Supplementary Material (ESI) for Chemical Communications

Supplementary Information for

Chiral Lutetium Benzamidinate Complexes

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Experimental Section:

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum (10^{-3} torr) line, or in an argon-filled M. Braun glove box. THF was distilled under nitrogen from potassium benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and *n*-pentane) were dried using an MBraun solvent purification system (SPS-800). All solvents for vacuum line manipulations were stored *in vacuo* over $LiAlH_4$ in resealable flasks. Deuterated solvents were obtained from Aldrich mbH (99 atom % D) and were degassed, dried, and stored *in vacuo* over Na/K alloy in resealable flasks. NMR spectra were recorded on a Bruker Avance II 300 MHz NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. IR spectra were obtained on a Bruker Tensor 34. Mass spectra were recorded at 70 eV on a Finnigan MAT 8200. Elemental analyses were carried out with an Elementar vario EL. $LuCl_3$[1], HPEBA[2], and KPEBA[2] were prepared according to literature procedures.

[{(S)-PEBA}$_2$LuCl]$_2$ ***(1)***

10 mL of THF was condensed onto a mixture of 154 mg (0.55 mmol) $LuCl_3$ and 400 mg (1.09 mmol) (S)-KPEBA and the reaction mixture was stirred overnight at room temperature. The colorless precipitate was filtered off and the solvent was removed under vacuum. After washing with *n*-pentane, the yellow product was recrystallized from toluene/*n*-pentane. – Yield: 115 mg, 0.13 mmol, 31 %. – ^{1}H-NMR (300 MHz, d_8-THF, 23 °C): δ (ppm) = 7.47 - 6.77 (m, 30 H, Ph), 4.15 (q, ^3J = 6.6 Hz, 4 H C*H*), 1.44 (d, ^3J = 6.6 Hz, 12 H, CH_3). – ^{13}C{^{1}H}-NMR (75 MHz, d_8-THF, 23 °C): δ (ppm) = 180.3 (N*C*N), 149.3 (*i*-Ph), 136.1 (*i*-Ph), 129.0 (Ph), 128.9 (Ph), 128.8 (Ph), 127.9 (Ph), 126.7 (Ph), 126.2

(Ph), 58.3 (*C*H), 26.6 (*C*H_3). – MS (EI, 70 eV): m/z (%) = 864 ([M]$^+$, 1), 849 ([M-Me]$^+$, 13), 829 ([M-Cl]$^+$, 57), 759 (16), 703 (9) 537 (9), 501 (7), 417 (6), 328 ([PEBA]$^+$, 68), 223 ([PEBA-PhEt]$^+$, 56), 180 (18), 120 (PhEtN]$^+$, 100), 105 ([PhEt]$^+$, 100), 91 ([Bz]$^+$, 17), 77 ([Ph]$^+$, 42), 57 (12), 42 ([C_2H_4N]$^+$, 13), 27 ([CHN]$^+$, 4). – IR (ATR): ν (cm^{-1}) = 3058 (w), 3023 (w), 2963 (m), 2923 (w), 1629 (w), 1488 (w), 1447 (w), 1406 (m), 1366 (m), 1299 (m), 1184 (m), 1154 (w), 1067 (w), 1021 (w), 970 (w), 908 (w), 750 (m), 696 (s), 696 (w), 616 (w), 588 (w), 532 (w). – $C_{46}H_{46}N_4ClLu \cdot ½C_7H_8$ (911.38): Calc.: C, 65.23; H, 5.53; N, 6.15; Found: C, 65.10; H, 5.57; N, 5.63.

*[{(S)-PEBA}$_2$Lu{N(SiMe$_3$)$_2$}] (**2**)*

Pathway A:

10 mL of toluene was condensed onto a mixture of 572 mg (0.87 mmol) [Lu{N(SiMe$_3$)$_2$}$_3$] and 573 mg (1.74 mmol) (*S*)-HPEBA and the reaction mixture was stirred overnight at 100 °C. After cooling to room temperature, the volatiles were removed under vacuum. After washing with 10 mL of *n*-pentane, colorless crystals were obtained from a hot *n*-heptane solution. Yield: 708 mg, 0.72 mmol, 82 %.

Pathway B:

10 mL of THF was condensed onto a mixture of 197 mg (0.24 mmol) of **1** and 45 mg (0.24 mmol) of KN(SiMe$_3$)$_2$ and the reaction mixture was stirred overnight at room temperature. The colorless precipitate was filtered off and the solvent was removed under vacuum. After washing with 10 mL of *n*-pentane, colorless crystals were obtained from a hot *n*-heptane solution. Yield: 46 mg, 0.05 mmol, 20 %.

– ^{1}H-NMR (300 MHz, C_6D_6, 25 °C): δ (ppm) = 7.28 - 6.82 (m, 30 H, Ph), 4.29 (br, 4 H, C*H*), 1.53 (d, ^3J = 6.8 Hz, 12 H, CH_3), 0.66 (s, 18 H, SiCH_3). – ^{13}C{^{1}H}-NMR (75 MHz, C_6D_6, 25 °C): δ (ppm) = 179.4 (N*C*N), 148.6 (*i*-Ph), 134.9 (*i*-Ph), 127.9 (Ph), 127.1 (Ph), 126.9 (Ph), 126.4 (Ph), 126.2 (Ph), 126.0 (Ph), 57.6 (*C*H), 27.1 (*C*H_3), 5.5 (Si*C*H_3).– ^{29}Si{^{1}H}-NMR (60 MHz, C_6D_6, 25 °C): δ (ppm) = -9.3. – MS (EI, 70 eV): m/z (%) = 989 ([M]$^+$, 1), 974 ([M-Me]$^+$, 34), 854 (11), 828 ([M-{N(SiMe$_3$)$_2$}]$^+$, 16), 723 ([M-{N(SiMe$_3$)$_2$}-PhEt]$^+$, 21), 662 ([M-PEBA]$^+$, 63), 579 (31), 480 (17), 380

(23), 328 ([PEBA]$^+$, 87), 223 ([PEBA-PhEt]$^+$, 68), 180 (77), 146 ([N(SiMe$_3$)$_2$]$^+$, 98), 120 ([PhEtN]$^+$, 96), 105 ([PhEt]$^+$, 100), 91 ([Bz]$^+$, 74), 77 ([Ph]$^+$, 90), 42 ([C_2H_4N]$^+$, 100). – IR (ATR): ν (cm^{-1}) = 3057 (w), 3023 (w), 2973 (w), 2954 (w), 2919 (w), 2919 (w), 2877 (w), 2857 (w), 1636 (m), 1598 (w), 1578 (w), 1483 (m), 1448 (m), 1360 (w), 1306 (w), 1266 (w), 1212 (w), 1142 (w), 1072 (w), 1027 (w), 1006 (w), 969 (w), 929 (w), 829 (w), 762 (m), 698 (s), 601 (w), 572 (w), 544 (m). – $C_{52}H_{64}N_5Si_2Lu \cdot 1½C_7H_8$ (1128.45): Calc.: C, 66.52; H, 6.79; N, 6.21; Found: C, 66.61; H, 6.46; N, 6.25.

Hydroamination Reactions: The catalyst was weighed under argon in an NMR tube. C_6D_6 (≈ 0.5 mL) was condensed into the NMR tube, and the mixture was frozen at –196 °C. The reactant was injected onto the solid mixture, and the whole sample was melted and mixed just before insertion into the core of the NMR machine (t_0). The ratio between the reactant and the product was calculated by comparison of the integrations of the corresponding signals. Ferrocene was used as an internal standard for the kinetic measurements. The substrates 2,2-diphenyl-pent-4-enylamine (**3a**),[3] C-(1-allyl-cyclohexyl)-methylamine (**4a**),[3] 2,2-dimethylpent-4-en-1-amine (**5a**),[3] 2,2-dimethylhex-5-en-1-amine (**6a**),[4] 5-phenylpent-4-yn-1-amine (**7a**)[5] and [1-(pent-2-ynyl)-cyclohexyl]methanamine (**8a**)[6] were synthesized according to literature procedures. The ^{1}H NMR spectra of 2-methyl-4,4-diphenylpyrrolidine (**3b**),[3] 3-methyl-2-aza-spiro-[4.5]decane (**4b**),[3] 2,4,4-trimethylpyrrolidine (**5b**),[3] 2,5,5-trimethylpiperidine (**6b**),[7] 2-benzyl-1-pyrroline (**7b**)[5] and 3-propyl-2-azaspiro[4.5]dec-2-ene (**8b**)[6] conform with the literature.

General procedure for preparation of Mosher amides: The cyclic amine (0.1-0.2 mmol) was dissolved in dry $CDCl_3$ (0.5 mL) in an NMR tube. Then 2 equiv of Et_3N and 2-5 equiv of

(*S*)-(+)-α-methoxy-α-trifluoromethylphenylacetic acid chloride were added. Afterwards, the enantiomeric excess was determined by ^{19}F NMR at 60-70 °C.[4]

Mosher adduct of

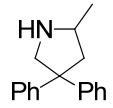
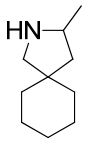
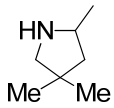
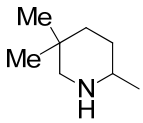
- **3b**: ^{19}F NMR ($CDCl_3$, 70 °C): δ = -69.3 (major isomer), -70.4 (minor isomer).
- **4b**: ^{19}F NMR ($CDCl_3$, 70 °C): δ = -69.7 (major isomer), -70.6 (minor isomer).
- **5b**: ^{19}F NMR ($CDCl_3$, 60 °C): δ = -69.7 (major isomer), -70.6 (minor isomer).

^{19}F NMR spectra are attached to the end of the document.

The ^{19}F NMR spectrum of the Mosher adduct of **6b** showed an indefinable mixture of products and the enantiomeric excess of **6b** was determined by chiral HPLC analysis of the corresponding 1-naphthoyl amide.

Determination of Enantiomeric Excess by chiral HPLC analysis: The hydroamination products were derivatized as 1-naphthoyl amides by treating with one equiv of 1-naphthoyl chloride and 3 equiv of Et_3N in CH_2Cl_2.[8] The values for enantiomeric excess of the products were determined by chiral stationary phase HPLC analysis using a Regis (*R*,*R*)-*β*-Gem1 column (i.d. = 4.6 mm, length = 250 mm, particle size = 5 mm). The HPLC conditions and enantiomeric excess values are shown in Table 1.

Table 1: HPLC conditions for determination of enantiomeric excess values.[a]

Entry	Compound	Eluent ratio hexane:*i*PrOH	Flow rate mL / min	Retention time [min] (absolute config)	ee [%]
1	 **3b**	75:25	1	7.4 (S) 11.6 (R)	67 (S)
2	 **4b**	75:25	1	6.2 (S) 9.1 (R)	70 (S)
3	 **5b**	75:25	1	6.2 (S) 9.2 (R)	80 (S)
4	 **6b**	90:10	0.5	15.7 (R) 18.5 (S)	33 (R)

[a] Regis (*R*,*R*)-*β*-Gem1 column (i.d. = 4.6 mm, length = 250 mm, particle size = 5 mm, injected volume: 1 µL.

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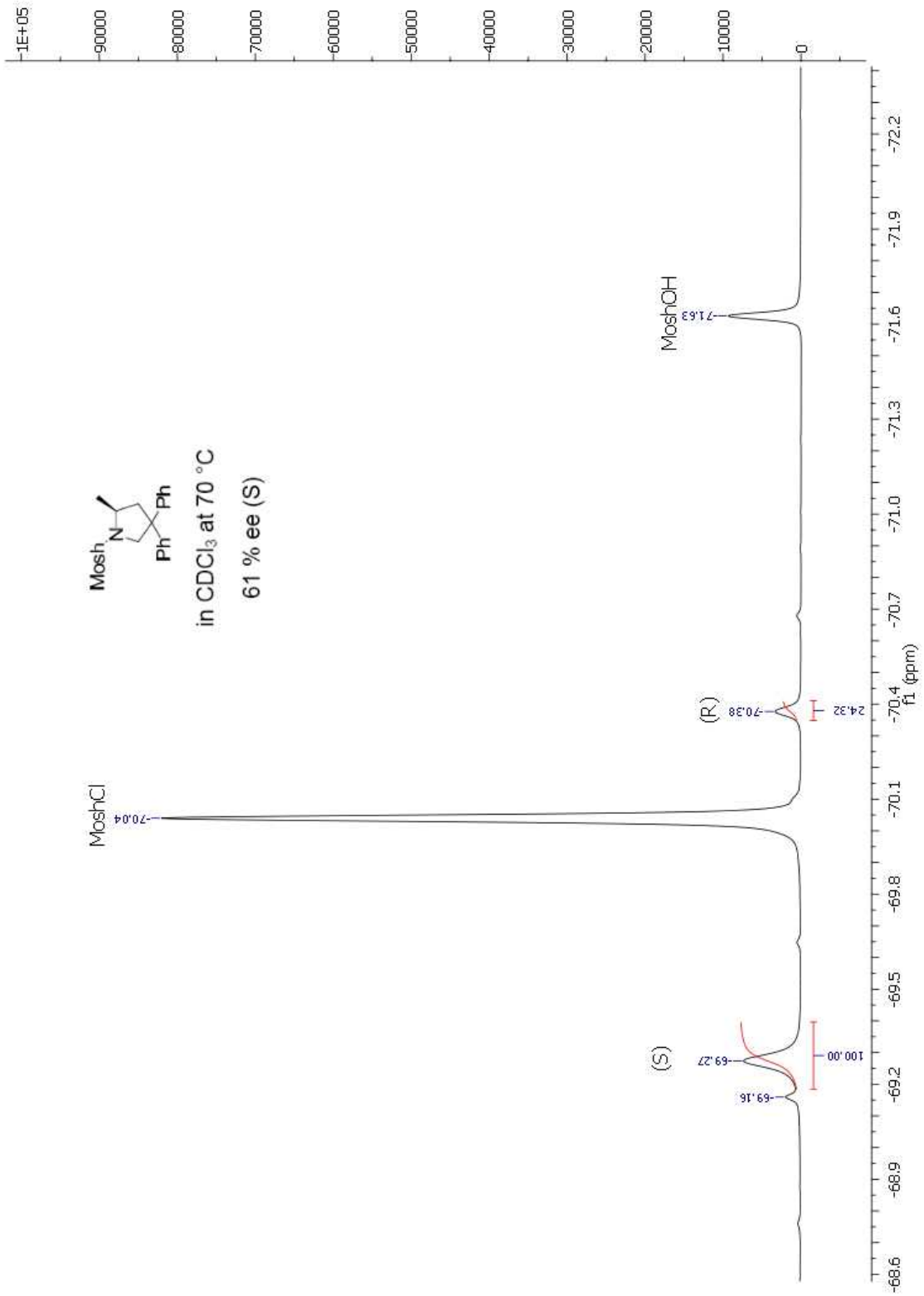
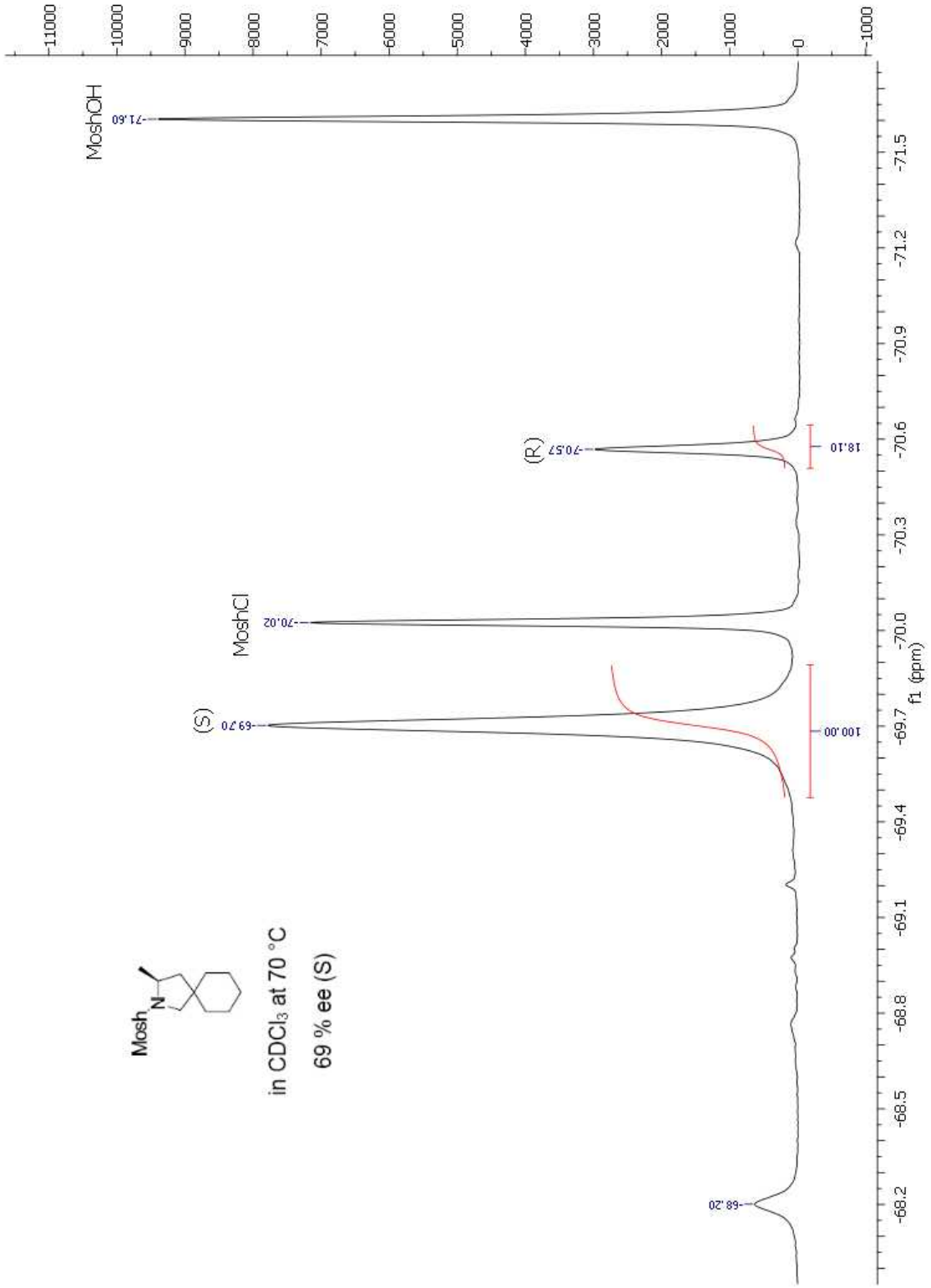
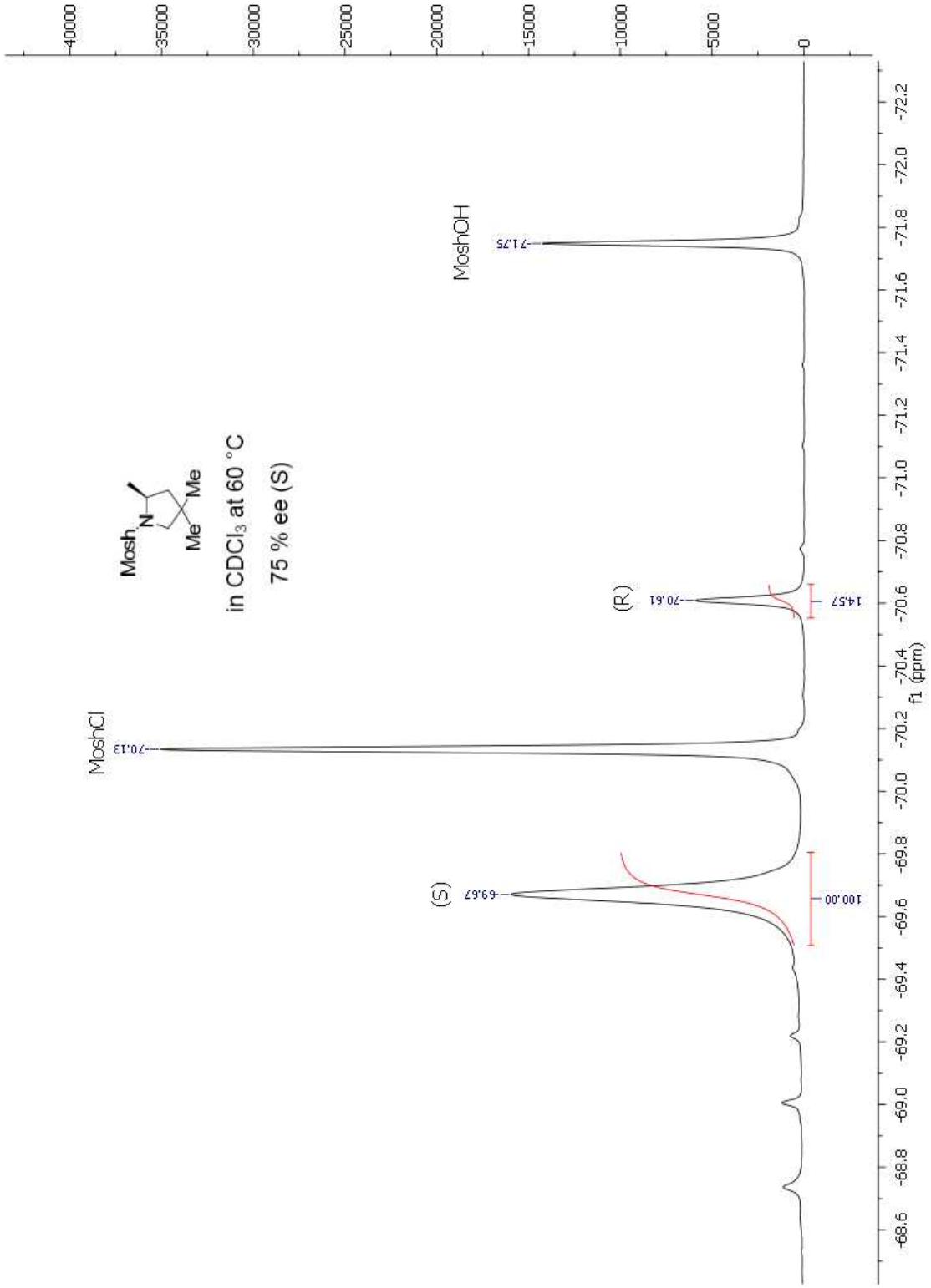

Mosh
Ph
Ph
in $CDCl_3$ at 70 °C
61 % ee (S)
MoshCl
MoshOH
(R)
(S)
-70.04
-70.38
-71.63
-69.27
-69.16
24.32
100.00
f1 (ppm)


MoshOH
-71.60
(R)
-70.57
18.10
MoshCl
-70.02
(S)
-69.70
100.00
-68.20
f1 (ppm)
Mosh
in CDCl3 at 70 °C
69 % ee (S)


MoshCl
70.13
(S)
69.67
100.00
(R)
70.61
14.57
MoshOH
71.75
Mosh
Me
Me
in CDCl3 at 60 °C
75 % ee (S)
f1 (ppm)