Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

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Chiral Neutral Zirconium Amidate Complexes for Asymmetric Hydroamination of Alkenes

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Experimental Section

General Procedures: Complexes **4a-c** and catalytic reactions were prepared using Schlenk line and/or glove box techniques under a nitrogen atmosphere. D_6-benzene and d_8-toluene were degassed and stored over 3 Å molecular sieves. Solvents used for the synthesis of complexes **4a-c** were purified and dried as follows: pentane, benzene and diethyl ether were sparged with nitrogen and dried using alumina and copper columns; THF, toluene and hexanes were sparged with nitrogen and dried using an alumina column. All other chemicals were commercially available and used as received unless stated otherwise. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on either a Bruker Avance 300 or Avance 400 spectrometer. Enantiopurity of the resolved bis((*S*)-Mosher amide) derivative of 2,2′-diamino-6,6′-dimethylbiphenyl was determined using an Agilent 6890N GC system with a 5973 mass selective detector. Mass spectrometry and elemental analyses were performed by the analytical laboratory in the Department of Chemistry at the University of British Columbia. Optical rotation was measured using a cylindrical glass cell (10mm I.D., 100mm path) on a Jasco P-1010 digital polarimeter at 589 nm. Single-crystal X-ray structure determinations were performed on a Bruker X8 APEX diffractometer using MoKα radiation (λ = 0.71073 Å). Resolution of the 2,2′-diamino-6,6′-dimethylbiphenyl, proligand synthesis and substrate synthesis were completed under ambient atmosphere. 2,2′-diamino-6,6′-dimethylbiphenyl,[1] 2,2-dimethyl-4-pentenylamine,[2] 2,2-diphenyl-4-pentenylamine,[2] 2,2-diphenyl-5-hexenylamine,[3] 2-allyl-methyl-4-pentenylamine[4] and *C*-(1-allyl-cyclohexyl)-methylamine[4] were prepared according to literature procedures. These substrates were distilled from CaH_2 and stored over 3 or 4 Å molecular sieves. Heterocyclic products 2-methyl-4,4-diphenylpyrrolidine,[2] 2-methyl-5,5-diphenylpiperidine,[2] 2,4,4-trimethylpyrrolidine,[2] 2,4-dimethyl-4-phenylpyrrolidine[2], 4-allyl-2,4-dimethylpyrrolidine[4] and 3-methyl-2-aza-spiro[4.5]decane[4] are known compounds. Enantiopurity of these products were determined using either ^{1}H or ^{19}F NMR spectroscopy (60 °C) of the (+)-(*S*)-α-methoxy-α-trifluoromethylphenylacetyl amide derivative.

Resolution of (-)-(*S*)-2,2′-diamino-6,6′-dimethylbiphenyl[5]: To a solution of racemic 2,2′-diamino-6,6′-dimethylbiphenyl (24 g, 113 mmol) in absolute ethanol (120 mL) heated to 80^{o}C, was added a solution of L-

(+)-tartaric acid (17 g, 113 mmol) in absolute ethanol (80 mL). The solution was cooled to room temperature and then placed in a refrigerator to aid crystallization. After 2 hours, the supernatant was decanted and the remaining crystalline solid was re-dissolved in absolute ethanol (100 mL) at 80 °C. The solution was cooled to room temperature for 2 hours and the supernatant was again decanted. This recrystallization process was repeated two additional times, then the remaining solid was neutralized with 1M NaOH (50 mL) and extracted with dichloromethane (3 x 100 mL). The combined dichloromethane extracts were dried on $MgSO_4$, filtered and reduced under vacuum to give (-)-(*S*)-2,2′-diamino-6,6′-dimethylbiphenyl as a beige solid (5.19 g, 21%). Specific rotation (10% HCl) $[\alpha]_D^{20}$ = -22°. Literature value: (10% HCl) $[\alpha]_D$ = -34°.[5] The enantiopurity was further improved by recrystallization of the neutral amine from dichloromethane and hexanes as two phases. This was achieved by dissolving **1** (5.19 g, 24.5 mmol) in dichloromethane (10 mL) and carefully layering this solution with hexanes (50 mL). The solution was left overnight at room temperature to produce large clear colorless prisms that form at the solvent interface (2.13 g). $[\alpha]_D^{20}$ = -35°. (10% HCl), % ee > 98% (determined by GCMS analysis of the bis[(*S*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride] derivative**).

Resolution of (+)-(*R*)-2,2′-diamino-6,6′-dimethylbiphenyl: The combined supernatants from the resolution of (-)-(*R*)-2,2′-diamino-6,6′-dimethylbiphenyl were reduced under vacuum, dissolved in 1M NaOH (50 mL), and extracted with dichloromethane (3 x 100 mL). The combined extracts were reduced to a beige solid (12.5 g). The (+)-enriched 2,2′-diamino-6,6′-dimethylbiphenyl (12.5 g, 59 mmol) was dissolved in absolute ethanol (50 mL) at 80 °C and D-(+)-tartaric acid (9.2 g, 61 mmol) was added as a solution in absolute ethanol (25 mL). The solution was cooled to room temperature and the supernatant was decanted to yield a white colorless crystalline solid. The above procedure was repeated once more, then the solid was neutralized with 1M NaOH (50 mL) and extracted with dichloromethane (3 x 100 mL). The combined extracts were dried on $MgSO_4$ and concentrated to a white solid. The solid was dissolved in dichloromethane (10 mL) and layered with hexanes (50 mL) and left at room temperature overnight to produce large clear colorless prisms (3.81 g). $[\alpha]_D^{20}$ = +37°. (10% HCl), ee > 98% (determined by GCMS analysis of the bis[(*S*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride] derivative**).

****Procedure for GC/MS analysis to determine the enantiopurity 2,2′-diamino-6,6′-dimethylbiphenyl as the bis[(*S*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride] derivative:** Resolved 2,2′-diamino-6,6′-dimethylbiphenyl (7.5 mg, 0.035 mmol) was placed in a scintillation vial and dissolved in $CHCl_3$. NEt_3 (10.7 mg, 0.106 mmol) and *S*-(+)-α-methoxy-α-trifluoromethylphenylacetyl chloride (26.8

mg, 0.106 mmol) were individually dissolved in $CHCl_3$ and added by pipette. The reaction vessel was heated to 50 ºC and progress was monitored by thin-layer chromatography (TLC). Two additional equivalents of Mosher's acid chloride (17.9 mg, 0.071 mmol) was added to the mixture and the solution was heated overnight. The resulting solution was passed through the GC-MS (Agilent HP-5ms GC column, split mode injection 1:10, 1 min at 150 ºC, ramp to 290 ºC at 20 ºC/min, held for 15 min at 290 ºC). Retention times: 14.3 min [*R*-(+)-enantiomer], 16.5 min [*S*-(-)-enantiomer]. MS (EI): *m/z* 644 (M^+), 455 (M^+ - $C_9H_8F_3O$).

General procedure for the preparation of proligands 3a-c:

Example: (+)-3a and (-)-3c. To a solution of resolved (+)-(*R*)- or (-)-(S)-2,2′-diamino-6,6′-dimethylbiphenyl (1.0 g, 4.67 mmol) and pyridine (2.0 g, 25 mmol) in toluene (20 mL) was added 2,4,6-trimethylbenzoyl chloride (2.55 g, 14.0 mmol) in one portion. The reaction mixture was stirred at 90 °C overnight. The following day the reaction mixture was cooled to room temperature and the toluene was removed under high vacuum. The remaining residue was dissolved in dichloromethane and flushed through a silica plug (2.5 cm length, 3 cm width). The collected solution was concentrated to a beige solid that was recrystallized by dissolving the solid in dichloromethane (3-5 mL) and layering with hexanes (25 mL) in two phases. The product was isolated as colourless clear needles (1.51g, 64%). The proligands were thoroughly milled with a mortar and pestle and dried under vacuum at 60°C prior to reaction with $Zr(NMe_2)_4$.

3a: ^{1}H NMR ($CDCl_3$, 300MHz): δ 7.97 (2H, d, J=8.1 Hz, Ar-*H*), 7.34 (2H, t, J=7.9 Hz, Ar-*H*), 7.15-7.13 (4H, m, Ar-*H*), 6.73 (4H, s, Mesityl-*H*), 2.20 (6H, s, -C*H*$_3$), 2.08 (12H, s, -C*H*$_3$), 1.95 (6H, s, -C*H*$_3$). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.32, 138.58, 137.31, 135.50, 134.36, 134.06, 129.34, 129.01, 128.25, 127.50, 121.90, 20.97, 19.93, 18.82. MS (ESI): *m/z* 528.2 (M^+ + Na); $C_{34}H_{36}N_4O_2$, Anal Calcd: C, 80.92; H, 7.19; N, 5.55. Found: C, 80.83; H, 7.33; N, 5.83. $[\alpha]_D^{20}$ = +139°. (**(+)-3a**, CH_2Cl_2).

3b: ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.21-8.10 (m, 4H, Ar*H*), 7.83-7.72 (m, 6H, Ar*H*), 7.47-7.18 (m, 10 H, Ar*H*), 2.03 (s, 6H, ArC*H*$_3$). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 168.27 (*C*=O), 137.76, 136.27, 134.15, 133.97, 131.40, 130.36, 129.54, 129.03, 128.60, 127.82, 127.61, 126.72, 125.39, 125.08, 121.64, 20.20 (Ar*C*H$_3$). MS (ESI): *m/z* 543.2 (M^+ + Na). Anal. Calcd. for $C_{36}H_{28}N_2O_2$: C, 83.05, H, 5.38, N, 5.42. Found: C, 82.90, H, 5.77, N, 5.55. $[\alpha]_D^{20}$ = +118°. (**(+)-3b**, CH_2Cl_2)

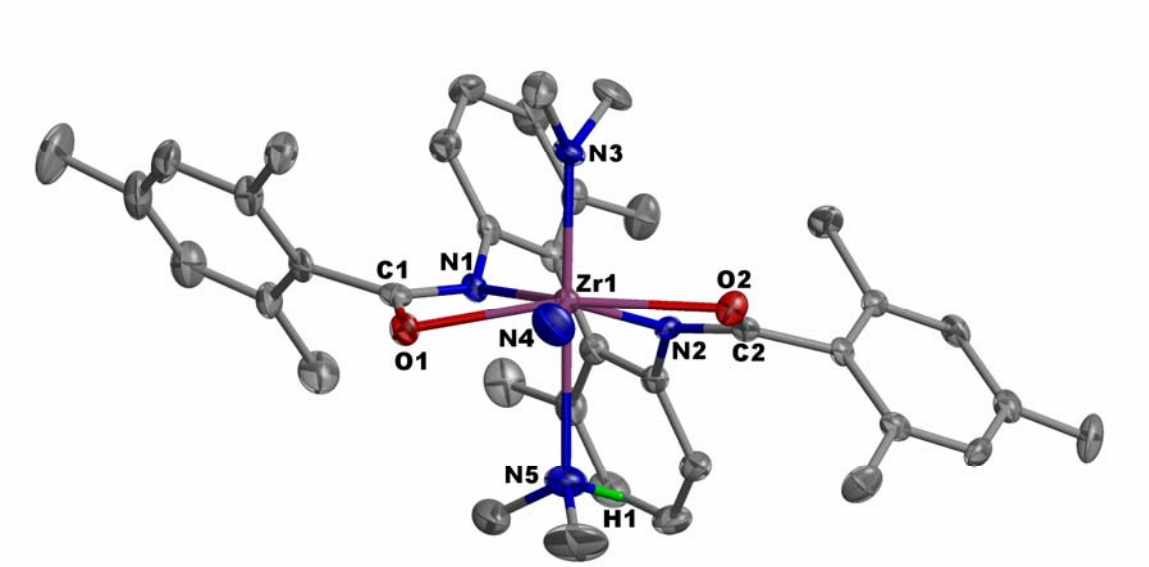
3c: ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.25 (d, 2H, J=8.1 Hz, Ar*H*) 7.34 (t, 2H, J=7.8 Hz, Ar*H*), 7.11 (d, 2H, J=7.8 Hz, Ar*H*), 6.96 (s, 2H, -N*H*), 1.97 (s, 6H, biphenyl-CH_3), 1.89 (m, 6H, Ad-*H*), 1.70-1.50 (m, 24H, Ad-*H*). ^{13}C-NMR (C_6D_6, 75.5 MHz): δ 176.74, 138.39, 138.36, 130.65, 127.70, 127.04, 121.15, 43.10,

40.47, 37.73, 29.60, 20.76. MS (ESI): *m/z* 559 (M^+ + Na), 537 (M^+ + H); $C_{36}H_{44}N_2O_2$, Anal Calcd: C, 80.56; H, 8.26; N, 5.22. Found: C, 80.29; H, 8.31; N, 5.44. $[\alpha]_D^{20}$ = +69°. (**(+)-3c**, CH_2Cl_2)

General Procedure for the preparation of complexes 4a-c.

Example: (+)-4a or (-)-4a. In a glove box, a solution of $Zr(NMe_2)_4$ (106 mg, 0.397 mmol) in benzene (2 mL) was added to a suspension of proligand **3a** (200mg, 0.397 mmol) in benzene (2 mL). Upon addition of the $Zr(NMe_2)_4$, the solution turned yellow and the insoluble proligand slowly dissolved upon reaction. The solution was stirred overnight at room temperature followed by concentration under vacuum to give a pale yellow solid (246 mg, 90%). It is important to note that hydroamination reactions with precatalysts **4a-c** were completed using non purified material, but recrystallization from pentane was achieved for structural analysis of the $HNMe_2$ adduct of **(+)-4a** by X-ray crystallography. ^{1}H NMR (C_6D_6, 300MHz): δ 6.88-6.75 (6H, m, Ar-*H*), 6.70 (2H, s, Mesityl-*H*), 6.49 (2H, s, Mesityl-*H*), 3.30 (12H, s, -N(C*H*$_3$)$_2$), 2.61 (6H, s, -C*H*$_3$), 2.00 (6H, s, -C*H*$_3$), 1.91 (6H, s, -C*H*$_3$), 1.81 (6H, s, -C*H*$_3$). ^{13}C NMR (C_6D_6, 400MHz): δ 189.85, 143.12, 139.13, 138.68, 136.43, 134.65, 132.95, 132.07, 128.77, 128.53, 128.16, 126.15, 121.50, 42.19, 20.83 (2 signals overlap), 20.06, 19.51. MS(EI): *m/z* 680 (M^+), 636 (M-NMe_2), 593 (M-2•NMe_2); $C_{38}H_{46}N_4O_2Zr$, Anal Calcd for **4a**: C, 66.92; H, 6.80; N, 8.21. Found: C, 67.30; H, 7.20; N, 8.00. $[\alpha]_D^{20}$ = +422°. (**(+)-4a**, benzene)

Crystallographic data for the $HNMe_2$ adduct of complex (+)-4a:



Ortep plot of (+)-4a (-CH_3 substituents omitted from N4 dimethylamido ligand for clarity) Selected interatomic distances [Å] and angles [°]: Zr1 – O1 2.2802(35), Zr1 – O2 2.2890(37), Zr1 – N1 2.3134(43), Zr1 – N2 2.3468(33), Zr1 – N3 2.0651(41), Zr1 – N4 2.0694(43), Zr1 – N5 2.5357(53); O1 – Zr1 – O2 166.68(0.13), N1 – Zr1 – N2 74.87(0.16), O1 – Zr1 – N1 56.81(0/13), O2 – Zr1 – N2 56.21(0.13), N3 – Zr1 – N5 177.95(0.17), O1 – C1 – N1 144.52(0.41), O2 – C2 – N2 113.47(0.42). biphenyl torsion angle [°]: 68.28(0.65).

Crystallographic data for **4a**: $C_{40}H_{53}N_5O_2Zr$; M_r = 527.1; T = 293(2) K; λ = 0.71073 Å (CCD diffractometer, $Mo_{K\alpha}$); triclinic; space group P -1; a = 10.3739(18) Å, b = 11.975(2) Å, c = 16.814(3) Å; α = 76.0480(10)°, β = 73.900(12)°, γ = 73.903(12)°; V = 1897.4(6) $Å^3$; Z = 2; D_c = 1.273 Mgm^{-3}; μ = 0.330 mm^{-1}; F_{000} = 768; crystal size = 0.3 x 0.25 x 0.2 mm; θ range for data collected = 2.39-25.05°; limiting indices = $-10 \le h \le 12$, $-14 \le k \le 14$, $-19 \le I \le 19$; 12020 reflection collected; 6349 reflections unique (R_{int} = 0.0623); Completeness to θ = 25.05: 94.4%; absorption correction: semiempirical from equivalents; max. and min. transmission: 1.1237 and 1.07; refinement method: full-matrix least-squares on F^2 ; data/restraints/parameters: 6349/0/437; GOF on F^2: 1.051; final R indices: ($I>2\sigma(I)$): R1 = 0.0561, wR2 = 0.1172; R indices (all data): R1 = 0.0954, wR2 = 0.1274; largest diff. peak and hole: 0.447 and -0.626 $e.A^{-3}$.

CCDC 611964 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of 2,2-Bis(2-propenyl)-4-pentenenitrile, (Table 2, Entry 4): Diisopropylamine (8.33 g, 11.54 mL, 82.3 mmol) was dissolved in THF (50 mL). The solution was cooled to -78 °C prior to the slow addition of *n*-BuLi (1.6 M in hexanes, 50 mL, 80 mmol). The cold bath was replaced with an ice bath and the reaction was warmed to 0°C and stirred for 45 minutes. During this time, a separate flask was charged with acetonitrile (1.15 g, 1.47 mL, 28.1 mmol) and THF (50 mL). This solution was cooled to -78 °C. A

third of the LDA solution (34 mL) was added slowly to the acetonitrile solution. After 15 minutes of stirring at -78 °C, allyl bromide (3.57 g, 2.50 mL, 29.5 mmol) was added. The reaction was warmed to room temperature with stirring for 30 minutes before being cooled to -78 °C again. Another equivalent of LDA solution (34 mL) was added, followed by 15 minutes of stirring, followed by the addition of another equivalent of allyl bromide (3.57 g, 2.50 mL, 29.5 mmol). The reaction was again warmed to room temperature with stirring for 30 minutes before being cooled to -78 °C. The remaining LDA solution was added, followed by 15 minutes of stirring, followed by the addition of a third equivalent of allyl bromide (3.57 g, 2.50 mL, 29.5 mmol). The reaction was allowed to warm to room temperature with stirring overnight. Workup of a small aliquot of the reaction mixture revealed incomplete alkylation by ^{1}H NMR. A fresh batch of LDA (2.84 g, 3.94 mL, 28.1 mmol of diisopropylamine, 17.5 mL, 28 mmol of *n*-BuLi) was prepared as described above. The nitrile solution was cooled to -78°C, followed by the slow addition of LDA. After 15 minutes of stirring, a fourth equivalent of allyl bromide (3.40 g, 2.40 mL, 28.1 mmol) was added. The reaction was warmed to room temperature with stirring for one hour. The reaction was then quenched by the addition of water (5 mL). The volatiles were removed under reduced pressure and the residue dissolved in 100 mL of diethyl ether. The organic phase was washed with 2 x 100 mL water, 1 x 100 mL brine, and dried over $MgSO_4$. The solvent was removed under reduced pressure to give the crude product, which was used in the next step without further purification. The yield was assumed to be quantitative. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.29 (d, 6H, J = 7.3 Hz, H_2C=CHCH_2-), 5.17 (m, 6H, H_2C=CH-), 5.80 (m, 3H, H_2C=CH-). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 40.16, 40.39, 120.51, 122.74, 131.78.

Synthesis of 2,2-Bis(2-propenyl)-4-pentenylamine, (Table 2, Entry 4): A flask was charged with lithium aluminum hydride (1.60 g, 42.2 mmol) and anhydrous diethyl ether (50 mL) and cooled to 0 °C. 2,2-Bis(2-propenyl)-4-pentenenitrile (4.52 g, 28.1 mmol) dissolved in anhydrous diethyl ether (50 mL) was added dropwise to the LAH suspension over a period of 10 minutes. The reaction was warmed to room temperature and stirred overnight. The reaction was again cooled to 0°C prior to the addition of water (4 mL) and 1 M NaOH (5 mL). The reaction was stirred at room temperature until no grey colour remained in the suspension. The solution was filtered through Celite, and the solid mass extracted with 3 x 50 mL of diethyl ether. The solvent was removed under reduced pressure to give the crude amine, which was determined to be pure by ^{1}H NMR. Calcium hydride was added to the oil which was stirred under nitrogen overnight. The product was degassed by several freeze-pump-thaw cycles before being filtered through a plug of Celite to remove any calcium hydride and calcium hydroxide. A GC/MS trace determined that the product was 93% pure; therefore, no further purification was undertaken. The impurity was found to have

negligible effect on catalytic efficiency. Yield: 3.48 g (75%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.98 (br s, 2H, -N*H*$_2$), 1.94 (d, 6H, *J* = 7.5 Hz, H_2C=CHC*H*$_2$-), 2.42 (s, 2H, -C*H*$_2$$NH_2$), 4.98 (m, 6H, *H*$_2$C=CH-), 5.73 (m, 3H, H_2C=C*H*-). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 39.28, 40.75, 47.52, 117.71, 134.63. HRMS (ESI), m/z calc'd for $C_{11}H_{20}N$ (M^+ + H): 166.1596, found: 166.1597.

General procedure for NMR-scale intramolecular aminoalkene hydroamination (Tables 1 and 2): All NMR scale hydroamination reactions were prepared in a nitrogen filled glove box. To a Teflon screw cap NMR tube was added the appropriate amino alkene substrate (0.2 mmol), the appropriate precatalyst (5 or 10 mol %) and d_6-benzene or d_8-toluene (500 mg). The NMR tube was then placed in an oil bath at the temperature and duration listed in Table 2. Reactions were monitored frequently to accurately obtain the reaction times for complete conversion. **Purification** (Yields listed in Tables 1 & 2): 2-methyl-4,4-diphenylpyrrolidine, 2-methyl-4,4-bis(2-propenyl)pyrrolidine, 3-methyl-2-aza-spiro[4.5]decane, 2-methyl-5,5-diphenylpiperidine and 2,5,5-trimethylpiperidine were purified by flash silica chromatography (length: 3cm, diameter: 2.5 cm) eluted first with 1:1 hexanes/ethyl acetate (100 mL) to remove proligand, followed by 89:10:1 dichloromethane/methanol/isopropylamine (200 mL) or 90:5:5 dichloromethane/methanol/ammonium hydroxide to isolate the product. 2,4,4-Trimethylpyrrolidine was purified as the benzoyl amide derivative according to a literature method.[2]

2-Methyl-4,4-bis(2-propenyl)pyrrolidine (Table 2, Entry 5): Purity: 92% by GC/MS. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.07 (dd, 1H, obscured by methyl signal; coupling constants not determined), 1.10 (d, 3H, *J* = 6.3 Hz, -C*H*$_3$), 1.71 (dd, 1H, *J* = 12.8 Hz, 6.7 Hz), 2.07 (m, 4H, H_2C=CHC*H*$_2$-), 2.62 (d, 1H, *J* = 11.3 Hz), 2.75 (d, 1H, *J* = 11.3 Hz), 3.12 (m, 1H), 4.99 (m, 4H, *H*$_2$C=CH-), 5.73 (m, 2H, H_2C=C*H*-). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 21.35, 42.84, 43.86, 45.59, 46.46, 54.60, 57.31, 117.54, 117.60, 135.32, 135.42. HRMS (ESI), m/z calc'd for $C_{11}H_{20}N$ (M^+ + H): 166.1596, found: 166.1595. ^{19}F NMR of Mosher's Amide ($CDCl_3$, 60°C, 300 MHz): δ -70.0 (integrated to 0.1485), -70.9 (integrated to 1.000); 74 % ee.

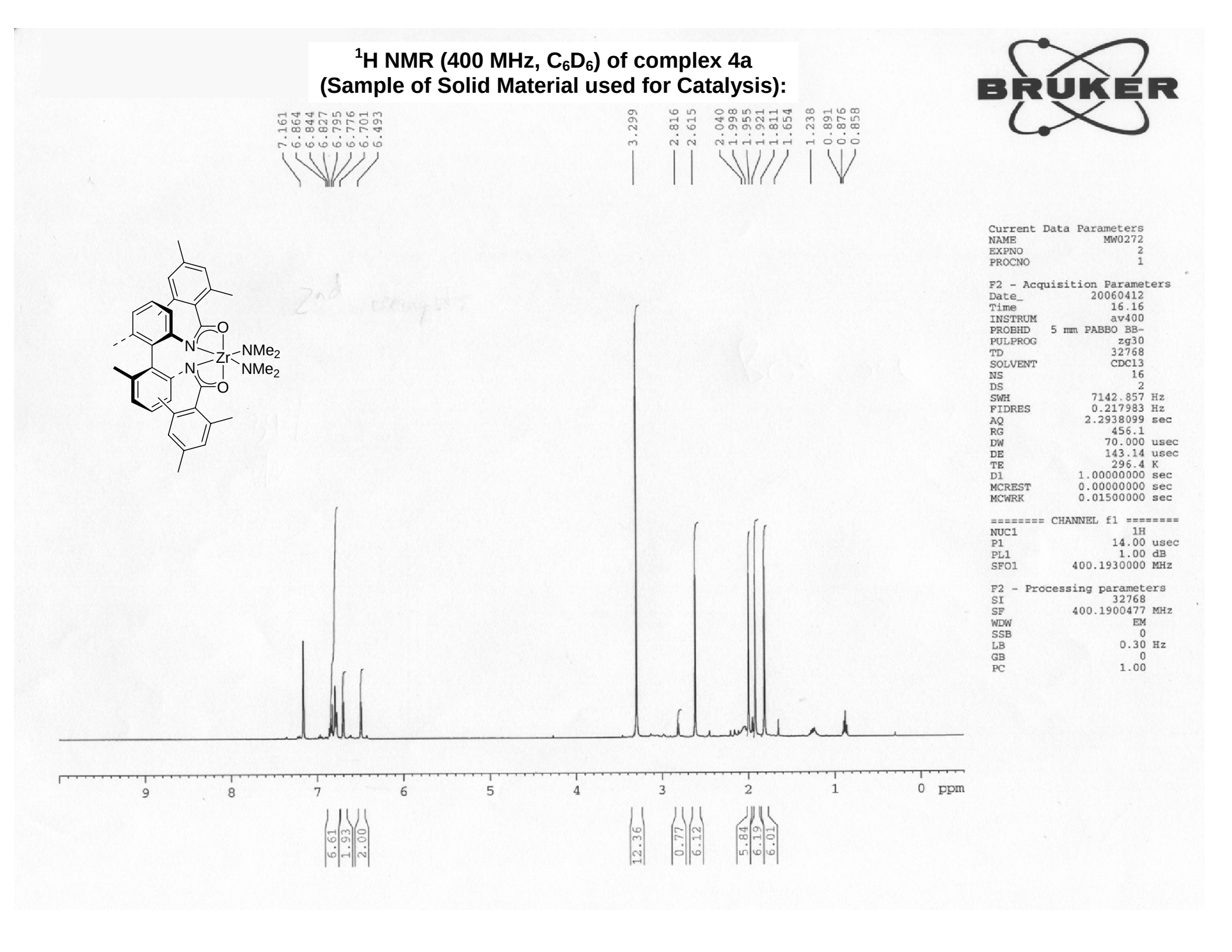
General procedure for the NMR scale preparation of Mosher amides for enantiopurity investigations of pyrrolidine and piperidine products (Tables 1 and 2): To a solution of the hydroamination product (5.0 mg, 0.021 mmol) and triethylamine (10 mg, 0.10 mmol) in dichloromethane (~1 mL) was added (*S*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (6.0 mg, 0.023 mmol) as a solution dichloromethane (~1 mL). The solution was immediately filtered through a silica gel plug (pipette column, eluent: dichloromethane, 5mL) and concentrated under vacuum to give a clear colorless residue. The % ee

was determined by ^{1}H NMR at room temperature or ^{19}F NMR at 60°C referenced to literature.[4] See ^{1}H NMR spectra below for examples of how enantiomeric excesses for select substrates was obtained.

References

[1] P. N. O'Shaughnessy, K. M.Gillespie, C. Morton, I. Westmoreland, P. Scott. *Organometallics*. **2002**, *21*, 4496 and references therein.
[2] J. A. Bexrud, J. D. Beard, D. C. Leitch, L. L. Schafer. *Org. Lett.* **2005**, *7*, 1959.
[3] D. V. Gribkov, K. C. Hultzsch, F. Hampel.. *J. Am. Chem. Soc.* **2006**, *128*, 3748.
[4] P. H. Martinez, K. C. Hultzsch, F. Hampel. *Chem. Commun*. **2006**, 2221.
[5] T. L. Marxen, B. J. Johnson, P. V. Nilsson, L. H. Pignolet. *Inorg. Chem.* **1984,** *23*, 4663

^{1}H NMR (400 MHz, C_6D_6) of complex 4a (Sample of Solid Material used for Catalysis):

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EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
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PULPROG                zg30
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FIDRES            0.217983 Hz
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TE                   296.4 K
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MCREST            0.00000000 sec
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======== CHANNEL f1 ========
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PL1                     1.00 dB
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F2 - Processing parameters
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WDW                      EM
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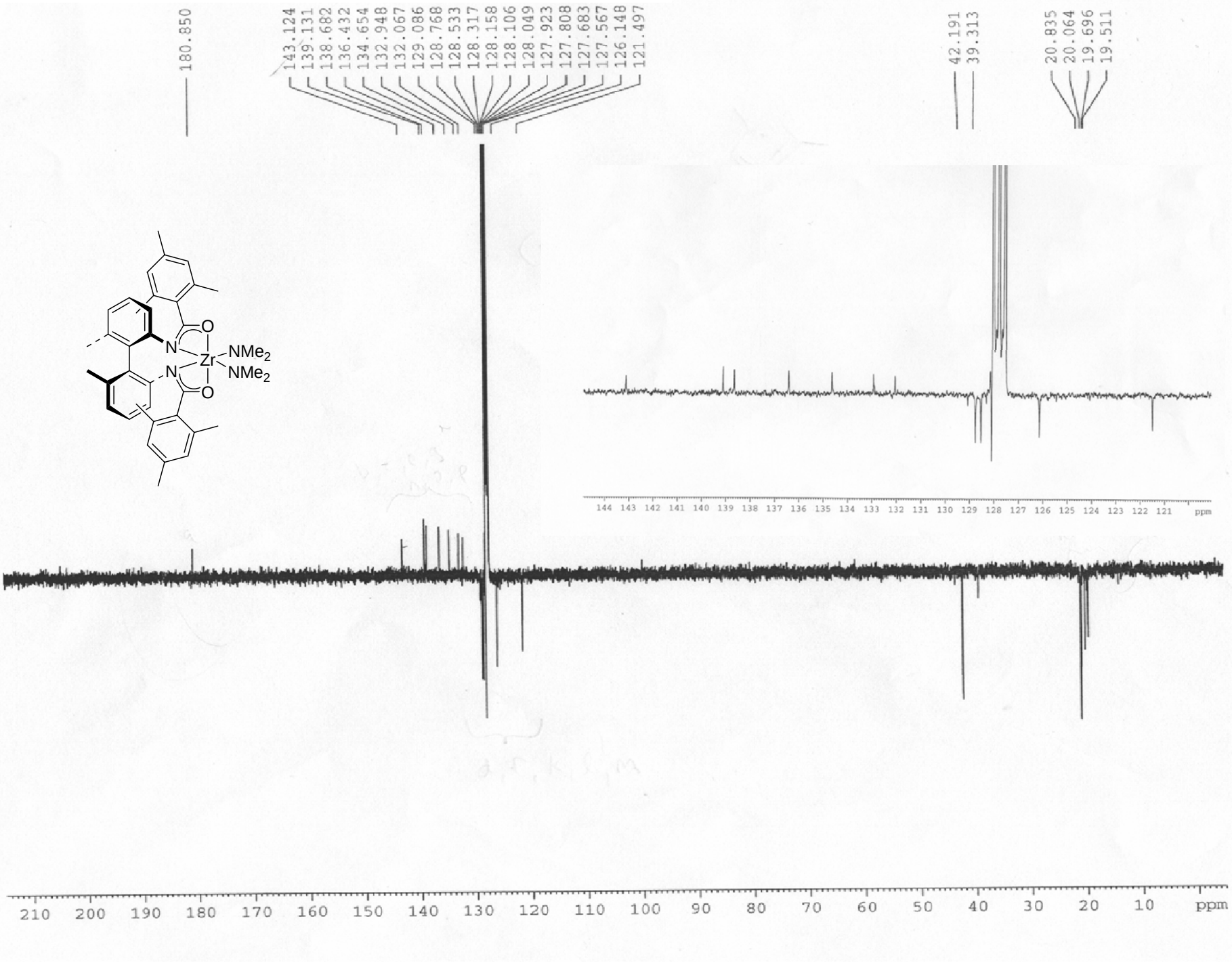
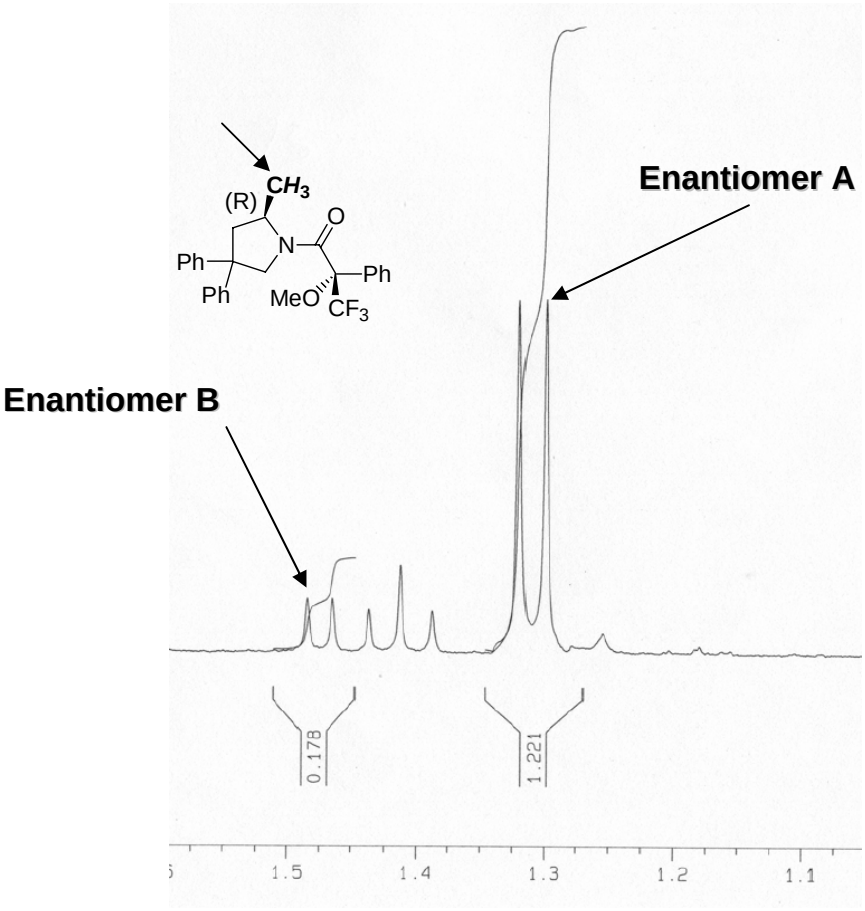
^{13}C NMR (APT45, C_6D_6) of complex 4a
(Sample of Solid Crude Material Used for Catalysis):



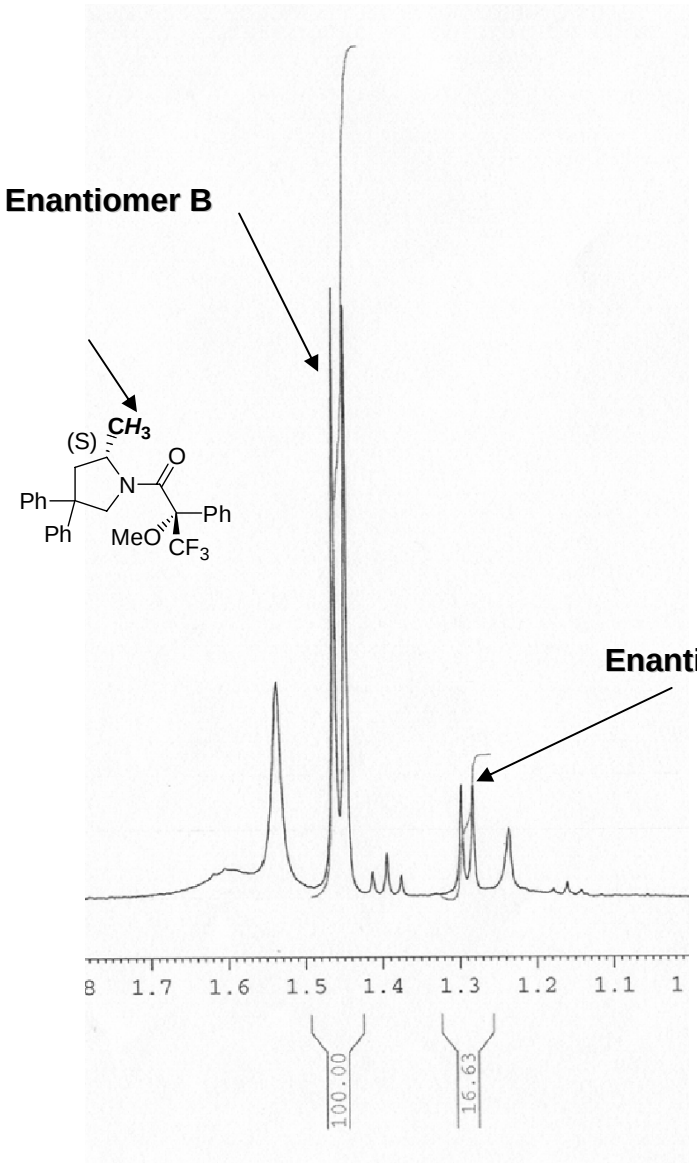
diphenylpyrrolidine prepared with precatalyst (+)-4a (Table 1, Entry 1):



% ee = $\frac{1.221 - 0.178}{2.847}$

= 74 %

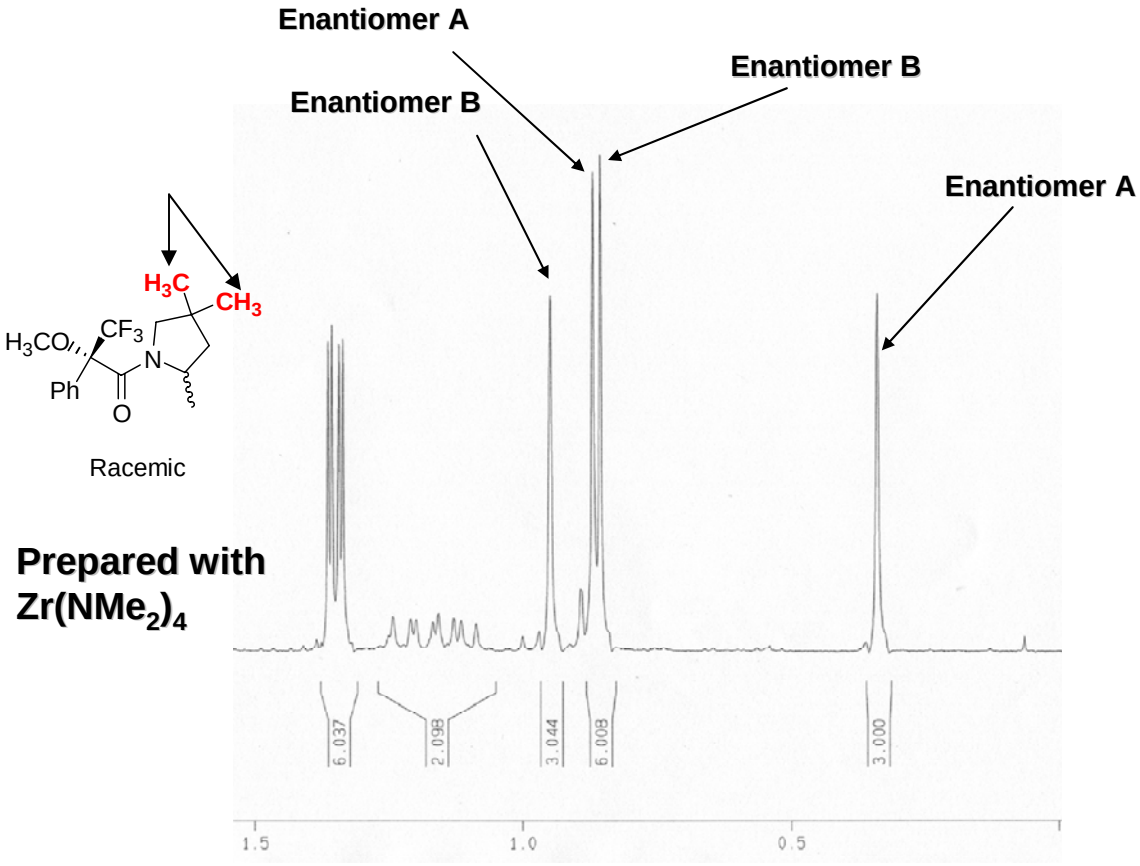
^{1}H NMR ($CDCl_3$) for Mosher amide derivative of 2-methyl-4,4-diphenylpyrrolidine prepared with precatalyst (-)-4a (Table 1, Entry 4):



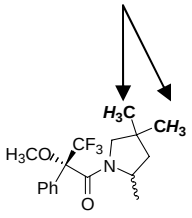
% ee = $\frac{100.00 - 16.63}{116.63}$

= 72 %

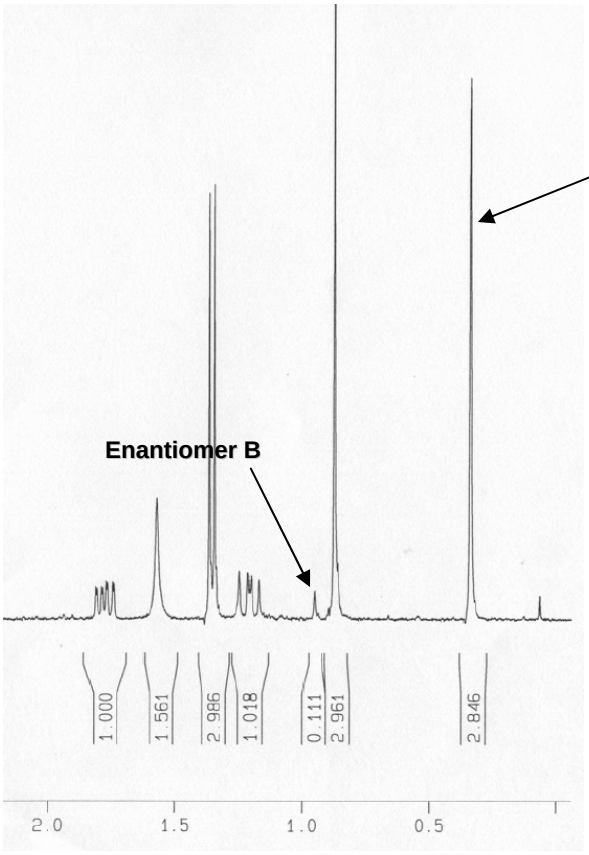
^{1}H NMR ($CDCl_3$) for Mosher amide derivative of 2,4,4-trimethylpyrrolidine prepared with $Zr(NMe_2)_4$ (RACEMIC):



^{1}H NMR ($CDCl_3$) for Mosher amide derivative of 2,4,4-trimethylpyrrolidine prepared with precatalyst (-)-4a (Table 2, Entry 2):



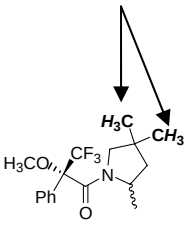
non-racemic



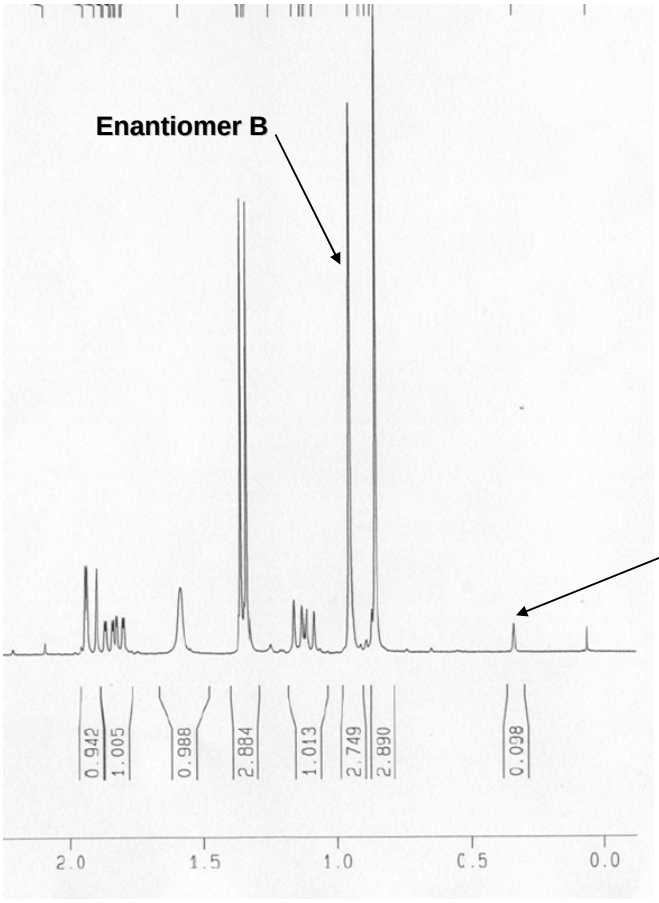
% ee = $\frac{2.846 - 0.111}{2.957}$

= 93 %

^{1}H NMR ($CDCl_3$) for Mosher amide derivative of 2,4,4-timethylpyrrolidine prepared with precatalyst (+)-4a (Table 2, Entry 1):



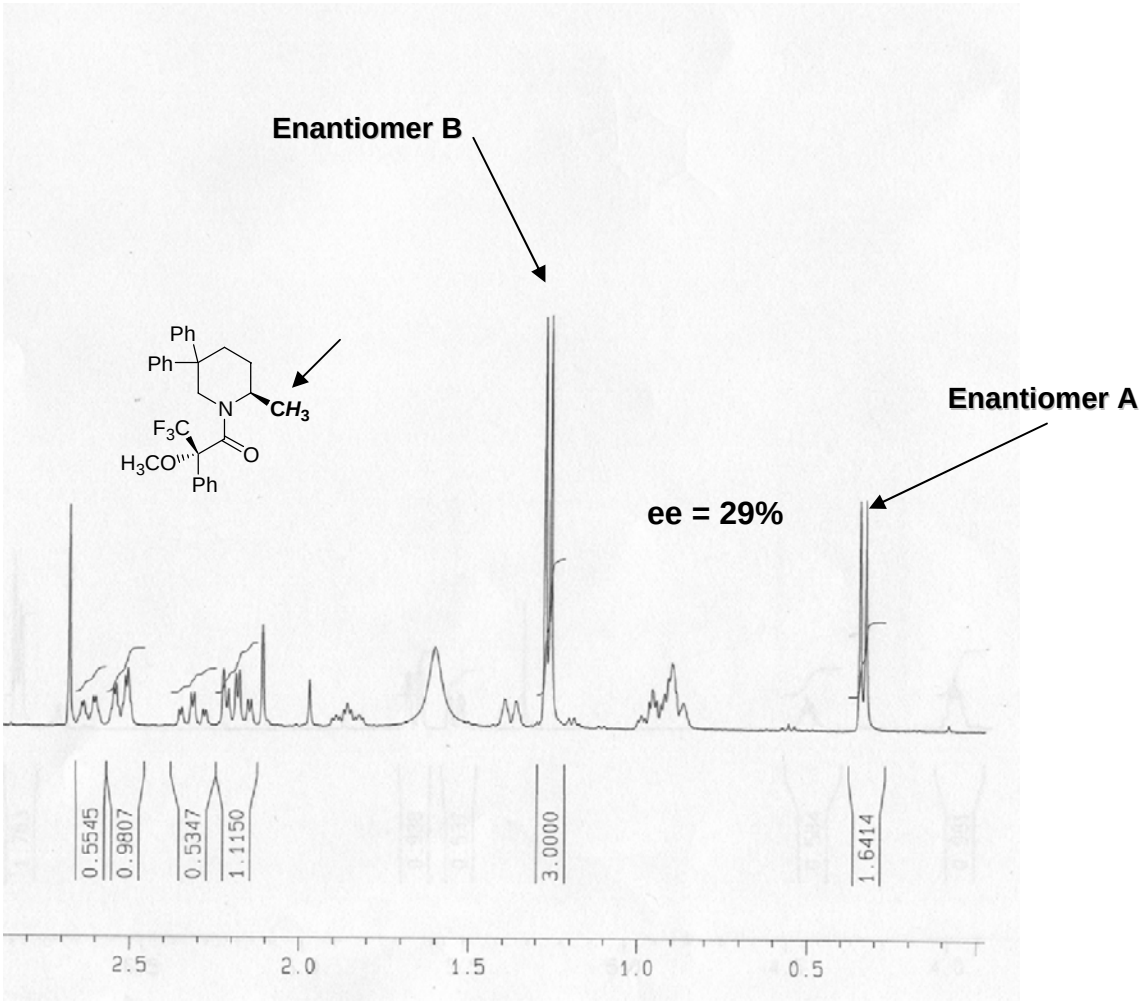
non-racemic



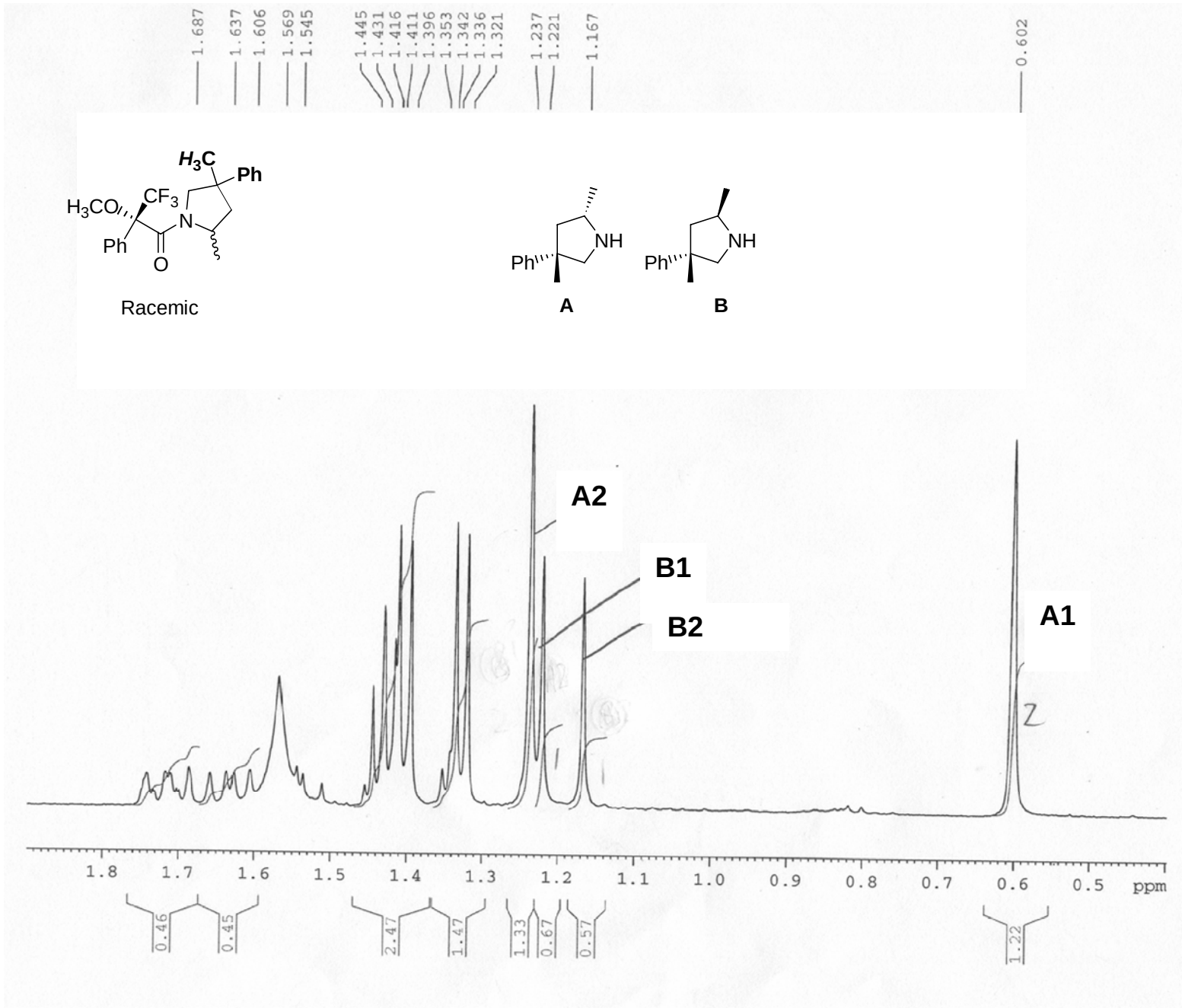
% ee = $\frac{2.749 - 0.098}{2.847}$

= 93 %

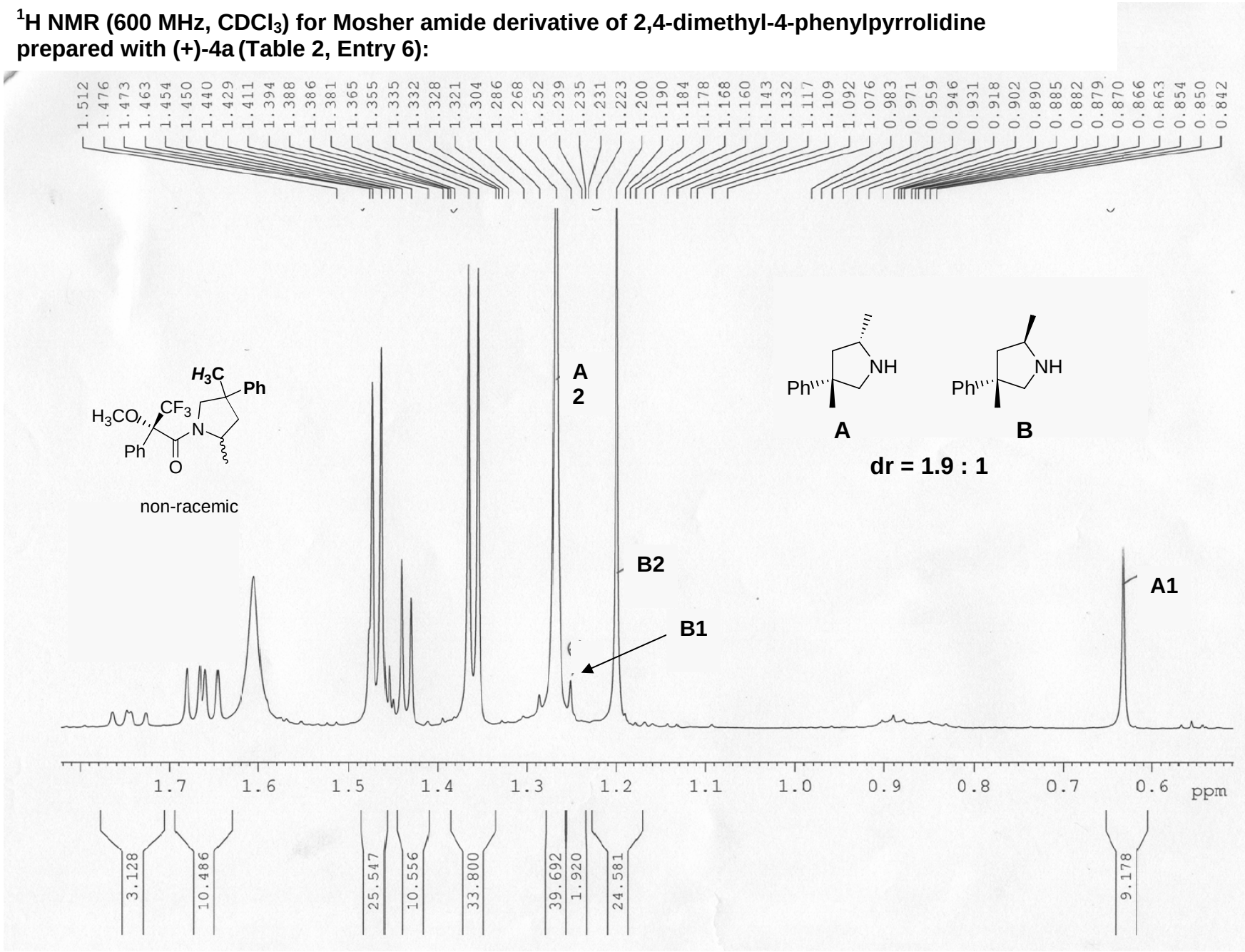
^{1}H NMR ($CDCl_3$) for Mosher amide derivative of 2-methyl-2,2-diphenylpiperidine prepared with precatalyst (+)-4a:



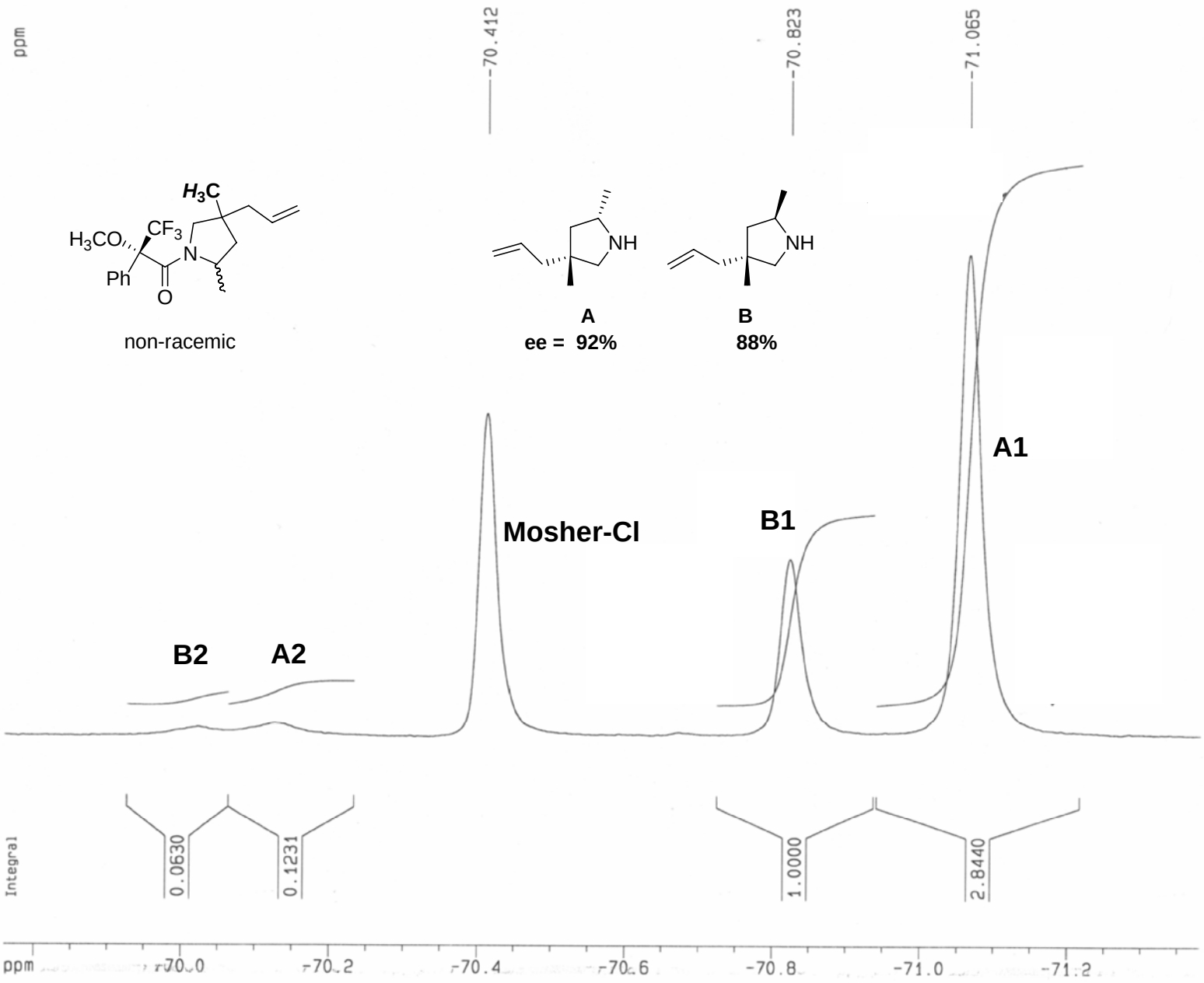
^{1}H NMR (400 MHz, $CDCl_3$) for Mosher amide derivative of 2,4-dimethyl-4-phenylpyrrolidine prepared with $Zr(NMe_2)_4$ (RACEMIC):



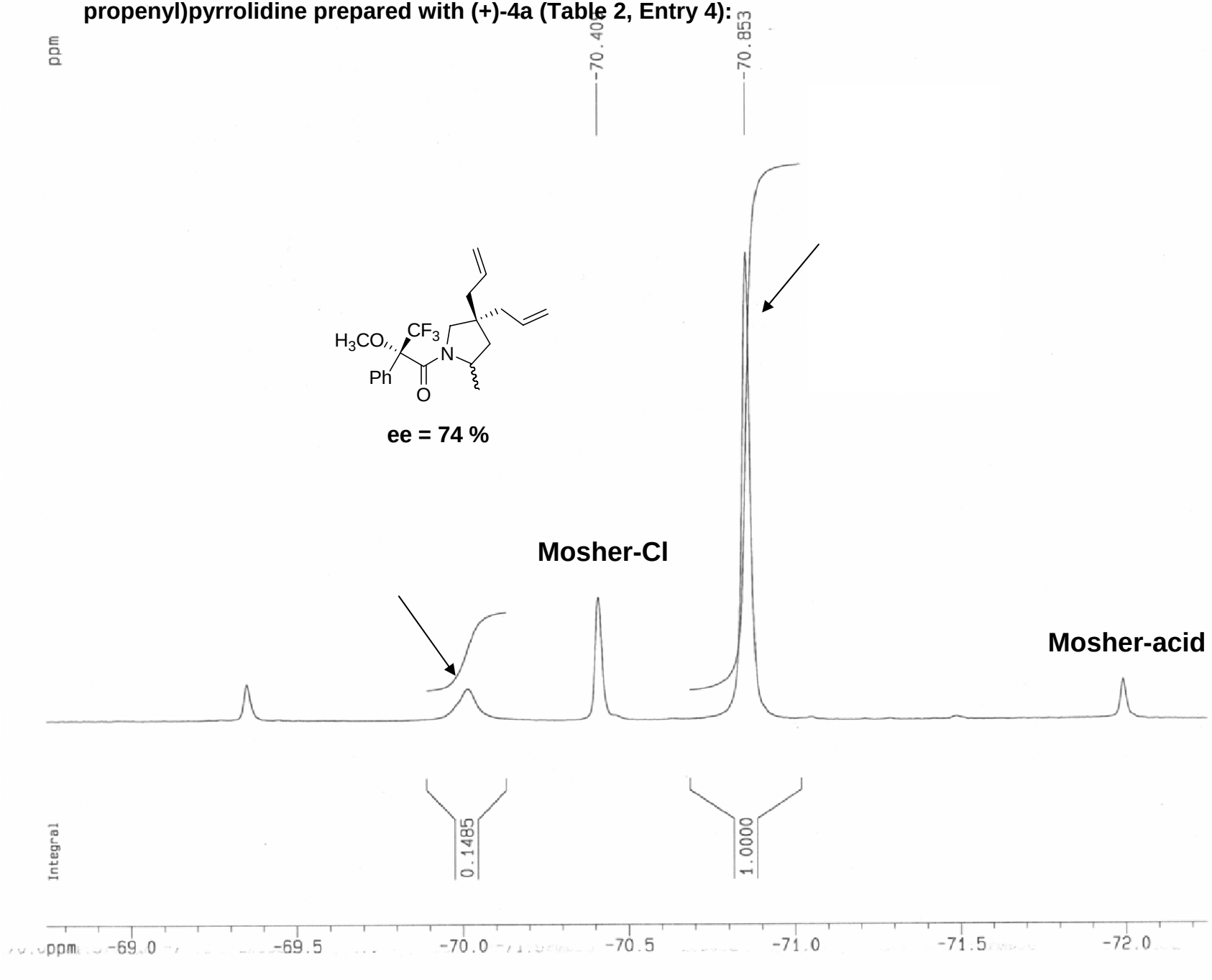
^{1}H NMR (600 MHz, $CDCl_3$) for Mosher amide derivative of 2,4-dimethyl-4-phenylpyrrolidine prepared with (+)-4a (Table 2, Entry 6):



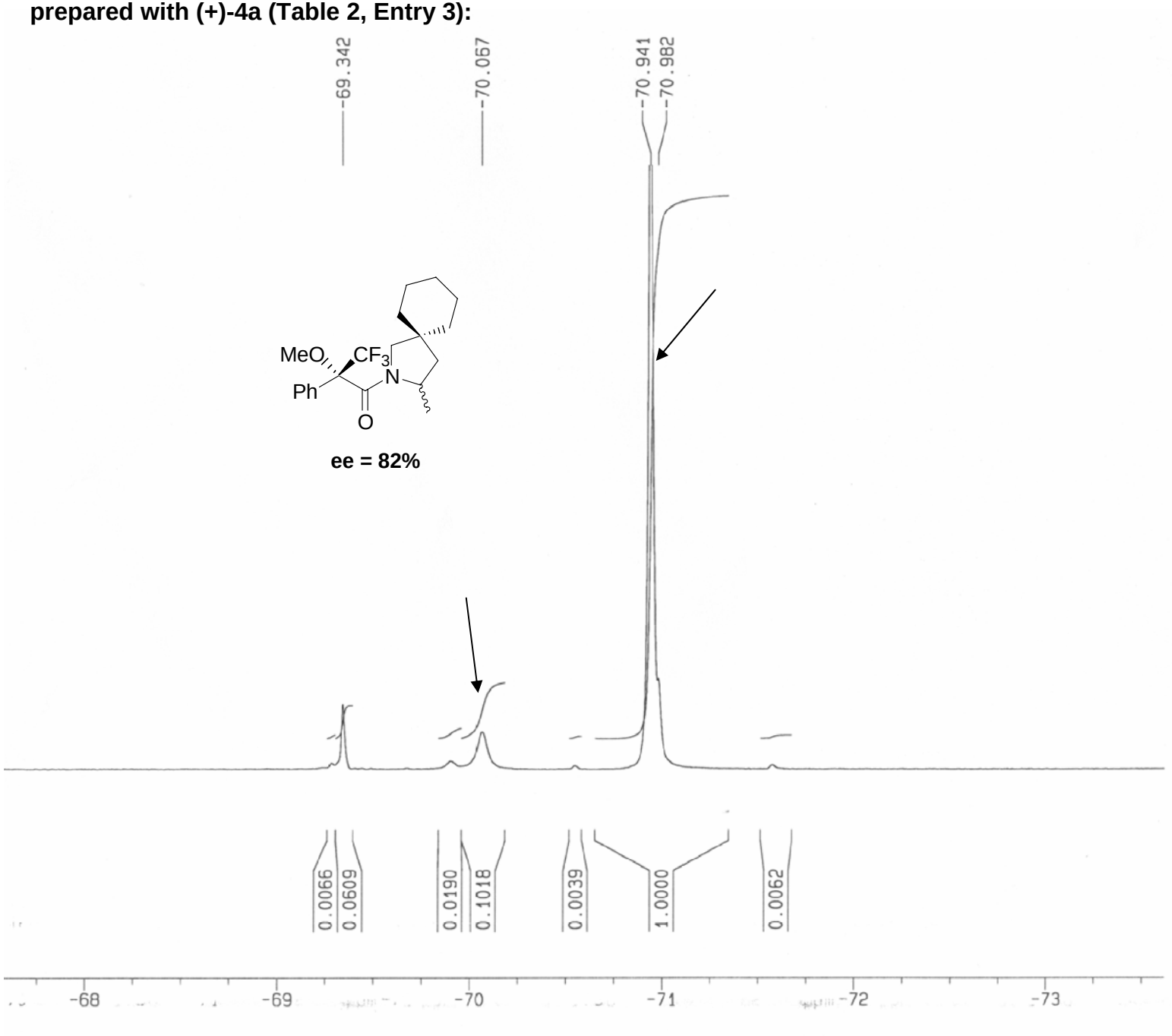
^{19}F NMR (300 MHz, $CDCl_3$, 60^{o}C) for Mosher amide derivative of 4-allyl-2,4-dimethylpyrrolidine prepared with (+)-4a (Table 2, Entry 4):



^{19}F NMR (300MHz, $CDCl_3$, 60oC) for Mosher amide derivative of 2-methyl-4,4-Bis(2-propenyl)pyrrolidine prepared with (+)-4a (Table 2, Entry 4):



^{19}F NMR (300 MHz, $CDCl_3$, 60^{o}C) for Mosher amide derivative of 3-methyl-2-aza-spiro[4.5]decane prepared with (+)-4a (Table 2, Entry 3):



ee = 82%