Supporting Information

for

Acid-catalyzed reaction of (4,4-diethoxybutyl)ureas with phenols as a novel approach to the synthesis of α -arylpyrrolidines.

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General experimental details.

Commercially available compounds were used without further purification. All solvents were purified and dried according to standard procedures. The ^1H NMR spectra were recorded on an MSL 400 instrument (Bruker) with the working frequency of 400.13 MHz. The ^{13}C NMR spectra were recorded on an Avance 600 instrument with the working frequency of 150.90 MHz. Signals of residual protons of solvent in ^1H NMR spectra were used as references for the measurements of chemical shift. IR spectra were recorded on a Vector 22 (Bruker) spectrometer. Melting points were determined on a Stuart SMP 10 apparatus and are uncorrected.

The X-Ray diffraction data for crystals of compounds **2b,c** were collected on a Bruker AXS Smart Apex II CCD diffractometer in the ω and ϕ -scan modes using graphite monochromated $\text{MoK}\alpha$ (λ 0.71073 Å) radiation. The structure was solved by direct method and refined by the full matrix least-squares using SHELXTL [1] and WinGX [2] programs. All Figures were made using PLATON [3].

[1] Sheldrick, G.M. SHELXTL v.6.12, Structure Determination Software Suite, Bruker AXS, Madison, Wisconsin, USA, **2000**.

[2] Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, 32, 837.

[3] Spek, A. L. *J. Appl. Cryst.* **2003**, 36, 7.

General procedure for the synthesis of ureas **1a-d**.

To the solution of appropriate amine (11.2 mmol) in dry dichloromethane (11 ml) CDI (2.0 g, 12.3 mmol) was added. Reaction mixture was stirred at 20°C for 5 days, then 4,4-diethoxybutan-1-amine (1.80 g, 11.2 mmol) was added and the mixture was stirred at 20°C for additional 3 days. Solvent was removed on rotary evaporator, residue washed thoroughly with water and dried in vacuo (2h, 0.01 torr, 20°C) to give desired compound **1**.

1-(sec-butyl)-3-(4,4-diethoxybutyl)urea (1a).

White solid (2.91 g, 67%), mp = 48-49°C. IR (KBr): 1622 (CO), 2845, 2928 (NH). ^1H NMR (CDCl_3 , 400 MHz): 0.80-0.87 (m, 3H, Me), 1.00-1.05 (m, 3H, Me), 1.09-1.18 (m, 6H, Me), 1.31-1.41 (m, 2H, CH_2), 1.43-1.62 (m, 4H, CH_2), 3.06-3.14 (m, 2H, CH_2O), 3.37-3.48 (m, 2H, CH_2O), 3.52-3.65 (m, 3H, CH, CH_2), 4.39-4.45 (m, 1H, CH-O), 4.71 (s, 1H, NH); 4.96 (s, 1H, NH). Anal. calcd for $\text{C}_{13}\text{H}_{28}\text{N}_2\text{O}_3$: C 59.97; H 10.84; N 10.76. Found: C 59.86; H 11.02; N 11.02.

1-(4,4-diethoxybutyl)-3-hexylurea (1b).

White solid (1.20 g, 37%), mp = 51-52°C. IR (KBr): 1623 (CO), 2838, 2935 (NH). ^1H NMR (CD_3OD , 400 MHz): 0.90-0.95 (m, 3H, Me), 1.19 (t, J = 7.05 Hz, 6H, Me), 1.30-1.39 (m, 6H, CH_2), 1.45-1.50

(m, 2H, CH₂), 1.55-1.58 (m, 2H, CH₂), 1.60-1.66 (m, 2H, CH₂), 3.09-3.16 (m, 4H, CH₂), 3.49-3.56 (m, 2H, CH₂O), 3.65-3.71 (m, 2H, CH₂O), 4.50-4.54 (m, 1H, CH-O). Anal. calcd for C₁₅H₃₂N₂O₃: C 62.46; H 11.18; N 9.71. Found: C 62.32; H 11.43; N 9.41.

1-cyclohexyl-3-(4,4-diethoxybutyl)urea (1c).

White solid (2.46 g, 76%), mp = 108-109°C. IR (KBr): 1624 (CO), 2854, 2930, 2974 (NH). ¹H NMR (CDCl₃, 400 MHz): 1.12-1.27 (m, 3H, CH₂), 1.19 (t, *J* = 7.05 Hz, 6H, Me), 1.32-1.43 (m, 2H, CH₂), 1.50-1.57 (m, 2H, CH₂), 1.59-1.66 (m, 2H, CH₂), 1.70-1.78 (m, 2H, CH₂), 1.84-1.91 (m, 2H, CH₂), 3.13 (t, *J* = 6.78 Hz, 2H, CH₂), 3.43-3.49 (m, 1H, CH), 3.50-3.56 (m, 2H, CH₂O), 3.63-3.71 (m, 2H, CH₂O), 4.50-4.54 (m, 1H, CH-O). Anal. calcd for C₁₅H₃₀N₂O₃: 62.90; H 10.56; N 9.78. Found: C 62.71; H 10.83; N 9.95.

1-(4,4-diethoxybutyl)-3-dodecylurea (1d).

White solid (2.58 g, 62%), mp = 77-78°C. IR (KBr): 1620 (CO), 2849, 2922 (NH). ¹H NMR (CDCl₃, 400 MHz): 0.91 (t, *J* = 6.78 Hz, 3H, Me), 1.19 (t, *J* = 7.07 Hz, 6H, Me), 1.29-1.37 (m, 18H, CH₂), 1.45-1.51 (m, 2H, CH₂), 1.52-1.58 (m, 2H, CH₂), 1.59-1.67 (m, 2H, CH₂), 3.08-3.17 (m, 4H, CH₂), 3.49-3.56 (m, 2H, CH₂O), 3.63-3.71 (m, 2H, CH₂O), 4.50-4.54 (m, 1H, CH-O). Anal. calcd for C₂₁H₄₄N₂O₃: C 67.70; H 11.90; N 7.52. Found: C 67.42; H 12.12; N 7.68.

General procedure for the synthesis of pyrrolidine-1-carboxamides 2a-d.

To the solution of appropriate urea **1** (0.58 mmol) in dry chloroform (5 ml) 2-naphthol (0.15 g, 0.58 mmol) and trifluoroacetic acid (0.07 g, 0.58 mmol) were added. Reaction mixture was stirred at 20°C for 3 days. Solvent was evaporated on rotary evaporator, crude product washed thoroughly with diethyl ether and dried in vacuo (2h, 0.01 torr, 20°C) to give desired compound **2**.

***N*-(sec-butyl)-2-(2-hydroxynaphthalen-1-yl)pyrrolidine-1-carboxamide (2a)**

White solid (0.13 g, 77%), mp = 179-180°C. IR (KBr): 1588 (Ar), 1608 (CO), 2874, 2967, 3052 (NH), 3395 (OH). ¹H NMR ((CD₃)₂SO, 400 MHz): 0.23 (t, *J* = 6.27 Hz, 1.7H, Me), 0.50 (d, *J* = 6.41 Hz, 1.4H, Me), 0.67 (t, *J* = 7.42 Hz, 1.4H, Me), 0.86 (d, *J* = 6.62 Hz, 1.6H, Me), 0.83-0.91 (m, 0.4H, CH₂), 0.95-1.04 (m, 0.6H, CH₂), 1.13-1.20 (m, 1H, CH₂), 1.85-1.96 (m, 1H, CH₂), 2.02-2.09 (m, 1H, CH₂), 2.11-2.22 (m, 1H, CH₂), 2.23-2.30 (m, 1H, CH₂), 3.27-3.41 (m, 1H, CH), 3.57-3.65 (m, 1H, CH₂), 3.73-3.82 (m, 1H, CH₂), 4.80-4.91 (m, 1H, CH), 5.59 (t, *J* = 8.38 Hz, 1H, NH), 7.16 (d, *J* =

8.87 Hz, 1H, Ar), 7.24 (t, $J = 7.12$ Hz, 1H, Ar), 7.41 (t, $J = 7.21$ Hz, 1H, Ar), 7.67 (d, $J = 9.83$ Hz, 1H, Ar), 7.76 (d, $J = 8.33$ Hz, 1H, Ar), 7.95 (t, $J = 7.80$ Hz, 1H, Ar). Anal. calcd for $C_{19}H_{24}N_2O_2$: C 73.05; H 7.74; N 8.97. Found: C 73.21; H 7.59; N 8.82.

***N*-hexyl-2-(2-hydroxynaphthalen-1-yl)pyrrolidine-1-carboxamide (2b).**

White solid (0.11 g, 53%), mp = 148-149°C. IR (KBr): 1589 (Ar), 1624 (CO), 2873, 2925, 2954 (NH), 3417 (OH). 1H NMR ($(CD_3)_2SO$, 400 MHz): 0.76 (t, $J = 7.00$ Hz, 3H, Me), 0.80-0.89 (m, 2H, CH_2), 0.95-1.02 (m, 2H, CH_2), 1.04-1.13 (m, 4H, CH_2), 1.83-1.97 (m, 1H, CH_2), 2.00-2.14 (m, 2H, CH_2), 2.21-2.32 (m, 1H, CH_2), 2.70-2.80 (m, 1H, CH_2), 2.83-2.93 (m, 1H, CH_2), 3.56-3.65 (m, 1H, CH_2), 5.12-5.21 (m, 1H, CH), 5.55-5.61 (m, 1H, NH), 7.13 (d, $J = 8.36$ Hz, 1H, Ar), 7.26 (t, $J = 7.25$ Hz, 1H, Ar), 7.40 (t, $J = 7.38$ Hz, 1H, Ar), 7.66 (d, $J = 8.96$ Hz, 1H, Ar), 7.77 (d, $J = 8.02$ Hz, 1H, Ar), 7.99 (d, $J = 8.71$ Hz, 1H, Ar). Anal. calcd for $C_{21}H_{28}N_2O_2$: C 74.08; H 8.29; N 8.23. Found: C 74.21; H 8.50; N 8.01.

***N*-cyclohexyl-2-(2-hydroxynaphthalen-1-yl)pyrrolidine-1-carboxamide (2c).**

White solid (0.18 g, 93%), mp = 191-192°C. IR (KBr): 1583 (Ar), 1610 (CO), 2855, 2929, 3059 (NH), 3415 (OH). 1H NMR ($(CD_3)_2SO$, 400 MHz): 0.54-0.64 (m, 1H, CH_2), 0.88-1.02 (m, 3H, CH_2), 1.03-1.16 (m, 2H, CH_2), 1.18-1.25 (m, 1H, CH_2), 1.28-1.39 (m, 2H, CH_2), 1.53-1.60 (m, 1H, CH_2), 1.84-1.96 (m, 1H, CH_2), 2.01-2.09 (m, 1H, CH_2), 2.10-2.20 (m, 1H, CH_2), 2.24-2.31 (m, 1H, CH_2), 3.18-3.26 (m, 1H, CH_2), 3.35-3.42 (m, 1H, CH_2), 3.57-3.64 (m, 1H, CH_2), 3.73-3.80 (m, 1H, CH_2), 4.79-4.86 (m, 1H, CH), 5.53-5.59 (m, 1H, NH), 7.16 (d, $J = 8.80$ Hz, 1H, Ar), 7.28 (t, $J = 7.90$ Hz, 1H, Ar), 7.42 (t, $J = 8.39$ Hz, 1H, Ar), 7.70 (d, $J = 8.94$ Hz, 1H, Ar), 7.79 (d, $J = 8.25$ Hz, 1H, Ar), 7.99 (d, $J = 8.52$ Hz, 1H, Ar). ^{13}C NMR ($(CD_3)_2SO$, 150 MHz): 24.0, 24.3 (C19), 25.1 (C18), 25.6 (C13), 32.8 (C12), 33.2 (C17), 47.5 (C14), 48.0 (C16), 54.0 (C11), 118.7 (C3), 118.8 (C1), 122.8

(C7), 123.0 (C9), 126.5 (C8), 129.2 (C4), 129.3 (C5), 129.4 (C6), 132.2 (C10), 153.2 (C2), 156.2 (C15). Anal. calcd for C₂₁H₂₆N₂O₂: C 74.52; H 7.74; N 8.28. Found: C 74.70; H 7.58; N 8.52.

***N*-dodecyl-2-(2-hydroxynaphthalen-1-yl)pyrrolidine-1-carboxamide (2d).**

White solid (0.09 g, 38%), mp = 142-143°C. IR (KBr): 1587 (Ar), 1606 (CO), 2861, 2945 (NH), 3371 (OH). ¹H NMR ((CD₃)₂SO, 400 MHz): 0.75-0.89 (m, 5H, Me, CH₂), 0.92-1.07 (m, 6H, CH₂), 1.15-1.28 (m, 12H, CH₂), 1.83-1.95 (m, 1H, CH₂), 1.98-2.16 (m, 2H, CH₂), 2.21-2.32 (m, 1H, CH₂), 2.69-2.78 (m, 1H, CH₂), 2.83-2.94 (m, 1H, CH₂), 3.56-3.65 (m, 1H, CH₂), 3.67-3.75 (m, 1H, CH₂), 5.54-5.61 (m, 1H, CH), 7.12 (d, *J* = 8.87 Hz, 1H, Ar), 7.24 (t, *J* = 7.59 Hz, 1H, Ar), 7.39 (t, *J* = 7.55 Hz, 1H, Ar), 7.64 (d, *J* = 8.87 Hz, 1H, Ar), 7.75 (d, *J* = 7.70 Hz, 1H, Ar), 7.98 (d, *J* = 8.65, 1H, Ar). ¹³C NMR ((CD₃)₂SO, 150 MHz): 13.01 (C27), 21.17 (C26), 23.85 (C13), 25.03 (C18), 27.79 (19, 24), 27.94 (C17), 28.07 (C20, 21, 22, 23), 28.65 (C16), 30.38 (C25), 31.87 (C12), 46.14 (C14), 52.85 (C11), 117.42 (C3), 117.86 (C1), 121.28 (C7), 121.60 (C9), 125.02 (C8), 127.69 (C4), 127.76 (C5), 127.80 (C6), 130.93 (C10), 151.64 (C2), 155.51 (C15). Anal. calcd for C₂₇H₄₀N₂O₂: C 76.37; H 9.50; N 6.60. Found: C 76.18; H 9.24; N 6.81.

General procedure for the synthesis of pyrrolidine-1-carboxamides 3a-d, 4a-d and 5a-d.

To the solution of urea **1** (0.58 mmol) in dry chloroform (5 ml) appropriate phenol (0.29 mmol) and trifluoroacetic acid (0.07 g, 0.58 mmol) were added. Reaction mixture was stirred at 20°C for 3 days. Solvent was evaporated on rotary evaporator, crude product washed thoroughly with diethyl ether and dried in vacuo (2h, 0.01 torr, 20°C) to give the target compound.

2,2'-(4,6-dihydroxy-1,3-phenylene)bis(*N*-(*sec*-butyl)pyrrolidine-1-carboxamide) (3a).

White solid (0.09 g, 71%), mp = 196-197°C. IR (KBr): 1589 (Ar), 1616 (CO), 2876, 2934, 2968 (NH), 3358 (OH). ¹H NMR ((CD₃)₂SO, 400 MHz): 0.59-0.70 (m, 2H, Me), 0.71-0.84 (m, 4H, Me), 0.86-0.93 (m, 2H, Me), 0.93-1.04 (m, 4H, Me), 1.13-1.38 (m, 4H, CH₂), 1.59-1.91 (m, 4H, CH₂), 1.93-2.19 (m, 2H, CH₂), 2.81-3.00 (m, 1H, CH), 3.25-3.60 (m, 5H, CH₂, CH), 3.91-4.04 (m, 0.2H, CH), 4.11-4.35 (m, 0.6H, CH), 4.77-5.06 (m, 1.2H, CH), 5.08-5.25 (br. m, 0.6H, NH), 5.27-5.41 (br. m, 0.4H, NH), 5.48-5.81 (br. m, 1H, NH), 6.14-6.32 (m, 1H, Ar), 6.43-6.47 (m, 0.15H, Ar), 6.62-6.80 (m, 0.75H, Ar). Anal. calcd for C₂₄H₃₈N₄O₄: C 64.55; H 8.58; N 12.55. Found: C 64.76; H 8.31; N 12.69.

2,2'-(4,6-dihydroxy-1,3-phenylene)bis(*N*-hexylpyrrolidine-1-carboxamide) (3b).

White solid (0.04 g, 29%), mp = 189-190°C. IR (KBr): 1593 (Ar), 1621 (C=O), 2937, 3134 (N-H), 3418 (O-H). ¹H NMR ((CD₃)₂SO, 400 MHz): 0.79-0.90 (m, 6H, Me), 1.09-1.28 (m, 12H, CH₂), 1.29-1.39 (m, 4H, CH₂), 1.62-1.72 (m, 2H, CH₂), 1.73-1.90 (m, 4H, CH₂), 1.98-2.13 (m, 2H, CH₂), 2.89-

3.01 (m, 4H, CH₂), 3.26-3.35 (m, 2H, CH₂), 3.36-3.48 (m, 2H, CH₂), 4.87-4.98 (m, 2H, CH), 5.44-5.92 (br. m, 2H, NH), 6.27 (s, 0.4H, Ar), 6.32 (s, 0.6H, Ar), 6.39 (s, 0.6H, Ar), 6.56 (s, 0.4H, Ar). ¹³C NMR ((CD₃)₂SO, 150 MHz): 14.34 (C15), 22.47 (C14), 23.16, 23.92 (C7), 26.43, 26.51 (C11), 30.31, 30.49 (C13), 31.50, 31.56 (C12), 32.93, 33.17 (C6), 46.43 (C8), 54.94 (C5), 103.28, 103.96 (C1), 120.30, 120.47 (C4), 123.71, 124.25 (C3), 153.71, 154.33 (C2), 156.66, 157.13 (C9). Anal. calcd for C₂₈H₄₆N₄O₄: C 66.90; H 9.22; N 11.15. Found: C 67.12; H 9.41; N 10.98.

2,2'-(4,6-dihydroxy-1,3-phenylene)bis(N-cyclohexylpyrrolidine-1-carboxamide) (3c).

White solid (0.1 g, 69%), mp = 215-216°C. IR (KBr): 1581 (Ar), 1623 (CO), 2933, 3141 (NH), 3436 (OH). ¹H NMR ((CD₃)₂SO, 400 MHz): 1.00-1.09 (m, 4H, CH₂), 1.10-1.25 (m, 6H, CH₂), 1.48-1.53 (m, 2H, CH₂), 1.55-1.62 (m, 4H, CH₂), 1.63-1.69 (m, 3H, CH₂), 1.70-1.74 (m, 3H, CH₂), 1.76-1.82 (m, 2H, CH₂), 2.03-2.12 (m, 2H, CH₂), 3.31-3.39 (m, 4H, CH₂, CH), 3.39-3.45 (m, 2H, CH₂), 4.87-4.93 (m, 2H, CH), 5.09-5.36 (br. m, 2H, NH), 6.29 (s, 0.15H, Ar), 6.31 (s, 0.85H, Ar), 6.44 (s, 0.85H, Ar), 6.60 (s, 0.15H, Ar). ¹³C NMR ((CD₃)₂SO, 150 MHz): 23.27, 23.93 (C12), 25.12, 25.76 (C13), 25.25, 25.29 (C7), 33.33, 33.63 (C6), 33.41 (C11), 46.48 (C8), 48.90, 49.09 (C10), 54.62, 54.80 (C5), 103.23, 103.74 (C1), 120.40, 120.66 (C3), 123.97, 124.38 (C4), 153.78, 154.25 (C2), 155.95, 156.32 (C9). Anal. calcd for C₂₈H₄₂N₄O₄: C 69.93; H 10.27; N 8.16. Found: C 67.63; H 8.27; N 11.51.

2,2'-(4,6-dihydroxy-1,3-phenylene)bis(N-dodecylpyrrolidine-1-carboxamide) (3d).

White solid (0.03 g, 16%), mp = 210-211°C. IR (KBr): 1598 (Ar), 1610 (CO), 2851, 2924, 3063 (NH), 3184 (OH). ¹H NMR ((CD₃)₂SO, 400 MHz): 0.81-0.90 (m, 6H, Me), 1.08-1.37 (m, 40H, CH₂), 1.61-1.71 (m, 2H, CH₂), 1.72-1.85 (m, 4H, CH₂), 1.97-2.12 (m, 2H, CH₂), 2.86-3.01 (m, 4H, CH₂), 3.25-3.46 (m, 4H, CH₂), 4.87-4.95 (m, 2H, CH), 5.54-5.79 (br. m, 2H, NH), 6.26 (s, 0.4H, Ar), 6.30 (s, 0.6H, Ar), 6.38 (s, 0.6H, Ar), 6.54 (s, 0.4H, Ar). Anal. calcd for C₄₀H₇₀N₄O₄: C 71.60; H 10.51; N 8.35. Found: C 71.73; H 10.36; N 8.53.

2,2'-(4,6-dihydroxy-5-methyl-1,3-phenylene)bis(N-(sec-butyl)pyrrolidine-1-carboxamide) (4a).

White solid (0.05 g, 35%), mp = 152-153°C. IR (KBr): 1591 (Ar), 1612 (CO), 2876, 2933, 2968 (NH), 3352 (OH). ¹H NMR ((CD₃)₂SO, 400 MHz): 0.70-0.82 (m, 6H, Me), 0.97-1.00 (m, 6H, Me), 1.28-1.44 (m, 4H, CH₂), 1.75-1.85 (m, 1H, CH₂), 1.87-1.96 (m, 3H, CH₂), 1.97-2.05 (m, 5H, Me, CH₂), 2.07-2.18 (m, 2H, CH₂), 3.29-3.61 (6H, CH₂, CH), 5.00-5.04 (m, 2H, CH), 5.52-5.63 (br. m, 1H, NH), 5.65-5.75 (br. m, 1H, NH), 6.52-6.57 (m, 0.5H, Ar), 6.62-6.66 (m, 0.5H, Ar). Anal. calcd for C₂₅H₄₀N₄O₄: C 65.19; H 8.75; N 12.16. Found: C 65.30; H 8.64; N 12.33.

2,2'-(4,6-dihydroxy-5-methyl-1,3-phenylene)bis(N-hexylpyrrolidine-1-carboxamide) (4b).

White solid (0.03 g, 24%), mp = 151-152°C. IR (KBr): 1584 (Ar), 1614 (CO), 2858, 2926, 3106 (NH), 3348 (OH). ¹H NMR ((CD₃)₂SO, 400 MHz): 0.85 (t, *J* = 6.9 Hz, 6H, Me), 1.15-1.27 (m, 12H, CH₂), 1.31-1.38 (m, 4H, CH₂), 1.89-1.96 (m, 2H, CH₂), 1.97-2.03 (m, 7H, CH₂, Me), 2.08-2.16 (m, 2H, CH₂), 2.94-3.01 (m, 4H, CH₂), 3.26-3.41 (m, 4H, CH₂), 4.98-5.03 (m, 2H, CH), 6.08-6.17 (br. m, 2H, NH), 6.62 (s, 1H, Ar). Anal. calcd for C₂₉H₄₈N₄O₄: C 67.41; H 9.36; N 10.84. Found: C 67.19; H 9.61; N 10.64.

2,2'-(4,6-dihydroxy-5-methyl-1,3-phenylene)bis(N-cyclohexylpyrrolidine-1-carboxamide) (4c).

White solid (0.11 g, 75%), mp = 184-185°C. IR (KBr): 1587 (Ar), 1613 (CO), 2756, 2879 (NH), 3341 (OH). ¹H NMR ((CD₃)₂SO, 400 MHz): 1.00-1.26 (m, 10H, CH₂), 1.47-1.56 (m, 2H, CH₂), 1.56-1.73 (m, 8H, CH₂), 1.76-1.87 (m, 1H, CH₂), 1.87-1.97 (m, 3H, CH₂), 1.97-2.05 (m, 5H, CH₂, Me), 2.07-2.19 (m, 2H, CH₂), 3.28-3.46 (m, 6H, CH₂, CH), 4.97-5.04 (m, 2H, CH), 5.53-5.67 (br. m, 1H, NH), 5.67-5.78 (br. m, 1H, NH), 6.56 (s, 0.5H, Ar), 6.63 (s, 0.5H, Ar). ¹³C NMR ((CD₃)₂SO, 150 MHz): 10.05 (C16), 24.53, 24.89 (C12), 25.30, 25.73 (C13), 25.38 (C7), 32.28, 32.50 (C6), 33.50, 33.79

(C11), 46.27, 46.33 (C8), 49.32, 49.44 (C10), 54.80, 54.94 (C5), 113.30, 113.38 (C1), 120.60, 120.70 (C3), 121.15, 121.37 (C4), 152.82, 153.20 (C2), 156.95, 157.19 (C9). Anal. calcd for $C_{29}H_{44}N_4O_4$: C 67.63; H 8.65; N 10.93. Found: C 67.81; H 8.78; N 10.69.

2,2'-(4,6-dihydroxy-5-methyl-1,3-phenylene)bis(N-dodecylpyrrolidine-1-carboxamide) (4d).

White solid (0.13 g, 63%), mp = 157-158°C. IR (KBr): 1583 (Ar), 1614 (CO), 2836, 2916, 3037 (NH), 3342 (OH). 1H NMR ($(CD_3)_2SO$, 400 MHz): 0.81-0.90 (m, 6H, Me), 1.11-1.29 (m, 36H, CH_2), 1.31-1.40 (m, 4H, CH_2), 1.76-1.85 (m, 1H, CH_2), 1.86-2.04 (m, 8H, Me, CH_2), 2.06-2.18 (m, 2H, CH_2), 2.94-2.99 (m, 4H, CH_2), 3.26-3.46 (m, 4H, CH_2), 4.98-5.02 (m, 2H, CH), 5.92-6.01 (br. m, 1H, NH), 6.03-6.11 (br. m, 1H, NH), 6.51-6.53 (br. s, 0.4H, Ar), 6.59-6.63 (br. s, 0.6H, Ar). Anal. calcd for $C_{41}H_{72}N_4O_4$: C 71.89; H 10.59; N 8.18. Found: C 71.08; H 10.59; N 7.97.

2,2'-(4,5,6-trihydroxy-1,3-phenylene)bis(N-(sec-butyl)pyrrolidine-1-carboxamide) (5a).

White solid (0.08 g, 61%), mp = 201-202°C. IR (KBr): 1586 (Ar), 1624 (CO), 2875, 2932, 2965 (NH), 3271 (OH). 1H NMR ($(CD_3)_2SO$, 400 MHz): 0.64-0.7 (m, 3H, Me), 0.74-0.83 (m, 3H, Me), 0.92-0.97 (m, 3H, Me), 0.97-1.02 (m, 3H, Me), 1.24-1.42 (m, 4H, CH_2), 1.71-1.80 (m, 2H, CH_2), 1.82-1.92 (m, 4H, CH_2), 2.03-2.15 (m, 2H, CH_2), 3.29-3.34 (m, 2H, CH_2), 3.38-3.46 (m, 2H, CH),

3.48-3.58 (m, 2H, CH₂), 4.93-5.00 (m, 2H, CH), 5.20-5.57 (br. s, 2H, NH), 6.13-6.19 (m, 1H, Ar).

Anal. calcd for C₂₄H₃₈N₄O₅: C 62.31; H 8.28; N 12.11. Found: C 62.57; H 8.49; N 11.92.

2,2'-(4,5,6-trihydroxy-1,3-phenylene)bis(N-hexylpyrrolidine-1-carboxamide) (5b).

White solid (0.07 g, 24%), mp = 176-177°C. IR (KBr): 1585 (Ar), 1616 (CO), 2866, 2928 (NH), 3332 (OH). ¹H NMR ((CD₃)₂SO, 400 MHz): 0.82-0.86 (m, 6H, Me), 1.12-1.27 (m, 12H, CH₂), 1.28-1.38 (m, 4H, CH₂), 1.71-1.81 (m, 2H, CH₂), 1.82-1.97 (m, 4H, CH₂), 2.03-2.14 (m, 2H, CH₂), 2.92-3.00 (m, 4H, CH₂), 3.28-3.42 (m, 4H, CH₂), 4.94-4.99 (m, 2H, CH), 5.74-5.89 (br. m, 1H, NH), 5.90-6.02 (br. m, 1H, NH), 6.11 (s, 0.5H, Ar), 6.21 (s, 0.5H, Ar). Anal. calcd for C₂₈H₄₆N₄O₅: C 64.84; H 8.94; N 10.80. Found: C 64.67; H 9.17; N 10.58.

2,2'-(4,5,6-trihydroxy-1,3-phenylene)bis(N-cyclohexylpyrrolidine-1-carboxamide) (5c).

White solid (0.08 g, 52%), mp = 168-169°C. IR (KBr): 1589 (Ar), 1637 (CO), 2974, 3123 (NH), 3355 (OH). ¹H NMR ((CD₃)₂SO, 400 MHz): 1.00-1.25 (m, 10H, CH₂), 1.48-1.55 (m, 2H, CH₂), 1.55-1.65 (m, 6H, CH₂), 1.66-1.72 (m, 2H, CH₂), 1.75-1.79 (m, 1H, CH₂), 1.81-1.97 (m, 5H, CH₂), 2.04-2.17 (m, 2H, CH₂), 3.27-3.45 (m, 6H, CH₂, CH), 4.92-4.98 (m, 2H, CH), 5.29-5.63 (m, 2H, NH), 6.14 (s,

0.5H, Ar), 6.23 (s, 0.5H, Ar). ^{13}C NMR ($(\text{CD}_3)_2\text{SO}$, 150 MHz): 23.93, 24.37 (C12), 25.23, 25.73 (C13), 25.32 (C7), 32.57, 32.79 (C6), 33.42, 33.59 (C11), 46.30, 46.39 (C8), 49.14, 49.28 (C10), 54.82, 55.01 (C5), 112.95 (C1), 121.15, 121.28 (C3), 134.21, 134.40 (C4), 142.58, 142.77 (C2), 156.48, 156.76 (C9). Anal. calcd for $\text{C}_{28}\text{H}_{42}\text{N}_4\text{O}_5$: C, 65.34; H, 8.23; N, 10.89. Found: C 65.21; H 8.41; N 11.02.

2,2'-(4,5,6-trihydroxy-1,3-phenylene)bis(N-dodecylpyrrolidine-1-carboxamide) (5d).

White solid (0.11 g, 51%), mp = 182-183°C. IR (KBr): 1584 (Ar), 1613 (CO), 2851, 2925 (NH), 3332 (OH). ^1H NMR ($(\text{CD}_3)_2\text{SO}$, 400 MHz): 0.82-0.90 (m, 6H, Me), 1.13-1.28 (m, 36H, CH_2), 1.29-1.38 (m, 4H, CH_2), 1.72-1.96 (m, 6H, CH_2), 2.03-2.12 (m, 2H, CH_2), 2.91-3.00 (m, 4H, CH_2), 3.26-3.45 (m, 4H, CH_2), 4.93-5.00 (m, 2H, CH), 5.73-5.86 (br. m, 1H, NH), 5.87-5.97 (br. m, 1H, NH), 6.11 (s, 0.65H, Ar), 6.20 (s, 0.35H, Ar). Anal. calcd for $\text{C}_{40}\text{H}_{70}\text{N}_4\text{O}_5$: C 69.93; H 10.27; N 8.16. Found: 69.72; H 10.08; N 7.99.

X-ray analysis of compounds 2b,c.

Crystal data for compound 2b: $\text{C}_{21}\text{H}_{28}\text{N}_2\text{O}_2$, $M = 340.45$, colorless crystal, monoclinic, space group Pc , $Z = 2$, $a = 7.409(4)$, $b = 9.594(5)$, $c = 13.178(7)\text{\AA}$, $V = 936.2(9)\text{\AA}^3$, $\rho_{\text{calc}} = 1.208\text{ g/cm}^3$, $\mu = 0.078\text{ mm}^{-1}$, 7123 reflections collected ($\pm h$, $\pm k$, $\pm l$), 3484 independent ($R_{\text{int}} 0.0546$) and 1759 observed reflections [$I \geq 2\sigma(I)$], 226 refined parameters, $R = 0.1004$, $wR^2 = 0.2763$, max. Residual electron density $0.481 (-0.723)\text{e}\text{\AA}^{-3}$.

Crystal data for compound 2c: $\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}_2$, $M = 338.44$, colorless crystal, orthorhombic, space group $P2_12_12_1$, $Z = 4$, $a = 7.974(7)$, $b = 14.15(1)$, $c = 16.34(1)\text{\AA}$, $V = 1843(3)\text{\AA}^3$, $\rho_{\text{calc}} = 1.219\text{ g/cm}^3$, $\mu = 0.079\text{ mm}^{-1}$, 13450 reflections collected ($\pm h$, $\pm k$, $\pm l$), 3626 independent ($R_{\text{int}} 0.0546$) and 2500 observed reflections [$I \geq 2\sigma(I)$], 230 refined parameters, $R = 0.0500$, $wR^2 = 0.1245$, max. Residual electron density $0.142 (-0.174)\text{e}\text{\AA}^{-3}$.

Table 1. H-bonds in crystals of **2b** and **2c**

H-bond	Symmetry operation	D – H, Å	H...A, Å	D...A, Å	D - H...A, °
2c					
O(11) --H(11) ..O(18)	1+x,y,z	1.05(5)	1.60(5)	2.635(3)	166(4)
C(9) --H(9) ..N(16)	intramolecular	0.93	2.44	3.052(4)	124
C(12) --H(12) ..O(11)	intramolecular	0.98	2.24	2.728(4)	110
C(12) --H(12) ..O(18)	1/2+x,1/2-y,-z	0.98	2.56	3.410(4)	145
2b					
N(17)-H(17)...O(24)	intramolecular	0.79(5)	2.40(5)	3.167(5)	164(6)
O(24)-H(24)...O(25)	-1+x,y,z	0.95(3)	1.68(3)	2.605(5)	164(4)
C(9)-H(9)...N(15)	intramolecular	0.95	2.55	3.122(7)	119
C(11)-H(11)...O(24)	intramolecular	1.00	2.19	2.713(6)	111

Fig. 1. H-bonds in crystal of **2b**.

The minor component of the disordered hexyl chain and H-atoms are omitted for clarity.

Fig. 2. H-bonds in crystal of **2c**.

Supporting Information

for

Acid-catalyzed reaction of (4,4-diethoxybutyl)ureas with phenols as a novel approach to the synthesis of α -arylpyrrolidines.

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Copies of NMR spectra for all synthesized compounds

7.99
7.97
7.77
7.75
7.66
7.64
7.41
7.40
7.38
7.38
7.27
7.25
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1.02
0.99
0.97
0.87
0.86
0.84
0.82
0.81

2d

immediatly after synthesis

2 months later

immediatly after synthesis

5c

2 months later