



Supporting Information

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New Soluble Lanthanide Salts ($\text{LnCl}_3 \cdot 2\text{LiCl}$; Ln = La, Ce, Nd) for the improved Addition of Magnesium Organometallics to Carbonyl Derivatives

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General All reactions were carried out under an argon atmosphere in dried glassware. All starting materials were purchased from commercial sources and used without further purification. THF was continuously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen. Grignard reagents were prepared using standard insertion methodology except *i*-PrMgCl·LiCl (Chemetall), PhMgCl (Chemetall), MeMgCl (Chemetall), Allylmagnesiumchloride (Aldrich). Yields refer to isolated yields of compounds estimated to be > 95 % pure as determined by ^1H -NMR and capillary GC.

Typical procedure for the preparation of $\text{LnCl}_3 \cdot 2\text{LiCl}$ -solutions:

Preparation of a solution of $\text{LaCl}_3 \cdot 2\text{LiCl}$ in THF:

In a 500 mL Schlenk-flask, commercially available $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$ (0.10 mol, 35.3 g) was mixed with LiCl (0.20 mol, 8.40 g) and water (100 mL) was slowly added under vigorous stirring. The resulting slurry was stirred in high vacuum (0.01 mm Hg) at RT for 4 h. Stirring was continued for 4 h at 40 °C, 4 h at 60 °C, 4 h at 80 °C, 4 h at 100 °C, 4 h at 120 °C, 4 h at 140 °C and finally 4 h at 160 °C. The slow increase of temperature and highly efficient stirring are essential. The resulting solid was cooled to room temperature and THF was added until a total volume of 300 mL was reached. Then, molecular sieves (50 g; 4 Å) were added and the resulting mixture was stirred vigorously for 1 d at RT. Finally, all insoluble material (mostly crushed molecular sieves) was filtered over a combined filter system (fresh molecular sieves/filter paper) under an argon atmosphere. By this procedure, a clear and colorless solution of $\text{LaCl}_3 \cdot 2\text{LiCl}$ was obtained that was stored until use at RT under argon.

Typical procedure for the reactions with ketones and imines (TP 1):

In a flame dried, argon-flushed 25 mL Schlenk-flask equipped with a septum and a magnetic stirring bar was placed $\text{LaCl}_3 \cdot 2\text{LiCl}$ in THF (0.33 M; 6.10 mL, 2.00 mmol, 1.00 equiv).

The ketone (2.00 mmol) was added neat and the resulting mixture was stirred for 1 h at RT. The reaction mixture was cooled to 0 °C and the Grignard reagent (solution in THF, 2.10 mmol, 1.05 equiv.) was added dropwise and the reaction mixture was allowed to stir at the same temperature. After GC-analysis of reaction aliquots showed complete conversion, sat. aq. NH₄Cl (2 mL) and water (2 mL) was added. The aqueous layer was extracted with ether (4 × 10 mL), the combined extracts were dried (Na₂SO₄) and evaporated *in vacuo*. The crude residue was purified by flash column chromatography.

Preparation of 1-isopropyl-cyclopentanol (4a):

According to TP 1 *i*-PrMgCl (3.30 mL; 3.30 mmol; 1.10 equiv) was reacted with cyclopentanone (252 mg; 3.00 mmol) in the presence of LaCl₃·2LiCl (0.33 M; 9.09 mL, 3.00 mmol, 1.00 equiv), the conversion was complete after 5 min (GC monitoring). After workup and careful evaporation of the solvents under reduced pressure, the desired product was obtained as colorless oil (353 mg, 92 %). The analytical data were found to be in accordance with the literature data.

C. S. A. Antunes, M. Bietti, O. Lanzalunga, M. Salamome, *J. Org. Chem.* **2004**, *16*, 5281.

Preparation of 1-isopropyl-cyclohexanol (4b):

According to TP 1 *i*-PrMgCl (3.30 mL; 3.30 mmol; 1.10 equiv) was reacted with cyclohexanone (294 mg; 3.00 mmol) in the

presence of $\text{LaCl}_3 \cdot 2\text{LiCl}$ (0.33 M; 9.09 mL, 3.00 mmol, 1.00 equiv), the conversion was complete after 5 min (GC monitoring). After workup and careful evaporation of the solvents under reduced pressure, the desired product was obtained as colorless oil (418 mg, 98 %). The analytical data were found to be in accordance with the literature data.

C. S. A. Antunes, M. Bietti, O. Lanzalunga, M. Salamome, J. *Org. Chem.* **2004**, *16*, 5281.

Preparation of 1-isopropyl-1,2,3,4-tetrahydro-naphthalen-1-ol (4c):

According to TP 1 *i*-PrMgCl (1.00 M; 2.10 mL, 2.10 mmol, 1.05 equiv) was reacted with α -tetralone (292 mg; 2.00 mmol) in the presence of $\text{LaCl}_3 \cdot 2\text{LiCl}$ in THF (0.33 M; 6.10 mL, 2.00 mmol, 1.00 equiv). After workup, the crude residue was purified by flash column chromatography (silica; pentane:Et₂O 10:1) to give 1-isopropyl-1,2,3,4-tetrahydro-naphthalen-1-ol (**4c**) as a colorless, crystalline solid, mp = 101 °C (361 mg; 1.90 mmol; 95 %). The analytical data were found to be in accordance with the literature data.

T. Imamoto, Y. Sugiyura, N. Takiyama, T. Hatojima, Y. Kamiya, *J. Am. Chem. Soc.* **1989**, *111*, 4392.

Preparation of 2-benzyl-3-methyl-1-phenyl-butan-2-ol (4d):

According to TP 1 *i*-PrMgCl (1.1 mL; 1.1 mmol; 1.1 equiv) was reacted with 1,3-diphenylacetone (210 mg; 1.0 mmol) in the

presence of $\text{LaCl}_3 \cdot 2\text{LiCl}$ (0.33 M; 3.0 mL, 1.00 mmol, 1.00 equiv), the conversion was complete after 5 min (GC monitoring). After workup and careful evaporation of the solvents under reduced pressure, the desired product was obtained as white solid, mp = 52 – 53 °C (241 mg, 95 %). The analytical data were found to be in accordance with the literature data.

G. Boche, K. Buckl, D. Martens, D. R. Schneider, *Liebigs Ann. Chem.* **1980**, 7, 1135.

Preparation of 4-(1-benzyl-1-hydroxy-2-phenyl-ethyl)-benzoic acid ethyl ester (4e)

According to TP 1 the Grignard reagent **2b** (freshly prepared via iodine-magnesium exchange^[8] from ethyl-4-iodobenzoate (607 mg, 2.20 mmol, 1.10 equiv) and *i*-PrMgCl·LiCl (1.00 M in THF; 2.16 mL, 2.16 mmol, 1.08 equiv) at -20 °C) was reacted with diphenylacetone (420 mg; 2.00 mmol) in the presence of $\text{LaCl}_3 \cdot 2\text{LiCl}$ (0.33 M; 6.06 mL, 2.00 mmol, 1.00 equiv). The crude product was recrystallized from heptane to give 4-(1-benzyl-1-hydroxy-2-phenyl-ethyl)-benzoic acid ethyl ester as crystalline, colorless solid, mp = 126 – 128 °C (662 mg, 92 %).

¹H-NMR (300 MHz, CDCl_3): δ [ppm] = 7.94 (d, 2 H, J = 8.45 Hz); 7.34 (d, 2 H, J = 8.45 Hz); 7.15 (m, 6 H); 6.95 (m, 4 H); 4.37

(q, $J = 7.14$ Hz); 3.32 (d, 2 H, $J = 13.48$ Hz); 3.13 (d, 2 H, $J = 13.48$ Hz); 1.99 (s, 1 H); 1.39 (q, $J = 7.14$ Hz).

^{13}C -NMR (300 MHz, CDCl_3): δ [ppm] = 166.6; 150.5; 135.8; 130.6; 129.1; 128.7; 128.0; 126.7; 125.9; 77.2; 60.9; 48.7; 14.3.

MS (EI): m/z (%) = 361 (0.4, $[\text{M}+\text{H}]^+$); 315 (5); 270 (19); 269 (100); 241 (3); 197 (6); 177 (22); 149 (6); 121 (3); 105 (10); 91 (14); 65 (3).

HR-MS: ($\text{C}_{24}\text{H}_{24}\text{O}_3$) calculated: 361.1804 ($[\text{M}+\text{H}]^+$) found: 361.1817.

IR (KBr): ν/cm^{-1} = 3500 (m); 3061 (w); 3030 (w); 2978 (w); 2920 (w); 1700 (vs); 1607 (s); 1571 (w); 1499 (m); 1477(m); 1454 (m); 1405 (m); 1371 (s); 1316 (m); 1283 (vs); 1245 (s); 1204 (m); 1185 (m); 1160 (m); 1132 (s); 1113 (s); 1092 (s); 1066 (w); 1038 (m); 1020 (s); 992 (m); 919 (w); 902 (w); 884 (m); 851 (m); 777 (s); 754 (m); 722 (m), 700 (s); 698 (s); 664 (w).

Preparation of 4-(1-benzyl-1-hydroxy-2-phenyl-ethyl)-benzonitrile (4f):

According to TP 1 the Grignard reagent **2c** (freshly prepared via bromine-magnesium exchange^[8] from 4-bromo-benzonitrile (1 mmol) and *i*-PrMgCl·LiCl (1.05 mmol, 1.05 equiv) at -20 °C) was reacted with diphenylacetone (210 mg; 1.00 mmol) in the presence of $\text{LaCl}_3 \cdot 2\text{LiCl}$ (0.33 M; 3.03 mL, 1.00 mmol, 1.00 equiv). The crude product was recrystallized from heptane to give the desired product as white solid, mp = 153 °C (268 mg, 86 %). The analytical data were found to be in accordance with the literature data.

K. Fukui et al. *J. Org. Chem.* **1972**, *37*, 3176.

Preparation of 4-(1-Hydroxy-cyclopentyl)-benzonitrile (4i):

According to TP 1 the Grignard reagent **2c** (freshly prepared via bromine-magnesium exchange^[8] from 4-bromo-benzonitrile (400 mg, 2.20 mmol, 1.1 equiv) and *i*-PrMgCl·LiCl (1.0 M in THF; 2.16 mL, 2.16 mmol, 1.08 equiv) at -20 °C) was reacted with cyclopentanone (168 mg; 2.00 mmol) in the presence of LaCl₃·2LiCl (0.33 M; 6.06 mL, 2.00 mmol, 1.00 equiv). The crude product was purified by flash column chromatography (silica; pentane:Et₂O, 7:3) to give the desired product as a colorless oil (355 mg, 95 %).

¹H-NMR (300 MHz, CDCl₃): δ [ppm] = 7.57 (s, 4 H); 2.04 (s, 1 H); 1.89 (m, 8 H).

¹³C-NMR (300 MHz, CDCl₃): δ [ppm] = 152.3; 131.9; 125.8; 118.9; 110.2; 83.1; 42.4; 24.0.

MS (EI): m/z (%) = 187 (27, M⁺); 168 (9); 159 (12); 158 (100); 154 (6); 145 (41); 140 (9); 130 (55); 116 (7); 89 (4); 76 (4); 63 (2); 55 (7); 51 (3).

HR-MS: (C₁₂H₁₃NO) calculated: 187.0997 found: 187.0982.

IR (KBr): ν/cm⁻¹ = 3436 (br); 2964 (s); 2874 (m); 2229 (vs); 1928 (w); 1725 (w); 1608 (s); 1503 (m); 1449 (w); 1402 (m); 1323 (w); 1183 (w); 1092 (w), 1040 (w); 1010 (s); 960 (w); 906 (w); 884 (w); 837 (s); 567 (s).

Preparation of 2-(6-bromo-pyridin-2-yl)-1-phenyl-propan-2-ol (4j):

According to TP 1 the Grignard reagent **2d** (freshly prepared via bromine-magnesium exchange^[8] from 2,5-dibromopyridine (391 mg, 1.65 mmol; 1.10 equiv) and *i*-PrMgCl·LiCl (1.00 M in THF; 1.62 mL, 1.62 mmol, 1.08 equiv) at -10 °C) was reacted with 1-phenyl-propan-2-one (201 mg; 1.50 mmol) in the presence of LaCl₃·2LiCl (0.33 M; 4.55 mL, 1.50 mmol, 1.00 equiv). The crude product was purified by flash column chromatography (silica; pentane:Et₂O, 9:1, 0.2 vol-% NEt₃) to give the desired product as colorless oil (355 mg, 81 %).

¹H-NMR (300 MHz, CDCl₃): δ [ppm] = 7.47 (t, 1 H; *J* = 7.75 Hz); 7.34 (d, 1 H, *J* = 7.81 Hz); 7.23 (d, 1 H, *J* = 7.81 Hz); 7.19 (m, 3 H); 6.98 (m, 2 H); 3.16 (d, 1 H; *J* = 13.54 Hz); 3.03 (d, 1 H; *J* = 13.54 Hz); 1.55 (s, 3 H).

¹³C-NMR (300 MHz, CDCl₃): δ [ppm] = 166.7; 140.5; 138.8; 136.6; 130.4; 127.9; 126.5; 126.1; 118.4; 74.8; 49.5; 27.6.

MS (EI): *m/z* (%) = 292 (0.1, M⁺); 274 (2); 272 (2); 260 (1); 202 (95); 200 (100); 184 (15); 182 (14); 158 (6); 120 (4); 102 (12); 92 (39); 91 (39); 78 (25); 65 (13); 51 (5).

HR-MS: (C₁₄H₁₅BrNO) calculated: 292.0337 found: 292.0325.

IR (KBr): $\tilde{\nu}$ /cm⁻¹ = 4062 (w); 3444 (br); 3085 (m); 3062 (m), 3028 (m); 2977 (m), 2922 (m); 2851 (w); 1950 (w); 1885 (w); 1808 (w); 1674 (w); 1581 (s); 1555 (s); 1496 (m); 1454 (s); 1430 (s); 1400 (s); 1366 (s); 1307 (s); 1232 (m); 1198 (m);

1159 (s); 1128 (s); 1080 (m); 1055 (m); 1031 (w); 987 (m); 951 (m); 909 (w); 872 (w); 797 (s); 781 (s); 739 (s); 702 (s); 676 (m); 659 (m); 643 (m); 624 (w); 566 (m); 465 (m).

Preparation of ethyl 4-(1-hydroxy-1-methyl-2-phenylethyl)-3-nitrobenzoate (4k):

According to TP 1 the Grignard reagent **2e** (freshly prepared via iodine-magnesium exchange^[8] from Ethyl-4-iodo-3-nitrobenzoate (353 mg, 1.10 mmol; 1.10 equiv) and PhMgBr·LiCl (0.95 M in THF; 1.13 mL, 1.07 mmol, 1.07 equiv) at -50 °C) was reacted with 1-phenyl-propan-2-one (201 mg; mmol) in the presence of LaCl₃·2LiCl (0.33 M; 6.06 mL, 2.00 mmol, 1.00 equiv). The crude product was purified by flash column chromatography (silica; pentane:Et₂O, 19:1) to give the desired product as yellow oil (231 mg, 73 %).

¹H-NMR (300 MHz, CDCl₃): δ [ppm] = 8.20 (m, 2 H); 7.80 (d, *J* = 8.13 Hz); 7.27 (m, 5 H); 4.40 (q, 2 H, *J* = 7.11 Hz); 3.66 (s, 1 H); 2.00 (s, 3 H); 1.39 (t, 2 H, *J* = 7.11 Hz).

¹³C-NMR (300 MHz, CDCl₃): δ [ppm] = 164.1; 145.7; 144.4; 132.4; 131.1; 129.2; 128.4; 127.8; 126.0; 125.3; 112.6; 75.9; 61.9; 42.0; 31.0; 14.2.

MS (EI): *m/z* (%) = 315 (0.4, M⁺); 300 (100); 270 (5); 238 (5); 223 (6); 222 (46); 194 (3); 178 (2); 165 (2); 152 (5); 121 (9); 105 (3); 103 (2); 77 (4); 43 (7).

HR-MS: (C₁₇H₁₇NO₅) calculated: 315.1107 found: 315.1093.

IR (KBr): ν/cm^{-1} = 2982 (s); 1724 (vs); 1617 (m); 1542 (vs); 1494 (m); 1448 (m); 1370 (s); 1289 (vs); 1131 (s); 1019 (s); 912 (m); 861 (m); 837 (m); 767 (s); 735 (m); 701 (s); 671 (w).

Preparation of 2-(2,4,6-trimethyl-phenyl)-propan-2-ol (41):

According to entry 12, Table 1:

According to TP 1 MeMgCl (2.90 M; 0.76 mL, 2.20 mmol, 1.10 equiv) was reacted with 1-(2,4,6-Trimethyl-phenyl)-ethanone (324 mg, 2.00 mmol) in the presence of $\text{LaCl}_3 \cdot 2\text{LiCl}$ (0.33 M; 6.06 mL, 2.00 mmol, 1.00 equiv). Column chromatographical purification (silica; pentane: Et_2O 9:1) afforded the desired product as colorless, crystalline solid, mp = 106-107 °C (217 mg, 61 %).

According to entry 13, Table 1:

Mesitylmagnesium bromide (1.20 M in THF; 1.83 mL; 2.20 mmol; 1.10 equiv) was placed in a flame dried schlenk flask under an argon atmosphere and cooled to 0 °C. At this temperature, $\text{LaCl}_3 \cdot 2\text{LiCl}$ (0.33 M; 6.06 mL, 2.00 mmol, 1.00 equiv) was slowly added. The resulting mixture was allowed to warm up to room temperature and stirred for 4 h. Then, after cooling to 0 °C, acetone (116 mg; 2.00 mmol) was added and the reaction was warmed up to room temperature and stirred for another hour at this temperature. When the end of the reaction was reached (GC-monitoring of aliquots), sat. aq. NH_4Cl (2 mL) and water (2 mL) were added. The aqueous layer was extracted with ether

(4 × 10 mL), the combined extracts were dried (Na₂SO₄) and evaporated *in vacuo*. Column chromatographical purification (silica; pentane:Et₂O 9:1) afforded the desired product as colorless, crystalline solid, mp = 106 - 107 °C (245 mg, 69 %). In both cases, the analytical data were found to be in accordance with the literature data.

J. W. Timberlake, D. Pan, J. Murray, B. S. Jursic, T. Chen, *J. Org. Chem.* **1995**, *16*, 5295.

Preparation of 1-tert-butyl-cyclohexanol (4m):

According to TP 1 *t*-BuMgCl·LiCl (1.01 M in THF 2.18 mL; 2.20 mmol; 1.10 equiv) was reacted with cyclohexanone (178 mg; 2.00 mmol) in the presence of LaCl₃·2LiCl (0.33 M; 6.06 mL, 2.00 mmol, 1.00 equiv). Column chromatographical purification (silica; pentane:Et₂O, 9:1) afforded the desired product as colorless oil, which started to crystallize after being chilled, mp = 49 - 50 °C (287 mg, 92 %). The analytical data were found to be in accordance with the literature data.

C. S. A. Antunes, M. Bietti, O. Lanzalunga, M. Salamome, *J. Org. Chem.* **2004**, *16*, 5281.

Preparation of 1,7,7-trimethyl-2-phenyl-bicyclo[2.2.1]heptan-2-ol (4n):

According to TP 1 PhMgBr·LiCl (1.00 M in THF 1.10 mL; 1.10 mmol; 1.10 equiv) was reacted with 1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (152 mg; 1.00 mmol) in the

presence of $\text{LaCl}_3 \cdot 2\text{LiCl}$ (0.33 M; 3.03 mL, 1.00 mmol, 1.00 equiv) at room temperature. Column chromatographical purification (silica; pentane: Et_2O , 9:1) afforded the desired product as colorless solid, mp = 41 – 42 °C (211 mg, 92 %). The analytical data were found to be in accordance with the literature data.

G. Rueedi, H.-J. Hansen, *Helv. Chim. Acta*, **2004**, *87*, 1968.

Preparation of 1,7,7-trimethyl-2-pyridin-2-yl-bicyclo[2.2.1]-heptan-2-ol (4o):

According to TP 1 2-PyMgCl·LiCl (1.00 M in THF 1.1 mL; 1.10 mmol; 1.10 equiv) was reacted with 1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (152 mg; 1.00 mmol) in the presence of $\text{LaCl}_3 \cdot 2\text{LiCl}$ (0.33 M; 3.03 mL, 1.00 mmol, 1.00 equiv) at -20 °C. Column chromatographical purification afforded the desired product as white solid, mp = 60 – 61 °C (212 mg, 92 %). The analytical data were found to be in accordance with the literature data.

W. A. Herrmann, J. J. Haider, J. Fridgen, G. M. Lobmaier, M. Spiegler, *J. Organomet. Chem.* **2000**, *503*, 69.

Preparation of 1-cyclopentyl-cyclohex-2-enol (7):

According to TP 1 cyclopentylmagnesiumbromide/LiCl (1.00 M; 2.10 mL; 2.10 mmol; 1.05 equiv) was reacted with cyclohexenone (192 mg; 2.00 mmol) in the presence of $\text{LaCl}_3 \cdot 2\text{LiCl}$ (0.33 M; 6.06 mL, 2.00 mmol, 1.00 equiv). Gel filtration (silica;

pentane:Et₂O 9:1, 0.5 vol-% NEt₃) afforded 1-Cyclopentyl-cyclohex-2-enol (**7**) as colorless oil (306 mg, 93 %).

¹H-NMR (300 MHz, CDCl₃): δ [ppm] = 5.82 (m, 1 H); 5.65 (brd, 1 H; *J* = 10.15 Hz).

¹³C-NMR (300 MHz, CDCl₃): δ [ppm] = 131.6; 130.4; 112.6; 71.0; 49.7; 41.7; 34.6; 26.9; 26.5; 26.0; 25.4; 18.7.

MS (EI): *m/z* (%) = 166 (0.1; M⁺); 149 (4); 138 (3); 97 (100); 79 (5); 77 (2); 69 (5); 67 (4).

HR-MS: (C₁₈H₁₈O) calculated: 166.1358 found: 166.1363.

IR (KBr): $\tilde{\nu}$ /cm⁻¹ = 3430 (br); 3023 (m); 2948 (vs); 2867 (s); 2833 (m); 1647 (w); 1452 (m); 1438 (m); 1402 (w); 1321 (w); 1172 (m); 1099 (w); 1063 (m); 981 (m); 966 (m); 930 (m); 884 (w); 851 (w); 734 (m); 533 (w).

Attempted preparation of 1-cyclopentyl-cyclohex-2-enol (7**), isolation of cyclohex-2-enol (**8**):**

Cyclopentylmagnesiumbromide/LiCl (1.00 M; 2.10 mL; 2.10 mmol; 1.05 equiv) was added to a solution of cyclohexenone (192 mg; 2.00 mmol) in absolute THF at 0 °C. After 15 min, GC and GC/MS monitoring indicated complete conversion to the reduction product, cyclohexenol (**8**). Then, sat. aq. NH₄Cl (2 mL) and water (2 mL) was added and the aqueous layer was extracted with ether (4 × 10 mL). The combined extracts were dried (Na₂SO₄) and carefully evaporated under reduced pressure. Gel filtration (silica; pentane: Et₂O, 9:1) afforded cyclohex-2-

enol (**8**) as colorless oil (151 mg, 77 %). The analytical data were found to be in accordance with the literature data.

P. Saravanan, A. DattaGupta, D. Bhuniya, V. K. Singh, *Tetrahedron* **1997**, *53*, 1855.

Preparation of 1-butyl-cyclopentanol (9): *n*-BuLi (1.53 M; 0.65 mL; 1.00 mmol; 1.00 equiv) was added to a solution of cyclopentenone (84 mg; 1.0 mmol) in the presence of $\text{LaCl}_3 \cdot 2\text{LiCl}$ (0.33 M; 3.00 mL, 1.00 mmol, 1.00 equiv) at 0 °C. After 2 min, sat. aq. NH_4Cl (2 mL) and water (2 mL) was added and the aqueous layer was extracted with ether (4 × 10 mL). The combined extracts were dried (Na_2SO_4) and carefully evaporated under reduced pressure to give analytically clean 1-butylcyclopentanol (**9**) as colorless oil (139 mg, 98 %). The analytical data were found to be in accordance with the literature data.

C. Walling, A. Padwa, *J. Am. Chem. Soc.* **1963**, *85*, 1597.

Preparation of (4-methoxy-phenyl)-(2-methyl-1-phenyl-propyl)-amine (10): According to TP 1 *i*-PrMgCl·LiCl (1.00 M in THF, 1.1 mL; 1.1 mmol; 1.10 equiv) was reacted with 4-methoxy-*N*-[(*E*)-phenylmethylidene]aniline (**10**) (212 mg; 1.00 mmol) in the presence of $\text{LaCl}_3 \cdot 2\text{LiCl}$ (0.33 M; 0.30 mL, 0.10 mmol, 0.10 equiv) at room temperature for 12 h. Column chromatographical purification afforded the desired product **11**

as colorless oil (214 mg, 84 %). The analytical data were found to be in accordance with the literature data.

S. Saito, K. Hatanaka, H. Yamamoto, *Syn. Lett.* **2001**, *12*, 1859.

Preparation allyl-(1-pyridin-3-yl-allyl)-amine (12):

According to TP 1 vinyl magnesium chloride (1.00 M in THF, 1.10 mL; 1.10 mmol; 1.10 equiv) was reacted with *N*-[(*E*)-3-pyridinylmethylidene]-2-propen-1-amine (**12**) (146 mg; 1.00 mmol) in the presence of $\text{LaCl}_3 \cdot 2\text{LiCl}$ (0.33 M; 0.30 mL, 0.10 mmol, 0.10 equiv) at room temperature for 1 h. Column chromatographical purification afforded the desired product **13** as colorless oil (151 mg, 87 %). The analytical data were found to be in accordance with the literature data.

C. Agami, F. Couty, G. Evano, *Tetrahedron: Asymmetry* **2000**, *11*, 4639.