Deoxygenation of Carbonyl Compounds using an Alcohol as Efficient Reducing Agent Catalyzed by Oxo-rhenium Complexes

Joana R. Bernardo and Ana C. Fernandes*

Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av.

Rovisco Pais, 1049-001 Lisboa, Portugal.

anacristinafernandes@tecnico.ulisboa.pt

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1. General Remarks

All the reactions were carried out under air atmosphere and without any dry solvent. Carbonyl compounds, alcohols and catalysts were obtained from commercial suppliers and were used without further purification. ReIO₂(PPh₃)₂¹ and ReOBr₃(PPh₃)₂,² ReOCl₃(SMe₂)(OPPh₃)³ were prepared according to literature procedures. Flash chromatography was performed on MN Kieselgel 60M 230-400 mesh. ¹H NMR and ¹³C NMR spectra were measured on a Bruker Avance II⁺ 400 MHz and 300 MHz spectrometers. Chemical shifts are reported in parts per million (ppm) downfield from an internal standard. Microanalyses were performed at Laboratório de Análises do Instituto Superior Técnico, using a Fisons Instruments EA1108 system and data acquisition, integration and handling were performed using the software package Eager-200 (Carlo Erba Instruments).

2. Deoxygenation of carbonyl compounds with the system 3-pentanol/ReOCl₃(SMe₂)(OPPh₃)

General procedure for the deoxygenation of carbonyl compounds with the system 3-pentanol/ReOCl₃(SMe₂)(OPPh₃)

The solution of $\text{ReOCl}_3(\text{SMe}_2)(\text{OPPh}_3)$ (5-10 mol%) and carbonyl compound (0.5 mmol) in 3-pentanol (2 ml) was stirred at 170 °C under air atmosphere in a closed Schlenk equipped with a J-Young tap without using any special pressure-controlling equipment (the reaction times are indicated in Tables 3 and 4, all reaction temperatures refer to bath temperatures). The reaction mixture of the less volatile products was evaporated and purified by silica gel column chromatography with *n*-hexane. The yields of more volatile deoxygenated products were determined directly by ¹H NMR spectroscopy using 1,2-dimethoxyethane as the internal standard.

Table 3 – Direct reductive deoxygenation of aryl ketones with the system 3-pentanol/ReOCl₃(SMe₂)(OPPh₃)^a





^aThe reactions were carried out with 0.5 mmol of ketone and 2 mL of 3-pentanol.

^bYields determined by ¹H NMR spectroscopy using 1,2-dimethoxyethane as the internal standard. ^cIsolated yield.

^dSubstrate.

^eYield of alcohol.

^fYield of ether.

Table	4	_	Direct	reductive	deoxygenation	of	aldehydes	with	the	system
3-penta	ano	l/Re	OCl ₃ (SN	Ae ₂)(OPPh ₃)) ^a					

	R H 3-pen	tanol, ReOCl ₃ (SMe ₂)(OPPh ₃) (10 n 170 ℃	nol%)	Ť
Entry	Aldehyde	Product	Time (h)	Yield (%)
1	CI O H	CI	17	90°
2	Br	Br	17	75 (19) ^{d,c}
3	CI	CI	17	66°
4	F	F	40	50 (40) ^{d,b}
5	MeO H	MeO	17	40 (50) ^{e,b}
6	MeS	Mes	17	79° (10) ^{f,b}
7	Р		17	79 (16) ^{f,c}

^aThe reactions were carried out with 0.5 mmol of aldehyde and 2 mL of alcohol.

^bYields determined by ¹H NMR spectroscopy using 1,2-dimethoxyethane as the internal standard. ^cIsolated yields. ^dYield of ether.

eYield of alcohol. ^fYield of alkane

3. Use of the complex ReOCl₃(SMe₂)(OPPh₃) as catalyst in several catalytic cycles

The solution of ReOCl₃(SMe₂)(OPPh₃) (5-10 mol%) and carbonyl compound (0.5 mmol) in 3-pentanol (3 ml) was stirred at 170 °C under air atmosphere in a closed Schlenk equipped with a J-Young tap during 17 h. The reaction mixture was cooled and the yield was determined by ¹H NMR spectroscopy using 1,2dimethoxyethane as the internal standard. In the next catalytic cycles, carbonyl compound (0.5 mmol) was added to the reaction mixture and stirred for 24 h at 170 °C. The reaction mixture was cooled at room temperature, and the yields were determined by ¹H NMR spectroscopy (the yields obtained for each cycles are indicated in Tables 5 and 6).

4. Compound characterization

Table 3, Entries 1 and 2



¹H NMR (CDCl₃, 400.1 MHz): δ 2.23-2.29 (m, 2 H, CH₂) 2.76 (t, J = 8.4 Hz, 2 H, CH₂), 3.80 (s, 3 H, OMe), 5.97-6.01 (m, 1 H, CH), 6.39 (d, J = 9.6 Hz, 1 H, CH), 6.64 (d, J = 7.6 Hz, 1 H, CH_{arom}), 6.72 (d, J = 8.4 Hz, 1 H, CH_{arom}), 7.06-7.10 (m, 1H, CH_{arom}) ppm. ¹³C NMR (CDCl₃, 100.6 MHz): δ 19.6, 22.8, 55.6, 109.7, 119.1, 123.2, 126.7, 127.7, 128.9, 135.2, 156.3 ppm. Anal. Calcd. for C₁₁H₁₂O: C, 82.46; H, 7.55. Found: C, 82.41; H, 7.48.

Table 3, Entries 3 and 4



¹H NMR (CDCl₃, 400.1 MHz): δ 2.28-2.33 (m, 2 H, CH₂), 2.80 (t, *J* = 8.0 Hz, 2 H, CH₂), 3.81 (s, 3 H, OMe), 5.89-5.94 (m, 1 H, CH), 6.44 (d, *J* = 8.0 Hz, 1 H, CH), 6.71 (d, *J* = 4.0 Hz, 2 H, CH_{arom}), 6.97 (d, *J* = 8.0 Hz, 1 H, CH_{arom}) ppm. ¹³C NMR (CDCl₃, 100.6 MHz): δ 23.1, 28.2, 55.4, 111.2, 113.9, 126.1, 127.0, 127.3, 137.3, 158.7 ppm.). Anal. Calcd. for C₁₁H₁₂O: C, 82.46; H, 7.55. Found: C, 82.43; H, 7.50.

Table 3, entries 5 and 6



¹H NMR (CDCl₃, 400.1 MHz): δ 2.30-2.32 (m, 2 H, CH₂), 2.75 (t, *J* = 8.0, 8.4 Hz, 2 H, CH₂), 3.79 (s, 3 H, OMe), 6.04-6.09 (m, 1 H, CH), 6.44 (d, *J* = 9.6 Hz, 1 H, CH), 6.63

(d, J = 2.4 Hz, 1 H, CH_{arom}), 6.69 (dd, J = 8.0, 2.4 Hz, 1H, CH_{arom}), 7.03 (d, J = 8.4 Hz, 1 H, CH_{arom}) ppm. ¹³C NMR (CDCl₃, 100.6 MHz): δ 23.7, 26.7, 55.4, 111.8, 112.0, 127.7, 127.9, 128.3, 129.5, 135.2, 158.4 ppm. Anal. Calcd. for C₁₁H₁₂O: C, 82.46; H, 7.55. Found: C, 82.31; H, 7.48.

Table 3, entry7

¹H NMR (CDCl₃, 300.1 MHz): δ 2.26-2.35 (m, 2 H, CH₂), 2.77 (t, *J* = 8.3 Hz, *J* = 8.2 Hz, 2 H, CH₂), 5.96-6.03 (m, 1 H, CH), 6.44 (d, *J* = 9.6 Hz, 1 H, CH), 6.99 (d, *J* = 6.8 Hz, 1 H, CH_{arom}), 7.09-7.11 (m, 3 H, CH_{arom}) ppm. ¹³C NMR (CDCl₃, 75.5 MHz): δ 23.3, 27.6, 126.0, 126.6, 127.0, 127.7, 127.9, 128.8, 134.4, 135.4 ppm.

Table 3, entry 8



¹H NMR (CDCl₃, 400.1 MHz): δ 1.81-1.87 (m, 1 H, CH₂), 2.05-2.09 (m, 1 H, CH₂), 2.75-2.89 (m, 3 H, CH₂ + OH), 2.94-3.01 (m, 1 H, CH₂), 3.09 (dd, J = 16.2, 4.3 Hz, 1H, CH₂), 4.15-4.19 (m, 1H, CH), 7.10-7.12 (m, 4 H, CH_{arom}) ppm.¹³C NMR (CDCl₃, 100.6 MHz): δ 27.1, 31.6, 38.5, 67.4, 126.0, 126.1, 128.7, 129.6, 134.4, 135.8ppm.

Table 3, entry 9



¹H NMR (CDCl₃, 400.1 MHz): δ 1.30 (d, *J* = 8.0 Hz, 3 H, Me) 2.14-2.21 (m, 1 H, CH₂), 2.49-2.56 (m, 1 H, CH₂), 2.95-3.03 (m, 1 H, CH), 5.97-5.60 (m, 1 H, CH), 6.50 (d, *J* = 8.0 Hz, 1 H, CH), 7.07-7.10 (m, 1 H, CH_{arom}), 7.19-7.22 (m, 3 H, CH_{arom}) ppm. ¹³C NMR (CDCl₃, 100.6 MHz): δ 20.3, 31.4, 31.8, 126.2, 126.3, 126.4, 127.3, 127.4, 127.6, 133.5, 140.6 ppm.

Table 3, entry 10



¹H NMR (CDCl₃, 400.1 MHz): δ 4.82 (dd, J = 1.8 Hz, J = 1.4 Hz, 2 H, CH₂), 5.78-5.74 (m, 1 H, CH), 6.42 (d, J = 8.1 Hz, 1 H, CH), 6.77 (d, J = 8.1 Hz, 1 H, CH_{arom}), 6.86 (t, J = 7.4 Hz, J = 7.3 Hz, 1 H, CH_{arom}), 6.94 (d, J = 7.3 Hz, 1 H, CH_{arom}), 7.08 (t, J = 7.3 Hz, J = 8.1 Hz, 1 H, CH_{arom}) ppm. ¹³C NMR (CDCl₃, 100.6 MHz): δ 65.7, 115.9, 121.5, 122.1, 122.5, 124.7, 126.7, 129.3, 154.2 ppm.

Table 3, entry 11



¹H NMR (CDCl₃, 400.1 MHz): δ 3.83 (s, 6 H, 2 OMe), 6.89 (d, J = 8.0 Hz, 4 H, CH_{arom}), 6.93 (s, 2 H, 2 CH), 7.43 (d, J = 8.0 Hz, 4 H, CH_{arom}) ppm. ¹³C NMR (CDCl₃, 100.6 MHz): δ 55.5, 114.3, 126.3, 127.6, 130.6, 159.2 ppm. Anal. Calcd. for C₁₆H₁₆O₂: C, 79.97; H, 6.71. Found: C, 79.90; H, 6.52.

Table 3, entry 12



¹H NMR (CDCl₃, 400.1 MHz): δ 7.11 (s, 2 H, CH), 7.25 (t, *J* = 4.0 Hz, 8.0 Hz, 2 H, CH_{arom}), 7.36 (t, *J* = 8.0 Hz, *J* = 4.0 Hz, 4 H, CH_{arom}), 7.52 (d, *J* = 8.0 Hz, 4 H, CH_{arom}), ppm. ¹³C NMR (CDCl₃, 100.6 MHz): δ 126.7, 127.8, 128.8, 137.5 ppm. Anal. Calcd. for C₁₄H₁₂: C, 93.29; H, 6.71. Found: C, 93.05; H, 6.49.

Table 3, entry 13



¹H NMR (CDCl₃, 400.1 MHz): $\delta 2.89$ (s, 4H, 2CH₂), 7.08 (d, J = 8.0 Hz, 2H,CH_{arom}), 7.14 (d, J = 7.6 Hz, 2H, CH_{arom}), 7.19-7.29 (m, 5H,CH_{arom}) ppm. ¹³C NMR (CDCl₃,

100.6 MHz): δ37.3, 37.9, 126.2, 128.5, 128.5, 128.6, 130.0, 131.8, 140.3, 141.4 ppm. Anal. Calcd. for C₁₄H₁₃Cl: C, 77.59; H, 6.05. Found: C, 77.48; H, 5.99.



¹H NMR (CDCl₃, 400.1 MHz): 0.69 (t, J = 7.2 Hz, 3H, Me), 0.74 (t, J = 7.2 Hz, 3H, CH₃), 1.32-1.42 (m, 4H, 2 CH₂), 2.83 (dd, J = 6.4 Hz, 1H, CH₂), 3.00-3.09 (m, 2H, CH+ H of CH₂), 4.45 (t, J = 6.8 Hz, 1H, CH), 7.15 (d, J = 8.0 Hz, 2H, CH_{arom}), 7.20 (d, J = 7.2 Hz, 2H, CH_{arom}), 7.24-7.29 (m, 5H, CH_{arom}) ppm.¹³C NMR (CDCl₃, 100.6 MHz): δ 8.7, 10.0, 24.7, 26.4, 45.4, 79.2, 80.4, 126.6, 127.3, 128.4, 128.5, 129.5, 133.1, 137.6, 142.2 ppm.

Table 3, entry 14



¹H NMR (CDCl₃, 400.1 MHz): δ 1.86 (s, 3 H, CH₃), 1.90 (s, 3 H, CH₃), 6.27 (s, 3 H, CH=C), 7.13-7.25 (m, 3 H, CH_{arom}), 7.31 (t, *J* = 8.0 Hz, 2 H, CH_{arom}) ppm. ¹³C NMR (CDCl₃, 100.6 MHz): δ 19.5, 27.0, 125.3, 125.9, 128.2, 128.9, 135.6, 138.8 ppm. Anal. Calcd. for C₁₀H₁₂: C, 90.85; H, 9.15. Found: C, 90.77; H, 9.01.

Table 4, entry 1



¹H NMR (CDCl₃, 400.1 MHz): δ 2.34 (s, 3 H, Me), 7.14 (s, 2 H, CH_{arom}), 7.35 (s, 1 H, CH_{arom}) ppm. ¹³C NMR (CDCl₃, 100.6 MHz): δ 19.6, 126.9, 128.9, 131.7, 132.1, 134.7, 135.1 ppm. Anal. Calcd. for C₇H₆Cl₂: C, 52.21; H, 3.76. Found: C, 52.17; H, 3.69.

Table 4, entry 2

¹H NMR (CDCl₃, 400.1 MHz): δ 2.31 (s, 3H, Me), 7.05 (d, J = 8.0 Hz, 2H, CH_{arom}), 7.35 (d, J = 8.0 Hz, 2H, CH_{arom}) ppm. ¹³C NMR (CDCl₃, 100.6 MHz): δ 21.0, 119.2, 130.9, 131.4, 136.9 ppm. Anal. Calcd. for C₇H₇Br: C, 49.16; H, 4.13. Found: C, 49.08; H, 4.02.



¹H NMR (CDCl₃, 400.1 MHz): δ 0.92 (t, *J* = 4.0, 8.0 Hz, 6 H, 2 Me), 1.52-1.59 (m, 4 H, 2 CH₂), 3.22-3.28 (m, 1 H, CH), 4.46 (s, 2 H, CH₂), 7.24 (d, *J* = 8.0 Hz, 2 H, CH_{arom}), 7.43 (d, *J* = 8.0 Hz, 2 H, CH_{arom}) ppm. ¹³C NMR (CDCl₃, 100.6 MHz): δ 9.7, 26.0, 70.1, 81.8, 121.3, 129.4, 131.5, 138.5 ppm.

Table 4, entry 3



¹H NMR (CDCl₃, 400.1 MHz): δ 2.32 (s, 3H, Me), 7.10 (d, J = 8.0 Hz, 2H, CH_{arom}), 7.24 (d, J = 8.0 Hz, 2H, CH_{arom}) ppm. ¹³C NMR (CDCl₃, 100.6 MHz): δ 21.0, 128.4, 130.5, 131.2, 136.4 ppm. Anal. Calcd. for C₇H₇Cl: C, 66.42; H, 5.57. Found: C, 66.25; H, 5.51.

Table 4, entry 4



¹H NMR (CDCl₃, 400.1 MHz): δ 2.29 (s, 3H, CH₃), 6.90 (t, *J* = 8.4 Hz, 2 H, CH_{arom}), 7.08 (t, *J* = 7.2 Hz, 2 H, CH_{arom}) ppm. ¹³C NMR (CDCl₃, 100.6 MHz): δ 20.6, 114.6, 115.4, 130.2, 130.5, 133.4, 133.5, 156.4, 166.1 ppm.



¹H NMR (CDCl₃, 400.1 MHz): δ 0.92 (t, J = 8.0 Hz, 6 H, 2 Me), 1.54-1.58 (m, 4 H, 2 CH₂), 3.24-3.27 (m, 1 H, CH), 4.47 (s, 2 H, CH₂), 7.02 (t, J = 8.0 Hz, 2 H, CH_{arom}),

7.32 (t, J = 8.0, 4.0 Hz, 2 H, CH_{arom}) ppm. ¹³C NMR (CDCl₃, 100.6 MHz): δ 9.8, 26.0,
70.2, 81,7, 115.1, 115.4, 129.5, 129.6, 135.1, 161.1, 163.6 ppm.
Table 4, entry 5



¹H NMR (CDCl₃, 400.1 MHz): δ 2.35 (s, 3 H, Me), 3.85 (s, 3 H, OMe), 7.19 (d, J = 7.6 Hz, 2 H, CH_{arom}), 7.88 (d, J = 7.2 Hz, 2 H, CH_{arom}) ppm. ¹³C NMR (CDCl₃, 100.6 MHz): δ 21.6, 51.9, 127.5, 167.1, 129.6, 129.1, 143.5 ppm.



¹H NMR (CDCl₃, 400.1 MHz): δ 2.46 (brs, 1H, OH), 3.89 (s, 3H, OMe), 4.73 (s, 2H, CH₂), 7.39 (d, *J* = 7.6 Hz, 2H, CH_{arom}), 7.98 (d, *J* = 8.0 Hz, 2H, CH_{arom}) ppm. ¹³C NMR (100.6 MHz, CDCl₃): δ 52.2, 64.7, 167.2, 126.6, 129.3, 129.9, 146.2 ppm.

Table 4, entry 6



¹H NMR (CDCl₃, 400.1 MHz): δ 0.91 (t, *J* = 8.0 Hz, 6H, 2Me), 1.51-1.58 (m, 4H, 2CH₂), 2.45 (s, 3H, Me), 3.21-3.27 (m, 1H, CH), 4.45 (s, 2H,CH₂), 7.22 (d, *J* = 8.0 Hz, 2 H, CH_{arom}), 7.27 (d, *J* = 8.0 Hz, 2 H, CH_{arom}) ppm. ¹³C NMR (CDCl₃, 100.6 MHz): δ 9.7, 16.2, 25.9, 70.4, 81.4, 126.8, 128.4, 136.3, 137.4 ppm. Anal. Calcd. for C₁₃H₂₀OS: C, 69.59; H, 8.98. Found: C, 69.47; H, 8.88.



¹H NMR (CDCl₃, 400.1 MHz): δ 2.41 (s, 3 H, Me), 2.70 (s, 3 H, Me), 7.33 (d, *J* = 8.1, 2 H, CH_{arom}), 7.54 (d, *J* = 11.1 Hz, 2 H, CH_{arom}) ppm. ¹³C NMR (CDCl₃, 100.6 MHz): δ 16.5, 20.9, 127.4, 129.6, 134.8, 135.0 ppm.

Table 4, entry 7



¹H NMR (CDCl₃, 400.1 MHz): δ 0.92 (t, *J* = 8.0 Hz, 6H, 2 Me), 1.52-1.59 (m, 4H, 2 CH₂), 2.33 (s, 3H, Me), 3.22-3.28 (m, 1H, CH), 4.47 (s, 2H, CH₂), 7.14 (d, *J* = 8.0 Hz, 2 H, CH_{arom}), 7.25 (d, *J* = 8.0 Hz, 2 H, CH_{arom}) ppm. ¹³C NMR (CDCl₃, 100.6 MHz): δ 9.7, 21.3, 26.0, 70.7, 81.3, 127.9, 129.1, 136.3, 137.1 ppm. Anal. Calcd. for C₁₃H₂₀O: C, 81.20; H, 10.48. Found: C, 81.11; H, 10.40.



¹H NMR (CDCl₃, 400.1 MHz): δ 2.36 (s, 6H, 2 Me), 7.12 (s, 4H, CH_{arom}) ppm. ¹³C NMR (CDCl₃, 100.6 MHz): δ 21.9, 129.1, 134.8 ppm. Anal. Calcd. for C₈H₁₀: C, 90.51; H, 9.49. Found: C, 90.43; H, 9.28.

5. NMR spectra of isolated compounds



Figure 1 – ¹H NMR spectrum (400.1 MHz) using CDCl₃ as solvent.



Figure 2 – 13 C NMR spectrum (100.6 MHz) using CDCl₃ as solvent.



Figure 3 – ¹H NMR spectrum (400.1 MHz) using $CDCl_3$ as solvent.





Figure 4 – 13 C NMR spectrum (100.6 MHz) using CDCl₃ as solvent.

Figure 5 – ¹H NMR spectrum (400.1 MHz) using CDCl₃ as solvent.



Figure 6 – 13 C NMR spectrum (100.6 MHz) using CDCl₃ as solvent.



Figure 7 – ¹H NMR spectrum (400.1 MHz) using CDCl₃ as solvent.



Figure 8 – 13 C NMR spectrum (100.6 MHz) using CDCl₃ as solvent.



Figure 9 – ¹H NMR spectrum (400.1 MHz) using $CDCl_3$ as solvent.



Figure 10 – 13 C NMR spectrum (100.6 MHz) using CDCl₃ as solvent.



Figure 11 – ¹H NMR spectrum (400.1 MHz) using CDCl₃ as solvent.



Figure 12–¹³C NMR spectrum (100.6 MHz) using CDCl₃ as solvent.



Figure 13 – ¹H NMR spectrum (400.1 MHz) using CDCl₃ as solvent.



Figure $14 - {}^{13}C$ NMR spectrum (100.6 MHz) using CDCl₃ as solvent.



Figure 15 – ¹H NMR spectrum (400.1 MHz) using CDCl₃ as solvent.



Figure 16 – 13 C NMR spectrum (100.6 MHz) using CDCl₃ as solvent.



Figure 17 – ¹H NMR spectrum (400.1 MHz) using CDCl₃ as solvent.



Figure 18 – ¹³C NMR spectrum (100.6 MHz) using CDCl₃ as solvent.



Figure 19 – ¹H NMR spectrum (400.1 MHz) using $CDCl_3$ as solvent.



Figure 20 – 13 C NMR spectrum (100.6 MHz) using CDCl₃ as solvent.



Figure 21 – ¹H NMR spectrum (400.1 MHz) using $CDCl_3$ as solvent.



Figure 22 – ¹³C NMR spectrum (100.6 MHz) using CDCl₃ as solvent.



Figure 23 – ¹H NMR spectrum (400.1 MHz) using CDCl₃ as solvent.



Figure 24 – ¹³C NMR spectrum (100.6 MHz) using CDCl₃ as solvent.



Figure 25 – ¹H NMR spectrum (400.1 MHz) using $CDCl_3$ as solvent.



Figure 26 – 13 C NMR spectrum (100.6 MHz) using CDCl₃ as solvent.

6. Synthesis of 3-pentanol-D



To a solution of sodium borodeuteride (0.84 g, 0.02 mol) in ethanol (15 mL) was added 3-pentanone (5 mL, 0.047 mol) with external cooling. The reaction was monitored by TLC and after the reaction is complete, water (25 mL) was added with strong stirring until complete dissolution of the white precipitated formed. The reaction mixture was extracted with diethyl ether (3x15 mL). To the organic phase was added sodium chloride saturated solution until pH=7. The organic phase was dried with magnesium sulfate anhydrous and the product was purified by fractional distillation.



Figure 27 – ¹H NMR spectrum (400.1 MHz) using CDCl₃ as solvent.



Figure 28 – ¹³C NMR spectrum (100.6 MHz) using CDCl₃ as solvent.

7. Deoxygenation of 2,4-dichlorobenzaldehyde with 3-pentanol-D catalyzed by ReOCl₃(SMe₂)(OPPh₃)



The solution of $\text{ReOCl}_3(\text{SMe}_2)(\text{OPPh}_3)$ (10 mol%) and 2,4-dichlorobenzaldehyde (87.5 mg, 0.5 mmol) in 3-pentanol-D (1 ml) was stirred at 170 °C under air atmosphere in a closed Schlenk equipped with a J-Young tap during 17 h. The reaction mixture was evaporated and purified by silica gel column chromatography with *n*-hexane.



Figure 29 – ¹H NMR spectrum (400.1 MHz) using CDCl₃ as solvent.

8. Synthesis of deuterated alcohol 7



The solution of $\text{ReOCl}_3(\text{SMe}_2)(\text{OPPh}_3)$ (10 mol%) and 2,4-dichlorobenzaldehyde (0.5 mmol) in 3-pentanol-D (1 ml) was stirred at 170 °C under air atmosphere in a closed Schlenk equipped with a J-Young tap. After 3 h, the reaction was stopped and the reaction mixture was evaporated and purified by silica gel column chromatography with *n*-hexane.



Figure 30 – ¹H NMR spectrum (400.1 MHz) using $CDCl_3$ as solvent.



Figure 31 – 13 C NMR spectrum (100.6 MHz) using CDCl₃ as solvent.

9. Oxidation of 3-pentanol

The mixture of ReOCl₃(SMe₂)(OPPh₃) (32.0 mg, 0.05 mmol) in 3-pentanol (1 mL) was stirred at 170 °C under air atmosphere in a closed Schlenk equipped with a J-Young tap during 17h. The reaction mixture was analysed by ¹H and ¹³C NMR.



Figure 32 – ¹H NMR spectrum (400.1 MHz) of the reaction mixture using $CDCl_3$ as solvent.



Figure 33 – 13 C NMR spectrum (100.6 MHz) of the reaction mixture using CDCl₃ as solvent.

10. References

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