Carbon Dioxide: A Reagent for the Simultaneous Protection of Nucleophilic Centers and the Activation of Alternative Locations to Electrophilic Attack. 17.[1] Substitution of *N*-Methyl-1- and *N*-Methyl-2-naphthylamine and Side-Chain Functionalization of *o*-Toluidine

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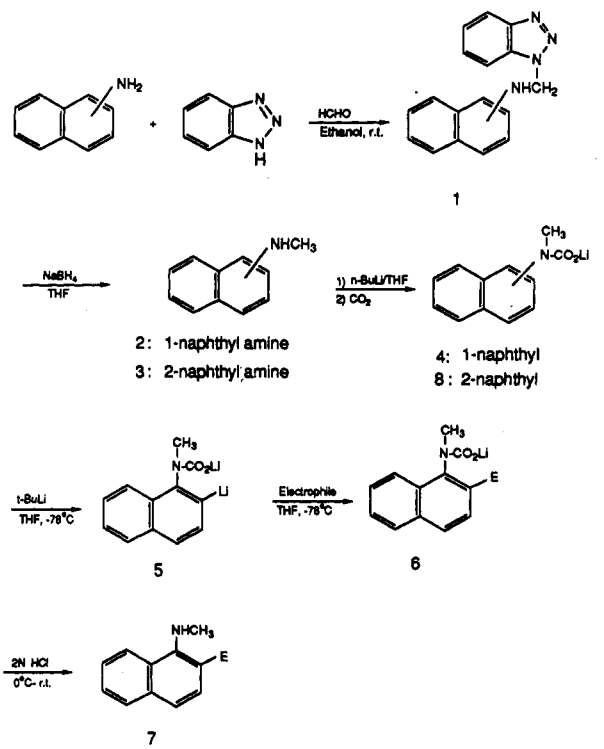
N-Methyl-1-naphthylamine is readily converted into a range of 2-substituted derivatives in one-pot sequences, using carbon dioxide for NH protection. Similarly, *N*-methyl-2-naphthylamine yields 3-substituted derivatives in the first direct preparation of 2,3-disubstituted naphthalenes. The intermediate lithium carbamates are further lithiated by *tert*-butyllithium at the 2-position for *N*-methyl-1-naphthylamine and at the 3-position for *N*-methyl-2-naphthylamine and then reacted with an electrophile; the products undergo acid-catalyzed decarboxylation during workup. *o*-Toluidine is converted into its methyl-functionalized derivatives in a similar way, except that 2 equiv of *tert*-butyllithium are used for the further lithiation of the intermediate lithium carbamate.

The preparation and further elaboration of amines is of considerable importance in organic synthesis and in medicinal chemistry. Synthetic equivalents of amine carbanions have become of increasing importance in the functionalization of amines by electrophilic substitution in the last decade.[2-6] However, most of these methods require three individual operations: protection, substitution, and deprotection. Furthermore, a number of functionalities commonly used to protect NH groups, such as amides and carbamates, are not suitable in carbanionic systems because of their susceptibility to nucleophilic attack. This problem can be partly overcome by the use of more hindered derivatives, but then the compounds usually require much harsher conditions for removing the protecting group.

Ortho-substituted aromatic amines are important starting materials for heterocyclic compounds and pharmaceuticals.[7] Available methods for the regiospecific ortho-functionalization of primary and secondary aromatic amines include the reaction of anilinodichloroborane with electrophiles,[8] heteroatom facilitated dilithiation of aromatic amines followed by electrophilic substitution,[9] and the lithiation of N-protected aromatic amines followed by reaction with electrophiles.[10] In recent contributions from our laboratory, carbon dioxide has been successfully used as an easily introduced and removed protecting group in such reactions. This one-pot synthetic sequence has been applied to the conversion of *N*-alkylanilines into ortho-substituted *N*-alkylanilines,[11] to the α-functionalization of benzylamine and benzyl alcohol,[12] to the side-chain elaboration of *N*-methyl-*o*-toluidine[1] and 2-methylindole,[13] and to the preparation of 4-substituted 2-pyridone.[14]

Scheme I[a]



[a] Electrophile: Ph_2CO, $3\text{-}CH_3C_6H_4CHO$, $(CH_3)_2CHCHO$, $PhCH_2Br$, *t*-BuNCO.

We have now studied the lithiation of *N*-methyl-1-naphthylamine (**2**), *N*-methyl-2-naphthylamine (**3**), and *o*-toluidine (**12**) as a further exploration of the scope of our protection methodology. A particular goal of this study

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Table I. Preparation of 2-Substituted *N*-Methyl-1-Naphthylamines 7, 3-Substituted *N*-Methyl-2-naphthylamines 11, and Side-Chain Substituted *o*-Toluidines 12

compd	electrophile	substituent (E)	yield (%)	mp (°C)	solvent
7a	Ph_2CO	$Ph_2C(OH)$	61	151–152	ethanol
7b	$(CH_3)_2CHCHO$	$(CH_3)_2CHCHOH$	52	oil	
7c	*m*-$CH_3C_6H_4CHO$	*m*-$CH_3C_6H_4CHOH$	56	102–104	ethanol
7d	*t*-BuNCO	*t*-BuNHCO	51	96–98	hexane
7e	$PhCH_2Br$	$PhCH_2$	48	oil	
11a	Ph_2CO	$Ph_2C(OH)$	18	160–162	ethanol
11b	*p*-$CH_3C_6H_4CHO$	*p*-$CH_3C_6H_4CHOH$	17	124–126	ethanol
11c	*t*-BuNCO	*t*-BuNHCO	14	156–158	hexane
11d	$PhCH_2Br$	$PhCH_2$	25	87–89	hexane
16a	Ph_2CO	$Ph_2C(OH)$	58	119–121	ethanol
16b	*p*-$CH_3C_6H_4CHO$	*p*-$CH_3C_6H_4CHOH$	59	105–106	EtOH/hexane
16c	$(CH_3)_2CHCHO$	$(CH_3)_2CHCHOH$	48	oil	
16d	CH_3I	CH_3	50	oil[a]	
17	*t*-BuNCO		51	174–175	hexane

[a] Lit.[21] bp 209–210 °C (760 mmHg); its ^1H NMR spectrum is consistent with the reported data.[22]

is the evaluation of the regioselectivity of carbon dioxide protective lithiation. For lithium carbamates derived from *N*-monoalkylnaphthylamines there are two possible positions for the C-lithiation, i.e., the 2- and 8-positions for *N*-methyl-1-naphthylamine and the 1- and 3-positions for *N*-methyl-2-naphthylamine. We wished also to discover if our CO_2-protection technique could be extended from the secondary aromatic amines used so far to primary aromatic amines.

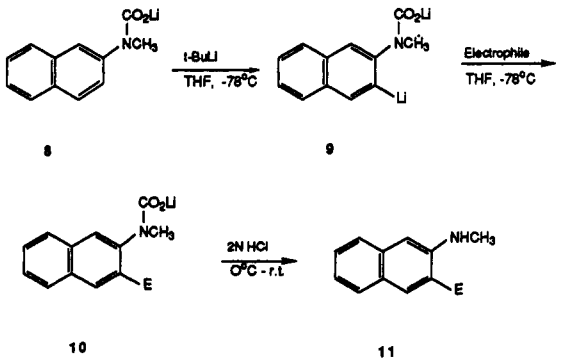
Results and Discussion

N-Methylation of Naphthylamines. The starting materials, *N*-methyl-1-naphthylamine (2) and *N*-methyl-2-naphthylamine (3), were prepared by the benzotriazole facilitated N-methylation[1,15] of the corresponding primary naphthylamines. Reaction of 1- or 2-naphthylamine, benzotriazole, and formaldehyde in ethanol at 20 °C afforded the corresponding *N*-(benzotriazol-1-ylmethyl)-naphthylamines (1), in nearly quantitative yields, which were then reduced by $NaBH_4$ in THF to give *N*-methyl-1-naphthylamine (2) and *N*-methyl-2-naphthylamine (3) in good yields (Scheme I).

Substitution of *N*-Methyl-1-naphthylamine and *N*-Methyl-2-naphthylamine. Substitution of *N*-methyl-1-naphthylamine was achieved by the same one-pot procedure as that previously described.[11-14] The sequence is composed of four operations as shown in Scheme I, viz. protection, C-lithiation, reaction with electrophiles, and decarboxylation.

A variety of different electrophiles were investigated, and the results (Table I) demonstrate that electrophiles reacted readily with the dilithiated intermediate 5 and substituted *N*-methyl-1-naphthylamines were formed in moderate yields. Two aldehydes and one ketone gave the expected secondary and tertiary alcohols, an isocyanate afforded the naphthyl acid amide, and an alkyl halide produced the alkyl-substituted naphthylamine. The functionalizations were regioselective for the 2-position based on the comparison of the ^1H NMR spectra of the products with that of the starting material 2. The doublet of the C-2 proton at 6.51 ppm[16] is absent in the spectra of the products. None of the 8-substituted products, which should have different proton NMR spectra, was observed. All the products obtained, most of which have not previously been reported, were characterized by elemental analysis and by their ^1H and ^{13}C NMR spectra.

Scheme II[a]



[a] Electrophile: Ph_2CO, 4-$CH_3C_6H_4CHO$, *t*-BuNCO, $PhCH_2Br$.

The lithiation and electrophilic substitution of *N*-methyl-2-naphthylamine (3) was carried out using the same procedure, as shown in Scheme II. Four different types of electrophile were employed. The results showed that the electrophiles reacted with the lithium carbamate 9 to give 3-substituted derivatives in about 40% yields based on the ^1H NMR of the crude products. The NMR spectra of the crude products showed that traces of 1-substituted *N*-methyl-2-naphthylamines were also formed, but we were unable to isolate any of these byproducts. Thus, 3-(hydroxylalkyl)-2-(methylamino)naphthalenes **11a** and **11b** (from benzophenone and 4-methylbenzaldehyde, respectively), 3-(*tert*-butylcarbamoyl)-2-(methylamino)-naphthalene (**11c**; from *tert*-butyl isocyanate), and 3-benzyl-2-(methylamino)naphthalene (**11d**; from benzyl bromide) were isolated from the crude product by column chromatography (silica gel/ether–hexane). The isolated yields of **11a–d** were low because the R_f values of 3-substituted 2-(methylamino)naphthalenes and their 1-substituted analogues were too close for complete separation to be achieved.

The evidence of dominant functionalization at the 3-position of 2-(methylamino)naphthalene comes from the ^1H NMR spectra of these products. There are two singlets in the aromatic region that are easily assigned to the C-1 and C-4 protons of 2,3-disubstituted naphthalenes. All four 3-substituted 2-(methylamino)naphthalenes **11a–d** are new compounds and were characterized by their ^1H and ^{13}C NMR and MS spectra. No previous direct method for the preparation of 3-substituted derivatives from 2-(alkylamino)- or 2-(dialkylamino)naphthalenes has been reported.

Extension to Primary Aromatic Amines. Extension of the CO_2 methodology to primary aromatic amines would involve the ortho lithiation of the dilithio derivative ArN-

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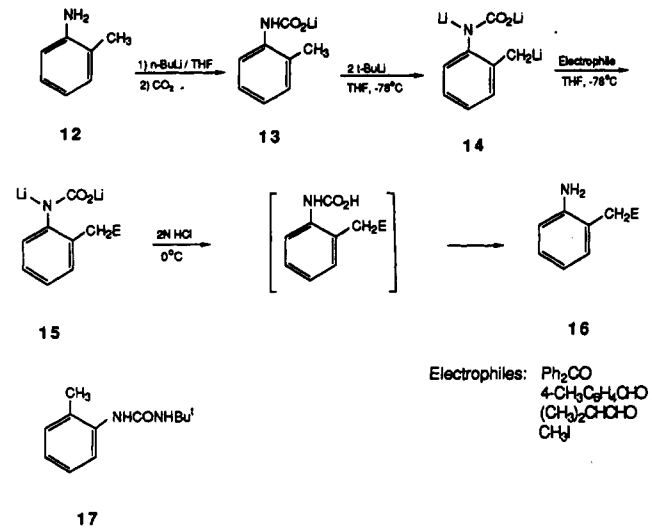
Scheme III



(Li)CO_2Li. Unfortunately, all attempts to achieve this with aniline failed. The side-chain substitution of *o*-toluidine and its analogues is an important alternative route to ortho-substituted aromatic amines and to the indole ring system.[17-19] We have recently reported that *N*-methyl-*o*-toluidine was readily converted into a range of side-chain functionalized derivatives in a one-pot sequence using carbon dioxide for N-protection. We also reported[12] that benzylamine was substituted at the α-position by lithiation of the intermediate carbamate using 2 equiv of *tert*-butyllithium, followed by reactions with various electrophiles. Considering these previous achievements, we anticipated that *o*-toluidine (**12**) would be lithiated as shown in Scheme III to allow the preparation of the side-chain-substituted *o*-toluidines **16**.

Our results showed that the carbon dioxide protection method is effective for the electrophilic substitution of *o*-toluidine at the methyl carbon. Benzophenone reacted with the trianion **14** to give the expected tertiary alcohol **16a**, *p*-methylbenzaldehyde and isobutyl aldehyde afforded secondary alcohols **16b** and **16c**, respectively, and methyl iodide produced *o*-ethylaniline (**16d**). The yields range from 48 to 59%. For these electrophiles, only products of reaction at the side-chain carbon were observed; the greater acidity of the methyl group compared to the ring protons permitted deprotonation to occur exclusively at the methyl carbon.

However, when *tert*-butyl isocyanate was used as the electrophile, a urea derivative, N^1-*tert*-butyl-N^2-(2-methylphenyl)urea (**17**) was obtained in 51% yield. Its ^{1}H NMR spectrum showed clearly a methyl resonance at 2.26 ppm instead of a methylene group as expected for side-chain substitution. The urea carbonyl resonance in the ^{13}C NMR spectrum appeared at 155.5 and the CH_3 signal at 29.2 ppm.

In summary, a range of 2-substituted *N*-methyl-1-naphthylamines and 3-substituted *N*-methyl-2- naphthylamines were synthesized in one-pot sequences by the reaction of their lithium carbamates with butyllithium as a key step. *o*-Toluidine was converted into several side-chain-substituted derivatives by a similar sequence. The present method is convenient, and the ease of introduction and removal of the N-protecting group, lithium carbamate, offers considerable advantages. The carbon dioxide protection method presently offers the easiest route to compounds of types **7**, **11**, and **16**.

Experimental Section

The ^{1}H NMR spectra were recorded at 300 MHz and the ^{13}C spectra at 75 MHz in $CDCl_3$ unless otherwise stated. Tetrahydrofuran (THF) was dried by refluxing with benzophenone and sodium and used directly after distillation under dry nitrogen. Carbon dioxide gas was dried by passage through anhydrous calcium sulfate.

***N*-(Benzotriazol-1-ylmethyl)-1-naphthylamine (1a).** A mixture of benzotriazole (29.8 g, 0.25 mol) and 1-naphthylamine(35.8 g, 0.25 mol) in ethanol (500 mL) was stirred continuously until completely dissolved, and aqueous formaldehyde (37% aqueous, 0.25 mol) was added at 25 °C. A white solid separated overnight and was collected by filtration, washed with ethanol, and dried (95% yield): mp 156–158 °C; ^{1}H NMR (DMSO-d_6) δ 8.20 (d, J = 9 Hz, 1 H), 8.15 (d, J = 8.1 Hz, 1 H), 7.94 (d, J = 8.1 Hz, 1 H), 7.74–7.60 (m, 2 H), 7.47–7.37 (m, 3 H), 7.30 (t, J = 8.1 Hz, 1 H), 7.25 (t, J = 7.8 Hz, 1 H), 7.17 (t, J = 8.1 Hz, 1 H), 7.01 (d, J = 7.5 Hz, 1 H), 6.29 (d, J = 6.6 Hz, 2 H, CH_2); ^{13}C NMR δ 145.7, 140.7, 133.7, 132.0, 127.8, 126.7, 125.9, 125.4, 124.3, 123.5, 122.7, 120.7, 118.8, 117.6, 110.8, 104.4, 57.2. Anal. Calcd for $C_{17}H_{14}N_4$: C, 74.45; H, 5.11; N, 20.44. Found: C, 74.13; H, 5.27; N, 20.71.

***N*-(Benzotriazol-1-ylmethyl)-2-naphthylamine (1b).** This intermediate was prepared as described for **1a**: yield 98%; mp 172–175 °C; ^{1}H NMR (DMSO-d_6) δ 8.08 (d, J = 8.4 Hz, 1 H), 7.95 (d, J = 8.4 Hz, 1 H), 7.62–7.43 (m, 5 H), 7.35–7.22 (m, 2 H), 7.15–7.07 (m, 3 H), 6.21 (d, J = 7.2 Hz, 2 H, CH_2); ^{13}C NMR δ 145.4, 143.2, 134.2, 132.0, 128.5, 127.1, 126.8, 125.9, 125.6, 123.6, 121.9, 118.8, 117.3, 110.8, 104.7, 56.9 (CH_2).

***N*-Methyl-1-naphthylamine (2).** To the benzotriazole derivative (**1a**; 27.4 g, 0.1 mole) suspended in 400 mL of freshly distilled THF was added $NaBH_4$ (8 g) over a 2-h period at 20 °C with vigorous stirring. Gas was evolved, and the solid gradually dissolved. The mixture was kept well-stirred overnight. The solvent was removed under reduced pressure and the residue poured into water and extracted with hexane (3 × 200 mL). The extract was washed with water and dried over anhydrous magnesium sulfate. The solvent was removed to give an oil, which was distilled to afford a colorless liquid (14.6 g, 89%): bp 160–165 °C (5 mmHg) [lit.[20] bp 175–176 °C (16 mmHg)].

***N*-Methyl-2-naphthylamine (3).** The procedure was the same as that for **2**: yield 80%, bp 160–163 °C (8 mmHg) [lit.[20] 165–170 °C (12 mmHg)].

General Procedure for the Carbon Dioxide Protected Lithiation. A Schlenk reactor was flushed with argon and charged with the amine (10 mmol) and THF (30 mL). The solution was cooled to −78 °C, and *n*-butyllithium (4 mL, 2.6 M *n*-hexane solution) was added dropwise. The solution was kept at −78 °C for a few minutes, and then the temperature was allowed to rise to 0 °C. Carbon dioxide gas was passed through for a few minutes, and the solvent was evaporated under reduced pressure. The argon flush was reinstated, and THF (30 mL) was added. The solution was cooled to −78 °C, and *tert*-butyllithium [7 mL (14 mL for *o*-toluidine), 1.6 M *n*-pentane solution] was added slowly. The cooling bath was changed to ice–salt, and the solution was kept at ca. −20 °C for 1 h. The mixture was cooled again to −78 °C, and the electrophile (11 mmol) in THF was added. The reaction was allowed to warm to room temperature and was stirred overnight. The solvent was removed, and aqueous hydrochloric acid (2 N) was added to the residue slowly at 0 °C. The solution was neutralized ($NaHCO_3$) and extracted with $CHCl_3$, washed with water, and dried over anhydrous $MgSO_4$. Evaporation of solvent

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(22) *The Sadtler Standard NMR Spectra*; Sadtler Research Laboratories: Philadelphia, 1973; Vol. 1, No. 111.

gave the crude product, which was purified either by recrystallization or by column chromatography.

1-(Methylamino)-2-(diphenylhydroxymethyl)naphthalene (7a): ^{1}H NMR δ 7.90 (d, J = 8.1 Hz, 1 H), 7.83 (d, J = 7.8 Hz, 1 H), 7.42–7.55 (m, 3 H), 7.20–7.35 (m, 10 H), 6.87 (d, J = 8.1 Hz, 1 H), 2.21 (s, 3 H, CH_3); ^{13}C NMR δ 147.6, 142.4, 139.4, 133.8, 130.4, 128.7, 128.2, 128.1, 127.7, 127.0, 126.4, 125.9, 123.9, 121.5, 83.3 (COH), 36.2 (CH_3). Anal. Calcd for $C_{24}H_{21}NO$: C, 84.96; H, 6.19; N, 4.13. Found: 85.17; H, 6.01; N, 4.39.

1-[1-(Methylamino)-2-naphthyl]-2-methyl-1-propanol (7b): ^{1}H NMR δ 8.00 (d, J = 8.0 Hz, 1 H), 7.71 (d, J = 7.9 Hz, 1 H), 7.40 (m, 2 H), 7.22 (d, J = 8.0 Hz, 1 H), 6.87 (d, J = 8.0 Hz, 1 H), 4.80 (br, 2 H, OH and NH), 4.38 (d, J = 7.5 Hz, 1 H, CHOH), 2.83 (s, 3 H, NCH_3), 2.00 (m, 1 H, CH), 1.10 (d, J = 7.1 Hz, 3 H, CH_3), 0.82 (d, 3 H, CH_3); ^{13}C NMR δ 143.6, 133.7, 130.9, 128.6, 127.9, 126.5, 125.1, 124.8, 123.2, 122.1, 80.1 (CHOH), 37.5, 34.5, 19.6, 19.4; HRMS calcd for $C_{15}H_{19}NO$ 229.3261, found 229.3267.

1-(Methylamino)-2-[(3-methylphenyl)hydroxymethyl]naphthalene (7c): ^{1}H NMR δ 7.95 (d, J = 8.1 Hz, 1 H), 7.67 (d, J = 7.5 Hz, 1 H), 7.32 (m, 3 H), 7.20–7.05 (m, 4 H), 6.92 (d, J = 7.8 Hz, 1 H), 5.85 (s, 1 H, CHOH), 2,48 (s, 3 H, NCH_3), 2.19 (s, 3 H, CH_3); ^{13}C NMR δ 144.0, 143.4, 137.2, 133.9, 131.6, 128.7, 128.0, 127.7, 127.3, 126.4, 125.3, 124.9, 123.0, 122.9, 122.4, 74.0 (CHOH), 36.5 (NCH_3), 21.0 (CH_3). Anal. Calcd for $C_{19}H_{19}NO$: C, 82.31; H, 6.86; N, 5.05. Found: C, 82.04; H, 6.99; H, 4.82.

2-(*N*-*tert*-Butylcarbamoyl)-1-(methylamino)naphthalene (7d): ^{1}H NMR δ 7.95 (d, J = 8.1 Hz, 1 H), 7.62 (d, J = 7.8 Hz, 1 H), 7.35 (m, 4 H), 7.10 (d, J = 7.8 Hz, 1 H), 5.40 (br, NH), 2.90 (s, 3 H, NCH_3), 1.30 (s, 9 H, t-Bu); ^{13}C NMR δ 168.4 (CONH), 147.8, 136.1, 128.9, 128.3, 127.4, 126.0, 125.6, 123.9, 122.1, 121.9, 51.6 (CMe_3), 38.0 (NCH_3), 29.3. Anal. Calcd for $C_{16}H_{20}N_2O$: C, 75.00; H, 7.81; N, 10.94. Found: C, 74.60; H, 8.03; N, 10.58.

2-Benzyl-*N*-methyl-1-naphthylamine (7e): ^{1}H NMR δ 8.25 (d, J = 8.0 Hz, 1 H), 7.82 (d, J = 7.8 Hz, 1 H), 7.58–7.20 (m, 8 H), 7.08 (d, J = 7.9 Hz, 1 H), 4.22 (s, 2 H, CH_2), 2.90 (s, 3 H, NCH_3); ^{13}C NMR δ 150.1, 138.7, 134.8, 129.1, 128.4, 128.3, 128.1, 126.9, 126.0, 125.7, 125.3, 123.7, 123.1, 115.5, 61.4 (CH_2), 41.6 (CH_3); HRMS calcd for $C_{18}H_{18}N$ (M^+ + 1) 248.1439, found 248.1431.

3-(Diphenylhydroxymethyl)-2-(methylamino)naphthalene (11a): ^{1}H NMR δ 7.69 (d, J = 8.0 Hz, 1 H), 7.45 (d, J = 8.0 Hz, 1 H), 7.39–7.14 (m, 2 H), 7.26 (s, 10 H), 7.01 (s, 1 H), 6.91 (s, 1 H), 2.76 (s, 3 H, NCH_3); ^{13}C NMR δ 145.6, 145.3, 134.6, 134.2, 129.6, 128.1, 128.0, 127.8, 127.5, 126.9, 126.6, 125.5, 122.8, 107.6, 82.7 (COH), 30.9 (CH_3); MS m/z 339 (M^+, 21), 320 (100), 244 (45), 77 (25). Anal. Calcd for $C_{24}H_{21}NO$: C, 84.94; H, 6.19; N. 4.11. Found: C, 84.26; H, 6.35; N, 3.94.

2-(Methylamino)-3-[(4-methylphenyl)hydroxymethyl]naphthalene (11b): ^{1}H NMR δ 7.65 (d, J = 8.1 Hz, 1 H), 7.60 (d, J = 8.0 Hz, 1 H), 7.42 (s, 1 H), 7.36 (t, J = 8.0 Hz, 1 H), 7.27 (d, J = 7.9 Hz, 2 H), 7.19 (t, J = 8.0 Hz, 1 H), 7.16 (d, J = 7.8 Hz, 2 H), 6.87 (s, 1 H), 5.96 (s, 1 H, C*H*OH), 2.82 (s, 3 H, NCH_3), 2.31 (s, 3 H, CH_3); ^{13}C NMR δ 145.7, 138.5, 137.5, 134.9, 129.9, 129.3, 127.8, 126.6, 126.5, 126.4, 125.6, 122.1, 122.0, 104.9, 75.1 (CH), 30.6 (NCH_3), 21.3 (CH_3); MS m/z 277 (M^+, 33), 258 (M – H_2O, 56), 244 (100), 122 (21). Anal. Calcd for $C_{19}H_{18}NO$: C, 82.31; H, 6.86; N, 5.05. Found: C, 81.89; H, 6.99; N, 4.84.

3-(*N*-*tert*-Butylcarbamoyl)-2-(methylamino)naphthalene (11c): ^{1}H NMR δ 7.76 (s, 1 H), 7.62 (d, J = 8.0 Hz, 1 H), 7.60 (d, J = 8.1 Hz, 1 H), 7.38 (t, J = 7.9 Hz, 1 H), 7.17 (t, J = 8.0 Hz, 1 H), 6.80 (s, 1 H), 6.05 (br, 1 H, NH), 2.90 (s, 3 H, NCH_3), 1.55 (s, 9 H, t-Bu); ^{13}C NMR δ 169.2 (CO), 146.5, 136.4, 128.7, 128.1, 127.7, 127.5, 125.6, 125.2, 122.0, 104.1, 51.8 (C), 30.1 (NCH_3), 28.8 (CH_3); MS m/z 256 (M^+, 90), 200, 183 (M^+ – $BuNH_2$, 100), 155 (M^+ – BuNHCO, 83). Anal. Calcd for $C_{16}H_{20}N_2O$: C, 75.00; H, 7.81; N, 10.94. Found: C, 75.38; H, 7.84; N, 10.73.

3-Benzyl-*N*-methyl-2-naphthylamine (11d): ^{1}H NMR δ 7.75–7.68 (m, 2 H), 7.39–7.03 (m, 8 H), 6.95 (s, 1 H), 4.62 (s, 2 H, CH_2), 3.05 (s, 3 H, NCH_3); ^{13}C NMR δ 147.7, 138.8, 135.1, 128.9 128.6, 128.5, 128.3, 127.5, 126.9, 126.2, 125.9, 122.0, 116.2, 56.8 (CH_2), 38.7 (CH_3); MS m/z 247 (M^+, 100), 170, 156 (27), 127, 91 (57). Anal. Calcd for $C_{18}H_{17}N$: C, 87.45; H, 6.88; N, 5.67. Found: C, 86.95; H, 7.07; N, 5.55.

2-(2-Aminophenyl)-1,1-diphenylethanol (16a): ^{1}H NMR δ 7.39 (m, 4 H), 7.29–7.19 (m, 6 H), 6.94 (t, J = 7.9 Hz, 1 H), 6.60 (d, J = 7.8 Hz, 1 H), 6.49–6.43 (m, 2 H), 3.90 (br, NH_2 and OH), 3.56 (s, 2H, CH_2); ^{13}C NMR δ 146.9, 145.8, 132.6, 127.7, 127.3, 126.7, 126.2, 122.7, 118.7, 116.8, 79.5 (COH), 43.5 (CH_2). Anal. Calcd for $C_{20}H_{19}NO$: C, 83.04; H, 6.57; N, 4.84. Found: C, 82.67; H, 6.70; N, 4.65.

2-(2-Aminophenyl)-1-(4-methylphenyl)ethanol (16b): ^{1}H NMR δ 7.23 (d, J = 7.8 Hz, 2 H), 7.12 (d, J = 7.8 Hz, 2 H), 7.04 (t, J = 7.9 Hz, 1 H), 6.95 (d, J = 7.9 Hz, 1 H), 6.70 (m, 2 H), 4.87 (X of ABX system, J_{AX} = 9.8 Hz, J_{BX} = 3.2 Hz, 1 H, CH_2CHOH), 3.50 (br, NH_2 and OH), 2.96 and 2.81 (AB of ABX system, J_{AB} = 15 Hz, 2 H, CH_2CHOH), 2.32 (s, 3 H, CH_3); ^{13}C NMR δ 145.2, 141.4, 137.1, 131.2, 129.0, 127.6, 125.5, 124.3, 119.1, 116.5, 75.4 (CHOH), 41.8 (CH_2), 21.1 (CH_3). Anal. Calcd for $C_{15}H_{17}NO$: C, 79.30; H, 7.49; N, 6.17. Found: C, 79.62; H, 7.23; N, 6.30.

1-(2-Aminophenyl)-3-methyl-2-butanol (16c): ^{1}H NMR δ 7.20–7.00 (m, 2 H), 6.85 (t, J = 7.8 Hz, 1 H), 6.61 (d, J = 7.6 Hz, 1 H), 3.85 (m, 4 H, CHOH and NH_2), 2.80 (d, J = 7.1 Hz, 2 H, CH_2), 1.80 (m, 1 H, CH), 0.98 (d, J = 7.0 Hz, 6 H, CH_3); ^{13}C NMR δ 142.0, 130.8, 127.5, 125.0, 119.5, 116.1, 78.0, 36.0, 33.8, 19.0; HRMS calcd for $C_{11}H_{17}NO$ 179.2653, found 179.2645.

***N*-*tert*-Butyl-*N'*-(2-methylphenyl)urea (17)**: ^{1}H NMR δ 7.43 (d, J = 7.8 Hz, 1 H), 7.18 (m, 2 H), 7.07 (t, J = 7.8 Hz, 1 H), 6.15 (br, 1 H, NH), 4.82 (br, 1 H, NH), 2.26 (s, 3 H, CH_3), 1.33 (s, 9 H, t-Bu); ^{13}C NMR δ 155.5, 136.6, 131.6, 130.9, 126.9, 125.2, 124.7, 50.6, 29.2, 17.9. Anal. Calcd for $C_{12}H_{18}N_2O$: C, 69.90; H, 8.74; N, 13.59. Found: C, 69.71; H, 8.95; N, 13.30.

Registry No. **1a**, 134627-19-3; **1b**, 134627-20-6; **2**, 2216-68-4; **3**, 2216-67-3; **7a**, 134627-21-7; **7b**, 134627-22-8; **7c**, 134627-23-9; **7d**, 134627-24-0; **7e**, 134627-25-1; **11a**, 134627-26-2; **11b**, 134627-27-3; **11c**, 134627-28-4; **11d**, 134627-29-5; **12**, 95-53-4; **16a**, 134627-30-8; **16b**, 134627-31-9; **16c**, 65826-92-8; **16d**, 578-54-1; **17**, 134627-32-0; Ph_2CO, 119-61-9; $(CH_3)_2CHCHO$, 78-84-2; *m*-$CH_3C_6H_4CHO$, 620-23-5; *t*-BuNCO, 1609-86-5; $PhCH_2Br$, 100-39-0; *p*-$CH_3C_6H_4CHO$, 104-87-0; CO_2, 124-38-9; benzotriazole, 95-14-7; 1-naphthylamine, 134-32-7; 2-naphthylamine, 91-59-8.