***Curtius Rearrangement of Aromatic Carboxylic Acids
to Access Protected Anilines and Aromatic Ureas***

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Supporting Information

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General: Unless otherwise noted, all non-aqueous reactions were performed under an oxygen-free atmosphere of argon with rigid exclusion of moisture from reagents and glassware. The solvents were dried using standard methods prior to use. NaN_3 and sodium *tert*-butoxide are commercially available and were purchased from Aldrich. Sodium *tert*-butoxide was handled under inert atmosphere. 2-allylbenzoic acid was prepared from 2-bromobenzoic acid according to the literature.¹ Other carboxylic acids are commercially available and were purified using standard methods prior to use. Analytical thin layer chromatography (TLC) was performed using EM Reagent 0.25 mm silica gel 60-F plates. Visualization of the developed chromatogram was performed by UV absorbance, aqueous cerium molybdate, ethanolic phosphomolybdic acid, or aqueous potassium permanganate. Flash chromatography was performed using EM Silica Gel 60 (230-400 mesh) with the indicated solvent system. Optical rotations were measured on a Perkin-Elmer 341 digital polarimeter at 589 nm. Data are reported as follows: $[\alpha]_D^{\text{temp}}$, concentration (*c* g/100mL), and solvent. ¹H NMR spectra were recorded in CDCl_3 , unless otherwise noted, on a Bruker AV-400, a Bruker ARX-400, a Bruker AMX-300 or a Bruker AV-300 spectrometers (400, 400, 300 and 300 MHz respectively). Chemical shifts are reported in ppm on the δ scale from an internal standard of residual chloroform (7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet and br = broad), coupling constant in Hz, integration. ¹³C NMR spectra were recorded in CDCl_3 , unless otherwise noted, on a Bruker AV-400, a Bruker ARX-400, a Bruker AMX-300 or a Bruker AV-300 spectrometers (100, 100, 75 and 75 MHz respectively) with complete proton decoupling. Chemical shifts are reported in ppm from the central peak of CDCl_3 (77.0 ppm) on the δ scale. 2DCOSY experiments were realized for complex structures. Mass spectra were obtained on a LC-MSD TOF (ESI) Agilent Technologies high resolution from the Centre régional de spectrométrie de masse de l'Université de Montréal. Analytical gas chromatography with a mass spectroscopy (GC-MS) was carried out on a Hewlett Packard 6890 series gas chromatograph equipped with a split mode capillary in/Jector and electron impact mass detector. Unless otherwise noted, in/Jector and detector temperatures were 250 °C and the carrier gas was hydrogen (2mL/min) with a HP-5MS column. Data are reported as follows: column type, oven temperature, and retention time (t_r).

¹ a) Inoue, A.; Kitawaga, K.; Shinorubo, H.; Oshima, K. *J. Org. Chem.* **2001**, *66*, 4333-4339. b) Bauer, M.; Maier, M. E. *Org. Lett.* **2002**, *4*, 2205-2208.

General procedure for the synthesis of aromatic Boc-carbamates

To a solution of sodium azide (0.097 g, 1.50 mmol), and carboxylic acid (1.00 mmol) in DME (10.0 mL) at 25 °C, was added di-*tert*-butyldicarbonate (250 μ L, 1.10 mmol). Then the resulting mixture was stirred at 75 °C. When the reaction is completed by GC analysis, a 10% solution of NaNO₂ (20 mL) was added. The mixture was then diluted with chloroform (20 mL), and the resulting mixture was stirred during 20 min at 25 °C. The aqueous layer was acidified with a 10% solution of HCl to pH = 4 and then extracted with chloroform (3 x 30 mL). The combined organic layers were washed with saturated NH₄Cl (2 x 20 mL), and brine (20 mL). The organic layer was dried over Na₂SO₄ and the solvent was removed under reduced pressure and the crude carbamate was purified by flash chromatography on silica gel with a pre-absorption on silica.

NB. Although we have conducted this procedure on a 10 mmol scale without any problem, extreme care should be taken when carried out this reaction, as potentially explosive azide-containing intermediates could be generated under these reaction conditions.

Characterization of aromatic Boc-carbamate

***tert*-Butyl phenylcarbamate (1).** The title compound was prepared from benzoic acid (122 mg, 1.00 mmol) according to the general procedure. The desired carbamate **1** (152 mg, 79%) was obtained as a white solid after flash chromatography (10% EtOAc/hexanes). *R_f* 0.62 (20% EtOAc/hexanes); mp 130 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.39-7.37 (m, 2H), 7.33-7.29 (m, 2H), 7.07-7.04 (m, 1H), 6.50 (s (br), 1H), 1.54 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 152.7, 138.3, 128.9, 122.9, 118.5, 80.4, 28.3; IR 3301, 3042, 2983, 2933, 1684, 1597, 1527, 1439, 1242, 1147, 1054, 743, 691 cm⁻¹; HMRS (ESI) calcd for C₁₁H₁₅NO₂Na [M+Na]⁺: 216.0995. Found: 216.0990.

***tert*-Butyl 2-allylphenylcarbamate (2).** The title compound was prepared from 2-allylbenzoic acid (162 mg, 1.00 mmol) according to the general procedure. The desired carbamate **2** (177 mg, 76%) was obtained as a colorless oil after flash chromatography (10% EtOAc/hexanes). *R_f* 0.71 (20% EtOAc/hexanes); ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 7Hz, 1H), 7.26 (t, *J* = 8Hz, 1H), 7.17 (d, *J* = 7Hz, 1H), 7.07 (t, *J* = 7Hz, 1H), 6.48 (s (br), 1H), 5.99 (ddt, *J* = 17, 10, 6 Hz, 1H), 5.20-5.17 (m, 1H), 5.11-5.07 (m, 1H), 3.39 (d, *J* = 6 Hz, 2H), 1.54 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 153.2, 136.4, 135.8, 130.0, 127.3, 123.9, 121.9, 116.5, 80.3, 36.5, 28.3; IR 3356, 2968, 2918, 1691, 1520, 1430, 1232, 1153, 1075, 1010, 842, 687 cm⁻¹; HMRS (ESI) calcd for C₁₄H₁₉NO₂ [M+Na]⁺: 256.1308. Found: 256.1302.

tert-Butyl 3,5-dimethylphenylcarbamate (3). The title compound was prepared from 3,5-dimethylbenzoic acid (150 mg, 1.00 mmol) according to the general procedure. The desired carbamate **3** (163 mg, 74%) was obtained as a white solid after flash chromatography (10% EtOAc/hexanes). R_f 0.69 (20% EtOAc/hexanes); mp 73 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.03 (s (br), 2H), 6.71 (s (br), 1H), 6.50 (s (br), 1H), 2.31 (s, 6H), 1.55 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.7, 138.6, 138.1, 124.7, 116.2, 80.2, 28.3, 21.3; IR 3356, 2968, 2918, 1691, 1520, 1430, 1232, 1153, 1075, 1010, 842, 687 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{13}\text{H}_{19}\text{NO}_2$ $[\text{M}+\text{Na}]^+$: 244.1308. Found: 244.1298.

General procedure for the synthesis of aromatic Alloc-, CBz-, Troc-carbamates

To a solution of sodium azide (0.110 g, 1.70 mmol), sodium *tert*-butoxide (14.4 mg, 0.150 mmol), and carboxylic acid (1.00 mmol) in DME (10.0 mL) at 25 °C, was added the chloroformate reagent (1.10 mmol) (Allylchloroformate: 120 μL , benzylchloroformate: 150 μL , or 2,2,2 trichloroethylchloroformate: 112 μL). Then the resulting mixture was stirred at 75 °C (85 °C for Troc derivatives). When the reaction is completed by GC analysis, the mixture was diluted with dichloromethane and a pre-absorption on silica was made. The crude carbamate was then purified by flash chromatography on silica gel.

Characterization of aromatic Alloc-, CBz-, Troc-carbamates

Allyl phenylcarbamate (4). The title compound was prepared from benzoic acid (122 mg, 1.00 mmol) according to the general procedure. The desired carbamate **4** (101 mg, 57 %) was obtained as a white solid after flash chromatography (10% EtOAc/hexanes). R_f 0.45 (20% EtOAc/hexanes); mp 48 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.40-7.38 (m, 2H), 7.33-7.29 (m, 2H), 7.07 (t, J = 7 Hz, 1H), 6.70 (s (br), 1H), 5.97 (ddt, J = 17, 10, 6 Hz, 1H), 5.39-5.34 (m, 1H), 5.28-5.25 (m, 1H), 4.68-4.66 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.2, 137.7, 132.4, 129.0, 123.4, 118.7, 118.1, 65.8; IR 3302, 3061, 2955, 1701, 1596, 1533, 1442, 1222, 1054, 936, 743, 692 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{10}\text{H}_{12}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 178.0863. Found: 178.0866.

Benzyl phenylcarbamate (5). The title compound was prepared from benzoic acid (122 mg, 1.00 mmol) according to the general procedure. The desired carbamate **5** (145 mg, 64%) was obtained after flash chromatography (15% EtOAc/hexanes), as a white solid. R_f 0.49 (20% EtOAc/hexanes); mp 38 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.42-7.29 (m, 9H), 7.10-7.05 (m, 1H), 6.70 (s (br), 1H), 5.21 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.2, 137.7, 132.4, 129.05, 128.96 (2C), 123.4, 118.6, 118.1, 65.8; IR 3267, 3135, 3076, 2953, 2894, 1686, 1598, 1542, 1443, 1315, 1236, 1223, 1055, 845, 735, 693 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{14}\text{H}_{14}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 228.1020. Found: 228.1019.

Allyl 3,5-dimethylphenylcarbamate (6). The title compound was prepared from 3,5-dimethylbenzoic acid (150 mg, 1.00 mmol) according to the general procedure. The desired carbamate **6** (135 mg, 66%) was obtained as a white solid after flash chromatography (10% EtOAc/hexanes). R_f 0.50 (20% EtOAc/hexanes); mp 37 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.04 (s (br), 2H), 6.80 (s (br), 1H), 6.72 (s (br), 1H), 6.03-5.93 (m, 1H), 5.39-5.35 (m, 1H), 5.28-5.25 (m, 1H), 4.68-4.66 (m, 2H), 2.29 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.2, 138.6, 137.5, 132.4, 125.1, 117.9, 116.4, 65.6, 21.2; IR 3316, 2919, 1704, 1614, 1548, 1450, 1218, 1084, 931, 841, 769 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{12}\text{H}_{16}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 206.1176. Found: 206.1168.

Benzyl 3,5-dimethylphenylcarbamate (7). The title compound was prepared from 3,5-dimethylbenzoic acid (150 mg, 1.00 mmol) according to the general procedure. The desired carbamate **7** (148 mg, 58%) was obtained as a white solid after flash chromatography (20% EtOAc/hexanes). R_f 0.49 (20% EtOAc/hexanes); mp 43 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.42-7.33 (m, 5H), 7.02 (s (br), 2H), 6.72 (s (br), 1H), 6.60 (s (br), 1H), 5.19 (s, 2H), 2.29 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.3, 138.7, 137.5, 136.1, 128.5, 128.2, 125.2, 116.4, 66.8, 21.3; IR 3289, 3034, 2917, 1694, 1531, 1453, 1269, 1215, 1078, 838, 739, 685 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{16}\text{H}_{18}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 256.1333. Found: 256.1332.

Allyl naphthalen-3-ylcarbamate (8). The title compound was prepared from 2-naphthanoic acid (172 mg, 1.00 mmol) according to the general procedure. The desired carbamate **8** (175 mg, 77%) was obtained as a pale brown solid after flash chromatography (20% EtOAc/hexanes). R_f 0.31 (20% EtOAc/hexanes); mp 98 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.90-7.88 (m, 3H), 7.69 (d, J = 8 Hz, 1H), 7.54-7.47 (m, 3H), 7.13 (s (br), 1H), 6.09-5.99 (m, 1H), 5.42 (d, J = 17 Hz, 1H), 5.31 (d, J = 10 Hz, 1H), 4.76 (d, J = 6 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.1, 133.9, 132.4, 132.3, 128.6, 126.7, 126.1, 125.9, 125.7, 125.0, 120.4, 119.1, 118.2, 66.0; IR 3265, 3050, 2940, 1693, 1525, 1501, 1253, 1230, 1103, 990, 785, 764 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{14}\text{H}_{14}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 228.1024. Found: 228.1019.

Benzyl naphthalen-3-ylcarbamate (9). The title compound was prepared from 2-naphthanoic acid (172 mg, 1.00 mmol) according to the general procedure. The desired carbamate **9** (152 mg, 55%) was

obtained after flash chromatography (20% EtOAc/hexanes), as a pale brown solid. R_f 0.30 (20% EtOAc/hexanes); mp 117 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.91-7.89 (m, 3H), 7.71 (d, J = 8Hz, 1H), 7.54-7.42 (m, 8H), 7.15 (s (br), 1H), 5.30 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.2, /36.0, /34.0, 132.3, 128.6, 128.5, 128.32, 128.29, 126.6, 126.1, 126.0, 125.7, 125.0, 120.4, 118.9, 67.2; IR 3277, 3031, 2950, 1688, 1534, 1502, 1235, 1068, 766, 694 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{18}\text{H}_{16}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 278.1188. Found: 278.1175.

Allyl 4-methoxyphenylcarbamate (10). The title compound was prepared from 4-methoxybenzoic acid (152 mg, 1.00 mmol) according to the general procedure. The desired carbamate **10** (93 mg, 45%) was obtained as a pale yellow oil after flash chromatography (20% EtOAc/hexanes). R_f 0.30 (20% EtOAc/hexanes); ^1H NMR (400 MHz, CDCl_3) δ 7.29 (s (br), 2H), 6.83 (d, J = 9Hz, 2H), 6.80 (s (br), 1H), 5.94 (ddt, J = 17, 10, 6 Hz, 1H), 5.35 (d, J = 17 Hz, 1H), 5.24 (d, J = 10 Hz, 1H), 4.64 (d, J = 6 Hz, 2H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.9, 153.6, 132.5, 130.8, 120.6, 118.0, 114.1, 65.7, 55.4; IR 3310, 2933, 1703, 1514, 1414, 1221, 1033, 828 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{11}\text{H}_{14}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 208.0960. Found: 208.0968.

Allyl 4-tert-butylphenylcarbamate (11). The title compound was prepared from 4-tert-butyl benzoic acid (178 mg, 1.00 mmol) according to the general procedure. The desired carbamate **11** (130 mg, 56 %) was obtained as a white solid after flash chromatography (10% EtOAc/hexanes). R_f 0.52 (20% EtOAc/hexanes); mp 72 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.33 (s (br), 4H), 6.81 (s (br), 1H), 5.98 (ddt, J = 17, 10, 6 Hz, 1H), 5.36 (d, J = 17 Hz, 1H), 5.26 (d, J = 10 Hz, 1H), 4.67 (d, J = 6 Hz, 2H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.4, 146.3, 135.1, 132.5, 125.8, 118.5, 118.0, 65.7, 34.2, 31.3; IR 3326, 2964, 2868, 1698, 1529, 1407, 1226, 1054, 992, 836, 768 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{14}\text{H}_{20}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 234.1495. Found: 234.1488.

Benzyl 4-methoxyphenylcarbamate (12). The title compound was prepared from 4-methoxybenzoic acid (152 mg, 1.00 mmol) according to the general procedure. The desired carbamate **12** (159 mg, 62%) was obtained after flash chromatography (20% EtOAc/hexanes), as a white solid. R_f 0.20 (20% EtOAc/hexanes); mp 88 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.41-7.28 (m, 8H), 6.87 (d, J = 9 Hz, 2H), 5.21 (s, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.8, 153.7, 136.1, 130.8, 128.5, 128.1 (2C), 120.6, 114.1, 66.8, 55.4; IR 3303, 3041, 2969, 2843, 1699, 1526, 1511, 1414, 1234, 1187, 1063, 1027, 823, 741 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{15}\text{H}_{16}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 258.1125. Found: 258.1131.

Benzyl 4-*tert*-butylphenylcarbamate (13). The title compound was prepared from 4-*tert*-butylbenzoic acid (178 mg, 1.00 mmol) according to the general procedure. The desired carbamate **13** (175 mg, 62%) was obtained after flash chromatography (10% EtOAc/hexanes), as a white solid. R_f 0.40 (20% EtOAc/hexanes); mp 64 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.43-7.33 (m, 9H), 6.71 (s (br), 1H), 5.21 (s, 2H), 1.31 (s (br), 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.3, 146.3, 136.1, 135.0, 128.6 (2C), 128.3, 125.8, 118.4, 66.9, 34.2, 31.3; IR 3335, 3051, 2955, 2900, 2865, 1694, 1596, 1533, 1410, 1229, 1065, 831, 740, 661 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{18}\text{H}_{22}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 284.1651. Found: 284.1645.

Allyl 4-nitrophenylcarbamate (14). The title compound was prepared from 4-nitrobenzoic acid (167 mg, 1.00 mmol) according to the general procedure. The desired carbamate **14** (173 mg, 78%) was obtained as a yellow solid after flash chromatography (30% EtOAc/hexanes). R_f 0.16 (20% EtOAc/hexanes); mp 94 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.19 (d, J = 9 Hz, 2H), 7.58-7.55 (m, 2H), 7.20 (s (br), 1H), 6.00-5.90 (m, 1H), 5.37 (d, J = 17 Hz, 1H), 5.29 (d, J = 10 Hz, 1H), 4.69 (d, J = 6 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.6, 143.9, 142.9, 131.7, 125.2, 118.9, 117.7, 66.4; IR 3376, 3092, 2947, 2887, 1731, 1546, 1508, 1493, 1321, 1204, 1056, 853, 747 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{10}\text{H}_{11}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 223.0713. Found: 223.0709.

Allyl 4-acetylphenylcarbamate (15). The title compound was prepared from 4-acetylbenzoic acid (164 mg, 1.00 mmol) according to the general procedure. The desired carbamate **15** (144 mg, 66%) was obtained as a white solid after flash chromatography (30% EtOAc/hexanes). R_f 0.11 (20% EtOAc/hexanes); mp 116 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, J = 9 Hz, 2H), 7.50 (d, J = 9 Hz, 2H), 7.09 (s (br), 1H), 5.94 (ddt, J = 17, 10, 6 Hz, 1H), 5.40-5.35 (m, 1H), 5.29-5.26 (m, 1H), 4.69-4.67 (m, 2H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.1, 152.8, 142.5, 131.98, 131.95, 129.8, 118.5, 117.6, 66.0, 26.3; IR 3297, 3191, 3112, 3065, 2949, 1724, 1660, 1588, 1531, 1410, 1208, 1053, 845, 697 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{12}\text{H}_{14}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 220.0968. Found: 220.0959.

Benzyl 4-nitrophenylcarbamate (16). The title compound was prepared from 4-nitrobenzoic acid (167 mg, 1.00 mmol) according to the general procedure. The desired carbamate **16** (228 mg, 84%) was obtained after flash chromatography (20% EtOAc/hexanes), as a yellow solid. R_f 0.24 (20% EtOAc/hexanes); mp 142 °C; ^1H NMR (400 MHz, DMSO) δ 10.52 (s (br), 1H), 8.18 (d, J = 9 Hz, 2H), 7.70 (d, J = 9 Hz, 2H), 7.46-7.33 (m, 5H), 5.20 (s, 2H); ^{13}C NMR (100 MHz, DMSO) δ 153.0, 145.6,

141.6, 136.0, 128.4, 128.3, 128.2, 125.0, 117.5, 66.4; IR 3330, 1738, 1599, 1544, 1492, 1328, 1213, 1061, 845, 727 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{14}\text{H}_{13}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 273.0870. Found: 273.0876.

Benzyl 4-acetylphenylcarbamate (17). The title compound was prepared from 4-acetylbenzoic acid (164 mg, 1.00 mmol) according to the general procedure. The desired carbamate **17** (215 mg, 80%) was obtained after flash chromatography (30% EtOAc/hexanes), as a white solid. R_f 0.12 (20% EtOAc/hexanes); mp 114 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, J = 9 Hz, 2H), 7.51 (d, J = 9 Hz, 2H), 7.39-7.34 (m, 6H), 5.19 (s, 2H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.1, 152.9, 142.4, 135.6, 132.0, 129.8, 128.6, 128.4, 128.2, 117.6, 67.2, 26.3; IR 3283, 3190, 3062, 2966, 1718, 1666, 1588, 1537, 1413, 1319, 1217, 1187, 1047, 959, 843, 695 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{16}\text{H}_{16}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 270.1125. Found: 270.1124.

Allyl 3-chlorophenylcarbamate (18). The title compound was prepared from 3-chlorobenzoic acid (156 mg, 1.00 mmol) according to the general procedure. The desired carbamate **18** (139 mg, 66%) was obtained as a yellow oil after flash chromatography (10% EtOAc/hexanes). R_f 0.38 (20% EtOAc/hexanes); ^1H NMR (400 MHz, CDCl_3) δ 7.54 (s (br), 1H), 7.28-7.20 (m, 2H), 7.06-7.04 (m, 1H), 6.94 (s (br), 1H), 6.02-5.92 (m, 1H), 5.38 (d, J = 17 Hz, 1H), 5.29 (d, J = 10 Hz, 1H), 4.69 (d, J = 5 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.0, 138.9, 134.7, 132.1, 129.9, 123.5, 118.7, 118.4, 116.6, 66.0; IR 3309, 3085, 1710, 1598, 1535, 1427, 1275, 1225, 1058, 879, 777 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{10}\text{H}_{11}\text{ClNO}_2$ $[\text{M}+\text{H}]^+$: 212.0473. Found: 212.0483.

Allyl 3-bromophenylcarbamate (19). The title compound was prepared from 3-bromobenzoic acid (201 mg, 1.00 mmol) according to the general procedure. The desired carbamate **19** (133 mg, 52%) was obtained as a colorless oil after flash chromatography (10% EtOAc/hexanes). R_f 0.38 (20% EtOAc/hexanes); ^1H NMR (400 MHz, CDCl_3) δ 7.68 (s (br), 1H), 7.31-7.28 (m, 1H), 7.23-7.16 (m, 2H), 6.72 (s(br), 1H), 5.98 (ddt, J = 17, 10, 6 Hz, 1H), 5.40-5.36 (m, 1H), 5.31-5.28 (m, 1H), 4.70-4.68 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.0, 139.0, 132.1, 130.2, 126.3, 122.6, 121.5, 118.4, 117.0, 66.0; IR 3311, 3082, 2948, 1704, 1589, 1525, 1480, 1274, 1215, 1055, 994, 771 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{10}\text{H}_{11}\text{NO}_2\text{Br}$ $[\text{M}+\text{H}]^+$: 255.9969. Found: 255.9967.

Benzyl 3-chlorophenylcarbamate (20). The title compound was prepared from 3-chlorobenzoic acid (156 mg, 1.00 mmol) according to the general procedure. The desired carbamate **20** (175 mg, 67%)

was obtained as a colorless oil after flash chromatography (15% EtOAc/hexanes). R_f 0.44 (20% EtOAc/hexanes); ^1H NMR (400 MHz, CDCl_3) δ 7.53 (s (br), 1H), 7.39-7.36 (m, 5H), 7.26-7.18 (m, 2H), 7.06-7.04 (m, 2H), 5.20 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.2, 138.9, 135.6, 134.5, 129.9, 128.5, 128.3, 128.2, 123.4, 118.6, 116.6, 67.1; IR 3310, 3033, 2955, 1704, 1594, 1530, 1426, 1213, 1054, 883, 697 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{14}\text{H}_{13}\text{NO}_2\text{Cl}$ $[\text{M}+\text{H}]^+$: 262.0632. Found: 262.0629.

Benzyl 3-bromophenylcarbamate (21). The title compound was prepared from 3-bromobenzoic acid (201 mg, 1.00 mmol) according to the general procedure. The desired carbamate **21** (220 mg, 72%) was obtained as a colorless oil after flash chromatography (15% EtOAc/hexanes). R_f 0.28 (20% EtOAc/hexanes); ^1H NMR (400 MHz, CDCl_3) δ 7.69 (s (br), 1H), 7.40-7.39 (m, 5H), 7.32-7.14 (m, 3H), 7.07 (s (br), 1H), 5.22 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.1, 139.0, 135.6, 130.2, 128.5, 128.3, 128.2, 126.3, 122.6, 121.5, 117.1, 67.1; IR 3310, 3032, 2955, 1700, 1588, 1522, 1421, 1274, 1211, 1051, 869, 769 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{14}\text{H}_{13}\text{NO}_2\text{Br}$ $[\text{M}+\text{H}]^+$: 306.0120. Found: 306.0124.

Allyl 2-bromophenylcarbamate (22). The title compound was prepared from 2-bromobenzoic acid (201 mg, 1.00 mmol) according to the general procedure. The desired carbamate **22** (212 mg, 83%) was obtained as a colorless oil after flash chromatography (10% EtOAc/hexanes). R_f 0.55 (20% EtOAc/hexanes); ^1H NMR (400 MHz, CDCl_3) δ 8.15 (d, J = 8 Hz, 1H), 7.51 (d, J = 8 Hz, 1H), 7.30 (t, J = 8 Hz, 1H), 7.19 (s (br), 1H), 6.92 (t, J = 8 Hz, 1H), 5.99 (ddt, J = 17, 10, 6 Hz, 1H), 5.40-5.36 (m, 1H), 5.30-5.27 (m, 1H), 4.70-4.68 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.7, 135.6, 132.2, 132.1, 128.3, 124.2, 120.1, 118.4, 112.5, 66.0; IR 3404, 2947, 1739, 1593, 1578, 1521, 1437, 1207, 1065, 750 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{10}\text{H}_{11}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 255.9966. Found: 255.9967.

Allyl 2-iodophenylcarbamate (23). The title compound was prepared from 2-iodobenzoic acid (248 mg, 1.00 mmol) according to the general procedure. The desired carbamate **23** (218 mg, 72%) was obtained as a colorless oil after flash chromatography (5% EtOAc/hexanes). R_f 0.61 (20% EtOAc/hexanes); ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, J = 8 Hz, 1H), 7.77 (d, J = 8 Hz, 1H), 7.35 (t, J = 8 Hz, 1H), 7.03 (s (br), 1H), 6.82 (t, J = 8 Hz, 1H), 6.02 (ddt, J = 17, 10, 6 Hz, 1H), 5.43-5.38 (m, 1H), 5.33-5.29 (m, 1H), 4.72-4.70 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.0, 138.8, 138.2, 132.2, 129.2, 125.1, 120.3, 118.5, 88.8, 66.1; IR 3385, 2959, 1733, 1585, 1516, 1434, 1204, 1038, 750 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{10}\text{H}_{11}\text{INO}_2$ $[\text{M}+\text{H}]^+$: 303.9829. Found: 303.9826.

Benzyl 2-bromophenylcarbamate (24). The title compound was prepared from 2-bromobenzoic acid (201 mg, 1.00 mmol) according to the general procedure. The desired carbamate **24** (278 mg, 91%) was obtained as a white solid, after flash chromatography (10% EtOAc/hexanes). R_f 0.45 (20% EtOAc/hexanes); mp 41 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.18 (d, J = 8 Hz, 1H), 7.51 (d, J = 8 Hz, 1H), 7.45-7.29 (m, 6H), 7.22 (s (br), 1H), 6.94 (t, J = 8 Hz, 1H), 5.23 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.0, 135.7, 132.3, 128.7, 128.5, 128.42, 128.38, 124.3, 120.1, 112.5, 67.3; IR 3288, 3056, 3031, 2954, 1698, 1579, 1522, 1437, 1233, 1068, 1025, 843, 738 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{14}\text{H}_{13}\text{NO}_2\text{Br}$ $[\text{M}+\text{H}]^+$: 306.0124. Found: 306.0124.

Benzyl 2-iodophenylcarbamate (25). The title compound was prepared from 2-iodobenzoic acid (248 mg, 1.00 mmol) according to the general procedure. The desired carbamate **25** (328 mg, 93%) was obtained as a white solid, after flash chromatography (20% EtOAc/hexanes). R_f 0.57 (20% EtOAc/hexanes); mp 49 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.10 (d, J = 8 Hz, 1H), 7.77 (d, J = 8 Hz, 1H), 7.46-7.33 (m, 6H), 7.05 (s (br), 1H), 6.81 (t, J = 8 Hz, 1H), 5.24 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.2, 151.4, 138.8, 138.2, 135.7, 129.2, 128.6, 128.3, 125.1, 120.3, 88.8, 67.2; IR 3383, 3031, 2953, 1732, 1586, 1514, 1432, 1201, 1036, 741 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{14}\text{H}_{12}\text{INO}_2$ $[\text{M}+\text{H}]^+$: 353.9985. Found: 353.9982.

2,2,2-Trichloroethyl 2-iodophenylcarbamate (26). The title compound was prepared from 2-iodobenzoic acid (248 mg, 1.00 mmol) according to the general procedure. The desired carbamate **26** (280 mg, 71%) was obtained as a white solid, after flash chromatography (5% EtOAc/hexanes). R_f 0.82 (20% EtOAc/hexanes); mp 61 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.99 (d (br), J = 7 Hz, 1H), 7.78 (d, J = 8 Hz, 1H), 7.35 (t, J = 8 Hz, 1H), 7.13 (s (br), 1H), 6.84 (t, J = 7 Hz, 1H), 4.83 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.9, 139.0, 137.5, 129.4, 125.9, 120.8, 95.1, 74.6; IR 3295, 3057, 2958, 1762, 1691, 1522, 1435, 1279, 1226, 1102, 990, 808, 712 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_9\text{H}_7\text{Cl}_3\text{INO}_2$ $[\text{M}+\text{H}]^+$: 393.8659. Found: 393.8653.

Allyl 2-chloro-5-(methylthio)phenylcarbamate (27). The title compound was prepared from 2-chloro-5-(methylthio)benzoic acid (203 mg, 1.00 mmol) according to the general procedure. The desired carbamate **27** (211 mg, 82%) was obtained as a colorless oil after flash chromatography (10% EtOAc/hexanes). R_f 0.50 (20% EtOAc/hexanes); ^1H NMR (400 MHz, CDCl_3) δ 8.14 (s (br), 1H), 7.24-7.21 (m, 2H), 6.87 (d, J = 8 Hz, 1H), 6.04-5.95 (m, 1H), 5.40 (d, J = 17 Hz, 1H), 5.30 (d, J = 10 Hz,

1H), 4.70 (d, $J = 5$ Hz, 2H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.6, 138.8, 134.7, 131.9, 128.8, 121.3, 118.5, 118.1, 116.6, 66.1, 15.6; IR 3413, 2922, 1739, 1577, 1516, 1407, 1272, 1209, 1067, 928, 765 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{11}\text{H}_{13}\text{ClNO}_2\text{S}$ $[\text{M}+\text{H}]^+$: 258.0350. Found: 258.0351.

Benzyl 2-chloro-5-(methylthio)phenylcarbamate (28). The title compound was prepared from 2-chloro-5-(methylthio)benzoic acid (203 mg, 1.00 mmol) according to the general procedure. The desired carbamate **28** (249 mg, 81%) was obtained as a white solid, after flash chromatography (10% EtOAc/hexanes). R_f 0.49 (20% EtOAc/hexanes); mp 42 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.17 (s (br), 1H), 7.45-7.35 (m, 5H), 7.23 (d, $J = 8$ Hz, 2H), 6.88 (d, $J = 8$ Hz, 1H), 5.24 (s, 2H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.7, 138.7, 135.5, 134.7, 128.8, 128.5, 128.4, 128.3, 121.3, 118.1, 116.6, 67.3, 15.5; IR 3408, 2921, 1737, 1577, 1515, 1407, 1206, 1063, 905, 697 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{15}\text{H}_{15}\text{NO}_2\text{SCl}$ $[\text{M}+\text{H}]^+$: 308.0518. Found: 308.0506.

Allyl benzofuran-2-ylcarbamate (29). The title compound was prepared from benzofuranbenzoic acid (162 mg, 1.00 mmol) according to the general procedure. The desired carbamate **29** (150 mg, 69%) was obtained as a yellow solid after flash chromatography (20% EtOAc/hexanes). R_f 0.30 (20% EtOAc/hexanes); mp 94 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.45-7.47 (m, 1H), 7.34-7.33 (m, 1H), 7.22-7.15 (m, 3H), 6.52 (s (br), 1H), 5.98 (ddt, $J = 17, 10, 6$ Hz, 1H), 5.42-5.37 (m, 1H), 5.32-5.29 (m, 1H), 4.75-4.73 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.7, 150.0, 147.7, 131.7, 129.4, 123.1, 122.5, 120.0, 118.8, 110.2, 88.9, 66.7; IR 3237, 3073, 2962, 1703, 1607, 1551, 1454, 1226, 1061, 938, 783 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{12}\text{H}_{12}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 218.0812. Found: 218.0817.

Benzyl benzofuran-2-ylcarbamate (30). The title compound was prepared from 2-benzofuranbenzoic acid (162 mg, 1.00 mmol) according to the general procedure. The desired carbamate **30** (214 mg, 80%) was obtained as a yellow solid, after flash chromatography (20% EtOAc/hexanes). R_f 0.41 (20% EtOAc/hexanes); mp 81 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.47-7.32 (m, 7H), 7.28 (s (br), 1H), 7.23-7.15 (m, 2H), 6.55 (s (br), 1H), 5.27 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.8, 150.1, 147.6, 135.3, 129.4, 128.65, 128.57, 128.4, 123.2, 122.5, 120.1, 110.2, 88.9, 67.9; IR 3287, 3149, 3063, 2962, 1703, 1608, 1542, 1454, 1215, 1058, 733 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{16}\text{H}_{14}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 268.0979. Found: 268.0968.

Allyl styrylcarbamate (31). The title compound was prepared from *trans*-cinamic acid (148 mg, 1.00 mmol) according to the general procedure. The desired carbamate **31** (106 mg, 52 %) was obtained as a

white solid after flash chromatography (20% EtOAc/hexanes). R_f 0.40 (20% EtOAc/hexanes); mp 68 °C; ^1H NMR (400 MHz, DMSO, 85 °C) δ 9.45 (s (br), 1H), 7.29-7.24 (m, 4H), 7.14-7.08 (m, 2H), 6.11 (d, J = 14 Hz, 1H), 5.97 (ddt, J = 17, 10, 6 Hz, 1H), 5.37-5.32 (m, 1H), 5.25-5.22 (m, 1H), 4.62-4.60 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.3, 136.1, 132.1, 128.6, 126.3, 125.3, 123.9, 118.4, 110.8, 66.2; IR 3291, 3060, 3027, 1698, 1656, 1530, 1252, 1055, 937, 748, 690 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{12}\text{H}_{13}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 204.1019. Found: 204.1017.

Benzyl styrylcarbamate (32). The title compound was prepared from *trans*-cinnamic acid (148 mg, 1.00 mmol) according to the general procedure. The desired carbamate **32** (129 mg, 51%) was obtained as a white solid after flash chromatography (20% EtOAc/hexanes). R_f 0.42 (20% EtOAc/hexanes); mp 94 °C; ^1H NMR (400 MHz, DMSO, 85 °C) δ 9.51 (s (br), 1H), 7.41-7.32 (m, 4H), 7.29-7.24 (m, 5H), 7.15-7.09 (m, 2H), 6.11 (d, J = 14 Hz, 1H), 5.16 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.4, 136.1, 135.7, 128.6 (2C), 128.4, 128.3, 126.3, 125.2, 123.8, 110.9, 67.4; IR 3276, 3032, 1710, 1659, 1517, 1496, 1221, 1051, 946, 746, 695 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{16}\text{H}_{16}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 254.1185. Found: 254.1175.

General procedure for the synthesis of aromatic ureas.

To a solution of sodium azide (0.110 g, 1.70 mmol), sodium *tert*-butoxide (14.4 mg, 0.150 mmol), and carboxylic acid (1.00 mmol) in DME (10.0 mL) at 25 °C, was added the phenylchloroformate (140 μL , 1.10 mmol). The resulting mixture was stirred at room temperature for 8 hours. The amine derivative (1.50 mmol) was then added and the reaction mixture was stirred at for 16 hours. The reaction mixture was cooled to room temperature and diluted with hexane (40 mL). The resulting solution is poured into ice-cold water with continuous stirring, 10 mL water was added and the stirring maintains during 20 minutes. The solid was filtered and recrystallized when needed.

Characterization of aromatic ureas.

1,3-Diphenylurea (33). The title compound was prepared from benzoic acid (122 mg, 1.00 mmol) and aniline (137 μL , 1.50 mmol) according to the general procedure. The desired urea **33** (189 mg, 89%) was obtained as a white solid after filtration. R_f 0.51 (40% EtOAc/hexanes); mp 219 °C; ^1H NMR (400 MHz, DMSO) δ 8.24 (s (br), 2H), 7.45 (d, J = 8 Hz, 4H), 7.27 (t, J = 8 Hz, 4H), 6.96 (t, J = 7 Hz, 2H); ^{13}C NMR (100 MHz, DMSO) δ 152.4, 139.6, 128.7, 121.7, 118.1; IR 3281, 3036, 1646, 1592, 1538, 1496, 1439, 1230, 893, 751 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{ONa}$ $[\text{M}+\text{Na}]^+$: 235.0842. Found: 235.0843.

1-(4-Nitrophenyl)-3-phenylurea (34). The title compound was prepared from 4-nitrobenzoic acid (167 mg, 1.00 mmol) and aniline (137 μ L, 1.50 mmol) according to the general procedure. The desired urea **34** (182 mg, 71%) was obtained as a pale yellow solid after filtration. R_f 0.34 (40% EtOAc/hexanes); mp 217 $^{\circ}$ C; ^1H NMR (400 MHz, DMSO) δ 9.43 (s (br), 1H), 8.91 (s (br), 1H), 8.19 (d, J = 9 Hz, 2H), 7.69 (d, J = 9 Hz, 2H), 7.47 (d, J = 8 Hz, 2H), 7.31 (t, J = 8 Hz, 2H), 7.02 (t, J = 7 Hz, 1H); ^{13}C NMR (100 MHz, DMSO) δ 151.9, 146.3, 140.9, 138.9, 128.8, 125.1, 122.5, 118.6, 117.4; IR 3288, 164, 1606, 1593, 1556, 1488, 1343, 1233, 1110, 856, 750 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{13}\text{H}_{12}\text{N}_3\text{O}_3$ $[\text{M}+\text{H}]^+$: 258.0872. Found: 258.0872.

1-(2-Iodophenyl)-3-phenylurea (35). The title compound was prepared from 2-iodobenzoic acid (248 mg, 1.00 mmol) and aniline (137 μ L, 1.50 mmol) according to the general procedure. The desired urea **35** (200 mg, 59%) was obtained as a white solid after filtration. R_f 0.64 (40% EtOAc/hexanes); mp 217 $^{\circ}$ C; ^1H NMR (400 MHz, DMSO) δ 9.42 (s (br), 1H), 7.88 (s (br), 1H), 7.85-7.82 (m, 2H), 7.47-7.45 (m, 2H), 7.36-7.27 (m, 3H), 6.98 (t, J = 7 Hz, 1H), 6.84 (t, J = 7 Hz, 1H); ^{13}C NMR (100 MHz, DMSO) δ 152.3, 139.8, 139.5, 138.9, 128.8, 128.5, 125.0, 123.0, 122.0, 118.1, 91.3; IR 3280, 1645, 1573, 1543, 1444, 1289, 1229, 1014, 897, 749 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O I}$ $[\text{M}+\text{H}]^+$: 338.9994. Found: 338.9988

1-Mesityl-3-phenylurea (36). The title compound was prepared from benzoic acid (122 mg, 1.00 mmol) and mesidine (211 μ L, 1.50 mmol) according to the general procedure. The desired urea **36** (203 mg, 80%) was obtained as a white solid after trituration in Et_2O . R_f 0.52 (40% EtOAc/hexanes); mp 226 $^{\circ}$ C; ^1H NMR (400 MHz, DMSO) δ 8.66 (s (br), 1H), 7.59 (s, 1H), 7.44-7.42 (m, 2H), 7.25-7.22 (m, 2H), 6.93-6.87 (m, 3H), 2.22 (s, 3H), 2.15 (s, 6H); ^{13}C NMR (100 MHz, DMSO) δ 153.5, 140.7, 135.2, 134.6, 132.9, 128.6, 128.2, 120.9, 117.5, 20.5, 18.3; IR 3279, 2917, 1641, 1595, 1550, 1495, 1228, 858, 694 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{16}\text{H}_{19}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 255.1492. Found: 255.1484.

1-Mesityl-3-(4-methoxyphenyl)urea (37). The title compound was prepared from 4-methoxybenzoic acid (152 mg, 1.00 mmol) and mesidine (211 μ L, 1.50 mmol) according to the general procedure. The desired urea **37** (173 mg, 61%) was obtained as a white solid after trituration in Et_2O . R_f 0.47 (40% EtOAc/hexanes); mp 244 $^{\circ}$ C; ^1H NMR (400 MHz, DMSO) δ 8.43 (s (br), 1H), 7.50 (s, 1H), 7.33 (d, J = 9 Hz, 2H), 6.87-6.82 (m, 4H), 3.69 (s, 3H), 2.22 (s, 3H), 2.15 (s, 6H); ^{13}C NMR (100 MHz, DMSO) δ 154.0, 153.4, 135.2, 134.7, 133.4, 132.7, 128.2, 119.5, 113.8, 55.1, 20.4, 18.1; IR 3288, 2916, 2835,

1637, 1599, 15554, 1508, 1247, 1222, 837, 683 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{17}\text{H}_{21}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 285.1595. Found: 285.1597.

1-Hydroxy-3-(4-nitrophenyl)urea (38). The title compound was prepared from 4-nitrobenzoic acid (167 mg, 1.00 mmol) and *N*-Hydroxylamine hydrochloride (139 mg, 1.00 mmol) according to the general procedure. After 20 hours of reaction, a 10% solution of NaNO_2 (20 ml) was added. The mixture was then diluted with ethyl acetate (20 ml), and the resulting mixture was stirred during 20 min at 25 °C. The aqueous layer was extracted with ethyl acetate (3 x 30 ml). The combined organic layers were washed with saturated NH_4Cl (2x20 ml), and brine (20 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure to afford a orange oil. The desired urea **38** (105 mg, 55%) was obtained as a yellow solid, after flash chromatography (5% MeOH/ CHCl_3). R_f 0.51 (5% MeOH/ CHCl_3); mp 140 °C; ^1H NMR (400 MHz, DMSO) δ 9.50 (s, 1H), 9.28 (s, 1H), 9.15 (s, 1H), 8.15 (d, J = 9 Hz, 2H), 7.92 (d, J = 9 Hz, 2H); ^{13}C NMR (100 MHz, DMSO) δ 157.6, 146.3, 141.1, 124.7, 118.3; IR 3288, 2938, 2835, 1628, 1508, 1443, 1245, 1167, 1026, 842, 768 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_7\text{H}_8\text{N}_3\text{O}_4$ $[\text{M}+\text{H}]^+$: 198.0509. Found: 198.0512.

1-(3,5-Dimethylphenyl)-3-((*R*)-1-phenylethyl)urea (39). The title compound was prepared from 3,5-dimethylbenzoic acid (150 mg, 1.00 mmol) and (*R*)-methylbenzyl amine (191 μL , 1.50 mmol) according to the general procedure. The desired urea **39** (182 mg, 63%) was obtained as a white solid after filtration. R_f 0.69 (40% EtOAc/hexanes); mp 167 °C; $[\alpha]_D^{25} = +6.6$ (c 1.0, MeOH); ^1H NMR (400 MHz, DMSO) δ 8.22 (s, 1H), 7.33-7.32 (m, 4H), 7.25-7.21 (m, 1H), 6.97 (s, 2H), 6.58 (d, J = 8 Hz, 1H), 6.52 (s, 1H), 4.80-4.76 (m, 1H), 2.17 (s, 6H), 1.37 (d, J = 7 Hz, 3H); ^{13}C NMR (100 MHz, DMSO) δ 154.3, 145.2, 140.2, 137.4, 128.2, 126.5, 125.7, 122.6, 115.2, 48.5, 23.0, 21.0; IR 3305, 2968, 2922, 1632, 1558, 1445, 1231, 850, 685 cm^{-1} ; HMRS (ESI) calcd for $\text{C}_{17}\text{H}_{20}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 269.1652. Found: 269.1652.