Highly selective *N*-Alkylation of amines promoted on silica: An efficient and recyclable surface

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Received 24th March 2009, Accepted 28th April 2009
First published as an Advance Article on the web 13th May 2009
DOI: 10.1039/b905878h

***N*-Alkylation of amines suffers from competing over alkylations. At the same time, use of strong base and other harsh conditions greatly limits providing a practical, generalized and selective procedure. Activated silica gel has been found to promote *N*-alkylations of amines. Here, we studied *N*-alkylation of amines with various types of alkyl halides, which finally constitute practical, highly selective and eco-friendly conditions for mono- or bis-alkylated amines at ambient temperature with recyclability of silica.**

Introduction

Amines and their derivatives are important functionalities in various natural products and important synthetic targets. They are widely used as basic intermediates to prepare solvents, fine chemicals, pharmaceuticals, agrochemicals and catalysts for polymerization.[1] As a result, the development of new methods to prepare these compounds has become the goal of many research groups over the years. Traditionally, amines are alkylated in solution phase using inorganic acids as the catalysts and alkyl halides or dimethyl sulfate as the alkylating agents,[2] besides methanol[3] and dimethyl carbonate.[4] However, yields or products selectivity (mono- or bis-alkylations) are, with few exceptions, low and depend on the nature of the catalysts and on the reaction conditions. From a methodological viewpoint, direct nucleophilic attack of amines to alkyl halides is the most straightforward procedure for the alkylation of amines.[5] The major synthetic problem for direct alkylation procedure is the competing over-alkylation, which leads to mixtures of secondary and tertiary amines and even quaternary ammonium salts, and the prevention of over-alkylation becomes more difficult when highly reactive alkylating agents such as methyl, ethyl, benzyl, and allyl halides are used as alkylating agents.[6] Thermal reaction between alkyl halides and amines in the presence of a base requires longer reaction time period and affords lower yields of desired product.[7] Inorganic bases like NaH,[8] K_2CO_3,[9] $CsOH{\cdot}H_2O$,[10] Cs_2CO_3[11] have been employed in *N*-alkylation of amines. Recently, Varma and his co-workers studied the formation of tertiary amines *via* *N*-alkylation in aqueous alkaline medium under microwave irradiation to evolve a greener procedure.[12] Use of strong inorganic bases, however, can lead to undesired products in the presence of base-sensitive functional groups and hydrolysis of the corresponding alkyl halides may also result. Copper-catalyzed Ullmann and Goldberg reactions[13] or Pd-catalyzed Buchwald–Hartwig reaction[14] have been established as versatile C–N bond-forming reactions. However, transition metal-free amination of electron-rich benzyl halides has remained largely unexplored.[15] Although most of the methods are apparently useful, many of them are limited by harsh reaction conditions, low yields, long reaction times and use of toxic solvents or catalysts. *N*-alkylations promoted on solid phase are often associated with strong basicity of the surface limiting the scopes of recyclability and selectivity.[16] Furthermore, the possibility of the concomitant over-alkylations, when the amine is employed as the limiting substrate, often reduces the application of these methods.[17] Therefore, development of mild, efficient, selective and environmentally benign method of *N*-alkylation of amines including diamines and heterocyclic compounds bearing acidic hydrogen atom attached to nitrogen has been a major challenge in organic synthesis.

Results and discussion

Organic reactions catalyzed or mediated on solid surfaces remain a strategic field of chemistry because of their implications to industry and environment. In continuation of our efforts to explore organic reactions using solid phases[18] we observed that aza-Michael additions of amines, including sterically hindered amines, can be done efficiently on the surface of silica gel.[18c] We reasoned that nucleophilic substitution of alkyl halides with amines might be accelerated using activated silica as the solid reaction medium and thus negating use of any other organic or inorganic bases. In this communication, we report our studies which constitute an efficient method for the synthesis of secondary and tertiary amines *via* *N*-alkylation of amines with alkyl halides in solid phase using silica at room temperature. The procedure is simple and extremely useful for the control of the mono-, bis- or over-alkylations by varying the reaction conditions and molar proportions of amines and alkyl halides. Furthermore, the silica gel, after purification and activation, can be reused for ten consecutive runs (tested) without any substantial reduction in the yield.

In order to develop a convenient and selective reaction procedure for *N*-alkylation of amines, we first chose the reaction of aniline with benzyl chloride, as the model case. According to our previous experience, commercially available silica gel (source: SRL, India; particle size: 60–120 Mesh) was activated by heating under vacuum at 150 °C until bubbling ceases and then was cooled to room temperature under vacuum. In a typical procedure, an equimolar or 1 : 2.2 mixture of aniline and benzyl

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Table 1 HPLC analyses of the reaction of aniline with benzyl chloride promoted on different silica surface at various temperature and time

Entry	Aniline : benzyl chloride	Silica gel (type)	Temp./°C	Time/h	% Conversion[b]	Mono :	Bis[c]
1a	1 : 1	Column[a]	5–10	1	36.46	76.1	23.9
1b	1 : 1	Column[a]	5–10	2	52.04	87.2	12.8
1c	1 : 1	Column[a]	5–10	3	78.82	83.8	16.2
1d	1 : 1	Column[a]	5–10	6	83.5	75.5	24.4
2a	1 : 1	Column[a]	25	0.5	71.93	84.7	15.3
2b	1 : 1	Column[a]	25	1	72.51	84	16
2c	1 : 1	Column[a]	25	1.5	85.86	80.9	19.1
2d	1 : 1	Column[a]	25	6	88.82	60.8	39.2
3a	1 : 1	Column[a]	60	1	94.09	35	65
3b	1 : 1	Column[a]	60	3	95.76	33.9	66
4a	1 : 2.2	Column[a]	5–10	1	48.7	91	9
4b	1 : 2.2	Column[a]	5–10	2	67.25	80.9	19
4c	1 : 2.2	Column[a]	5–10	3	86.31	68.8	31.2
5a	1 : 2.2	Column[a]	25	5	90.86	33	67
5b	1 : 2.2	Column[a]	25	8	91.24	24	76
5c	1 : 2.2	Column[a]	25	16	93.11	14	86
6a	1 : 2.2	Column[a]	60	1.5	89.9	57.7	42.3
6b	1 : 2.2	Column[a]	60	4	93.3	45.5	54.5
7a	1 : 1	Tlc[d]	5–10	1	38.1	70.1	29.8
7b	1 : 1	Tlc[d]	5–10	2	52.16	90.6	9.4
7c	1 : 1	Tlc[d]	5–10	4	58.38	87	12.9
8a	1 : 1	Tlc[d]	25	0.5	54.73	90.8	9
8b	1 : 1	Tlc[d]	25	1	74.82	95.7	4.3
8c	1 : 1	Tlc[d]	25	1.5	87.95	93.1	6.8
8d	1 : 1	Tlc[d]	25	2.5	89.89	88.4	11.6
9a	1 : 1	Tlc[d]	60	1	81.9	78.5	21.6
9b	1 : 1	Tlc[d]	60	3	87.32	43	57
10a	1 : 2.2	Tlc[d]	5–10	0.5	19.89	80	20
10b	1 : 2.2	Tlc[d]	5–10	2	40.23	90.3	9.7
10c	1 : 2.2	Tlc[d]	5–10	4	66.8	70.7	29.2
11a	1 : 2.2	Tlc[d]	25	2	79.1	66.6	33.4
11b	1 : 2.2	Tlc[d]	25	8	89.4	33.7	66.3
11c	1 : 2.2	Tlc[d]	25	18	92.2	10	90
12a	1 : 2.2	Tlc[d]	60	0.5	87.9	55.5	44.4
12b	1 : 2.2	Tlc[d]	60	1	89.7	63	27
12c	1 : 2.2	Tlc[d]	60	2	92.9	33.3	66.6
12d	1 : 2.2	Tlc[d]	60	4	94.1	11.3	88.7

[a] Particle size: 60–120 Mesh. [b] Based on unreacted aniline. [c] Analysed by HPLC data. [d] Particle size: –325 Mesh.

chloride was mixed with activated silica (1 g mmol^{-1}) and the solid mixture was stirred at varying temperature and time. The product composition was checked taking a small amount of the solid reaction mixture in methanol and analysed by HPLC (Table 1). We observed that the aniline can be benzylated to produce both mono- and bis-*N*-benzylated anilines along with the starting aniline (about 5–15%). In the case of equimolar mixture of reactants, the ratio of mono- and bis- products was obtained in 3 : 1 at 5 °C for 6 h, with an overall 84% conversion, while at room temperature (25 °C for 1.5 h) the ratio was 4 : 1 with an overall 86% conversion. At high temperature (60 °C), however, the bis-alkylation was mostly favoured with slight better overall conversion. On the other hand, similar reaction in the ratios of 1 : 2.2 (25 °C/16 h) yielded *N*-benzylaniline and *N*,*N*-dibenzylaniline in 1 : 6 proportions with an overall 93% conversion.

Since, commercially available silica gel for tlc was found to be active in aza-Michael reaction,[18c] similar experiments were also performed using commercially available silica gel for tlc (source: SRL, India; particle size: –325 Mesh) with the aim of improving the yield and/or selectivity. Activity of the silica gel (for tlc) was indeed found to be little better in comparison to silica gel for column. Thus an equimolar mixture of the aniline and benzyl chloride stirred (25 °C/1.5 h) on the surface of activated silica gel (for tlc) afforded the mono- and bis-benzylated anilines in 13 : 1 with an overall 88% conversion. Similarly, use of reactants in 1 : 2.2 proportions yielded the mono- and bis-benzylated anilines in the ratios of 1 : 9 with an overall 92% conversion, when the reaction was performed at room temperature for 18 h. Thus, the selectivity for mono- or bis-alkylations greatly depends on temperature, time of the reaction, proportion of the reactants and also partly on the type of silica gel. A clear optimization of the reaction conditions is revealed from our study by which one can control the preparation of mono- or bis-*N*-benzylated anilines.

Such remarkable selectivity under mild and simple reaction conditions on silica gel surface was unprecedented and prompted us to investigate the reactivity and selectivity of a series of different classes of amines with both active and inactive alkyl halides. The results are presented in Table 2. The reaction of 4-anisidine or 4-toluidine with benzyl chloride afforded similar results (entries 3–6). Other active halides like allyl or propargyl bromide also showed notable selectivity for mono- and bis- alkylation, when treated with 4-anisidine (entries 7–10). Anilines bearing different groups such as Br or NO_2 also worked similarly and efficiently to yield the corresponding

Table 2 Reaction of amine and alkyl halide on a surface of silica (type: for tlc; particle size:–325 Mesh) under different conditions

Entry	Amine	Alkyl halide	Amine : Alkyl Halide	Time/h	Temp.	*N*-mono-substituted	*N*-bis-substituted	Mono : Bis
1	$C_6H_5NH_2$	$PhCH_2Cl$	1 : 1	1.5	RT	80	8	10 : 1
2	$C_6H_5NH_2$	$PhCH_2Cl$	1 : 2.2	18	RT	10	81	1 : 8
3	1,4-$H_3COC_6H_4NH_2$	$PhCH_2Cl$	1 : 1	1.5	RT	79	13	6 : 1
4	1,4-$H_3COC_6H_4NH_2$	$PhCH_2Cl$	1 : 2.2	12	RT	11	84	1 : 7.6
5	1,4-$CH_3C_6H_4NH_2$	$PhCH_2Cl$	1 : 1	1	RT	81	10	8 : 1
6	1,4-$CH_3C_6H_4NH_2$	$PhCH_2Cl$	1 : 2.2	14	RT	8	88	1 : 11
7	1,4-$H_3COC_6H_4NH_2$	$HC{\equiv}C{-}CH_2Br$	1 : 1	2	RT	79	10	8 : 1
8	1,4-$H_3COC_6H_4NH_2$	$HC{\equiv}C{-}CH_2Br$	1 : 2.2	12	RT	12	83	1 : 7
9	1,4-$H_3COC_6H_4NH_2$	$CH_2{=}CH{-}CH_2Br$	1 : 1	1.5	RT	70	14	5 : 1
10	1,4-$H_3COC_6H_4NH_2$	$CH_2{=}CH{-}CH_2Br$	1 : 2.2	5	RT	12	84	1 : 7
11	1,4-$BrC_6H_4NH_2$	$CH_2{=}CH{-}CH_2Br$	1 : 1	1	RT	75	12	6.3 : 1
12	1,4-$BrC_6H_4NH_2$	$CH_2{=}CH{-}CH_2Br$	1 : 2.2	8	RT	Trace	84	—
13	1,4-$NO_2C_6H_4NH_2$	$CH_2{=}CH{-}CH_2Br$	1 : 2.2	12	RT	58	35	1.6 : 1
14	1,2-$IC_6H_4NH_2$	$CH_2{=}CH{-}CH_2Br$	1 : 1	1	RT	85	Trace	—
15	1,2-$IC_6H_4NH_2$	$CH_2{=}CH{-}CH_2Br$	1 : 2.2	10	RT	7	89	1 : 12.7
16	2,4,6-$Br_3C_6H_2NH_2$	$PhCH_2Cl$	1 : 2.2	15	RT	93	Trace	
17	1,4-$H_3COC_6H_4NH_2$	$Me{-}(CH_2)_4Br$	1 : 2.2	14	RT	75	12	6.3 : 1
18	1,4-$H_3COCC_6H_4NH_2$	$Me{-}(CH_2)_4Br$	1 : 2.2	6	60 °C	75	Nil	—
19	1,4-$CH_3C_6H_4NH_2$	$Me{-}(CH_2)_{11}Br$	1 : 2.2	26	RT	75	12	6.3 : 1
20	Me-$(CH_2)_3$-NH_2	$PhCH_2Cl$	1 : 2.2	3	RT	Trace	78	—
21	(iso-Prop)$_2$NH	$PhCH_2Cl$	1 : 1	40	RT	52		
22	Piperidine	$PhCH_2Cl$	1 : 1	1	RT	86		
23	Morpholine	$PhCH_2Cl$	1 : 1	8	RT	82		
24	Morpholine	$HC{\equiv}C{-}CH_2Br$	1 : 1	1	RT	75		
25	Morpholine	$Me(CH_2)_6Br$	1 : 1	11	RT	89		
26	1,2,3-Benzotriazole	$PhCH_2Cl$	1 : 1	28	RT	89		
27	1,2,3-Benzotriazole	$CH_2{=}CH{-}CH_2Br$	1 : 1	6	RT	93		
28	$NH_2(CH_2)_2NH_2$	$PhCH_2Cl$	1 : 5	4	60 °C	Nil	73	—
29	$NH_2(CH_2)_2NH_2$	$CH_2{=}CH\text{-}CH_2Br$	1 : 5	4	60 °C	Nil	79	—

Yields and ratio of mono : bis represent the products as obtained after column chromatographic separation.

N-alkylated anilines depending upon the conditions employed (entries 11–13). It is interesting to observe that 2-iodoaniline can afford both mono- or bis-*N*-alkylated anilines under selective conditions (entries 14–15), whereas sterically hindered aniline such as 2,4,6-tribromoaniline gave only the corresponding mono-*N*-benzylated product, when reacted with benzyl chloride (entry 16).

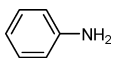
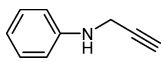
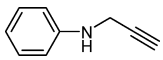
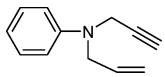
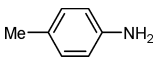
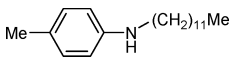
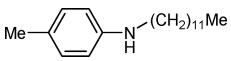
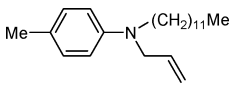
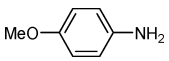
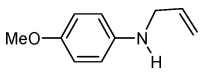
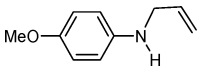
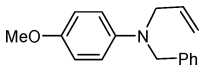
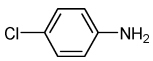
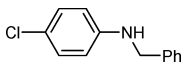
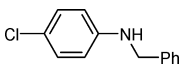
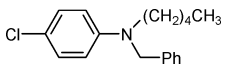
On the other hand, unactivated alkyl halides reacted with anilines to produce preferably the mono-alkylated anilines in major quantities, even after using excess alkyl halide and continuing the reaction for prolonged time (entries 17–19). Primary aliphatic amine on reaction with benzyl chloride gave bis-benzylated amine in fairly good yield, while diisopropyl amine gave the corresponding *N*-benzylated product in 52% yield only even after stirring for 40 h at room temperature (entry 21). Finally, we found that cyclic amines including benzotriazole can be alkylated easily in excellent yields, when equimolar quantities of the amine and alkyl halide were stirred on silica surface for several hours at room temperature (entries 22–27). The method was further applied successfully to aliphatic bis-amine, such as ethylene diamine and reaction with benzyl chloride or allyl bromide afforded the desired tetra-alkylated product in 73–79% yields (entries 28–29).

Selectivity of mono- and bis-alkylations under different conditions has been further broadened to synthesise unsymmetrical trialkyl/aryl amines. The results are shown in Table 3. Thus, aniline was first mono-alkylated with propargyl bromide under selective conditions, the resulting product was then treated with allyl bromide to prepare *N*-allyl-*N*-(prop-2-ynyl) benzeneamine either at room temperature (40 h) or at 55 °C for 1.5 h in 92% overall yield (Table 3, entry 1–2). Similarly, 4-toluidine was smoothly converted to *N*-benzyl-*N*-hexadecyl-4-methylbenzeneamine in 76% overall yield by stepwise selective alkylations (Table 3, entry 3–4). The procedure was further extended with 4-anisidine and 4-chloroaniline (Table 3, entries 5–8).

Subsequently, recycling of silica was examined and it was found that it could be reused without any significant loss of activity for ten cycles (tested). The silica was recovered after the reaction, washed with methanol, dried and activated for subsequent applications. The reaction was studied with 4-anisidine and benzyl chloride in molar ratios of 1 : 2.2 and the data are presented in Table 4. The *N*,*N*-dibenzyl-4-anisidine was obtained after chromatographic purification in 80–84% yield with 10–14% formation of mono-benzylated product.

Solid phase mediated reactions are generally governed by the nature and availability of the functional groups on the solid surface. Functional groups on the surface of silica are either silanol (≡SiOH) or siloxane bridges (≡SiOSi≡), and their concentrations depend greatly on the temperature of the pretreatment.[19] It is known that upon heating, silanols condense to produce siloxane bridges and higher the temperature, accessible silanol (≡SiOH) groups per nm^2 of silica surface decrease. Since silanol (≡SiOH) groups are believed to be responsible for the Lewis or Brønsted acidity of silica, partial dehydroxylation and forming more siloxane bridges (≡SiOSi≡) might result even poorer acidity of the preheated or activated silica.[20] The strength of acidity of silica has been increased by impregnating various transition

Table 3 Synthesis of unsymmetrical trialkyl/aryl amines by stepwise selective alkylations on silica (type: for tlc; particle size: –325 Mesh)

Entry	Amine	Alkyl halide	Amine : alkyl halide	Time/h	Temp.	Product	Yield[a] (%)
1			1 : 1	1.5	RT		79
2			1 : 1	40 1.5	RT 55 °C		92
3		$Me(CH_2)_{11}Br$	1 : 1	25	RT		75
4			1 : 1	35 2	RT 55 °C		76
5			1 : 1	1	RT		75
6			1 : 1	6	RT		85
7			1 : 1	1.5	RT		79
8		$CH_3(CH_2)_4Br$	1 : 1	35 24	RT 55 °C		65

[a] Yields represent the products as obtained after column chromatographic separation.

Table 4 Recycling experiments using 4-anisidine and benzyl chloride

Sl. No.	Cycle	Yield (%)[a]	
		N-benzyl-4-anisidine	*N*,*N*-dibenzyl-4-anisidine
1	0	11	84
2	1	10	82
3	2	10	80
4	3	14	81
5	4	11	83
6	5	12	82
7	6	13	80
8	7	13	82
9	8	12	80
10	9	11	83
11	10	13	81

[a] Yield represents after column chromatographic purification.

metal oxides and reported to use in *N*-alkylations.[21] However, use of commercially available silica (pH of 10% aqueous solution is ~7) for selective *N*-alkylation reactions is unique and studied for the first time. Scaling up of the process up to ten mmol of reagents is achieved without any difficulty and having similar selectivity.

Conclusion

Based on the above observations, it may be concluded that the nature of silica and the nature of alkyl halide along with temperature greatly control the overall selectivity in the alkylation of amines. Use of preheated silica and controlled access of the alkyl halide can give mono-alkylated product selectively, whereas excess use of the alkylating agent and longer reaction time favours bis-alkylations. We underline the selectivity and versatility of the method described above for the clean and selective *N*-alkylation of all classes of amines, including synthesis of unsymmetrical trialkyl/aryl amines, under mild conditions on a cheap, neutral environmentally benign and recyclable surface of silica gel.

Experimental

General procedure for mono *N*-alkylation

An equimolar mixture of an amine and alkyl halide was intimately mixed with pre-activated silica (type: used for tlc; particle size: –325 Mesh) in a mortar pestle and the solid mixture was transferred into a flask. Gentle agitation was then provided by a magnetic spin bar at room temperature. The progress of the reaction was monitored by tlc. After the reaction for the time mentioned in the Table 2, the reaction mixture was washed repeatedly with diethyl ether and combined ethereal layer was dried over anhydrous Na_2SO_4 and concentrated. The crude product was then purified by column chromatography over silica gel. The purified products were identified on the basis of ^1H and ^{13}C NMR spectra, and/or by comparison with the data reported in the literature.

A similar procedure was also performed for bis-alkylation using the amine (1 mmol) and alkyl halide (2.2 mmol) and

stirring was continued for a longer reaction time, as shown in Table 2. After the usual work up and purification by column chromatography, the bis-alkylated products were characterised by NMR spectra.†

Acknowledgements

We are grateful to the Department of Science and Technology, New Delhi for financial support (Grant No. SR/S1/OC-49/2006). S. P. thanks CSIR, New Delhi for awarding senior research fellowship.

Notes and references

† ^{1}H and ^{13}C NMR spectral data of some selected compounds: *N*-allyl-4-methoxybenzenamine; Table 2, Entry 9: ^{1}H NMR ($CDCl_3$, δ ppm^{-1} relative to TMS): 3.65–3.84 (6H, m, $-OCH_3$, –NH, $-NCH_2$); 5.12–5.29 (2H, m, $=CH_2$); 5.89–5.98 (1H, m, =CH); 6.58 (2H, d, J = 8.7 Hz, 2 aromatic proton); 6.77 (2H, d, J = 8.7 Hz, 2 aromatic protons). ^{13}C NMR ($CDCl_3$, δ ppm^{-1}): 47.6 ($-NCH_2$); 55.8 ($-OCH_3$); 114.4 (2 =CH, 2 aromatic carbon); 114.9 (2 =CH, 2 aromatic carbon); 116.2 (=CH); 135.8 ($=CH_2$); 142.3 (>C<); 152.3 (>C<). *N*,*N*-diallyl-4-methoxybenzenamine; Table 2, Entry 9: ^{1}H NMR ($CDCl_3$, δ ppm^{-1} relative to TMS): 3.74 (3H, s, OCH_3); 3.85 (4H, d, J = 4.8 Hz, $2CH_2N$–); 5.12–5.20 (4H, m, 2 $=CH_2$); 5.90–5.78 (2H, m, 2 =CH); 6.69 (2H, d, J = 6.9 Hz, 2 aromatic protons); 6.79 (2H, d, J = 6.9 Hz, 2 aromatic protons). ^{13}C NMR ($CDCl_3$, δ ppm^{-1}): 53.6 ($2CH_2N$–); 55.7 (OCH_3); 114.5 (2 $=CH_2$); 114.6 (2 =CH aromatic); 116.1 (2 =CH aromatic); 134.6 (2 =CH); 143.5 (>C<); 151.5 (>C<). 1-Benzyl-1H-benzo[d][1,2,3]triazole; Table 2, Entry 27: ^{1}H NMR ($CDCl_3$, δ ppm^{-1} relative to TMS): 5.82 (2H, s, $-CH_2$); 7.25–7.41 (8H, m, aromatic proton); 8.05 (1H, d, J = 7.8 Hz, aromatic proton). ^{13}C NMR ($CDCl_3$, δ ppm^{-1}): 52.2 (CH_2); 109.7 (=CH); 120.0 (=CH); 123.9 (=CH); 127.4 (=CH, aromatic); 127.6 (2 =CH); 128.4 (=CH); 128.9 (2 =CH); 132.8 (=C); 134.8 (=C); 146.3 (=C). N^1,N^1,N^2,N^2-tetraallylethane-1,2-diamine; Table 2, Entry 29: ^{1}H NMR ($CDCl_3$, δ ppm^{-1} relative to TMS): 2.57 (4H, s, $2CH_2$); 3.10 (8H, d, J = 6.6 Hz, $4CH_2$); 5.12–5.19 (8H, m, 4 $=CH_2$); 5.79–5.92 (4H, m, 4 =CH). ^{13}C NMR ($CDCl_3$, δ ppm^{-1}): 50.6 ($2CH_2$); 57.3 ($4CH_2$); 117.7 (4 $=CH_2$); 135.5 (4 =CH). *N*-(prop-2-ynyl) benzeneamine; Table 3, Entry 1: ^{1}H NMR ($CDCl_3$, δ ppm^{-1} relative to TMS): 2.21 (1H, s, ≡CH); 3.93 (2H, s, $-NCH_2$); 4.12 (1H, s, –NH); 6.67–6.81 (3H, m, 3 aromatic proton); 7.19–7.24 (2H, m, 2 aromatic proton). ^{13}C NMR ($CDCl_3$, δ ppm^{-1}): 33.6 ($-NCH_2$); 71.3 (≡CH); 81.0 (>C<); 113.5 (2 =CH, 2 aromatic carbon); 118.7 (=CH, aromatic carbon); 129.2 (2 =CH, 2 aromatic carbon); 146.8 (>C<). *N*-allyl-*N*-(prop-2-ynyl) benzeneamine; Table 3, Entry 2: ^{1}H NMR ($CDCl_3$, δ ppm^{-1} relative to TMS): 2.24 (1H, s, ≡CH); 3.49 (2H, d, J = 6.6 Hz, $-CH_2C$=); 3.88 (2H, s, $-NCH_2C$≡); 5.11–5.06 (2H, m, $=CH_2$); 5.95–6.10 (1H, m, =CH); 7.10–7.32 (5H, m, 5 aromatic protons). ^{13}C NMR ($CDCl_3$, δ ppm^{-1}): 34.9 ($-NCH_2C$≡); 42.5 ($-CH_2C$=); 72.9 (≡CH); 79.4 (–*C*≡CH); 115.8 (2 =CH, 2 aromatic carbon); 122.5–130.3 (aromatic carbons); 135.9 (=CH); 137.6 (=CH, aromatic carbon); 148.2 (>C<). *N*-dodecyl-4-methylbenzenamine; Table 3, Entry 3: ^{1}H NMR ($CDCl_3$, δ ppm^{-1} relative to TMS): 0.87 (3H, d, J = 7.2 Hz, CH_3); 1.26 (18H, s, 9 CH_2); 1.57 (2H, t, J = 6.6 Hz, CH_2); 2.23 (3H, s, aromatic CH_3); 3.04 (2H, t, J = 7.2 Hz, $-NCH_2$); 3.35 (1H, br s, –NH); 6.51 (2H, d, J = 8.1 Hz, 2 aromatic proton); 6.95 (2H, d, J = 7.8 Hz, 2 aromatic proton). ^{13}C NMR ($CDCl_3$, δ ppm^{-1}): 14.1 ($-CH_3$); 20.4 ($-CH_2CH_3$); 22.7 ($-CH_3$, aromatic); 27.3–29.7 ($-CH_2$, aliphatic carbons); 31.9 ($-CH_2$, aliphatic); 44.4 ($-NCH_2$); 112.9 (2 =CH, aromatic carbons); 126.2 (>C<); 129.7 (2 =CH, aromatic carbons); 146.3 (>C<). *N*-allyl-*N*-dodecyl-4-methylbenzenamine; Table 3, Entry 4: ^{1}H NMR ($CDCl_3$, δ ppm^{-1} relative to TMS): 0.86–1.26 (23H, m, aliphatic CH_2, CH_3); 2.23 (3H, s, CH_3, aromatic); 3.24 (2H, t, J = 7.5 Hz, $-NCH_2$); 3.87 (2H, d, J = 4.8 Hz, $-NCH_2$); 5.10–5.17 (2H, m, $=CH_2$); 5.72–5.98 (1H, m, =CH); 6.59 (2H, d, J = 8.4 Hz, 2 aromatic proton); 7.01 (2H, d, J = 8.4 Hz, 2 aromatic proton). ^{13}C NMR ($CDCl_3$, δ ppm^{-1}): 14.2 ($-CH_3$, aliphatic); 20.2 ($-CH_2CH_3$); 22.7 ($-CH_3$, aromatic); 27.2–31.9 ($-CH_2$, aliphatic carbons); 51.0 ($-NCH_2$); 53.4 ($-NCH_2$); 112.3 (2 =CH, aromatic carbon); 115.7 ($=CH_2$, allylic); 124.8 (>C<, aromatic); 129.6 (2 =CH, aromatic carbon); 134.6 (=CH); 146.3 (>C<, aromatic). *N*-allyl-*N*-benzyl-4-methoxybenzenamine; Table 3, Entry 6: ^{1}H NMR ($CDCl_3$, δ ppm^{-1} relative to TMS): 3.73 (3H, s, OCH_3); 3.93 (2H, d, J = 4.5 Hz, $-NCH_2$); 4.46 (2H, s, $-NCH_2$); 5.18 (2H, t, J = 8.4 Hz, $=CH_2$); 5.83–5.92 (1H, m, =CH); 6.68 (2H, d, J = 9 Hz, 2 =CH, 2 aromatic proton); 6.78 (2H, d, J = 9 Hz, 2 =CH, 2 aromatic proton); 7.23–7.33 (5H, m, 5 aromatic protons). ^{13}C NMR ($CDCl_3$, δ ppm^{-1}): 53.8 ($-NCH_2$); 54.9 ($-NCH_2Ph$); 55.7 (OCH_3); 114.4–116.4 (aromatic carbons); 126.8–128.5 (aromatic carbons); 134.2 (=CH, aliphatic); 139.3 (>C<, aromatic); 143.6 (>C<, aromatic); 151.6 (>C<, aromatic). *N*-benzyl-4-chlorobenzenamine; Table 3, Entry 7: ^{1}H NMR ($CDCl_3$, δ ppm^{-1} relative to TMS): 3.96 (1H, br s, NH); 4.19 (2H, s, $-NCH_2Ph$); 6.44 (2H, d, J = 8.7 Hz, 2 =CH, 2 aromatic proton); 7.04 (2H, d, J = 8.7 Hz, 2 =CH, 2 aromatic proton); 7.10–7.27 (5H, m, 5 aromatic proton). ^{13}C NMR ($CDCl_3$, δ ppm^{-1}): 48.2 ($-NCH_2$); 113.8 (2 =CH, 2 aromatic carbon); 121.9 (>C<); 127.3–129.0 (aromatic carbons); 138.9 (>C<); 146.6 (>C<). *N*-benzyl-4-chloro-*N*-pentylbenzenamine; Table 3, Entry 8: ^{1}H NMR ($CDCl_3$, δ ppm^{-1} relative to TMS): 0.89 (3H, d, J = 6.9 Hz, CH_3); 1.31 (4H, s, 2 $-CH_2$); 1.61 (2H, s, CH_2); 3.35 (2H, t, J = 7.5 Hz, $-NCH_2$); 4.51 (2H, s, $-CH_2Ph$); 6.56 (2H, d, J = 8.1 Hz, 2 aromatic proton); 7.09 (2H, d, J = 8.4 Hz, 2 aromatic proton); 7.17–7.30 (5H, m, 5 aromatic proton). ^{13}C NMR ($CDCl_3$, δ ppm^{-1}): 14.1 ($-CH_3$); 22.6 ($-CH_2$ CH_3); 26.7 ($-CH_2CH_2CH_3$); 29.3 ($-CH_2CH_2CH_2CH_3$); 51.6 ($-NCH_2CH_2$); 54.6 ($-NCH_2Ph$); 113.1–138.6 (aromatic carbons).

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