_2$), 2.00–2.10 m (4H, $C^{2',7'}H_2$), 3.44–3.52 m (1H, $C^{1'}H$), 3.65 br.s (1H, NH), 6.59 d (2H, $C^{2,6}H$, J 8 Hz), 6.70–6.75 m (1H, $C^{4}H$), 7.20 t (2H, $C^{3,5}H$, J 8 Hz). ^{13}C NMR spectrum, δ, ppm: 24.44 ($C^{4',5'}$), 28.39 ($C^{3',6'}$), 34.86 ($C^{2',7'}$), 54.66 ($C^{1'}$), 113.23 ($C^{2,6}$), 116.77 (C^{4}), 129.29 ($C^{3,5}$), 147.38 (C^{1}). Mass spectrum, *m/z* (I_{rel}, %): 189 (38) $[M]^+$, 160 (5), 146 (17), 132 (100), 106 (17), 93 (20), 77 (12).

***N*-Isopropylaniline (15).** Yield 53%, yellow oily liquid, bp 68–70°C (15 mmHg) {105–106°C (27 mmHg) [18]}. ^{1}H NMR spectrum, δ, ppm: 1.37 t (6H, C^{7,9}H$_3$, *J* 8 Hz), 3.60–3.70 m (1H, C^{8}H), 4.05 br.s (1H, NH), 6.54 d (2H, C^{2,6}H, *J* 8 Hz), 6.55–6.75 m (1H, C^{4}H), 7.18 t (2H, C^{3,5}H, *J* 8 Hz). ^{13}C NMR spectrum, δ, ppm: 22.80 (C^{7,9}), 44.19 (C^8), 113.22 (C^{2,6}), 116.93 (C^4), 129.04 (C^{3,5}), 146.92 (C^1). Mass spectrum, *m/z* (I_rel, %): 135 (30) [*M*]$^+$, 121 (8), 120 (100), 120 (100), 106 (10), 93 (18), 77 (12).

***N*-(Butan-2-yl)aniline (16).** Yield 55%, light-yellow oily liquid, bp 99–100°C (10 mmHg) {74–75°C (0.15 mmHg) [15]}. ^{1}H NMR spectrum, δ, ppm: 0.98 t (3H, C^{10}H$_3$, *J* 8 Hz), 1.20 d (3H, C^{7}H$_3$, *J* 4 Hz), 1.55–1.70 m (2H, C^{9}H), 4.05–4.20 m (1H, C^{8}H), 4.05 s (1H, NH), 6.60 d (2H, C^{2,6}H, *J* 8 Hz), 6.65–6.75 m (1H, C^{4}H), 7.18 t (2H, C^{3,5}H, *J* 8 Hz). ^{13}C NMR spectrum, δ, ppm: 10.20 (C^{10}), 20.29 (C^7), 29.66 (C^9), 49.86 (C^8), 113.09 (C^{2,6}), 116.47 (C^4), 129.26 (C^{3,5}), 147.33 (C^1). Mass spectrum, *m/z* (I_rel, %): 149 (19) [*M*]$^+$, 134 (11), 121 (13), 120 (100), 103 (5), 93 (7), 77 (10).

1-Phenylpyrrolidine (22). Yield 98%, colorless oily liquid, bp 105–106°C (5 mmHg) {89–90°C (1 mmHg) [19]}. ^{1}H NMR spectrum, δ, ppm: 2.00–2.05 m (4H, C$^{2',3'}$H), 3.31 t (4H, C$^{1',4'}$H), 6.60 d (2H, C^{2,6}H, *J* 8 Hz), 6.66–6.74 m (1H, C^{4}H), 7.26 t (2H, C^{3,5}H, *J* 8 Hz). ^{13}C NMR spectrum, δ, ppm: 25.47 (C$^{1',2'}$), 47.57 (C$^{3',4'}$), 111.63 (C^{2,6}), 115.35 (C^4), 129.14 (C^{3,5}), 148.04 (C^1). Mass spectrum, *m/z* (I_rel, %): 147 (82) [*M*]$^+$, 146 (100), 119 (10), 106 (23), 91 70), 77 (31).

***N*-Benzylaniline (23).** Yield 80%, light-yellow oily liquid, bp 140–142°C (6 mmHg) {125°C (3 mmHg) [11]}. ^{1}H NMR spectrum, δ, ppm: 4.45 s (2H, C^{7}H$_2$), 4.80 s (1H, NH), 6.50–6.80 m (2H, C^{2,6}H), 6.85–6.95 m (1H, C^{4}H), 7.20–7.40 m (2H, C^{3,5}H), 7.45–7.50 m (5H, C$^{2'-6'}$H). ^{13}C NMR spectrum, δ, ppm: 48.40 (C^7), 112.81 (C^{2,6}), 117.68 (C^4), 127.37 (C$^{4'}$), 127.65 (C^{3,5}), 129.42 (C$^{2',6'}$), 128.79 (C$^{3',5'}$), 139.61 (C$^{1'}$), 148.30 (C^1). Mass spectrum, *m/z* (I_rel, %): 184 (14) [*M*]$^+$, 183 (58), 106 (18), 91 (100), 77 (15), 65 (17).

***N*,*N*-Dibenzylaniline (27).** Yield 20%, mp 59–60°C (60°C [20]). Mass spectrum, *m/z* (I_rel, %): 273 (63) [*M*]$^+$, 196 (17), 182 (18), 91 (100), 77 (20), 65 (13).

***N*-Benzyl-3-chloroaniline (24).** Yield 74%, light-yellow oily liquid, bp 150–152°C (2 mmHg) {182–186°C (5 mmHg) [21]}. ^{1}H NMR spectrum, δ, ppm: 4.07 s (1H, NH), 4.36 s (2H, C^{7}H$_2$), 6.72 s (1H, C^{2}H), 6.50–7.20 m (3H, C$^{4-6}$H), 7.20–7.50 m (5H, C$^{2'-6'}$H). ^{13}C NMR spectrum, δ, ppm: 48.30 (C^7), 111.64 (C^{2,6}), 117.87 (C^4), 127.59 (C$^{4'}$), 127.62 (C$^{2',6'}$), 128.76 (C^{3,5}), 130.26 (C^5), 135.02 (C^3), 137.86 (C$^{1'}$), 148.72 (C^1). Mass spectrum, *m/z* (I_rel, %): 217 (40) [*M*]$^+$, 182 (5), 140 (10), 91 (100), 77 (5).

***N*,*N*-Dibenzyl-3-chloroaniline (28).** Yield 24%, yellow oily liquid, bp 165–167°C (0.02 mmHg). ^{1}H NMR spectrum, δ, ppm: 4.70 s (2H, C^{7,8}H), 6.72 s (1H, C^{2}H), 6.50–7.20 m (1H, C$^{4-6}$H), 7.20–7.50 m (5H, C$^{2'-6',2''-6''}$H). ^{13}C NMR spectrum, δ, ppm: 47.89 (C^{7,8}), 110.69 (C^6), 112.26 (C^2), 116.71 (C^4), 127.53 (C$^{4',4''}$), 127.72 (C$^{2',2'',6',6''}$), 128.76 (C$^{3',3'',5',5''}$), 129.04 (C^5), 135.18 (C^3), 138.44 (C$^{1',1''}$), 148.72 (C^1). Mass spectrum, *m/z* (I_rel, %): 309 (25) [*M*]$^+$, 307 (65), 230 (15), 216 (30), 111 (10), 91 (100), 77 (5).

***N*-Benzyl-2-methoxyaniline (25).** Yield 62%, yellow oily liquid, bp 155–157°C (2 mmHg) {183–187°C (5 mmHg) [21]}. ^{1}H NMR spectrum, δ, ppm: 3.90 s (3H, OCH$_3$), 4.41 s (2H, C^{7}H$_2$), 4.62 s (1H, NH), 6.55–6.75 m (1H, C^{6}H), 6.75–6.92 m (3H, C$^{3-5}$H), 7.20–7.50 m (5H, C$^{2'-6'}$H). ^{13}C NMR spectrum, δ, ppm: 48.16 (C^7), 55.51 (OCH$_3$), 109.51 (C^3), 110.25 (C^6), 116.80 (C^4), 121.38 (C^5), 127.62 (C$^{2',6'}$), 127.67 (C$^{3',5'}$), 127.72 (C$^{4'}$), 138.17 (C^1), 139.65 (C$^{1'}$), 146.92 (C^2). Mass spectrum, *m/z* (I_rel, %): 213 (75) [*M*]$^+$, 198 (23), 120 (10), 91 (100), 77 (13).

***N*,*N*-Dibenzyl-2-methoxyaniline (29).** Yield 34%, yellow oily liquid, bp 144–146°C (0.02 mmHg). ^{1}H NMR spectrum, δ, ppm: 3.90 s (3H, OCH$_3$), 4.41 s (2H, C^{7,8}H$_2$), 6.55–6.70 m (4H, C$^{3-6}$H), 7.20–7.50 m (5H, C$^{2'-6',2''-6''}$H). ^{13}C NMR spectrum, δ, ppm: 48.41 (C^{7,8}), 55.51 (OCH$_3$), 109.51 (C^3), 110.53 (C^6), 116.80 (C^4), 121.53 (C^5), 127.66 (C$^{2',2'',6',6''}$), 127.75 (C$^{4',4''}$), 128.87 (C$^{3',3'',5',5''}$), 138.17 (C^1), 139.65 (C$^{1',1''}$), 146.92 (C^2). Mass spectrum, *m/z* (I_rel, %): 303 (100) [*M*]$^+$, 213 (10), 180 (7), 91 (88), 77 (6).

***N*-Benzyl-2-chloroaniline (26).** Yield 78%, yellow oily liquid, bp 150–152°C (2 mmHg) {162–163°C (4 mmHg) [22]}. ^{1}H NMR spectrum, δ, ppm: 4.00 s (1H, NH), 4.47 s (2H, C^{7}H$_2$), 6.50–7.80 m (4H, C$^{3-6}$H), 6.50–7.80 m (5H, C$^{2'-6'}$H). ^{13}C NMR spectrum, δ, ppm: 47.97 (C^7), 111.82 (C^6), 117.68 (C^3), 119.30 (C^{2,4}), 127.39 (C$^{4'}$), 127.46 (C$^{2',6'}$), 127.91 (C^5), 128.81 (C$^{3',5'}$), 138.72 (C$^{1'}$), 143.78 (C^1). Mass spectrum, *m/z* (I_rel, %): 217 (35) [*M*]$^+$, 180 (5), 140 (10), 91 (100), 77 (10).

***N*,*N*-Dibenzyl-2-chloroaniline (30).** Yield 20%, yellow oily liquid, bp 160–162°C (0.02 mmHg). ^{1}H

NMR spectrum, δ, ppm: 4.47 s (2H, $C^{7,8}H$), 6.50–7.80 m (4H, $C^{3–6}H$), 6.50–7.80 m (5H, $C^{2'–6',2''–6''}H$). ^{13}C NMR spectrum, δ, ppm: 48.20 ($C^{7,8}$), 111.82 (C^{6}), 117.68 (C^{3}), 119.30 ($C^{2,4}$), 127.39 ($C^{4',4''}$), 127.46 ($C^{2',2'',6',6''}$), 127.91 (C^{5}), 129.21 ($C^{3',3'',5',5''}$), 134.55 ($C^{1',1''}$), 143.78 (C^{1}). Mass spectrum, *m/z* (I_{rel}, %): 309 (25) $[M]^+$, 307 (68), 230 (10), 216 (5), 180 (7), 91 (100), 77 (3).

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