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SUPPORTING INFORMATION

Title: Salt-Free Synthesis of Tertiary Amines by Ruthenium-Catalyzed Amination of Alcohols
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Ref. No.: O200800671

General Remarks: All reactions were carried out under an argon atmosphere. Chemicals were purchased from Aldrich, Fluka, Acros and Strem and unless otherwise noted were used without further purification. Amines were distilled under argon. All compounds were characterized by ^{1}H NMR, ^{13}C NMR, MS, HRMS and FTIR spectroscopy. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV 300, AV 400 and AV 500 spectrometers operating at 300.13 MHz, 400.13 MHz and 500.13 MHz (^{1}H), and 75.5 MHz, 100.6 MHz and 125.8 MHz (^{13}C). The ^{1}H and ^{13}C NMR chemical shifts are reported relative to the solvent resonance ($CDCl_3$: δ (^{1}H) = 7.25, δ (^{13}C) = 77.0) or TMS (δ (^{1}H) = 0). EI mass spectra were recorded on an MAT 95XP spectrometer (70 eV, Thermo ELECTRON CORPORATION). FTIR spectra were recorded on a Nicolet 6700 (Thermo ELECTRON CORPORATION) and ATR with the same spectrometer equipped with a SMART ENDURANCE (Thermo ELECTRON CORPORATION). GC was performed on a Hewlett-Packard HP 6890 chromatograph with a Optima 5 amine column (Company: Machery-Nagel, 30m x 0.25µm, 0.5µm film thickness, 50-8-200/5-8-260/5-8-280/5-8-300/20).

General procedure for N-alkylation reaction with solvent

In a pressure tube (ACE) under an argon atmosphere [$Ru_3(CO)_{12}$] (0.02 mmol) and ligand (0.06 mmol) were dissolved in *tert*-amylalcohol (0.2 – 0.5 mL). Then the corresponding alcohol (1.5 or 3 mmol) and secondary amine (1 mmol) were added. The pressure tube was fitted with a Teflon cap and stirred at 120 - 140 °C for 24 h. The solvent was removed in vacuo, and the crude product was purified by column chromatography.

General procedure for N-alkylation reaction without solvent

In a pressure tube (ACE) under an argon atmosphere [$Ru_3(CO)_{12}$] (0.2 mmol) and ligand (0.6 mmol) were dissolved in the corresponding alcohol (50 mmol) and secondary amine (10 mmol). The pressure tube was fitted with a Teflon cap and stirred at 130 - 140 °C for 24 h. The excess alcohol was distilled, and the crude product was purified by column chromatography.

1-(1-Phenyl-ethyl)-piperidine (1)[1]:

In a pressure tube (ACE) under an argon atmosphere [$Ru_3(CO)_{12}$] (12.8 mg, 0.02 mmol) and *N*-phenyl-2-(dicyclohexylphosphino)pyrrol (20.4 mg, 0.06 mmol) were dissolved in *tert*-amylalcohol (0.3 mL). Then, 1-phenylethanol (183.2 mg, 1.5 mmol) and piperidine (85.2 mg, 1 mmol) were added. After stirred at 140 °C for 24 h the solvent was removed in vacuo.

Purification by column chromatography (ethyl acetate/chloroform = 1:2); pale yellow oil; 92% (0.175 g) isolated yield (97% GC).

^{1}**H NMR** (400 MHz, $CDCl_3$): δ = 1.36 (d, J = 6.8 Hz, 3H), 1.33-1.40 (m, 2H), 1.50-1.56 (m, 4H), 2.27-2.42 (m, 4H), 3.38 (q, J = 6.8 Hz, 1H), 7.19-7.30 (m, 5H) ppm.

^{13}**C NMR** (100 MHz, $CDCl_3$): δ = 19.5 (CH_3), 24.7 (CH_2), 26.3 (CH_2), 51.6 (CH_2), 65.2 (CH), 126.7 (CH, C_{Ar}), 127.8 (CH, C_{Ar}), 128.0 (CH, C_{Ar}), 144.0 (C_q, C_{Ar}) ppm.

FTIR (neat): 3082, 3061, 3025, 2970, 2933, 2852, 2791, 2751, 1601, 1491, 1451, 1157, 1134, 1117, 939, 769, 756, 701, 542 cm^{-1}.

GC/MS (EI, 70 eV): *m/z* (rel. int.): 189 (7) [M^+], 175 (13), 174 (100), 112 (20), 105 (18), 91 (10), 84 (7), 77 (8).

HRMS (EI): *m/z*: calcd. for $C_{13}H_{19}N$: 189.15120. Found: 189.151283.

1-(1-Phenyl-ethyl)-pyrrolidine (2)[2]:

In a pressure tube (ACE) under an argon atmosphere [$Ru_3(CO)_{12}$] (12.8 mg, 0.02 mmol) was dissolved in *tert*-amylalcohol (0.2 mL). Then, 1-phenylethanol (183.2 mg, 1.5 mmol) and pyrrolidine (71.1 mg, 1 mmol) were added. After stirred at 120 °C for 24 h the solvent was removed in vacuo. Purification by column chromatography (ethyl acetate/chloroform = 1:1); pale yellow oil; 83% (0.145 g) isolated yield (88% GC yield).

^{1}**H NMR** (300 MHz, $CDCl_3$): δ = 1.39 (d, J = 6.6 Hz, 3H), 1.75 (m, 4H), 2.30-2.42 (m, 2H), 2.48-2.60 (m, 2H), 3.17 (q, J = 6.6 Hz, 1H), 7.18-7.35 (m, 5H) ppm.

^{13}**C NMR** (75 MHz, $CDCl_3$): δ = 23.2 (CH_3), 23.4 (CH_2), 52.9 (CH_2), 66.0 (CH), 126.7 (CH, C_{Ar}), 127.1 (CH, C_{Ar}), 128.2 (CH, C_{Ar}), 145.7 (C_q, C_{Ar}) ppm.

FTIR (neat): 3082, 3061, 3026, 2969, 2931, 2874, 2779, 2718, 1604, 1491, 1452, 1368, 1314, 1286, 1209, 1144, 971, 762, 701, 541 cm^{-1}.

GC/MS (EI, 70 eV): *m/z* (rel. int.): 175 (9) [M^+], 161 (18), 160 (100), 105 (22), 98 (32), 91 (17), 77 (14), 70 (8).

HRMS (EI): *m/z*: calcd. for $C_{12}H_{17}N$: 175.13555. Found: 175.135521.

2-Methyl-1-(1-phenyl-ethyl)-pyrrolidine (3):

In a pressure tube (ACE) under an argon atmosphere [$Ru_3(CO)_{12}$] (12.8 mg, 0.02 mmol) and *N*-phenyl-2-(dicyclohexylphosphino)pyrrol (20.4 mg, 0.06 mmol) were dissolved in *tert*-amylalcohol (0.25 mL). Then, 1-phenylethanol (183.2 mg, 1.5 mmol) and 2-methylpyrrolidine (85.2 mg, 1 mmol) were added. After stirred at 130 °C for 24 h the solvent was removed in vacuo. Purification (the crude product is a diastereomeric mixture, ratio =

1:1, determined by GC) by column chromatography (pentane/ethyl acetate = 1:2); pale yellow oil; 69% (0.131 g) isolated yield (81% GC yield). After column chromatography in two fractions either **3a** or **3b** were in excess.

Diastereomer **3a ((*S*)-2-methyl-1-[(*S*)-1-phenylethyl]pyrrolidin) (*rac*)**[3]: **^{1}H NMR** (300 MHz, $CDCl_3$, TMS): δ = 0.85 (d, J = 6.2 Hz, 3H), 1.35 (d, J = 6.7 Hz, 3H), 1.35-1.45 (m, 1H), 1.57-1.81 (m, 2H), 1.85-1.98 (m, 1H), 2.44 (dt, J = 9.4 Hz, J = 8.0 Hz, 1H), 2.76 (ddd, J = 9.4 Hz, J = 8.0 Hz, J = 3.9 Hz, 1H), 2.91 (m, 1H), 3.67 (q, J = 6.7 Hz, 1H), 7.17-7.40 (m, 5H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.4 (CH_3), 19.4 (CH_3), 22.3 (CH_2), 32.9 (CH_2), 49.8 (CH_2), 56.2 (CH), 60.4 (CH), 126.6 (CH, C_{Ar}), 127.6 (CH, C_{Ar}), 128.0 (CH, C_{Ar}), 145.7 (C_q, C_{Ar}) ppm.

Diastereomer **3b ((*R*)-2-methyl-1-[(*S*)-1-phenylethyl]pyrrolidin) (*rac*)**: **^{1}H NMR** (300 MHz, $CDCl_3$, TMS): δ = 1.10 (d, J = 6.2 Hz, 3H), 1.34-1.43 (m, 1H), 1.46 (d, J = 6.9 Hz, 3H), 1.50-1.62 (m, 1H), 1.65-1.88 (m, 2H), 2.40 (dt, J = 9.0 Hz, J = 8.0 Hz, 1H), 2.53 (m, 1H), 2.86 (ddd, J = 9.0 Hz, J = 8.0 Hz, J = 3.5 Hz, 1H), 3.86 (q, J = 6.9 Hz, 1H), 7.20-7.34 (m, 5H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.0 (CH_3), 21.7 (CH_3) 21.8 (CH_2), 32.5 (CH_2), 48.2 (CH_2), 54.8 (CH), 58.6 (CH), 126.7 (CH, C_{Ar}), 127.8 (CH, C_{Ar}), 128.1 (CH, C_{Ar}), 141.8 (C_q, C_{Ar}) ppm.

FTIR (ATR): 3083, 3061, 3026, 2961, 2870, 2789, 1602, 1492, 1452, 1370, 1149, 760, 698 cm^{-1}.

GC/MS (EI, 70 eV): *m/z* (rel. int.): 189 (12) [M^+], 175 (14), 174 (100), 112 (21), 105 (63), 103(10), 91 (9), 79 (12), 77 (16), 70 (50), 41 (8).

HRMS (EI): *m/z*: calcd. for $C_{13}H_{19}N$: 189.15120. Found: 189.151359.

4-(1-Phenyl-ethyl)-morpholine (4)[2b,4]**:**

In a pressure tube (ACE) under an argon atmosphere [$Ru_3(CO)_{12}$] (12.8 mg, 0.02 mmol) and *N*-phenyl-2-(dicyclohexylphosphino)pyrrol (20.4 mg, 0.06 mmol) were dissolved in *tert*-amylalcohol (0.5 mL). Then, 1-phenylethanol (366.5 mg, 3 mmol) and morpholine (87.1 mg, 1 mmol) were added. After stirred at 140 °C for 24 h the solvent was removed in vacuo. Purification by column chromatography (*tert*-butylmethylether/chloroform = 2:1); colourless oil; 37% (0.070 g) isolated yield (47% GC yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.34 (d, J = 6.7 Hz, 3H), 2.30-2.40 (m, 2H), 2.43-2.54 (m, 2H), 3.29 (q, J = 6.7 Hz, 1H), 3.68 (m, 4H), 7.19-7.33 (m, 5H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.8 (CH_3), 51.3 (CH_2), 65.4 (CH), 67.2 (CH_2), 126.9 (CH, C_{Ar}), 127.6 (CH, C_{Ar}), 128.3 (CH, C_{Ar}), 143.9 (C_q, C_{Ar}) ppm.

FTIR (ATR): 3083, 3061, 3026, 2957, 2852, 2805, 2755, 2692, 1600, 1492, 1450, 1319, 1140, 1116, 948, 918, 865, 758, 700 cm^{-1}.

GC/MS (EI, 70 eV): *m/z* (rel. int.): 191 (9) [M^+], 177 (13), 176 (100), 114 (14), 105 (42), 91 (7), 77 (11), 56 (8).

HRMS (EI): *m/z*: calcd. for $C_{12}H_{17}NO$: 191,13047. Found: 191.130987.

1-Methyl-4-(1-phenyl-ethyl)-piperazine (5):

In a pressure tube (ACE) under an argon atmosphere [$Ru_3(CO)_{12}$] (0.128 g, 0.2 mmol) was dissolved in 1-phenylethanol (6.11 g, 50 mmol) and 1-methylpiperazine (1.0 g, 10 mmol). After stirred at 140 °C for 24 h the excess alcohol was distilled and the residue was purified by column chromatography (pentane/ethyl acetate) = 1:2) and gave 1.41 g (69%) **5** as a pale yellow oil (90% GC yield).

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.36 (d, *J* = 6.8 Hz, 3H), 2.26 (s, 3H), 2.34-2.50 (br m, 8H), 3.34 (q, *J* = 6.7 Hz, 1H), 7.18-7.32 (m, 5H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.9 (CH_3), 46.0 (CH_3), 50.5 (CH_2), 55.4 (CH_2), 64.9 (CH), 126.8 (CH, C_{Ar}), 127.6 (CH, C_{Ar}), 128.1 (CH, C_{Ar}), 144.1 (C_q, C_{Ar}) ppm.

FTIR (ATR): 3061, 3026, 2968, 2934, 2792, 2761, 1600, 1491, 1450, 1291, 1163, 1154, 1012, 947, 809, 759, 699 cm^{-1}.

GC/MS (EI, 70 eV): *m/z* (rel. int.): 205 (11), 204 (71) [M^+], 189 (65), 146 (41), 145 (33), 133 (33), 132 (73), 127 (13), 120 (13), 105 (88), 104 (14), 103(20), 99 (100), 91 (23), 79 (21), 77 (31), 72 (16), 71 (10), 70 (36), 58 (18), 57 (11), 56 (68), 44 (16), 43 (24), 42 (36).

HRMS (EI): *m/z*: calcd. for $C_{13}H_{20}N_2$: 204.16210. Found: 204.162434.

1-Benzyl-4-(1-phenyl-ethyl)-piperazine (6):

In a pressure tube (ACE) under an argon atmosphere [$Ru_3(CO)_{12}$] (0.128 g, 0.2 mmol) was dissolved in 1-phenylethanol (6.11 g, 50 mmol) and 1-benzylpiperazine (1.76 g, 10 mmol). After stirred at 140 °C for 24 h the excess alcohol was distilled and the residue was purified by column chromatography (pentane/ethyl acetate) = 2:1) and gave 2.21 g (79%) **6** as a colourless oil (97% GC yield).

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.35 (d, *J* = 6.7 Hz, 3H), 2.33-2.63 (br, 8H), 3.35 (q, *J* = 6.7 Hz, 1H), 3.48 (s, 2H), 7.17-7.26 (m, 2H), 7.26-7.31 (m, 8H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.9 (CH_3), 50.5 (CH_2), 53.3 (CH_2), 63.0 (CH_2), 65.0 (CH), 126.8 (CH, C_{Ar}), 126.9 (CH, C_{Ar}), 127.6 (CH, C_{Ar}), 128.1 (CH, C_{Ar}), 128.1 (CH, C_{Ar}), 129.2 (CH, C_{Ar}), 138.1 (C_q, C_{Ar}), 143.9 (C_q, C_{Ar}) ppm.

FTIR (ATR): 3083, 3061, 3026, 2971, 2932, 2806, 2765, 1600, 1493, 1451, 1372, 1346, 1288, 1238, 1152, 1140, 1010, 949, 824, 760, 736, 697 cm^{-1}.

GC/MS (EI, 70 eV): *m/z* (rel. int.): 280 (20) [M^+], 265 (10), 189 (17), 176 (11), 175 (87), 148 (11), 146 (21), 134 (12), 132 (23), 105 (55), 91 (100), 77 (11).

HRMS (EI): *m/z*: calcd. for $C_{19}H_{24}N_2$: 280.19340. Found: 280.193511.

1-(1-Methyl-heptyl)-piperidine (8):

In a pressure tube (ACE) under an argon atmosphere [$Ru_3(CO)_{12}$] (12.8 mg, 0.02 mmol) and *N*-phenyl-2-(dicyclohexylphosphino)pyrrol (20.4 mg, 0.06 mmol) were dissolved in *tert*-amylalcohol (0.25 mL). Then, 2-octanol (195.3 mg, 1.5 mmol) and piperidine (85.2 mg, 1 mmol) were added. After stirred at 140 °C for 24 h the solvent was removed in vacuo. Purification by column chromatography (ethyl acetate/ethanol = 20:1); pale yellow oil; 79% (0.155 g) isolated yield (91% GC yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86 (t, J = 7.0 Hz, 3H), 0.93 (d, J = 6.6 Hz, 3H), 1.20-1.30 (m, 9H), 1.39 (m, 2H), 1.48-1.59 (m, 5H), 2.35-2.51 (m, 5H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_3), 14.1 (CH_3), 22.6 (CH_2), 25.0 (CH_2), 26.5 (CH_2), 27.2 (CH_2), 29.6 (CH_2), 31.9 (CH_2), 33.5 (CH_2), 49.4 (CH_2), 59.8 (CH) ppm.

FTIR (ATR): 2957, 2928, 2854, 2791, 1466, 1454, 1442, 1379, 1363, 1342, 1172, 1106, 1036, 861, 758, 722 cm^{-1}.

GC/MS (EI, 70 eV): *m/z* (rel. int.): 197 (2) [M^+], 182 (14), 113 (11), 112 (100).

HRMS (EI): *m/z*: calcd. for $C_{13}H_{27}N$: 197.21380. Found: 197.213543.

1-(1-Furan-2-yl-ethyl)-piperidine (9):

In a pressure tube (ACE) under an argon atmosphere [$Ru_3(CO)_{12}$] (0.128 g, 0.2 mmol) was dissolved in 1-(2-furyl)-ethanol (5.61 g, 50 mmol) and piperidine (0.852 g, 10 mmol). After stirred at 140 °C for 24 h the excess alcohol was distilled and the residue was purified by column chromatography (ethyl acetate/ethanol) = 20:1) and gave 0.930 g (52%) **9** as a colourless oil (75% GC yield).

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 1.39 (d, J = 7.0 Hz, 3H), 1.33-1.42 (m, 2H), 1.52-1.62 (m, 4H), 2.40 (m, 4H), 3.72 (q, J = 7.0 Hz, 1H), 6.11 (m, 1H), 6.31 (dd, J = 3.2 Hz, J = 1.8 Hz, 1H), 7.36 (dd, J = 1.9 Hz, J = 0.8 Hz, 1H) ppm.

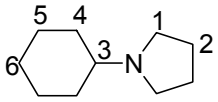
^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 15.6 (CH_3), 24.5 (CH_2), 26.2 (CH_2), 50.5 (CH_2), 57.7 (CH), 106.7 (CH, C_{Ar}), 109.5 (CH, C_{Ar}), 141.2 (CH, C_{Ar}), 156.0 (C_q, C_{Ar}) ppm.
FTIR (ATR): 3110, 2973, 2931, 2851, 2798, 2749, 1501, 1443, 1335, 1303, 1222, 1148, 1108, 1009, 944, 913, 803, 759, 736, 722 cm^{-1}.
GC/MS (EI, 70 eV): *m/z* (rel. int.): 179 (9) [M^+], 165 (12), 164 (100), 95 (35), 41 (9).
HRMS (EI): *m/z*: calcd. for $C_{11}H_{17}NO$: 179.13047. Found: 179.130534.

1-(1-Methyl-heptyl)-pyrrolidine (10):
In a pressure tube (ACE) under an argon atmosphere [$Ru_3(CO)_{12}$] (12.8 mg, 0.02 mmol) and *N*-phenyl-2-(dicyclohexylphosphino)pyrrol (20.4 mg, 0.06 mmol) were dissolved in *tert*-amylalcohol (0.4 mL). Then, 2-octanol (390.7 mg, 3 mmol) and pyrrolidin (71.1 mg, 1 mmol) were added. After stirred at 120 °C for 24 h the solvent was removed in vacuo. Purification by column chromatography (ethyl acetate/methanol = 20:1); pale yellow oil; 54% (0.099 g) isolated yield (89% GC yield).
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.84 (t, *J* = 6.8 Hz, 3H), 1.04 (d, *J* = 6.4 Hz, 3H), 1.18-1.37 (m, 9H), 1.50-1.62 (m, 1H), 1.69-1.80 (m, 4H), 2.14-2.25 (m, 1H), 2.53 (m, 4H) ppm.
^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 (CH_3), 17.9 (CH_3), 22.6 (CH_2), 23.3 (CH_2), 25.8 (CH_2), 29.7 (CH_2), 31.8 (CH_2), 35.4 (CH_2), 51.4 (CH_2), 59.4 (CH) ppm.
FTIR (ATR): 2958, 2927, 2872, 2857, 2777, 1460, 1378, 1332, 1193, 1166, 1113, 873, 724 cm^{-1}.
GC/MS (EI, 70 eV): *m/z* (rel. int.): 183 (1) [M^+], 168 (10), 99 (7), 98 (100).
HRMS (EI): *m/z*: calcd. for $C_{12}H_{25}N$: 183.19815. Found: 183.197876.

1-(1-Methyl-2-phenyl-ethyl)-pyrrolidine (11):
In a pressure tube (ACE) under an argon atmosphere [$Ru_3(CO)_{12}$] (12.8 mg, 0.02 mmol) and *N*-phenyl-2-(dicyclohexylphosphino)pyrrol (20.4 mg, 0.06 mmol) were dissolved in *tert*-amylalcohol (0.4 mL). Then, 1-phenyl-2-propanol (408.6 mg, 3 mmol) and pyrrolidine (71.1 mg, 1 mmol) were added. After stirred at 120 °C for 24 h the solvent was removed in vacuo. Purification by column chromatography (ethyl acetate/chloroform = 1:1); pale yellow oil; 72% (0.137 g) isolated yield (85% GC yield).
^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.98 (d, *J* = 6.2 Hz, 3H), 1.82 (m, 4H), 2.41 (dd, *J* = 12.7 Hz, *J* = 10.2 Hz, 1H), 2.48-2.61 (m, 1H); 2.61-2.77 (m, 4H), 3.14 (dd, *J* = 12.7 Hz, *J* = 3.3 Hz, 1H), 7.14-7.20 (m, 3H), 7.24-7.30 (m, 2H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.6 (CH_3), 23.4 (CH_2), 41.9 (CH_2), 51.4 (CH_2), 61.0 (CH), 125.8 (CH, C_{Ar}), 128.2 (CH, C_{Ar}), 129.4 (CH, C_{Ar}), 140.2 (C_q, C_{Ar}) ppm.
FTIR (neat): 3085, 3062, 3026, 2966, 2931, 2874, 2781, 2717, 1603, 1494, 1454, 1378, 1337, 1165, 996, 744, 700, 515 cm^{-1}.
GC/MS (EI, 70 eV): *m/z* (rel. int.): 189 (0.2) [M^+], 188 (1) [M-H]$^+$, 174 (3), 99 (15), 98 (100), 91 (20), 56 (20).
HRMS (EI): *m/z*: calcd. for $C_{13}H_{18}N$ [M-H]$^+$: 188.14338. Found: 188.142872.

1-Cyclohexyl-pyrrolidine (12)[5]:
In a pressure tube (ACE) under an argon atmosphere [$Ru_3(CO)_{12}$] (12.8 mg, 0.02 mmol) and *N*-phenyl-2-(dicyclohexylphosphino)pyrrol (20.4 mg, 0.06 mmol) were dissolved in *tert*-amylalcohol (0.25 mL). Then, cyclohexanol (150.2 mg, 1.5 mmol) and pyrrolidine (71.1 mg, 1 mmol) were added. After stirred at 120 °C for 24 h the solvent was removed in vacuo. Purification by column chromatography (ethyl acetate/methanol = 2:1); yellow oil; 76% (0.116 g) isolated yield (92% GC yield).



^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.06-1.33 (m, 5H, 4-H_{ax}, 5-H_{ax}, 6-H_{ax},), 1.55-1.64 (m, 1H, 6-H_{eq},), 1.69-1.83 (m, 6H, 2-H, 5-H_{eq}), 1.89-2.02 (m, 3H, 3-H, 4-H_{eq}), 2.58 (m, 4H, 1-H) ppm.
^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.1 (CH_2, C2), 25.2 (CH_2, C5), 26.0 (CH_2, C6), 32.1 (CH_2, C4), 51.5 (CH_2, C1), 63.8 (CH, C3) ppm.
FTIR (ATR): 2925, 2853, 2775, 1448, 1375, 1348, 1193, 1140, 1128, 1077, 885, 787 cm^{-1}.
GC/MS (EI, 70 eV): *m/z* (rel. int.): 153 (13) [M^+], 111 (9), 110 (100), 97 (10), 96 (9).
HRMS (EI): *m/z*: calcd. for $C_{10}H_{19}N$: 153.15120. Found: 153.151671.

1-(1-Methoxy-2-butyl)-pyrrolidine (13):
In a pressure tube (ACE) under an argon atmosphere [$Ru_3(CO)_{12}$] (0.128 g, 0.2 mmol) and *N*-phenyl-2-(dicyclohexylphosphino)pyrrol (0.204 g, 0.6 mmol) were dissolved in 1-methoxy-2-butanol (5.21 g, 50 mmol) and pyrrolidine (0.711 g, 10 mmol). After stirred at 130 °C for 24 h the excess alcohol was distilled and the residue was purified by column chromatography (*tert*-butylmethylether/methanol) = 20:1) and gave 0.984 g (63%) **14** as a pale yellow oil (85% GC yield).

^{1}**H NMR** (300 MHz, $CDCl_3$): δ = 0.92 (t, J = 7.5 Hz, 3H), 1.47-1.70 (m, 2H), 1.77 (m, 4H), 2.27 (br, 1H), 2.62 (br, 4H), 3.33 (s, 3H), 3.46 (m, AB part of ABX system, ^{2}J = 10.0 Hz, 2H) ppm.

^{13}**C NMR** (75 MHz, $CDCl_3$): δ = 10.3 (CH_3), 22.8 (CH_2), 23.2 (CH_2), 51.5 (CH_2), 58.9 (CH_3), 64.7 (CH), 73.0 (CH_2) ppm.

FTIR (neat): 2966, 2874, 2806, 1459, 1380, 1350, 1196, 1153, 1120, 1060, 1029, 977, 962, 880 cm^{-1}.

GC/MS (EI, 70 eV): *m/z* (rel. int.): 157 (1) [M^{+}], 128 (6), 113 (9), 112 (100), 70 (9), 41 (5).

HRMS (EI): *m/z*: calcd. for $C_9H_{19}NO$: 157.14612. Found: 157.145560.

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