

### Supporting Information Available

For ms 'Smooth synthesis of aryl- and alkylamines by photoheterolysis of haloanilines in the presence of aromatics and alkenes' by Fagnoni, Mella and Albini

$^1\text{H}$  (with decoupling) and  $^{13}\text{C}$  NMR (with DEPT-135) data in  $\text{CDCl}_3$ .

**3a**  $^1\text{H}$  NMR,  $\delta$  2.55 (s, 6H), 3.05 (s, 6H), 6.9 (d, 1H,  $J=8$  Hz), 6.76 and 7.45 (AA'BB' system, 4H), 7.14 (dd, 1H,  $J=8, 2$  Hz), 7.18 (d, 1H,  $J=2$ Hz).

$^{13}\text{C}$  NMR,  $\delta$  40.4 ( $\text{CH}_3$ ), 43.9 ( $\text{CH}_3$ ), 112.3 (CH), 118.6 (CH), 126.3, 126.5 (CH), 128.9, 129.0 (CH), 130.9 (CH), 135.8, 149.4, 149.8.

**3b**  $^1\text{H}$  NMR,  $\delta$  2.55 (s, 6H), 3.02 (s, 6H), 6.75 and 7.48 (AA'BB' system, 4H), 6.7-6.95 (m, 3 H).

$^{13}\text{C}$  NMR,  $\delta$  40.4 ( $\text{CH}_3$ ), 43.5 ( $\text{CH}_3$ ), 112.1 (CH), 112.6 (d, CH), 117.4 (d, CH), 118.6 (d, CH), 121.7, 128.4, 129.1 (CH), 147.3, 149.4, 158.1 (d).

**5**  $^1\text{H}$  NMR,  $\delta$  0.9 (t, 3H,  $J=7$  Hz), 1.3-1.5 (m, 6H), 2.9 (s, 6H), 2.95 (AB part of an ABX system, 2H), 4.0 (X part, 1H), 6.75 and 7.05 (AA'BB', 4H)

$^{13}\text{C}$  NMR,  $\delta$  13.9 ( $\text{CH}_3$ ), 22.1 ( $\text{CH}_2$ ), 28.5 ( $\text{CH}_2$ ), 37.0 ( $\text{CH}_2$ ), 40.5 ( $\text{CH}_3$ ), 44.0 ( $\text{CH}_2$ ), 64.6 (CH), 112.5 (CH), 125.9, 129.9 (CH), 149.3

**6**  $^1\text{H}$  NMR,  $\delta$  0.85 (t, 3H,  $J=7$  Hz), 1.3-1.9 (m, 6H), 2.9 (s, 6H), 2.8 (m, 1H), 3.6 (AB part of an ABX system), 6.75 and 7.05 (AA'BB', 4H)

$^{13}\text{C}$  NMR,  $\delta$  13.9 ( $\text{CH}_3$ ), 22.5 ( $\text{CH}_2$ ), 29.5 ( $\text{CH}_2$ ), 32.5 ( $\text{CH}_2$ ), 40.5 ( $\text{CH}_3$ ), 47.1 (CH), 50.1 ( $\text{CH}_2$ ), 112.5 (CH), 126.8, 128.2 (CH), 149.4.

(compounds **5** and **6** were obtained as a mixture, and NMR characterization is referred to it. Satisfactory separation and characterization was obtained by GC/MS).

**7**  $^1\text{H}$  NMR,  $\delta$  1.95 (m, 1H), 2.2 (m, 1H), 2.35-2.45 (m, 2H), 2.8 and 2.95 (AB part of an ABX system, 2H), 2.9 (s, 6H), 4.65 (m, 1H), 6.65 and 7.05 (AA'BB', 4H)

$^{13}\text{C}$  NMR,  $\delta$  26.6 ( $\text{CH}_2$ ), 28.5( $\text{CH}_2$ ), 40.0 ( $\text{CH}_2$ ), 40.5 ( $\text{CH}_2$ ), 81.1 (CH), 112.9 (CH), 123.5, 129.9 (CH), 149.4, 177.3.

**9**  $^1\text{H}$  NMR,  $\delta$  1.45 (s, 6H), 1.6 (bs, 3H), 2.98 (s, 6H), 4.85 (bd, 1H,  $J=2$  Hz), 4.97 (bd, 1H,  $J=2$  Hz), 6.7 and 7.2 (AA'BB', 4H)

$^{13}\text{C}$  NMR,  $\delta$  20.0 ( $\text{CH}_3$ ), 28.3 ( $\text{CH}_3$ ), 40.5 ( $\text{CH}_3$ ), 42.3, 108.7 ( $\text{CH}_2$ ), 112.3 (CH), 126.6 (CH), 136.3, 148.5, 153.2.