The Electronic Role of 3-Iminophosphine Ligands in Palladium-Catalyzed Intermolecular Hydroamination

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Supporting Information

I. Kinetic data and reaction rate determinations

Reaction order in amine: Pyrrolidine (0.25, 0.50 or 1.0 mmol) was added to a mixture of benzene (0.5 mmol), C_6D_6 (800 µl) and **3c** (0.025 mmol)**,** followed by addition of cyclohexylallene (0.50 mmol). ^{1}H NMR spectra were recorded every 2 minutes with the temperature preset to 25 ^{o}C.

[Pyrrolidine] M	Trial 1 (h^{-1})	Trial 2 (h^{-1})
0.28	0.0721	0.0866
0.55	0.1262	0.1366
1.09	0.2714	0.2375

Table S1. k_{obs} determined by initial rate method for different [pyrrolidine].

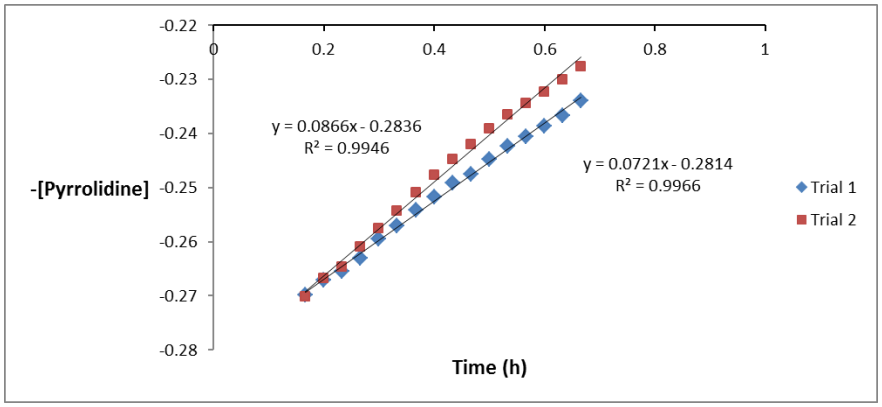


Figure S1. k_{obs} obtained for 0.28 M pyrrolidine.

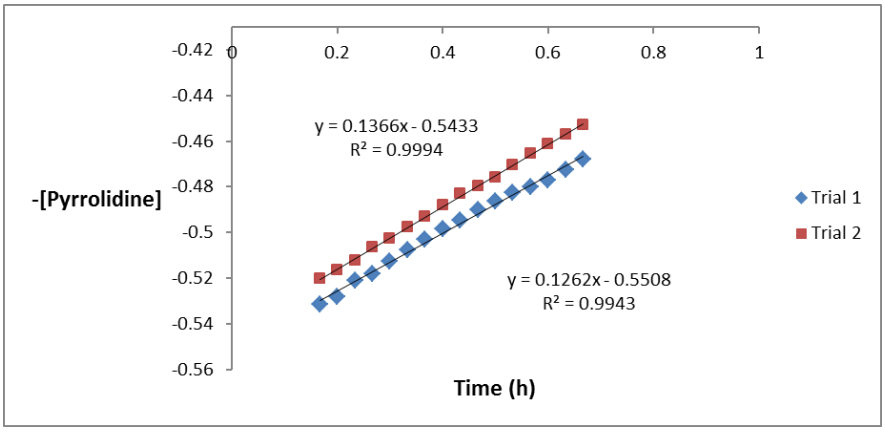


Figure S2. k_{obs} obtained for 0.55 M pyrrolidine.

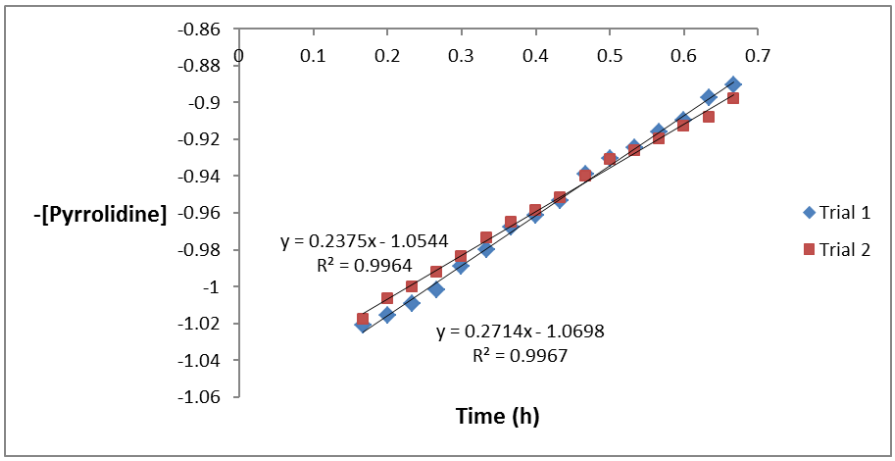


Figure S3. k_{obs} obtained for 1.09 M pyrrolidine.

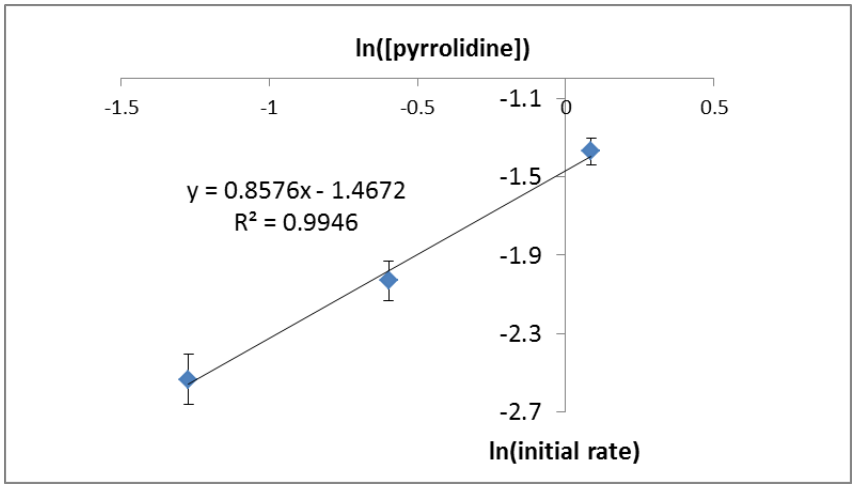


Figure S4. Plot of ln(initial rate) versus ln([pyrrolidine]).

Reaction order in cyclohexylallene: Pyrrolidine (0.50 mmol) was added to a mixture of benzene (0.50 mmol) in 800 µl of C_6D_6 containing **3c** (0.025 mmol)**,** followed by addition of 0.025, 0.50 and 1.0 mmol cyclohexylallene in separate experiments. ^{1}H NMR data was collected every two minutes with temperature preset to 25 ^{o}C.

[Allene] M	Trial 1 (h^{-1})	Trial 2 (h^{-1})
0.29	0.1145	0.1281
0.55	0.1262	0.1366
1.01	0.1362	0.1308

Table S2. k_{obs} determined by initial rate method for different [cyclohexylallene].

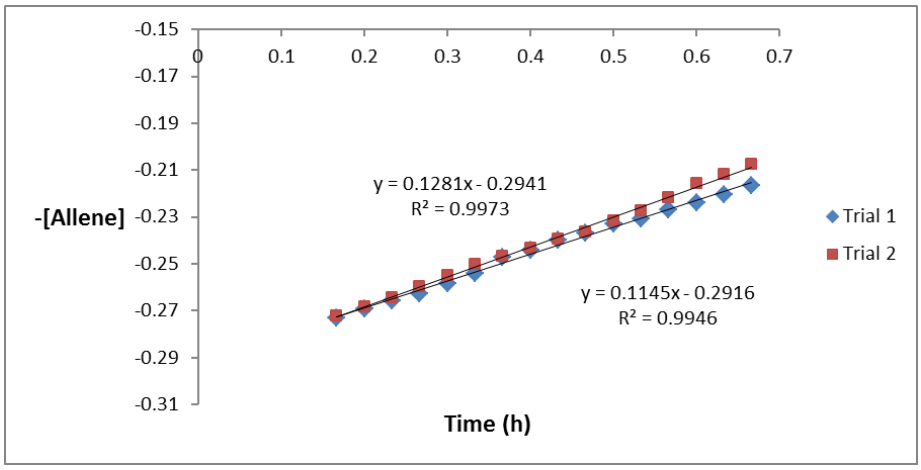


Figure S5. k_{obs} obtained for 0.29 M cyclohexylallene.

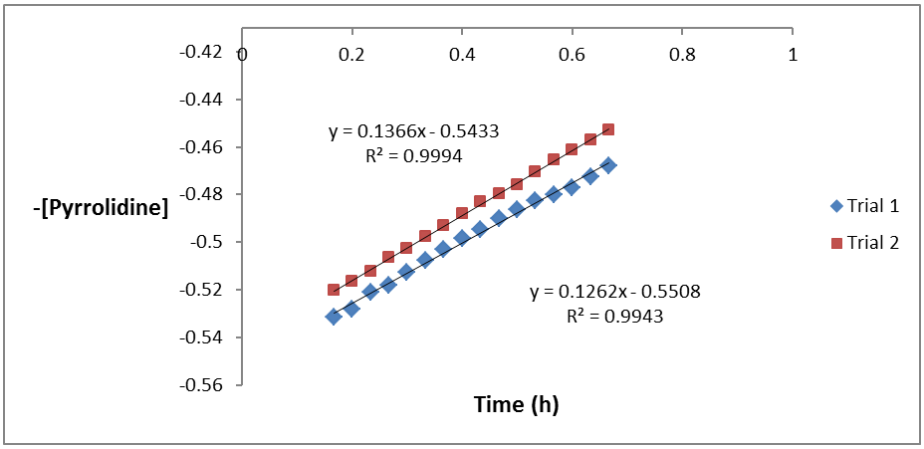


Figure S6. k_{obs} obtained for 0.55 M cyclohexylallene.

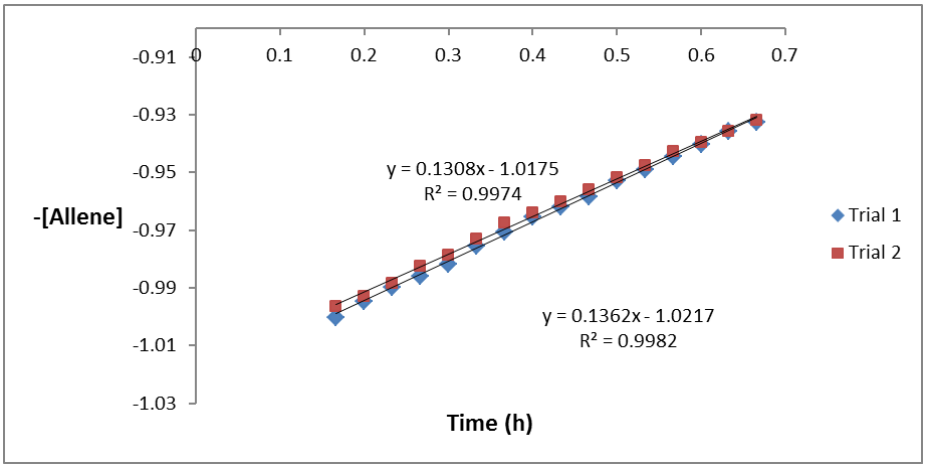


Figure S7. k_{obs} obtained for 1.01 M cyclohexylallene.

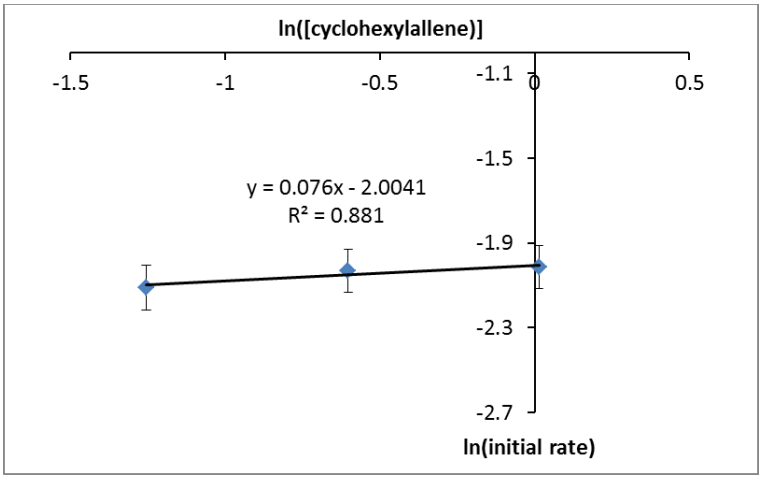


Figure S8. Plot of ln(initial rate) versus ln([allene]).

Catalytic reaction in the presence of triethylamine

It was observed that at long reaction times, first order kinetic plots showed deviation from linearity (Figure S9). This was attributed to competitive inhibition by the product (tertiary amine) that can reversibly coordinate to the catalyst. To test this hypothesis, the hydroamination reaction of cyclohexylallene and pyrrolidine catalyzed by **3d** was performed in the presence of 1 equiv. of triethylamine (0.5 mmol) and the rate constant was determined and compared to the rate constant of the reaction without triethylamine (0.0423 versus 0.2217 h^{-1}, Figure S10). The decreased rate constant suggests that reversible coordination of triethylamine competes with coordination of secondary amine and slows the catalytic reaction.

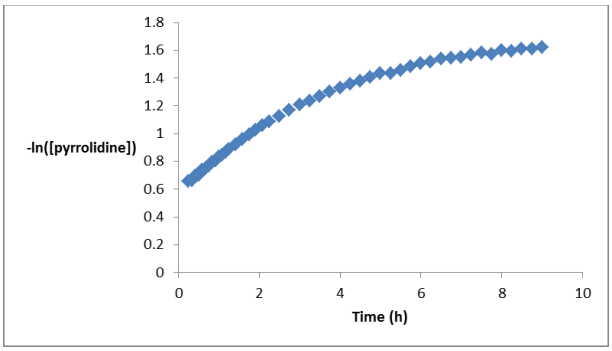


Figure S9. Plot of ln([pyrrolidine]) vs. time for 9 hours of reaction using **3d**.

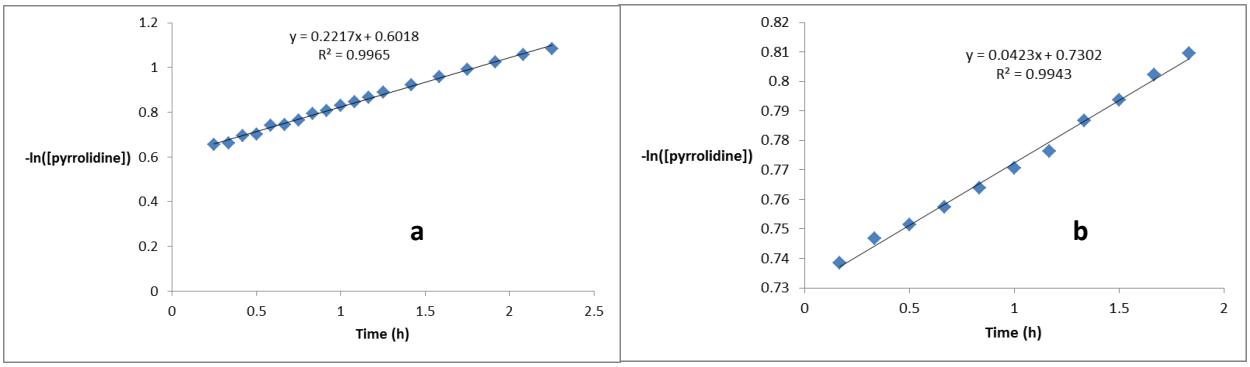


Figure S10. Hydroamination reactions of pyrrolidine catalyzed by **3d**, **a)** under catalytic conditions **b)** in presence of triethylamine (1 equiv.).

This deviation occurs in all of the reported catalytic reactions; therefore, early time points were utilized for rate constant determination. This will have a slight effect on the calculated values for rate constants. However, even when using different maximum time for plotting first order kinetics and determining the rate constant, it was observed that the new values of the rate constant still follow the same trend in the Hammett plot (See the next section for catalytic reactions of piperidine).

Rate of hydroamination reactions with catalysts 3a-f for pyrrolidine:

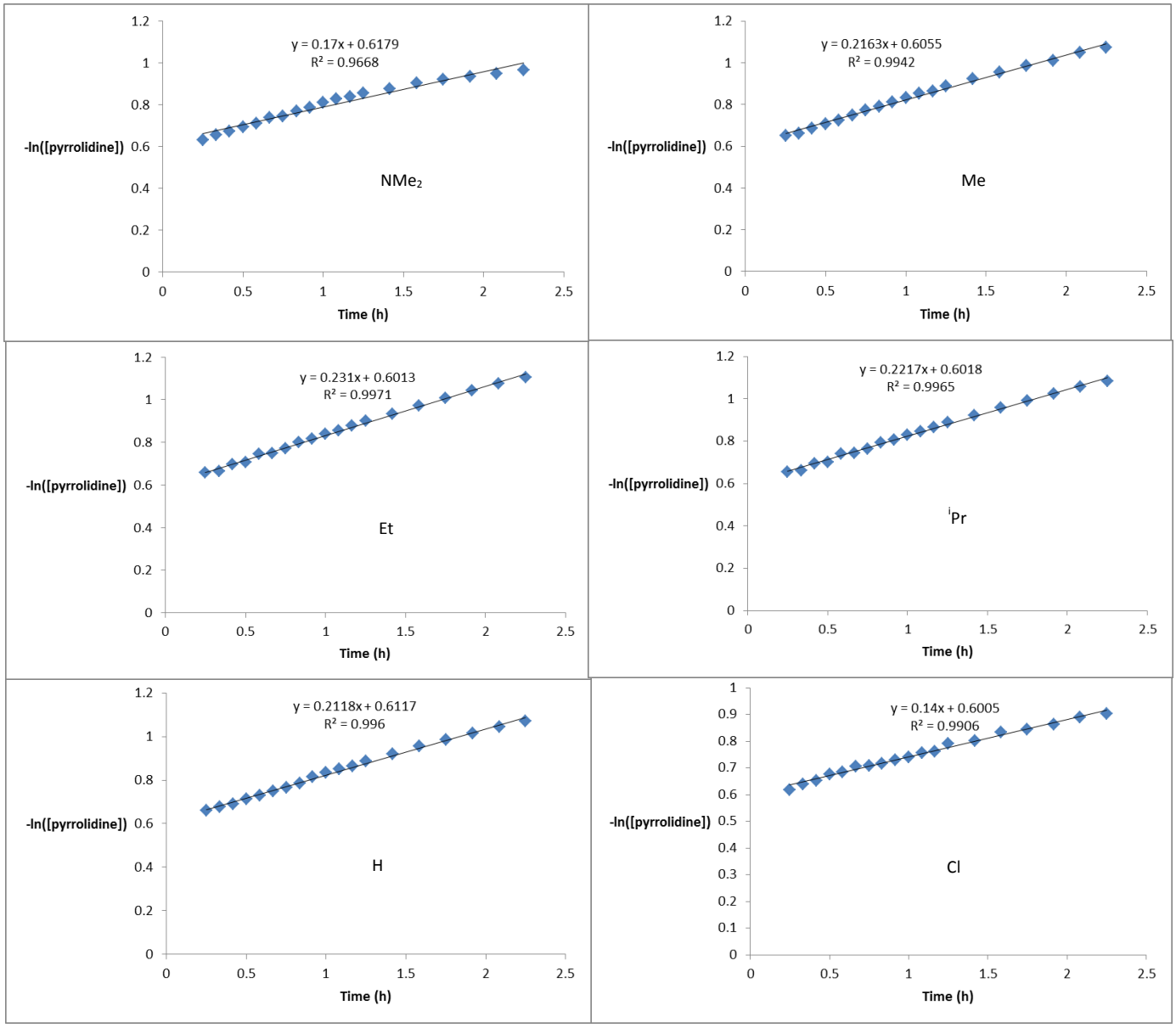


Figure S11. Plots of –ln([pyrrolidine]) versus time in hydroamination of cyclohexylallene with pyrrolidine, with the slope representing rate constant (h^{-1}).

Rate of hydroamination reactions with catalysts 3a-f for piperidine (1.2 h):

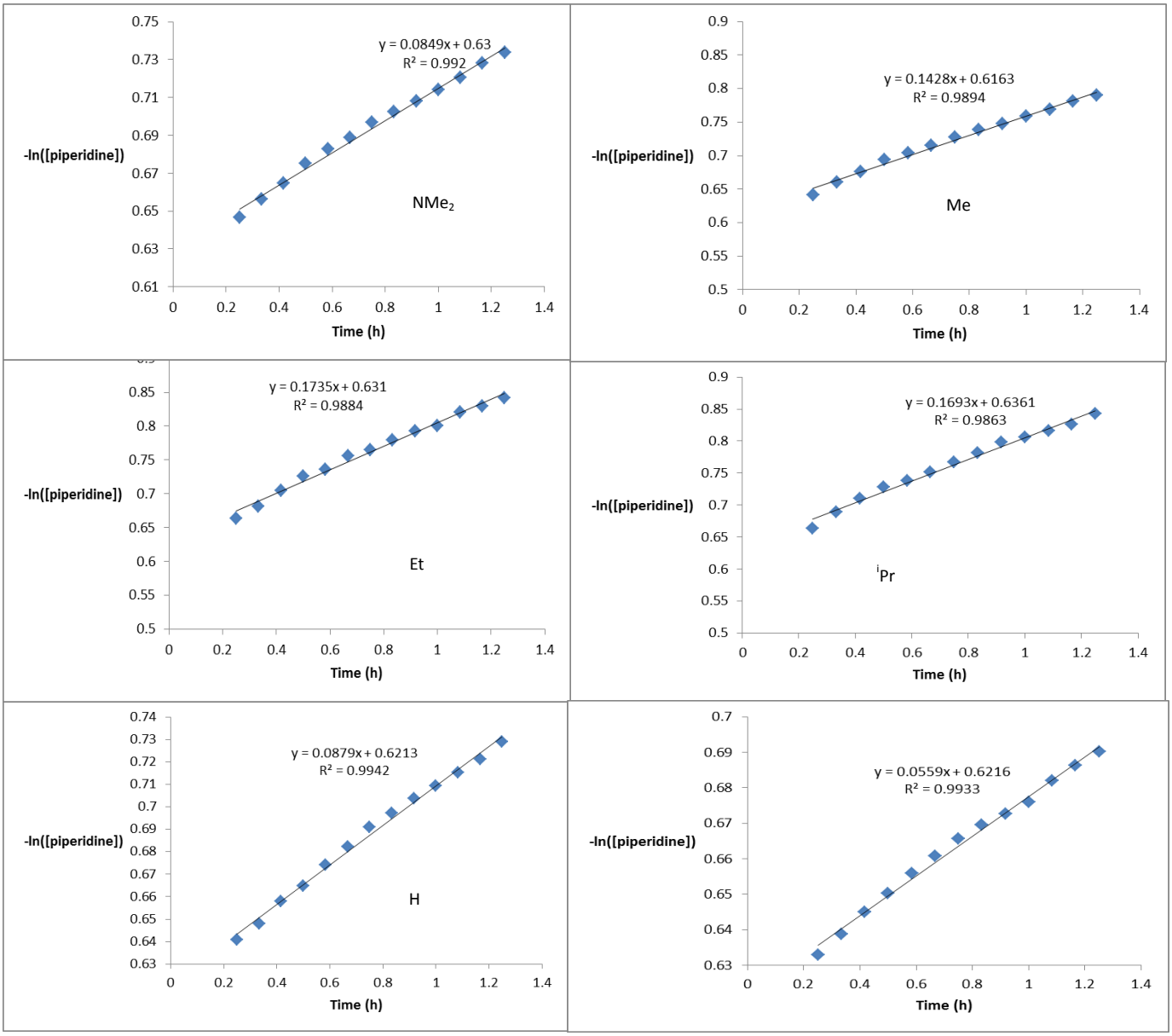


Figure S12. Plots of –ln([piperidine]) versus time in hydroamination of cyclohexylallene with piperidine, with the slope representing rate constant (h^{-1}).

Rate of hydroamination reactions with catalysts 3a-f for piperidine (0.8 h):

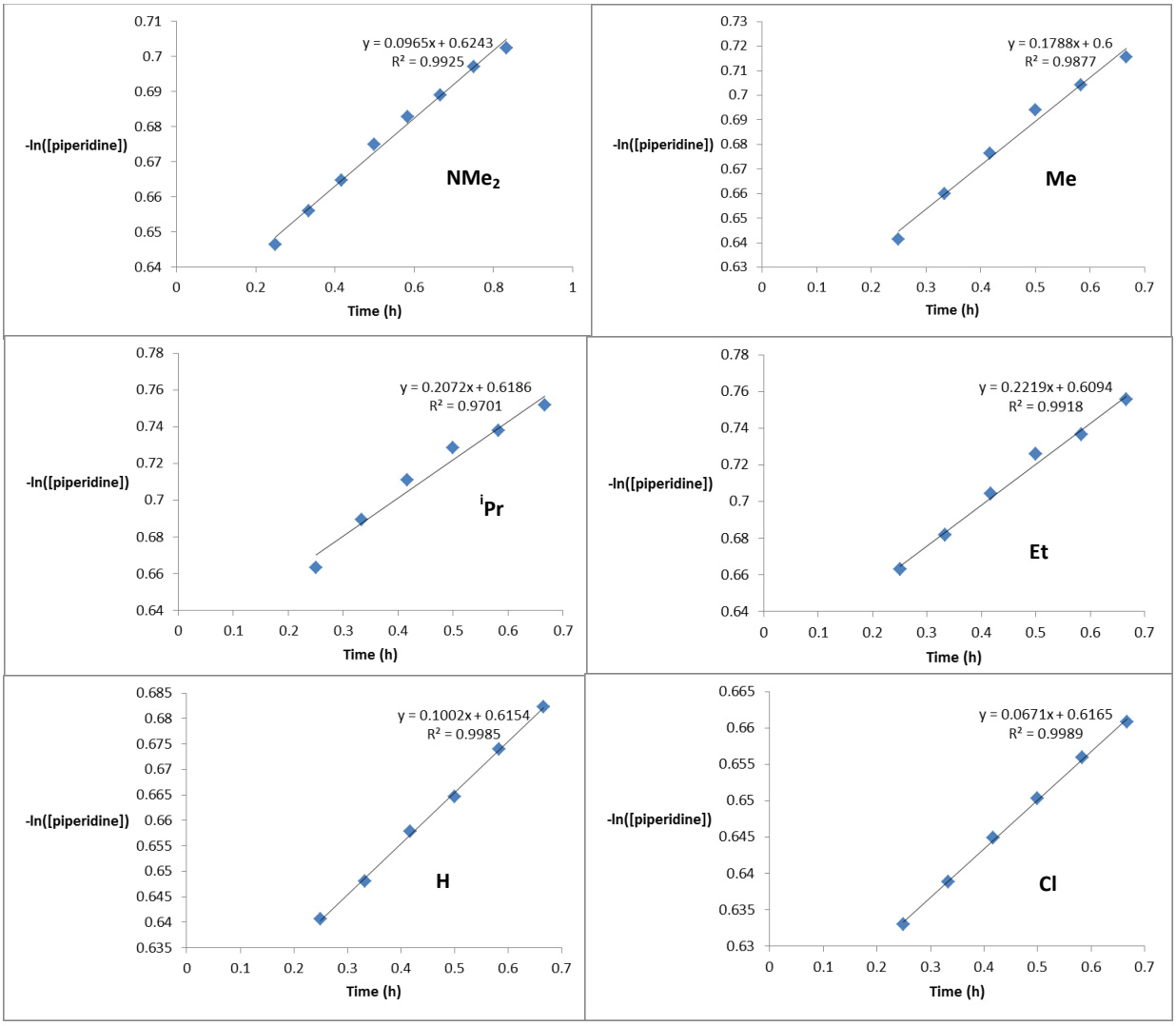


Figure S13. Plots of –ln([piperidine]) versus time in hydroamination of cyclohexylallene with piperidine, with the slope representing rate constant (h^{-1}).

Rate of hydroamination reactions with catalysts 3a-f for morpholine:

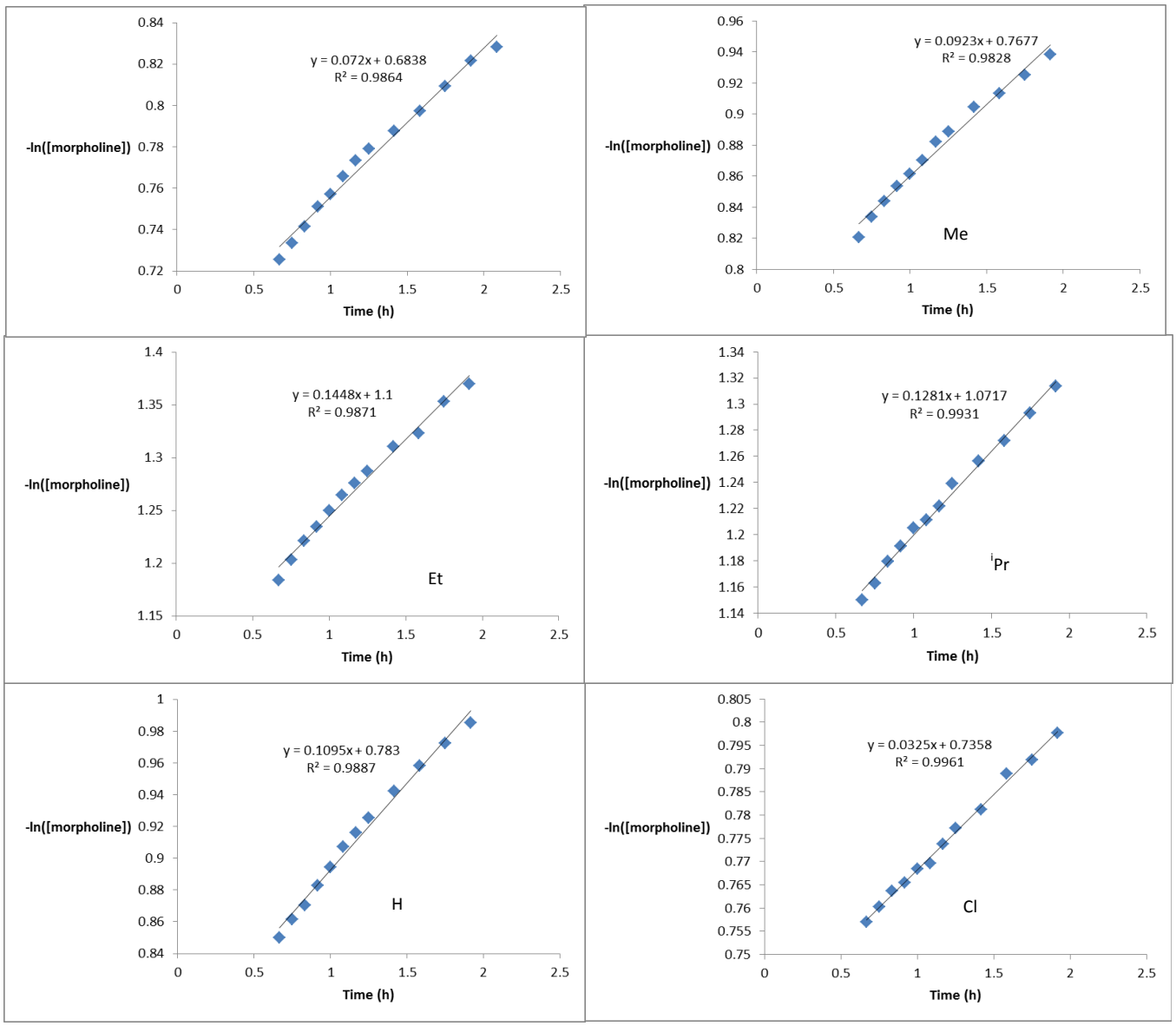
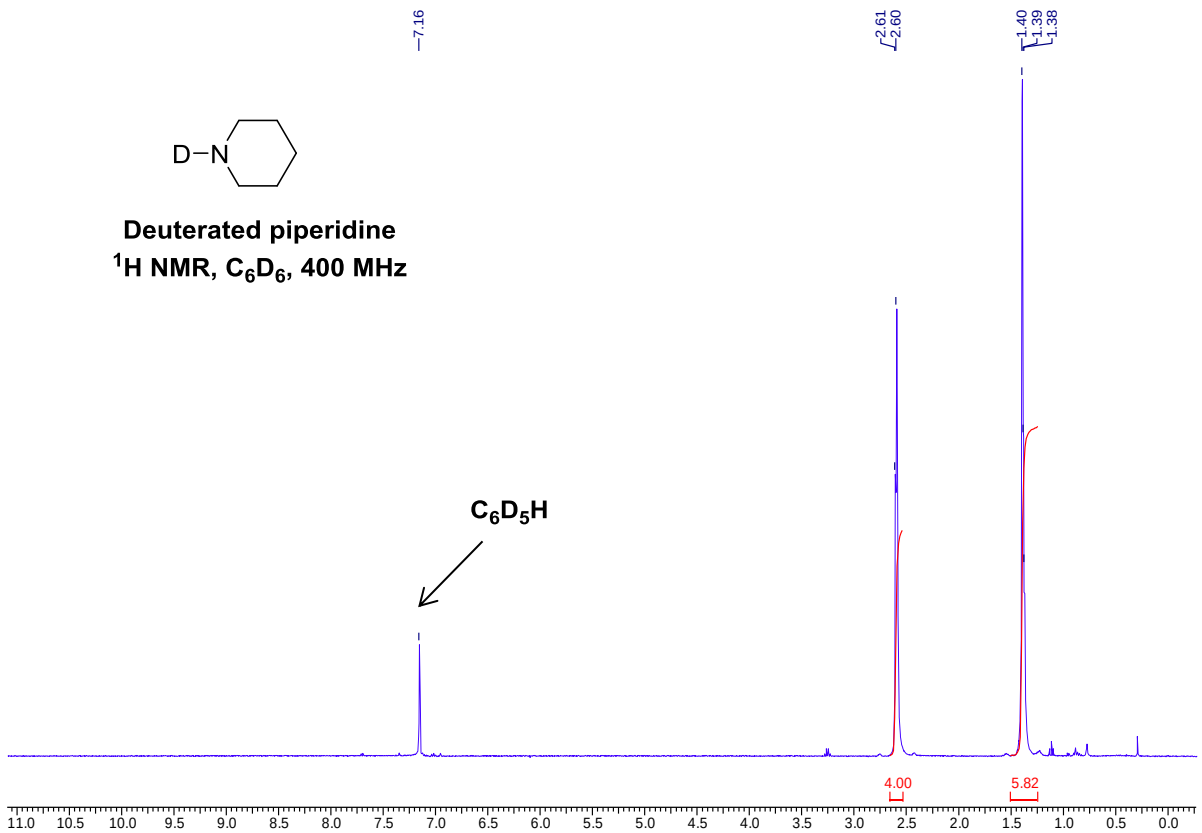


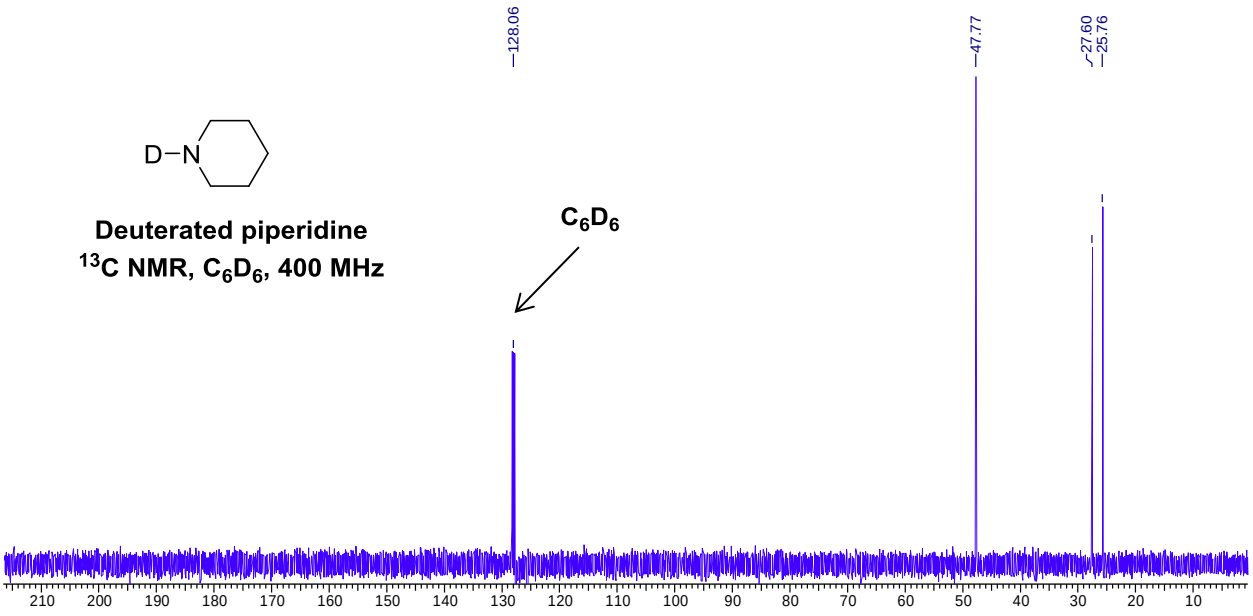
Figure S14. Plots of –ln([morpholine]) versus time in hydroamination of cyclohexylallene with morpholine, with the slope representing rate constant (h^{-1}).

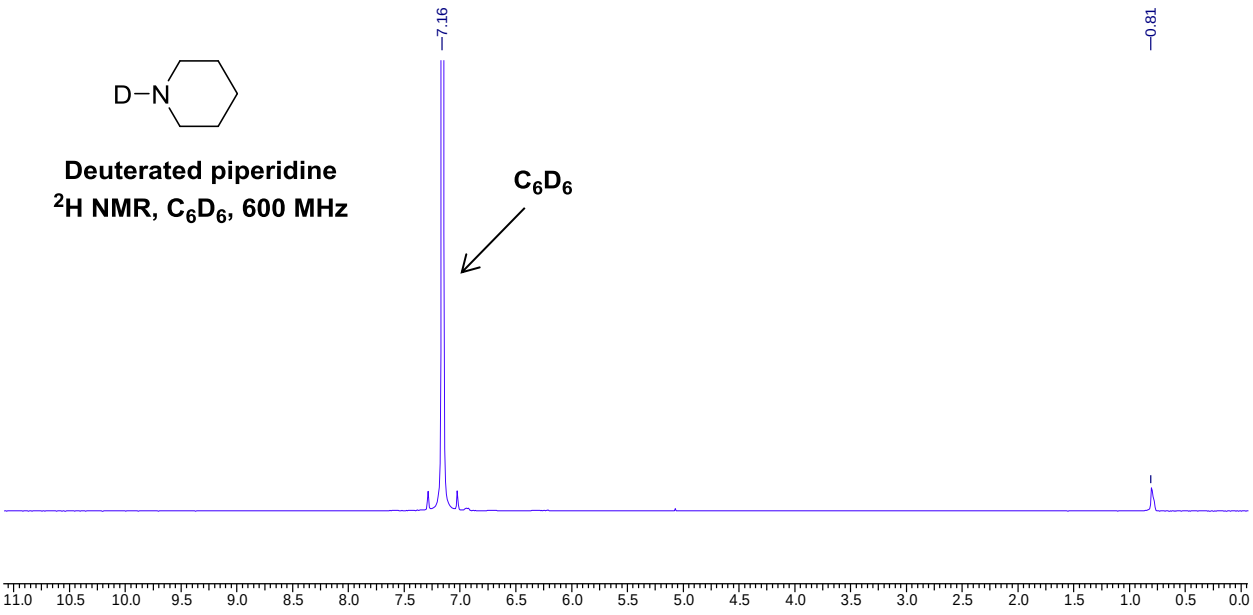
II. Characterization and spectral data

Piperidine-d_1: To a solution of piperidine in diethylether (previously dried over $MgSO_4$ and degassed by passing nitrogen through the solution) was added n-butyllithium (0.9 eq.) at 0 ^oC. The reaction was warmed to ambient temperature and stirred for 4h. This was then concentrated and stored in the freezer at -21 ^oC overnight. The lithiated piperidine precipitated as a white solid from the concentrated solution. The supernatant was filtered and the solid compound was washed with pentane to remove unreacted piperidine. The lithiated piperidine was dissolved in the minimum amount of diethylether and deuterium oxide (1.1 eq.) was added while the reaction flask was cooled in an ice bath at 0 ^oC. The product piperidine-d_1 was extracted into pentane (3 times), dried over calcium hydride, freeze-pump-thawed three times and solvent was removed under vacuum (at 0 ^oC) before transferring to the glovebox for further usage. Colorless liquid, yield: 79%; ^1H NMR (C_6D_6) δ 2.69-2.59 (m, 4H), 1.41-1.37 (m, 6H)**;** $^{13}C\{^1H\}$ NMR (C_6D_6) δ 47.8, 27.6, 25.8; ^2H NMR (C_6D_6) δ 0.81.

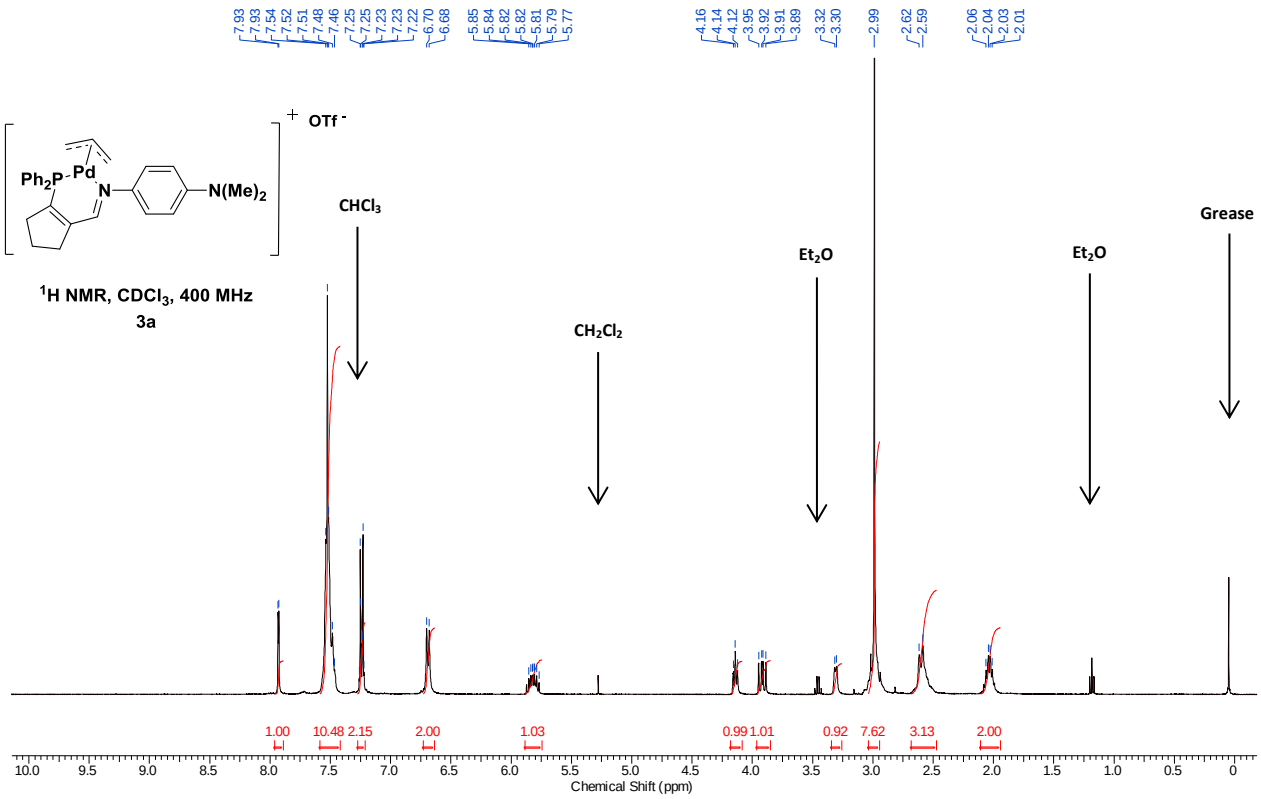
NMR spectra for deuterated piperidine:

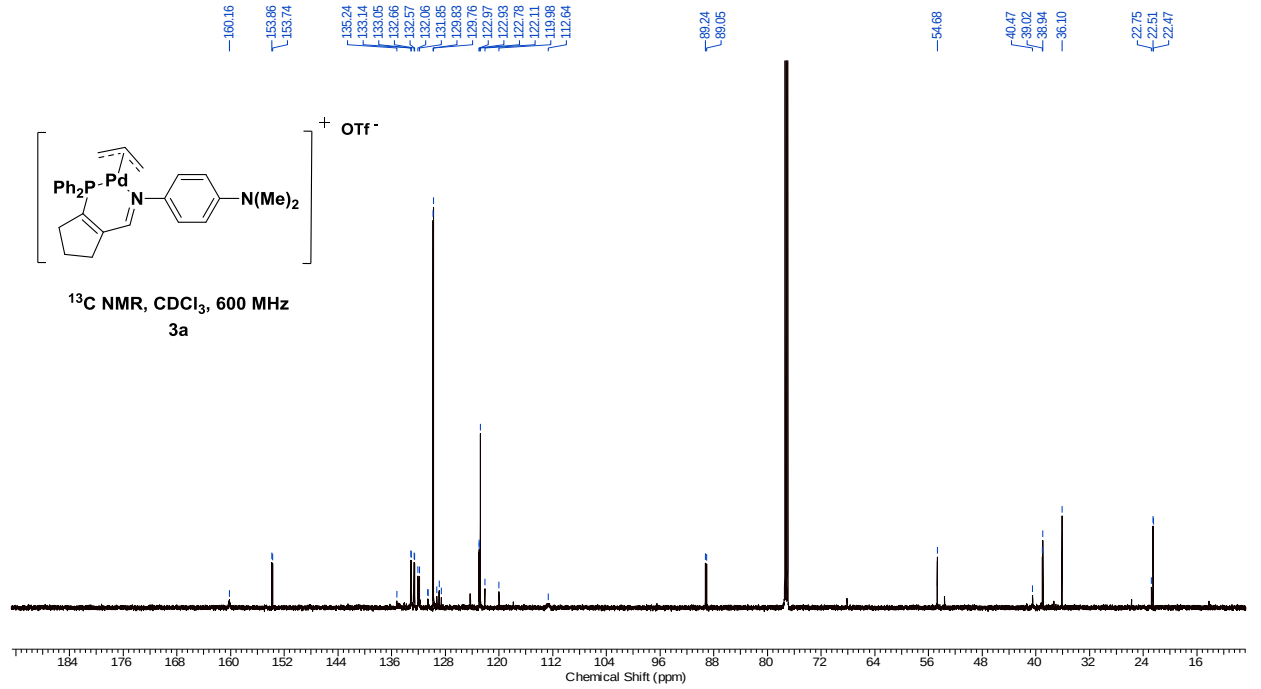


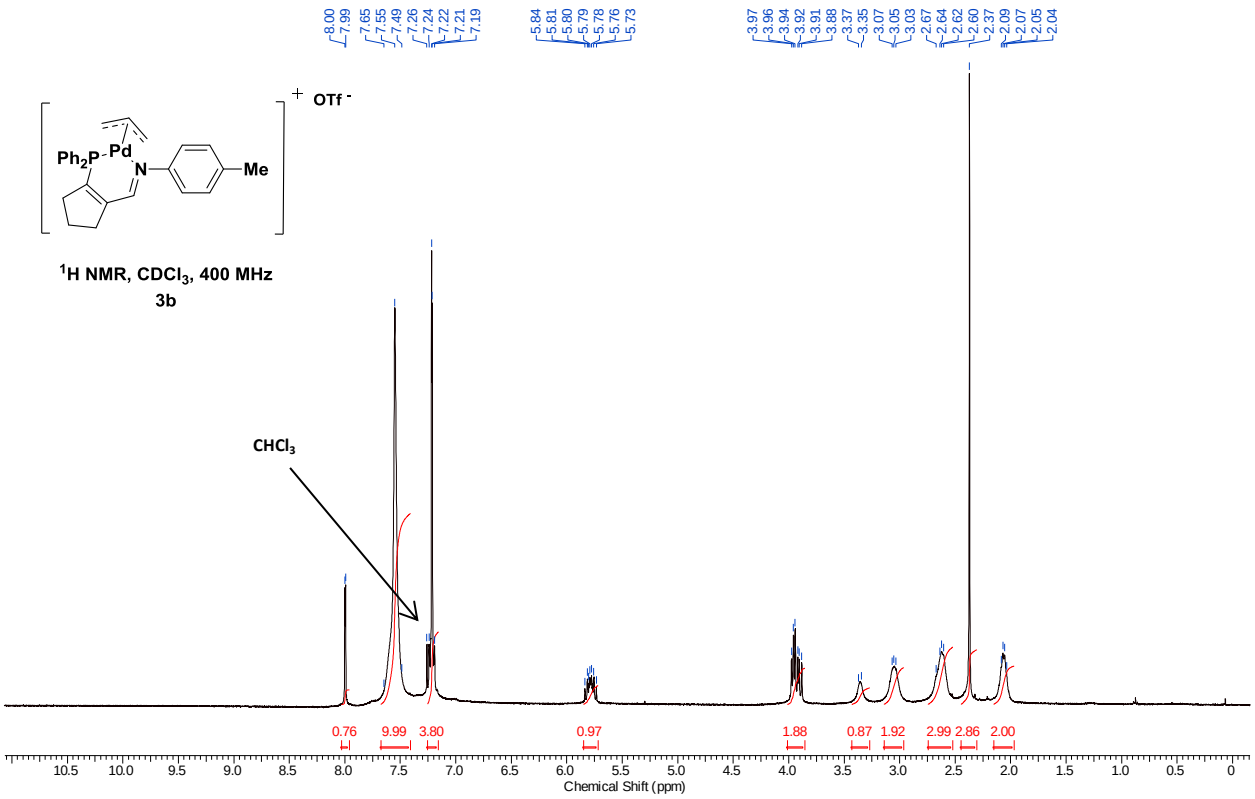

128.06
47.77
27.60
25.76
D–N
Deuterated piperidine
^{13}C NMR, C_6D_6, 400 MHz
C_6D_6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10


7.16
0.81
D–N
Deuterated piperidine
^{2}H NMR, C_6D_6, 600 MHz
C_6D_6
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

^{1}H and ^{13}C NMR of complexes (3a-f):



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5.80
5.79
5.78
5.76
5.73
3.97
3.96
3.94
3.92
3.91
3.88
3.37
3.35
3.07
3.05
3.03
2.67
2.64
2.62
2.60
2.37
2.09
2.07
2.05
2.04
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Ph2P-Pd
N
Me
1H NMR, CDCl3, 400 MHz
3b
CHCl3
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0.97
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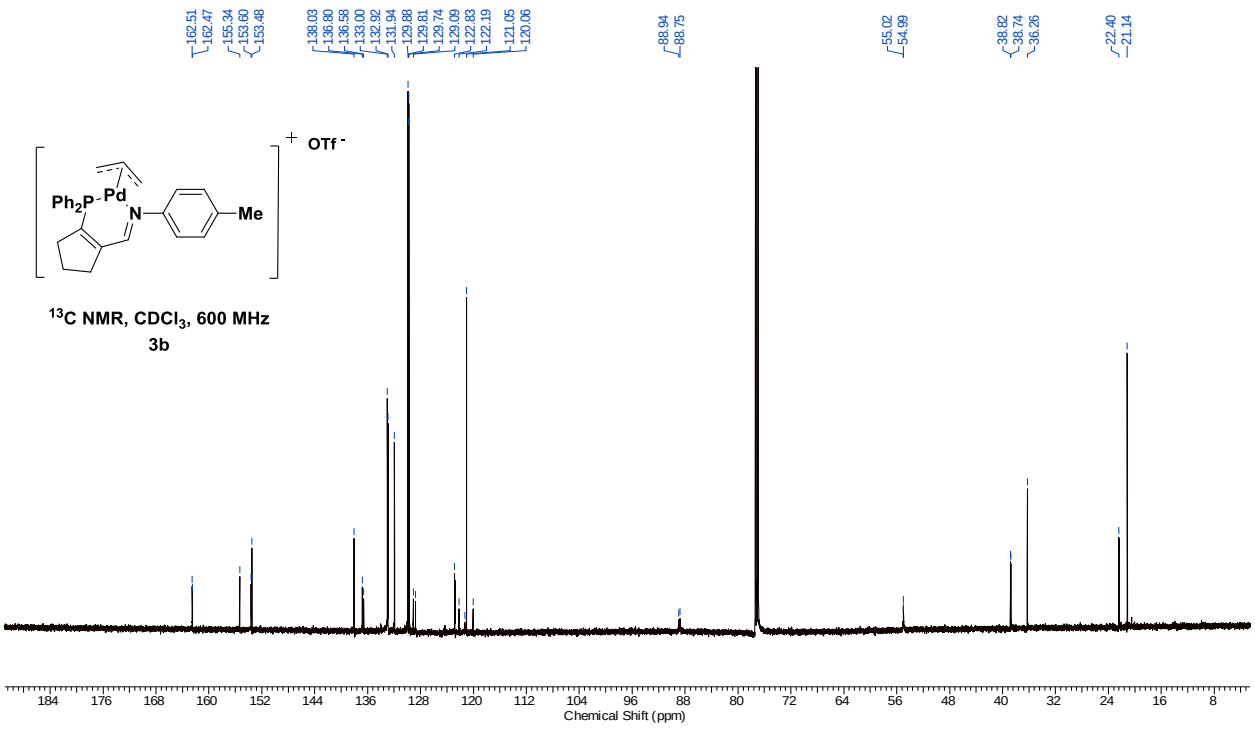
0.87
1.92
2.99
2.86
2.00
Chemical Shift (ppm)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121.05
120.06
88.94
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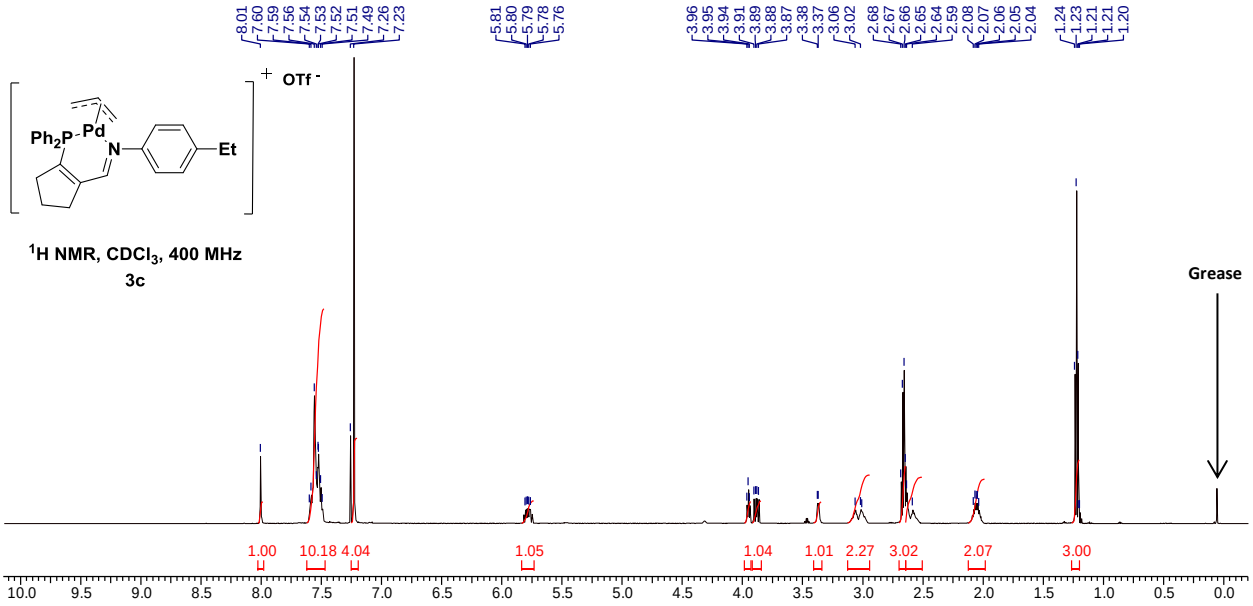
Me
13C NMR, CDCl3, 600 MHz
3b
Chemical Shift (ppm)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2.05
2.04
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1.23
1.21
1.21
1.20
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Ph2P-Pd
N
Et
1H NMR, CDCl3, 400 MHz
3c
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4.04
1.05
1.04
1.01
2.27
3.02
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3.00
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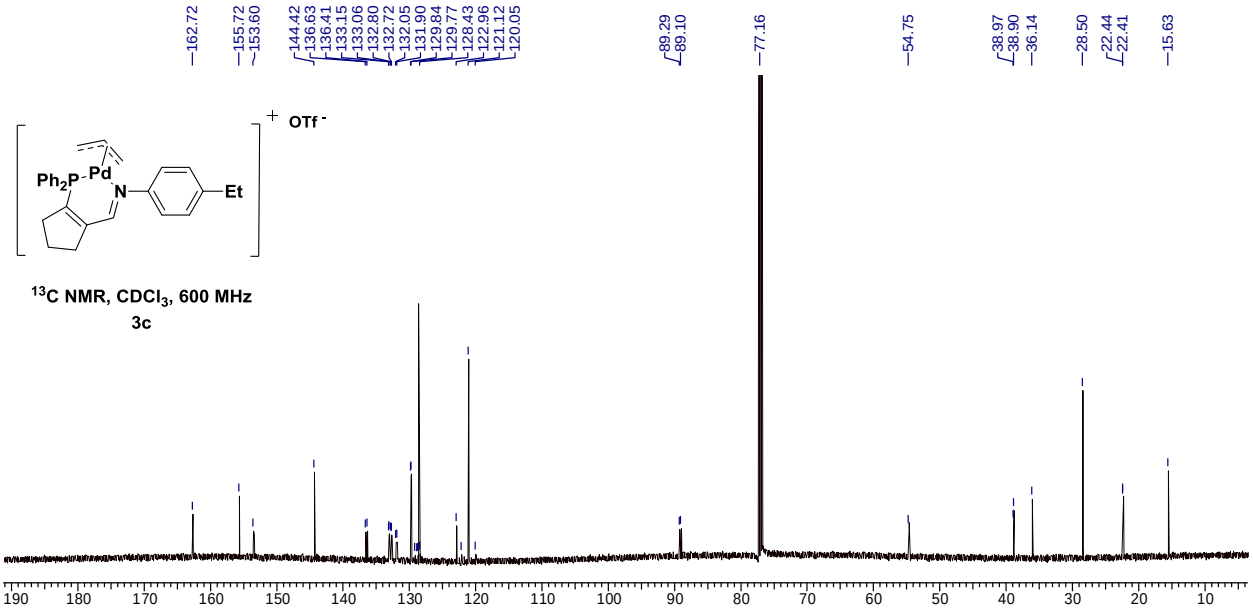
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28.50
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22.41
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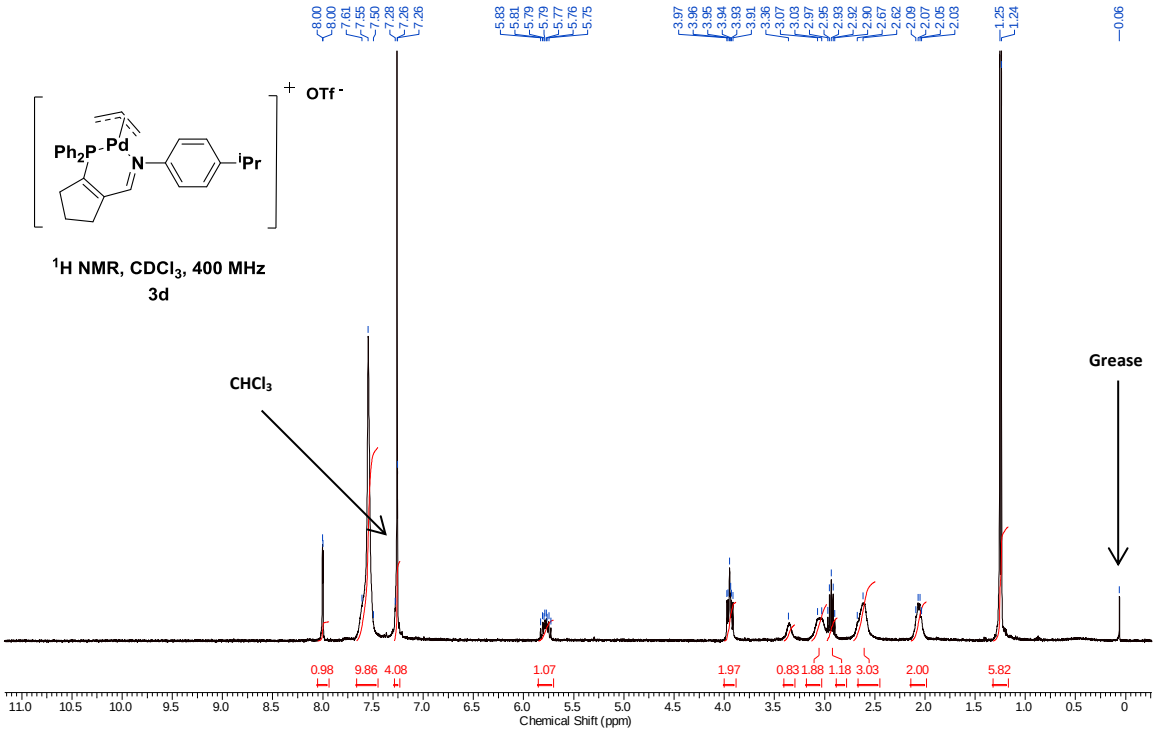
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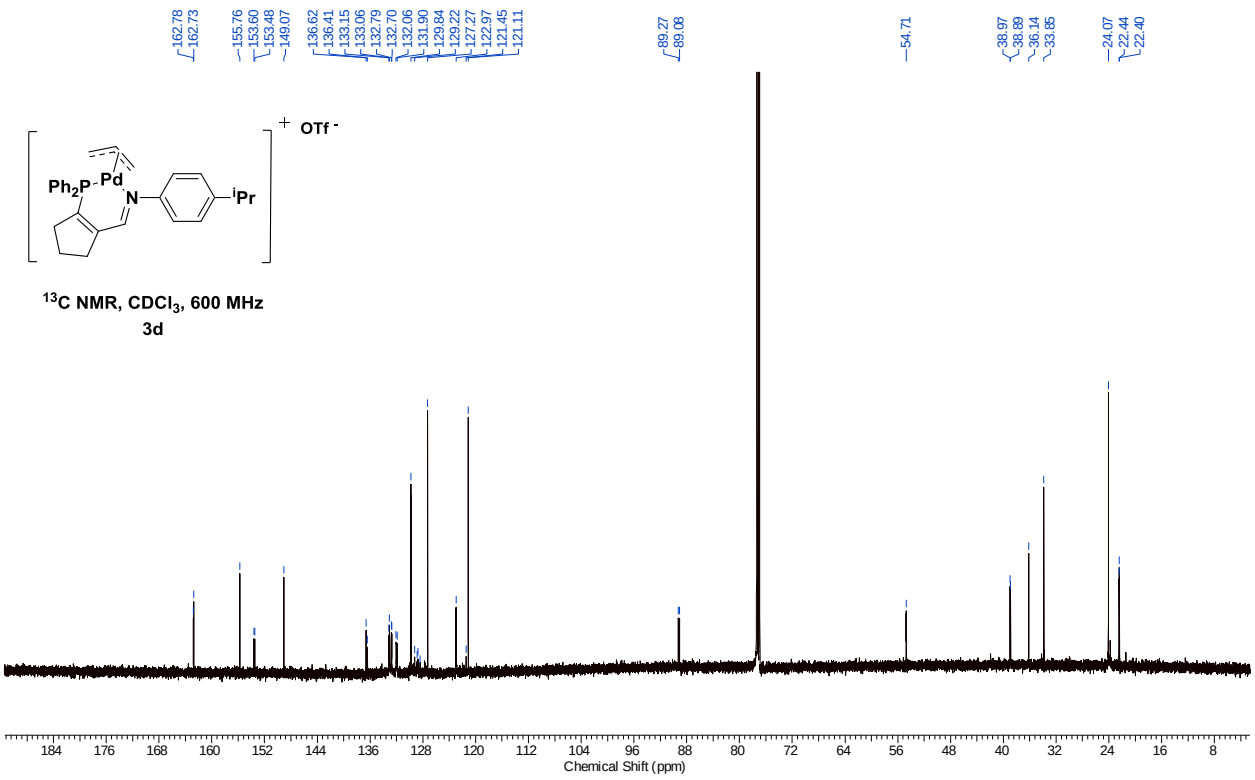
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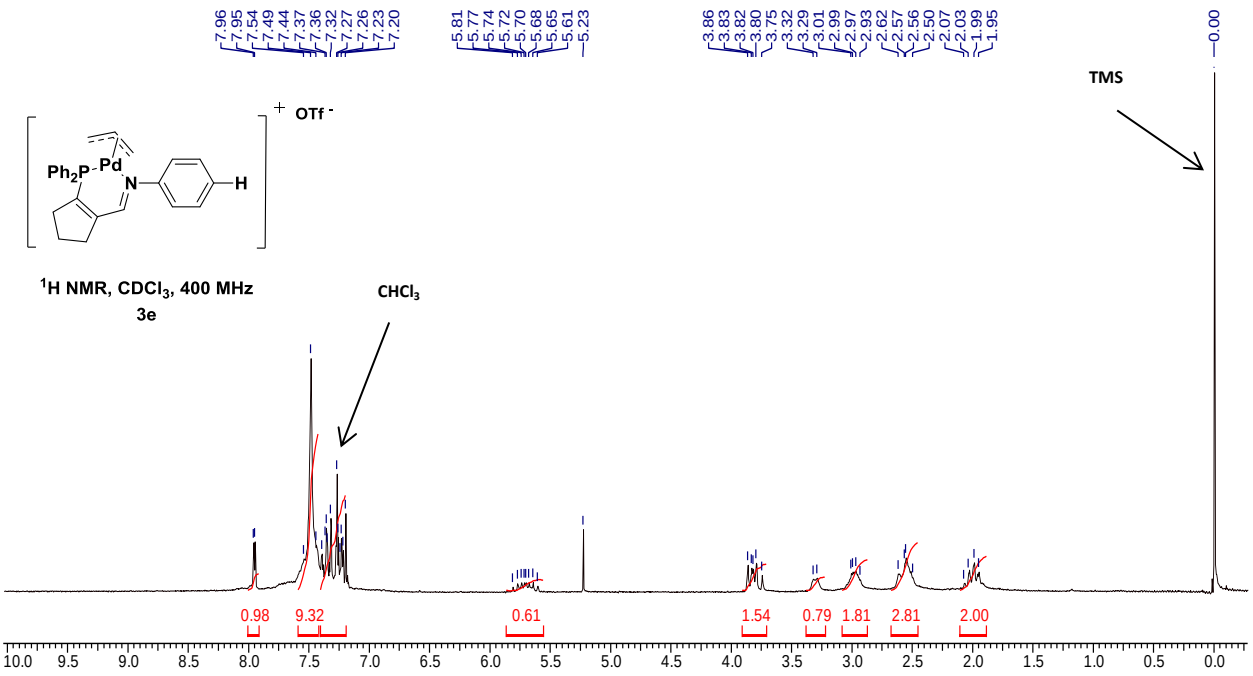
13C NMR, CDCl3, 600 MHz
3d
Chemical Shift (ppm)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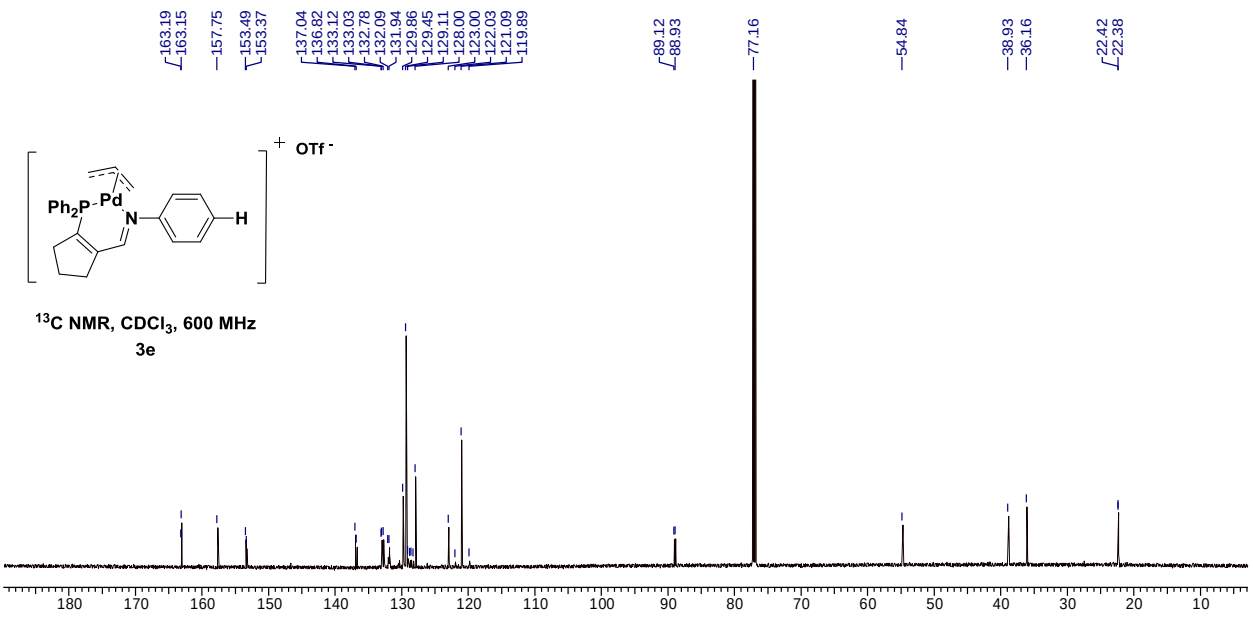
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22.38
OTf -
Ph2P-Pd
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H
13C NMR, CDCl3, 600 MHz
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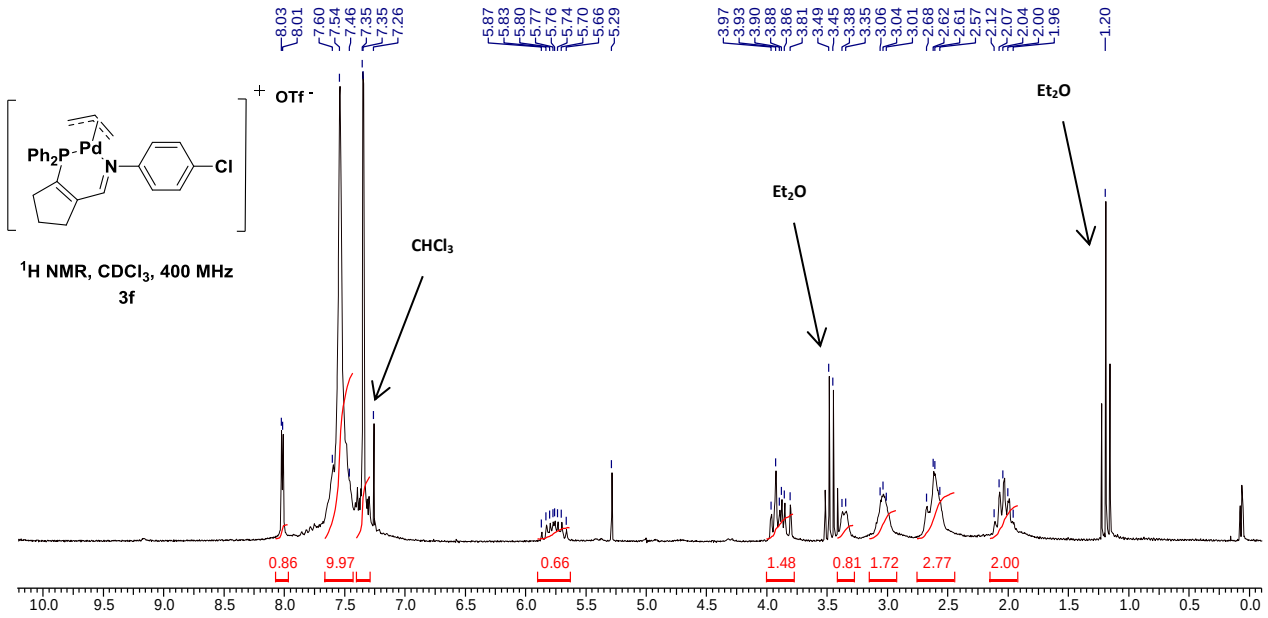
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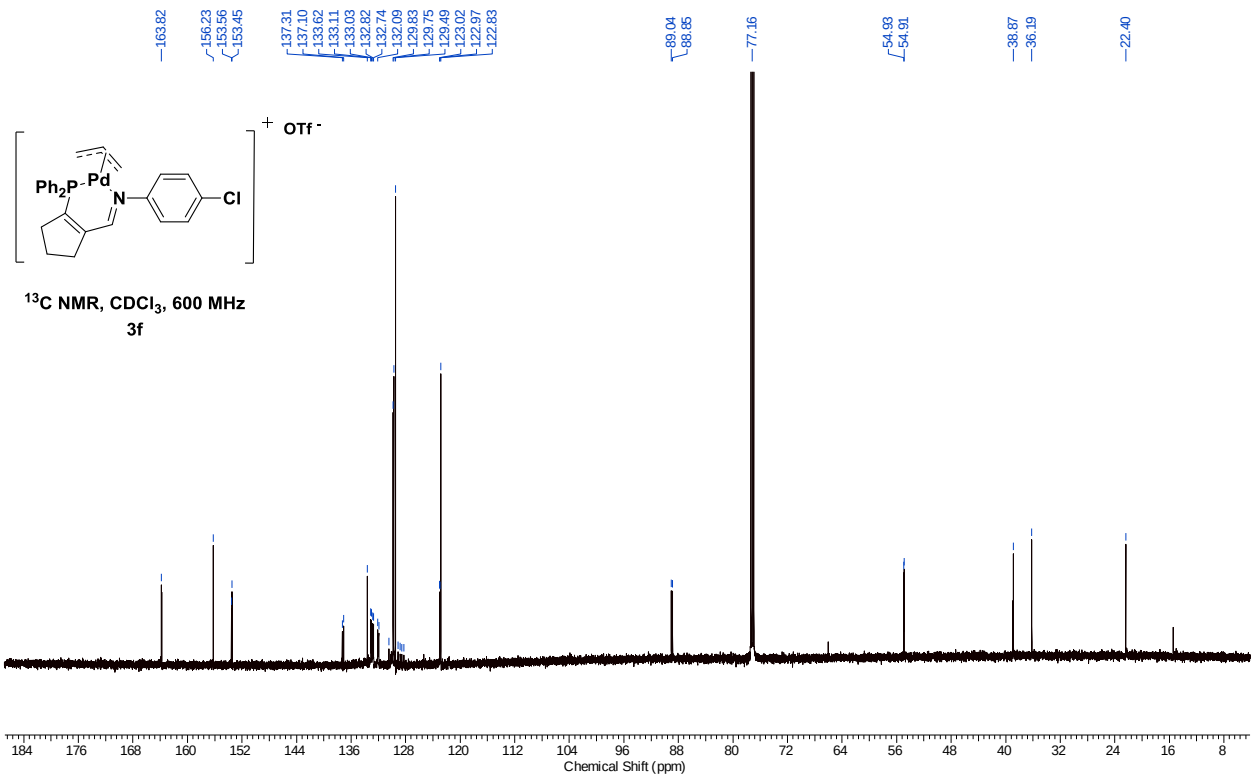
3.90
3.88
3.86
3.81
3.49
3.45
3.38
3.35
3.06
3.04
3.01
2.68
2.62
2.61
2.57
2.12
2.07
2.04
2.00
1.96
1.20
OTf -
Ph2P-Pd
N
Cl
1H NMR, CDCl3, 400 MHz
3f
CHCl3
Et2O
Et2O
0.86
9.97
0.66
1.48
0.81
1.72
2.77
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


163.82
156.23
153.56
153.45
137.31
137.10
133.62
133.11
133.03
132.82
132.74
132.09
129.83
129.75
129.49
123.02
122.97
122.83
89.04
88.85
77.16
54.93
54.91
38.87
36.19
22.40
OTf -
Ph2P-Pd
N
Cl
13C NMR, CDCl3, 600 MHz
3f
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

^{1}H NMR studies of catalyst resting state

To understand the catalyst resting state, catalytic hydroaminations with piperidine catalyzed by **3a**, **3d**, and **3f** were conducted with higher catalyst loading (25 mol%) and ^{1}H NMR was taken at various time points as well as after reaction completion. It was observed that during the catalytic reaction, the imine moiety of the ligand was consistently dissociated from palladium (detected by ^{1}H NMR with the dissociated imine peak appearing near 9.8 ppm in C_6D_6). After reaction completion, the imine was again coordinated to palladium, as noted by the disappearance of the peak at 9.8 ppm (coordination shifts this peak into the aromatic region).

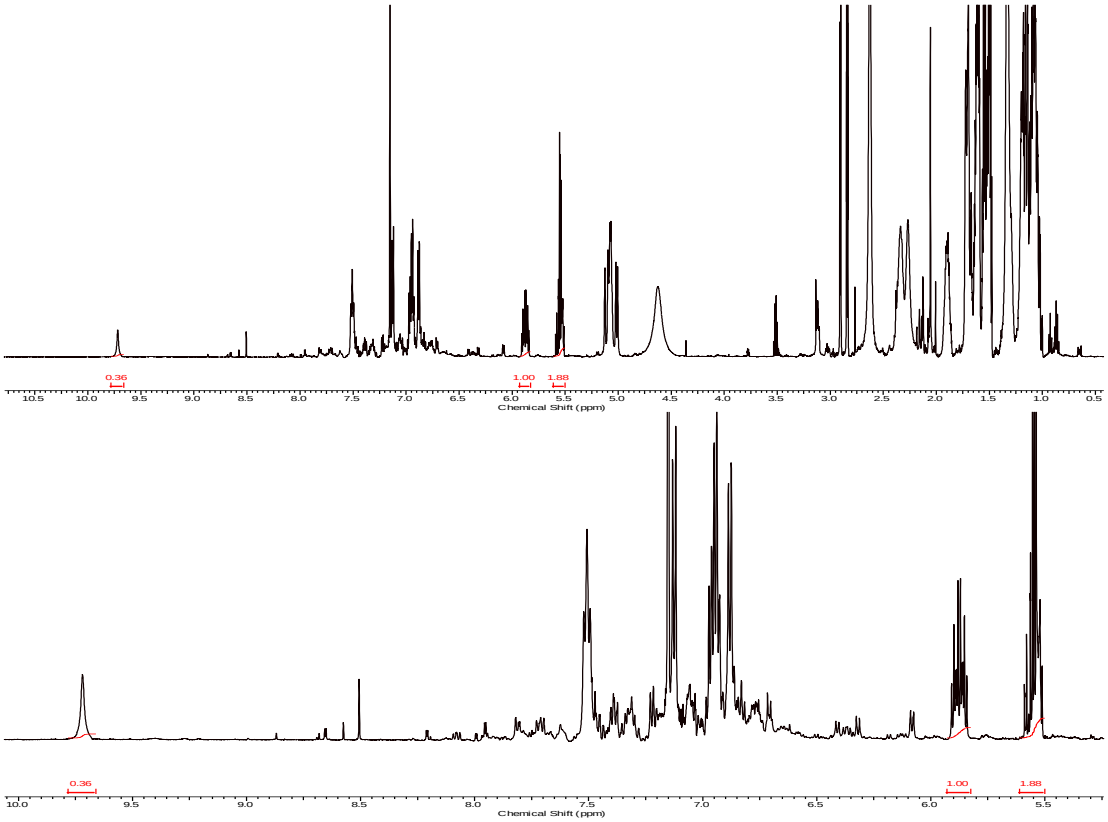


Figure S15. Catalytic hydroamination of cyclohexylallene with piperidine catalyzed by **3a** (25 mol%) after 30 minutes (top: full spectrum; bottom: expanded low field region).

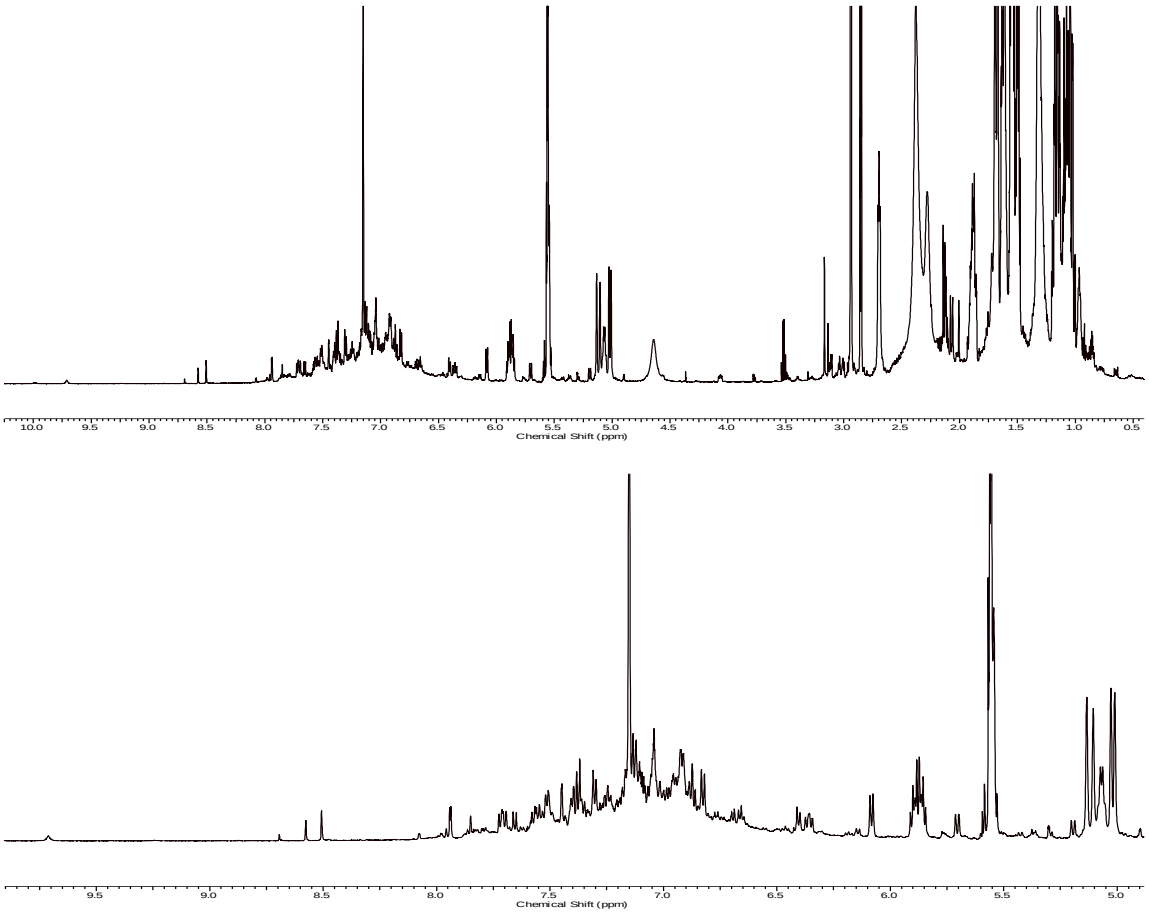
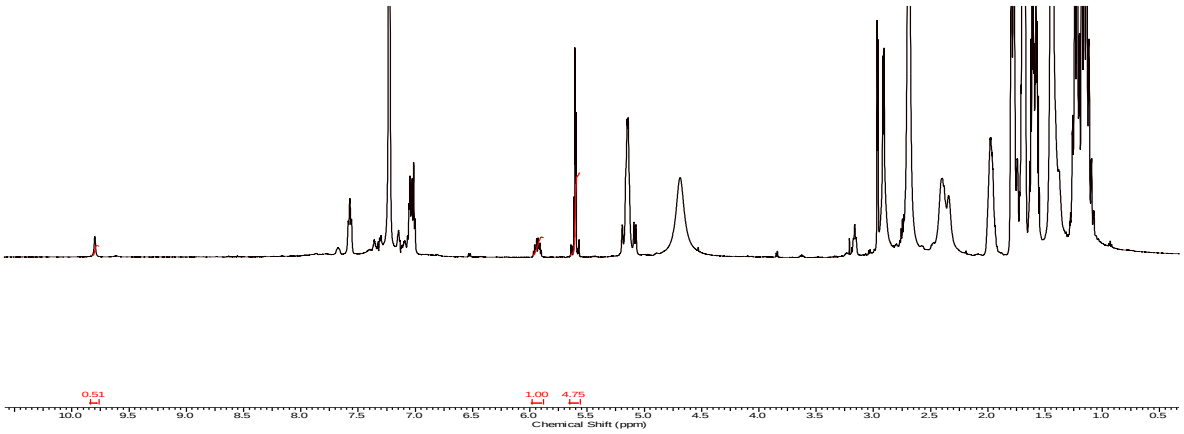


Figure S16. Catalytic hydroamination of cyclohexylallene with piperidine catalyzed by **3a** (25 mol%) after reaction completion (top: full spectrum; bottom: expanded low field region).



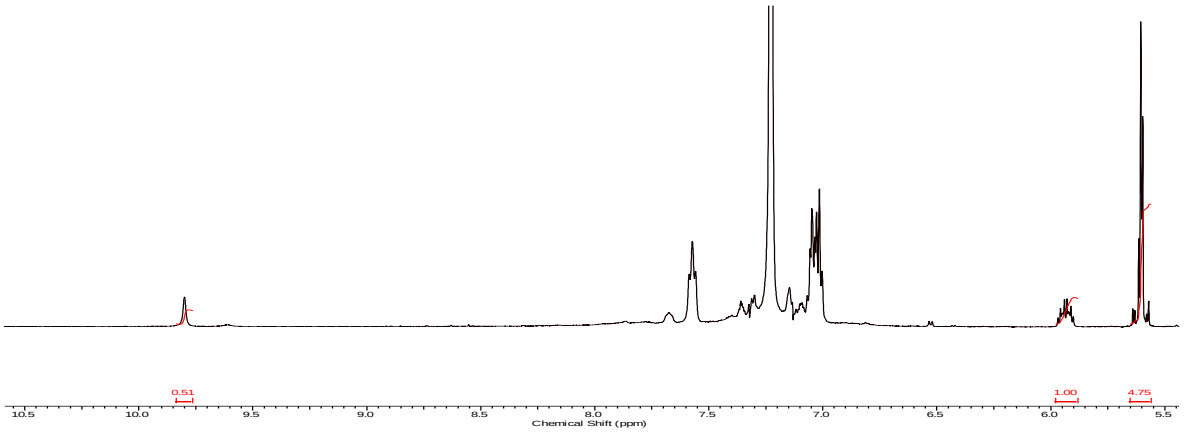


Figure S17. Catalytic hydroamination of cyclohexylallene with piperidine catalyzed by **3d** (25 mol%) after 30 minutes (top: full spectrum; bottom: expanded low field region).

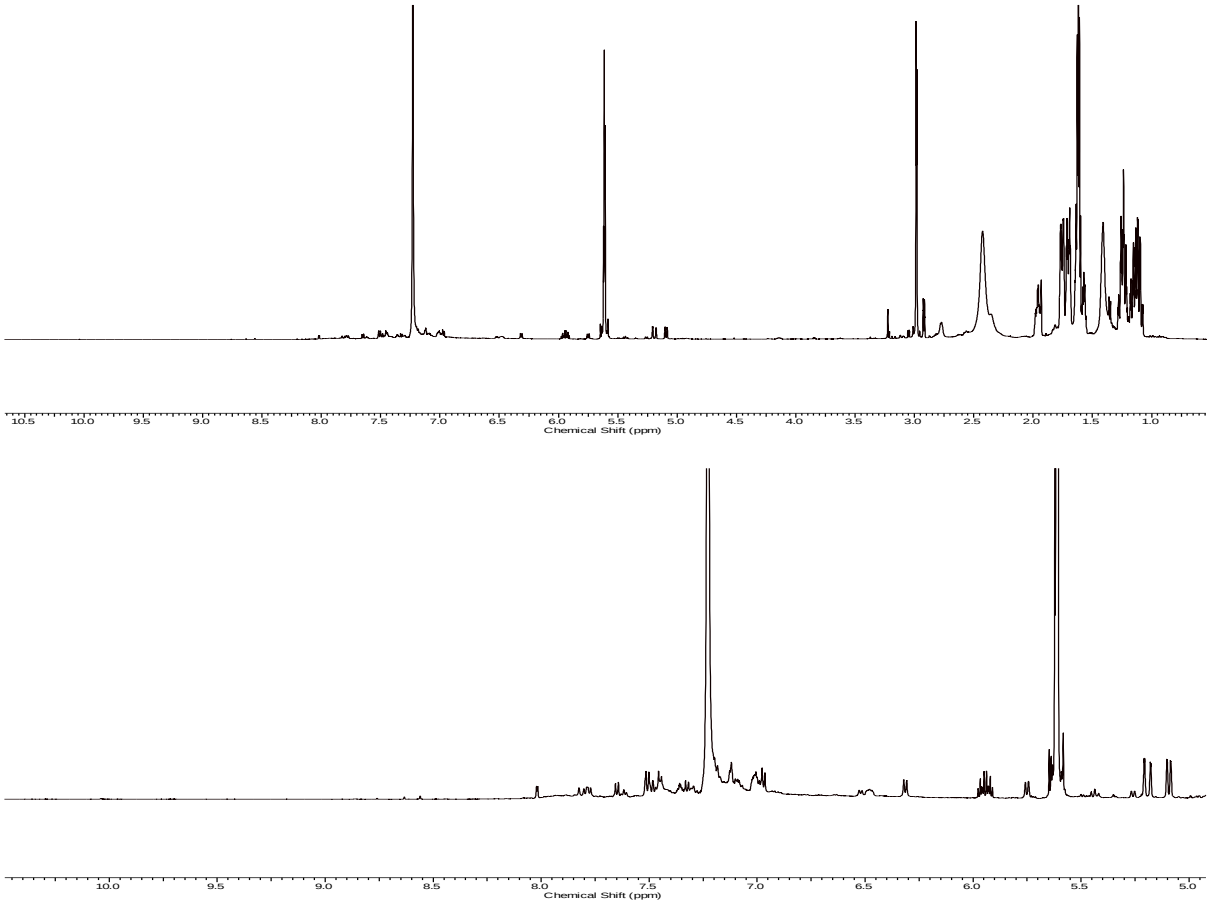


Figure S18. Catalytic hydroamination of cyclohexylallene with piperidine catalyzed by **3d** (25 mol%) after reaction completion (top: full spectrum; bottom: expanded low field region).

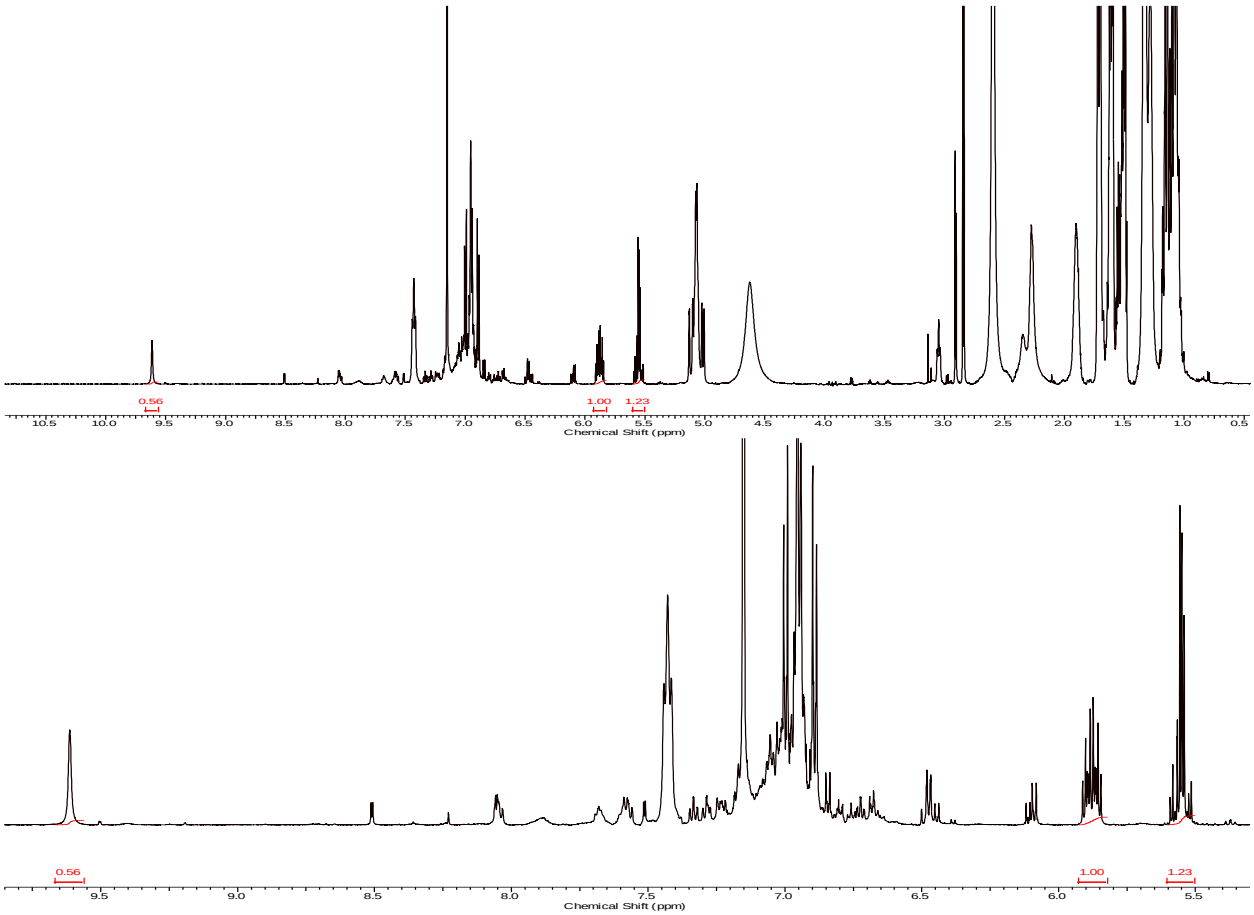


Figure S19. Catalytic hydroamination of cyclohexylallene with piperidine catalyzed by **3f** (25 mol%) after 30 minutes (top: full spectrum; bottom: expanded low field region).

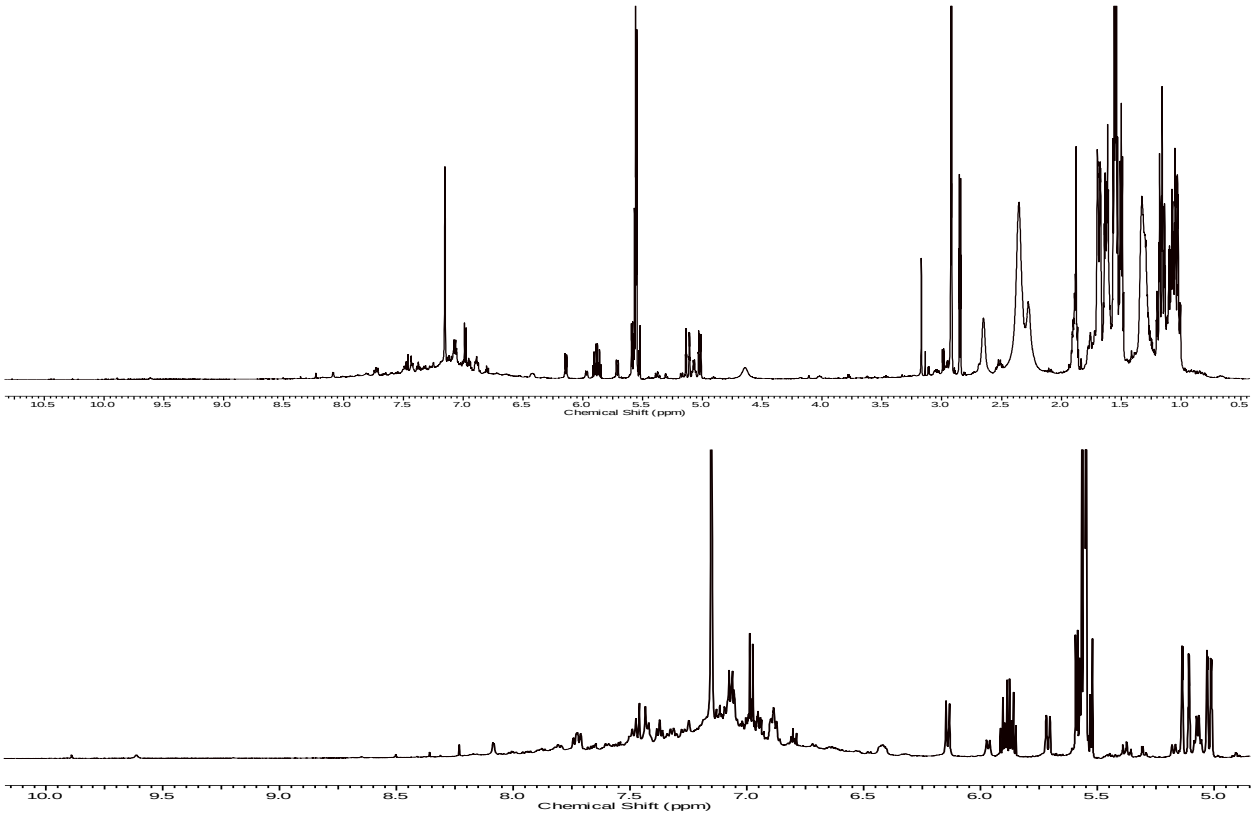


Figure S20. Catalytic hydroamination of cyclohexylallene with piperidine catalyzed by **3f** (25 mol%) after reaction completion (top: full spectrum; bottom: expanded low field region).