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Synthesis of N-substituted anilines *via* Smiles rearrangement

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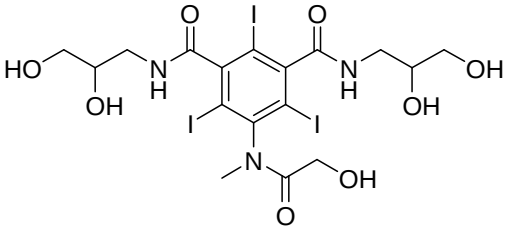
ABSTRACT

A new method for the synthesis of N - alkyl anilines from phenols is described via Smiles rearrangement. The resulting anilines are versatile intermediates for further synthetic transformations.

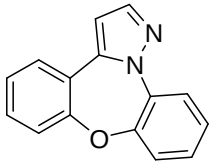
Key words: N-Alkyl aryl amines, Rearrangement, Base, N-alkyl amines.

INTRODUCTION

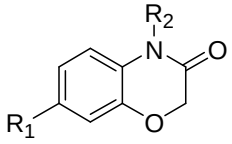
C-N bonded compounds are omnipresent in bioactive agents and the C-N bond formation continues [1] to be active area of research. The Buchwald and Hartwig [2]transition metal catalyzed C-N bond forming reaction has become one of the major reactions in the medicinal chemistry laboratories. Other efforts for C-N bond formation using Pd or Ni catalyzed coupling of phenolic derivatives are aryl sulfonates[3], ethers[4], esters[5], sulfamates[6] and carbamates[5,7].



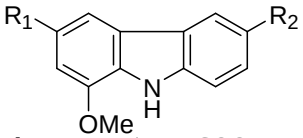
Iomeprol



dibenzo[b,f]pyrazole[1,5-d]
[1,4] oxazepines



Benzo[1,4]oxazin-3(4H)-ones

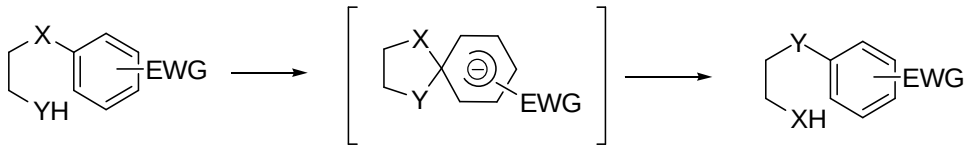


Mukonine (R1 = COOMe, R2 = H)
Calusenine (R1 = Me, R2 = OMe)
Murrayafoline (R1 = Me, R2 = H)

Figure 1. Synthetic routes Structures of Iomeprol , dibenzo [b,f] pyrazole [1,5-d][1,4] oxazepines, Benzo[1,4]oxazin-3(4H)-ones and carbazole alkaloids

Smiles rearrangement is an established procedure [8, 9d, e, j] for converting phenols to anilines (C-O bond into C-N bond). The procedure has been useful for the preparation of Iomeprol,9a (Iodinated X-ray contrast media), rare heterocyclic systems such as dibenzo [b,f] pyrazole [1,5-d] [1,4] oxazepines[9b], dibenzoxazepinones[9c], Benzo[1,4]oxazin-3(4H)-ones[9f], pyrido[1,4]thiazinone derivatives[9g] and carbazole based alkaloids such as mukonine, calusenine and murrayafoline A[9h] (Figure 1). Smiles rearrangement is also studied in combination with Ugi reaction in the creation of diversified molecules [9i].

The mechanism of this base catalyzed rearrangement is studied well and is thought to proceed via Meisenheimer complex.[10]



Scheme 1. Schematic representation of the Smiles rearrangement

N-cyclo propyl anilines are interesting compounds for the preparation of quinoline antibiotics. We used Smiles rearrangement strategy to prepare these anilines in good yields [11].

Klopman[12] et al reported N-1-tert-butyl substituted quinolines (PD 161314 and PD 161315) (Figure 2) are comparable to ciprofloxacin against *Mycobacterium avium-Mycobacterium intracellulare complex.*

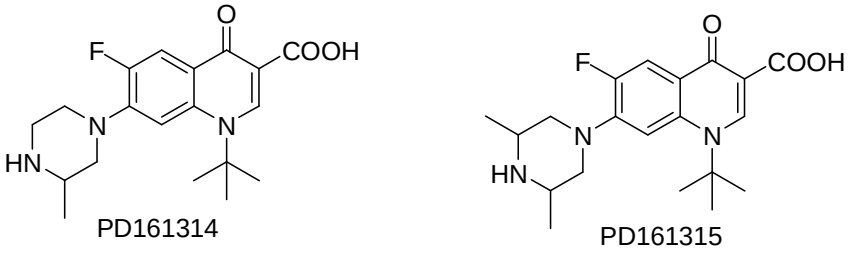


Figure 2. Structures of N-1-t-Butyl substituted Quinolines

MATERIALS AND METHODS

General: All solvents were used as commercial anhydrous grade without further purification. ^{1}H (400MHz) and ^{13}C (100MHz) NMR spectra were recorded by using a Bruker 400 Spectrometer with TMS as internal standard. IR spectra were recorded on a PerkinElmer Spectrum 100 FTIR Spectrophotometer as KBr pellets or with the neat products. Mass spectra were recorded on a API 2000 LC-MS/MS-Applied bio-Systems MDS Sciex spectrometer. Microanalysis was performed on a Perkin Elmer-240CHN elemental analyzer. Analytical TLC was conducted on E-Merck 60F254 aluminum-packed plates of silica gel (0.2mm). Developed plates were visualized by using UV light or in an iodine chamber. HPLC spectra were recorded on shimadzu 2010.

Typical procedure for the synthesis of chloro-acetamide. t-butyl amine (100.0 g, 1.36 moles) was added to a stirred solution of 5N NaOH solution (700 mL) in DCM (1 L), and the mixture was cooled to 5–10 °C. $ClCH_2COCl$ (190.0 g, 1.68 moles) was added at 5–10 °C over 1 h. The mixture was maintained at 20–25 °C for 2 h at room temperature. The compound was extracted with diethyl ether (200 mL), then washed with brine solution (200 mL), dried over anhydrous sodium sulfate (20 g), and then the solvent was evaporated under vacuum at 30 °C. The product was isolated by filtration and washed with *n*-hexane (100 mL) to give **2** as a white solid.

2-chloro-N-t-butyl acetamide (2). White solid, Yield 184 g (90%). mp 82.4-84.3°C (lit. mp 80-84°C). IR (KBr): 3309, 3079, 2980, 1684, 1553, 1253, 944, 800 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.38 (br s, 1H), 3.94 (s, 2H), 1.40 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8, 51.5, 42.7, 28.3. Mass: (m/z) 150.1 [M+1]. Anal. Calcd for $C_6H_{12}ClNO$: C, 48.17; H, 8.08; N, 9.36. Found: C, 48.18; H, 8.07; N, 9.34.

2-Chloro-N-cyclobutyl-acetamide (5). White solid; Yield: 85.5 g (90%); mp 89.5-90.8°C. IR (KBr): 3277, 2973, 2985, 1665, 1563, 1401, 1251, 951, 809, 757 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 6.66 (br s, 1H), 4.45-4.35 (m, 1H), 4.01 (s, 2H), 2.40-2.33 (m, 2H), 1.98-1.88 (m, 2H), 1.80-1.76 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 44.7, 42.4, 30.8, 14.9. Mass: (m/z) 148.1 [M+1]. Anal. Calcd for $C_6H_{10}ClNO$: C, 48.82; H, 6.83; N, 9.49. Found: C, 48.84; H, 6.79; N, 9.47.

2-Chloro-N-cyclopentyl-acetamide (8). White solid; Yield: 34 g (90%); mp 78-80°C. IR (KBr): 3283, 2964, 2873, 1652, 1561, 1241 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 6.47 (br s, 1H), 4.26-4.17 (s, 1H), 4.02 (s, 2H), 2.05-1.99 (m, 2H), 1.75-1.69 (m, 2H), 1.67-1.60 (m, 2H), 1.57-1.44 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 51.4, 42.5, 32.7, 23.5. Mass: (m/z) 162.1 [M+1]. Anal. Calcd for $C_7H_{12}ClNO$: C, 52.02; H, 7.48; N, 8.67. Found: C, 51.98; H, 7.51; N, 8.65.

2-Chloro-N-cyclohexyl-acetamide (11). White solid; Yield: 80 g (90%); mp 106.5-108.3°C (lit. mp 105-106°C). IR (KBr): 3280, 2942, 2921, 2856, 1651, 1556, 1447, 1415, 1338, 1245, 1231, 1091, 780 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 6.44 (s, 1H), 4.00 (s, 2H), 3.80-3.75 (m, 1H), 1.91-1.88 (m, 2H), 1.72-1.59 (m, 3H), 1.40-1.31 (m, 2H), 1.22-1.17 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 48.5, 42.6, 32.6, 25.2, 24.5. Mass: (m/z) 176.3 [M+1].

Typical procedure for the synthesis of amide. 4-Chloro phenol (**1a**; 9.0 g, 0.069 moles) and 2-chloro-N-t-butyl acetamide (**2**; 8.0 g, 0.053 moles) were added to a stirred soln of K_2CO_3 (20.00 g, 0.144 moles) in toluene (200 mL) at 20–25 °C. The mixture was heated at 105–110 °C for 6–8 h then the solvent was then evaporated under vacuum at 50 °C. The residue was added to 10% aq NaOH (200 mL) at 20–25 °C and the mixture was stirred for 2 h at 20–25 °C. The precipitate was isolated by filtration and washed with H_2O (20 mL) to give **3a** as a white solid.

N-tert-Butyl-2-(4-chloro-phenoxy)-acetamide (3a). White solid, yield 11.0 g (85%) [Yield based on recovered phenol **1a**] mp 120.4-121.6°C. IR (KBr): 3288, 2976, 1659, 1553, 1492, 1222, 1068, 819 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.25-7.23 (d, *J* = 8.72 Hz, 2H), 6.84-6.82 (d, *J* = 8.72 Hz, 2H), 6.29 (br s, 1H), 4.31 (s, 2H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 155.6, 129.5, 126.9, 115.9, 67.8, 51.2, 28.6. Mass: (m/z) 242.2 [M+1]. Anal. Calcd for $C_{12}H_{16}ClNO_2$: C, 59.63; H, 6.67; N, 5.79. Found: C, 59.58; H, 6.64; N, 5.74.

N-tert-Butyl-2-(naphthalen-2-yloxy)-acetamide (3b). Brown color solid; Yield: 12.5 g (92%); mp 81.6-84.5°C. IR (KBr): 3401, 2969, 1674, 1529, 1258, 1216, 845 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.80-7.73 (m, 3H), 7.49-7.45 (t, *J* = 7.42 Hz, 1H), 7.40-7.37 (t, *J* = 7.41 Hz, 1H), 7.20-7.15 (m, 2H), 6.43 (br s, 1H), 4.50 (s, 2H), 1.42 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 154.9, 134.2, 129.7, 129.3, 127.5, 126.9, 126.6, 124.2, 118.0, 107.6, 67.6, 51.2, 28.6. Mass: (m/z) 258.2 [M+1].

2-(Biphenyl-4-yloxy)-N-tert-butyl-acetamide (3c). Off-white solid; Yield: 16.1 g (85%); mp 109.8-112.4°C. IR (KBr): 3269, 3085, 2969, 1659, 1566, 1225, 1076, 761 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.57-7.55 (d, *J* = 7.31 Hz, 4H), 7.45-7.41 (t, *J* = 7.01 Hz, 2H), 7.35-7.33 (d, *J* = 6.89 Hz, 1H), 7.01-6.99 (d, *J* = 7.90 Hz, 2H), 6.41 (br s, 1H), 4.42 (s, 2H), 1.43 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 156.6, 140.2, 135.0, 128.7, 128.3, 126.8, 126.6, 114.9, 67.7, 51.2, 28.6. Mass: (m/z) 284.2 [M+1]. Anal. Calcd for $C_{18}H_{21}NO_2$: C, 76.29; H, 7.47; N, 4.94. Found: C, 76.30; H, 7.46; N, 4.89.

N-tert-Butyl-2-p-tolyloxy-acetamide (3d). Off-white solid; Yield: 10.0 g (85%); mp 96.8-98.0°C (lit. 98°C). IR (KBr): 3285, 2974, 1655, 1557, 1510, 1228, 1214, 1074, 809 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.10-7.08 (d, *J* = 7.44 Hz, 2H), 6.81-6.79 (d, *J* = 7.48 Hz, 2H), 6.38 (br s, 1H), 4.32 (s, 2H), 2.28 (s, 3H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3, 155.0, 131.2, 130.0, 114.4, 51.0, 28.6, 20.3. Mass: (m/z) 222.2 [M+1].

N-tert-Butyl-2-phenoxy-acetamide (3e). White solid; Yield: 16.0 g (82%); mp 57.6-59.4°C. IR (KBr): 3275, 3090, 2966, 1660, 1563, 1219, 1084, 754 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.34-7.30 (t, *J* = 7.88 Hz, 2H), 7.04-7.01 (t, *J* = 7.32 Hz, 1H), 6.93-6.91 (d, *J* = 8.16 Hz, 2H), 6.37 (br s, 1H), 4.36 (s, 2H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 157.1, 129.6, 121.9, 114.6, 67.6, 51.1, 28.6. Mass: (m/z) 208.3 [M+1].

N-tert-Butyl-2-(3-chloro-phenoxy)-acetamide (3f). Off-white solid; Yield: 16.0 g (97%); mp 76.4-78.0°C. IR (KBr): 3275, 3085, 2967, 1659, 1479, 1226, 1084 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.23-7.19 (t, *J* = 8.06 Hz, 1H), 6.99-6.97 (d, *J* = 7.75 Hz, 1H), 6.91 (s, 1H), 6.79-6.77 (d, *J* = 7.52 Hz, 1H), 6.28 (s, 1H), 4.33 (s, 2H), 1.38 (s,

9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 157.7, 135.0, 130.4, 122.1, 115.4, 112.7, 67.6, 51.2, 28.6. Mass: (m/z) 242.2 [M+1]. Anal. Calcd for $C_{12}H_{16}ClNO_2$: C, 59.63; H, 6.67; N, 5.79. Found: C, 59.61; H, 6.69; N, 5.78.

N-tert-Butyl-2-(3-methoxy-phenoxy)-acetamide (3g). White solid; Yield:10.5 g (82%); mp 52.1-54.6°C. IR (KBr): 3313, 3076, 2967, 1677, 1603, 1154, 1044, 764 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-7.16 (m, 1H), 6.59-6.56 (dd, *J* = 1.64, 1.71 Hz, 1H), 6.52-6.47 (m, 2H), 6.34 (br s, 1H), 4.35 (s, 2H), 3.80 (s, 3H), 1.42 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 160.8, 158.3, 130.1, 107.5, 106.6, 101.2, 67.6, 55.2, 51.1, 28.6. Mass: (m/z) 238.2 [M+1]. Anal. Calcd for $C_{13}H_{19}NO_3$: C, 65.80; H, 8.07; N, 5.90. Found: C, 65.81; H, 8.05; N, 5.87.

2-(3-Bromo-phenoxy)-N-tert-butyl-acetamide (3h). Brown color solid; Yield: 13.0 g (85%); mp 76.4-78.1°C. IR (KBr): 3273, 3085, 2968, 1659, 1565, 1476, 1224, 1082, 940 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20-7.14 (m, 2H), 7.10 (s, 1H), 6.86-6.83 (m, 1H), 6.28 (br s, 1H), 4.33 (s, 2H), 1.41 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 157.7, 130.7, 125.1, 122.9, 118.3, 113.1, 67.6, 51.2, 28.6. Mass: (m/z) 288.2 [M+1]. Anal. Calcd for $C_{12}H_{16}BrNO_2$: C, 50.37; H, 5.64; N, 4.89. Found: C, 50.36; H, 5.66; N, 4.87.

N-tert-Butyl-2-(naphthalen-1-yloxy)-acetamide (3i). Brown color solid; Yield: 12.5 g (92%); mp 110.0-112.5°C. IR (KBr): 3420, 3266, 3089, 2970, 1662, 1570, 1273, 1230, 768 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19-8.17 (m, 1H), 7.86-7.83 (m, 1H), 7.55-7.50 (m, 3H), 7.40-7.36 (t, *J* = 7.91 Hz, 1H), 6.82-6.80 (d, *J* = 7.58 Hz, 1H), 6.50 (br s, 1H), 4.58 (s, 2H), 1.44 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 152.8, 134.5, 127.7, 126.5, 125.7, 125.6, 125.1, 121.6, 121.0, 105.7, 68.0, 51.2, 28.7. Mass: (m/z) 258.3 [M+1]. Anal. Calcd for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.44. Found: C, 74.71; H, 7.41; N, 5.42.

N-tert-Butyl-2-(4-fluoro-phenoxy)-acetamide (3j). White color solid; Yield: 11.5 g (96%); mp 76.6-77.8°C. IR (KBr): 3272, 3077, 2977, 1659, 1559, 1505, 1200, 1070, 821 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02-6.98 (t, *J* = 8.52 Hz, 2H), 6.88-6.84 (m, 2H), 6.32 (br s, 1H), 4.33 (s, 2H), 1.42 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 158.9, 156.5, 153.2, 115.7, 68.3, 51.1, 28.6. Mass: (m/z) 226.2 [M+1]. Anal. Calcd for $C_{12}H_{16}FNO_2$: C, 63.98; H, 7.16; N, 6.22. Found: C, 63.89; H, 7.18; N, 6.18.

N-Cyclobutyl-2-(naphthalen-2-yloxy)-acetamide(6a). Off-white color solid; Yield: 1.45 g (84%); mp 118.1-122.9°C. IR (KBr): 3274, 2969, 1650, 1542, 1258, 1216, 842 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81-7.74 (m, 3H), 7.49-7.46 (t, *J* = 7.45 Hz, 1H), 7.41-7.37 (t, *J* = 7.41 Hz, 1H), 7.22-7.19 (dd, *J* = 2.30, 2.34 Hz, 1H), 7.156-7.152 (d, *J* = 1.79 Hz, 1H), 6.72 (br s, 1H), 4.58 (s, 2H), 4.55-4.49 (m, 1H), 2.42-2.36 (m, 2H), 1.97-1.92 (m, 2H), 1.78-1.72 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 154.9, 134.1, 129.8, 129.3, 127.5, 126.9, 126.6, 124.2, 117.9, 107.5, 67.2, 44.1, 31.0, 15.0. Mass: (m/z) 256.3 [M+1]. Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.24; H, 6.69; N, 5.48.

2-(Biphenyl-4-yloxy)-N-cyclobutyl-acetamide (6b). White color solid; Yield: 1.60 g (84%); mp 160.1-162.3°C. IR (KBr): 3278, 2976, 2941, 1651, 1543, 1248, 1071, 764 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.55 (m, 4H), 7.45-7.41 (t, *J* = 7.60 Hz, 2H), 7.35-7.31 (t, *J* = 7.27 Hz, 1H), 7.02-6.99 (d, *J* = 8.62 Hz, 2H), 6.70 (br s, 1H), 4.52-4.49 (m, 1H), 4.48 (s, 2H), 2.41-2.35 (m, 2H), 1.98-1.92 (m, 2H), 1.77-1.72 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 156.6, 140.2, 135.1, 128.6, 128.3, 126.9, 126.6, 114.9, 67.3, 44.1, 31.0, 15.0. Mass: (m/z) 282.1 [M+1]. Anal. Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98. Found: C, 76.75; H, 6.78; N, 4.92.

N-Cyclobutyl-2-p-tolyloxy-acetamide (6c). White color solid; Yield: 1.26 g (85%); mp 96.8-98.3°C. IR (KBr): 3290, 2969, 2947, 1653, 1511, 1236, 1053, 811 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13-7.11 (d, *J* = 8.33 Hz, 2H), 6.83-6.81 (d, *J* = 8.4 Hz, 2H), 6.69 (br s, 1H), 4.54-4.46 (m, 1H), 4.42 (s, 2H), 2.39-2.36 (m, 2H), 2.30 (s, 3H), 1.95-1.90 (m, 2H), 1.76-1.71 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 155.0, 131.3, 130.0, 114.4, 67.4, 44.0, 30.9, 20.3, 15.0. Mass: (m/z) 220.2 [M+1]. Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39. Found: C, 71.23; H, 7.79; N, 6.40.

2-(3-Chloro-phenoxy)-N-cyclobutyl-acetamide (6d). White color solid; Yield: 1.3 g (80%); mp 68.0-70.8°C. IR (KBr): 3293, 2986, 2972, 1658, 1593, 1557, 1479, 1268, 1228, 1076, 758 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.23 (d, *J* = 8.15 Hz, 1H), 7.03-7.01 (d, *J* = 7.97 Hz, 1H), 6.96 (s, 1H), 6.83-6.80 (dd, *J* = 2.06, 2.06 Hz, 1H), 6.60 (br s, 1H), 4.52-4.46 (m, 1H), 4.43 (s, 2H), 2.40-2.35 (m, 2H), 1.96-1.91 (m, 2H), 1.77-1.72 (m, 2H). ^{13}C NMR

(100 MHz, $CDCl_3$): δ 166.4, 157.7, 135.1, 130.4, 122.3, 115.4, 112.6, 67.2, 44.1, 30.9, 15.0. Mass: (m/z) 240.3 [M+1]. Anal. Calcd for $C_{12}H_{14}ClNO_2$: C, 60.13; H, 5.89; N, 5.84. Found: C, 60.15; H, 5.84; N, 5.81.

N-Cyclobutyl-2-(naphthalen-1-yloxy)-acetamide(6e). White color solid; Yield: 1.41 g (82%); mp 90.4-93.8°C. IR (KBr): 3273, 2985, 2937, 1665, 1555, 1263, 764 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.23-8.20 (m, 1H), 7.87-7.84 (m, 1H), 7.56-7.51 (m, 3H), 7.41-7.37 (t, *J* = 4.01 Hz, 1H), 6.82-6.80 (d, *J* = 7.58 Hz, 1H), 6.73 (br s, 1H), 4.66 (s, 2H), 4.56-4.50 (m, 1H), 2.40-2.39 (m, 2H), 1.96-1.89 (m, 2H), 1.78-1.70 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 152.8, 134.5, 127.7, 126.6, 125.6, 125.6, 125.0, 121.7, 121.1, 105.7, 67.7, 44.1, 31.0, 15.0. Mass: (m/z) 256.2 [M+1]. Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.23; H, 6.68; N, 5.47.

N-Cyclopentyl-2-(naphthalen-2-yloxy)-acetamide(9a). Brown color solid; Yield: 6.0 g (90%); mp 99.5-102.6°C. IR (KBr): 3296, 2956, 2870, 1652, 1537, 1256, 1215, 1180, 835 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.80-7.74 (m, 3H), 7.49-7.46 (t, *J* = 7.6 Hz, 1H), 7.41-7.37 (t, *J* = 7.56 Hz, 1H), 7.21-7.18 (dd, *J* = 2.44, 2.40 Hz, 1H), 7.158-7.154 (d, *J* = 1.76 Hz, 1H), 6.51 (br s, 1H), 4.59 (s, 2H), 4.35-4.30 (m, 1H), 2.05-2.01 (m, 2H), 1.68-1.61 (m, 4H), 1.46-1.42 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 154.9, 134.1, 129.7, 129.3, 127.5, 126.8, 126.6, 124.2, 107.9, 89.8, 67.3, 50.6, 32.9, 23.5. Mass: (m/z) 270.2 [M+1].

2-(Biphenyl-4-yloxy)-N-cyclopentyl-acetamide (9b). White color solid; Yield: 7.0 g (96%); mp 154.3-156.0°C. IR (KBr): 3294, 2955, 2870, 1651, 1541, 1520, 1246, 761 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.56-7.54 (d, *J* = 7.18 Hz, 4H), 7.44-7.32 (m, 2H), 7.18-7.16 (d, *J* = 7.34 Hz, 1H), 7.00-6.98 (d, *J* = 7.57 Hz, 2H), 6.52 (br s, 1H), 4.50 (s, 2H), 4.33-4.31 (m, 1H), 2.04-2.02 (m, 2H), 1.68-1.64 (m, 4H), 1.45-1.44 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.5, 156.6, 140.2, 135.1, 128.6, 128.3, 126.9, 126.6, 114.9, 67.5, 50.6, 32.9, 23.5. Mass: (m/z) 296.3 [M+1]. Anal. Calcd for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17; N, 4.74. Found: C, 77.21; H, 7.15; N, 4.71.

N-Cyclopentyl-2-p-tolyloxy-acetamide (9c). White color solid; Yield: 5.5 g (95%); mp 105.5-108.0°C. IR (KBr): 3267, 2952, 2921, 2872, 1651, 1558, 1513, 1456, 1244 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.10-7.09 (d, *J* = 7.8 Hz, 2H), 6.81-6.79 (d, *J* = 7.90 Hz, 2H), 6.49 (br s, 1H), 4.42 (s, 2H), 4.31-4.26 (m, 1H), 2.29 (s, 3H), 2.01-1.99 (m, 2H), 1.67-1.60 (m, 4H), 1.44-1.41 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 155.0, 131.3, 130.0, 114.4, 67.5, 50.5, 32.8, 23.5, 20.3. Mass: (m/z) 234.2 [M+1]. Anal. Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00. Found: C, 72.11; H, 8.17; N, 5.98.

2-(3-Chloro-phenoxy)-N-cyclopentyl-acetamide(9d). Off-white color solid; Yield: 5.2 g (90%); mp 63.1-64.6°C. IR (KBr): 3295, 2964, 2869, 1659, 1593, 1552, 1480, 1227, 1099 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.25-7.21 (t, *J* = 8.14 Hz, 1H), 7.01-6.99 (d, *J* = 8.00 Hz, 1H), 6.93 (s, 1H), 6.81-6.78 (dd, *J* = 1.72, 1.88 Hz, 1H), 6.40 (br s, 1H), 4.43 (s, 2H), 4.31-4.24 (m, 1H), 2.03-1.99 (m, 2H), 1.70-1.60 (m, 4H), 1.44-1.39 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 157.7, 135.1, 130.4, 122.2, 115.4, 112.6, 67.4, 50.6, 32.9, 23.5. Mass: (m/z) 254.1 [M+1]. Anal. Calcd for $C_{13}H_{16}ClNO_2$: C, 61.54; H, 6.36; N, 5.52. Found: C, 61.47; H, 6.38; N, 5.48.

N-Cyclopentyl-2-(naphthalen-1-yloxy)-acetamide(9e). Brown color solid; Yield: 6.0 g (90%); mp 73.0-80.0°C. IR (KBr): 3292, 2945, 2864, 1651, 1554, 1242, 1108, 771 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.19-8.16 (q, 1H), 7.86-7.84 (q, 1H), 7.56-7.53 (m, 3H), 7.41-7.37 (t, *J* = 7.98 Hz, 1H), 6.83-6.81 (d, *J* = 7.56 Hz, 1H), 6.54 (br s, 1H), 4.67 (s, 2H), 4.39-4.30 (m, 1H), 2.06-2.00 (m, 2H), 1.69-1.64 (m, 4H), 1.48-1.42 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 152.8, 134.5, 127.7, 126.5, 125.6, 125.6, 125.1, 121.7, 121.0, 105.8, 67.8, 50.7, 29.9, 23.5. Mass: (m/z) 270.2 [M+1]. Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.78; H, 7.08; N, 5.18.

2-(4-Chloro-phenoxy)-N-cyclohexyl-acetamide (12a). White color solid; Yield: 12.2 g (98%); mp 122.1-124.0°C. IR (KBr): 3273, 2932, 2920, 2855, 1657, 1562, 1490, 1232, 824, 642 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.28-7.26 (d, *J* = 8.36 Hz, 2H), 6.86-6.84 (d, *J* = 8.76 Hz, 2H), 6.36 (br s, 1H), 4.43 (s, 2H), 3.90-3.81 (m, 1H), 1.93-1.91 (m, 2H), 1.73-1.66 (m, 3H), 1.40-1.36 (m, 2H), 1.22-1.16 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 115.7, 129.5, 126.9, 115.8, 67.5, 47.7, 32.8, 25.3, 24.6. Mass: (m/z) 268.1 [M+1]. Anal. Calcd for $C_{14}H_{18}ClNO_2$: C, 62.80; H, 6.78; N, 5.23. Found: C, 62.78; H, 6.81; N, 5.21.

N-Cyclohexyl-2-(naphthalen-2-yloxy)-acetamide (12b). Off-white color solid; Yield: 12.5 g (94%); mp 116.2-119.8°C. IR (KBr): 3305, 2934, 2853, 1650, 1538, 1258, 1216, 1052, 833, 745 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.80-7.77 (d, *J* = 8.42 Hz, 2H), 7.74-7.72 (d, *J* = 8.03 Hz, 1H), 7.48-7.45 (t, *J* = 7.31 Hz, 1H), 7.40-7.36 (t, *J* = 7.24

Hz, 1H), 7.20-7.18 (d, *J* = 8.82 Hz, 1H), 7.14 (s, 1H), 6.49 (br s, 1H), 4.58 (s, 2H), 3.92-3.89 (m, 1H), 1.96-1.93 (m, 2H), 1.73-1.61 (m, 3H), 1.43-1.34 (m, 2H), 1.24-1.15 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 154.9, 134.1, 129.7, 129.3, 127.5, 126.9, 126.6, 124.2, 117.9, 107.6, 67.3, 47.8, 32.9, 25.3, 24.7. Mass: (m/z) 284.2 [M+1].

2-(Biphenyl-4-yloxy)-N-cyclohexyl-acetamide (12c). Off-white color solid; Yield: 13.2 g (93%); mp 152.8-162.5°C. IR (KBr): 3296, 2932, 2853, 1652, 1539, 1487, 1243, 834, 761, 692 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.54 (d, *J* = 8.51 Hz, 4H), 7.45-7.41 (t, *J* = 7.60 Hz, 2H), 7.34-7.31 (t, *J* = 7.26 Hz, 1H), 7.01-6.99 (d, *J* = 8.62 Hz, 2H), 6.44 (br s, 1H), 4.51 (s, 2H), 3.93-3.85 (m, 1H), 1.96-1.93 (m, 2H), 1.74-1.64 (m, 3H), 1.41-1.38 (m, 2H), 1.23-1.20 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 156.6, 140.2, 135.1, 128.7, 128.3, 126.9, 126.6, 114.9, 67.4, 47.8, 32.9, 25.3, 24.7. Mass: (m/z) 310.3 [M+1]. Anal. Calcd for $C_{20}H_{23}NO_2$: C, 77.64; H, 7.49; N, 4.53. Found: C, 77.58; H, 7.50; N, 4.51.

N-Cyclohexyl-2-p-tolyloxy-acetamide (12d). White color solid; Yield: 11.0 g (94%); mp 98.1-99.6°C. IR (KBr): 3318, 2937, 2853, 1651, 1241 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12-7.10 (d, *J* = 8.30 Hz, 2H), 6.82-6.80 (d, *J* = 8.41 Hz, 2H), 6.43 (br s, 1H), 4.43 (s, 2H), 3.90-3.82 (m, 1H), 2.30 (s, 3H), 1.94-1.90 (m, 2H), 1.73-1.69 (m, 3H), 1.40-1.37 (m, 2H), 1.20-1.17 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 155.1, 131.3, 130.0, 114.4, 67.5, 47.6, 32.8, 25.3, 24.6, 20.3. Mass: (m/z) 176.3 [M+1]. Anal. Calcd for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56; N, 5.66. Found: C, 72.79; H, 8.57; N, 5.62.

N-Cyclohexyl-2-phenoxy-acetamide (12e). White color solid; Yield: 10.5 g (95%); mp 88.7-89.9°C (lit. mp 91°C). IR (KBr): 3341, 2936, 2913, 2852, 1650, 1537, 1498, 1242, 1060, 753 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.30 (t, *J* = 7.92 Hz, 2H), 7.05-7.01 (t, *J* = 7.32 Hz, 1H), 6.94-6.91 (d, *J* = 8.16 Hz, 2H), 6.43 (br s, 1H), 4.47 (s, 2H), 3.91-3.83 (m, 1H), 1.94-1.91 (m, 2H), 1.73-1.59 (m, 3H), 1.40-1.37 (m, 2H), 1.21-1.16 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 157.1, 129.6, 121.9, 114.6, 67.3, 47.7, 32.8, 25.3, 24.6. Mass: (m/z) 234.2 [M+1].

2-(3-Chloro-phenoxy)-N-cyclohexyl-acetamide(12f). White color solid; Yield: 12.0 g (98%); mp 82.8-84.5°C. IR (KBr): 3321, 2935, 2853, 1650, 1542, 1279, 1228, 1063, 767 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23-7.19 (t, *J* = 7.79 Hz, 1H), 6.99-6.97 (d, *J* = 7.62 Hz, 1H), 6.92 (s, 1H), 6.79-6.77 (d, *J* = 8.04 Hz, 1H), 6.36 (br s, 1H), 4.42 (s, 2H), 3.86-3.84 (m, 1H), 1.92-1.89 (m, 2H), 1.71-1.59 (m, 3H), 1.40-1.31 (m, 2H), 1.21-1.16 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 157.7, 135.0, 130.4, 122.1, 115.4, 112.6, 67.3, 47.7, 32.8, 25.3, 24.6. Mass: (m/z) 268.2 [M+1]. Anal. Calcd for $C_{14}H_{18}ClNO_2$: C, 62.80; H, 6.78; N, 5.23. Found: C, 62.74; H, 6.75; N, 5.21.

N-Cyclohexyl-2-(3-methoxy-phenoxy)-acetamide (12g). White color solid; Yield: 9.5 g (76 %); mp 65.4-66.4°C. IR (KBr): 3302, 2935, 2854, 1643, 1541, 1195, 1152, 1063, 852, 770 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23-7.19 (t, *J* = 8.2 Hz, 1H), 6.59-6.57 (dd, *J* = 1.84, 1.88 Hz, 1H), 6.52-6.48 (m, 2H), 6.40 (br s, 1H), 4.45 (s, 2H), 3.88-3.85 (m, 1H), 3.80 (s, 3H), 1.95-1.91 (m, 2H), 1.73-1.60 (m, 3H), 1.40-1.37 (m, 2H), 1.21-1.18 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 160.8, 158.3, 130.1, 107.5, 106.6, 101.2, 67.3, 55.2, 47.7, 32.8, 25.3, 24.6. Mass: (m/z) 264.2[M+1]. Anal. Calcd for $C_{15}H_{21}NO_3$: C, 68.42; H, 8.04; N, 5.32. Found: C, 68.43; H, 8.01; N, 5.28.

2-(3-Bromo-phenoxy)-N-cyclohexyl-acetamide (12h). Brown color solid; Yield: 11.2 g (95%); mp 90.0-92.5°C. IR (KBr): 3322, 2932, 2853, 1651, 1591, 1543, 1471, 1279, 1225, 1059, 865, 855, 766 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20-7.15 (m, 2H), 7.11 (s, 1H), 6.86-6.84 (m, 1H), 6.34 (br s, 1H), 4.44 (s, 2H), 3.91-3.82 (m, 1H), 1.94-1.91 (m, 2H), 1.73-1.61 (m, 3H), 1.40-1.37 (m, 2H), 1.20-1.17 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 157.7, 130.7, 125.1, 122.9, 118.4, 113.9, 67.4, 47.8, 32.8, 25.3, 24.6. Mass: (m/z) 312.1[M+1]. Anal. Calcd for $C_{14}H_{18}BrNO_2$: C, 53.86; H, 5.81; N, 4.49. Found: C, 53.79; H, 5.78; N, 4.46.

N-Cyclohexyl-2-(naphthalen-1-yloxy)-acetamide (12i). Brown color solid; Yield: 12.5 g (94%); mp 121.1-123.8°C. IR (KBr): 3343, 2929, 2849, 1652, 1239, 1107, 790, 765 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20-8.18 (m, 1H), 7.86-7.83 (m, 1H), 7.55-7.50 (m, 3H), 7.40-7.36 (t, *J* = 7.95 Hz, 1H), 6.82-6.80 (d, *J* = 7.64 Hz, 1H), 6.52-6.51 (d, *J* = 6.51 Hz, 1H), 4.67 (s, 2H), 3.96-3.88 (m, 1H), 1.96-1.93 (m, 2H), 1.73-1.69 (m, 3H), 1.42-1.38 (m, 2H), 1.24-1.16 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 152.8, 134.5, 127.7, 126.5, 125.6, 125.6, 125.1, 121.7, 121.0, 105.7, 67.8, 47.7, 32.8, 25.3, 24.6. Mass: (m/z) 284.2 [M+1]. Anal. Calcd for $C_{18}H_{21}NO_2$: C, 76.29; H, 7.47; N, 4.94. Found: C, 76.27; H, 7.45; N, 4.89.

N-Cyclohexyl-2-(4-fluoro-phenoxy)-acetamide (12j). White color solid; Yield: 11.0 g (96%); mp 77.7-78.7°C. IR (KBr): 3280, 2935, 2853, 1653, 1562, 1509, 1447, 1455, 1246, 1223, 1214, 1101, 828 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.03-6.99 (t, *J* = 8.58 Hz, 2H), 6.88-6.85 (m, 2H), 6.38 (br s, 1H), 4.42 (s, 2H), 3.90-3.82 (m, 1H), 1.94-1.91 (m, 2H), 1.73-1.70 (m, 3H), 1.40-1.37 (m, 2H), 1.23-1.15 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 159.0, 116.2, 153.2, 115.7, 68.0, 47.7, 32.8, 25.3, 24.6. Mass: (m/z) 252.2 [M+1]. Anal. Calcd for $C_{14}H_{18}FNO_2$: C, 66.91; H, 7.22; N, 5.57. Found: C, 66.85; H, 7.18; N, 5.53.

Typical procedure for the synthesis of amine. Amide **3a** (10.0 g, 0.0414 moles) was added to a stirred soln of KOH (6.90 g, 0.124 moles) and NMP (50 mL) in toluene (200 mL) at 20–25 °C. The mixture was heated to 120–130 °C for 12 h then cooled to 40–45 °C. H_2O (200 mL) was added with stirring. The layers were separated and the aqueous layer was extracted with toluene (100 mL). The organic layers were combined, washed with H_2O (2 × 200 mL), and concentrated to give **4a** as a yellow liquid.

tert-Butyl-(4-chloro-phenyl)-amine (4a). Yellow liquid, Yield: 4.6 g (61%). IR (Neat): 3420, 2976, 1597, 1493, 1217, 817, 758 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.12-7.09 (dd, *J* = 1.58, 1.41 Hz, 2H), 6.68-6.66 (dd, *J* = 1.52, 1.56 Hz, 2H), 3.42 (br s, 1H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 128.6, 122.9, 118.3, 51.4, 29.8. Mass: (m/z) 184.2 [M+1].

tert-Butyl-naphthalen-2-yl-amine (4b). White solid; Yield: 4.7 g (60%). mp 47.4-48.7°C. IR (KBr): 3412, 2969, 1628, 1523, 1229, 813, 750 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.68-7.66 (d, *J* = 8.06 Hz, 1H), 7.63-7.60 (d, *J* = 8.58 Hz, 2H), 7.38-7.34 (t, *J* = 7.46 Hz, 1H), 7.22-7.19 (t, *J* = 7.41 Hz, 1H), 7.05-7.04 (d, *J* = 1.69 Hz, 1H), 6.92-6.89 (dd, *J* = 2.06, 2.06 Hz, 1H), 3.71 (br s, 1H), 1.45 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.3, 134.8, 128.5, 127.8, 127.4, 126.0, 126.0, 122.1, 120.8, 109.2, 51.4, 29.8. Mass: (m/z) 200.2 [M+1].

Biphenyl-4-yl-tert-butyl-amine (4c). White solid; Yield:7.0 g (59%). mp 63.4-65.6°C. IR (KBr): 3415, 2967, 1610, 1518, 1484, 1222, 821, 757, 697 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.57-7.55 (d, *J* = 7.54 Hz, 2H), 7.44-7.40 (t, *J* = 8.04 Hz, 4H), 7.29-7.27 (d, *J* = 7.86 Hz, 1H), 6.83-6.81 (d, *J* = 8.25 Hz, 2H), 3.61 (br s, 1H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.2, 141.1, 130.6, 128.5, 127.5, 126.2, 126.0, 117.0, 51.3, 29.9. Mass: (m/z) 226.2 [M+1].

tert-Butyl-p-tolyl-amine (4d). Colourless liquid; Yield: 4.1 g (55%). IR (Neat): 3405, 2971, 1617, 1515, 1219, 831, 560 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.00-6.98 (d, *J* = 8.10 Hz, 2H), 6.72-6.70 (d, *J* = 8.33 Hz, 2H), 3.20 (br s, 1H), 2.26 (s, 3H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.1, 129.2, 128.4, 119.0, 51.6, 30.0, 20.3. Mass: (m/z) 164.1 [M+1].

tert-Butyl-phenyl-amine (4e). Colourless liquid; Yield: 1.6 g (53%). IR (Neat): 3413, 2973, 1601, 1497, 1220, 753 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.18-7.14 (t, *J* = 7.77 Hz, 2H), 6.77-6.74 (m, 3H), 3.44 (br s, 1H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.7, 128.8, 118.2, 117.4, 51.3, 30.0. Mass: (m/z) 150.1 [M+1].

tert-Butyl-(3-chloro-phenyl)-amine (4f). Yellow liquid; Yield: 3.6 g (51%). IR (Neat): 3416, 2975, 1595, 1506, 1483, 1222, 991, 762 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.06-7.02 (t, *J* = 7.99 Hz, 1H), 6.70-6.67 (m, 2H), 6.58-6.56 (dd, *J* = 1.74, 1.44 Hz, 1H), 3.60 (s, 1H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.0, 134.4, 129.7, 117.3, 115.8, 114.5, 51.3, 29.7. Mass: (m/z) 184.2 [M+1].

tert-Butyl-(3-methoxy-phenyl)-amine (4g). Colourless liquid; Yield: 3.6 g (47%). IR (Neat): 3400, 2967, 1613, 1221, 1160, 1054, 757 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.08-7.04 (t, *J* = 8.34 Hz, 1H), 6.34-6.30 (m, 3H), 3.74 (s, 3H), 3.49 (br s, 1H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2, 148.1, 129.4, 109.9, 102.8, 102.8, 54.9, 51.3, 29.9. Mass: (m/z) 180.3 [M+1].

(3-Bromo-phenyl)-tert-butyl-amine (4h). Brown colour liquid; Yield: 3.0 g (42%). IR (Neat): 3412, 2974, 1592, 1503, 1479, 1221, 986, 760 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.01-6.91 (t, *J* = 7.97 Hz, 1H), 6.86 (s, 1H), 6.83-6.81 (d, *J* = 7.82 Hz, 1H), 6.63-6.61 (d, *J* = 8.14 Hz, 1H), 3.59 (br s, 1H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 130.0, 122.7, 120.2, 118.7, 114.8, 51.3, 29.7. Mass: (m/z) 230.1 [M+1].

tert-Butyl-naphthalen-1-yl-amine (4i). White solid; Yield: 2.2 g (30%); mp 37.8-39.8 °C. IR (KBr): 3441, 2971, 1579, 1527, 1232, 769 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88-7.83 (m, 2H), 7.49-7.47 (m, 2H), 7.40-7.38 (d, *J* = 7.80 Hz, 1H), 7.33-7.32 (d, *J* = 7.95 Hz, 1H), 7.02-7.00 (d, *J* = 7.39 Hz, 1H), 4.20 (br s, 1H), 1.50 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.7, 134.6, 128.7, 126.0, 125.3, 125.3, 124.6, 120.3, 117.8, 109.9, 51.6, 29.9. Mass: (m/z) 200.3 [M+1].

tert-Butyl-(4-fluoro-phenyl)-amine (4j). Colourless liquid; Yield: 2.2 g (30%). IR (Neat): 3416, 2972, 1506, 1214, 822, 780 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.90-6.86 (t, *J* = 8.64 Hz, 2H), 6.76-6.73 (m, 2H), 3.20 (br s, 1H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.4, 142.5, 120.7, 115.2, 51.9, 29.9. Mass: (m/z) 168.2 [M+1].

Cyclobutyl-naphthalen-2-yl-amine (7a). White solid; Yield: 0.5 g (65%); mp 44.1-46.2°C. IR (KBr): 3382, 2980, 2928, 1627, 1275 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67-7.59 (m, 3H), 7.37-7.33 (t, *J* = 7.41 Hz, 1H), 7.20-7.16 (t, *J* = 7.41 Hz, 1H), 6.86-6.83 (dd, *J* = 2.11, 2.05 Hz, 1H), 6.73-6.72 (d, *J* = 1.70 Hz, 1H), 4.07-4.00 (m, 2H), 2.52-2.51 (m, 2H), 1.94-1.80 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 135.1, 128.8, 127.5, 127.3, 126.1, 125.7, 121.8, 117.8, 104.7, 48.8, 31.1, 15.2. Mass: (m/z) 198.2 [M+1]. Anal. Calcd for C14H15N: C, 85.24; H, 7.66; N, 7.10. Found: C, 85.28; H, 7.58; N, 7.06.

Biphenyl-4-yl-cyclobutyl-amine (7b). White solid; Yield: 0.9 g (81%); mp 69.9-71.9°C. IR (KBr): 3381, 2982, 2954, 2932, 1607, 1518, 1483, 1165, 830, 766 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54-7.52 (d, *J* = 7.48 Hz, 2H), 7.44-7.36 (m, 4H), 7.28-7.23 (m, 1H), 6.63-6.61 (d, *J* = 8.40 Hz, 2H), 3.99-3.91 (m, 2H), 2.49-2.45 (m, 2H), 1.72-1.96 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5, 141.2, 130.1, 128.5, 127.8, 126.1, 125.9, 113.1, 48.8, 31.1, 15.1. Mass: (m/z) 224.3 [M+1]. Anal. Calcd for $C_{16}H_{17}N$: C, 86.05; H, 7.67; N, 6.27. Found: C, 85.98; H, 7.53; N, 6.31.

Cyclobutyl-p-tolyl-amine (7c). Colourless liquid; Yield: 0.46 g (57%). IR (Neat): 3407, 2929, 2853, 1596, 1499, 1480, 1321, 985, 759 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.00-6.98 (d, *J* = 7.85 Hz, 2H), 6.51-6.49 (d, *J* = 7.85 Hz, 2H), 3.93-3.88 (m, 1H), 3.5 (br s, 1H), 2.43-2.42 (m, 2H), 2.25 (s, 3H), 1.83-1.74 (m, 4H). ^{13}C NMR (100 MHz, CDCl3): δ 144.8, 129.6, 126.4, 113.1, 49.2, 31.1, 20.2, 15.1. Mass: (m/z) 162.1 [M+1].

(3-Chloro-phenyl)-cyclobutyl-amine (7d). Yellow liquid; Yield: 0.6 g (80%). IR (Neat): 3410, 2969, 2935, 1599, 1498, 1482, 1323, 1162, 988, 763 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07-7.03 (t, *J* = 8.0 Hz, 1H), 6.65-6.63 (d, *J* = 7.67 Hz, 1H), 6.50 (s, 1H), 6.42-6.39 (d, *J* = 8.08 Hz, 1H), 3.89 (br s, 2H), 2.43-2.42 (m, 2H), 1.82-1.75 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2, 134.8, 130.0, 116.9, 112.3, 111.1, 48.6, 30.9, 16.1. Mass: (m/z) 182.1 [M+1]. Anal. Calcd for $C_{10}H_{12}ClN$: C, 66.12; H, 6.66; N, 7.71. Found: C, 66.08; H, 6.58; N, 7.69.

Cyclobutyl-naphthalen-1-yl-amine (7e). White solid; Yield: 0.9 g (68%); mp 43.5-44.6°C. IR (KBr): 3404, 2975, 2958, 1582, 1522, 1476, 1406, 1286, 1153, 766 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81-7.77 (m, 2H), 7.45-7.43 (m, 2H), 7.35-7.31 (t, *J* = 7.86 Hz, 1H), 7.26-7.22 (t, *J* = 7.21 Hz, 1H), 6.53-6.51 (d, *J* = 7.43 Hz, 1H), 4.5 (br s, 1H), 4.12-4.08 (m, 1H), 2.57-2.55 (m, 2H), 1.99-1.84 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.1, 134.2, 128.5, 126.5, 125.5, 124.5, 123.2, 119.8, 117.2, 104.9, 49.1, 31.0, 15.4. Mass: (m/z) 198.2 [M+1]. Anal. Calcd for $C_{14}H_{15}N$: C, 85.24; H, 7.66; N, 7.10. Found: C, 85.13; H, 7.68; N, 7.04.

Cyclopentyl-naphthalen-2-yl-amine (10a). Colourless liquid; Yield: 3.2 g (67%). IR (Neat): 3405, 2955, 2867, 1628, 1603, 1520, 1480, 1397, 828, 743 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67-7.65 (d, *J* = 8.06 Hz, 1H); 7.62-7.60 (d, *J* = 8.45 Hz, 2H), 7.37-7.33 (t, *J* = 7.46 Hz, 1H), 7.20-7.16 (t, *J* = 7.40 Hz, 1H), 6.87-6.84 (dd, *J* = 2.15, 2.13 Hz, 1H), 6.82 (s, 1H), 3.93-3.92 (m, 1H), 3.90 (s, 1H), 2.13-2.08 (m, 2H), 1.76-1.71 (m, 2H), 1.69-1.65 (m, 2H), 1.57-1.52 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.5, 135.1, 128.7, 127.5, 127.2, 126.1, 125.7, 121.6, 118.2, 104.8, 54.6, 33.4, 24.0. Mass: (m/z) 212.2 [M+1].

Biphenyl-4-yl-cyclopentyl-amine (10b). White solid; Yield: 4.0 g (80%); mp 66.3-67.6°C. IR (KBr): 3409, 2951, 2866, 1610, 1521, 1485, 1184, 820, 759, 696 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.53 (d, *J* = 7.6 Hz, 2H), 7.47-7.37 (m, 4H), 7.25-7.23 (d, *J* = 7.36 Hz, 1H), 6.68-6.66 (d, *J* = 8.56 Hz, 2H), 3.87-3.80 (m, 1H), 3.74 (s, 1H), 2.08-2.03 (m, 2H), 1.77-1.73 (m, 2H), 1.66-1.63 (m, 2H), 1.55-1.48 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3, 141.2, 129.6, 128.5, 127.8, 126.1, 125.8, 123.2, 54.5, 33.5, 24.0. Mass: (m/z) 238.3 [M+1]. Anal. Calcd for $C_{17}H_{19}N$: C, 86.03; H, 8.07; N, 5.90. Found: C, 85.96; H, 8.01; N, 5.88.

Cyclopentyl-p-tolyl-amine (10c). Colourless liquid; Yield: 3.2 g (76%). IR (Neat): 3400, 2955, 2867, 1619, 1518, 1303, 807 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 6.99-6.97 (d, *J* = 8.12 Hz, 2H), 6.55-6.53 (d, *J* = 8.19 Hz, 2H), 3.78-3.74 (m, 1H), 3.50 (br s, 1H), 2.24 (s, 3H), 2.04-1.99 (m, 2H), 1.74-1.70 (m, 2H), 1.63-1.60 (m, 2H), 1.48-1.44 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.7, 129.5, 126.0, 113.3, 54.8, 33.4, 23.9, 20.2. Mass: (m/z) 176.3 [M+1].

(3-Chloro-phenyl)-cyclopentyl-amine (10d). Yellow liquid; Yield: 3.0 g (86%). IR (Neat): 3414, 2957, 2869, 1598, 1500, 1482, 1326, 762 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.07-7.03 (t, *J* = 8.00 Hz, 1H), 6.63-6.61 (d, *J* = 7.87 Hz, 1H), 6.56 (s, 1H), 6.46-6.44 (t, *J* = 4.02 Hz, 1H), 3.73 (br s, 2H), 2.04-1.98 (m, 2H), 1.72-1.67 (m, 2H), 1.65-1.59 (m, 2H), 1.48-1.43 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.0, 134.8, 129.9, 116.5, 112.4, 111.3, 54.4, 33.3, 23.9. Mass: (m/z) 196.2 [M+1]. Anal. Calcd for $C_{11}H_{14}ClN$: C, 67.51; H, 7.21; N, 7.16. Found: C, 67.48; H, 7.22; N, 7.14.

Cyclopentyl-naphthalen-1-yl-amine (10e). Yellow liquid; Yield: 2.8g (68%). IR (Neat): 3427, 2954, 2866, 1581, 1523, 1477, 1408, 767 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.80-7.78 (d, *J* = 7.86 Hz, 2H), 7.47-7.40 (m, 2H), 7.38-7.34 (t, *J* = 7.79 Hz, 1H), 7.25-7.21 (t, *J* = 8.09 Hz, 1H), 6.66-6.64 (d, *J* = 7.51 Hz, 1H), 4.35 (br s, 1H), 3.98-3.97 (m, 1H), 2.17-2.11 (m, 2H), 1.82-1.80 (m, 2H), 1.72-1.62 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.0, 134.2, 128.6, 126.5, 125.5, 124.4, 123.3, 119.7, 116.7, 105.0, 54.6, 33.6, 24.2. Mass: (m/z) 212.0 [M+1].

(4-Chloro-phenyl)-cyclohexyl-amine (13a). White solid; Yield: 2.3 g (66%); mp 48.1-50.8°C. IR (KBr): 3415, 2936, 2856, 1599, 1498, 1313, 1092, 816 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.07-7.04 (dd, *J* = 3.12, 3.04 Hz, 2H), 6.54-6.49 (dd, *J* = 8.72, 1.72 Hz, 2H), 3.52 (br s, 1H), 3.21-3.17 (m, 1H), 2.04-2.01 (m, 2H), 1.78-1.73 (m, 3H), 1.38-1.35 (m, 2H), 1.26-1.12 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.8, 128.9, 121.1, 114.0, 51.7, 33.2, 25.7, 24.8. Mass: (m/z) 210.2 [M+1].

Cyclohexyl-naphthalen-2-yl-amine (13b). White solid; Yield: 6.5 g (69%); mp 77.7-78.9°C. IR (KBr): 3420, 3044, 2921, 2854, 2840, 1627, 1601, 1523, 827, 808, 753 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.67-7.59 (m, 3H), 7.37-7.33 (t, *J* = 7.52 Hz, 1H), 7.20-7.16 (t, *J* = 7.41 Hz, 1H), 6.87-6.84 (dd, *J* = 2.12, 2.11 Hz, 1H), 6.81 (s, 1H), 3.71 (br s, 1H), 3.41-3.39 (m, 1H), 2.16-2.13 (m, 2H), 1.83-1.68 (m, 3H), 1.46-1.40 (m, 2H), 1.28-1.20 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 135.2, 128.8, 127.5, 127.1, 126.1, 125.6, 121.6, 118.1, 104.6, 51.6, 33.2, 25.9, 24.9. Mass: (m/z) 226.1 [M+1].

Biphenyl-4-yl-cyclohexyl-amine (13c). White solid; Yield: 7.4 g (76%); mp 79.8-82.1°C. IR (KBr): 3384, 3024, 2928, 2853, 1612, 1527, 1493, 1327, 1190, 825, 760, 696 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.55-7.53 (d, *J* = 7.66 Hz, 2H), 7.44-7.37 (m, 4H), 7.25 (t, *J* = 3.26 Hz, 1H), 6.67-6.65 (d, *J* = 8.09 Hz, 2H), 3.63 (br s, 1H), 3.33-3.28 (m, 1H), 2.11-2.08 (m, 2H), 1.80-1.66 (m, 3H), 1.42-1.36 (m, 2H), 1.29-1.15 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.7, 141.2, 129.5, 128.5, 127.8, 126.1, 125.8, 113.2, 51.6, 33.3, 25.8, 24.9. Mass: (m/z) 252.3 [M+1]. Anal. Calcd for $C_{18}H_{21}N$: C, 86.01; H, 8.42; N, 5.57. Found: C, 85.92; H, 8.34; N, 5.48.

Cyclohexyl-p-tolyl-amine (13d). White solid; Yield: 1.6 g (46%); mp 46.0-47.6°C. IR (KBr): 3415, 2926, 2853, 1615, 1519, 1448, 1256, 805 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 6.98-6.96 (d, *J* = 8.0 Hz, 2H), 6.53-6.51 (d, *J* = 8.16 Hz, 2H), 3.36 (br s, 1H), 3.23-3.21 (m, 1H), 2.23 (s, 3H), 2.06-2.03 (m, 2H), 1.78-1.63 (m, 3H), 1.38-1.34 (m, 2H), 1.31-1.11 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.0, 129.6, 125.9, 113.3, 51.9, 33.4, 25.9, 24.9, 20.2. Mass: (m/z) 190.1 [M+1].

Cyclohexyl-phenyl-amine (13e). Colourless liquid; Yield:6.0 g (80%). IR (Neat): 3400, 3051, 3019, 2929, 2853, 1601, 1504, 1320, 1255, 747, 692 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.18-7.14 (t, *J* = 7.23 Hz, 2H), 6.68-6.64 (t, *J* = 7.16 Hz, 1H), 6.60-6.58 (d, *J* = 7.89 Hz, 2H), 3.51 (br s, 1H), 3.28-3.23 (m, 1H), 2.08-2.05 (m, 2H), 1.78-1.64 (m, 3H), 1.39-1.33 (m, 2H), 1.24-1.14 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3, 129.1, 116.7, 113.0, 51.5, 33.4, 25.8, 24.9. Mass: (m/z) 176.3 [M+1].

(3-Chloro-phenyl)-cyclohexyl-amine (13f). Yellow liquid; Yield: 8.5 g (90%). IR (Neat): 3412, 2929, 2853, 1598, 1501, 1324, 1114, 1089, 989, 883, 836, 761 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.06-7.02 (t, *J* = 8.0 Hz, 1H), 6.61-6.59 (d, *J* = 7.96 Hz, 1H), 6.556-6.551 (d, *J* = 1.72 Hz, 1H), 6.45-6.42 (dd, *J* = 1.76, 1.8 Hz, 1H), 3.61 (br s, 1H),

3.24-3.19 (m, 1H), 2.05-2.02 (m, 2H), 1.79-1.64 (m, 3H), 1.40-1.13 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 134.9, 130.0, 116.4, 112.3, 111.3, 51.4, 33.1, 25.7, 24.8. Mass: (m/z) 210.2 [M+1].

Cyclohexyl-(3-methoxy-phenyl)-amine (13g). Colourless liquid; Yield: 5.0 g (72%). IR (Neat): 3394, 2928, 2852, 1614, 1511, 1209, 1161, 1048, 828, 754, 688 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07-7.03 (t, *J* = 8.06 Hz, 1H), 6.24-6.19 (t, *J* = 8.34 Hz, 2H), 6.15 (s, 1H), 3.77 (s, 3H), 3.54 (s, 1H), 3.25-3.20 (m, 1H), 2.07-2.04 (m, 2H), 1.77-1.63 (m, 3H), 1.38-1.32 (m, 2H), 1.23-1.12 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.7, 148.6, 129.8, 106.2, 101.6, 99.0, 54.9, 51.6, 33.3, 25.8, 24.9. Mass: (m/z) 206.2 [M+1].

(3-Bromo-phenyl)-cyclohexyl-amine (13h). Yellow liquid; Yield: 7.2 g (89%). IR (Neat): 3408, 3061, 2929, 2853, 1596, 1498, 1322, 985, 759, 682 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.00-6.96 (t, *J* = 8.00 Hz, 1H), 6.76-6.74 (d, *J* = 7.88 Hz, 1H), 6.71 (s, 1H), 6.49-6.47 (d, *J* = 7.47 Hz, 1H), 3.59 (s, 1H), 3.21 (br s, 1H), 2.05-2.01 (m, 2H), 1.79-1.64 (m, 3H), 1.39-1.33 (m, 2H), 1.24-1.13 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.5, 130.3, 123.2, 119.3, 115.2, 111.6, 51.4, 33.1, 25.7, 24.8. Mass: (m/z) 254.1 [M+1]. Anal. Calcd for $C_{12}H_{16}BrN$: C, 56.71; H, 6.35; N, 5.51. Found: C, 56.69; H, 6.32; N, 5.48.

Cyclohexyl-naphthalen-1-yl-amine (13i). White solid; Yield: 3.0 g (64%); mp 52.0-54.5°C. IR (KBr): 3427, 3057, 2928, 2852, 1580, 1526, 1408, 1121, 766 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80-7.77 (m, 2H), 7.45-7.40 (m, 2H), 1.36-1.29 (m, 3H), 7.36-7.32 (t, *J* = 7.86 Hz, 1H), 7.21-7.19 (d, *J* = 8.09 Hz, 1H), 6.66-6.64 (d, *J* = 7.59 Hz, 1H), 4.28 (br s, 1H), 3.51-3.46 (m, 1H), 2.21-2.18 (m, 2H), 1.85-1.81 (m, 2H), 1.75-1.65 (m, 1H), 1.48-1.41 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2, 134.4, 128.6, 126.5, 125.4, 124.3, 123.2, 119.7, 116.5, 104.5, 51.6, 33.2, 25.9, 24.9. Mass: (m/z) 226.2 [M+1].

Cyclohexyl-(4-fluoro-phenyl)-amine (13j). Colourless liquid; Yield: 5.0 g (66%). IR (Neat): 3411, 2930, 2854, 1508, 1219, 818, 769 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.88-6.84 (t, *J* = 8.51 Hz, 2H), 6.53-6.50 (m, 2H), 3.36 (br s, 1H), 3.19-3.14 (t, *J* = 9.90 Hz, 1H), 2.05-2.03 (m, 2H), 1.77-1.74 (m, 2H), 1.67-1.64 (m, 1H), 1.37-1.31 (m, 2H), 1.23-1.11 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.2, 143.6, 115.4, 113.9, 52.3, 33.3, 25.8, 24.9. Mass: (m/z) 194.3 [M+1].

RESULT AND DISCURSION

In order to demonstrate the versatility the method we describe here in the preparation of different aryl anilines such as N-t-butyl anilines, N-cyclo butyl anilines, N-cyclo pentyl anilines and N-cyclo hexyl anilines in good yields (Figure 3).

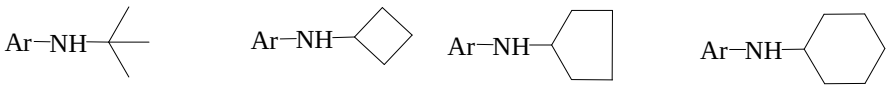
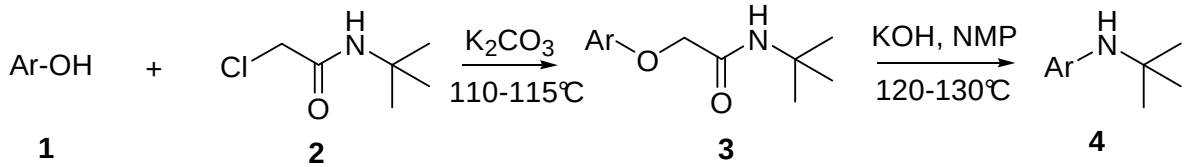


Figure 3. Structures of Substituted anilines

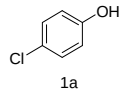
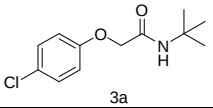
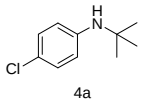
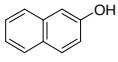
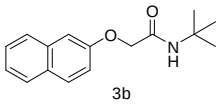
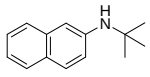
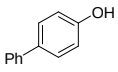
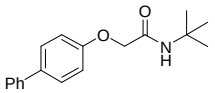
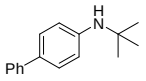
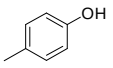
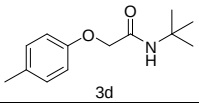
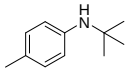
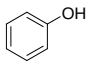
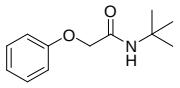
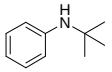
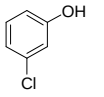
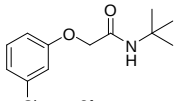
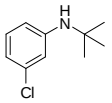
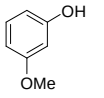
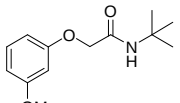
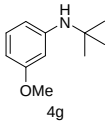
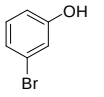
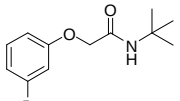
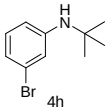
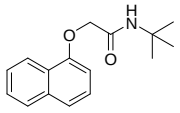
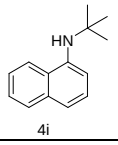
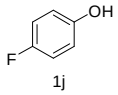
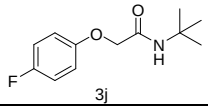
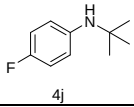
The present method for the preparation of t-butyl anilines [13] involves high pressure reaction of anilines with isobutylene. We developed a simple method using Smiles rearrangement method as shown in Scheme 2. The yields are 30-90% over two steps and the details are given in Table 1. Intermediate amides are characterized thoroughly and the final amines are also characterized completely.



1 **2** **3** **4**

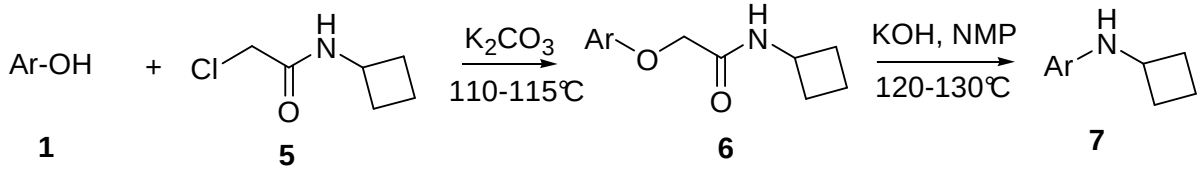
Scheme 2. Synthesis of N-1-t-butyl aniline

Table 1. Preparation of amide 3 and *N*-1-t-butyl aniline 4

Entry	Ar-OH **1**	Amide **3**	Yield[a] (%) of **3**	Amine **4**	Yield[b] (%) of **4**
1	 1a	 3a	85	 4a	61[13g, f]
2	 1b	 3b	92[17]	 4b	60[13e]
3	 1c	 3c	85	 4c	59[21]
4	 1d	 3d	85[18]	 4d	55[13g, f]
5	 1e	 3e	82[19]	 4e	53[13g, f]
6	 1f	 3f	97	 4f	51[13g, f]
7	 1g	 3g	82	 4g	47[13g, f]
8	 1h	 3h	85	 4h	42[15c]
9	 1i	 3i	92	 4i	30[22]
10	 1j	 3j	96	 4j	30[13g, f]

[a] yields calculated on the basis of the recovered starting phenol.
[b] Isolated yield

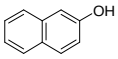
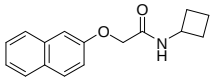
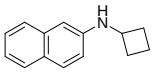
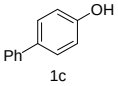
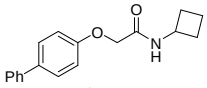
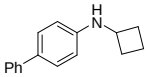
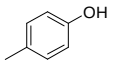
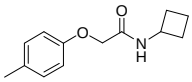
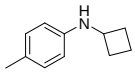
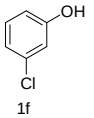
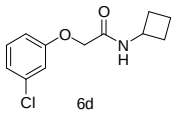
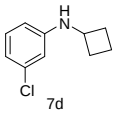
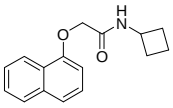
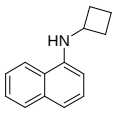
Similarly N-1-cyclo butyl anilines are prepared using the same strategy as shown in Scheme 3. The data are given in Table 2, and both intermediates and final anilines are characterized completely.



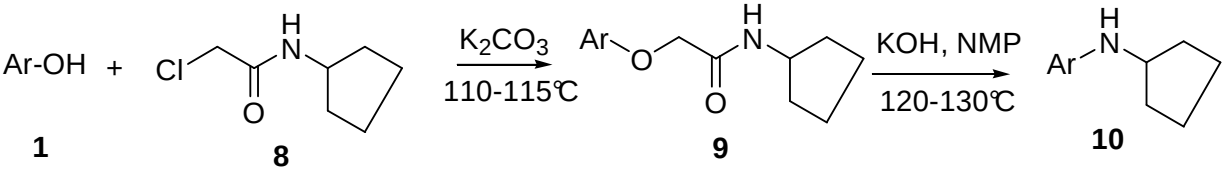
1 **5** **6** **7**

Scheme 3. Synthesis of *N*-1-cyclo butyl aniline

Table 2. Preparation of amide 6 and *N*-1-cyclo butyl aniline 7

Entry	Ar-OH **1**	Amide **6**	Yield[a] (%) of **6**	Amine **7**	Yield[b] (%) of **7**
1	 1b	 6a	84	 7a	65
2	 1c	 6b	84	 7b	81
3	 1d	 6c	85	 7c	57[14]
4	 1f	 6d	80	 7d	80
5	 1i	 6e	82	 7e	68
[a] yields calculated on the basis of the recovered starting phenol. *[b] Isolated yield*					

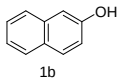
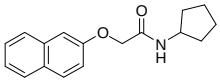
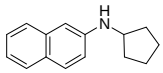
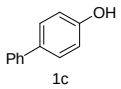
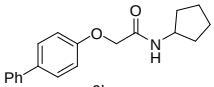
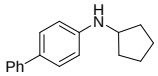
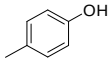
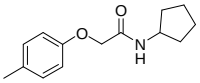
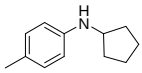
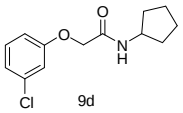
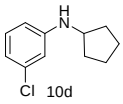
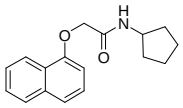
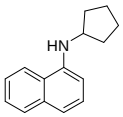
Generally cyclo pentyl anilines and cyclo hexyl anilines are prepared by two methods. The preferred one by many is by reductive alkylation of anilines with ketones[14]. The second one is alkylation of halo cyclopentanes or halo cyclohexanes with anilines and is studied extensively with number of catalysts [15]. We report here in the preparation of these amines by Smiles rearrangement method which can be performed without any metal contamination in the amines. The reaction sequence and the yield data are given in the following schemes and tables.



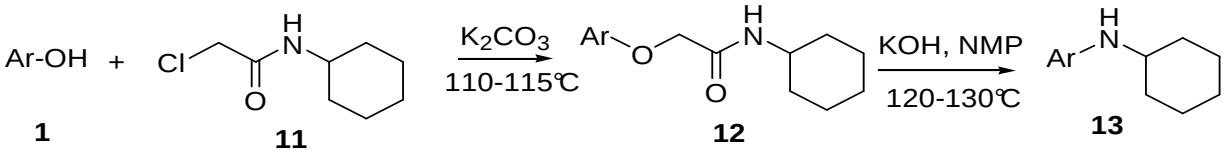
1 **8** **9** **10**

Scheme 4. Synthesis of *N*-1-cyclo pentyl aniline

Table 3. Preparation of amide 9 and *N*-cyclo pentyl aniline 10

Entry	Ar-OH **1**	Amide **9**	Yield[a] (%) of **9**	Amine **10**	Yield[b] (%) of **10**
1	 1b	 9a	90[17]	 10a	67[14b]
2	 1c	 9b	96	 10b	80
3	 1d	 9c	95	 10c	76[14a]
4	 1f	 9d	90	 10d	86
5	 1i	 9e	90	 10e	68[14b]

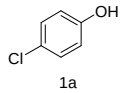
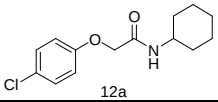
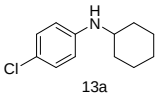
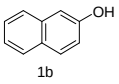
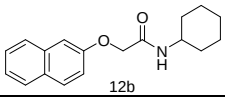
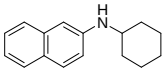
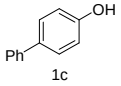
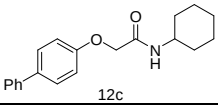
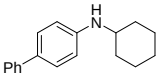
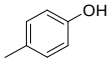
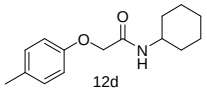
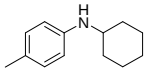
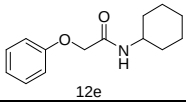
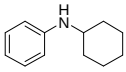
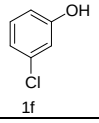
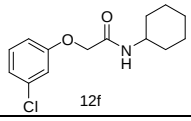
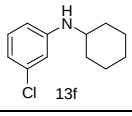
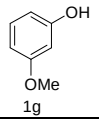
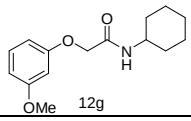
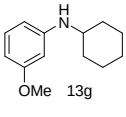
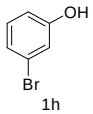
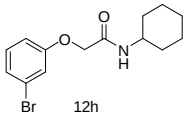
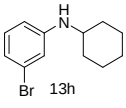
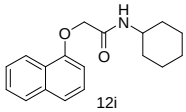
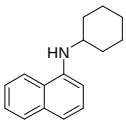
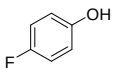
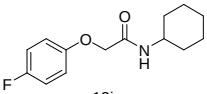
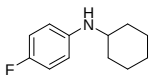
[a] yields calculated on the basis of the recovered starting phenol.
[b] Isolated yield



1 **11** **12** **13**

Scheme 5. Synthesis of *N*-1-cyclo hexyl aniline

Table 4. Preparation of amide 12 and *N*-1-cyclo hexyl aniline 13

Entry	Ar-OH **1**	Amide **12**	Yield[a] (%) of **12**	Amine **13**	Yield[b] (%) of **13**
1	 1a	 12a	98	 13a	66[14b]
2	 1b	 12b	94[17]	 13b	69[14b]
3	 1c	 12c	93	 13c	76
4	 1d	 12d	94	 13d	46[23]
5	 1e	 12e	95[20]	 13e	80[14b]
6	 1f	 12f	98	 13f	90[24]
7	 1g	 12g	76	 13g	72[25]
8	 1h	 12h	95	 13h	89
9	 1i	 12i	94	 13i	64[14b]
10	 1j	 12j	96	 13j	66[14b]

[a] yields calculated on the basis of the recovered starting phenol.
[b] Isolated yield

CONCLUSION

In conclusion, we have developed a simple and efficient two step strategy for the industrially useful N-alkyl aryl amines. This method produces a convenient, inexpensive, and scalable method of preparation of N-alkyl anilines.

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