Electronic Supplementary Information for:

Reactivity of functionalized indoles with rare-earth metal amides. Synthesis, characterization and catalytic activity of rare-earth metal complexes incorporating indolyl ligands

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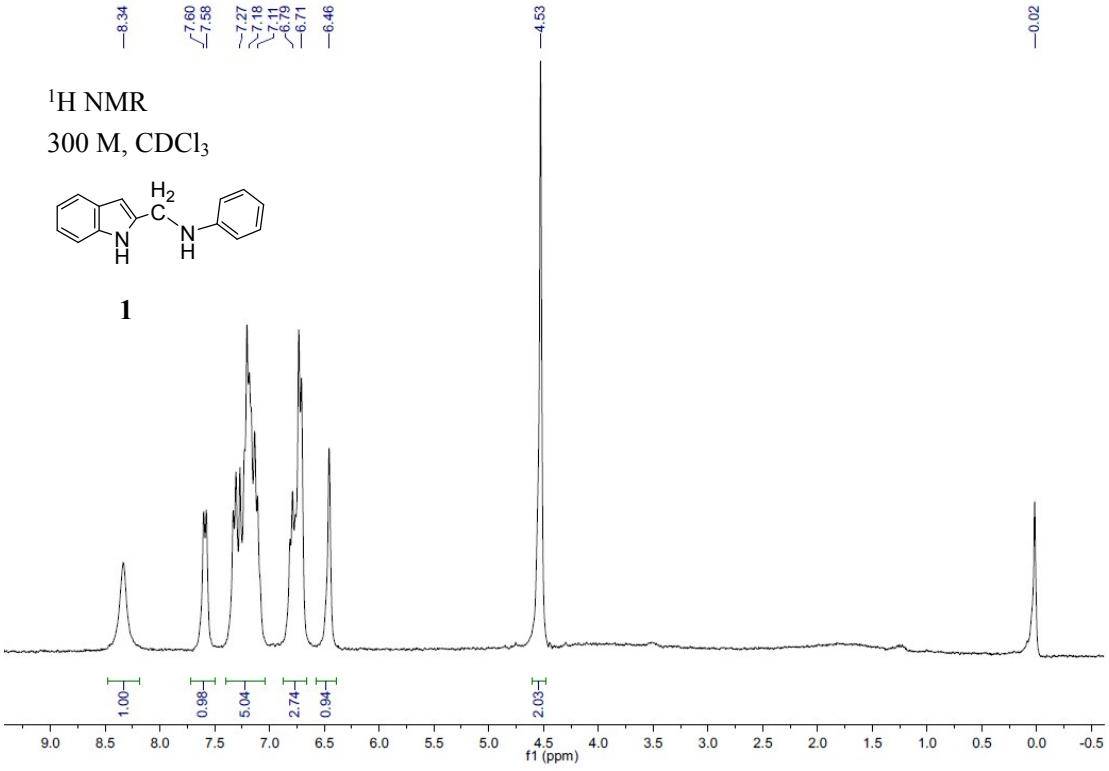
Characterization Spectra for Compound 1 and 2.



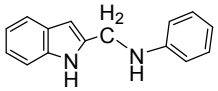
^{1}H NMR

300 M, $CDCl_3$

1

^{13}C NMR

125 M, $CDCl_3$



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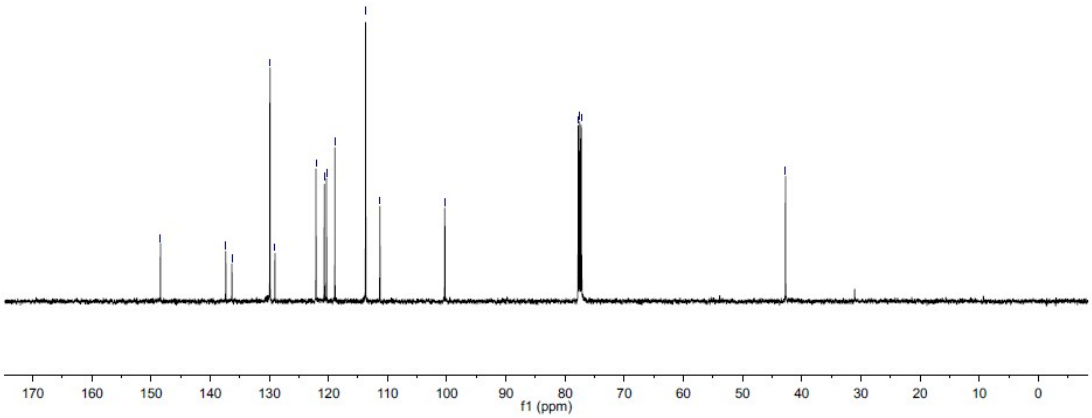
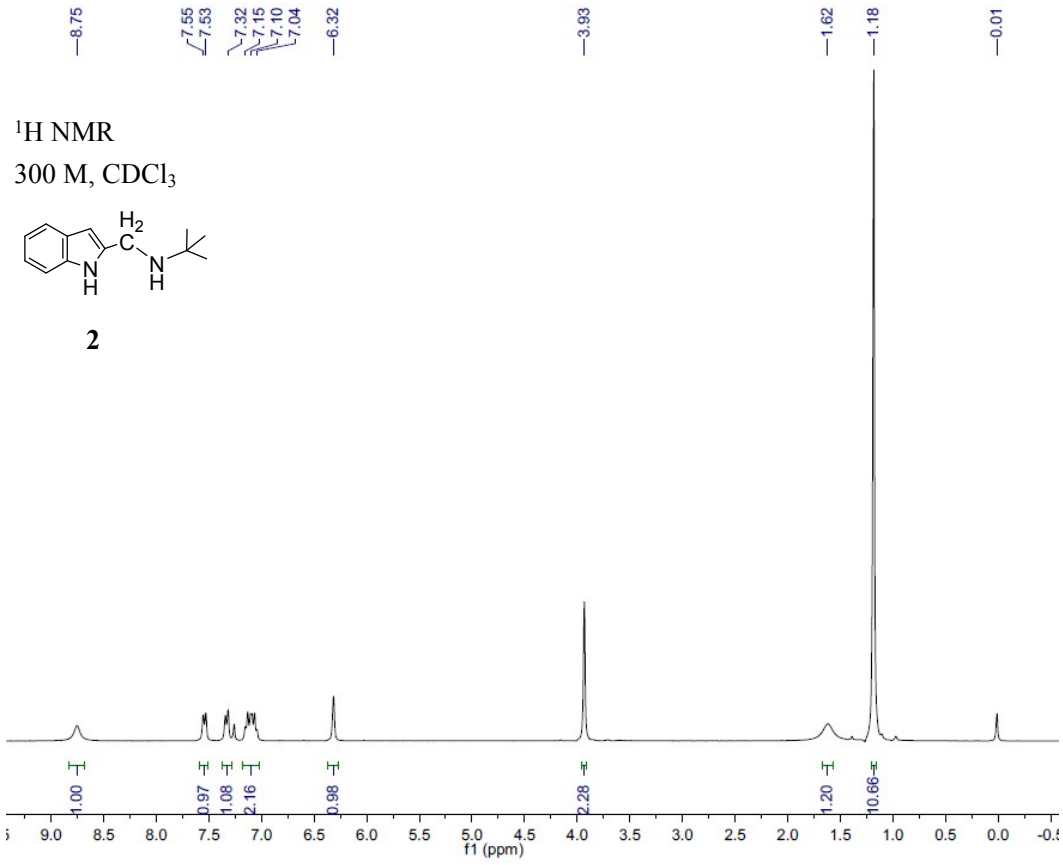
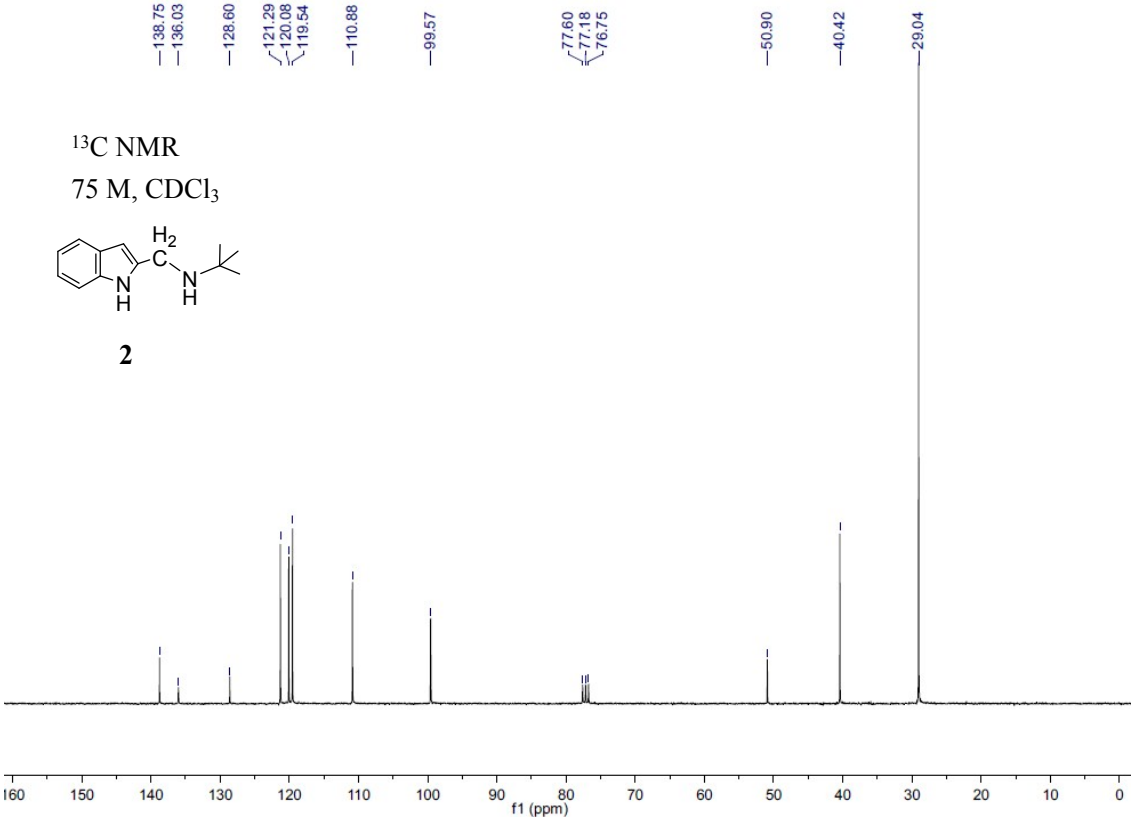




^{1}H NMR

300 M, $CDCl_3$

2

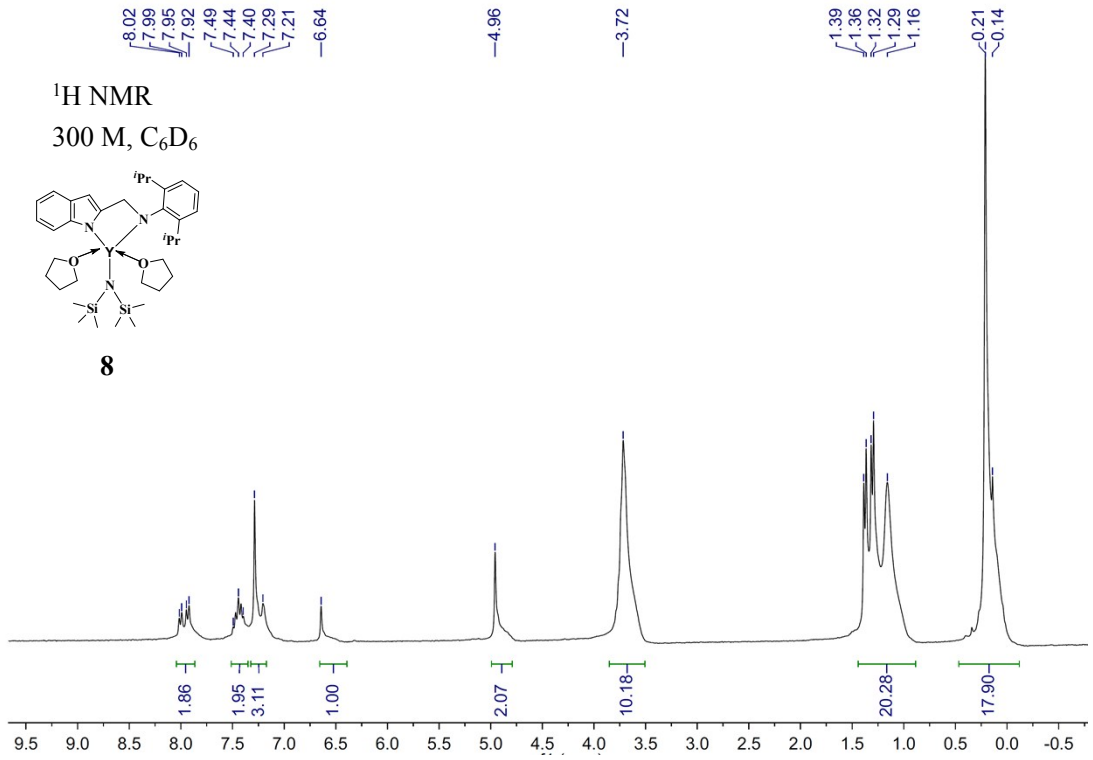


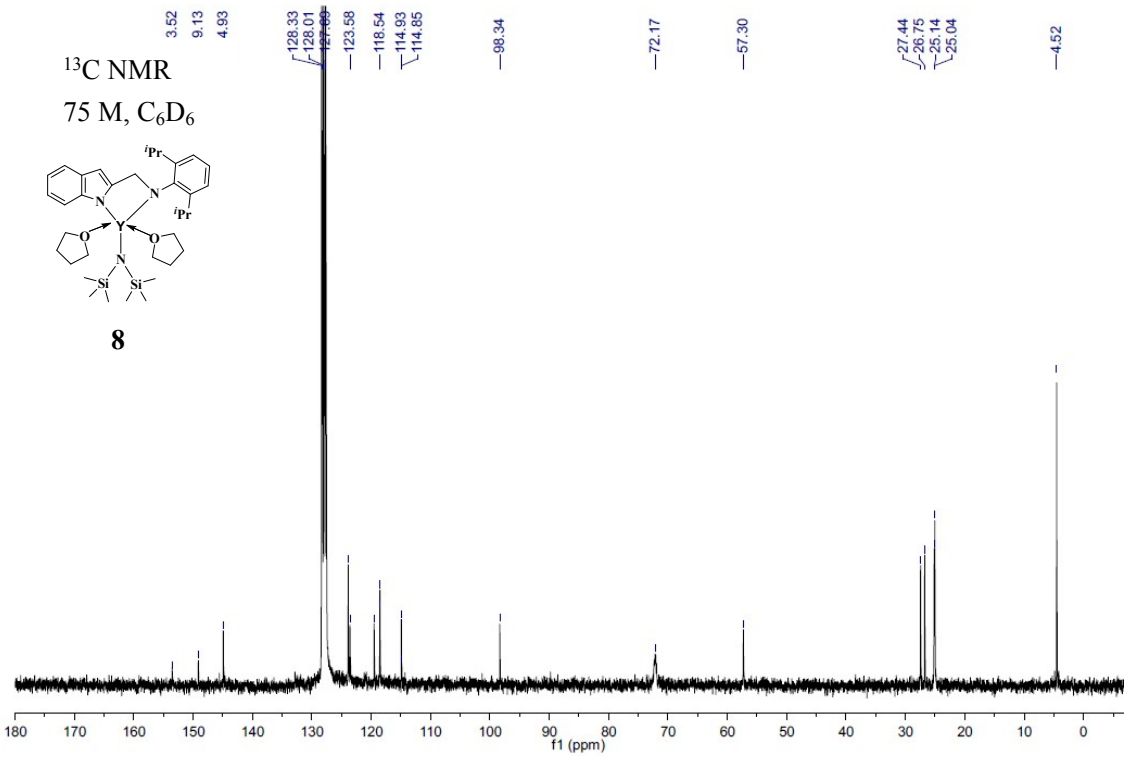
^{13}C NMR

75 M, $CDCl_3$

2

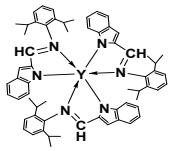
NMR Spectra of Complexes 8 and 11–14.





^{1}H NMR

500 M, C_6D_6



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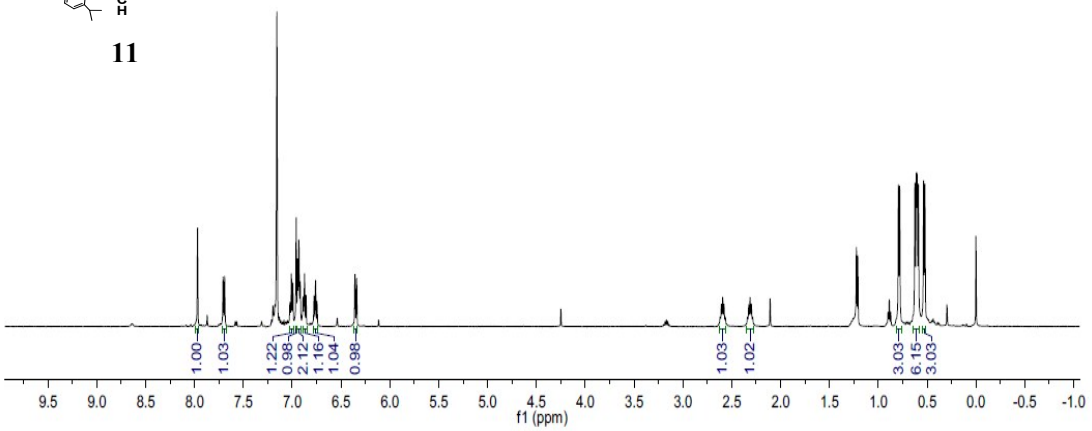
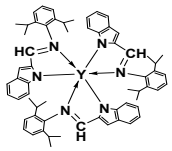


^{13}C NMR

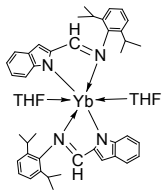
125 M, C_6D_6



11

^{1}H NMR

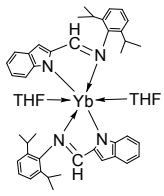
500 M, THF-d_8



12

^{13}C NMR

125 M, THF-d_8



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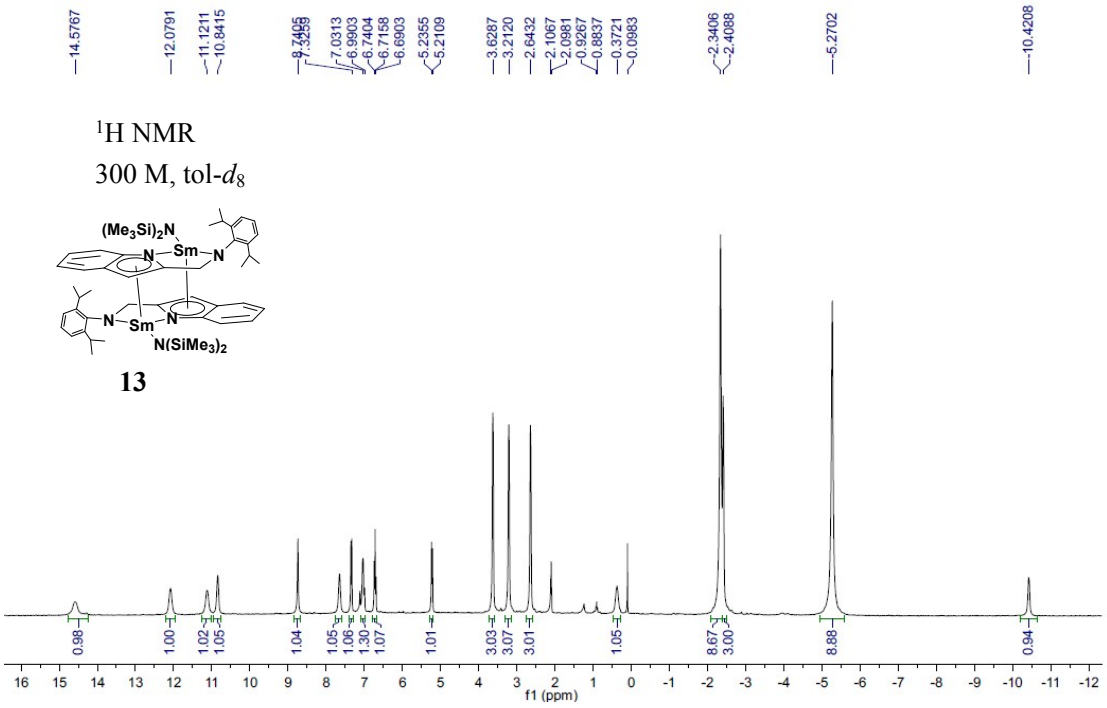
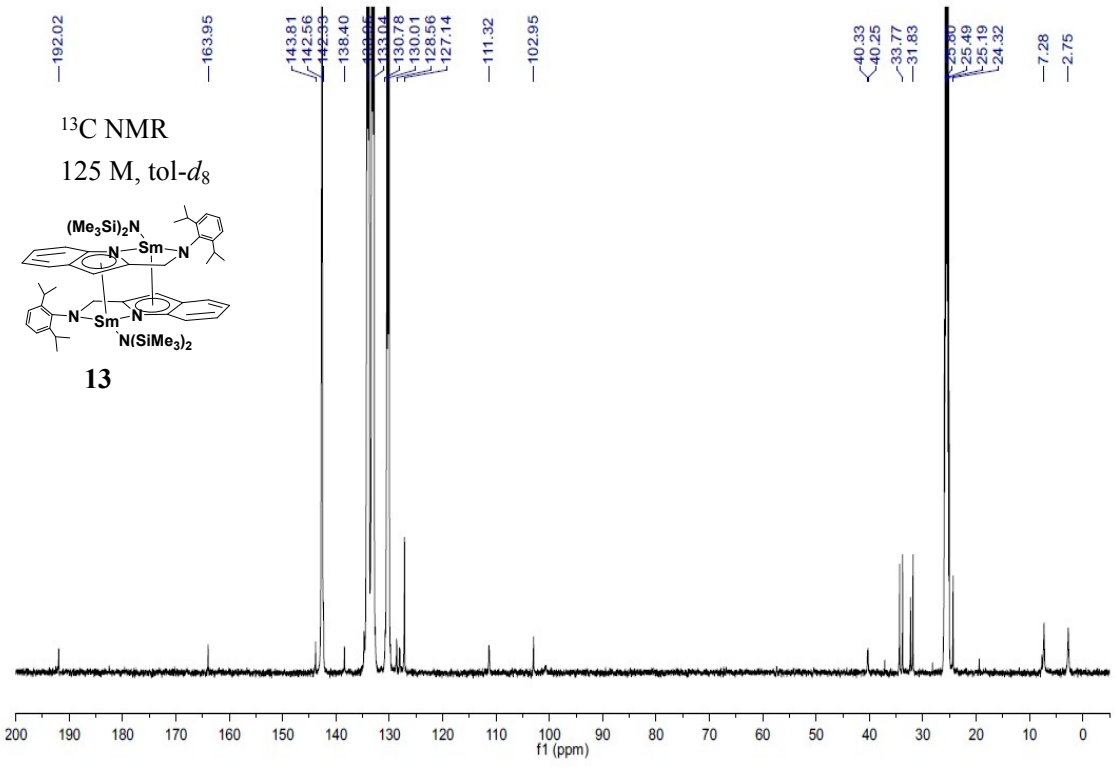


^{1}H NMR

300 M, tol-d_8

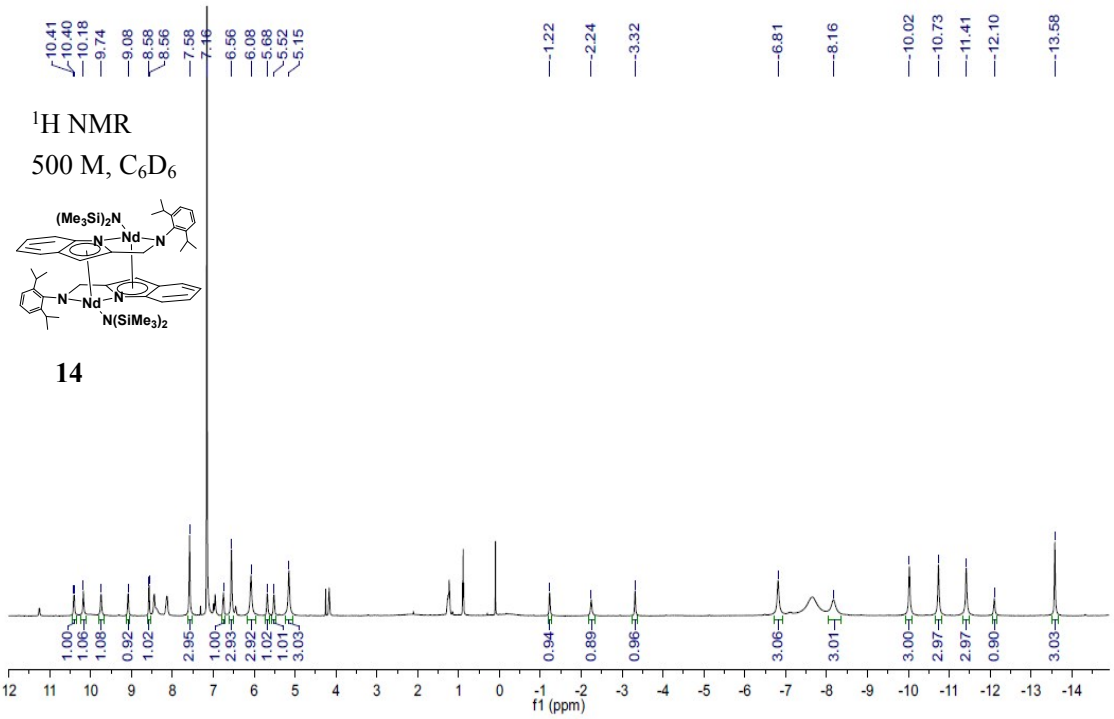
13



^{13}C NMR

125 M, tol-d_8

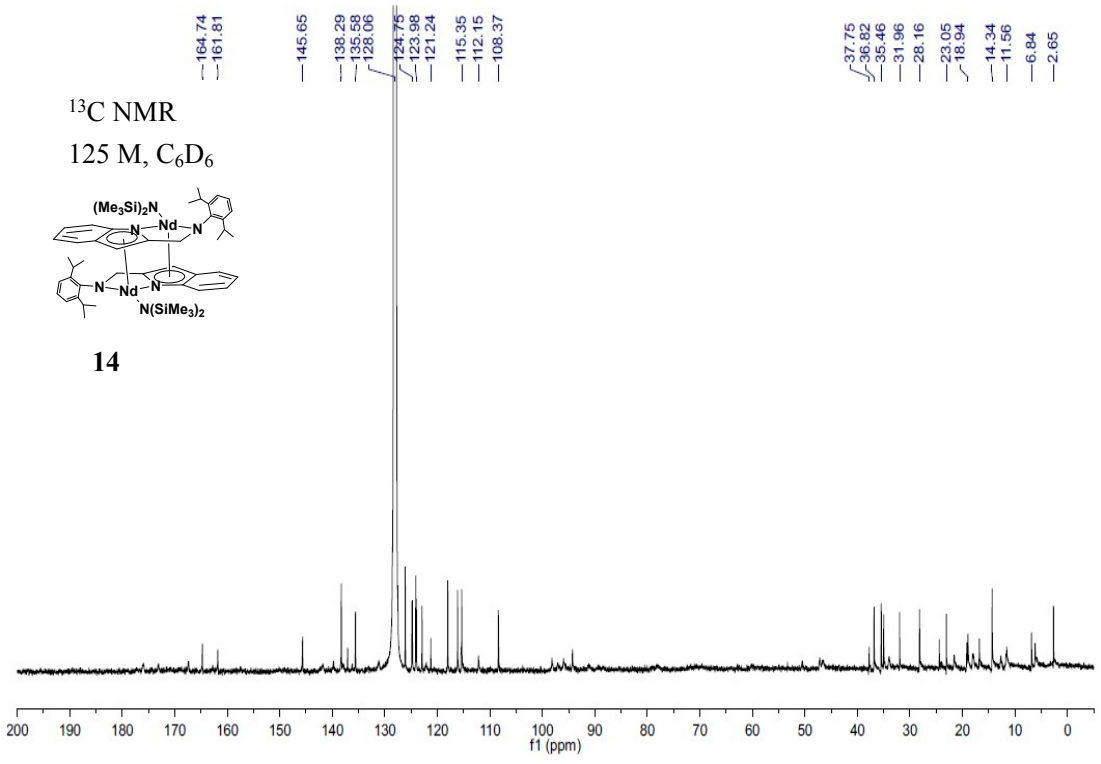
13



^{1}H NMR

500 M, C_6D_6

14

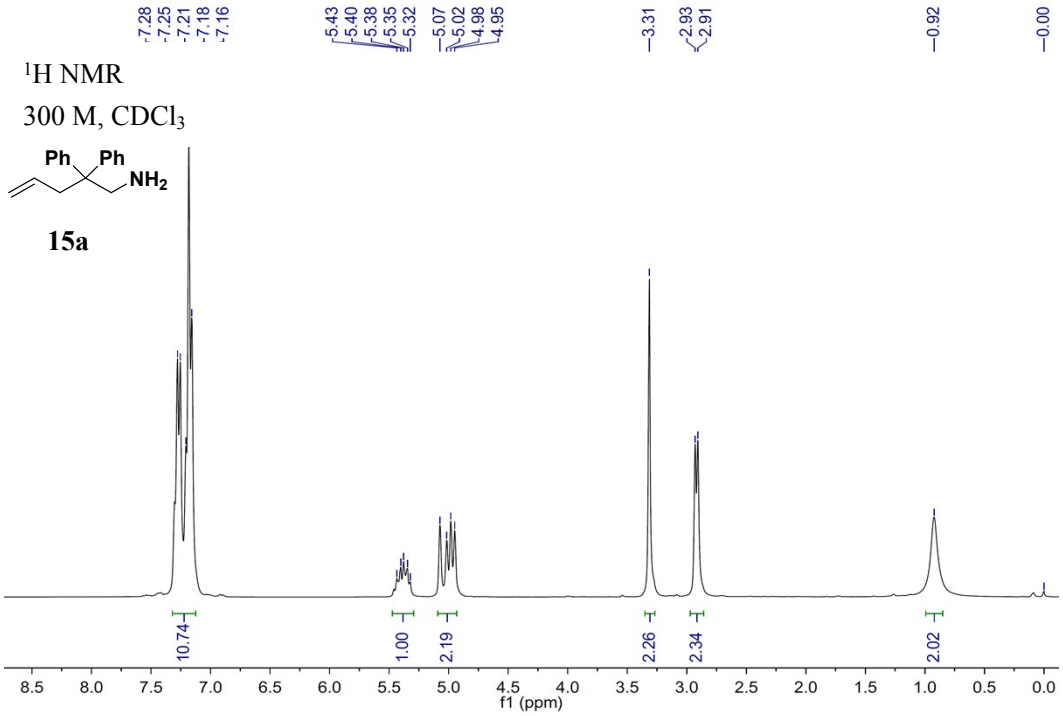


^{13}C NMR

125 M, C_6D_6

14

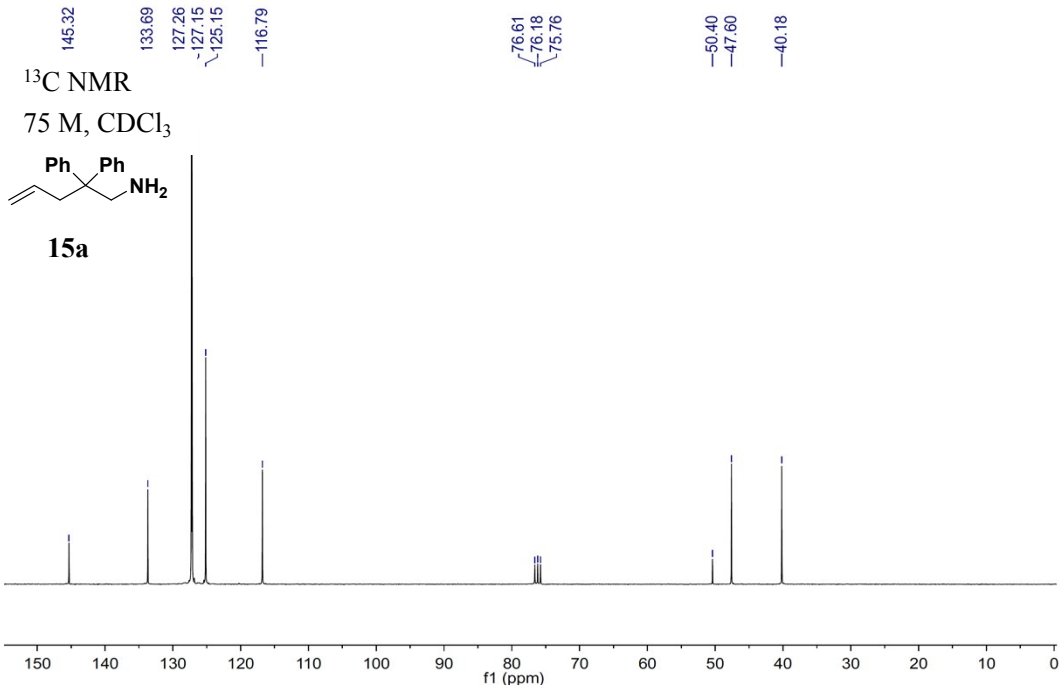
NMR Spectra of Aminoalkene Substrates 15a–i.



^{1}H NMR

300 M, $CDCl_3$

15a



^{13}C NMR

75 M, $CDCl_3$

15a

^{1}H NMR

300 M, $CDCl_3$

15b

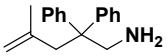
^{13}C NMR

75 M, $CDCl_3$

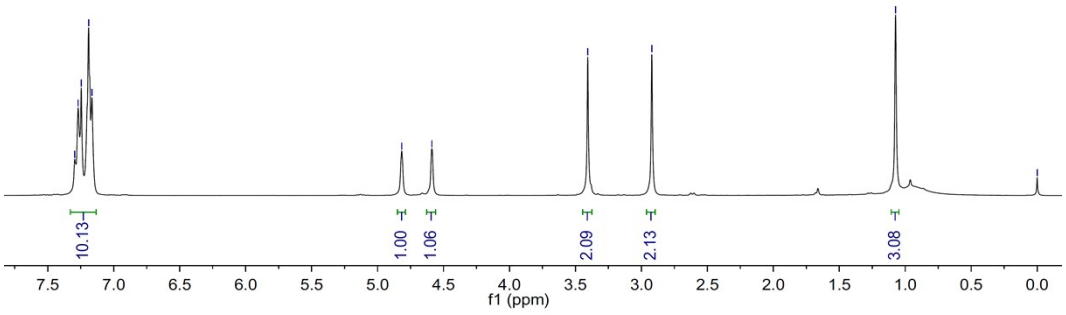
15b

^{1}H NMR

300 M, $CDCl_3$

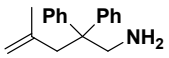


15c

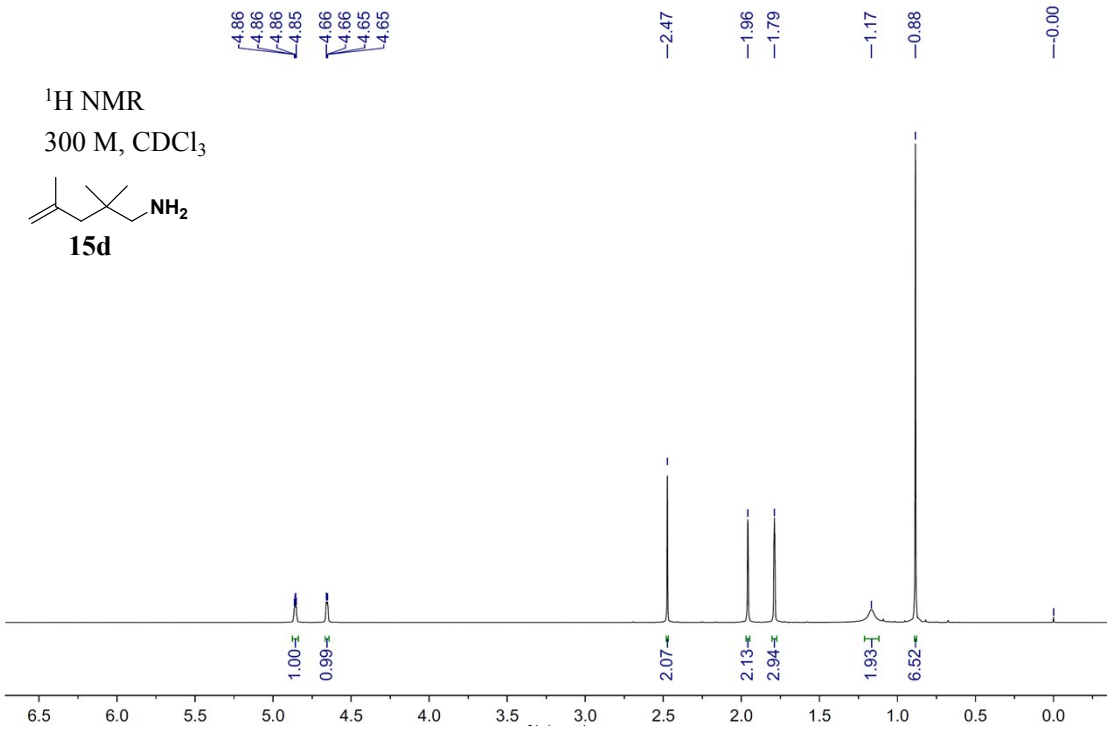


^{13}C NMR

75 M, $CDCl_3$



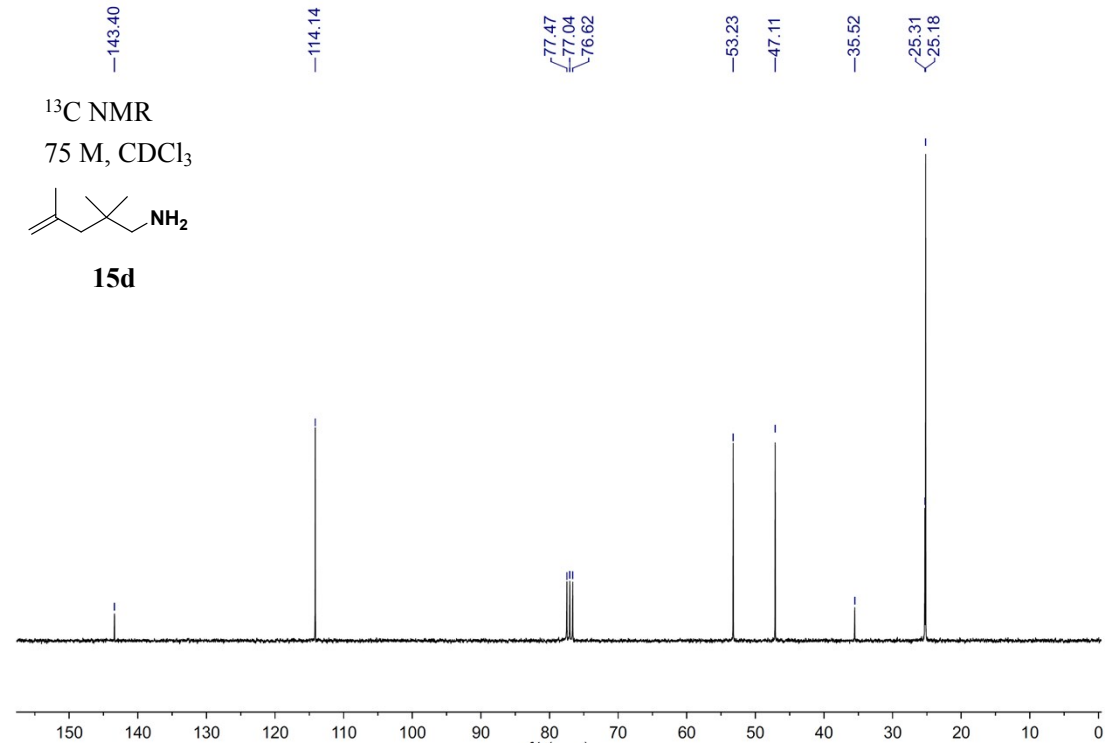
15c



^{1}H NMR

300 M, $CDCl_3$

15d



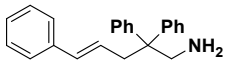
^{13}C NMR

75 M, $CDCl_3$

15d

^{1}H NMR

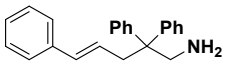
300 M, $CDCl_3$



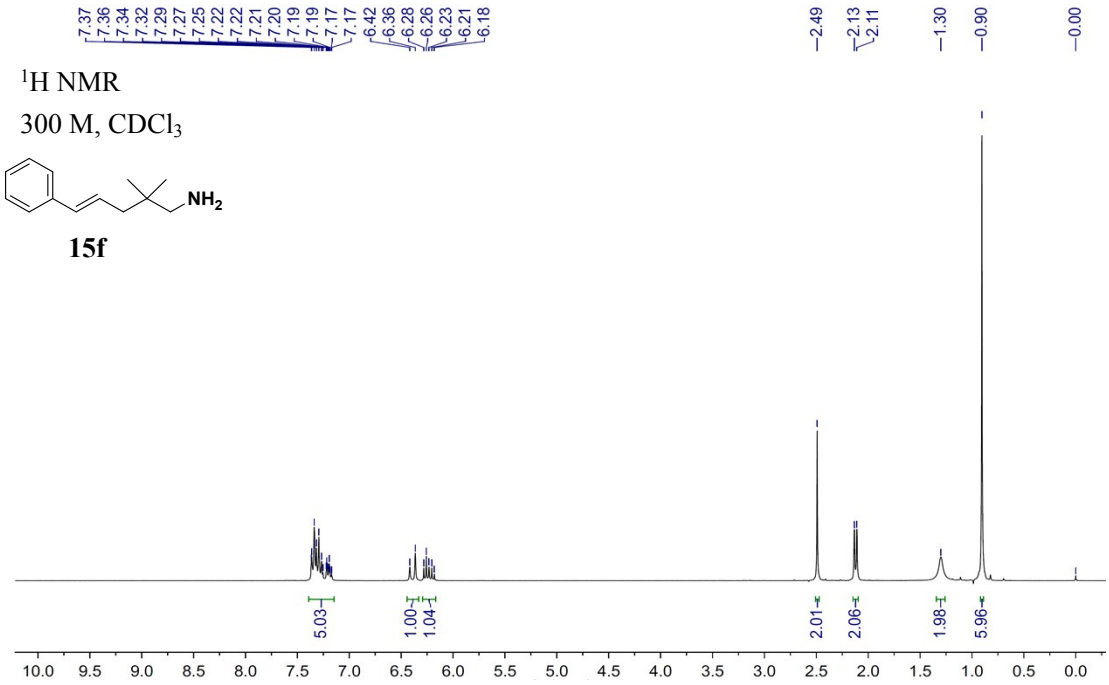
15e

^{13}C NMR

125 M, $CDCl_3$



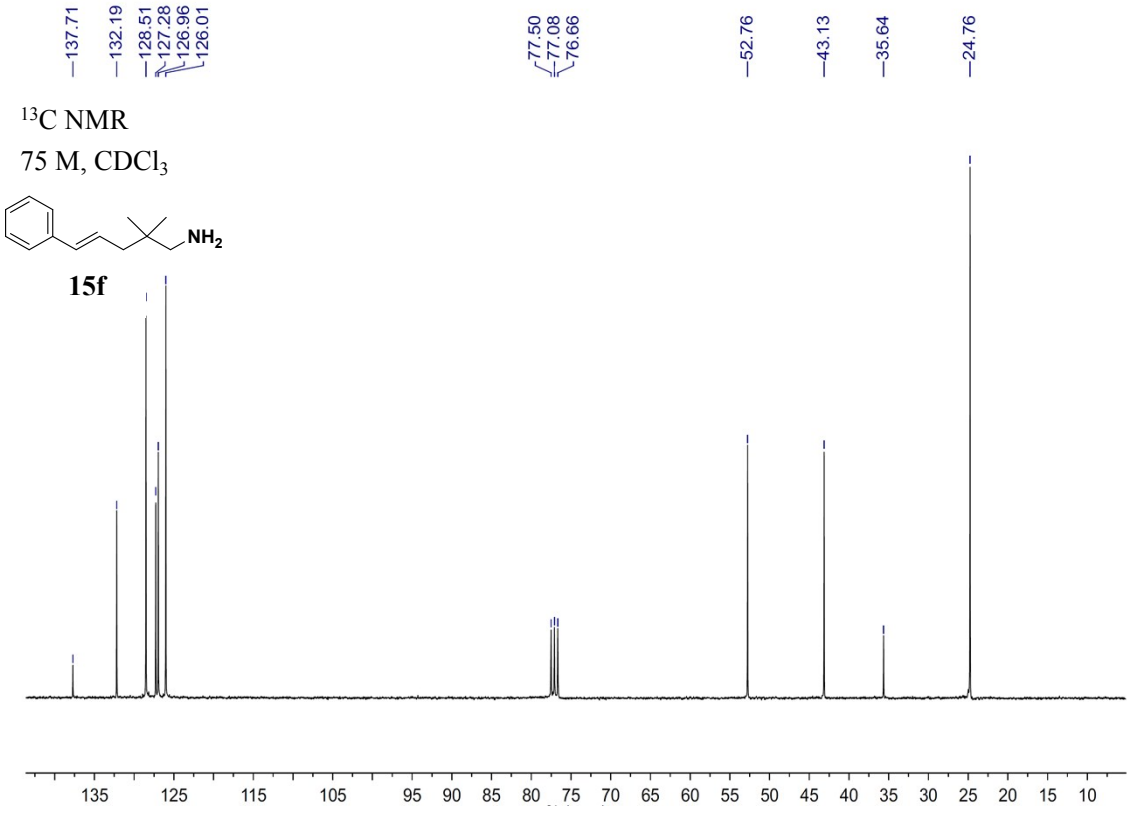
15e



^{1}H NMR

300 M, $CDCl_3$

15f



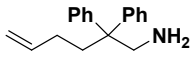
^{13}C NMR

75 M, $CDCl_3$

15f

^{1}H NMR

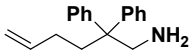
300 M, $CDCl_3$



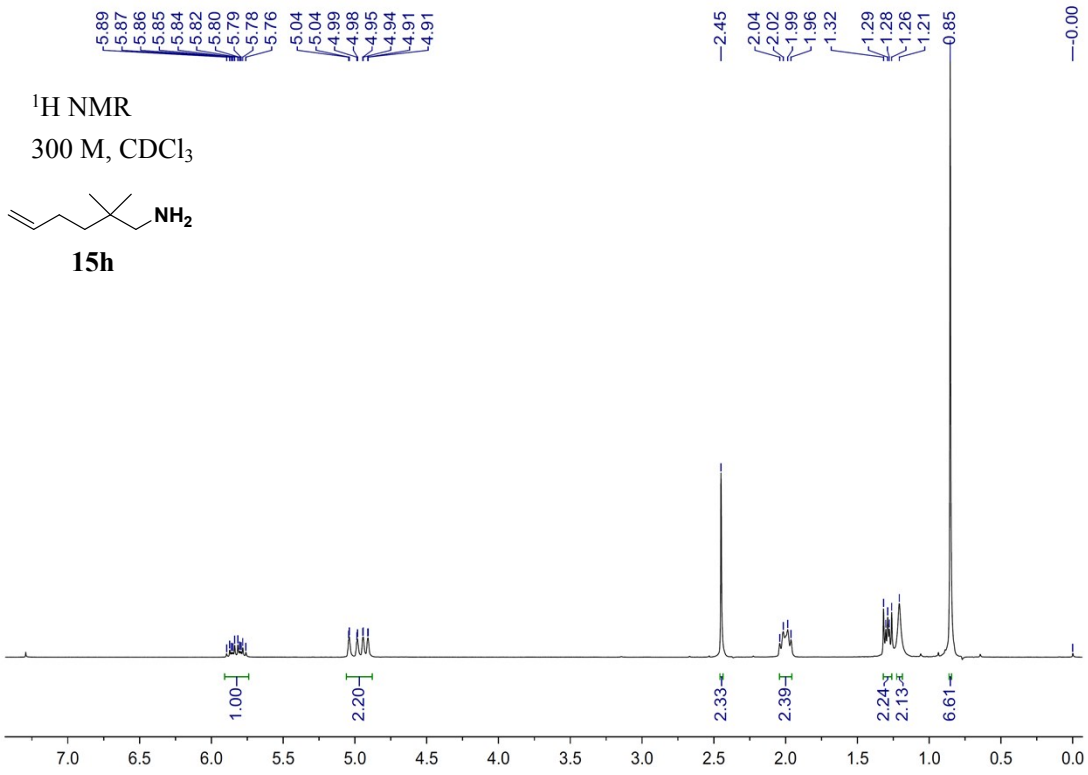
15g

^{13}C NMR

125 M, $CDCl_3$



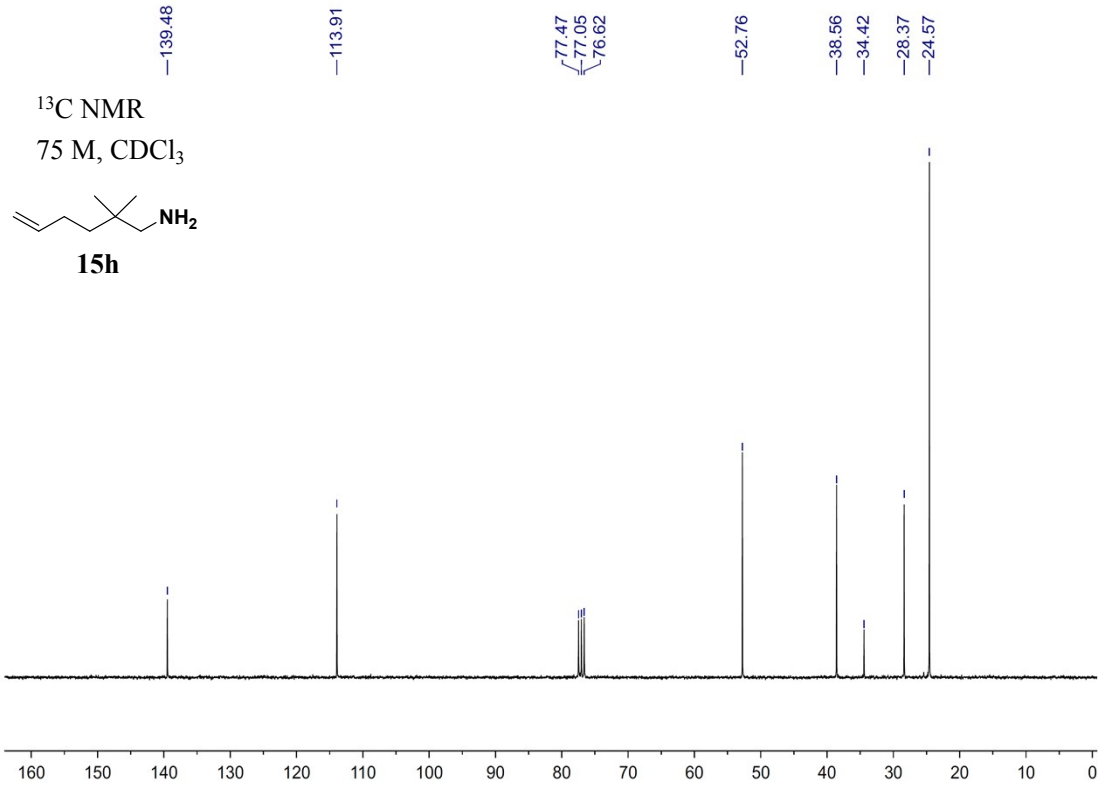
15g



^{1}H NMR

300 M, $CDCl_3$

15h



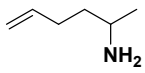
^{13}C NMR

75 M, $CDCl_3$

15h

^{1}H NMR

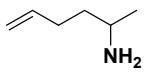
300 M, $CDCl_3$



15i

^{13}C NMR

75 M, $CDCl_3$



15i

^{1}H NMR Monitoring of Hydroamination of 15a–i Using Complex 8.

Table 5, Entry 1 ^{1}H NMR, 300 M, C_6D_6, ferrocene as internal standard
Substrate: 15**a** (0.32 mmol), Catalyst: **8** (2.0 % mol), Temperature: 25 ^{o}C

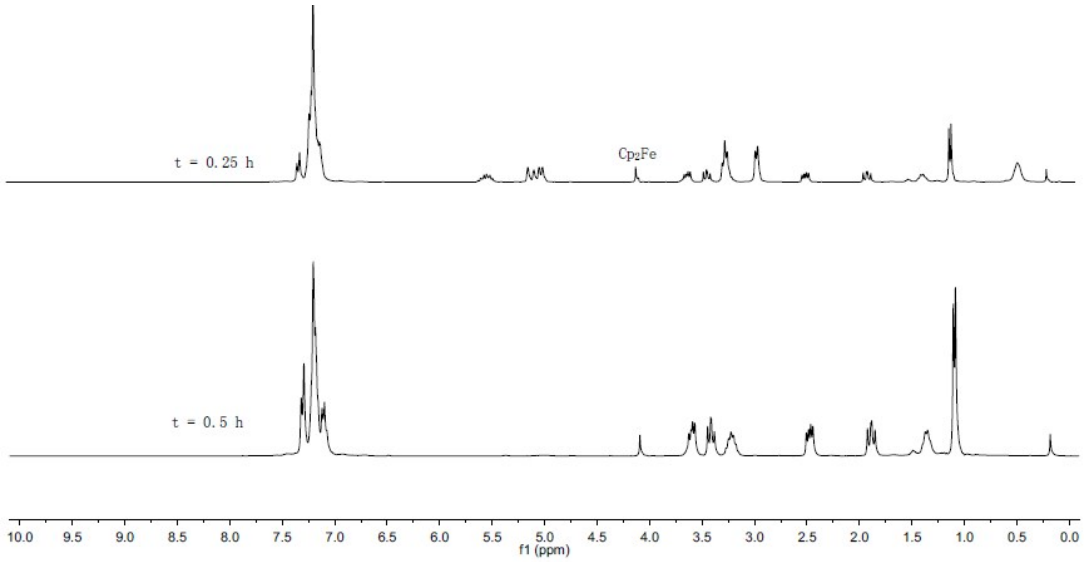


Table 5, Entry 2 ^{1}H NMR, 300 M, C_6D_6, ferrocene as internal standard
Substrate: 15**b** (0.32 mmol), Catalyst: **8** (2.0 % mol),
Temperature: 25 ^{o}C

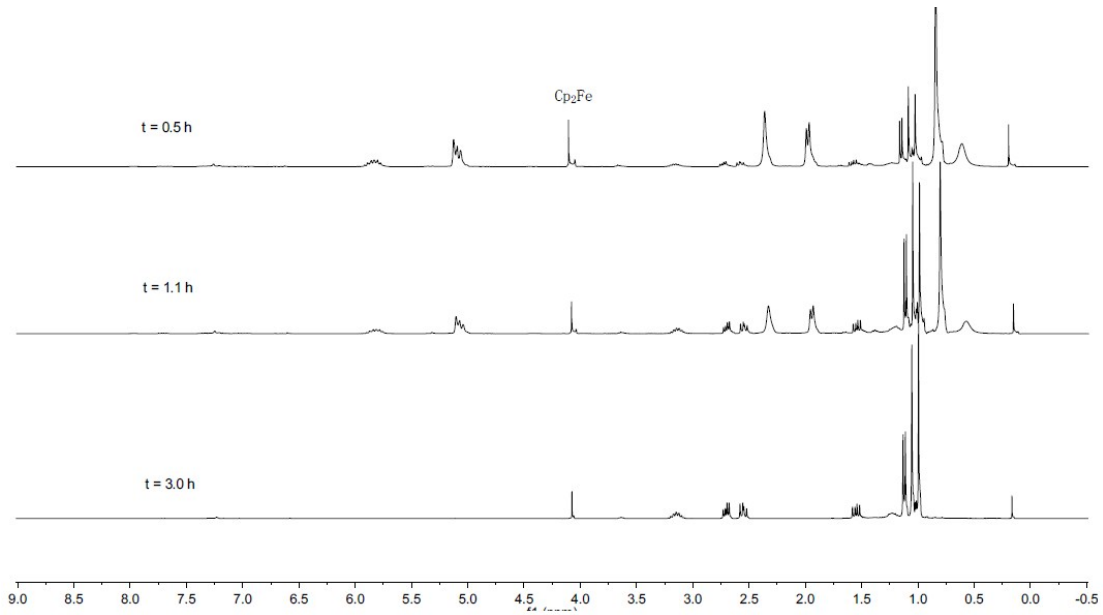


Table 5, Entry 3 ^{1}H NMR, 300 M, C_6D_6, ferrocene as internal standard
Substrate: 15**c** (0.32 mmol), Catalyst: **8** (2.0 % mol), Temperature: 25 ^{o}C

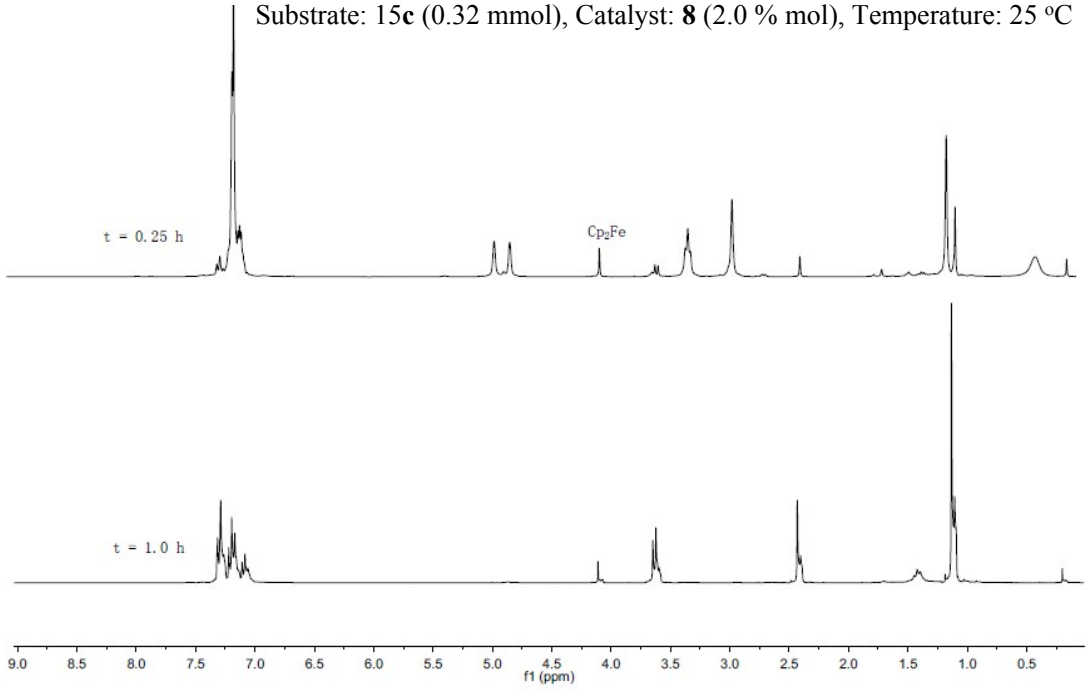


Table 5, Entry 4 ^{1}H NMR, 300 M, C_6D_6, ferrocene as internal standard
Substrate: 15**d** (0.32 mmol), Catalyst: **8** (2.0 % mol),
Temperature: 50 ^{o}C

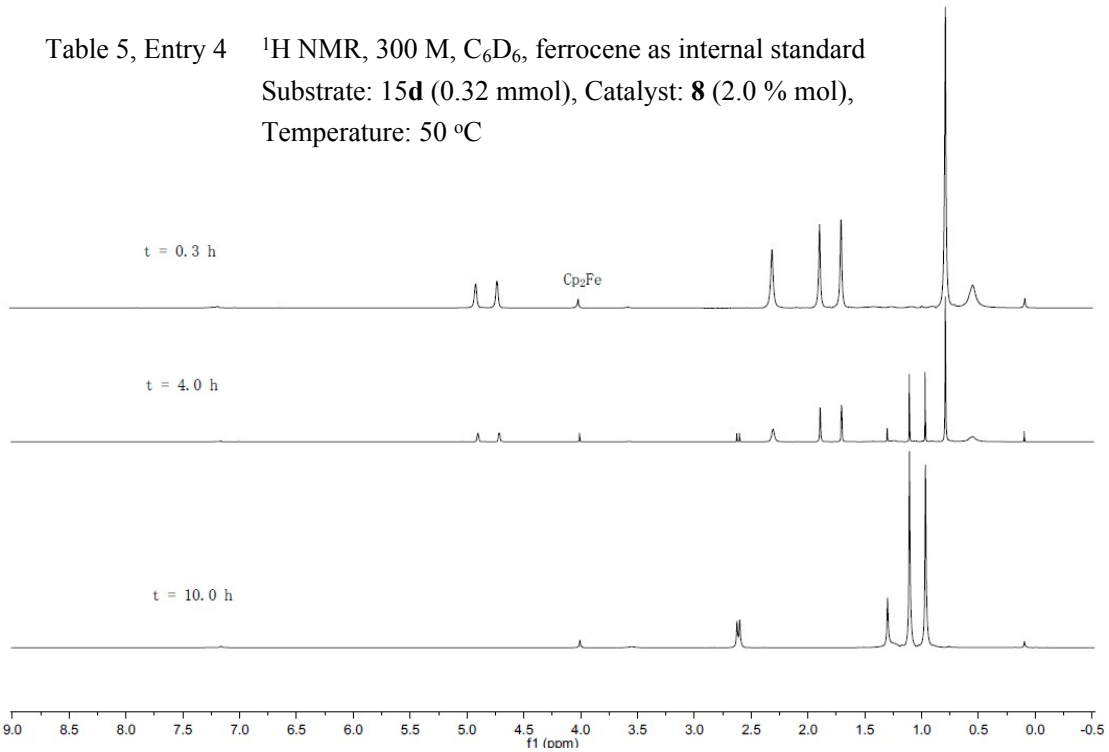


Table 5, Entry 5

^{1}H NMR, 300 M, C_6D_6, ferrocene as internal standard
Substrate: 15**e** (0.32 mmol), Catalyst: **8** (5.0 % mol),
Temperature: 25 ^{o}C

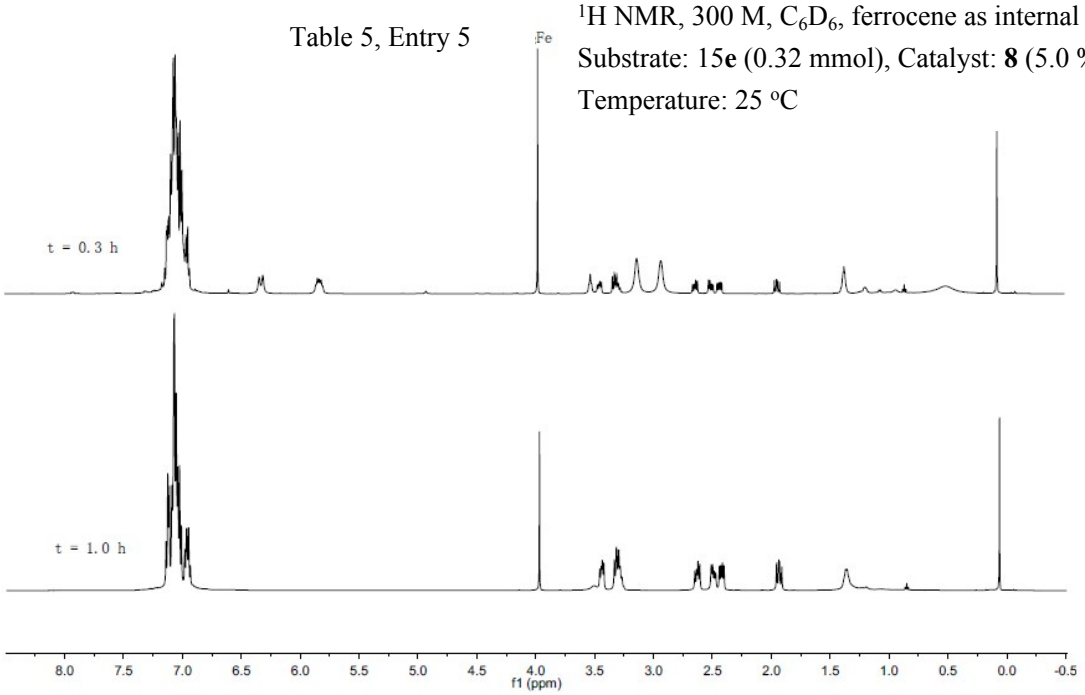


Table 5, Entry 6

^{1}H NMR, 300 M, C_6D_6, ferrocene as internal standard
Substrate: 15**f** (0.32 mmol), Catalyst: **8** (5.0 % mol),
Temperature: 50 ^{o}C

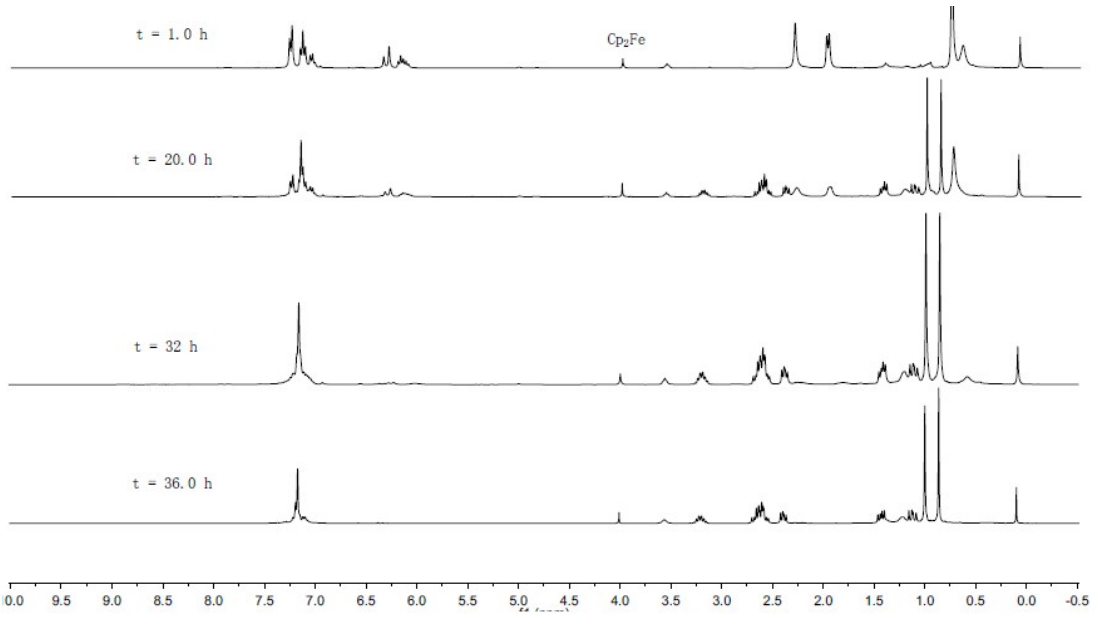


Table 5, Entry 7 ^{1}H NMR, 300 M, C_6D_6, ferrocene as internal standard

Substrate: 15**g** (0.32 mmol), Catalyst: **8** (4.0 % mol), Temperature: 50 ^{o}C

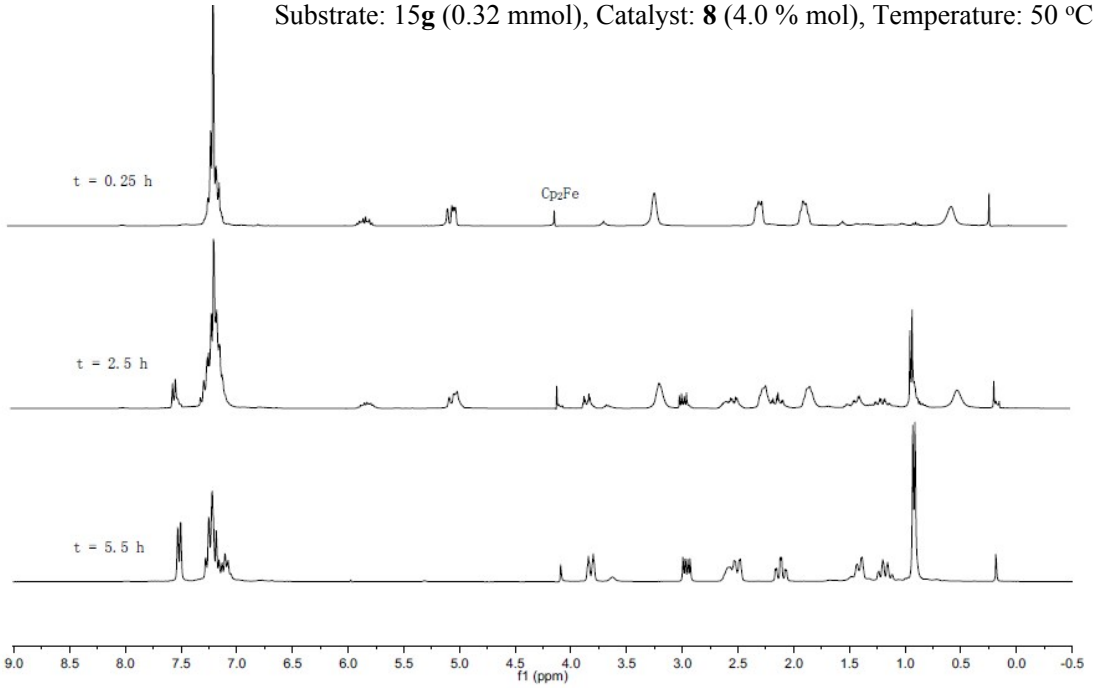


Table 5, Entry 8 ^{1}H NMR, 300 M, C_6D_6, ferrocene as internal standard

Substrate: 15**h** (0.32 mmol), Catalyst: **8** (4.0 % mol),

Temperature: 50 ^{o}C

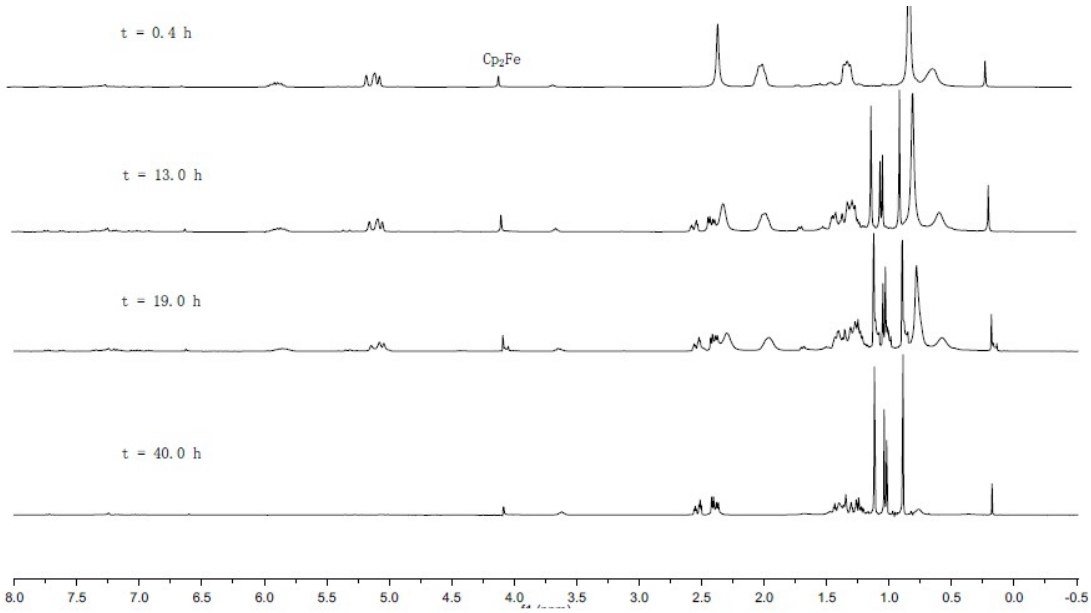
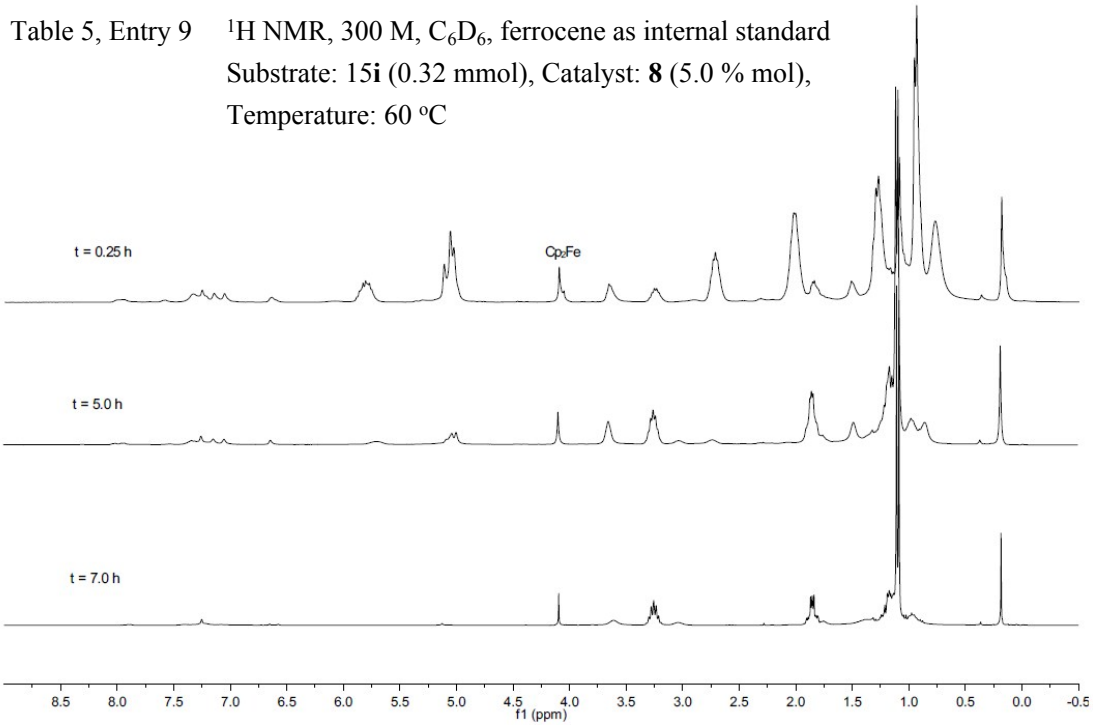
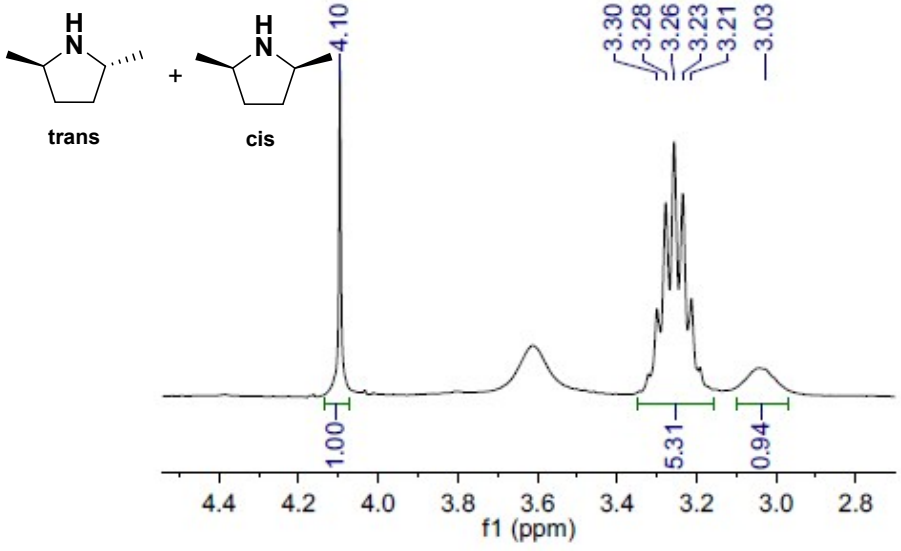
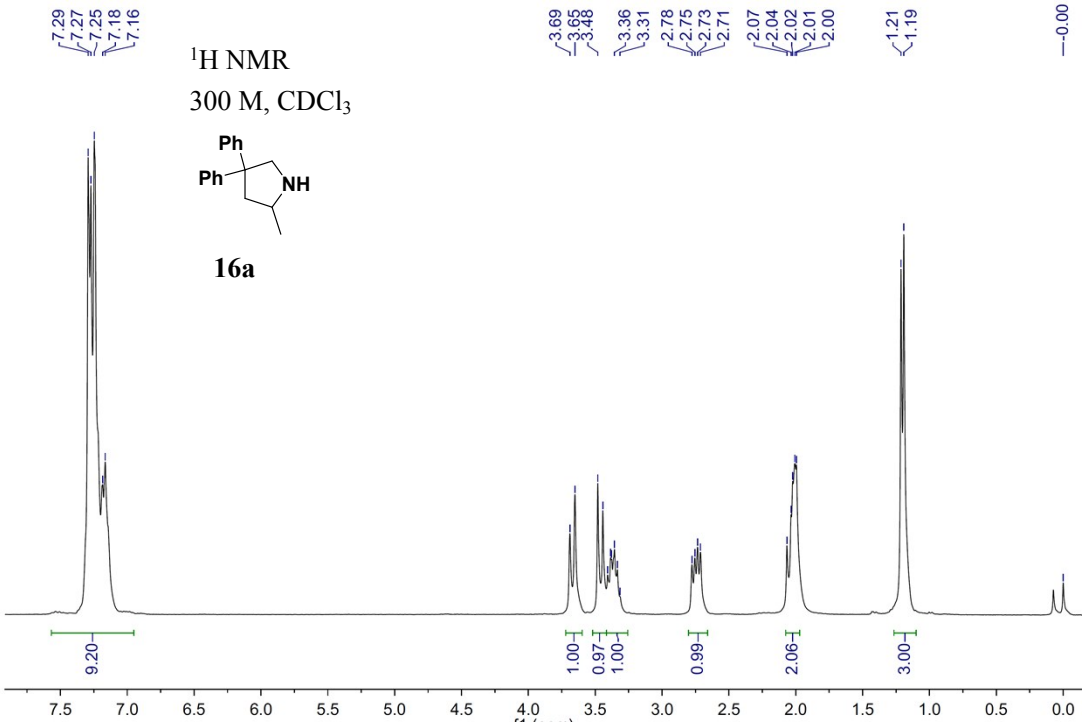


Table 5, Entry 9 ^{1}H NMR, 300 M, C_6D_6, ferrocene as internal standard
Substrate: 15**i** (0.32 mmol), Catalyst: **8** (5.0 % mol),
Temperature: 60 ^{o}C



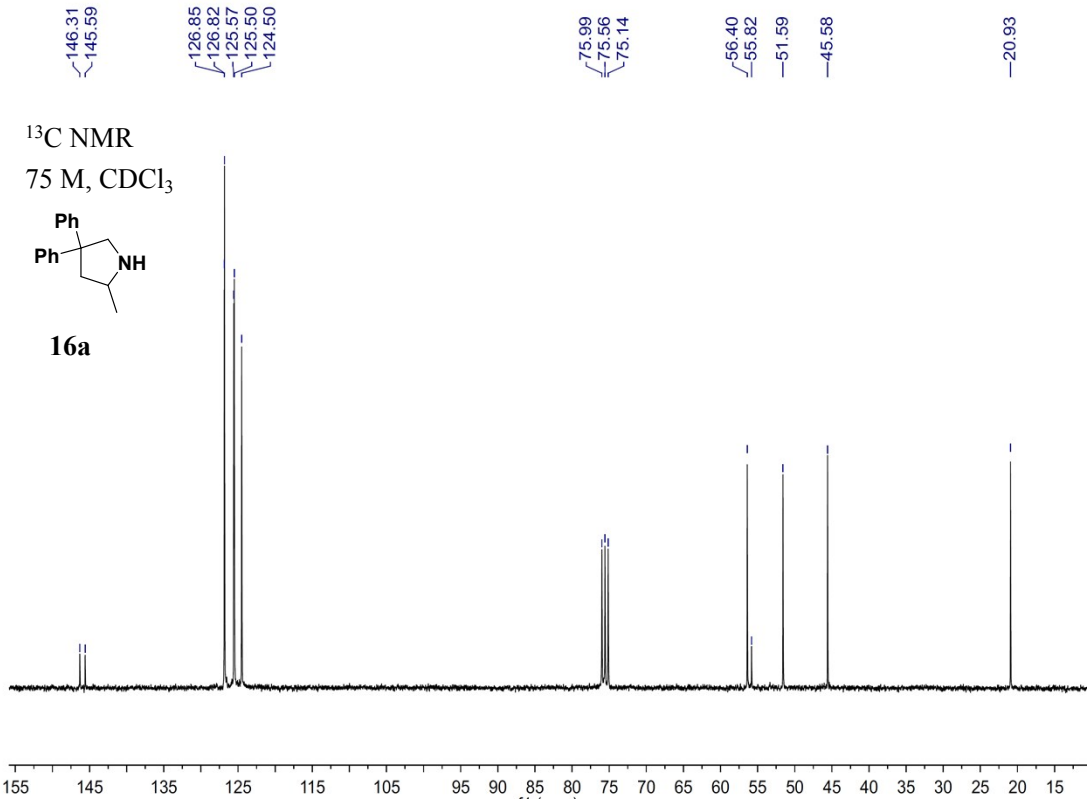


NMR Spectra of Isolated 16a, 16c, 16e, 16g.



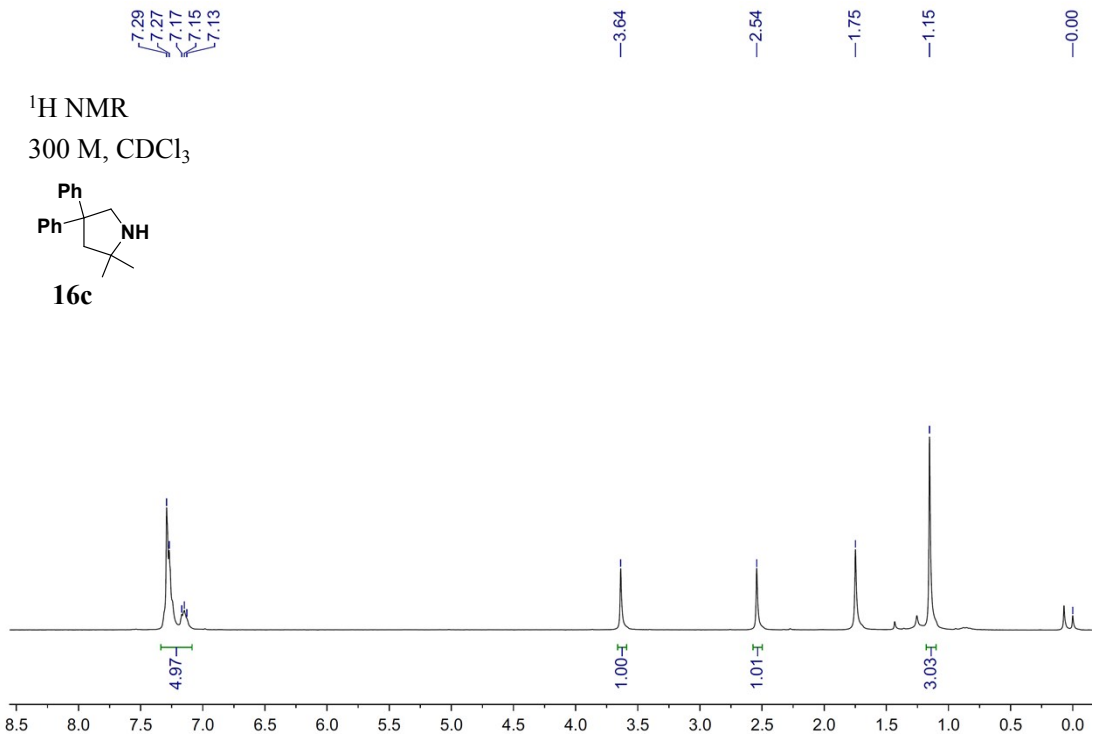
^{1}H NMR
300 M, $CDCl_3$

16a



^{13}C NMR
75 M, $CDCl_3$

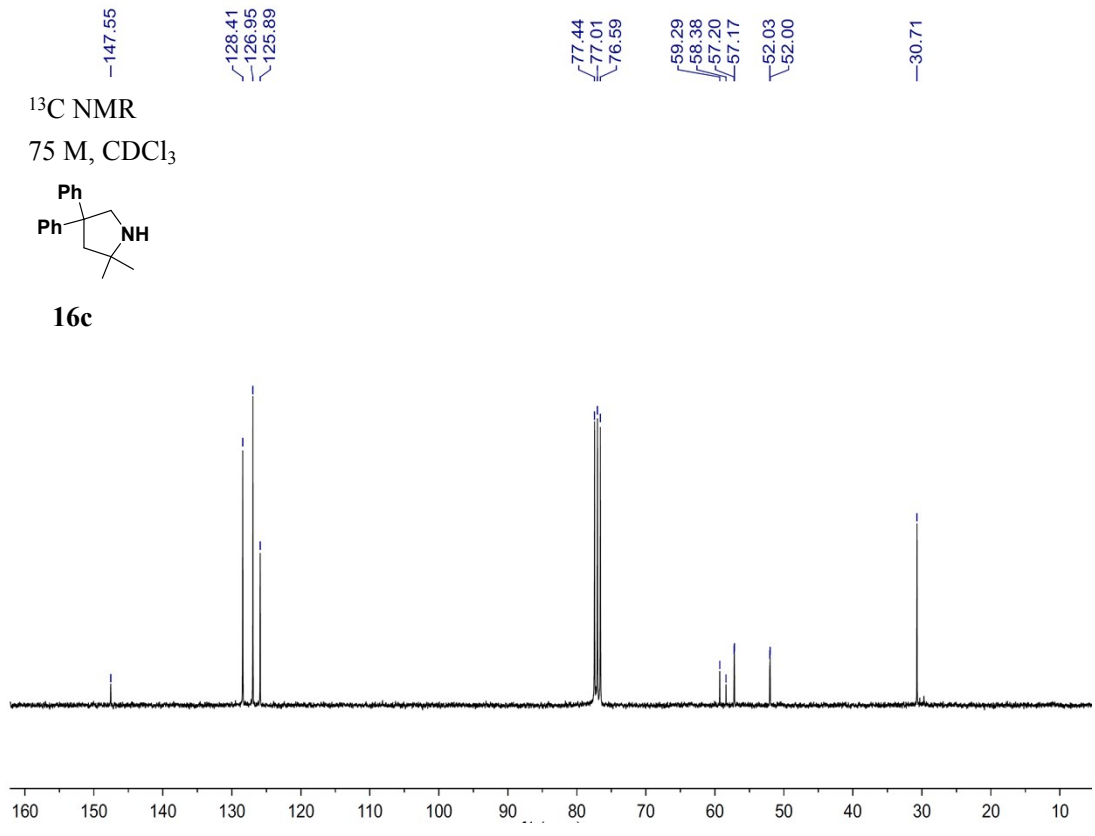
16a



^{1}H NMR

300 M, $CDCl_3$

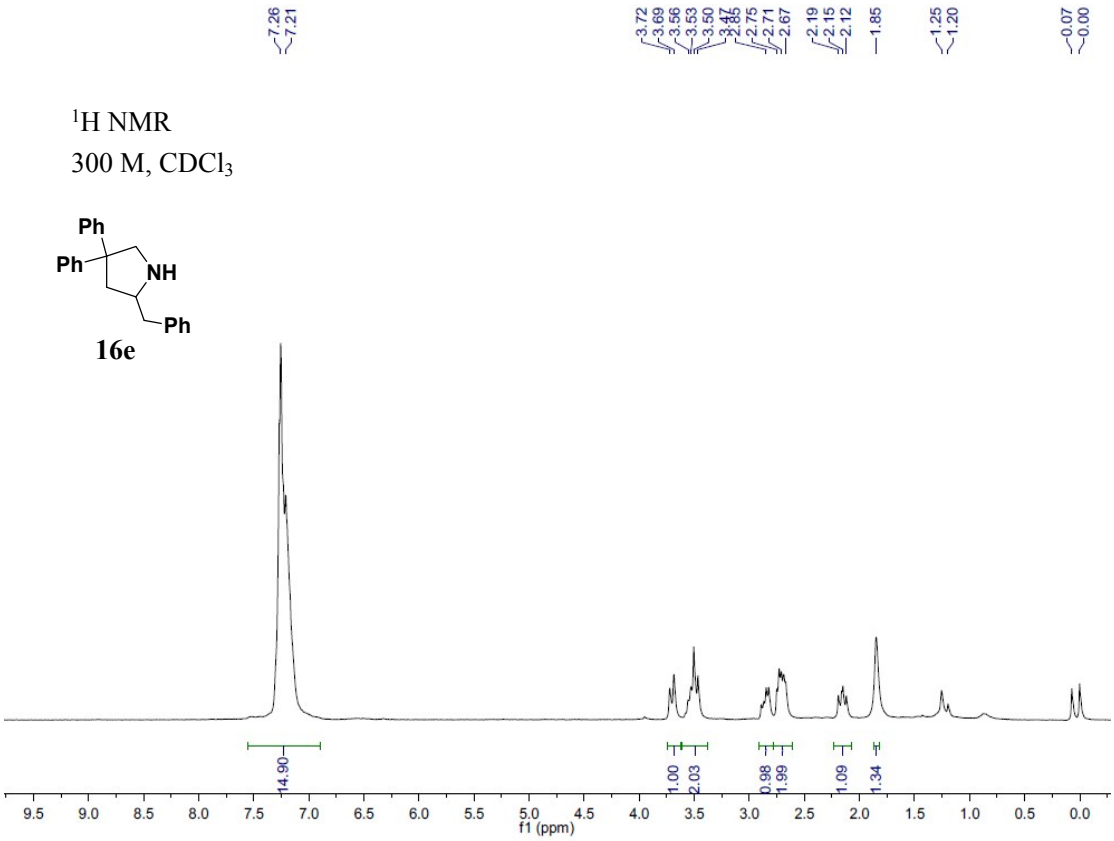
16c



^{13}C NMR

75 M, $CDCl_3$

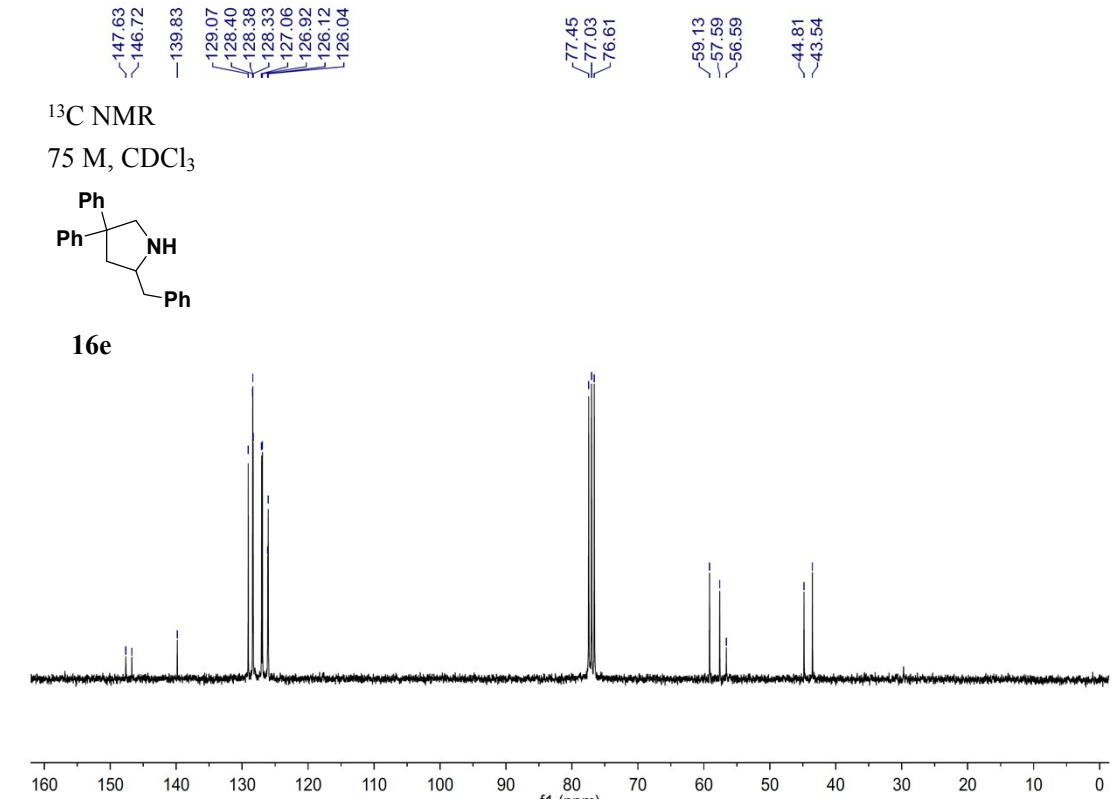
16c



^{1}H NMR

300 M, $CDCl_3$

16e



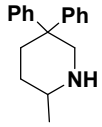
^{13}C NMR

75 M, $CDCl_3$

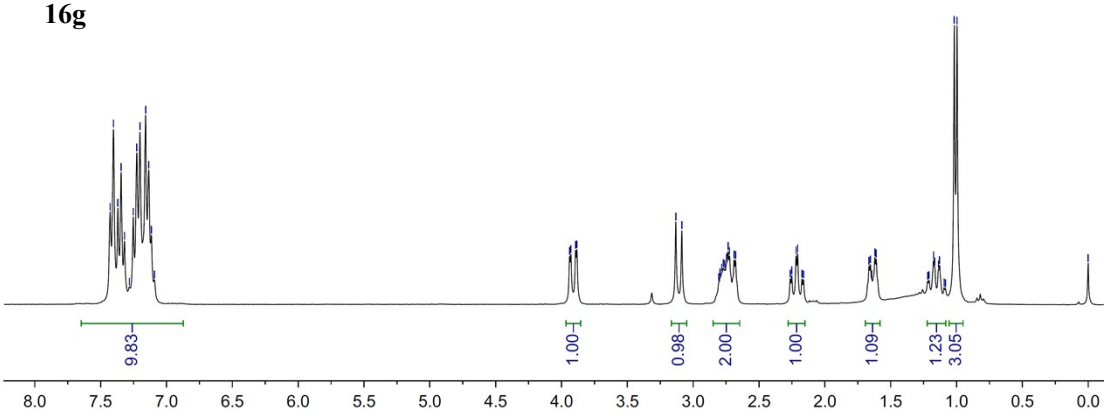
16e

^{1}H NMR

300 M, $CDCl_3$

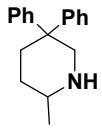


16g



^{13}C NMR

75 M, $CDCl_3$



16g

Molecular Structures and Selected Bond Distances and Angles of the Complexes 4–6, 8–14.

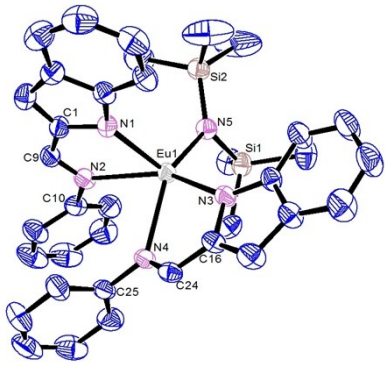


Figure S1. Structure of complex **4** (Ellipsoids at 30% probability level). Hydrogen atoms were omitted for clarity. Selected bond distances (Å) and angles (°): Eu1-N1 2.341(3), Eu1-N2 2.525(3), Eu1-N3 2.363(3), Eu1-N4 2.517(3), Eu1-N5 2.236(3), C9-N2 1.288(5), C24-N4 1.292(5), N2-C9-C1 121.5(4), C9-N2-C10 122.0(4), N4-C24-C16 121.5(3), C24-N4-C25 117.9(3), N5-Eu1-N1 113.03(11), N5-Eu1-N3 107.59(11), N1-Eu1-N3 100.43(11), N5-Eu1-N4 148.59(11), N1-Eu1-N4 97.92(10), N3-Eu1-N4 70.09(10), N5-Eu1-N2 102.36(11), N1-Eu1-N2 69.35(11), N3-Eu1-N2 149.95(11), N4-Eu1-N2 83.08(10).

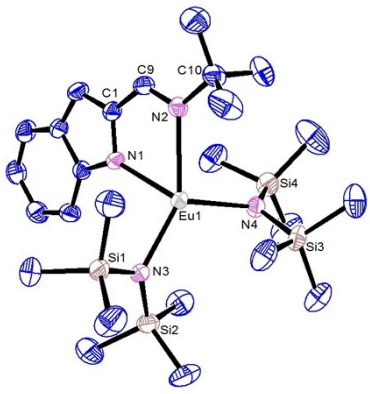


Figure S2. Structure of complex **5** (Ellipsoids at 30% probability level). Hydrogen atoms were omitted for clarity. Selected bond distances (Å) and angles (°): Eu1-N1 2.351(2), Eu1-N2 2.565(2), Eu1-N3 2.251(2), Eu1-N4 2.254(2), C9-N2 1.279(3), N3-Eu1-N4 115.40(9), N3-Eu1-N1 97.65(8), N4-Eu1-N1 125.38(8), N3-Eu1-N2 140.88(8), N4-Eu1-N2 100.93(8), N1-Eu1-N2 70.45(7), N2-C9-C1 123.3(3), C9-N2-C10 119.6(2).

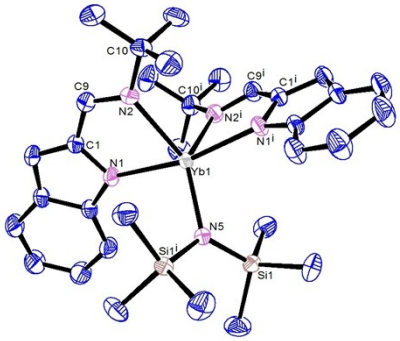


Figure S3. Structure of complex **6** (Ellipsoids at 30% probability level). Hydrogen atoms were omitted for clarity. Selected bond distances (Å) and angles (°): N1-Yb1 2.2740(16), N2-Yb1 2.4458(16), N5-Yb1 2.165(2), Yb1-N1$^{\#1}$ 2.2740(16), Yb1-N2$^{\#1}$ 2.4458(16), C9-N2 1.288(3), N5-Yb1-N1 96.53(4), N5-Yb1-N1$^{\#1}$ 96.53(4), N1-Yb1-N1$^{\#1}$ 166.94(8), N5-Yb1-N2 132.31(4), N1-Yb1-N2 72.94(6), N1$^{\#1}$-Yb1-N2 98.06(6), N5-Yb1-N2$^{\#1}$ 132.31(4), N1-Yb1-N2$^{\#1}$ 98.06(6), N1$^{\#1}$-Yb1-N2$^{\#1}$ 72.94(6), N2-Yb1-N2$^{\#1}$ 95.39(8), N2-C9-C1 122.08(18), C9-N2-C10 120.10(17).

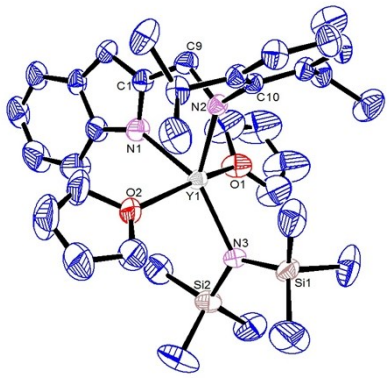


Figure S4. Structure of complex **8** (Ellipsoids at 30% probability level). Hydrogen atoms were omitted for clarity. Selected bond distances (Å) and angles (°): Y1-N1 2.294(3), Y1-N2 2.182(2), Y1-N3 2.275(2), Y1-O1 2.361(2), Y1-O2 2.357(2), C9-N2 1.474(4), N2-Y1-N3 132.01(9), N2-Y1-N1 80.00(10), N3-Y1-N1 147.91(10), N2-Y1-O2 101.89(9), N3-Y1-O2 89.17(9), N1-Y1-O2 85.20(11), N2-Y1-O1 97.30(9), N3-Y1-O1 89.04(9), N1-Y1-O1 83.49(11), O2-Y1-O1 155.64(10), C1-N1-Y1 108.9(2), C10-N2-Y1 137.78(19), C9-N2-Y1 112.47(18), C10-N2-C9 109.7(2), N2-C9-C1 115.2(3).

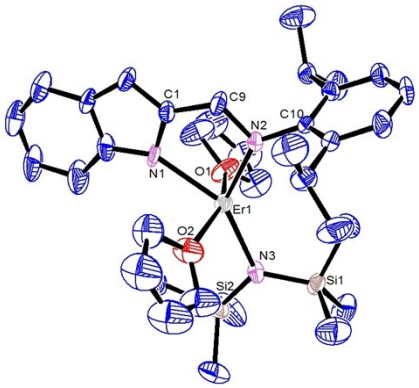


Figure S5. Structure of complex **9** (Ellipsoids at 30% probability level). Hydrogen atoms were omitted for clarity. Selected bond distances (Å) and angles (°): Er1-N1 2.293(12), Er1-N2 2.161(12), Er1-N3 2.257(12), Er1-O2 2.336(13), Er1-O1 2.351(12), C9-N2 1.455(18), N2-Er1-N3 131.9(4), N2-Er1-N1 80.4(5), N3-Er1-N1) 147.7(5), N2-Er1-O2 97.5(5), N3-Er1-O2 89.7(5), N1-Er1-O2 83.6(6), N2-Er1-O1 101.3(5), N3-Er1-O1 89.2(4), N1-Er1-O1 84.5(5), O2-Er1-O1 155.7(6), C10-N2-C9 108.7(11), N2-C9-C1 112.3(13).

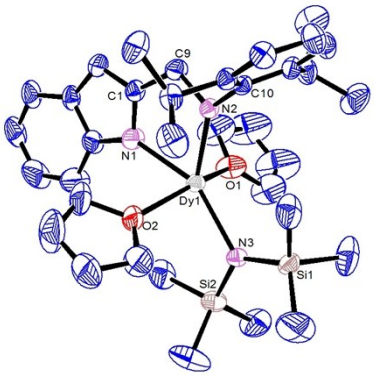


Figure S6. Structure of complex **10** (Ellipsoids at 30% probability level). Hydrogen atoms were omitted for clarity. Selected bond distances (Å) and angles (°): Dy1-N1 2.316(4), Dy1-N2 2.190(3), Dy1-N3 2.300(4), Dy1-O1 2.378(4), Dy1-O2 2.387(4), N2-C9 1.467(5), N2-Dy1-N3, 134.11(12), N2-Dy1-N1 78.82(14), N3-Dy1-N1 146.97(13), N2-Dy1-O2 102.13(14), N3-Dy1-O2 89.21(13), N1-Dy1-O2 84.69(17), N2-Dy1-O(1) 97.08(13), N3-Dy1-O1 89.09(13), N1-Dy1-O1 83.10(18), O2-Dy1-O1 154.74(16), C1-N1-Dy1 109.0(3), C9-N2-Dy1 114.2(3), C10-N2-Dy1 136.1(2), C10-N2-C9 109.6(3), N2-C9-C1 113.9(4).

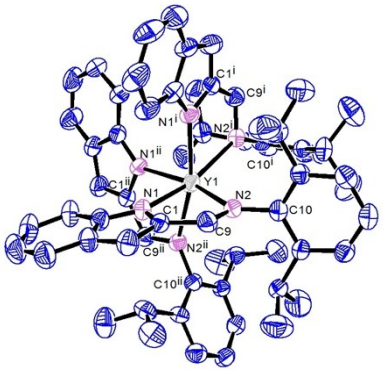


Figure S7. Structure of complex **11** (Ellipsoids at 30% probability level). Hydrogen atoms were omitted for clarity. Selected bond distances (Å) and angles (°): N1-Y1 2.356(2), Y1-N1$^{\#1}$ 2.356(2), Y1-N1$^{\#2}$ 2.356(2), N2-Y1 2.496(2), Y1-N2$^{\#1}$ 2.496(2), Y1-N2$^{\#2}$ 2.496(2), C9-N2 1.363(3), N2-C9-C1 119.0(2), C9-N2-C10 112.1(2), N1-Y1-N1$^{\#1}$ 92.24(7), N1-Y1-N1$^{\#2}$ 92.24(7), N1$^{\#1}$-Y1-N1$^{\#2}$ 92.25(7), N1-Y1-N2 71.19(7), N1$^{\#1}$-Y1-N2 89.01(6), N1$^{\#2}$-Y1-N2 163.42(7), N1-Y1-N2$^{\#2}$ 89.01(6), N1$^{\#1}$-Y1-N2$^{\#2}$ 163.43(7), N1$^{\#2}$-Y1-N2$^{\#2}$ 71.19(7), N2-Y1-N2$^{\#2}$ 107.00(5), N1-Y1-N2$^{\#1}$, 163.43(7), N1$^{\#1}$-Y1-N2$^{\#1}$ 71.19(7), N1$^{\#2}$-Y1-N2$^{\#1}$ 89.01(6), N2-Y1-N2$^{\#1}$ 107.00(5), N2$^{\#2}$-Y1-N2$^{\#1}$ 107.00(5).

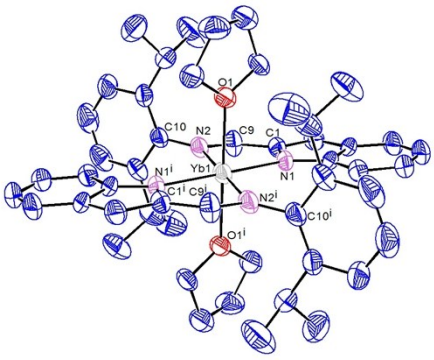


Figure S8. Structure of complex **12** (Ellipsoids at 30% probability level). Hydrogen atoms were omitted for clarity. Selected bond distances (Å) and angles (°): N1-Yb1 2.271(5), Yb1-N1$^{\#1}$ 2.271(5), Yb1-N2 2.420(7), Yb1-N2$^{\#1}$ 2.420(7), O1-Yb1 2.297(5), Yb1-O1$^{\#1}$ 2.297(5), N1$^{\#1}$-Yb1-N1 180.0, N1$^{\#1}$-Yb1-O1 90.01(18), N1-Yb1-O1 89.99(18), N1$^{\#1}$-Yb1-O1$^{\#1}$ 89.99(18), N1-Yb1-O1$^{\#1}$ 90.01(18), O1-Yb1-O1$^{\#1}$ 179.998(1), N1$^{\#1}$-Yb1-N2$^{\#1}$ 74.02(18), N1-Yb1-N2$^{\#1}$ 105.99(18), O1-Yb1-N2$^{\#1}$ 89.44(18), O1$^{\#1}$-Yb1-N2$^{\#1}$ 90.56(18), N1$^{\#1}$-Yb1-N2 105.98(18), N1-Yb1-N2

74.02(18), O1-Yb1-N2 90.56(18), O1$^{\#1}$-Yb1-N2 89.44(18), N2$^{\#1}$-Yb1-N2 179.999(2), N2-C9-C1 118.7(7), C9-N2-C10 111.6(6).

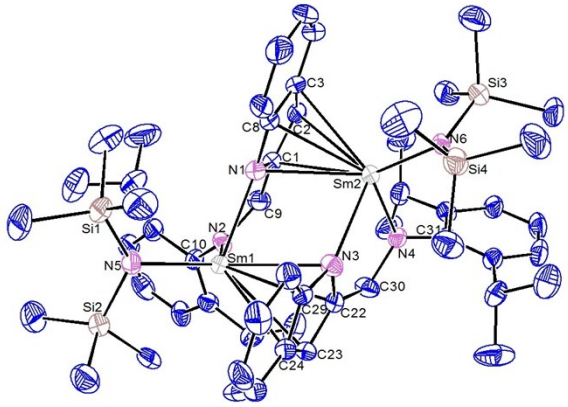


Figure S9. Structure of complex **13** (Ellipsoids at 30% probability level). Hydrogen atoms were omitted for clarity. Selected bond distances (Å) and angles (°): N1-Sm1 2.444(8), Sm1-N2 2.238(9), Sm1-N5 2.276(8), Sm1-N3 2.813(9), Sm1-C22 2.949(10), Sm1-C23 2.957(10), Sm1-C24 2.873(10), Sm1-C29 2.780(10), N2-C9 1.487(14), Sm2-N3 2.447(8), Sm2-N4 2.216(8), Sm2-N6 2.266(8), N1-Sm2 2.804(9), C1-Sm2 2.933(11), C2-Sm2 2.980(10), Sm2-C3 2.889(10), Sm2-C8 2.772(10), N4-C30 1.464(13), N2-Sm1-N5 114.1(3), N2-Sm1-N1 73.5(3), N5-Sm1-N1 109.4(3), N2-Sm1-N3 106.8(3), N5-Sm1-N3 137.5(3), N1-Sm1-N3 71.5(3), C10-N2-C9 111.9(9), N2-C9-C1 113.7(9), N4-Sm2-N6 112.5(3), N4-Sm2-N3 71.8(3), N6-Sm2-N3 110.9(3), N4-Sm2-N1 106.5(3), N6-Sm2-N1 139.6(3), N3-Sm2-N1 71.6(3), C31-N4-C30 114.4(8), N4-C30-C22 112.1(9), Sm2-N3-Sm1 107.3(3), Sm1-N1-Sm2 107.7(3).

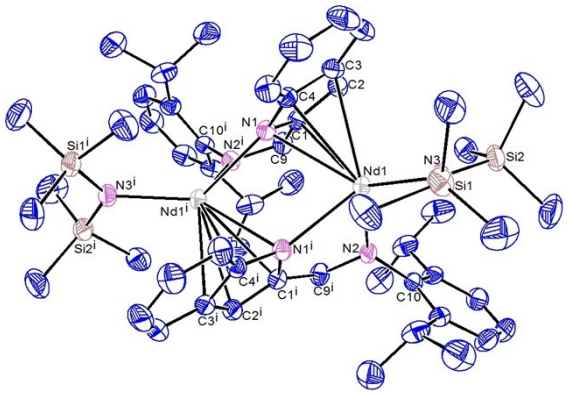


Figure S10. Structure of complex **14** (Ellipsoids at 30% probability level). Hydrogen atoms were omitted for clarity. Selected bond distances (Å) and angles (°): N1-Nd1$^{\#1}$

2.519(2), N1-Nd1 2.802(2), Nd1-N1$^{\#1}$ 2.519(2), Nd1-N2 2.263(2), Nd1-N3 2.292(2), C1-Nd1 2.855(3), Nd1-C2 2.924(3), Nd1-C3 2.963(3), Nd1-C4 2.867(3), N2-C9$^{\#1}$ 1.463(4), C9-N2$^{\#1}$ 1.463(4), Nd1$^{\#1}$-N1-Nd1 106.99(8), N2-Nd1-N3 112.13(9), N2-Nd1-N1$^{\#1}$ 69.91(8), N3-Nd1-N1$^{\#1}$ 129.81(8), N2-Nd1-N1 109.43(7), N3-Nd1-N1 138.13(8), N1$^{\#1}$-Nd1-N1 70.20(9), C10-N2-C9$^{\#1}$ 114.5(2), N2$^{\#1}$-C9-C1 111.5(2).

Table S1. Crystallographic Data for **4**–**6**, **11**, **12**.

	4	**5**	**6**	**11**	**12**
formula	$C_{36}H_{40}N_5Si_2Eu$	$C_{25}H_{51}N_4Si_4Eu$	$C_{32}H_{48}N_5Si_2Yb$	$C_{63}H_{69}N_6Y$	$C_{50}H_{62}N_4O_2Yb$
Fw	750.87	672.02	731.97	999.15	924.08
T(K)	293(2)	293(2)	293(2)	293(2)	293(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	Triclinic	Monoclinic	Monoclinic	Rhombohedral	Triclinic
space group	*P*-1	$P2_1/c$	*C*c	*R*-3	*P*-1
a (Å)	12.5496(8)	18.2694(9)	15.4846(8)	18.6067(12)	10.244(2)
b (Å)	12.7106(8)	11.7290(6)	15.5616(9)	18.6067(12)	10.812(2)
c (Å)	13.0429(8)	17.2018(9)	15.9167(9)	36.828(2)	12.997(3)
α(deg)	91.9700(10)	90	90	90	69.120(3)
β(deg)	98.0050(10)	108.6700(10)	111.3640(10)	90	72.005(3)
γ(deg)	116.3170(10)	90	90	120	86.183(3)
V (Å^3)	1835.8(2)	3492.1(3)	3571.8(3)	11042.0(12)	1277.7(5)
Z	2	4	4	6	1
D_{calcd} (mg/m^3)	1.358	1.278	1.361	0.902	1.201
μ(mm^{-1})	1.804	1.952	2.712	0.825	1.867
F(000)	764	1392	1492	3168	476
θ range (deg)	1.80–27.60	2.10–27.57	1.93–27.59	1.66–27.63	1.76–27.44
reflections collected / unique	16050/8309	29837/8056	15241/4127	32154/5696	5676/5676

R(int)	0.0295	0.0339	0.0194	0.0695	0.0000
goodness-of-fit on F^2	0.999	1.068	1.028	1.061	1.067
R_1,wR_2 [$I>2\sigma(I)$]	0.0381, 0.0745	0.0308, 0.0649	0.0171, 0.0413	0.0655, 0.1840	0.0661,0 .1696
R_1,wR_2(all data)	0.0666, 0.0872	0.0515, 0.0715	0.0187, 0.0424	0.1446, 0.2005	0.1035, 0.1866
Largest diff. peak and hole (e Å^{-3})	0.550 and –0.647	0.543 and –0.441	0.484 and –0.537	0.353 and –0.210	1.260 and –1.640

Table S2. Crystallographic Data for **8**–**10**, **13**, **14**.

	8	**9**	**10**	**13**	**14**
formula	$C_{35}H_{58}N_3O_2Si_2Y$	$C_{35}H_{58}N_3O_2Si_2Er$	$C_{35}H_{58}N_3O_2Si_2Dy$	$C_{54}H_{84}N_6Si_4Sm_2$	$C_{54}H_{84}N_6Si_4Nd_2$
Fw	697.93	776.28	771.52	1230.33	1218.12
T(K)	293(2)	293(2)	293(2)	293(2)	293(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	P-1	$P2/c$
a (Å)	10.6351(8)	10.571(4)	10.6543(7)	9.814(3)	15.9322(9)
b (Å)	32.280(3)	32.187(11)	32.270(2)	15.222(4)	12.3743(7)
c (Å)	11.9849(9)	12.964(3)	12.0034(8)	21.286(6)	16.8816(9)
α(deg)	90	90	90	73.257(3)	90
β(deg)	110.0440(10)	120.23(2)	110.3490(10)	86.632(3)	117.4350(10)
γ(deg)	90	90	90	77.623(3)	90
V (Å^3)	3865.3(5)	3811(2)	3869.4(5)	2974.4(13)	2953.9(3)
Z	4	4	4	2	4
D_{calcd} (mg/m^3)	1.199	1.353	1.324	1.374	1.370

μ(mm^{-1})	1.602	2.297	2.024	2.073	1.857
F(000)	1488	1604	1596	1260	1252
θ range (deg)	1.92–27.61	1.93–25.00	2.13–27.00	1.49–25.00	1.65–27.44
reflections collected / unique	33292/8879	23852/6531	31980/8399	20155/10296	24812/6720
R(int)	0.0554	0.0444	0.0238	0.0488	0.0373
goodness-of-fit on F^2	1.011	1.094	1.210	1.066	1.048
R_1,wR_2 [$I>2\sigma(I)$]	0.0498, 0.1075	0.0929, 0.2421	0.0357, 0.0783	0.0614, 0.1575	0.0276, 0.0598
R_1,wR_2(all data)	0.1061, 0.1280	0.0981, 0.2450	0.0426, 0.0810	0.0932, 0.1793	0.0483, 0.0666
Largest diff. peak and hole (e Å^{-3})	0.306 and −0.462	1.943 and −4.220	0.470 and −1.288	2.231 and −2.381	0.718 and −0.388