Conformation and Stereodynamics of 2,2'-Disubstituted N,N'-Diaryl Ureas

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SUPPORTING INFORMATION

1,3-Bis(2-fluorophenyl)urea **2a**. —2-Fluoroaniline (0.28 g, 0.19 cm³, 2.5 mmol), was dissolved in CH₂Cl₂ (10 cm³) at RT, 2-fluorophenylisocyanate (0.34 g, 0.22 cm³, 2.5 mmol) added dropwise and stirred at RT for 18 h. The white precipitate was isolated and recrystallised from EtOAc-pentane to give *1,3-bis(2-fluorophenyl)urea* **2a** (0.56 g, 90 %), as white plates, m.p. 219-221 °C (from EtOAc-pentane); R_f (EtOAc-pentane, 1:4) 0.22; v_{max} (film)/cm⁻¹ 1652 (C=O) and 1310 (C-F); δ_H (300 MHz; d_6 -DMSO) 9.03 [2 H, s, (NH)_A and (NH)_B], 8.16 (2 H, td, *J* 8.0 and 1.5, CH-d), 7.22 (2 H, ddd, *J* 12.0, 8.0 and 1.0, CH-a), 7.13 (2 H, td, *J* 8.0 and 1.0, CH-c) and 6.99 (2 H, tdd, *J* 8.0, 5.0 and 1.5, CH-b); δ_C (75 MHz; d_6 -DMSO) 152.7 (C=O), 152.6 (C-F, d, *J* 240), 128.0 (C, d, *J* 10.3), 125.2 (CH, d, *J* 3.5), 123.3 (CH, d, *J* 7.4), 121.2 (CH) and 115.7 (CH, d, *J* 18.9); m/z (CI) 249 (20 %); (Found: M+H⁺, 249.0833, C₁₃H₁₁N₂OF₂ requires *M*+*H*, 249.0834). Elem. Anal. for C₁₃H₁₀N₂OF₂: calcd: C, 62.90 %; H, 4.06 %; N, 11.29; F, 15.31; found: C, 62.77 %; H, 4.18 %; N, 11.08 %; F, 15.55 %.

1,3-Bis(2-chlorophenyl)urea 2b. —2-Chloroaniline (1.3 g, 10 mmol) was dissolved in CH₂Cl₂ (20 cm³) at 0 °C and triethylamine (2.2 g, 3.1 cm³, 22 mmol) added in one portion. Diphosgene (0.99 g, 0.60 cm³, 5.0 mmol) was added dropwise and the reaction mixture allowed to warm to room temperature over 18 h. The white precipitate was recrystallised from EtOAc-pentane to give *1,3-bis*(2-chlorophenyl)urea 2b (2.0 g, 70 %), as white cubes, m.p. 240-242 °C (from EtOAc-pentane); $R_{\rm f}$ (EtOAc-pentane, 1:4) 0.41; $\nu_{\rm max}$ (film)/cm⁻¹ 1645 (C=O) and 807 (C–Cl); $\delta_{\rm H}$ (400 MHz; *d*₆-DMSO) 9.12 [2 H, s, (NH)_A and (NH)_B], 8.02 (2 H, dd, *J* 8.0 and 1.0, CH-a), 7.44 (2 H, dd, *J* 8.0 and 1.0, CH-d), 7.28 (2 H, td, *J* 8.0 and 1.0, CH-c) and 7.04 (2 H, td, *J* 8.0 and 1.0, CH-b); $\delta_{\rm C}$ (100 MHz; *d*₆-DMSO) 153.0 (C=O), 136.5 (C), 130.0 (CH), 128.1 (CH), 124.6 (CH), 123.7 (C) and 123.3 (CH); m/z (ESI) 281 (100, M+H⁺); (Found: M+H⁺, 281.0242, C₁₃H₁₀N₂OCl₂ requires *M*+*H*, 281.0243). *t*_R = 3.52 min.

1,3-Bis(2-bromophenyl)urea 2c. —2-Bromoaniline (1.7 g, 10 mmol) was dissolved in CH₂Cl₂ (20 cm³) at room temperature and triethylamine (2.2 g, 22 mmol) added in one portion. Triphosgene (0.50 g, 1.6 mmol) was added in small portions, the reaction mixture stirred for 20 min and the solvent was evacuated under reduced pressure. The residue was recrystallised from EtOAc-petrol to give *1,3-bis(2-bromophenyl)urea* 2c (2.40 g, 65 %), as white cubes, m.p. 229-232 °C (from EtOAc-petrol); R_f (EtOAc-petrol, 1:4) 0.23; v_{max} (film)/cm⁻¹ 1710 (C=O) and 745 (C-Br); δ_H (300 MHz; d_6 -DMSO) 8.94 [2 H, s, (NH)_A and (NH)_B], 7.95 (2 H, dd, *J* 8.0 and 2.0, CH-a), 7.65 (2 H, dd, *J* 8.0 and 1.0, CH-d), 7.38 (2 H, td, *J* 8.0 and 1.0, CH-c), 7.08 (2 H, td, *J* 8.0 and 2.0, CH-b) and 3.22 [6 H, s, (NCH₃)_A and (NCH₃)_B]; δ_C (75 MHz; d_6 -DMSO) 153.0 (C=O), 137.5 (C), 133.2 (CH), 128.6 (CH), 125.3 (CH), 124.3 (CH) and 114.7 (C); m/z (CI) 369 (20 %, M+H⁺) and 289 (40, M+H⁺ – Br); (Found: M+H⁺, 368.9233, C₁₃H₁₁N₂OBr₂: calcd: C, 42.20%; H, 2.72%; N, 7.57%; Br, 43.19%; found : C, 42.51%; H, 2.90%; N, 7.36%; Br, 43.10%.

1,3-Bis(2-methylphenyl)urea 2d. —2-Aminotoluene (1.1 g, 1.1 cm³, 10 mmol) was dissolved in CH₂Cl₂ (20 cm³) at 0 °C and triethylamine (2.2 g, 3.1 cm³, 22 mmol) added in one portion. Diphosgene (0.99 g, 0.60 cm³, 5.0 mmol) was added dropwise and the reaction mixture allowed to warm to room temperature over 18 h. The white precipitate was recrystallised from EtOAc-pentane to give *1,3-bis(2-methylphenyl)urea* 2d (2.26 g, 94 %), as white cubes, m.p. 222-224 °C (from EtOAc-pentane); $R_{\rm f}$ (EtOAc-pentane, 3:7) 0.36; $v_{\rm max}$ (film)/cm⁻¹ 3301 and 3294 (N–H) and 1639 (C=O); $\delta_{\rm H}$ (400 MHz; d_6 -DMSO) 8.76 [2 H, s, (NH) × 2], 7.75 (2 H, dd, *J* 8.0 and 1.0, CH-d), 7.13 (2 H, dd, *J* 8.0 and 1.0, CH-a), 7.10 (2 H, td, *J* 8.0 and 1.0, CH-b) and 2.28 [6 H, s, (CH₃) × 2]; $\delta_{\rm C}$ (100 MHz; d_6 -DMSO) 153.9 (C=O), 138.4 (C), 130.8 (CH), 128.7 (C), 126.6 (CH), 123.2 (CH), 122.2 (CH) and 19.0 (CH₃); m/z (CI) 241 (100, M+H⁺); (Found: M+H⁺, 241.1333, C₁₅H₁₆N₂O requires $M_{+}^{+}H$, 241.1336). $t_{\rm R}$ = 3.34 min.

(1,3-bis(2-Ethylphenyl)urea, 2e. —2-Ethylaniline (1.2 g, 1.23 cm³, 10 mmol) was dissolved in CH₂Cl₂ (20 cm³) at 0 °C and triethylamine (2.2 g, 3.1 cm³, 22 mmol) added in one portion. Diphosgene (0.99 g, 0.60 cm³, 5.0 mmol) was added dropwise and the reaction mixture allowed to warm to room temperature over 18 h. The white precipitate was recrystallised from EtOAc-pentane to give *1,3-bis(2-Ethylphenyl)urea* 2e (2.57 g, 96 %), as white cubes, m.p. 177-179 °C (from EtOAc-pentane); $R_{\rm f}$ (EtOAc-pentane, 3:7) 0.46; $\nu_{\rm max}$ (film)/cm⁻¹ 3285 and 3295 (N–H) and 1633 (C=O); $\delta_{\rm H}$ (400 MHz; d_6 -DMSO) 8.74 [2 H, s, (NH) × 2], 7.68 (2 H, dd, *J* 8.0 and 1.0, CH-d), 7.15 (2 H, dd, *J* 8.0 and 1.0, CH-a), 7.10 (2 H, td, *J* 8.0 and 1.0, CH-c), 6.96 (2 H, td, *J* 8.0 and 1.0, CH-b), 2.68 [4 H, q, *J* 7.0, (CH₂) × 2] and 1.15 [6 H, t, *J* 7.0, (CH₃) × 2]; $\delta_{\rm C}$ (100 MHz; d_6 -DMSO) 154.4 (C=O), 137.6 (C), 135.2 (C), 129.0 (CH), 126.5 (CH), 123.8 (CH), 123.5 (CH) 24.7 (CH₂) and 15.0 (CH₃); m/z (CI) 269 (100 %, M+H⁺); (Found: M+H⁺, 269.1647, C₁₇H₂₀N₂O requires *M*+*H*, 269.1649).

1-(2-Ethylphenyl)-3-(2-isopropylphenyl)urea, 2f. —4-Nitrophenyl 2-isopropylphenylcarbamate (0.45 g, 1.5 mmol) was dissolved in DMSO (3.0 cm³) at room temperature and diisopropylethylamine (0.51 cm³, 4.5 mmol) was added dropwise. 2-Ethylaniline was added dropwise and stirred at room temperature for 18 h. EtOAc (30 cm³) was added, washed with water (3 \times 20 cm³), HCl (1M, 3 \times 20 cm³), NaOH (1M, 3 \times 20 cm³), brine (2 \times 20 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. The residue was purified by recrystallisation from EtOAc to give 1-(2-ethylphenyl)-3-(2-isopropylphenyl)urea 2f (0.40 g, 95 %), as white blocks, m.p. 182-184 °C (from EtOAc); R_f (EtOAc-petrol, 3:7) 0.5; v_{max} (film)/cm⁻¹ 3428 (NH) and 1636 (C=O); δ_H (400 MHz; d₆-DMSO) 8.20 [1 H, s, (NH)_A], 8.09 [1 H, s, (NH)_B], 7.71 (1 H, dd, J 8.0 and 1.0, CH-d), 7.57 (1 H, dd, J 8.0 and 2.0, CH-h), 7.26 (1 H, dd, J 8.0 and 2.0, CH-e), 7.17 (1 H, dd, J 8.0 and 1.0, CH-a), 7.12 (2 H, m, CH-c and CH-g), (1 H, td, J 8.0 and 2.0, CH-f), 6.98 (1 H, td, J 8.0 and 1.0, CH-b), 3.19 [1 H, hept, J 7.0, (CH)], 2.62 [2 H, q, J 7.0, (CH₂)] and 1.21-1.16 [9 H, m, (CH₃) and (CH₃) × 2]; δ_{C} (100 MHz; d_{6} -DMSO) 154.4 (C=O), 140.6 (C), 137.4 (C), 136.3 (C), 134.7 (C), 129.0 (CH), 126.7 (CH), 126.4 (CH), 125.9 (CH), 125.0 (CH), 124.7 (CH), 123.9 (CH), 123.3 (CH), 27.5 (CH), 24.5 (CH₂), 23.8 [(CH₃) × 2] and 14.5 (CH₃); (Found: M+H⁺, 283.1804, C₁₈H₂₂N₂O requires M+H, 283.1805). 1,3-bis(2-Isopropylphenyl)urea, 2g. -2-Isopropylaniline (1.35 g, 1.42 cm³, 10 mmol), was dissolved in CH₂Cl₂ (20 cm³) at 0 °C and triethylamine (2.2 g, 3.1 cm³, 22 mmol) added in one portion. Diphosgene (0.99 g, 0.60 cm³, 5.0 mmol) was added dropwise and the reaction mixture allowed to warm to room temperature over 18 h. The white precipitate was isolated and recrystallised from EtOAc-pentane to give 1,3-bis(2-isopropylphenyl)urea **2g** (2.87 g, 97 %), as white plates, m.p. 188-190 °C (from EtOAc-pentane); $R_{\rm f}$ (EtOAc-pentane, 3:7) 0.50; $v_{\rm max}$ (film)/cm⁻¹ 3318 and 3302 (N–H) and 1647 (C=O); δ_H (400 MHz; d₆-DMSO) 8.63 [2 H, s, (NH) × 2], 7.57 (2 H, dd, J 8.0 and 2.0, CH-d), 7.24 (2 H, dd, J 8.0 and 2.0, CH-a), 7.10 (2 H, td, J 8.0 and 2.0, CH-c), 7.03 (2 H, td, J 8.0 and 2.0, CH-b), 3.31 [2 H, hept, J 7.0, (CH) × 2] and 1.20 [12 H, d, J 7.0 (CH₃) × 4]; δ_C (100 MHz; d₆-DMSO) 154.9 (C=O), 140.6 (C), 136.7 (C), 126.2 (CH), 125.8 (CH), 124.8 (CH), 124.4 (CH), 27.5 (CH) and 23.9 (CH₃); m/z (CI) 297 (100 %, M+H⁺); (Found: M+H⁺, 297.1959, C₁₉H₂₄N₂O requires M+H, 297.1962).

I-(2-tert-Butylphenyl)-3-(2-methylphenyl)urea, **2h**. —2-Methylaniline (0.21 g, 0.21 cm³, 2 mmol), was dissolved in CH₂Cl₂ (10 cm³) at room temperature, 2-*tert*-butylphenyl isocyanate (0.35 g, 0.35 cm³, 2.0 mmol) added dropwise and stirred for 24 h. The solvent was removed under reduced pressure and the residue recrystallised from EtOAc-petrol to give *1-(2-tert-butylphenyl)-3-o-tolylurea* **2h** (0.55 g, 98 %), as white plates cubes, m.p. 225-227 °C (from EtOAc-petrol); R_f (EtOAc-petrol) 0.56; v_{max} (film)/cm⁻¹ 1649 (C=O); δ_H (300 MHz; CDCl₃) 8.15 [1 H, s, (NH)_A], 7.85 [1 H, s, (NH)_B], 7.75 (1 H, d, *J* 8.0, CH-h), 7.38 (1 H, dd, *J* 8.0 and 1.0, CH-d), 7.26-7.05 (5 H, m, CH-a, CH-c, CH-e, CH-f and CH-g), 6.91 (1 H, t, *J* 8.0, CH-b), 2.23 [3 H, s, CH₃] and 1.36 [9 H, s, (CH₃) × 3]; δ_C (75 MHz; CDCl₃) 154.6 (C=O), 145.6 (C), 138.5 (C), 136.8 (C), 136.7 (C), 131.5 (CH), 130.8 (CH), 128.3 (CH), 126.7 (CH), 126.3 (CH), 123.2 (CH), 122.1 (CH), 35.3 (C), 31.3 [(CH₃) × 3] and 18.7 (CH₃); m/z (ESI⁺) 283 (100 %, M+H⁺); (Found: M+H⁺, 283.1808, C₁₈H₂₃N₂O requires *M*+*H*, 283.1805). Elem. Anal. for C₁₈H₂₂N₂O: calcd: C, 76.56 %; H, 7.85 %; N, 9.92; found: C, 76.84 %; H, 7.75 %; N, 9.83 %.

1-(2-tert-Butylphenyl)-3-(2-ethylphenyl)urea, **2i**. —2-Ethylaniline (0.24 g, 0.25 cm³, 2 mmol), was dissolved in CH₂Cl₂ (10 cm³) at room temperature, 2-*tert*-butylphenyl isocyanate (0.35 g, 0.35 cm³, 2.0 mmol) added dropwise and stirred for 24 h. The solvent was removed under reduced pressure and the residue recrystallised from EtOAc-petrol to give *1-(2-tert-butylphenyl)-3-(2-ethylphenyl)urea* **2i** (0.57 g, 97 %), as white plates cubes, m.p. 234-236 °C (from EtOAc-petrol); R_f (EtOAc-petrol, 1:4) 0.58; v_{max} (film/cm⁻¹ 1660 (C=O); δ_H (300 MHz; CDCl₃) 8.17 (1 H, s, NH), 7.89 (1 H, s, NH), 7.75 (1 H, dd, *J* 8.0 and 1.0, CH-h), 7.40 (1 H, d, *J* 8.0, CH-d), 7.30-7.09 (5 H, m, CH-a, CH-c, CH-e, CH-f and CH-g), 7.01 (1 H, td, *J* 8.0 and 2.0, CH-b), 2.66 [2 H, q, *J* 7.5, (CH₂)], 1.40 [9 H, s, (CH₃) × 3] and 1.21 [3 H, t, *J* 7.5, (CH₃)]; δ_C (75 MHz; CDCl₃) 154.9 (C=O), 145.7 (C), 137.7 (C), 136.9 (C), 131.6 (CH), 129.1 (CH), 127.0 (CH), 126.9 (CH), 126.7 (CH), 126.4 (CH), 123.3 (CH), 35.3 (C), 31.3 [(CH₃) × 3], 24.7 (CH₂) and 14.9 (CH₃); m/z (ESI⁺) 297 (100 %, M+H⁺); (Found: M+H⁺, 297.1966, C₁₉H₂₄N₂O requires *M*+*H*, 297.1961). Elem. Anal. for C₁₉H₂₄N₂O: calcd: C, 76.99 %; H, 8.16 %; N, 9.45; found: C, 77.15 %; H, 8.26 %; N, 9.30 %.

1,3-bis(2-tert-Butylphenyl)urea, 2k. —2-tert-Butylaniline (0.254 g, 0.26 cm³, 1.70 mmol), was dissolved in CH2CL2 (10 cm³) at RT, 2-tert-butyl phenylisocyanate (0.298 g, 0.29 cm³, 1.70 mmol) added dropwise and stirred at RT for 18 h. The white precipitate was isolated and recrystallised from EtOAc-pentane to give *1,3-bis*(2-tert-butylphenyl)urea **2k** (0.61 g, 98 %), as white plates, m.p. 259-261 °C (from EtOAc-petrol); R_f (EtOAc-petrol, 1:1) 0.56; v_{max} (film)/cm⁻¹ 1653 (C=O); δ_H (300 MHz; d_6 -DMSO) 7.85 [2 H, s, (NH)_A and (NH)_B], 7.39 (2 H, dd, *J* 8.0 and 2.0, CH-a), 7.28 (2 H, dd, *J* 8.0 and 2.0, CH-d), 7.21 (2 H, td, *J* 8.0 and 2.0, CH-c), 7.15 (2 H, td, *J* 8.0 and 2.0, CH-b) and 1.42 [9 H, s, (CH₃) × 3]; δ_C (75 MHz; d_6 -DMSO) 155.6 (C=O), 145.3 (C), 137.2 (C), 131.2 (CH), 126.9 (CH), 126.8 (CH) and 126.1 (CH); m/z (CI) 369 (20 %, M+H⁺) and 289 (40, M+H⁺ - Br); (Found: M+H⁺, 368.9233, C₁₃H₁₁N₂OBr₂ requires *M*+*H*, 368.9233). Elem. Anal. for C₂₁H₁₈N₂O: calcd: C, 77.74 %; H, 8.70 %; N, 8.63; found: C, 77.94 %; H, 8.40 %; N, 8.60 %.

1-(2-Fluorophenyl)-3-(2,6-dimethylphenyl)urea, **21**. —2-Fluroroaniline (1.1 g, 10 mmol), was dissolved in CH₂Cl₂ (20 cm³) at room temperature. 2,6-Mimethylphenyl isocyanate (1.47 g, 1.40 cm³, 10 mmol) added dropwise and stirred for 24 h. The solvent was removed under educed pressure and the residue recrystallised from EtOAc-petrol to give *1-(2-fluorophenyl)-3-(2,6-dimethylphenyl)urea* **21** (2.0 g, 80 %), as white cubes, m.p. 225-227 °C (from EtOAc-pentane); R_f (EtOAc-pentane, 1:4) 0.36; v_{max} (film)/cm⁻¹ 1645 (C=O); δ_H (400 MHz; d_6 -DMSO) 8.57 [1 H, br., (NH)_A], 8.12 (2 H, td, *J* 8.0 and 2.0, CH-b and CH-c), 7.25-7.15 (1 H, m, CH-d), 7.11-7.02 [4 H, m, CH-a, CH-e and (NH)_B], 6.98-6.92 (1 H, m, CH-f) and 2.19 [6 H, s, (CH₃) × 2]; δ_C (100 MHz; d_6 -DMSO) 153.4 (C=O), 136.0 (C), 135.7 (C), 128.8 (CH), 128.4 (CH), 126.7 (CH), 125.1 (CH), 122.6 (C), 120.9 (C), 115.7 (CH), 115.5 (CH) and 18.9 (CH₃); m/z (ESI⁺) 259 (100 %, M+H⁺); (Found: M+H⁺, 259.1238, C₁₅H₁₅N₂OF requires *M*+*H*, 259.1241).

1-(2-Chlorophenyl)-3-(2,6-dimethylphenyl)urea, 2m. —2-Chloroaniline (1.27 g, 10 mmol), was dissolved in CH₂Cl₂ (20 cm³) at room temperature, 2,6-dimethylphenyl isocyanate (1.47 g, 1.40 cm³, 10 mmol) added dropwise and stirred for 24 h. The solvent was removed under educed pressure and the residue recrystallised from EtOAc-petrol to give *1-(2-chlorophenyl)-3-(2,6-dimethylphenyl)urea* 2m (2.50 g, 93 %), as white blocks, m.p. 234-236 °C (from EtOAc-pentane); R_f (EtOAc-pentane, 1:4) 0.38; v_{max} (film/cm⁻¹ 1644 (C=O); δ_H (400 MHz; d_6 -DMSO) 8.47 [1 H, s, (NH)_A], 8.31 [1 H, br., (NH)_B], 8.14 (1 H, dd, *J* 8.0 and 2.0, CH-d), 7.40 (1 H, dd, *J* 8.0 and 1.0, CH-a) 7.24 (1 H, td, *J* 8.0 and 1.0, CH-c), 7.06 (3 H, m, CH-b and CH-e), 6.97 (1 H, td, *J* 8.0 and 2.0, CH-f) and 2.20 [6 H, s, (CH₃) × 2]; δ_C (100 MHz; d_6 -DMSO) 153.4 (C=O), 137.2 (C), 136.1 (C), 135.6 (C), 129.8 (CH), 128.5 (CH), 128.2 (CH), 126.8 (CH), 123.5 (CH), 122.2 (C), 121.6 (CH) and 18.9 (CH₃); m/z (CI) 275 (100 %, M+H⁺); (Found: M+H⁺, 275.0944, C₁₅H₁₅N₂OCI requires *M*+H, 275.0946).

I-(2-Bromophenyl)-3-(2,6-dimethylphenyl)urea, **2n**. —2-Bromoaniline (1.7 g, 10 mmol), was dissolved in CH₂Cl₂ (20 cm³) at room temperature. 2,6-Dimethylphenyl isocyanate (1.47 g, 1.40 cm³, 10 mmol) added dropwise and stirred for 24 h. The solvent was removed under educed pressure and the residue recrystallised from EtOAc-petrol to give *I-(2-bromophenyl)-3-(2,6-dimethylphenyl)urea* **2n** (2.50 g, 78 %), as white cubes, m.p. 256-258 °C (from EtOAc-pentane); R_f (EtOAc-pentane, 1:4) 0.36; v_{max} (film)/cm⁻¹ 1644 (C=O) and 746 (C-Br); δ_H (400 MHz; d_6 -DMSO) 8.51 [1 H, s, (NH)_A], 8.13 [1 H, br., (NH)_B], 8.06 (1 H, dd, *J* 7.0 and 2.0, CH-d), 7.57 (1 H, dd, *J* 7.0 and 1.0, CH-a) 7.28 (1 H, td, *J* 7.0 and 1.0, CH-c), 7.06 (3 H, m, CH-b and CH-e), 6.92 (1 H, td, *J* 8.0 and 2.0, CH-f) and 2.21 [6 H, s, (CH₃) × 2]; δ_C (100 MHz; d_6 -DMSO) 153.4 (C=O), 138.3 (C), 136.0 (C), 135.6 (C), 133.1 (CH), 128.7 (CH), 128.5 (CH), 126.8 (CH), 122.5 (CH), 113.4 (C) and 18.9 (CH₃); m/z (ESI⁺) 319 (100 %, M+H⁺); (Found: M+H⁺, 319.0438, C₁₅H₁₅N₂OBr requires *M*+*H*, 319.0441).

1-(2-Iodophenyl)-3-(2,6-dimethylphenyl)urea, **20**. —2-Iodoaniline (2.2 g, 10 mmol), was dissolved in CH₂Cl₂ (20 cm³) at room temperature, 2,6-Dimethylphenyl isocyanate (1.47 g, 1.40 cm³, 10 mmol) added dropwise and stirred for 24 h. The solvent was removed under reduced pressure and the residue recrystallised from EtOAc-petrol to give *1-(2-iodophenyl)-3-(2,6-dimethylphenyl)urea* **20** (4.0 g, 86 %), as white cubes, m.p. 260-262 °C (from EtOAc-pentane); $R_{\rm f}$ (EtOAc-pentane, 1:4) 0.34; $v_{\rm max}$ (film)/cm⁻¹ 1640 (C=O); $\delta_{\rm H}$ (400 MHz; d_6 -DMSO) 8.43 [1 H, s, (NH)_A], 7.88-7.76 [3 H, m, CH-a, CH-d and (NH)_B], 7.30 (1 H, td, *J* 8.0 and 2.0, CH-c), 7.10-7.04 (3 H, m, CH-e and CH-f), 6.79 (1 H, td, *J* 8.0 and 2.0, CH-b) and 2.22 [6 H, s, (CH₃) × 2]; $\delta_{\rm C}$ (100 MHz; d_6 -DMSO) 153.7 (C=O), 141.0 (C), 139.5 (CH), 136.2 (C), 135.7 (CH), 130.2 (CH), 129.3 (CH), 128.5 (CH), 126.8 (C), 125.4 (CH), 91.9 (C) and 19.0 (CH₃); m/z (ESI⁺) 367 (100 %, M+H⁺); (Found: M+H⁺, 367.0298, C₁₅H₁₅N₂OI requires *M*+H, 367.0302).

1-(2-Methyphenyl)-3-(2,6-dimethylphenyl)urea, **2p**. —2-Methylaniline (0.54 g, 0.53 cm³, 5.0 mmol), was dissolved in CH₂Cl₂ (10 cm³) at room temperature and 2,6-dimethylphenyl isocyanate (0.74 g, 0.70 cm³, 5.0 mmol) was added dropwise and stirred for 20 h. The solvent was removed under reduced pressure and the residue recrystallised from EtOAc-petrol to give *1-(2-methylphenyl)-3-(2,6-dimethylphenyl)urea* **2p** (1.1 g, 86 %), as white cubes, m.p. 225-227 °C (from EtOAc-pentane); $R_{\rm f}$ (EtOAc-pentane, 1:4) 0.45; $v_{\rm max}$ (film)/cm⁻¹ 1637 (C=O); $\delta_{\rm H}$ (400 MHz; *d*₆-DMSO) 8.02 [1 H, s, (NH)_A], 7.88 [1 H, br., (NH)_B], 7.77 (1 H, d, *J* 8.0, CH-d), 7.14 (1 H, d, *J* 8.0, CH-a), 7.09 (1 H, t, *J* 8.0, CH-c), 7.06-7.01 (3 H, m, CH-e and CH-f), 6.90 (1 H, td, *J* 8.0 and 1.0, CH-b), 2.23 [3 H, s, (CH₃)] and 2.21 [6 H, s, (CH₃) × 2]; $\delta_{\rm C}$ (100 MHz; *d*₆-DMSO) 154.0 (C=O), 138.6 (C), 136.1 (C), 130.8 (CH), 128.4 (CH), 126.5 (CH), 123.2 (CH), 123.1 (CH), 121.7 (C), 119.2 (C), 19.0 (CH₃) and 18.6 (CH₃); m/z (ESI⁺) 255 (100 %, M+H⁺); (Found: M+H⁺, 255.1476, C₁₉H₂₄N₂O requires *M*+H, 255.1492). Purity by LC-MS analysis.

1-(2-Ethylphenyl)-3-(2,6-dimethylphenyl)urea, **2q**. —2-Ethylaniline (0.61 g, 0.62 cm³, 5.0 mmol), was dissolved in CH₂Cl₂ (10 cm³) at room temperature. 2,6-Dimethylphenyl isocyanate (0.74 g, 0.70 cm³, 5.0 mmol) was added dropwise and stirred for 20 h. The solvent was removed under reduced pressure and the residue recrystallised from EtOAc-petrol to give *1-(2-ethylphenyl)-3-(2,6-dimethylphenyl)urea* **2q** (1.3 g, 97 %), as white cubes, m.p. 230-232 °C (from EtOAc-pentane); $R_{\rm f}$ (EtOAc-pentane, 1:4) 0.28; $v_{\rm max}$ (film)/cm⁻¹ 1632 (C=O); $\delta_{\rm H}$ (400 MHz; *d*₆-DMSO) 7.99 [1 H, s, (NH)_A], 7.86 [1 H, br., (NH)_B], 7.70 (1 H, dd, *J* 8.0 and 1.0, CH-d), 7.15 (1 H, dd, *J* 8.0 and 1.0, CH-a), 7.10 (1 H, td, *J* 8.0 and 1.0, CH-c), 7.07-7.01 (3 H, m, CH-e and CH-f), 6.96 (1 H, td, *J* 8.0 and 1.0, CH-b), 2.61 [2 H, q, *J* 8.0, (CH₂)], 2.21 [6 H, s, (CH₃) × 2] and 1.17 [3 H, t, *J* 8.0, (CH₃)]; $\delta_{\rm C}$

(100 MHz; d₆-DMSO) 154.2 (C=O), 137.7 (C), 136.2 (C), 136.1 (C), 134.5 (C), 129.1 (CH), 128.4 (CH), 126.7 (CH), 126.5 (CH), 123.7 (CH), 123.0

(CH), 24.6 (CH₂), 18.9 (CH₃) and 14.9 (CH₃); m/z (ESI⁺) 269 (100 %, M+H⁺); (Found: M+H⁺, 269.1646, C₁₇H₂₀N₂O requires M+H, 269.1649). *1-(2-Isopropylphenyl)-3-(2,6-dimethylphenyl)urea*, **2r**. —2-Isopropylaniline (0.68 g, 0.71 cm³, 5.0 mmol), was dissolved in CH₂Cl₂ (10 cm³) at room temperature. 2,6-Dimethylphenyl isocyanate (0.74 g, 0.70 cm³, 5.0 mmol) added dropwise and stirred for 20 h. The solvent was removed under reduced pressure and the residue recrystallised from EtOAc-petrol to give 1-(2-isopropylphenyl)-3-(2,6-dimethylphenyl)urea 2r (1.5 g, 98 %), as white cubes, m.p. 255-257 °C (from EtOAc-pentane); R_f (EtOAc-pentane, 1:4) 0.29; v_{max} (film)/cm⁻¹ 1631 (C=O); δ_H (400 MHz; d₆-DMSO) 7.92 [1 H, s, (NH)_A], 7.89 [1 H, br., (NH)_B], 7.58 (1 H, dd, J 8.0 and 2.0, CH-d), 7.24 (1 H, dd, J 8.0 and 2.0, CH-a), 7.10 (1 H, td, J 8.0 and 2.0, CH-c), 7.07-6.98 (4 H, m, CH-b, CH-e and CH-f), 3.18 [1 H, hept, J 7.0, (CH)], 2.21 [6 H, s, (CH₃) × 2] 1.20 [3 H, s, (CH₃)_A] and 1.18 [3 H, s, (CH₃)_B]; $\delta_{\rm C}$ (100 MHz; d₆-DMSO) 154.2 (C=O), 140.2 (C), 136.8 (C), 136.3 (C), 136.2 (C), 128.4 (CH), 126.5 (CH), 126.4 (CH), 125.8 (CH), 124.5 (CH), 124.4 (CH), 125.4 (CH), 27.6 (CH), 23.7 (CH₃) and 18.9 (CH₃); m/z (ESI⁺) 283 (100 %, M+H⁺); (Found: M+H⁺, 283.1804, C₁₈H₂₂N₂O requires M+H, 367.0302).

1-(2-tert-Butylphenyl)-3-(2,6-dimethylphenyl)urea, 2s. —2-tert-Butylaniline (0.75 g, 0.78 cm³, 5.0 mmol), was dissolved in CH₂Cl₂ (10 cm³) at room temperature, 2,6-dimethylphenyl isocyanate (0.74 g, 0.70 cm³, 5.0 mmol) added dropwise and stirred for 20 h. The solvent was removed under reduced pressure and the residue recrystallised from EtOAc-petrol to give 1-(2-tert-butylphenyl)-3-(2,6-dimethylphenyl)urea 2s (1.4 g, 98 %), as white cubes, m.p. 269-271 °C (from EtOAc-pentane); $R_{\rm f}$ (EtOAc-pentane, 1:4) 0.51; $v_{\rm max}$ (film)/cm⁻¹ 1633 (C=O); $\delta_{\rm H}$ (400 MHz; d_6 -DMSO) 7.99 [1 H, s, (NH)_A], 7.49 [1 H, br., (NH)_B], 7.33 (1 H, dd, J 8.0 and 1.0, CH-d), 7.28 (1 H, br., CH-a), 7.15 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-d), 7.28 (1 H, br., CH-a), 7.15 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-d), 7.28 (1 H, br., CH-a), 7.15 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-d), 7.28 (1 H, br., CH-a), 7.15 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-d), 7.28 (1 H, br., CH-a), 7.15 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-d), 7.28 (1 H, br., CH-a), 7.15 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-d), 7.28 (1 H, br., CH-a), 7.15 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and 1.0, CH-c), 7.08 (1 H, td, J 8.0 and b), 7.06-6.99 (3 H, m, CH-e and CH-f), 2.22 [6 H, s, (CH₃) × 2] and 1.37 [9 H, s, (CH₃) × 2]; $\delta_{\rm C}$ (100 MHz; d_6 -DMSO) 154.7 (C=O), 137.3 (C), 136.4 (C), 136.2 (C), 136.1 (C), 128.4 (CH), 126.8 (CH), 126.6 (CH), 126.5 (CH), 125.8 (CH), 125.7 (CH), 35.2 (C), 31.2 [(CH₃) × 2] and 19.0 [(CH₃) × 2]; m/z (ESI⁺) 297 (100 %, M+H⁺); (Found: M+H⁺, 297.1944, C₁₉H₂₄N₂O requires M+H, 297.1962); Purity by LC-MS analysis.

1-(2-Methoxyphenyl)-3-(2,6-dimethylphenyl)urea, 2t. -2-Methoxyaniline (0.62 g, 0.56 cm³, 5.0 mmol), was dissolved in CH₂Cl₂ (10 cm³) at room temperature, 2,6-dimethylphenyl isocyanate (0.74 g, 0.70 cm³, 5.0 mmol) added dropwise and stirred for 20 h. The solvent was removed under reduced pressure and the residue recrystallised from EtOAc-petrol to give *1-(2-methoxyphenyl)-3-(2,6-dimethylphenyl)urea* **2t** (1.30 g, 96 %), as white cubes, m.p. 248-250 °C (from EtOAc); R_f (EtOAc) 0.44; v_{max} (film)/cm⁻¹ 1644 (C=O); δ_H (400 MHz; d_6 -DMSO) 8.34 [1 H, s, (NH)_A], 8.20 [1 H, br., (NH)_B], 8.11 (1 H, dd, J 8.0 and 2.0, CH-d), 7.08-7.02 (3 H, m, CH-e and CH-f), 6.98 (1 H, dd, J 8.0 and 2.0, CH-a), 6.89 (1 H, td, J 8.0 and 2.0, CH-b), 6.84 (1 H, td, *J* 8.0 and 2.0, CH-c), 3.86 [3 H, s, (CH₃)] and 2.19 [6 H, s, (CH₃) × 2]; $\delta_{\rm C}$ (100 MHz; *d*₆-DMSO) 153.6 (C=O), 148.0 (C), 136.0 (C), 129.9 (C), 128.4 (CH), 128.3 (CH), 126.5 (C), 122.0 (CH), 121.2 (CH), 118.6 (CH), 111.3 (CH), 56.4 (CH₃) and 19.0 (CH₃); m/z (APCI⁺) 271 (100 %, $M+H^+$); (Found: $M+H^+$, 271.1424, $C_{16}H_{18}N_2O_2$ requires M+H, 271.1441). Purity by LC-MS analysis.

1-(2,6-Dimethylphenyl)-3-(2-(trifluoromethoxy)phenyl)urea, 2u. —2-(Trifluoromethoxy)aniline (0.89 g, 0.68cm³, 5.0 mmol), was dissolved in CH₂Cl₂ (10 cm³) at room temperature, 2,6-dimethylphenyl isocyanate (0.74 g, 0.70 cm³, 5.0 mmol) added dropwise and stirred for 20 h. The solvent was removed under reduced pressure and the residue recrystallised from EtOAc-petrol to give 1-(2,6-dimethylphenyl)-3-(2-(trifluoromethoxy)phenyl)urea 2u (0.54 g, 33 %), as white cubes, m.p. 242-244 °C (from EtOAc); $R_{\rm f}$ (EtOAc) 0.48; $v_{\rm max}$ (film)/cm⁻¹ 1643 (C=O); $\delta_{\rm H}$ (400 MHz; d₆-DMSO) 8.46 [1 H, s, (NH)_A], 8.32 [1 H, br., (NH)_B], 8.15 (1 H, dd, J 8.0 and 2.0, CH-d), 7.37-7.20 (3 H, m, CH-a, CH-b and CH-c), 7.06-7.00 (3 H, m, CH-e and CH-f), 2.19 [6 H, s, (CH₃) × 2]; δ_{C} (100 MHz; d₆-DMSO) 153.4 (C=O), 136.1 (C), 135.6 (C), 133.5 (C), 128.5 (CH), 128.4 (CH), 126.7 (CH), 123.0 (CH), 122.3 (CH), 122.0 (CH), 119.4 (C), 110.3 (C) and 18.8 (CH₃); m/z (APCI⁺) 325 (100 %, M+H⁺); (Found: M+H⁺, 325.1139, C₁₆H₁₅N₂O₂F₃ requires *M*+*H*, 325.1159). Purity by LC-MS analysis.

1,3-bis(2-Fluorophenyl)-1,3-dimethylurea 3a. -1,3-bis(2-Fluorophenyl)urea 2a (0.45 g, 1.79 mmol) was dissolved in THF (40 cm³) and cooled to 0 °C. Sodium hydride (0.21 g, 5.37 mmol) was added portionwise and stirred at room temperature for 1 h. Methyl iodide (0.45 cm³, 7.16 mmol) was added and stirred at room temperature for 18 h. Water (10 cm³) was added and extracted with EtOAc (3×20 cm³). The combined organic fractions were dried (MgSO₄), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO₂; 20 % EtOAc in pentane) to give 1,3-bis(2-fluorophenyl)-1,3-dimethylurea 3a (0.43 g, 98 %), as white prisms, m.p. 176-178 °C; R_f (EtOAc-pentane, 1:1) 0.64; v_{max} $(\text{film})/\text{cm}^{-1}$ 1656 (C=O); δ_{H} (300 MHz; CDCl₃) 6.99-6.77 (3 H, m, CH-a, CH-c and CH-d), 6.73 (1 H, t, *J* 8.0, CH-b), and 3.16 [6 H, s, (NCH₃)_A and (CH₃)_B]; δ_C (75 MHz; CDCl₃) 160.7 C=O), 157.5 (C-F, d, J 249), 132.7 (C, d, J 11.5), 128.4 (CH), 127.7 (CH, d, J 8.0), 124.4 (CH, d, J 4.3), 116.1 (CH, d, J 20) and 38.6 (NCH₃); m/z (CI) 277 (100 %, M+H⁺); (Found: M+H⁺, 277.1150, $C_{15}H_{15}N_2OF_2$ requires M+H, 277.1147). Elem. Anal. for C₁₅H₁₄N₂OF₂: calcd: C, 65.21 %; H, 5.11 %; N, 10.14; F, 13.75; found: C, 65.55 %; H, 5.24 %; N, 9.84 %; F, 13.82 %.

1,3-bis(2-Chlorophenyl)-1,3-dimethylurea, 3b. -1,3-bis(2-Chlorophenyl)urea 2a (2.00 g, 7.10 mmol) was dissolved in THF (40 cm³) and cooled to 0 °C. Sodium hydride (0.71 g, 17.8 mmol) was added portionwise and stirred at room temperture for 1 h. Methyl iodide (1.33 cm³, 21.3 mmol) was added and stirred at room temperature for 18 h. Water (30 cm³) was added and extracted with EtOAc (3×30 cm³). The combined organic fractions were dried (MgSO₄), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO₂; 15 % EtOAc in pentane) to give 1,3-bis(2-chlorophenyl)-1,3-dimethylurea **3b** (2.08 g, 95 %), as colourless prisms, m.p. 195-197 °C; R_f (EtOAc-pentane, 1:4) 0.29; υ_{max} (film)/cm⁻¹ 1643 (C=O); δ_H (400 MHz; CDCl₃) 7.04 (2 H, dd, J 7.0 and 2.0, CH-a), 6.90-6.80 (4 H, m, CH-b and CH-c), 6.70 (2 H, dd, J 8.0 and 2.0, CH-d) and 3.08 [6H, s, (NCH₃)]; δ_{C} (100 MHz; CDCl₃) 160.4 (C=O), 142.2 (C), 132.4 (C), 130.2 (CH), 129.2 (CH), 127.6 (CH), 127.5 (CH) and 38.6 (NCH₃); m/z (CI) 309 (100 %, M+H⁺); (Found: M+H⁺, 309.0556, $C_{15}H_{14}N_2OCl_2$ requires M+H, 309.0556).

1,3-Bis(2-bromophenyl)-1,3-dimethylurea 3c. —2-Bromo-N-methylaniline (0.19 g, 1.0 mmol), was dissolved in CH₂Cl₂ (5 cm³) at room temperature and triethylamine (0.22 g, 2.2 mmol) added in one portion. Triphosgene (0.05 g, 0.16 mmol) was added in small portions and the reaction mixture stirred for 1 h. The solvent was concentrated under reduced pressure, the residue dissolved in toluene (10 cm³) and heated to reflux for 18 h. After cooling, water (20 cm³) was added and extracted with EtOAc (3 \times 30 cm³). The combined organic fractions were dried (MgSO₄), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO₂; EtOAc-petrol, 15:85) to give 1,3-bis(2bromophenyl)-1,3-dimethylurea 3c (0.04 g, 65 %), as white cubes, m.p. 91-93 °C (from EtOAc-petrol); R_f (EtOAc-petrol, 1:4) 0.23; v_{max} (film)/cm⁻¹ 1710 (C=O) and 742 (C-Br); $\delta_{\rm H}$ (300 MHz; CDCl₃) 7.31 (2 H, dd, J 8.0 and 2.0, CH-a), 6.88 (4 H, m, CH-b and CH-c), 6.72 (2 H, dd, J 8.0 and 1.0, CH-d), and 3.14 [6 H, s, (NCH₃)_A and (NCH₃)_B]; δ_{C} (75 MHz; CDCl₃) 143.7 (C), 133.5 (CH), 129.6 (CH), 128.3 (CH), 127.7 (CH), 123.1 (C) and 38.9 (NCH₃); m/z (CI) 397 (50 %, M+H⁺) and 317 (60, M+H⁺ – Br); (Found: M+H⁺, 396.9537, C₁₅H₁₅N₂Br requires *M*+*H*, 396.9546).

Alternatively, sodium hydroxide (0.09 g, 2.0 mmol), potassium carbonate (0.06 g, 0.5 mmol), tetrabutylammonium hydrogen sulphate (0.03 g, 0.01 mmol) and 1,3-bis(2-bromophenyl)urea 2c (0.15 g, 0.5 mmol) were suspended in toluene (5 cm³) and the mixture heated to reflux for 1 h. Dimethyl sulfate (0.09 cm³, 1.1 mmol) was added dropwise and reflux continued for 18 h. After cooling to room temperature, the mixture was filtered, the filtrate washed with 1N hydrochloric acid (3×10 cm³) and water (2×5 cm³), dried (MgSO₄), filtered and concentrated under reduced pressure. The residue was recrystallised from EtOAc-petrol to give 1,3-bis(2-bromophenyl)-1,3-dimethylurea 3c (0.115 g, 70%), as white cubes with identical data to above.

1,3-bis(2-Methylphenyl)-1,3-dimethylurea, 3d. -1,3-bis(2-Methylphenyl)urea 2d (1.39 g, 5.8 mmol) was dissolved in THF (50 cm³) and cooled to 0 °C. Sodium hydride (0.58 g, 14.5 mmol) was added portionwise and stirred at room temperture for 1 h. Methyl iodide (1.1 cm³, 17.4 mmol) was added and stirred at room temperature for 21 h. Water (40 cm³) was added and extracted with EtOAc (3×40 cm³). The combined organic fractions were dried (MgSO₄), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO₂; 10 % EtOAc in pentane) to give *1,3-bis(2-methylphenyl)-1,3-dimethylurea* **3d** (1.48 g, 95 %), as colourless cubes, m.p. 232-234 °C (from EtOAc-pentane); *R*_f (EtOAc-pentane, 3:7) 0.58; v_{max} (film)/cm⁻¹ 1667 (C=O); δ_{H} (400 MHz; CDCl₃) 6.87 (4 H, m, CH-c and CH-d), 6.78 (2 H, m, CH-b), 6.52 (2 H, d, *J* 8.0, CH-a), 3.04 [6H, s, (NCH₃) × 2] and 1.92 [6 H, s, (CH₃) × 2]; δ_{C} (100 MHz; CDCl₃) 162.3 (C=O), 144.1 (C), 135.6 (C), 130.7 (CH), 127.7 (CH), 126.7 (CH), 126.4 (CH), 38.9 (NCH₃) and 17.4 (CH₃); m/z (ESI⁺) 269 (100 %, M+H⁺); (Found: M+H⁺, 269.1652, C₁₇H₂₀N₂O requires *M*+*H*, 269.1649).

1,3-bis(2-*Ethylphenyl)-1,3-dimethylurea*, 3e. -1,3-*bis*(2-Ethylphenyl)urea 2e (1.56 g, 5.8 mmol) was dissolved in THF (50 cm³) and cooled to 0 °C. Sodium hydride (0.58 g, 14.5 mmol) was added portionwise and stirred at room temperture for 2 h. Methyl iodide (1.1 cm³, 17.4 mmol) was added and stirred at room temperature for 20 h. Water (40 cm³) was added and extracted with EtOAc (3 × 40 cm³). The combined organic fractions were dried (MgSO₄), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO₂; 10 % EtOAc in pentane) to give *1,3-bis*(2-*ethylphenyl)-1,3-dimethylurea* 3e (1.60 g, 93 %), as colourless cubes, m.p. 190-192 °C (from EtOAc-pentane); *R*_f (EtOAc-pentane, 3:7) 0.60; v_{max} (film)/cm⁻¹ 1660 (C=O); δ_{H} (400 MHz; CDCl₃) 6.96-6.89 (4 H, m, CH-c and CH-d), 6.80-6.72 (2 H, m, CH-b), 6.47 (2 H, d, *J* 8.0, CH-a), 3.03 [6 H, s, (NCH₃) × 2], 2.27 [4 H, br. s, (CH₂) × 2] and 1.06 [6 H, t, *J* 7.0, (CH₃) × 2]; δ_{C} (100 MHz; CDCl₃) 162.4 (C=O), 143.6 (C), 140.9 (C), 128.4 (CH), 127.9 (CH), 126.6 (CH), 126.4 (CH), 39.6 (NCH₃), 23.0 (CH₂) and 14.1 (CH₃); m/z (ESI⁺) 297 (100 %, M+H⁺); (Found: M+H⁺, 297.1967, C₁₉H₂₄N₂O requires *M*+*H*, 297.1962).

1-(2-Ethylphenyl)-3-(2-isopropylphenyl)-1,3-dimethylurea, **3f**. —1-(2-Ethylphenyl)-3-(2-*iso*propylphenyl)urea **2f** (0.45 g, 1.6 mmol) was dissolved in THF (20 cm³) and cooled to 0 °C. Sodium hydride (0.16 g, 4.0 mmol) was added portionwise and the suspension stirred at room temperature for 1 h. Methyl iodide (0.30 cm³, 4.5 mmol) was added and stirred at room temperature for 18 h. Water (20 cm³) was added and extracted with EtOAc (3 × 20 cm³). The combined organic fractions were dried (MgSO₄), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO₂; 10 % EtOAc in pentane) to give *1-(2-ethylphenyl)-3-(2-isopropylphenyl)-1,3-dimethylurea* **3f** (0.40 g, 81 %), as an orange oil; $R_{\rm f}$ (EtOAc-pentane, 1:4) 0.56; $v_{\rm max}$ (film)/cm⁻¹ 1650 (C=O); $\delta_{\rm H}$ (400 MHz; CDCl₃) 7.10 (1 H, dd, *J* 8.0 and 1.0, CH-d), 7.07-6.91 (3 H, m, CH-a, CH-e and CH-h), 6.86-6.60 (2 H, m, CH-c and CH-g), 6.30-6.20 (2 H, m, CH-b and CH-f), 3.07 [3 H, s, (NCH₃)_A], 3.02 [3 H, s, (NCH₃)_B], 2.91 [1 H, hept, *J* 7.0, (CH)], 2.35 [2 H, br., (CH₂)] and 1.12 [9 H, m, (CH₃) and (CH₃) × 2]; $\delta_{\rm C}$ (100 MHz; CDCl₃) 160.8 (C=O), 146.0 (C), 144.1 (C), 142.6 (C), 141.1 (C), 128.5 (CH), 128.4 (CH), 127.2 (CH), 127.0 (CH), 126.6 (CH), 126.5 (CH), 126.2 (CH), 125.9 (CH), 40.1 (NCH₃)_A, 39.9 (NCH₃)_B, 29.8 [(CH₃) × 2], 27.4 (CH), 22.8 (CH₂) and 14.1 (CH₃); m/z (ESI⁺) 311 (100 %, M+H⁺); (Found: M+H⁺, 311.2098, C₂₀H₂₆N₂O requires M+H, 311.2118).

2], 27.4 (CH), 22.8 (CH₂) and 14.1 (CH₃); m/z (ESI⁺) 311 (100 %, M+H⁺); (Found: M+H⁺, 311.2098, C₂₀H₂₆N₂O requires *M*+*H*, 311.2118). *I,3-bis(2-Isopropylphenyl)-1,3-dimethylurea* **3g**. —1,3-*bis*(2-Isopropylphenyl)urea **2g** (1.72 g, 5.8 mmol) was dissolved in THF (50 cm³) and cooled to 0 °C. Sodium hydride (0.58 g, 14.5 mmol) was added portionwise and stirred at room temperature for 1 h. Methyl iodide (1.1 cm³, 17.4 mmol) was added and stirred at room temperature for 18 h. Water (40 cm³) was added and extracted with EtOAc (3 × 40 cm³). The combined organic fractions were dried (MgSO₄), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO₂; 10 % EtOAc in pentane) to give *1,3-bis(2-isopropylphenyl)-1,3-dimethylurea* **3g** (1.65 g, 88 %), as white prisms, m.p. 195-197 °C (from EtOAc-pentane); $R_{\rm f}$ (EtOAc-pentane, 3:7) 0.61; $v_{\rm max}$ (film)/cm⁻¹ 1646 (C=O); $\delta_{\rm H}$ (400 MHz; CDCl₃) 7.05 (2 H, d, *J* 7.0, CH-d), 6.91 (2 H, t, *J* 7.0, CH-c), 6.55 (2 H, br., CH-a), 6.07 (2 H, br., CH-b), 2.97 [6 H, s, (NCH₃) × 2], 2.86 [2 H, br., (CH) × 2] and 1.05 (12 H, br., (CH₃) × 4]; $\delta_{\rm C}$ (100 MHz; CDCl₃) 162.9 (C=O), 146.0 (C), 142.9 (C), 128.3 (CH), 126.9 (CH), 126.6 (CH), 126.3 (CH), 40.2 (NCH₃), 27.3 (CH), 25.9 (CH₃) and 23.5 (CH₃); m/z (ESI⁺) 325 (100 %, M+H⁺); (Found: M+H⁺, 325.2274 C₂₁H₂₉N₂O requires *M*+*H*, 325.2270). Elem. Anal. for C₂₁H₂₈N₂O: calcd: C, 77.74%; H, 8.70%; N, 8.63%; found : C, 77.68%; H, 8.79%; N, 8.63%.

I-(2-tert-Butylphenyl)-3-(2-methylphenyl)-1,3-dimethylurea, **3h**. —1-(2-*tert*-Butylphenyl)-3-o-tolylurea **2h** (0.44 g, 1.56 mmol) was dissolved in THF (20 cm³) and cooled to 0 °C. Sodium hydride (0.08 g, 2.0 mmol) was added portionwise and stirred at room temperature for 1 h. Methyl iodide (0.15 cm³, 2.25 mmol) was added and stirred at room temperature for 18 h. Water (20 cm³) was added and extracted with EtOAc (3 × 20 cm³). The combined organic fractions were dried (MgSO₄), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO₂; 10 % EtOAc in pentane) to give *1-(2-tert-butylphenyl)-1,3-dimethyl-3-o-tolylurea* **3h** (0.47 g, 96 %), as colourless cubes, m.p. 221-223 °C (from EtOAc-petrol); R_f (EtOAc) 0.72; v_{max} (film)/cm⁻¹ 1655 (C=O); δ_H (300 MHz; CDCl₃) 7.29 (1 H, dd, *J* 8.0 and 2.0, CH-h), 7.10-6.90 (5 H, m, CH-a, CH-c, CH-d, CH-e and CH-g), 6.62 (1 H, br., CH-f), 6.26 (1 H, br., CH-b), 3.04 [3 H, br., (NCH₃)_A], 2.93 [3 H, br., (NCH₃)_B], 1.99 [3 H, br., (CH₃)] and 1.35 [9 H, s, (CH₃) × 3]; δ_C (75 MHz; CDCl₃) 162.3 (C=O), 146.5 (C), 145.2 (C), 142.6 (C), 135.7 (C), 131.3 (CH), 131.0 (CH), 128.6 (CH), 127.7 (CH), 127.1 (CH), 126.9 (CH), 126.5 (CH), 41.1 (NCH₃)_A, 39.5 (NCH₃)_B, 36.0 (C), 32.1 [(CH₃) × 3] and 17.7 (CH₃); m/z (ESI⁺) 311 (100 %, M+H⁺); (Found: M+H⁺, 311.2114, C₂₀H₂₇N₂O requires *M*+*H*, 311.2118). Elem. Anal. for C₁₈H₂₂N₂O: calcd: C, 76.56 %; H, 7.85 %; N, 9.92; found: C, 76.84 %; H, 7.75 %; N, 9.83 %.

1-(2-tert-Butylphenyl)-3-(2-ethylphenyl)-1,3-dimethylurea, 3i. -1-(2-tert-Butylphenyl)-3-(2-ethylphenyl)urea 3i (0.45 g, 1.52 mmol) was dissolved in THF (20 cm³) and cooled to 0 °C. Sodium hydride (0.08 g, 2.0 mmol) was added portionwise and stirred at room temperature for 1 h. Methyl iodide (0.15 cm³, 2.25 mmol) was added and stirred at room temperature for 18 h. Water (20 cm³) was added and extracted with EtOAc (3 × 20 cm³). The combined organic fractions were dried (MgSO₄), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO₂; 10 % EtOAc in pentane) to give 1-(2-tert-Butylphenyl)-3-(2-ethylphenyl)-1,3-dimethylurea 3i (0.46 g, 95 %), as colourless cubes, m.p. 223-224 °C (from EtOAc-petrol); R_f (EtOAc) 0.80; υ_{max} (film)/cm⁻¹ 1653 (C=O); δ_H (300 MHz; CDCl₃) 7.25 (1 H, d, J 8.0, CH-h), 7.09-6.95 (3 H, m, CH-a, CH-d and CH-e), 6.95-6.75 (2 H, m, CH-c and CH-g), 6.56 (1 H, br., CH-f), 6.20 (1 H, br., CH-b), 2.99 [3 H, br., (NCH₃)_A], 2.91 $[3 \text{ H}, \text{ br.}, (\text{NCH}_3)_B], 2.41 [2 \text{ H}, \text{ br.}, (\text{CH}_2)], 1.31 [9 \text{ H}, \text{ s}, (\text{CH}_3) \times 3]$ and 1.20-0.95 [3 H, m., (CH₃)]; δ_C (75 MHz; CDCl₃) 162.5 (C=O), 146.5 (C), 144.6 (C), 142.6 (C), 141.1 (C), 131.4 (CH), 128.6 (CH), 128.5 (CH), 127.6 (CH), 127.5 (CH), 126.8 (CH), 126.7 (CH), 126.4 (CH), 41.3 (NCH₃)_A, 40.1 (NCH₃)_B, 35.9 (C), 32.1 [(CH₃) × 3], 22.8 (CH₂) and 14.0 (CH₃); m/z (ESI⁺) 325 (100 %, M+H⁺); (Found: M+H⁺, 325.2278, C₂₁H₂₉N₂O requires *M*+*H*, 325.2274). Elem. Anal. for C₂₁H₂₈N₂O: calcd: C, 77.74 %; H, 8.70 %; N, 8.63; found: C, 77.52 %; H, 8.98 %; N, 8.70 %. 1-(2-tert-Butylphenyl)-3-(2-isopropylphenyl)-1,3-dimethylurea, 3j. —Diphosgene (0.90 cm³, 7.5 mmol) was dissolved in CH2CL2 (10 cm³) at room temperature and 2-tert-butyl aniline [0.78cm³, 5.0 mmol in CH₂Cl₂ (10 cm³)], added dropwise. Triethylamine [1.4 cm³, 10.0 mmol in CH₂Cl₂ (5 cm³)] added dropwise and stirred for 30 min. The mixture was concentrated under reduced pressure, the residue redissolved in CH₂Cl₂ (10 cm³), 2-isopropyl aniline (0.70 cm³, 5.0 mmol) added dropwise and stirred at RT for 18 h. The mixture was concentrated under reduced pressure, the residue suspended between water (10 cm³) and acetone (10 cm³), the white precipitate collected and dissolved in THF (60 cm³) at room temperature and cooled to 0 °C. Sodium hydride (0.45 g, 11.8 mmol) was added portionwise and stirred at room temperature for 30 min. Methyl iodide (0.50 cm³, 11.1 mmol) was added dropwise and stirred at room temperature for 18 h. Water (40 cm³) was added and the aqueous layer extracted with EtOAc (3×30 cm³). The combined organic fractions were dried (MgSO₄), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO₂; EtOAc-petrol, 1:9) to give 1-(2-tert-butylphenyl)-3-(2-isopropylphenyl)-1,3-dimethylurea 3j (1.34 g, 79 %), as colourless blocks, m.p. 230-232 °C (from EtOAc-petrol); R_f (EtOAc-petrol, 3:7) 0.50; v_{max} (film)/cm⁻¹ 1628 (C=O); δ_H (300 MHz; CDCl₃) 7.37 (1 H, d, J 8.0, CH-h), 7.17 (1 H, d, J 8.0, CH-d), 7.15-6.91 (2 H, br., CH-a and CH-e), 6.90-6.42 (2 H, br., CH-c and CH-g), 6.40-5.98 (2 H, br., CH-b and CH-f), 3.22-2.78 [7 H, br., (CH) and (NCH₃) × 2], 1.40 [9 H, s, (CH₃) × 3] and 1.39-1.05 [6 H, br, (CH₃) × 2]; δ_C (75 MHz; CDCl₃) 161.7 (C=O), 146.7 (C), 146.2 (C), 143.5 (C), 141.8 (C), 131.5 (CH), 128.7 (CH), 127.0 (CH), 126.9 (CH), 126.8 (CH), 126.7 (CH), 126.6 (CH), 126.5 (CH), 41.8 (NCH₃)_A, 40.9 (NCH₃)_B, 36.0 (C), 32.1 (CH), 27.2 [(CH₃) × 3] and 23.7 [(CH₃) × 2]; m/z (CI) 339 (100 %, M+H⁺); (Found: M+H⁺, 339.2430, C₂₂H₃₁N₂O

requires *M*+*H*, 339.2431). Elem. Anal. for C₂₂H₃₀N₂O: calcd: C, 78.06 %; H, 8.93 %; N, 8.28; found: C, 77.90 %; H, 8.90 %; N, 8.34 %.

1,3-bis(2-tert-Butylphenyl)-1,3-dimethylurea, **3k**. -1, *3-bis(2-tert-Butylphenyl)urea* **2k** (0.40 g, 1.23 mmol) was dissolved in THF (30 cm³) and cooled to 0 °C. Sodium hydride (0.15 g, 3.69 mmol) was added portionwise and stirred at room temperature for 1 h. Methyl iodide (0.31 cm³, 4.92 mmol) was added and stirred at room temperature for 18 h. Water (15 cm³) was added and extracted with EtOAc (3 × 10 cm³). The combined organic fractions were dried (MgSO₄), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO₂; 20 % EtOAc in petrol) to give *1,3-bis(2-tert-butylphenyl)-1,3-dimethylurea* **3k** (0.41 g, 95 %), as an inseparable mixture of conformers in a 3:1 ratio, as colourless prisms, m.p. 240-242 °C; R_f (EtOAc-petrol, 1:1) 0.74; v_{max} (film)/cm⁻¹ 1659 (C=O); δ_H (300 MHz; CDCl₃) 7.51 (1 H, dd, *J* 8.0 and 1.5, CH-a^{min}), 7.44 (1 H, dd, *J* 8.0 and 1.5, CH-a^{maj}), 7.30-7.17 (2 H, m, CH-d^{maj} and CH-d^{min}), 7.16-7.07 (2 H, m, CH-e^{maj} and CH-e^{min}), 6.93 (1 H, br., CH-b^{maj}), 6.73 (1 H, br., CH-b^{min}), 3.19 [6 H, s, (NCH₃)_{A^{maj}} and (NCH₃)_{B^{maj}}], 2.98 [6 H, s, (NCH₃)_{A^{min}} and (NCH₃)_{B^{min}}], 1.51 [9 H, s, (CH₃)^{maj}, × 3] and 1.44 [9 H, s, (CH₃)^{min} × 3]; δ_C (75 MHz; CDCl₃) 146.6 (C=O)^{maj} and ^{min}, 145.8 (C)^{maj} and ^{min}, 144.2 (C)^{maj} and ^{min}, 131.5 (CH)^{maj}, 130.8 (CH)^{min}, 129.5 (CH)^{min}, 128.6 (CH)^{maj}, 127.4 (CH)^{min}, 127.2 (CH)^{min}, 127.1 (CH)^{maj}, 43.0 (NCH₃)^{min}, 42.6 (NCH₃)^{maj}, 36.1 (C)^{min}, 36.0 (C)^{maj} and 32.2 [(CH₃)^{maj} and ^{min} × 3]; m/z (CI) 314 (100 %, M+H⁺); (Found: M+H⁺, 314.1388, C₁₆H₂₆NO₃S requires *M*+H, 314.1387). Elem. Anal. for C₂₃H₃₂N₂O: calcd: C, 78.36 %; H, 9.15 %; N, 7.95; found: C, 78.23 %; H, 9.00 %; N, 8.10 %.

1-(2-Fluorophenyl)-1,3-dimethyl-3-(2,6-dimethylphenyl)urea, **31.** —1-(2-Fluorophenyl)-3-(2,6-dimethylphenyl)urea **21** (0.37 g, 1.5 mmol) was dissolved in THF (20 cm³) and cooled to 0 °C. Sodium hydride (0.15 g, 3.8 mmol) was added portionwise and the suspension stirred at room temperture for 1 h. Methyl iodide (0.30 cm³, 4.5 mmol) was added and stirred at room temperature for 18 h. Water (20 cm³) was added and extracted with EtOAc (3 × 20 cm³). The combined organic fractions were dried (MgSO₄), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO₂; 10 % EtOAc in pentane) to give *1-(2-fluorophenyl)-1,3-dimethyl-3-(2,6-dimethylphenyl)urea* **31** (0.40 g, 97 %), as white plates, m.p. 95-97 °C (from EtOAc-pentane), R_f (EtOAc-pentane, 1:4) 0.48; v_{max} (film)/cm⁻¹ 1639 (C=O); δ_H (400 MHz; CDCl₃) 6.87 (1 H, m, CH-d), 6.77-6.57 (6 H, m, CH-a, CH-b, CH-c, CH-e¹, CH-e² and CH-f), 3.05 [3 H, s, (NCH₃)_A], 3.00 [3 H, s, (NCH₃)_B] and 1.93 [6 H, s, (CH₃) × 2]; δ_C (100 MHz; CDCl₃) 161.0 (C=O), 159.3 (C), 156.8 (C), 141.6 (C), 132.6 (C), 128.8 (CH), 127.8 (CH), 126.7 (CH), 124.3 (CH), 116.0 (CH), 39.4 (NCH₃)_A, 37.2 (NCH₃)_B and 18.0 [(CH₃) × 2]; m/z (ESI⁺) 287 (100 %, M+H⁺); (Found: M+H⁺, 287.1549, C₁₇H₁₉N₂OF requires M+H, 287.1554).

1-(2-Chlorophenyl)-1,3-dimethyl-3-(2,6-dimethylphenyl)urea, **3m**. —1-(2-Chlorophenyl)-3-(2,6-dimethylphenyl)urea **2m** (1.50 g, 5.5 mmol) was dissolved in THF (30 cm³) and cooled to 0 °C. Sodium hydride (0.55 g, 13.5 mmol) was added portionwise and the suspension stirred at room temperature for 1 h. Methyl iodide (1.05 cm³, 16.5 mmol) was added and stirred at room temperature for 20 h. Water (30 cm³) was added and extracted with EtOAc (3 × 30 cm³). The combined organic fractions were dried (MgSO₄), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO₂; 10 % EtOAc in pentane) to give *1-(2-chlorophenyl)-1,3-dimethyl-3-(2,6-dimethylphenyl)urea* **3m** (1.60 g, 96 %), as white prisms, m.p. 157-159 °C (from EtOAc-pentane), R_f (EtOAc-pentane, 1:4) 0.41; v_{max} (film)/cm⁻¹ 1650 (C=O) and 759 (C–Cl); δ_H (400 MHz; CDCl₃) 6.99 (1 H, d, *J* 8.0, CH-d), 6.79 (1 H, t, *J* 8.0, CH-c), 6.71-6.62 (2 H, m, CH-a and CH-b), 6.62-6.53 (2 H, m, CH-e¹ and CH-f), 6.36 (1 H, d, *J* 8.0, CH-e²), 2.96 [3H, s, (NCH₃)_A], 2.91 [3H, s, (NCH₃)_B] and 1.85 [6 H, br., (CH₃) × 2]; δ_C (100 MHz; CDCl₃) 161.1 (C=O), 142.1 (C), 141.8 (C), 136.0 (C), 132.5 (CH), 129.8 (CH), 129.3 (CH), 128.6 (CH), 127.4 (CH), 126.6 (CH), 38.8 (NCH₃)_A, 37.1 (NCH₃)_B and 18.0 (CH₃); m/z (ESI⁺) 303 (100 %, M+H⁺); (Found: M+H⁺, 303.1255, C₁₇H₁₉N₂O₁Cl requires *M*+*H*, 303.1259).

I-(2-Bromophenyl)-1,3-dimethyl-3-(2,6-dimethylphenyl)urea, **3n**. —1-(2-Bromophenyl)-3-(2,6-dimethylphenyl)urea **2n** (3.40 g, 10.6 mmol) was dissolved in THF (50 cm³) and cooled to 0 °C. Sodium hydride (1.0 g, 26.5 mmol) was added portionwise and the suspension stirred at room temperture for 2 h. Methyl iodide (1.90 cm³, 31.2 mmol) was added and stirred at room temperature for 22 h. Water (50 cm³) was added and extracted with EtOAc (3 × 40 cm³). The combined organic fractions were dried (MgSO₄), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO₂; 10 % EtOAc in pentane) to give *1-(2-bromophenyl)-1,3-dimethyl-3-(2,6-dimethylphenyl)urea* **3n** (3.60 g, 98 %), as off-white blocks, m.p. 162-164 °C (from EtOAc-pentane), $R_{\rm f}$ (EtOAc-pentane, 1:4) 0.35; $v_{\rm max}$ (film)/cm⁻¹ 1651 (C=O) and 761 (C–Br); $\delta_{\rm H}$ (400 MHz; CDCl₃) 7.22 (1 H, d, *J* 8.0, CH-d), 6.80-6.46 (5 H, br., CH-a, CH-b, CH-c, CH-e¹ and CH-f), 6.35 (1 H, d, *J* 7.0, CH-e²), 3.00 [3H, s, (NCH₃)_A], 2.95 [3H, s, (NCH₃)_B] and 1.90 [6 H, br., (CH₃) × 2]; $\delta_{\rm C}$ (100 MHz; CDCl₃) 161.1 (C=O), 143.6 (C), 141.9 (C), 136.2 (C), 133.1 (CH), 129.6 (CH), 128.7 (CH), 128.1 (CH), 127.7 (CH), 126.6 (CH), 123.0 (CH), 38.9 (NCH₃)_A, 37.1 (NCH₃)_B and 18.1 (CH₃); m/z (ESI⁺) 347 (100 %, M+H⁺); (Found: M+H⁺, 347.0748, C₁₇H₁₉N₂OBr requires *M*+H, 347.0754).

1-(2-Iodophenyl)-1,3-dimethyl-3-(2,6-dimethylphenyl)urea **30**. —1-(2-Iodophenyl)-3-(2,6-dimethylphenyl)urea **20** (0.68 g, 1.5 mmol) was dissolved in THF (20 cm³) and cooled to 0 °C. Sodium hydride (0.15 g, 3.8 mmol) was added portionwise and stirred at room temperture for 1 h. Methyl iodide (0.30 cm³, 4.5 mmol) was added and stirred at room temperature for 18 h. Water (20 cm³) was added and extracted with EtOAc (3 × 20 cm³). The combined organic fractions were dried (MgSO₄), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO₂; 10 % EtOAc in pentane) to give *1-(2-iodophenyl)-1,3-dimethyl-3-(2,6-dimethylphenyl)urea* **30** (0.57 g, 77 %), off-white blocks, m.p. 165-167 °C (from EtOAc-pentane); R_f (EtOAc-pentane, 1:4) 0.30; v_{max} (film/cm⁻¹ 1650 (C=O); δ_H (400 MHz; CDCl₃) 7.53 (1 H, d, *J* 8.0, CH-a), 6.83-6.69 (3 H, m, CH-b, CH-c and CH-d), 6.62 (1 H, t, *J* 8.0, CH-f), 6.56 (1 H, br., CH-e¹), 6.34 (1H, d, *J* 7.0, CH-e²), 3.03 [3H, s, (NCH₃)_A], 2.97 [3H, s, (NCH₃)_B], 2.02 [3H, s, (CH₃)_A] and 1.80 [3H, s, (CH₃)_B]; δ_C (100 MHz; CDCl₃) 160.9 (C=O), 146.8 (C), 142.1 (C), 139.5 (CH), 136.6 (C), 136.0 (C), 129.2 (CH), 129.0 (CH), 128.7 (CH), 128.4 (CH), 127.9 (CH), 126.6 (CH), 98.6 (C), 39.2 (NCH₃)_A, 37.3 (NCH₃)_B, 18.4 (CH₃)_A and 18.2 (CH₃)_B; m/z (ESI⁺) 395 (100 %, M+H⁺); (Found: M+H⁺, 395.06066, C₁₇H₁₉N₂OI requires *M*+H, 395.0615).

1-(2-Methylphenyl)-1,3-dimethyl-3-(2,6-dimethylphenyl)urea, **3p**. -1-(2-Methylphenyl)-3-(2,6-dimethylphenyl)urea **2p** (0.5 g, 2.0 mmol) was dissolved in THF (30 cm³) and cooled to 0 °C. Sodium hydride (0.20 g, 5.0 mmol) was added portionwise and stirred at room temperature for 1 h. Methyl iodide (0.37 cm³, 6.0 mmol) was added and stirred at room temperature for 18 h. Water (30 cm³) was added and extracted with EtOAc (3 × 30 cm³). The combined organic fractions were dried (MgSO₄), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO₂; 10 % EtOAc in pentane) to give *1-(2-methylphenyl)-1,3-dimethyl-3-(2,6-dimethylphenyl)urea* **3p** (0.53 g, 96 %), off-white blocks, m.p. 130-132 °C (from EtOAc-pentane); R_f (EtOAc-pentane, 1:4) 0.35; v_{max} (film)/cm⁻¹ 1644 (C=O); δ_H (400 MHz; CDCl₃) 6.86-6.79 (2 H, m, CH-a and CH-d), 6.75 (1 H, t, *J* 7.0, CH-c), 6.71-6.56 (3 H, m, CH-b, CH-e¹ and CH-f), 6.36 (1 H, d, *J* 7.0, CH-e²), 2.95 [3H, s, (NCH₃)_A], 2.94 [3 H, s, (NCH₃)_B], 1.86 [6 H, s, (CH₃) × 2] and 1.81 [3 H, br., (CH₃)]; δ_C (100 MHz; CDCl₃) 162.6 (C=O), 143.8 (C), 142.3 (C), 135.6 (C), 130.7 (CH), 128.5 (CH), 127.6 (CH), 126.6 (CH), 126.5 (CH), 39.2 (NCH₃)_A, 37.1 (NCH₃)_B, 17.8 (CH₃), 17.2 [(CH₃) × 2]; m/z (ESI⁺) 283 (100 %, M+H⁺); (Found: M+H⁺, 283.1787, C₁₈H₂₂N₂O requires *M*+*H*, 283.1805). Purity by LC-MS analysis.

1-(2-Ethylphenyl)-1,3-dimethyl-3-(2,6-dimethylphenyl)urea, **3q**. —1-(2-Ethylphenyl)-3-(2,6-dimethylphenyl)urea **2q** (1.05 g, 3.9 mmol) was dissolved in THF (30 cm³) and cooled to 0 °C. Sodium hydride (0.39 g, 9.8 mmol) was added portionwise and stirred at room temperature for 1 h. Methyl iodide (0.80 cm³, 11.7 mmol) was added and stirred at room temperature for 18 h. Water (40 cm³) was added and extracted with EtOAc (3 × 30 cm³). The combined organic fractions were dried (MgSO₄), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO₂; 10 % EtOAc in pentane) to give *1-(2-ethylphenyl)-1,3-dimethyl-3-(2,6-dimethylphenyl)urea* **3q** (1.1 g, 97 %), off-white blocks, m.p. 82-84 °C (from EtOAc-pentane); R_f (EtOAc-pentane, 1:4) 0.47; v_{max} (film)/cm⁻¹ 1647 (C=O); δ_H (400 MHz; CDCl₃) 6.96-6.86 (2 H, m, CH-a and CH-d), 6.80-6.54 (4 H, m, CH-b, CH-c, CH-e¹ and CH-f), 6.34 (1H, d, *J* 8.0, CH-e²), 3.00 [3H, s, (NCH₃)_A], 2.94 [3H, s, (NCH₃)_B], 2.38-2.12 [2 H, br., (CH₂)] 1.88 [3H, s, (CH₃)_A] and 1.74 [3H, s, (CH₃)_B]; δ_C (100 MHz; CDCl₃) 163.0 (C=O), 143.2 (C), 142.4 (C), 141.2 (C), 136.3 (C), 129.6 (CH),

128.7 (CH), 128.3 (CH), 127.8 (CH), 126.7 (CH), 126.6 (CH), 126.5 (CH), 39.9 (NCH₃)_A, 37.2 (NCH₃)_B, 22.8 (CH₂), 18.0 (CH₃)_A, 17.9 (CH₃)_B and 14.2 (CH₃); m/z (ESI⁺) 297 (100 %, M+H⁺); (Found: M+H⁺, 297.1943, C₁₉H₂₄N₂O requires *M*+*H*, 297.1962). Purity by LC-MS analysis.

I-(2-Isopropylphenyl)-1,3-dimethyl-3-(2,6-dimethylphenyl)urea, **3r**. —1-(2-Isopropylphenyl)-3-(2,6-dimethylphenyl)urea **2r** (1.20 g, 4.2 mmol) was dissolved in THF (30 cm³) and cooled to 0 °C. Sodium hydride (0.42 g, 11.5 mmol) was added portionwise and stirred at room temperature for 1 h. Methyl iodide (0.86 cm³, 12.6 mmol) was added and stirred at room temperature for 18 h. Water (40 cm³) was added and extracted with EtOAc (3 × 30 cm³). The combined organic fractions were dried (MgSO₄), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO₂; 10 % EtOAc in pentane) to give *1-(2-isopropylphenyl)-1,3-dimethyl-3-(2,6-dimethylphenyl)urea* **3r** (1.24 g, 94 %), off-white blocks, m.p. 90-92 °C (from EtOAc-pentane); R_f (EtOAc-pentane, 1:4) 0.73; v_{max} (film)/cm⁻¹ 1632 (C=O); δ_H (400 MHz; CDCl₃) 7.12 (1 H, d, J 7.0, CH-d), 7.05 (1 H, d, J 7.0, CH-a), 6.90 (2 H, br., CH-b and CH-c), 6.71 (2 H, br., CH-e¹ and CH-e²), 6.19 (1 H, br., CH-f), 3.07 [3 H, s, (NCH₃)_A], 3.02-2.90 [4 H, br., (CH) and (NCH₃)_B], 2.08 [3 H, s, (CH₃)_A], 1.63 [3 H, s, (CH₃)_B] and 1.11 [6 H, s, 2 × (CH₃)]; δ_C (100 MHz; CDCl₃) 164.4 (C=O), 146.6 (C), 143.0 (C), 142.3 (C), 136.8 (C), 136.4 (C), 128.8 (CH), 128.7 (CH), 128.6 (CH), 127.2 (CH), 126.8 (CH), 126.2 (CH), 40.4 (NCH₃)_A, 37.4 (NCH₃)_B, 27.4 (CH), 25.6 (CH₃)_A, 23.4 (CH₃)_B, 18.0 (CH₃)_C and 17.9 (CH₃)_D; m/z (ESI⁺) 311 (100 %, M+H⁺); (Found: M+H⁺, 311.2018). Purity by LC-MS analysis.

1-(2-tert-Butylphenyl)-1,3-dimethyl-3-(2,6-dimethylphenyl)urea, **3s**. -1-(2-*tert*-Butylphenyl)-3-(2,6-dimethylphenyl)urea **2s** (1.12 g, 3.9 mmol) was dissolved in THF (40 cm³) and cooled to 0 °C. Sodium hydride (0.16 g, 9.8 mmol) was added portionwise and stirred at room temperature for 1 h. Methyl iodide (0.73 cm³, 11.7 mmol) was added and stirred at room temperature for 18 h. Water (30 cm³) was added and extracted with EtOAc (3 × 30 cm³). The combined organic fractions were dried (MgSO₄), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO₂; 10 % EtOAc in pentane) to give *1-(2-tert-butylphenyl)-1,3-dimethyl-3-(2,6-dimethylphenyl)urea* **3s** (1.14 g, 90 %), off-white blocks, m.p. 170-172 °C (from EtOAc-pentane); R_f (EtOAc-pentane, 1:4) 0.38; v_{max} (film)/cm⁻¹ 1636 (C=O); δ_H (400 MHz; CDCl₃) 7.30 (1 H, d, J 8.0, CH-d), 7.09-6.84 (3 H, m, CH-a, CH-b and CH-c), 6.76-6.51 (2 H, br., CH-e¹ and CH-e²), 6.17 (1 H, br., CH-f), 3.07 [3H, s, (NCH₃)_A], 2.89 [3 H, s, (NCH₃)_B], 2.21 [3 H, s, (CH₃)_A], 1.68 [3 H, br., (CH₃)_B] and 1.35 [9 H, s, (CH₃) × 3]; δ_C (100 MHz; CDCl₃) 162.0 (C=O), 146.7 (C), 146.5 (C), 143.4 (C), 136.5 (C), 135.8 (C), 131.5 (CH), 128.8 (CH), 128.6 (CH), 127.7 (CH), 127.0 (CH), 126.9 (CH), 126.3 (CH), 41.3 (C), 37.8 (NCH₃)_A, 36.2 (NCH₃)_B, 32.4 [(CH₃) × 3], 18.3 (CH₃)_A, and 18.2 (CH₃); m/z (ESI⁺) 325 (100 %, M+H⁺); (Found: M+H⁺, 325.2254, C₂₁H₂₈N₂O requires *M*+*H*, 325.2275). Elem. Anal. for C₂₁H₂₈N₂O: calcd: C, 77.74 %; H, 8.70 %; N, 8.63; found: C, 77.80 %; H, 8.98 %; N, 8.55 %.

I-(2-Methoxyphenyl)-1,3-dimethyl-3-(2,6-dimethylphenyl)urea, **3t**. —1-(2-Methoxyphenyl)-3-(2,6-dimethylphenyl)urea **2t** (1.15 g, 4.3 mmol) was dissolved in THF (40 cm³) and cooled to 0 °C. Sodium hydride (0.43 g, 10.8 mmol) was added portionwise and stirred at room temperature for 1 h. Methyl iodide (0.87 cm³, 12.9 mmol) was added and stirred at room temperature for 18 h. Water (30 cm³) was added and extracted with EtOAc (3 × 40 cm³). The combined organic fractions were dried (MgSO₄), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO₂; 10 % EtOAc in pentane) to give *1-(2-methoxyphenyl)-1,3-dimethyl-3-(2,6-dimethylphenyl)urea* **3t** (0.84 g, 66 %), off-white blocks, m.p. 156-158 °C (from EtOAc-pentane); R_f (EtOAc-pentane, 1:4) 0.31; v_{max} (film)/cm⁻¹ 1639 (C=O); δ_H (400 MHz; CDCl₃) 6.80 (1 H, t, *J* 7.0, CH-f), 6.67 (1 H, t, *J* 8.0, CH-b), 6.56 (2 H, d, *J* 7.0, CH-e¹ and CH-e²), 6.50 (1 H, d, *J* 8.0, CH-d), 6.42 (1 H, t, *J* 8.0, CH-c), 6.36 (1 H, d, *J* 8.0, CH-a), 3.46 [3 H, s, (OCH₃)], 2.96 [3 H, s, (NCH₃)_A], 2.92 [3 H, s, (NCH₃)_B] and 1.86 [6 H, s, (CH₃) × 2]; δ_C (100 MHz; CDCl₃) 161.5 (C=O), 154.7 (C), 142.0 (C), 136.0 (C), 133.2 (C), 128.3 (CH), 128.0 (CH), 127.4 (CH), 126.1 (CH), 120.4 (CH), 110.6 (CH), 54.9 (OCH₃), 38.6 (NCH₃)_A, 37.1 (NCH₃)_B, and 18.0 [(CH₃) × 2]; m/z (ESI⁺) 299 (100 %, M+H⁺); (Found: M+H⁺, 299.1736, C₁₈H₂₂N₂O₂ requires *M*+H, 299.1754). Purity by LC-MS analysis.

1,3-Dimethyl-1-(2,6-dimethylphenyl)-3-(2-(trifluoromethoxy)phenyl)urea, **3u**. —1-(2,6-Dimethylphenyl)-3-(2-(trifluoromethoxy)phenyl)urea **2u** (0.30 g, 0.93 mmol) was dissolved in THF (10 cm³) and cooled to 0 °C. Sodium hydride (0.09 g, 2.3 mmol) was added portionwise and stirred at room temperature for 1 h. Methyl iodide (0.20 cm³, 2.8 mmol) was added and stirred at room temperature for 18 h. Water (10 cm³) was added and extracted with EtOAc (3 × 10 cm³). The combined organic fractions were dried (MgSO₄), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO₂; 10 % EtOAc in pentane) to give 1,3-dimethyl-1-(2,6-dimethylphenyl)-3-(2-(trifluoromethoxy)phenyl)urea **3u** (0.31 g, 95 %), off-white blocks, m.p. 140-142 °C (from EtOAc-pentane); R_f (EtOAc-pentane, 1:4) 0.40; v_{max} (film)/cm⁻¹ 1659 (C=O); $\delta_{\rm H}$ (400 MHz; CDCl₃) 7.03-6.91 (2 H, m, CH-a and CH-d), 6.89-6.77 (2 H, m, CH-b and CH-c), 6.75-6.67 (2 H, m, CH-e¹ and CH-f), 6.65 (1 H, d, J 7.0 CH-e²), 3.09 [3 H, s, (NCH₃)_A], 3.04 [3 H, s, (NCH₃)_B], 1.97 [6 H, s, 2 × (CH₃)]; $\delta_{\rm C}$ (100 MHz; CDCl₃) 161.1 (C=O), 145.1 (C), 141.8 (C), 137.2 (C), 136.0 (CH), 129.3 (CH), 128.5 (CH), 127.4 (CH), 126.7 (CH), 126.5 (CH) 121.6 (C), 119.1 (C), 39.4 (NCH₃)_A, 37.2 (NCH₃)_B and 18.0 [(CH₃) × 2]; m/z (APCI⁺) 353 (100 %, M+H⁺); (Found: M+H⁺, 353.1448, C₁₈H₁₉N₂O₂F₃ requires M+H, 353.1472). Elem. Anal. for C₁₈H₁₉N₂O₂F₃: calcd: C, 61.36 %; H, 5.44 %; F, 16.18; N, 7.95; found: C, 61.50 %; H, 5.40 %; F, 16.00 N, 8.15 %.