ELECTRONIC SUPPORTING INFORMATION

For New Journal of Chemistry

Synthesis and Structural Characterization of Amido Heteroscorpionate Rare-Earth Metals Complexes. Hydroamination of Aminoalkenes

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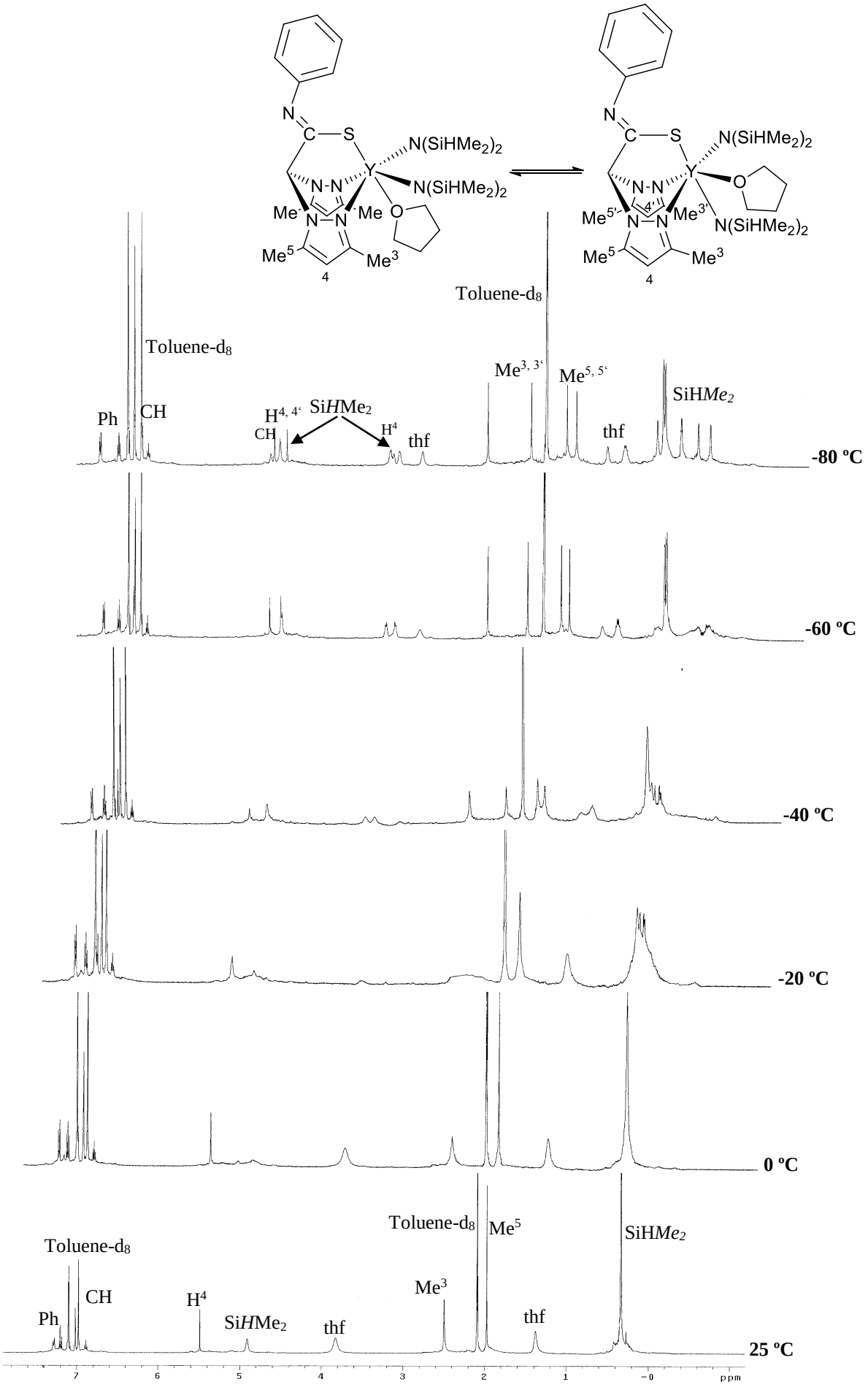


Fig. S1. Variable temperature ^{1}H NMR spectra for compound **2** in toluene-d$_8$

General procedure for catalytic intramolecular hydroamination. In a typical small scale experiment, 0.01 mmol (0.0078 g) of catalyst [Y{N(SiHMe$_2$)$_2$}$_2${κ^3-(*S*)-mbpam}thf] (**11**) and 1 mmol (0.2377 g) of aminoalkene 2,2-diphenyl-4-penten-1-amine (**13**), were dissolved in 0.75 mL of toluene-d_8 and placed in a J. Young style NMR tube with a re-sealable Teflon valve. The tube was closed, and placed into an oil bath that was preheated at the temperature desired. The reaction was monitored at regular intervals by ^{1}H NMR spectroscopy to determine the optimum conversion.

Representative example: Catalytic conversion of 2,2-diphenyl-4-penten-1-amine (**13**), into 2-methyl-4,4-diphenylpyrrolidine (**17**) using 1 mol % [Y{N(SiHMe$_2$)$_2$}$_2${κ^3-(*S*)-mbpam}thf] (**11**) as a catalyst is described. In the glovebox a 0.35 mL solution in toluene-d_8 containing a known concentration of 2,2-diphenyl-4-penten-1-amine (**13**) (1 mmol, 0.2377 g) and the appropriate internal standard ferrocene (0.048 mmol, 0.009 g) was prepared using a glass vial. This solution was added by a 1 mL glass syringe to a solution of catalyts **11** (0.01 mmol, 0.0078 g) in 0.45 mL of toluene-d_8. The resultant solution was quickly transferred to a J.Young style re-sealable NMR tube which was immediately placed into an oil bath that was preheated at 70 ºC. Single scan spectra were acquired automatically at different time intervals. The concentration of substrate and product at any given time were determined by integration of substrate and product resonances relative to the integration of the internal standard.

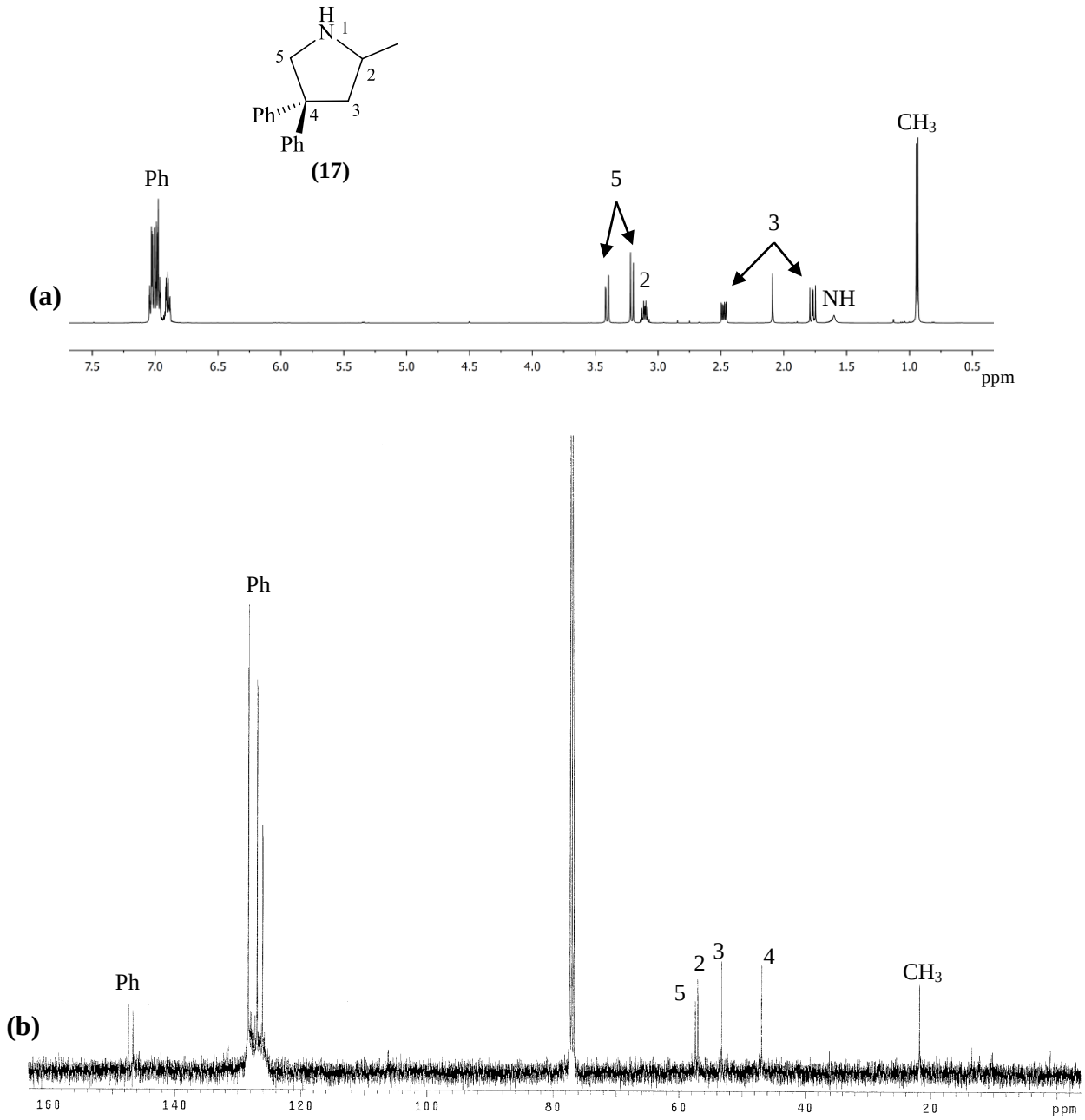


Fig. S2. (a) ^{1}H NMR spectrum in C_6D_6 of pure pyrrolidine **17** after vacuum transfer (removal of catalyst). (b) $^{13}C\{^{1}H\}$ NMR spectrum in $CDCl_3$ of pure pyrrolidine **17**.

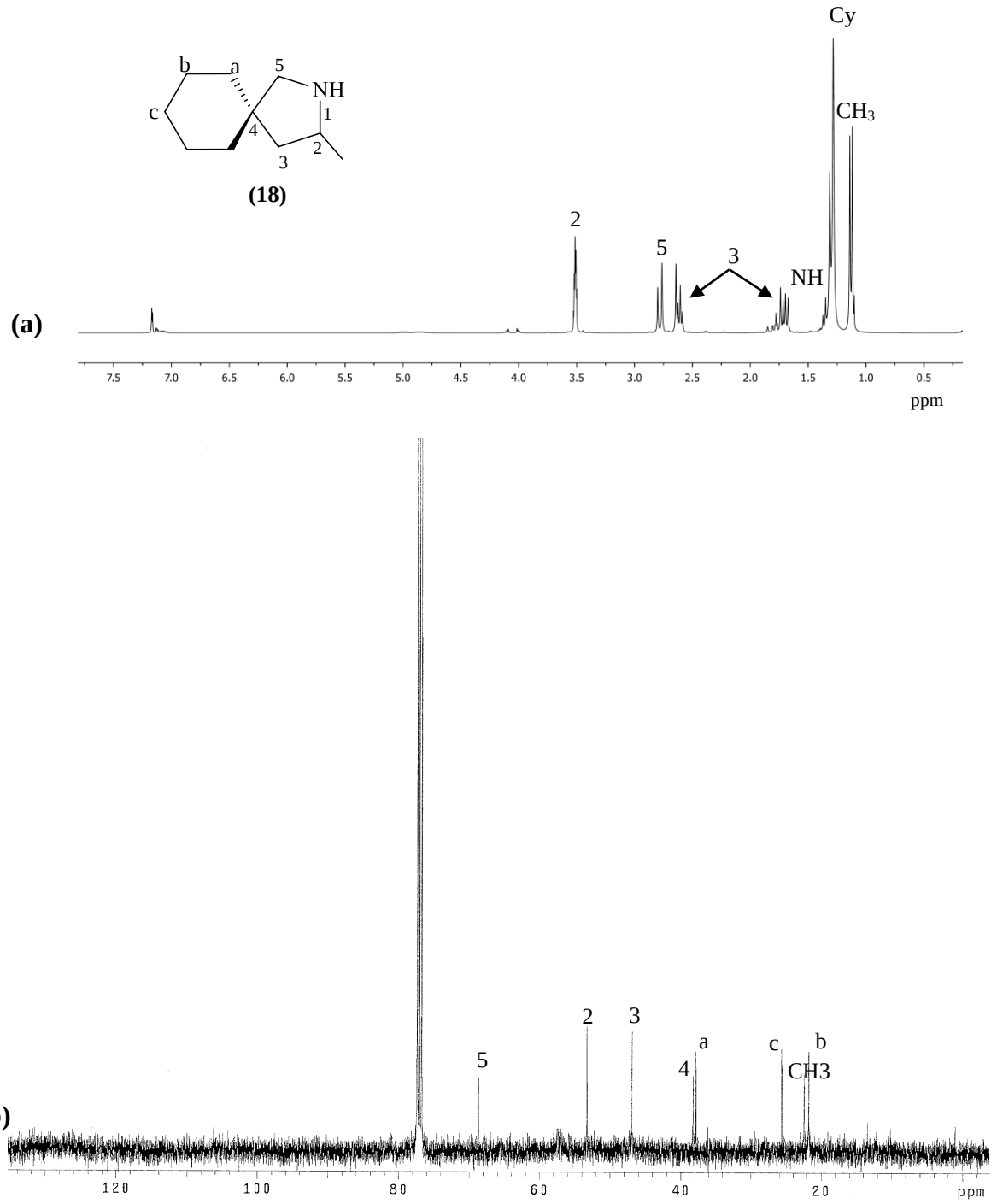


Fig. S3. (a) ^{1}H NMR spectrum in C_6D_6 of pure pyrrolidine **18** after vacuum transfer (removal of catalyst). (b) $^{13}C\{^{1}H\}$ NMR spectrum in $CDCl_3$ of pure pyrrolidine **18**.

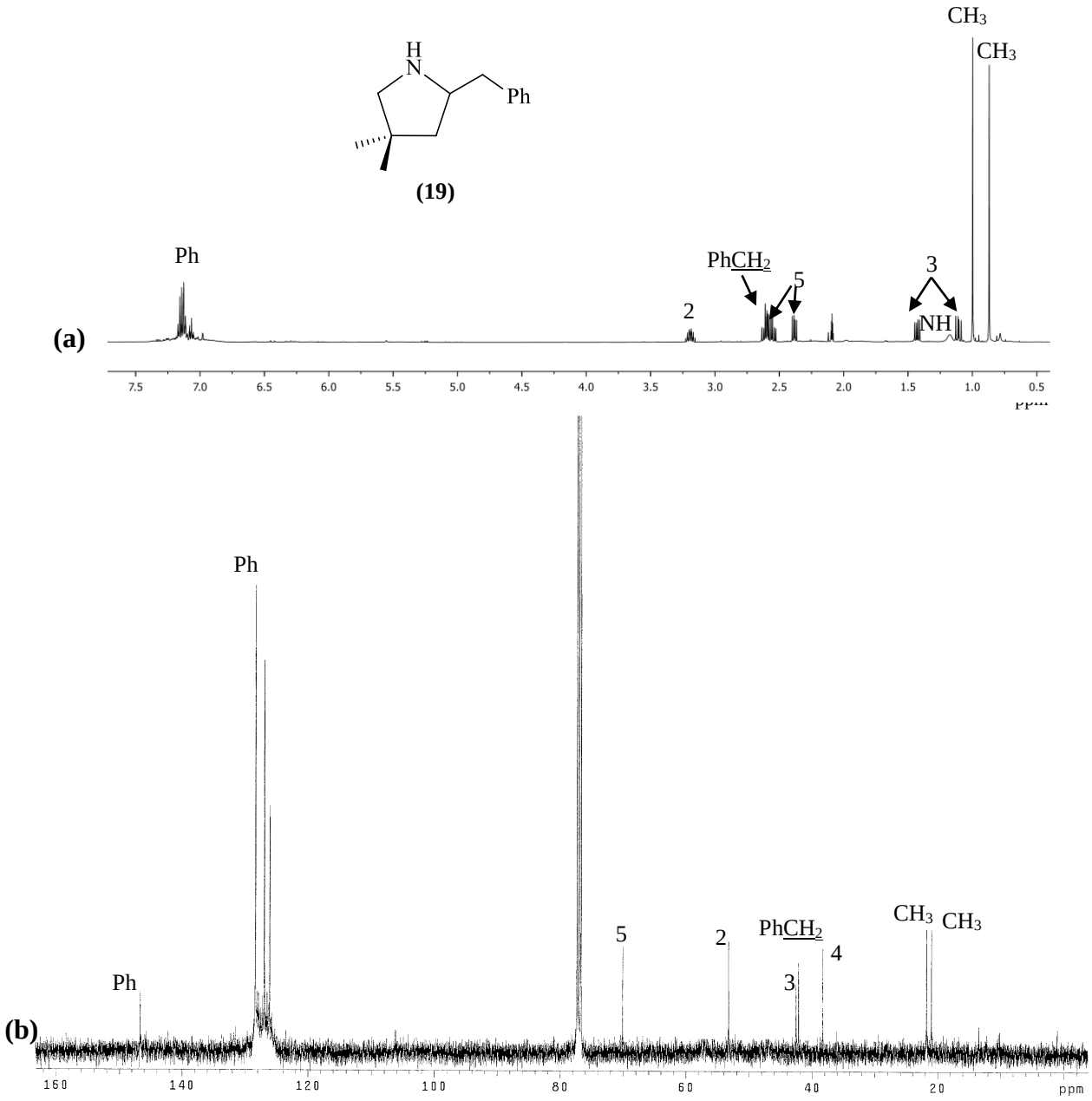


Fig. S4. (a) ^{1}H NMR spectrum in C_6D_6 of pure pyrrolidine **19** after vacuum transfer (removal of catalyst). (b) $^{13}C\{^{1}H\}$ NMR spectrum in $CDCl_3$ of pure pyrrolidine **19**.

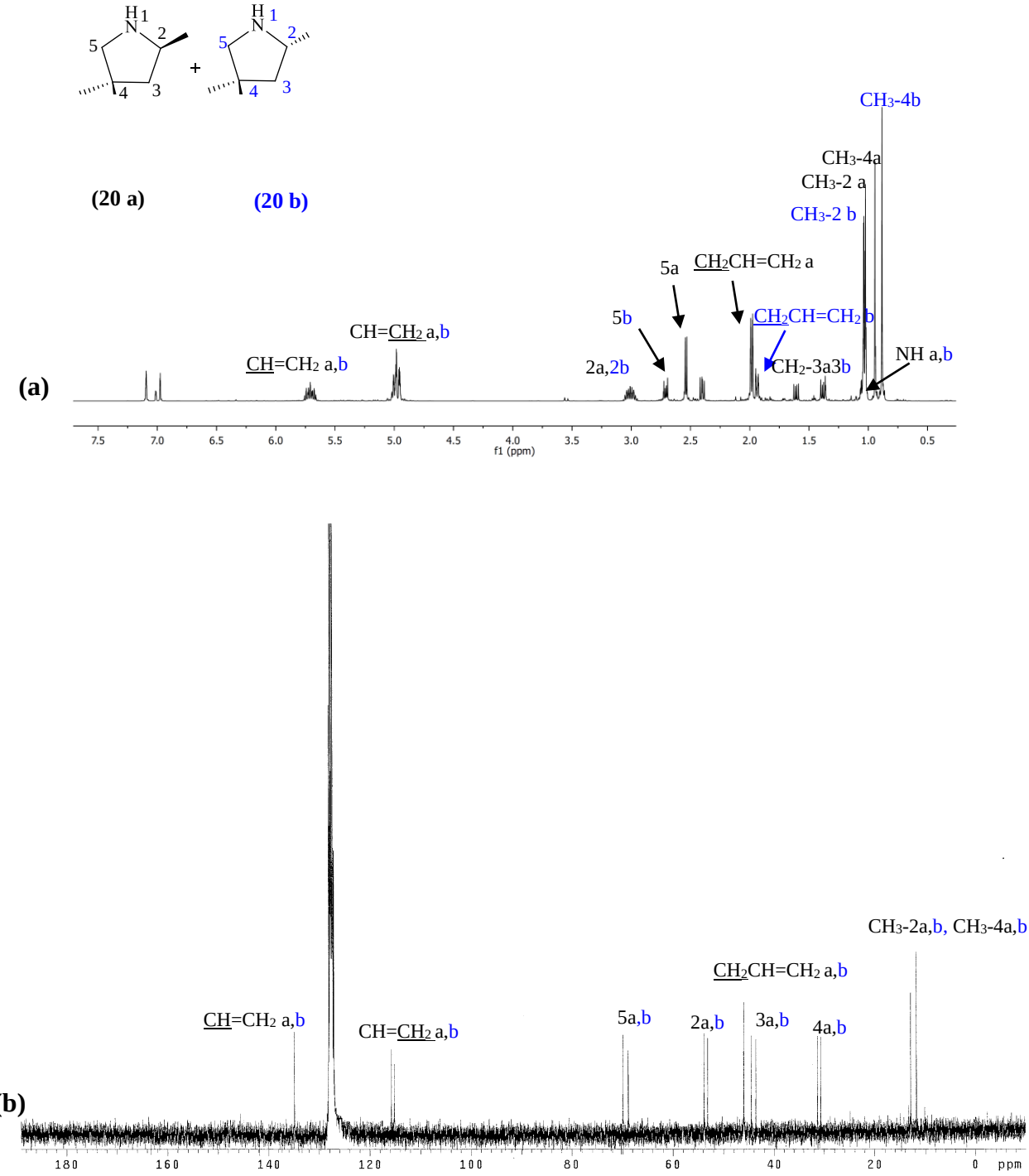


Fig. S5. (a) ^{1}H NMR spectrum in C_6D_6 of the mixture of diastereoisomers of pyrrolidine **20** after vacuum transfer (removal of catalyst). (b) $^{13}C\{^{1}H\}$ NMR spectrum in C_6D_6 of pure pyrrolidine **20**.

General procedure for kinetic measurements. All kinetic measurements were conducted by monitoring the reaction with ^{1}H NMR spectroscopy by using a Varian, Unity Innova FT-500 spectrometer. In a glovebox, a J. Young style NMR tube was charged with of the catalyst, internal

standard ferrocene and the substrate in 0.85 or 0.75 mL of toluene-d_8. The conversion was monitored by ^{1}H NMR spectroscopy by following the disappearance of the olefinic signals of the substrate relative to the internal standard ferrocene. NMR spectra were taken in appropriate time intervals (e.g. 1, 2, 3, 4, 5……60 min) using the multizg script from the Varian package.

Initial rate Kinetic Measurements at 25 ºC.

The initial rates for the hydroamination of 2,2-diphenyl-4-penten-1-amine (**13**) were measured for several substrate concentrations (0.40, 0.50, 0.60, 0.70 M) at constant catalyst **11** concentration (0.020 M). Linear regresion fits for [**13**] versus time were obtained for the first 60 min, indicating that the reactions are zero-order in substrate concentration (Fig. S6).

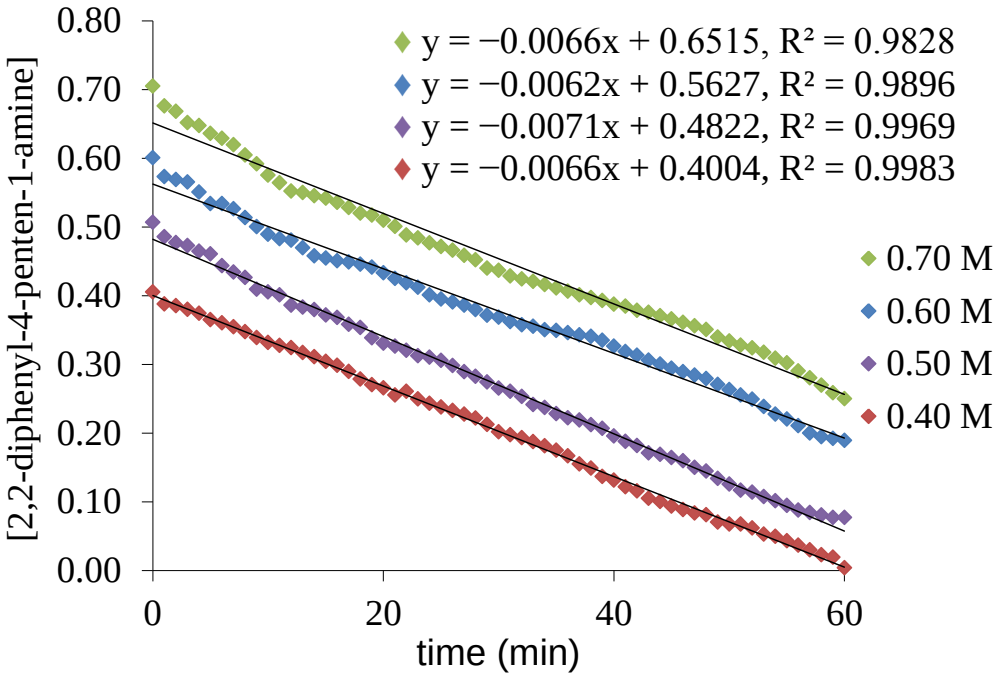


Fig. S6. Plot of [2,2-diphenyl-4-penten-1-amine] vs. time, illustrating zero-order dependence on [2,2-diphenyl-4-penten-1-amine]. The concentration of catalyst [**11**] is 0.020M.

The initial rates for the hydroamination of 2,2-diphenyl-4-penten-1-amine (**13**) were measured for several catalyst **11** concentrations (0.020, 0.025, 0.030, 0.035 M) at constant substrate [**13**] concentration (0.40 M). Linear regresion fits for ln[2,2-diphenyl-4-penten-1-amine] versus time were obtained for the first 30 min (Fig. S7). Plot of k_{obs} (from Fig. S7) versus concentration of [Y{N(SiHMe$_2$)$_2$}$_2${κ^3-(*S*)-mbpam}thf]

(**11**) for the cyclization of 2-diphenyl-4-penten-1-amine (**13**) showing first-order dependence on catalyst concentration (Fig. S8).

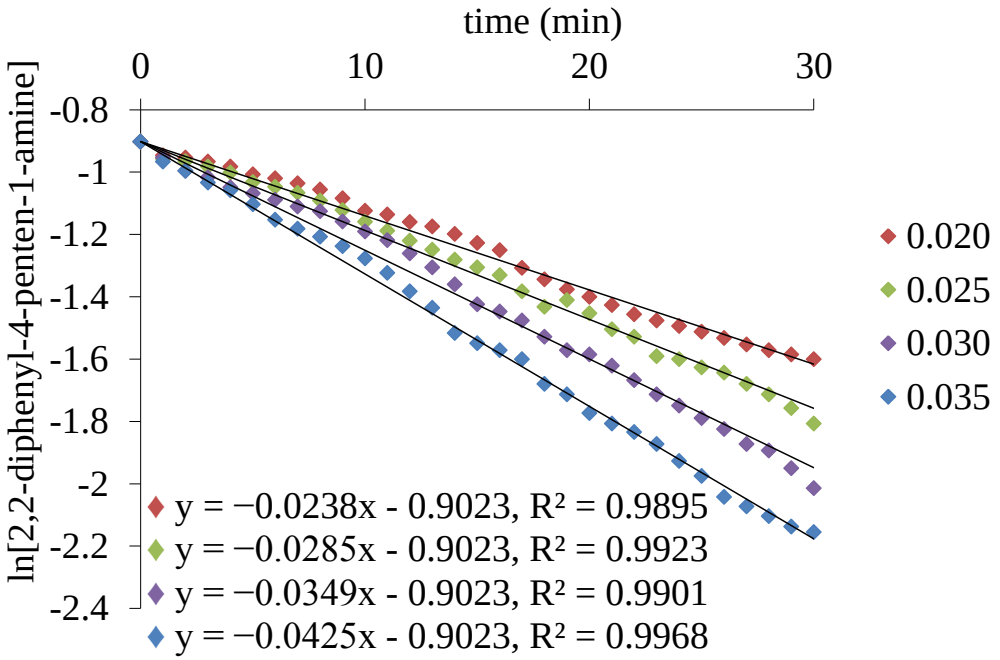
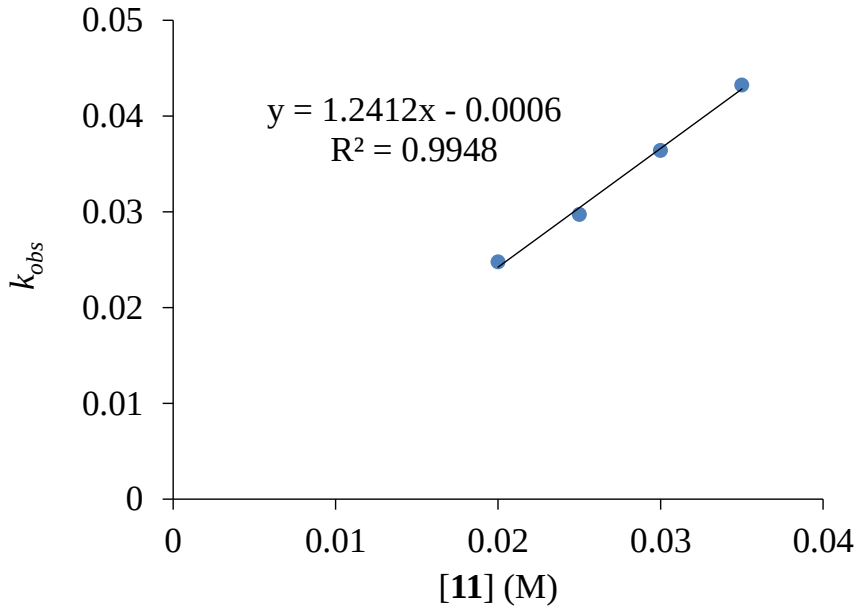


Fig. S7. Plot of ln[2,2-diphenyl-4-penten-1-amine] vs. time for several catalyst **11** concentrations (0.020, 0.025, 0.030, 0.035 M). The concentration of substrate [**13**] is 0.40 M.



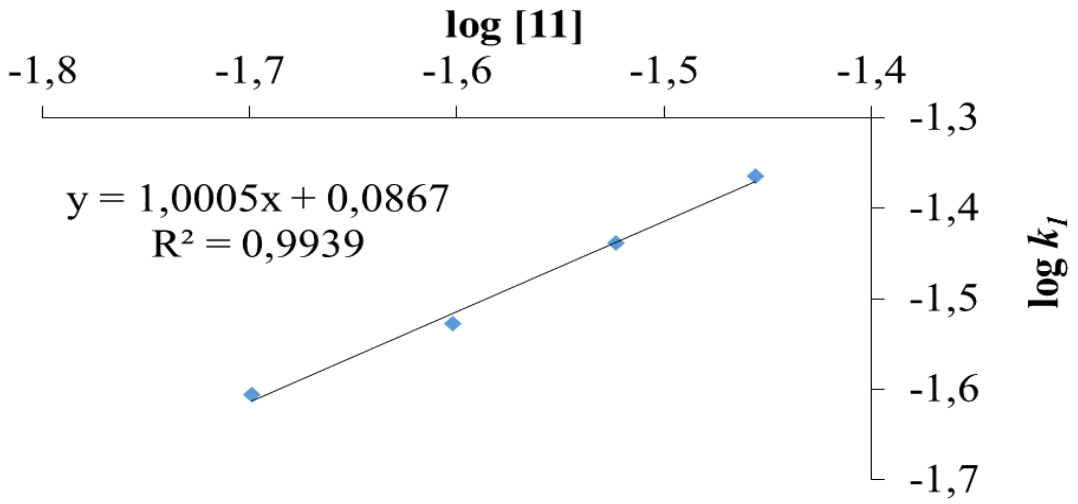
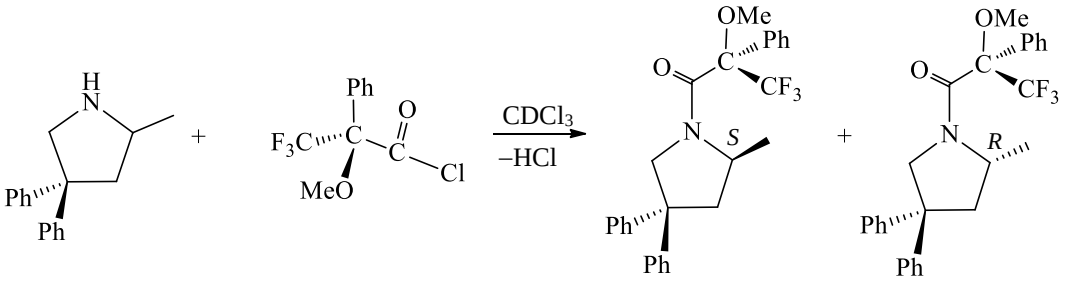


Fig. S8. Plot of k_{obs} (from Fig. S7) versus concentration of [Y{N(SiHMe$_2$)$_2$}$_2${κ^3-(*S*)-mbpam}thf] (**11**) for the cyclization of 2,2-diphenyl-4-penten-1-amine (**4**) showing first order dependence on catalyst concentration.

General procedure for preparation of Mosher amides. The amine (0.10 mmol) was dissolved in $CDCl_3$ (0.5 mL) in a NMR tube. (R)-(+)-α-methoxy-α-trifluoromethylphenylacetic acid chloride (0.040 mg, 0.15 mmol) was added. Enantiomeric excess was then determined by ^{19}F NMR at 70 ºC. For ^{19}F NMR data of Mosher amides of pyrrolidines, **17** and **18** see ref. 1.



Representative examples:

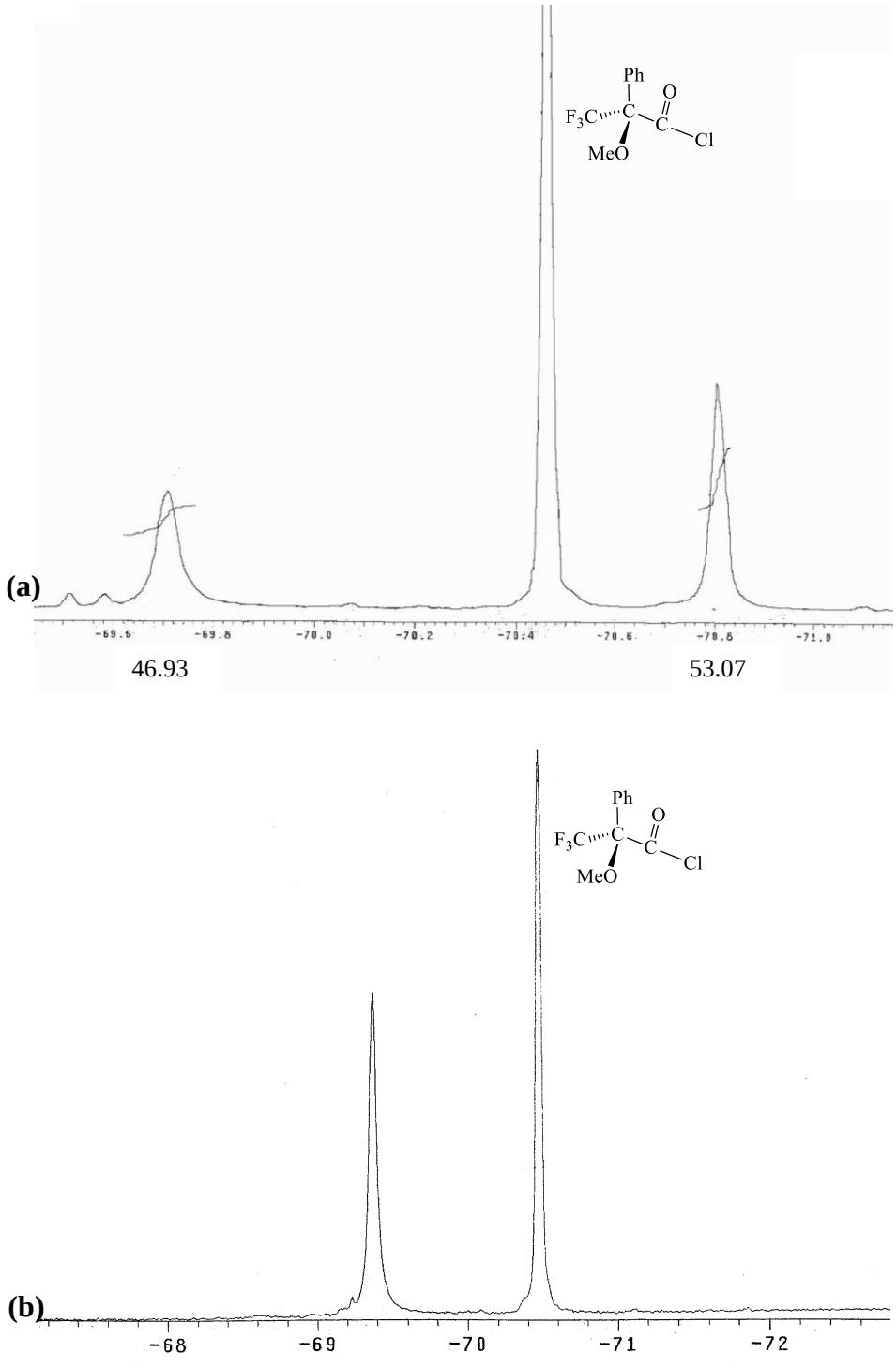


Fig. S9. ^{19}F NMR spectrum in $CDCl_3$ at 70 ºC of Mosher adduct from pyrrolidine **17**. (a) racemic product. (b) isolated with 99% ee in entry 12.

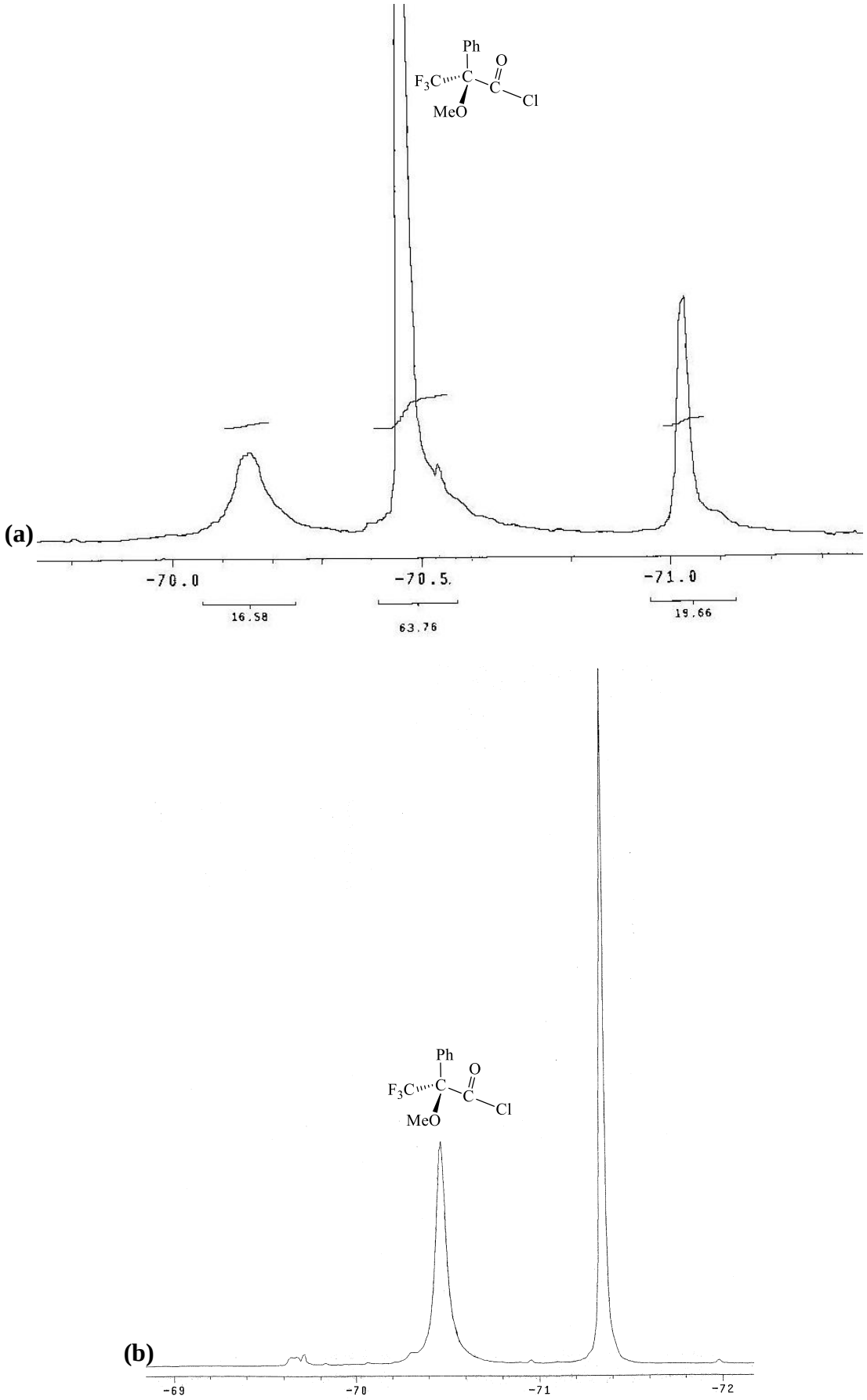


Fig. S10. ^{19}F NMR spectrum in $CDCl_3$ at 70 ºC of Mosher adduct from pyrrolidine **18.** (a) racemic product. (b) isolated with 93% ee in entry 14.

REFERENCES

(1) D. V. Gribkov, K. C. Hultzsch, F. Hampel, *Chem. Eur. J.*, 2003, **9**, 4796–4810; *(b)* D. V. Gribkov, K. C. Hultzsch, F. Hampel, *J. Am. Chem. Soc*., 2006, **128**, 3748–3759.