Supporting Information

Catalyst-Free Microwave-Assisted Amination of 2-Chloro-5-nitrobenzoic Acid

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Contents

1. Experimental	S2
2. General procedure for the synthesis of the products 3a-w	S2-S3
3. Analytical data of the synthesized compounds (3a-w)	S3-S14
4. ¹ H-NMR (500 MHz, DMSO- <i>d</i> ₆) and ¹³ C-NMR (126 MHz, DMSO- <i>d</i> ₆) spectra of final products 3a-w	S15-S37
5. References	S38

1. Experimental

General: All materials were used as purchased. Thin-layer chromatography was performed using TLC aluminum sheets silica gel 60 F₂₅₄. Colored compounds were visible at daylight; other compounds were visualized under UV light (254 nm). ¹H- and ¹³C-NMR data were collected using DMSO-*d*₆ as a solvent. Chemical shifts are reported in parts per million (ppm) relative to the deuterated solvent (DMSO-*d*₆), δ ¹H: 2.49 ppm, ¹³C: 39.7 ppm, coupling constants *J* are given in Hertz and spin multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), sext (sextet), m (multiplet), br (broad). The purities of isolated products were determined by ESI-mass spectra obtained on an LCMS instrument (LCMS/MS) using the following procedure: the compounds were dissolved at a concentration of 0.5 mg/ml in H₂O : MeOH = 1 : 1, containing 2 mM NH₄CH₃COO. Then, 10 μ l of the sample was injected into an HPLC column (C18, 50 x 2.00 mm). Elution was performed with a gradient of water : methanol (containing 2 mM NH₄CH₃COO) from 90 : 10 to 0 : 100 for 30 min at a flow rate of 250 μ l/min, starting the gradient after 10 min. UV absorption was detected from 200 to 950 nm using a diode array detector. Purity of the compounds was determined at 254 nm. Melting points were measured on a melting point apparatus and are uncorrected. For microwave reactions a CEM FocusedTM Microwave Synthesis type Discover LabMate (Corporation, Matthews, NC) apparatus was used. The reaction temperatures were measured and controlled using an IR sensor.

2. General procedure for the synthesis of the products 3a-w

To an 80 mL microwave reaction sealed vessel equipped with a magnetic stirring bar were added 5-nitro-2-chlorobenzoic acid (2.520 g, 12.5 mmol) and an excess (typically 6 eq.) of the appropriate aliphatic or aromatic amine derivative (75 mmol) to obtain a homogenous mixture. The mixture was irradiated in a microwave oven (80-100 W) for 5-30 min at 80-120 °C. Then the reaction mixture was cooled to rt, and the product was purified using the following procedure. The contents of the vial were dissolved in ca. 300 mL of dichloromethane and the organic solution was extracted with diluted aq. sodium hydroxide solution (ca. 500 mL). The extraction procedure was repeated until the aqueous layer became light yellow (3-4 times). Then the aqueous layer was collected and acidified using concentrated aq. hydrochloric acid

(37 %) until $\text{pH} \leq 3$ and the desired product precipitated in the acidic medium. The precipitated solid was filtered off and washed several times (2-3 times) with 100 mL of water each to remove the remaining sodium chloride as well as hydrochloric acid. The product was dried in an oven at 100 °C. The purity of the product was $\geq 95\%$ as determined by LC-MS.

Analytical data of the synthesized compounds:

5-Nitro-2-phenylaminobenzoic acid (3a):¹

Reaction conditions: according to the general procedure: 10 min, 100 °C, 80 W; pressure up to 10 bar. **Analytical data:** yellow solid, mp 251-253 °C (lit. 250 °C). **¹H-NMR:** δ 7.11 (d, 1H, $J = 9.5$ Hz), 7.26 (ddd, 1H, $J = 0.8$ Hz, $J = 7.3$ Hz, $J = 7.6$ Hz), 7.35 (dd, 2H, $J = 0.8$ Hz, $J = 8.9$ Hz), 7.45 (m, 2H), 8.15 (dd, 1H, $J = 2.9$ Hz, $J = 9.5$ Hz), 8.70 (d, 1H, $J = 2.9$ Hz), 10.35 (br, 1H, NH), 13.7 (br, 1H, COOH). **¹³C-NMR:** δ 111.1, 113.4, 124.2, 126.0, 128.6, 129.5, 129.9, 136.73, 138.3, 152.5, 168.8. **LC-MS (m/z):** 259 $[\text{M}]^+$, 276 $[\text{M}+\text{NH}_4]^+$, 257 $[\text{M}]^-$, 213 $[\text{M}-\text{COO}]^-$. Purity by **HPLC-UV (254 nm)**-ESI-MS: 99%.

2-(4-Fluorophenylamino)-5-nitrobenzoic acid (3b):²

Reaction conditions: according to the general procedure: 10 min, 120 °C, 100 W; pressure up to 10 bar. **Analytical data:** greenish yellow solid, mp 234-236 °C (lit. 234-235 °C, 235-236 °C). **¹H-NMR:** δ 6.96 (d, 1H, $J = 9.5$ Hz), 7.28 (m, 2H), 7.38 (m, 2H), 8.13 (dd, 1H, $J = 2.9$ Hz, $J = 9.5$ Hz), 8.69 (d, 1H, $J = 2.8$ Hz), 10.28 (br, 1H, NH). **¹³C-NMR:** δ 111.1, 113.2, 116.6, 116.8, 126.9, 127.0, 128.6, 129.4, 134.68,

134.70, 136.7, 153.0, 159.1, 161.1, 168.7. **LC-MS (m/z):** 277 [M]⁺, 294 [M+NH₄⁺]⁺, 275 [M]⁻, 230 [M-COO⁻]⁻. Purity by **HPLC-UV (254 nm)-ESI-MS:** 99%.

2-(2-Chlorophenylamino)-5-nitrobenzoic acid (3c):³

Reaction conditions: according to the general procedure: 30 min, 150 °C, 150 W; pressure up to 10 bar. **Analytical data:** yellowish green solid, mp 282-284 °C. **¹H-NMR:** δ 6.97 (d, 1H, *J* = 9.5 Hz), 7.31 (ddd, 1H, *J* = 1.3 Hz, *J* = 7.6 Hz, *J* = 7.9 Hz), 7.44 (ddd, 1H, *J* = 1.3 Hz, *J* = 7.3 Hz, *J* = 7.9 Hz), 7.59 (dd, 1H, *J* = 1.3 Hz, *J* = 7.9 Hz), 7.63 (dd, 1H, *J* = 1.3 Hz, *J* = 7.9 Hz), 8.19 (dd, 1H, *J* = 2.9 Hz, *J* = 9.5 Hz), 8.72 (d, 1H, *J* = 2.9 Hz), 10.44 (br, 1H, NH). **¹³C-NMR:** δ 111.8, 113.7, 126.1, 127.5, 128.38, 128.42, 128.5, 129.5, 130.6, 135.5, 137.4, 151.8, 168.8. **LC-MS (m/z):** 291 [M]⁻, 247 [M-COO⁻]⁻. Purity by **HPLC-UV (254 nm)-ESI-MS:** 99%.

2-(3-Chlorophenylamino)-5-nitrobenzoic acid (3d):⁴

Reaction conditions: according to the general procedure: 30 min, 120 °C, 150 W; pressure up to 10 bar. **Analytical data:** yellowish green solid, mp 274-276 °C. **¹H-NMR:** δ 7.18 (d, 1H, *J* = 9.5 Hz), 7.29 (dd, 1H, *J* = 1.3 Hz, *J* = 7.9 Hz), 7.33 (dd, 1H, *J* = 1.3 Hz, *J* = 7.9 Hz), 7.45 (m, 2H), 8.19 (dd, 1H, *J* = 2.9 Hz, *J* = 9.5 Hz), 8.70 (d, 1H, *J* = 2.9 Hz), 10.34 (br, 1H, NH), 13.8 (br, 1H, COOH). **¹³C-NMR:** δ 112.0, 114.0, 122.4, 123.6, 125.5, 128.4, 129.5, 131.4, 134.1, 137.3, 140.2, 151.8, 168.6. **LC-MS (m/z):** 291 [M]⁻, 247 [M-COO⁻]⁻. Purity by **HPLC-UV (254 nm)-ESI-MS:** 97%.

2-(3-Bromophenylamino)-5-nitrobenzoic acid (3e):

Reaction conditions: according to the general procedure: 15 min, 120 °C, 100 W; pressure up to 10 bar. **Analytical data:** greenish yellow solid, mp 274-276 °C. **¹H-NMR:** δ 7.17 (d, 1H, J = 9.1 Hz), 7.40 (m, 3H), 7.58 (m, 1H), 8.19 (dd, 1H, J = 2.9 Hz, J = 9.5 Hz), 8.70 (d, 1H, J = 2.8 Hz), 10.33 (br, 1H, NH), 13.6 (br, 1H, COOH). **¹³C-NMR:** δ 112.0, 113.9, 122.4, 122.9, 126.5, 128.4, 129.5, 131.6, 137.3, 140.3, 141.8, 168.5. **LC-MS (m/z):** 337 [M]⁺, 354 [M+NH₄⁺]⁺, 335 [M]⁻, 291 [M-COO⁻]⁻. Anal. Calcd. for C₁₅H₁₄N₂O₄: C, 46.32; H, 2.69; N, 8.31. Found: C, 46.18; H, 2.68; N, 8.32. Purity by **HPLC-UV (254 nm)-ESI-MS:** 95%.

2-(2-Methoxyphenylamino)-5-nitrobenzoic acid (3f):⁵

Reaction conditions: according to the general procedure: 15 min, 120 °C, 100 W; pressure up to 10 bar. **Analytical data:** green solid, mp 216-219 °C (lit. 265-267 °C, 218-224 °C). **¹H-NMR:** δ 3.81 (s, 3H, OCH₃), 7.00 (m, 2H), 7.17 (dd, 1H, J = 1.3 Hz, J = 8.2 Hz), 7.25 (ddd, 1H, J = 1.6 Hz, J = 7.6 Hz, J = 8.2 Hz), 7.40 (dd, 1H, J = 1.6 Hz, J = 7.6 Hz), 8.15 (dd, 1H, J = 2.8 Hz, J = 9.5 Hz), 8.71 (d, 1H, J = 2.8 Hz), 10.28 (br, 1H, NH), 13.7 (br, 1H, COOH). **¹³C-NMR:** δ 55.89, 111.1, 112.5, 113.5, 120.9, 124.2, 126.8, 126.9, 128.5, 129.3, 136.6, 152.4, 152.7, 168.8. **LC-MS (m/z):** 289 [M]⁺, 306 [M+NH₄⁺]⁺, 287 [M]⁻, 243 [M-COO⁻]⁻. Purity by **HPLC-UV (254 nm)-ESI-MS:** 100%.

2-(3-Methoxyphenylamino)-5-nitrobenzoic acid (3g):⁵

Reaction conditions: according to the general procedure: 10 min, 110 °C, 100 W; pressure up to 10 bar. **Analytical data:** yellowish green solid, mp 252-254 °C (lit. 258-261 °C, 253-254 °C). **¹H-NMR:** δ 3.77 (s, 3H, OCH₃), 6.83 (m, 1H), 6.91 (m, 2H), 7.18 (d, 1H, $J = 9.5$ Hz), 7.35 (dd, 1H, $J = 8.2$ Hz, $J = 8.5$ Hz), 8.16 (dd, 1H, $J = 2.9$ Hz, $J = 9.5$ Hz), 8.70 (d, 1H, $J = 2.9$ Hz), 10.32 (br, 1H, NH), 13.7 (br, 1H, COOH). **¹³C-NMR:** δ 55.4, 109.6, 111.2, 111.7, 113.7, 116.0, 128.5, 129.4, 130.7, 136.8, 139.5, 152.4, 160.5, 168.7. **LC-MS (m/z):** 289 [M]⁺, 306 [M+NH₄⁺]⁺, 287 [M]⁻, 243 [M-COO⁻]⁻. Purity by **HPLC-UV (254 nm)-ESI-MS:** 95%.

2-(2-Ethylphenylamino)-5-nitrobenzoic acid (3h):

Reaction conditions: according to the general procedure: 20 min, 120 °C, 150 W; pressure up to 10 bar. **Analytical data:** yellowish green solid, mp 186-187 °C. **¹H-NMR:** δ 1.10 (t, 3H, CH₃, $J = 7.6$ Hz), 2.55 (q, 2H, CH₂, $J = 7.6$ Hz), 6.72 (d, 1H, $J = 9.5$ Hz), 7.31 (m, 3H), 7.40 (d, 1H, $J = 6.9$ Hz), 8.13 (dd, 1H, $J = 2.2$ Hz, $J = 9.2$ Hz), 8.71 (d, 1H, $J = 2.2$ Hz), 10.28 (br, 1H, NH), 13.5 (br, 1H, COOH). **¹³C-NMR:** δ 14.6, 24.2, 110.5, 113.0, 126.3, 127.2, 127.4, 128.6, 129.5, 129.9, 136.1, 136.4, 139.7, 153.6, 169.0. **LC-MS (m/z):** 287 [M]⁺, 304 [M+NH₄⁺]⁺, 285 [M]⁻, 241 [M-COO⁻]⁻. Anal. Calcd. for C₁₅H₁₄N₂O₄·1/3H₂O: C, 61.64; H, 5.06; N, 9.58. Found: C, 61.71; H, 4.97; N, 9.13. Purity by **HPLC-UV (254 nm)-ESI-MS:** 95%.

2-(3-Ethylphenylamino)-5-nitrobenzoic acid (3i):

Reaction conditions: according to the general procedure: 5 min, 80 °C, 80 W; pressure up to 10 bar. **Analytical data:** yellow solid, mp 246-248 °C. **¹H-NMR:** δ 1.19 (t, 3H, CH₃, *J* = 7.6 Hz), 2.62 (q, 2H, CH₂, *J* = 7.6 Hz), 7.11 (d, 2H, *J* = 9.5 Hz), 7.13 (m, 2H), 7.35 (dd, 1H, *J* = 7.6 Hz, *J* = 7.7 Hz), 8.15 (dd, 1H, *J* = 2.9 Hz, *J* = 9.5 Hz), 8.70 (d, 1H, *J* = 2.8 Hz), 10.33 (br, 1H, NH), 13.7 (br, 1H, COOH). **¹³C-NMR:** δ 15.5, 28.1, 111.0, 113.4, 121.4, 123.5, 125.5, 128.6, 129.5, 129.8, 136.6, 138.3, 145.9, 152.6, 168.8. **LC-MS (m/z):** 287 [M]⁺, 304 [M+NH₄⁺]⁺, 285 [M]⁻, 241 [M-COO⁻]⁻. Anal. Calcd. for C₁₅H₁₄N₂O₄: C, 62.93; H, 4.93; N, 9.78. Found: C, 62.78; H, 4.99; N, 9.71. Purity by **HPLC-UV (254 nm)-ESI-MS:** 99%.

2-(4-Ethylphenylamino)-5-nitrobenzoic acid (3j):

Reaction conditions: according to the general procedure: 10 min, 100 °C, 80 W; pressure up to 10 bar. **Analytical data:** dark green solid, mp 206-208 °C. **¹H-NMR:** δ 1.19 (t, 3H, CH₃, *J* = 7.6 Hz), 2.62 (q, 2H, CH₂, *J* = 7.6 Hz), 7.05 (d, 1H, *J* = 9.5 Hz), 7.23 (d, 2H, *J* = 8.5 Hz), 7.28 (d, 2H, *J* = 8.5 Hz), 8.11 (dd, 1H, *J* = 2.9 Hz, *J* = 9.5 Hz), 8.72 (d, 1H, *J* = 2.9 Hz), 10.81 (br, 1H, NH). **¹³C-NMR:** δ 15.7, 27.8, 112.8, 124.0, 128.6, 128.9, 129.2, 136.2, 136.4, 141.3, 152.8, 168.9. **LC-MS (m/z):** 287 [M]⁺, 304 [M+NH₄⁺]⁺, 285 [M]⁻, 241 [M-COO⁻]⁻. Anal. Calcd. for C₁₅H₁₄N₂O₄·H₂O: C, 59.53; H, 5.29; N, 9.20. Found: C, 59.53; H, 5.19; N, 8.15. Purity by **HPLC-UV (254 nm)-ESI-MS:** 99%.

2-(2-Ethoxyphenylamino)-5-nitrobenzoic acid (3k):

Reaction conditions: according to the general procedure: 15 min, 120 °C, 100 W; pressure up to 10 bar. **Analytical data:** yellowish green solid, mp 222-224 °C. **¹H-NMR:** δ 1.28 (t, 3H, CH₃, J = 7.4 Hz), 4.08 (q, 2H, CH₂, J = 7.4 Hz), 7.00 (ddd, 1H, J = 2.0 Hz, J = 8.8 Hz, J = 8.9 Hz), 7.15 (m, 3H), 7.44 (dd, 1H, J = 2.0 Hz, J = 8.8 Hz), 8.16 (dd, 1H, J = 2.9 Hz, J = 9.5 Hz), 8.71 (d, 1H, J = 2.9 Hz), 10.45 (br, 1H, NH), 13.7 (br, 1H, COOH). **¹³C-NMR:** δ 14.7, 64.1, 111.3, 113.4, 113.5, 120.8, 123.0, 126.3, 127.3, 128.5, 129.3, 136.6, 151.4, 151.9, 168.8. **LC-MS (m/z):** 303 [M]⁺, 320 [M+NH₄⁺]⁺, 301 [M]⁻, 257 [M-COO⁻]⁻. Anal. Calcd. for C₁₅H₁₄N₂O₄: C, 59.60; H, 4.67; N, 9.27. Found: C, 59.28; H, 4.66; N, 9.15. Purity by **HPLC-UV (254 nm)-ESI-MS:** 99%.

2-(4-Ethoxyphenylamino)-5-nitrobenzoic acid (3l):⁶

Reaction conditions: according to the general procedure: 5 min, 100 °C, 100 W; pressure up to 10 bar. **Analytical data:** green solid, mp 199-201 °C. **¹H-NMR:** δ 1.33 (t, 3H, CH₃, J = 9.6 Hz), 4.04 (q, 2H, CH₂, J = 9.6 Hz), 6.88 (d, 1H, J = 9.5 Hz), 7.00 (d, 2H, J = 8.8 Hz), 7.24 (d, 1H, J = 9.2 Hz), 8.11 (dd, 1H, J = 2.8 Hz, J = 9.5 Hz), 8.68 (d, 1H, J = 2.9 Hz), 10.17 (br, 1H, NH), 13.8 (br, 1H, COOH). **¹³C-NMR:** δ 14.8, 63.5, 110.4, 113.0, 115.6, 126.7, 128.7, 129.4, 130.7, 136.2, 153.6, 157.0, 168.8. **LC-MS (m/z):** 303 [M]⁺, 320 [M+NH₄⁺]⁺, 301 [M]⁻, 257 [M-COO⁻]⁻. Purity by **HPLC-UV (254 nm)-ESI-MS:** 100%.

2-(2,3-Dimethylphenylamino)-5-nitrobenzoic acid (3m):⁷

Reaction conditions: according to the general procedure: 30 min, 120 °C, 100 W; pressure up to 10 bar. **Analytical data:** yellowish green solid, mp 262-264 °C (lit. 265-266 °C). **¹H-NMR:** δ 2.08 (s, 3H, CH₃), 2.29 (s, 3H, CH₃), 6.58 (d, 1H, J = 9.5 Hz), 7.16 (m, 3H), 8.10 (dd, 1H, J = 2.9 Hz, J = 9.5 Hz), 8.70 (d, 1H, J = 2.9 Hz), 10.18 (br, 1H, NH), 13.6 (br, 1H, COOH). **¹³C-NMR:** δ 13.9, 20.2, 110.3, 113.1, 124.1, 126.6, 128.5, 128.6, 129.5, 132.8, 136.2, 136.5, 138.5, 153.6, 168.9. **LC-MS (m/z):** 287 [M]⁺, 304 [M+NH₄⁺]⁺, 285 [M]⁻, 241 [M-COO⁻]⁻. Purity by **HPLC-UV (254 nm)-ESI-MS:** 95%.

2-(2,4-Dimethylphenylamino)-5-nitrobenzoic acid (3n):³

Reaction conditions: according to the general procedure: 10 min, 100 °C, 100 W; pressure up to 10 bar. **Analytical data:** yellowish green solid, mp 234-236 °C. **¹H-NMR:** δ 2.12 (s, 3H, CH₃), 2.30 (s, 3H, CH₃), 6.61 (d, 1H, J = 9.5 Hz), 7.05 (dd, 1H, J = 2.1 Hz, J = 8.2 Hz), 7.16 (d, 2H, J = 8.2 Hz), 8.10 (dd, 1H, J = 2.9 Hz, J = 9.5 Hz), 8.69 (d, 1H, J = 2.9 Hz), 10.11 (br, 1H, NH). **¹³C-NMR:** δ 17.5, 20.7, 110.3, 113.0, 126.1, 127.7, 128.7, 129.5, 132.0, 133.8, 134.1, 136.2, 136.4, 153.6, 168.9. **LC-MS (m/z):** 287 [M]⁺, 304 [M+NH₄⁺]⁺, 285 [M]⁻, 241 [M-COO⁻]⁻. Purity by **HPLC-UV (254 nm)-ESI-MS:** 95%.

2-(2,5-Dimethylphenylamino)-5-nitrobenzoic acid (3o):

Reaction conditions: according to the general procedure: 20 min, 120 °C, 100 W; pressure up to 10 bar. **Analytical data:** yellowish green solid, mp 235-237 °C. **¹H-NMR:** δ 2.13 (s, 3H, CH₃), 2.25 (s, 3H, CH₃), 6.70 (d, 1H, *J* = 9.5 Hz), 7.05 (dd, 1H, *J* = 2.0 Hz, *J* = 7.9 Hz), 7.13 (br, 1H), 7.24 (d, 1H, *J* = 7.6 Hz), 8.12 (dd, 1H, *J* = 2.9 Hz, *J* = 9.2 Hz), 8.70 (d, 1H, *J* = 2.9 Hz), 10.20 (br, 1H, NH), 13.7 (br, 1H, COOH). **¹³C-NMR:** δ 17.1, 20.6, 110.5, 113.1, 126.3, 127.6, 128.6, 129.5, 130.5, 131.2, 136.3, 136.5, 136.6, 153.2, 168.9. **LC-MS (m/z):** 287 [M]⁺, 304 [M+NH₄]⁺, 285 [M]⁻, 241 [M-COO]⁻. Anal. Calcd. for C₁₅H₁₄N₂O₄: C, 62.93; H, 4.93; N, 9.78. Found: C, 62.07; H, 4.89; N, 9.49. Purity by **HPLC-UV (254 nm)-ESI-MS:** 97%.

2-(3,5-Dimethylphenylamino)-5-nitrobenzoic acid (3p):

Reaction conditions: according to the general procedure: 10 min, 120 °C, 100 W; pressure up to 10 bar. **Analytical data:** yellow solid, mp 278-279 °C. **¹H-NMR:** δ = 2.48 (s, 6H, 2CH₃), 6.88 (br, 1H), 6.93 (br, 2H), 7.11 (d, 1H, *J* = 9.5 Hz), 8.13 (dd, 1H, *J* = 2.9 Hz, *J* = 9.5 Hz), 8.70 (d, 1H, *J* = 2.9 Hz), 10.47 (br, 1H, NH), 13.5 (br, 1H, COOH). **¹³C-NMR:** δ = 20.9, 111.7, 113.3, 121.5, 127.3, 128.5, 129.2, 136.5, 138.2, 139.2, 152.5, 168.8. **LC-MS (m/z):** 287 [M]⁺, 304 [M+NH₄]⁺, 285 [M]⁻, 241 [M-COO]⁻. Anal. Calcd. for C₁₅H₁₄N₂O₄·0.5H₂O: C, 61.00; H, 5.12; N, 9.49. Found: C, 61.18; H, 4.86; N, 9.44. Purity by **HPLC-UV (254 nm)-ESI-MS:** 99%.

2-(2-Methyl-4-chlorophenylamino)-5-nitrobenzoic acid (3q):

Reaction conditions: according to the general procedure: 30 min, 120 °C, 100 W; pressure up to 10 bar. **Analytical data:** dark green solid, mp >400 °C. **¹H-NMR:** δ 2.20 (s, 3H, CH₃), 6.81 (d, 1H, *J* = 9.2 Hz), 7.27 (dd, 1H, *J* = 2.3 Hz, *J* = 8.6 Hz), 7.34 (d, 1H, *J* = 8.6 Hz), 7.40 (d, 1H, *J* = 7.3 Hz), 8.01 (dd, 1H, *J* = 2.8 Hz, *J* = 9.2 Hz), 8.75 (d, 1H, *J* = 3.2 Hz), 12.30 (br, 1H, COOH). **¹³C-NMR:** δ 17.7, 111.7, 118.6, 124.8, 126.8, 127.4, 128.4, 128.6, 130.8, 134.6, 136.4, 137.3, 152.5, 168.9. **LC-MS (m/z):** 307 [M]⁺, 324 [M+NH₄⁺]⁺, 305 [M]⁻, 261 [M-COO⁻]⁻. Anal. Calcd. for C₁₅H₁₄N₂O₄Cl·2/3H₂O: C, 52.76; H, 3.90; N, 8.79. Found: C, 52.70; H, 3.32; N, 8.56. Purity by **HPLC-UV (254 nm)-ESI-MS:** 97%.

2-Cyclopentylamino-5-nitrobenzoic acid (3r):⁸

Reaction conditions: according to the general procedure: 5 min, 120 °C, 100 W; pressure up to 10 bar. **Analytical data:** pale yellow solid, mp 235-237 °C. **¹H-NMR:** δ 1.47 (m, 2H), 1.64 (m, 4H), 2.04 (m, 2H), 3.99 (m, 1H), 6.87 (d, 1H, *J* = 9.8 Hz), 8.13 (dd, 1H, *J* = 2.9 Hz, *J* = 9.5 Hz), 8.60 (d, 1H, *J* = 2.9 Hz), 8.77 (d, 1H, NH, *J* = 6.7 Hz), 13.4 (br, 1H, COOH). **¹³C-NMR:** δ 23.7, 32.9, 53.6, 109.2, 112.3, 128.7, 129.5, 134.7, 154.2, 168.9. **LC-MS (m/z):** 251 [M]⁺, 268 [M+NH₄⁺]⁺, 249 [M]⁻, 205 [M-COO⁻]⁻. Purity by **HPLC-UV (254 nm)-ESI-MS:** 100%.

2-Cyclohexylamino-5-nitrobenzoic acid (3s):⁹

Reaction conditions: according to the general procedure: 5 min, 120 °C, 100 W; pressure up to 10 bar. **Analytical data:** pale yellow solid, mp 260-261 °C (lit. 186-189 °C). **¹H-NMR:** δ 1.29 (m, 3H), 1.40 (m, 2H), 1.55 (m, 1H), 1.65 (m, 2H), 1.91 (m, 2H), 3.59 (m, 1H), 6.91 (d, 1H, $J = 9.8$ Hz), 8.11 (dd, 1H, $J = 2.8$ Hz, $J = 9.5$ Hz), 8.62 (d, 1H, $J = 2.9$ Hz), 8.79 (d, 1H, NH, $J = 6.7$ Hz), 13.7 (br, 1H, COOH). **¹³C-NMR:** δ 23.9, 25.2, 32.0, 50.2, 109.0, 112.0, 129.0, 129.5, 134.5, 153.8, 169.0. **LC-MS (m/z):** 265 [M]⁺, 282 [M+NH₄⁺]⁺, 263 [M]⁻, 219 [M-COO⁻]⁻. Purity by **HPLC-UV (254 nm)-ESI-MS:** 100%.

2-Benzylamino-5-nitrobenzoic acid (3t):¹⁰

Reaction conditions: according to the general procedure: 10 min, 120 °C, 100 W; pressure up to 10 bar. **Analytical data:** yellow solid, mp 239-241 °C. **¹H-NMR:** δ 4.62 (d, 2H, CH₂, $J = 6.0$ Hz), 6.83 (d, 1H, $J = 9.5$ Hz), 7.27 (m, 1H), 7.34 (m, 4H), 8.11 (dd, 1H, $J = 2.9$ Hz, $J = 9.2$ Hz), 8.65 (d, 1H, $J = 2.9$ Hz), 9.17 (t, 1H, NH, $J = 4.5$ Hz), 13.5 (br, 1H, COOH). **¹³C-NMR:** δ 46.0, 109.9, 112.2, 127.2, 127.4, 128.7, 128.8, 129.5, 135.2, 138.1, 154.7, 168.7. **LC-MS (m/z):** 273 [M]⁺, 290 [M+NH₄⁺]⁺, 271 [M]⁻, 227 [M-COO⁻]⁻. Purity by **HPLC-UV (254 nm)-ESI-MS:** 100%.

5-Nitro-2-phenethylaminobenzoic acid (3u):¹¹

Reaction conditions: according to the general procedure: 10 min, 120 °C, 100 W; pressure up to 10 bar. **Analytical data:** pale yellow solid, mp 219-220 °C. **¹H-NMR:** δ 2.92 (t, 2H, CH₂, J = 6.9 Hz), 3.59 (q, 2H, CH₂, J = 7.2 Hz), 6.94 (d, 1H, J = 9.5 Hz), 7.22 (m, 1H), 7.30 (m, 4H), 8.15 (dd, 1H, J = 2.9 Hz, J = 9.5 Hz), 8.61 (d, 1H, J = 2.9 Hz), 8.80 (t, 1H, NH, J = 4.5 Hz), 13.4 (br, 1H, COOH).

¹³C-NMR: δ 34.49, 43.92, 109.33, 111.82, 126.53, 128.56, 128.69, 128.95, 129.54, 134.84, 138.79, 154.63, 168.75. **LC-MS (m/z):** 287 [M]⁺, 304 [M+NH₄]⁺, 285 [M]⁻.

Purity by **HPLC-UV (254 nm)-ESI-MS:** 100%.

2-Dipropylamino-5-nitrobenzoic acid (3v):

Reaction conditions: according to the general procedure: 5 min, 100 °C, 100 W; pressure up to 10 bar. **Analytical data:** pale yellow solid, mp 100-102 °C. **¹H-NMR:** δ 0.80 (t, 6H, 2CH₃, J = 7.3 Hz), 1.53 (sext, 4H, 2CH₂, J = 7.3 Hz, J = 7.6 Hz), 3.29 (t, 4H, 2NCH₂, J = 7.3 Hz), 7.12 (d, 1H, J = 9.5 Hz), 8.09 (dd, 1H, J = 2.9 Hz, J = 9.5 Hz), 8.27 (d, 1H, J = 2.8 Hz), 13.6 (br, 1H, COOH). **¹³C-NMR:** δ 11.1, 20.1, 53.9, 117.4, 120.6, 126.8, 127.3, 136.7, 153.7, 168.3. **LC-MS (m/z):** 267 [M]⁺, 265 [M]⁻, 221 [M-COO]⁻. Anal. Calcd. for C₁₅H₁₄N₂O₄: C, 58.64; H, 6.81; N, 10.52. Found: C, 58.14; H, 6.67; N, 10.22. Purity by **HPLC-UV (254 nm)-ESI-MS:** 97%.

5-Nitro-2-pyrrolidin-1-ylbenzoic acid (3w):¹²

Reaction conditions: according to the general procedure: 5 min, 80 °C, 100 W; pressure up to 10 bar. **Analytical data:** pale yellow solid, mp 222-223^d °C (lit. 224-266 °C). **¹H-NMR:** δ 1.92 (m, 4H, 2CH₂), 3.34 (m, 4H, 2NCH₂), 6.86 (d, 1H, J = 9.5 Hz), 8.08 (dd, 1H, J = 2.9 Hz, J = 9.5 Hz), 8.29 (d, 1H, J = 2.9 Hz), 13.2 (br, 1H, COOH). **¹³C-NMR:** δ 25.4, 51.1, 114.1, 116.8, 126.7, 127.3, 134.9, 150.8, 168.15. **LC-MS (m/z):** 237 [M]⁺, 235 [M]⁻, 191 [M-COO]⁻. Purity by **HPLC-UV (254 nm)**-ESI-MS: 97%.

^1H and ^{13}C NMR spectra of final products **3a-w**

5-Nitro-2-phenylaminobenzoic acid (3a):

2-(4-Fluorophenylamino)-5-nitrobenzoic acid (3b):

2-(2-Chlorophenylamino)-5-nitrobenzoic acid (3c):

2-(3-Chlorophenylamino)-5-nitrobenzoic acid (3d):

2-(3-Bromophenylamino)-5-nitrobenzoic acid (3e):

2-(2-Methoxyphenylamino)-5-nitrobenzoic acid (3f):

2-(3-Methoxyphenylamino)-5-nitrobenzoic acid (3g):

2-(2-Ethylphenylamino)-5-nitrobenzoic acid (3h):

2-(3-Ethylphenylamino)-5-nitrobenzoic acid (3i):

2-(4-Ethylphenylamino)-5-nitrobenzoic acid (3j):

2-(2-Ethoxyphenylamino)-5-nitrobenzoic acid (3k):

2-(4-Ethoxyphenylamino)-5-nitrobenzoic acid (3l):

2-(2,3-Dimethylphenylamino)-5-nitrobenzoic acid (3m):

2-(2,4-Dimethylphenylamino)-5-nitrobenzoic acid (3n):

2-(2,5-Dimethylphenylamino)-5-nitrobenzoic acid (3o):

2-(3,5-Dimethylphenylamino)-5-nitrobenzoic acid (3p):

2-(2-Methyl-4-chlorophenylamino)-5-nitrobenzoic acid (3q):

2-Cyclopentylamino-5-nitrobenzoic acid (3r):

2-Cyclohexylamino-5-nitrobenzoic acid (3s):

2-Benzylamino-5-nitrobenzoic acid (3t):

5-Nitro-2-phenethylaminobenzoic acid (3u):

2-Dipropylamino-5-nitrobenzoic acid (3v):

5-Nitro-2-pyrrolidin-1-ylbenzoic acid (3w):

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