Supporting Information

Dehydrogenation of Secondary Amines: Synthesis, and Characterization of Rare-Earth Metal Complexes Incorporating Imino- or Amido-Functionalized Pyrrolyl Ligands

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Table 1. Crystallographic data for complexes 3a, 3b, 3c

	3a	**3b**	**3c**
empirical formula	$C_{24}H_{44}N_5Si_4Y$	$C_{24}H_{44}N_5Si_2Dy$	$C_{24}H_{44}N_5Si_2Yb$
formula weight	547.73	621.32	631.86
T((K)	293(2)	293(2)	293(2)
λ(Å)	0.71073	0.71073	0.71073
crystal system	Triclinic	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	9.2007(12)	9.2378(9)	9.2342(9)
b (Å)	9.3829(12)	9.3434(9)	9.3375(9)
c (Å)	19.864(3)	19.929(2)	19.846(2)
α(deg)	88.008(2)	87.8880(10)	86.9250(10)
β(deg)□	84.805(2)	84.6720(10)	84.6240(10)
γ(deg)	85.998(2)	86.2540(10)	85.8500(10)
V (Å^3)	1702.9(4)	1708.2(3)	1697.3(3)
Z	2	2	2
D_{calcd} (g cm^{-3})	1.068	1.208	1.236
μ (mm^{-1})	1.799	2.274	2.842
F(000)	580	634	642
θ□ range (deg.)	2.06 to 26.00	2.05 to 26.00	2.06 to 26.00
reflcns collcd/unique	13222/6612 [R_{int} = 0.0406]	13010/6605 [R_{int} = 0.0187]	13050/6589 [R(int) = 0.0198]
data/restraints/params	6612/579/485	6605/579/496	6589/567/497
Goodness of fit	0.968	0.955	1.066
R_1 [$I > 2\sigma$(□*I*)]	0.0510	0.0290	0.0247
wR_2	0.1280	0.0851	0.0651
largest diff. Peak and hole(e·Å^{-3})	0.316 and -0.271	0.919 and -0.507	0.689 and -0.973

Table 2. Crystallographic data for complexes 3d, 4a, 4b

	3d	**4a**	**4b**
empirical formula	$C_{24}H_{44}N_5Si_2Eu$	$C_{32}H_{60}N_5Si_2Y$	$C_{32}H_{60}DyN_5Si_2$
formula weight	610.78	659.94	733.53
T((K)	293(2)	293(2)	293(2)
λ(Å)	0.71073	0.71073	0.71073
crystal system	Triclinic	Monoclinic	Monoclinic
space group	$P\bar{1}$	*C2/c*	*C2/c*
a (Å)	9.2289(11)	16.3948(15)	16.4062(18)
b (Å)	9.3704(11)	16.9374(15)	16.8967(19)
c (Å)	20.064(2)	13.8194(12)	13.8325(16)
α(deg)	87.8760(10)	90	90
β(deg)□	84.7400(10	99.0520(10)	99.5270(10)
γ(deg)	86.2930(10)	90	90
V (Å^3)	1723.3(3)	3789.7(6)	3781.6(7)
Z	2	4	4
D_{calcd} (g cm^{-3})	1.177	1.157	1.288
μ (mm^{-1})	1.906	1.628	2.065
F(000)	628	1416	1524
θ□ range (deg.)	2.04 to 27.65	1.74 to 26.00	2.15 to 26.00
reflcns collcd/unique	14561/7754 [R(int) = 0.0253]	14518/3726 [R(int) = 0.0327]	14343/3717 [R(int) = 0.0279]
data/restraints/params	7754 / 561 / 496	3726/0/191	3717/0/191
Goodness of fit	1.037	1.017	1.049
R_1 [$I > 2\sigma$(□I)]	0.0383	0.0342	0.0197
wR_2	0.0879	0.0802	0.0492
largest diff. Peak and hole(e·Å^{-3})	0.788 and -0.914	0.339 and -0.210	0.557 and -0.802

Table 3. Crystallographic data for complexes4c, 4c', 5

	4c	**4c'**	**5**
empirical formula	$C_{32}H_{60}ErN_5Si_2$	$C_{43}H_{72}ClErLi_2N_6O$	$C_{30}H_{66}Li_4N_6Si_4$
formula weight	738.29	905.66	651.01
T((K)	293(2)	293(2)	293(2)
λ(Å)	0.71073	0.71073	0.71073
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	*C2/c*	$P2_1/c$	$P2_1/n$
a (Å)	16.3623(12)	11.0210(14)	10.8200(9)
b (Å)	16.8981(13)	20.302(3)	13.6124(12)
c (Å)	13.8066(10)	22.096(3)	14.8062(13)
α(deg)	90	90	90
β(deg)□	99.0760(10)	103.906(2)	90.2780(10)
γ(deg)	90	90	90
V (Å^3)	3769.6(5)	4799.1(11)	2180.7(3)
Z	4	4	2
D_{calcd} (g cm^{-3})	1.301	1.253	0.991
μ (mm^{-1})	2.316	1.840	0.161
F(000)	1532	1884	712
θ□ range (deg.)	1.74 to 26.00	1.38 to 27.54	2.03 to 27.50
reflcns collcd/unique	14472/3703 [R(int) = 0.0311]	40943/10962 [R(int) = 0.0310]	18610/4990 [R(int) = 0.0415]
data/restraints/params	3703/0/191	10962/196/555	4990/0/208
Goodness of fit	1.029	1.008	1.002
R_1 [$I > 2\sigma$(□I)]	0.0251	0.0368	0.0512
wR_2	0.0549	0.0967	0.1265
largest diff. Peak and hole(e·Å^{-3})	0.747 and -0.484	1.465 and -0.758	0.224 and -0.218

Table 4. Crystallographic data for complexes 7a, 7b, 7c

	7a	**7b**	**7c**
empirical formula	$C_{46}H_{80}N_6Si_4Nd_2$	$C_{46}H_{80}N_6Si_4Sm_2$	$C_{46}H_{80}Er_2N_6Si_4$
formula weight	1118.00	1130.22	1164.04
T (K)	293(2)	293(2)	293(2)
λ (Å)	0.71073	0.71073	0.71073
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	*C2/c*	*C2/c*	*P21/c*
a (Å)	26.619(5)	26.5814(13)	22.377(5)
b (Å)	12.344(3)	12.3473(6)	19.276(4)
c (Å)	17.358(4)	17.3550(9)	12.747(3)
α (deg)	90	90	90
β (deg)□	103.536(2)	103.6210(10)	101.327(3)
γ (deg)	90	90	90
V (Å^3)	5545(2)	5535.9(5)	5391(2)
Z	4	4	4
D_{calcd} (g cm^{-3})	1.339	1.356	1.434
μ (mm^{-1})	1.972	2.221	2360
F(000)	2296	2312	3.215
θ□ range (deg.)	1.83 to 25.99	1.58 to 25.98	1.41 to 26.00
reflcns collcd/unique	19673/5423 [R_{int} = 0.0520]	21076/5421 [R_{int} = 0.0260]	39994/10566 [R_{int} = 0.0724]
data/restraints/params	5423/0/272	5421/0/272	10566/15/543
Goodness of fit	1.107	1.025	1.037
R_1 [$I > 2\sigma$(□I)]	0.0396	0.0231	0.0443
wR_2	0.0911	0.0544	0.0992
largest diff. Peak and hole(e·Å^{-3})	1.763 and -0.986	0.562 and -0.403	2.175 and -1.544

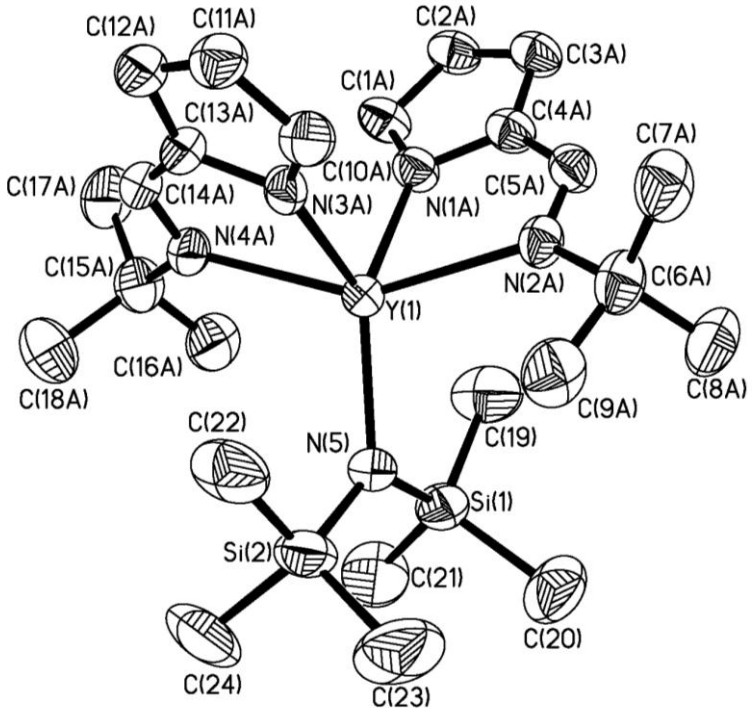


Figure 1. Molecular structure of the compound **3a**, hydrogen atoms and disorder are omitted for clarity. Selected bond lengths (Å) and angles (°): C(5A)-N(2A) 1.282(6), C(5B)-N(2B) 1.283(9), C(14A)-N(4A) 1.288(6), C(14B)-N(4B) 1.283(9), Y(1)-N(1A) 2.303(4), Y(1)-N(1B) 2.331(8), Y(1)-N(2A) 2.420(5), Y(1)-N(2B) 2.392(15), Y(1)-N(3A) 2.318(4), Y(1)-N(3B) 2.312(8), Y(1)-N(4A) 2.433(4), Y(1)-N(4B) 2.395(15), Y(1)-N(5) 2.245(4), N(2A)-C(5A)-C(4A) 123.2(6), N(2B)-C(5B)-C(4B) 113.9(19), N(4A)-C(14A)-C(13A) 122.5(5), N(4B)-C(14B)-C(13B) 119.6(16).

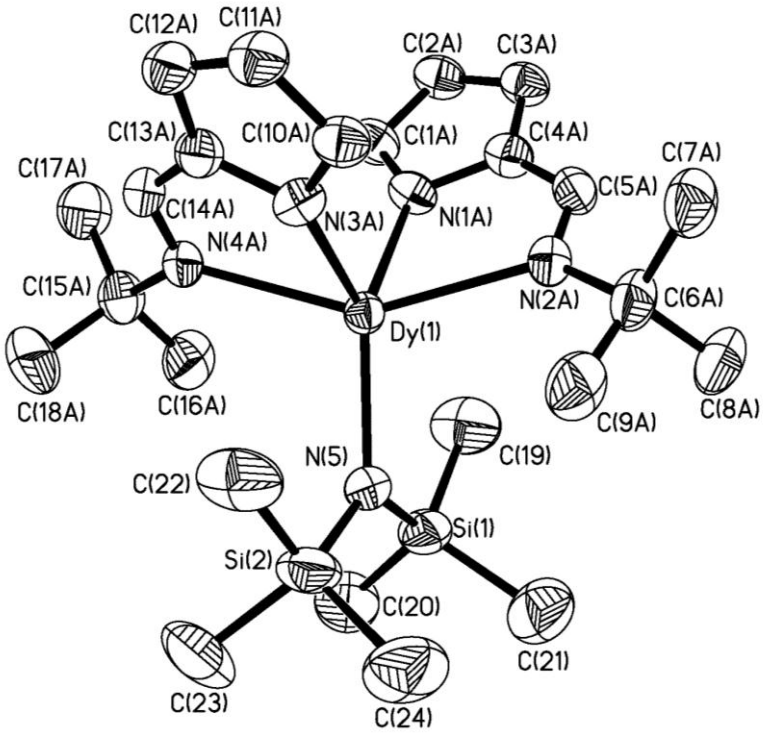


Figure 2. Molecular structure of the compound **3b**, hydrogen atoms and disorder are omitted for clarity. Selected bond lengths (Å) and angles (°):N(2A)-C(5A) 1.286(6), N(2B)-C(5B) 1.289(9), N(4A)-C(14A) 1.287(6), N(4B)-C(14B) 1.285(9), Dy(1)-N(1A) 2.332(7), Dy(1)-N(1B) 2.33(2), Dy(1)-N(2A) 2.439(4), Dy(1)-N(2B) 2.458(11), Dy(1)-N(3A) 2.345(9), Dy(1)-N(3B) 2.301(17), Dy(1)-N(4A) 2.453(4), Dy(1)-N(4B) 2.419(12), Dy(1)-N(5) 2.230(3), N(2A)-C(5A)-C(4A) 123.0(5), N(2B)-C(5B)-C(4B) 120.3(15), N(4A)-C(14A)-C(13A) 122.9(5), N(4B)-C(14B)-C(13B) 121.4(12).

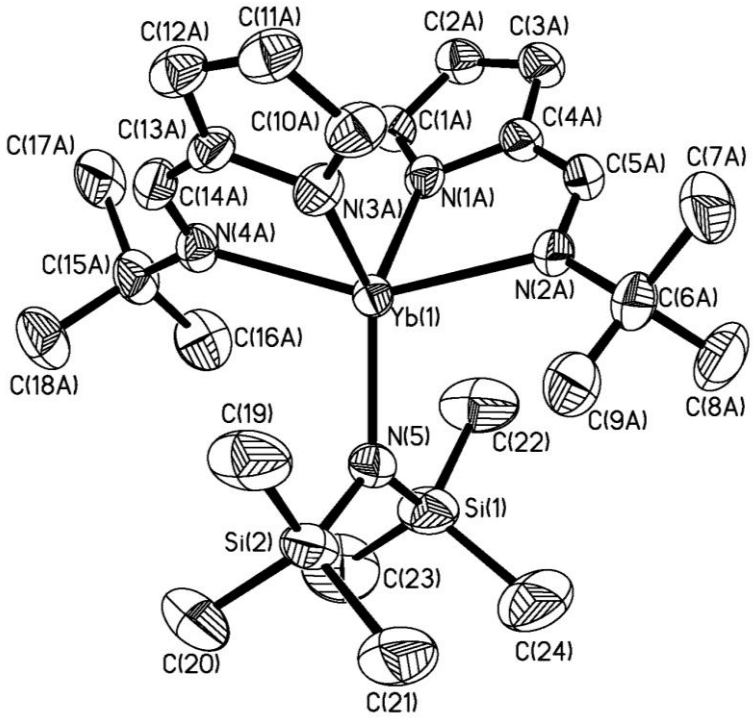


Figure 3. Molecular structure of the compound **3c**, hydrogen atoms and disorder are omitted for clarity. Selected bond lengths (Å) and angles (°): N(2A)-C(5A) 1.282(6), N(2B)-C(5B) 1.282(8), C(14A)-N(4A) 1.292(6), C(14B)-N(4B) 1.282(8), Yb(1)-N(1A) 2.271(6), Yb(1)-N(1B) 2.294(11), Yb(1)-N(2A) 2.407(4), Yb(1)-N(2B) 2.354(9), Yb(1)-N(3A) 2.277(7), Yb(1)-N(3B) 2.332(16), Yb(1)-N(4A) 2.389(4), Yb(1)-N(4B) 2.405(9), Yb(1)-N(5), 2.188(3), N(2A)-C(5A)-C(4A) 122.5(5), N(2B)-C(5B)-C(4B) 124.7(13), N(4A)-C(14A)-C(13A) 122.0(5), N(4B)-C(14B)-C(13B) 120.8(10).

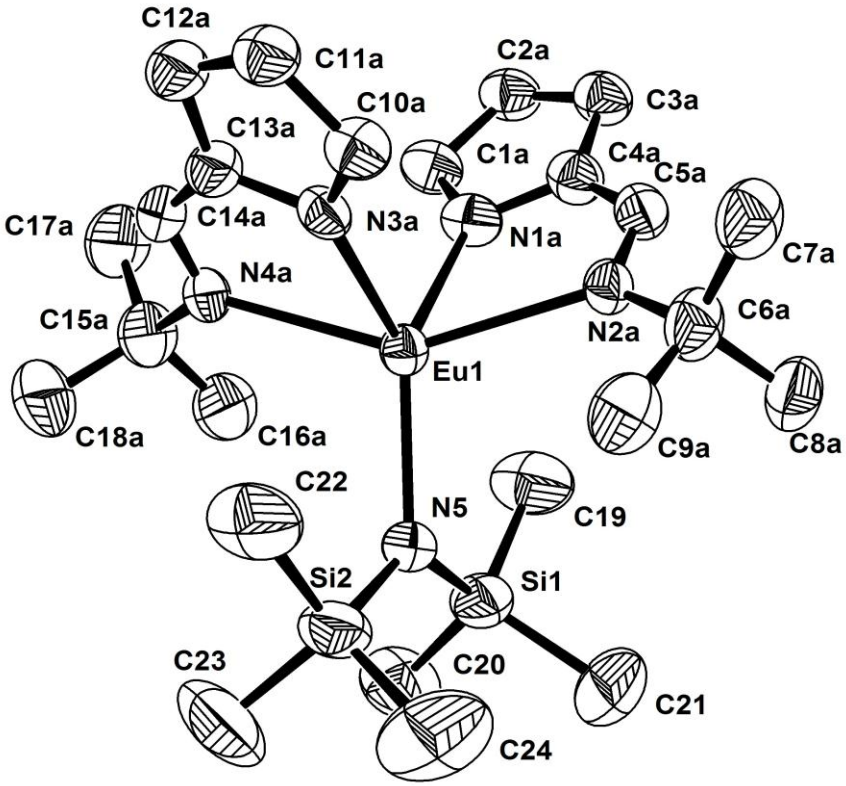


Figure 4. Molecular structure of the compound **3d**, hydrogen atoms and disorder are omitted for clarity. Selected bond lengths (Å) and angles (°): N(2A)-C(5A) 1.296(6), N(2B)-C(5B) 1.294(9), C(14A)-N(4A) 1.295(6), C(14B)-N(4B) 1.292(9), Eu(1)-N(1A) 2.374(10), Eu(1)-N(1B) 2.40(3), Eu(1)-N(2A) 2.482(4), Eu(1)-N(2B) 2.491(14), Eu(1)-N(3A) 2.387(7), Eu(1)-N(3B) 2.38(3), Eu(1)-N(4A) 2.491(4), Eu(1)-N(4B) 2.417(15), Eu(1)-N(5), 2.268(4), N(2A)-C(5A)-C(4A) 122.9(6), N(2B)-C(5B)-C(4B) 118.7(18), N(4A)-C(14A)-C(13A) 123.0(5), N(4B)-C(14B)-C(13B) 114.6(14).

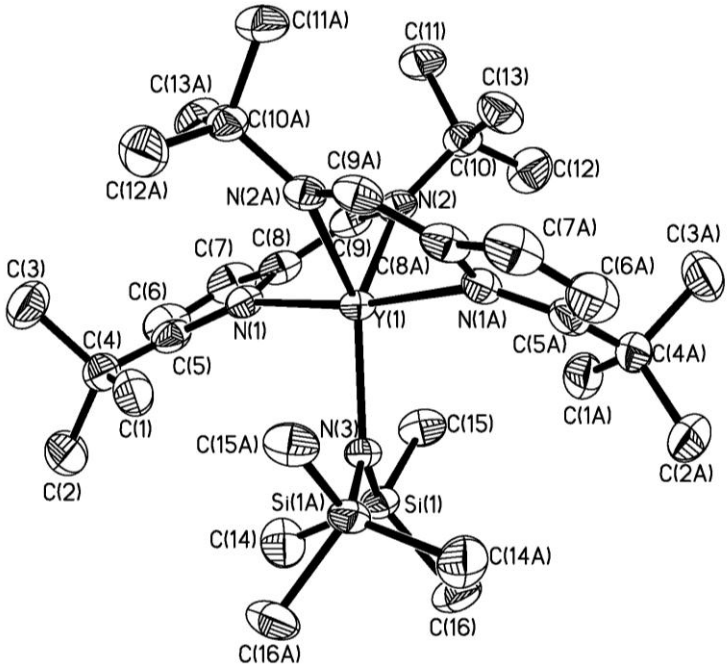


Figure 5. Molecular structure of the compound **4a**, hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Y(1)-N(1) 2.4098(19), Y (1)-N(2) 2.4007(19), Y (1)-N(3) 2.240(2), C(9)-N(2) 1.301(3), N(3)-Y(1)-N(1) 93.97(4), N(3)-Y(1)-N(2) 131.70(5), N(1)-Y(1)-N(2) 73.49(7), N(1)-Y(1)-N(1A) 172.05(9), N(1)-Y(1)-N(2A) 101.06(7), N(2)-Y(1)-N(2A) 96.61(9), N(2)-C(9)-C(8) 124.4(2).

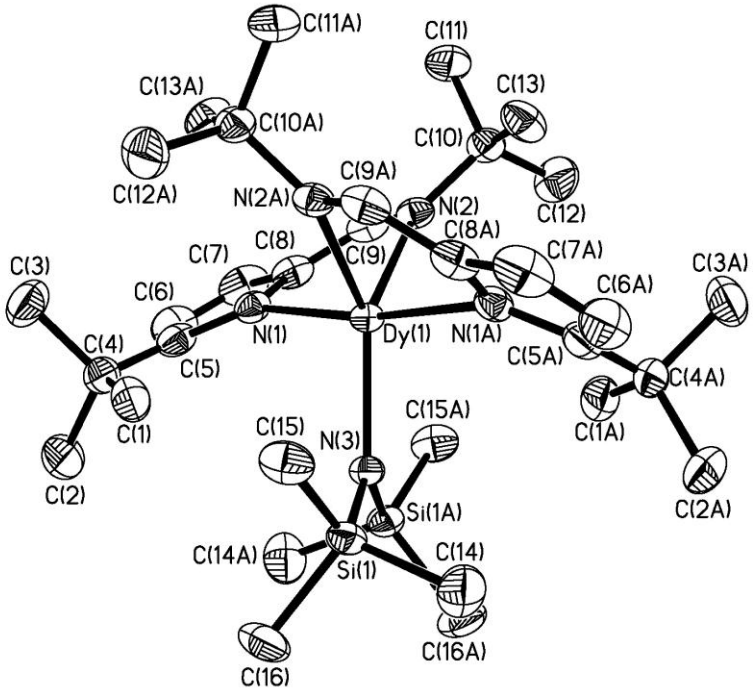


Figure 6. Molecular structure of the compound **4b**, hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Dy(1)-N(1) 2.421(2), Dy(1)-N(2) 2.4136(19), Dy(1)-N(3) 2.232(3), C(9)-N(2) 1.302(3), N(3)-Dy(1)-N(1) 94.14(4), N(3)-Dy(1)-N(2) 131.93(5), N(1)-Dy(1)-N(2) 73.12(7), N(1)-Dy(1)-N(1A) 171.72(9), N(1)- Dy(1)-N(2A) 101.19(7), N(2)-Dy(1)-N(2A) 96.13(9), N(2)-C(9)-C(8) 124.6(2).

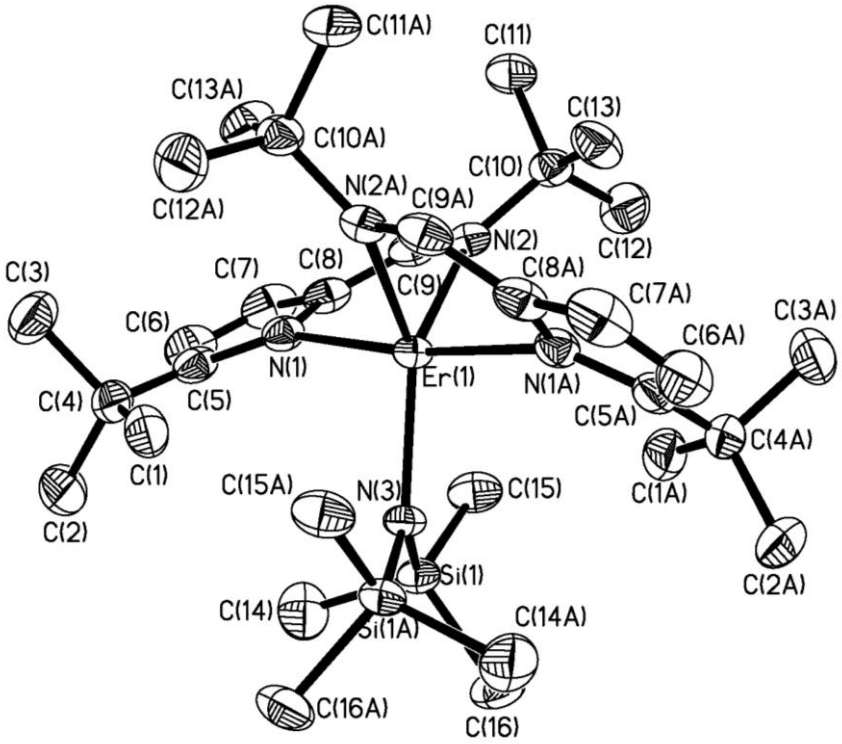


Figure 7. Molecular structure of the compound **4c**, hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Er(1)-N(1) 2.393(3), Er(1)-N(2) 2.383(2), Er(1)-N(3) 2.223(3), C(9)-N(2) 1.311(4), N(3)-Er(1)-N(1) 93.68(6), N(3)-Er(1)-N(2) 131.38(6), N(1)-Er(1)-N(2) 73.94(9), N(1)-Er(1)-N(1A) 172.63(12), N(1)-Er(1)-N(2A) 101.05(9), N(2)-Er(1)-N(2A) 97.24(12), N(2)-C(9)-C(8) 124.5(3).

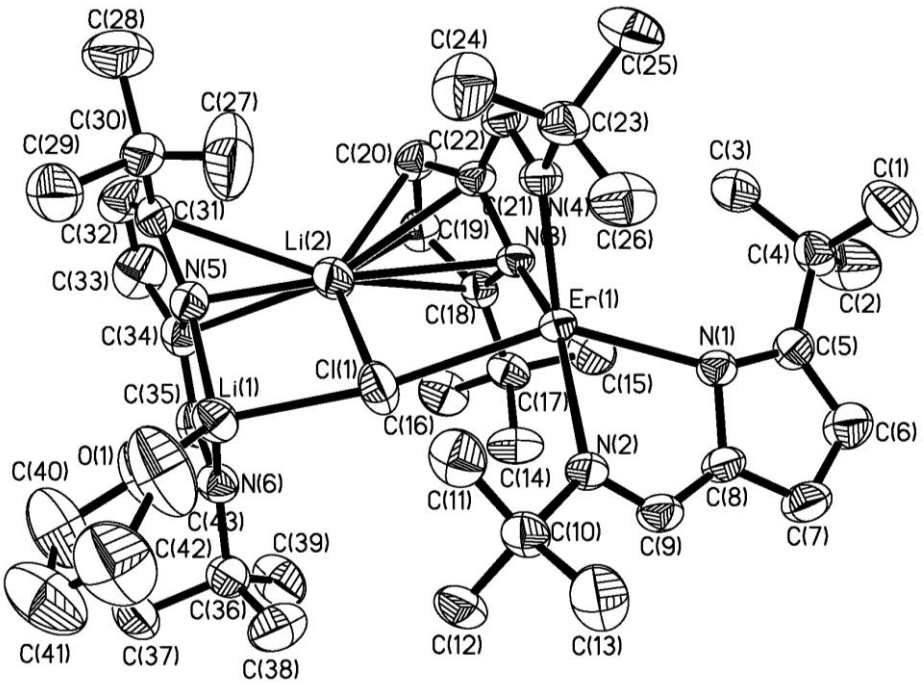


Figure 8. Molecular structure of the compound **4c'**, hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Er(1)-N(1) 2.346(3), Li(1)-N(5) 2.040(8), Er(1)-N(2) 2.458(3), Li(1)-N(6) 2.044(8), Er(1)-N(3) 2.300(3), Li(1)-O(1) 1.904(8), Er(1)-N(4) 2.126(3), Cl(1)-Li(1) 2.442(8), Er(1)-Cl(1) 2.6743(11), N(3)-Li(2) 2.710(8), N(2)-C(9) 1.278(5), C(18)-Li(2) 2.570(9), N(4)-C(22) 1.458(5), C(19)-Li(2) 2.339(9), N(6)-C(35) 1.285(6), C(20)-Li(2) 2.328(9), Li(2)-N(5) 2.138(8), C(21)-Li(2) 2.566(9), C(34)-Li(2) 2.765(9), C(31)-Li(2) 2.771(9), N(2)-C(9)-C(8) 124.1(4), C(22)-N(4)-C(23) 115.3(3), N(4)-C(22)-C(21) 111.2(3), C(22)-N(4)-Er(1) 115.9(2), N(6)-C(35)-C(34) 121.7(4), C(23)-N(4)-Er(1) 128.8(3).

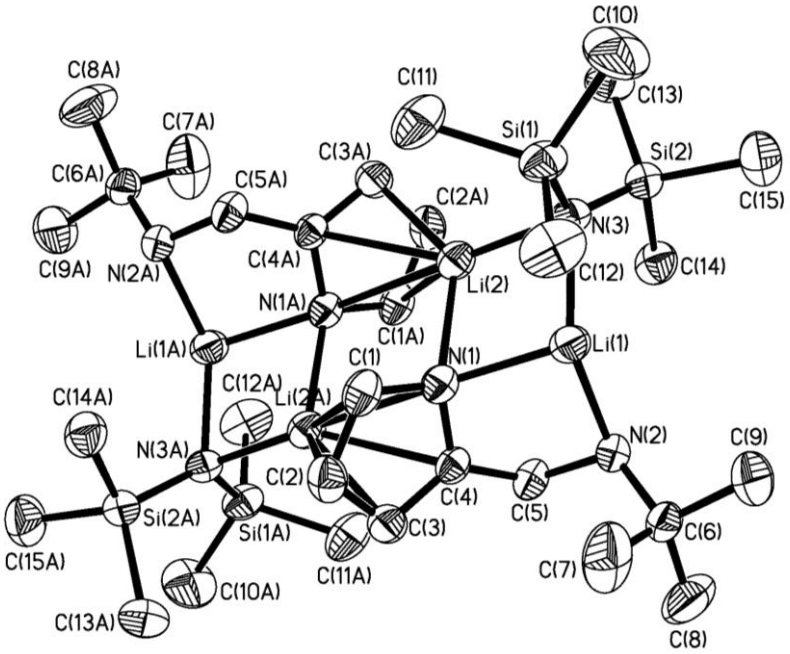


Figure 9. Molecular structure of the compound **5**, hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Li(1)-N(1) 2.057(4), Li(2)-N(1A) 2.693(4), Li(1)-N(2) 2.057(4), Li(2)-C(1A) 2.536(5), Li(1)-N(3) 1.960(4), Li(2)-C(2A) 2.332(4), Li(2)-N(1) 2.134(4), Li(2)-C(3A) 2.339(4), Li(2)-N(3),2.064(4), Li(2)-C(4A) 2.553(4), C(5)-N(2) 1.484(3), N(2)-C(5)-C(4) 111.59(18).

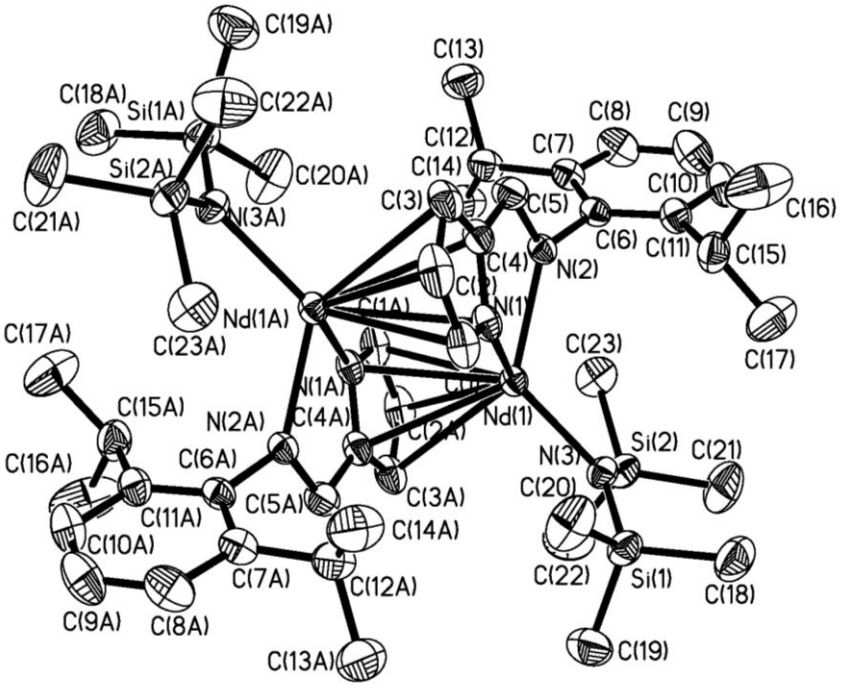


Figure 10. Molecular structure of the compound **7a**, hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Nd(1)-N(1) 2.511(4), Nd(1)-N(2) 2.259(4), Nd(1)-N(3) 2.302(5), C(5)-N(2) 1.451(7), Nd(1)-N(1A) 2.791(5), Nd(1)-C(1A) 2.760(6), Nd(1)-C(2A) 2.816(6), Nd(1)-C(3A) 2.883(6), Nd(1)-C(4A) 2.880(6), Nd(1)-Pyr 2.826(6), N(1)-Nd(1)-N(3) 130.49(16), N(1)-Nd(1)-N(2) 70.60(15), N(1)-Nd(1)-N(1A) 76.38(15), N(2)-Nd(1)-N(3) 121.48(17), N(2)-Nd(1)-N(1A) 97.68(15), N(3)-Nd(1)-N(1A) 136.90(16), N(2)-C(5)-C(4) 112.3(5).

Nd(1)-Pyr means the average bond distances between neodymium ion and the pyrrolyl ring.

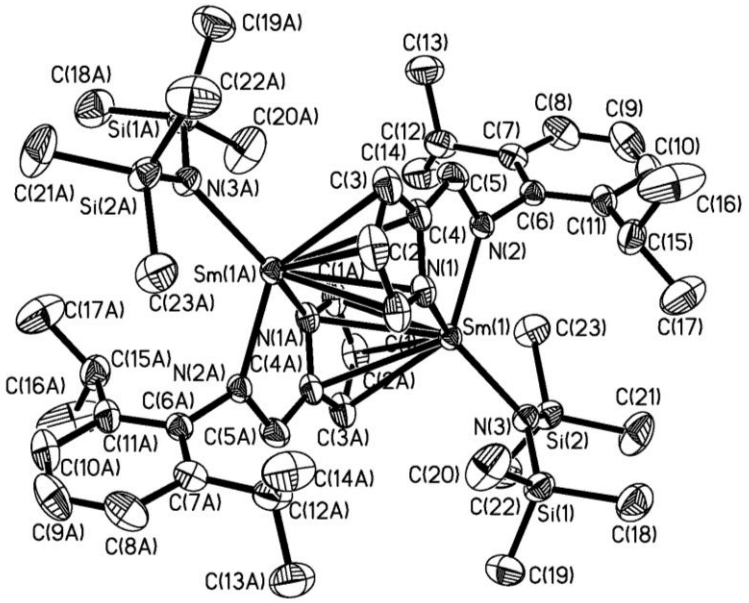


Figure 11. Molecular structure of the compound **7b**, hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Sm(1)-N(1) 2.472(2), Sm(1)-N(2) 2.234(2), Sm(1)-N(3) 2.278(2), C(5)-N(2) 1.460(4), Sm(1)-N(1A) 2.770(2), Sm(1)-C(1A) 2.725(3), Sm(1)-C(2A) 2.783(3), Sm(1)-C(3A) 2.851(3), Sm(1)-C(4A) 2.855(3), Sm(1)-Pyr 2.797(3), N(1)-Sm(1)-N(3) 130.49(8), N(1)-Sm(1)-N(2) 71.37(8), N(1)-Sm(1)-N(1A) 76.22(8), N(2)-Sm(1)-N(3) 120.64(8), N(2)-Sm(1)-N(1A) 98.17(8), N(3)-Sm(1)-N(1A) 137.12(8), N(2)-C(5)-C(4) 112.3(2).

Sm(1)-Pyr means the average bond distances between samarium ion and the pyrrolyl ring.

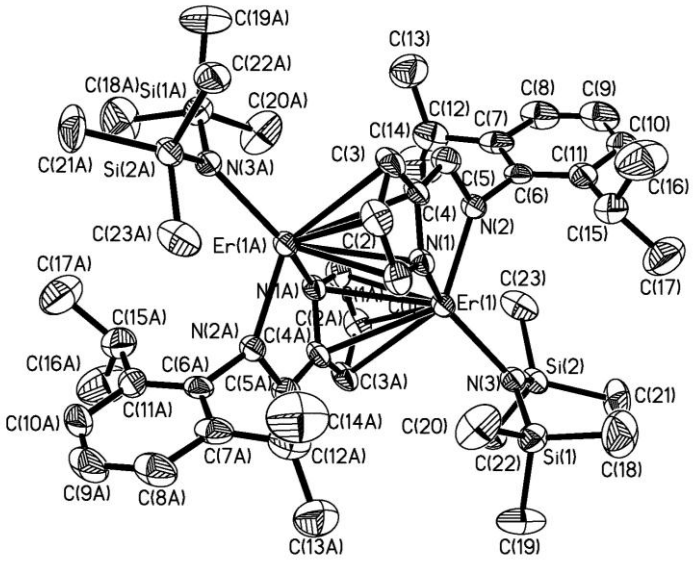
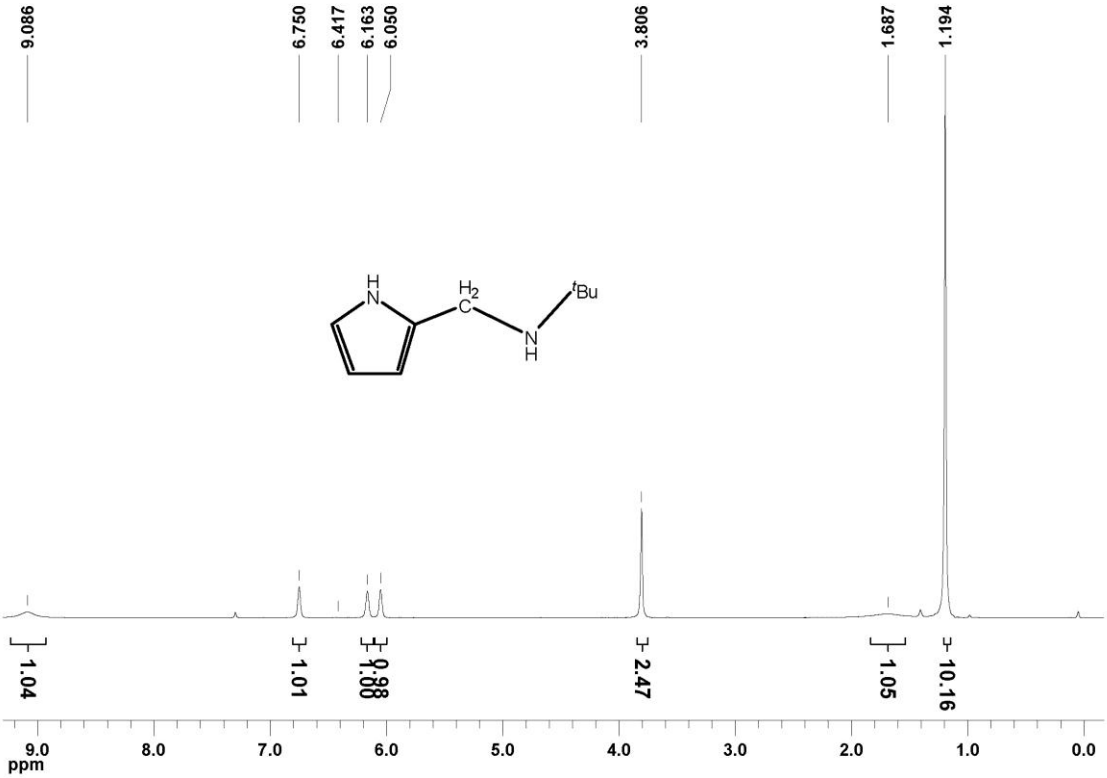


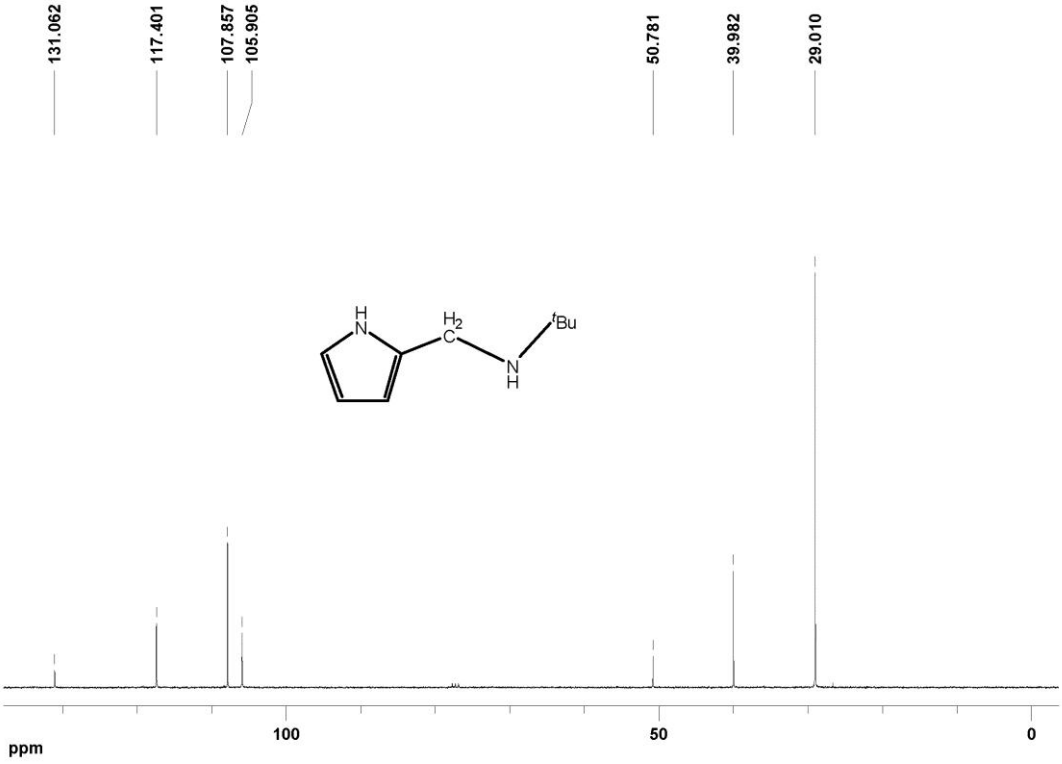
Figure 12. Molecular structure of the compound **7c**, hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Er(1)-N(1) 2.353(6), Er(1')-N(1') 2.356(5), Er(1)-N(2) 2.166(6), Er(1')-N(2') 2.177(5), Er(1)-N(3) 2.213(6), Er(1')-N(3') 2.201(5), C(5)-N(2) 1.467(9), C(5')-N(2') 1.459(7), Er(1)-N(1A), 2.728(6), Er(1')-N(1'A) 2.701(5), Er(1)-C(1A) 2.643(8), Er(1')-C(1'A) 2.650(6), Er(1)-C(2A) 2.676(8), Er(1')-C(2'A) 2.711(7), Er(1)-C(3A) 2.807(7), Er(1')-C(3'A) 2.786(7), Er(1)-C(4A) 2.805(7), Er(1')-C4'A) 2.792(6), Er(1)-Pyr 2.732(8), Er(1')-Pyr 2.728(7), N(2)-C(5)-C(4) 113.7(6), N(2')-C(5')-C(4') 111.6(5).

Er(1)-Pyr means the average bond distances between erbium ion and the pyrrolyl ring.

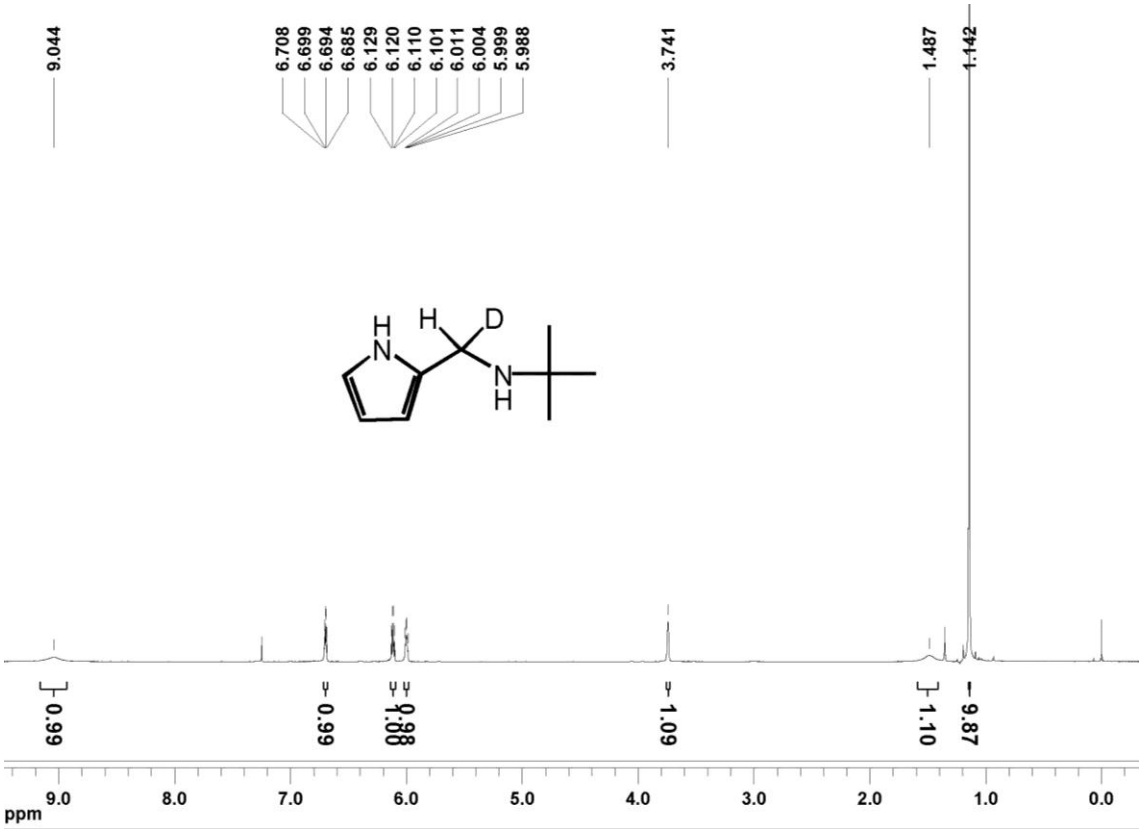
Copy of ^{1}H and ^{13}C NMR spectra



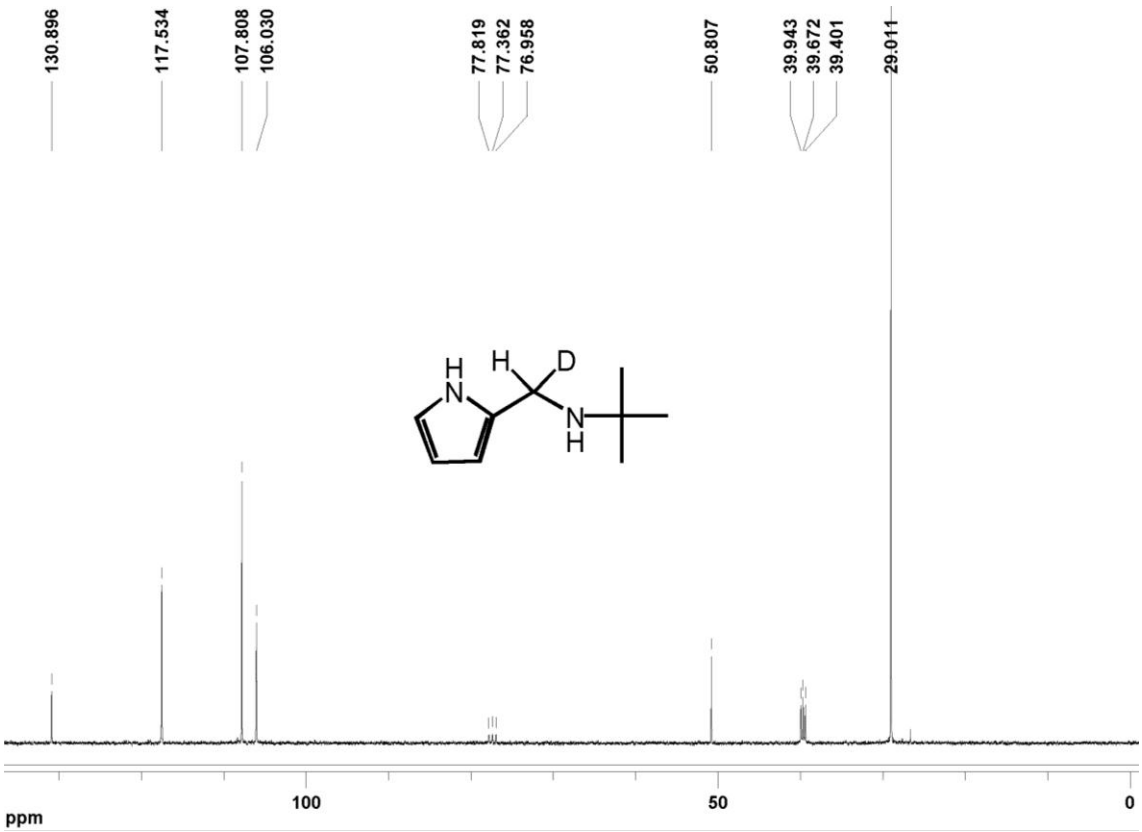
^{1}H NMR spectrum of compound **1**



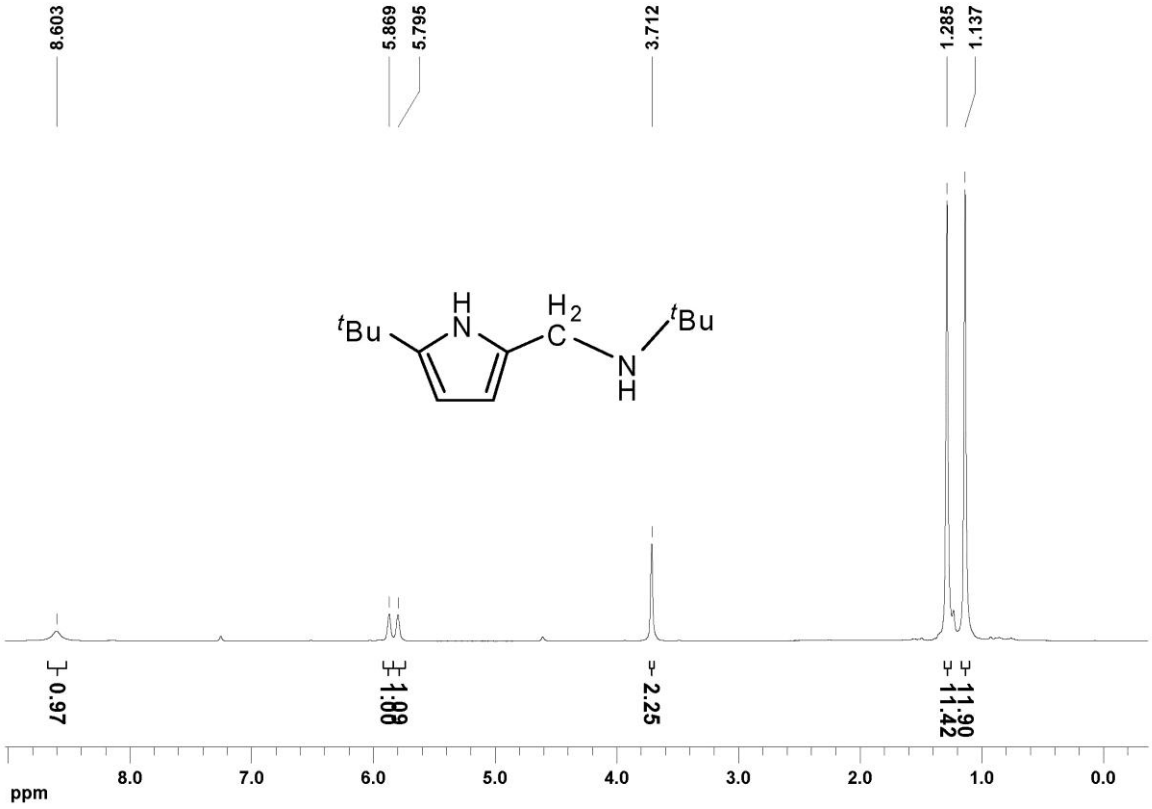
^{13}C NMR spectrum of compound **1**



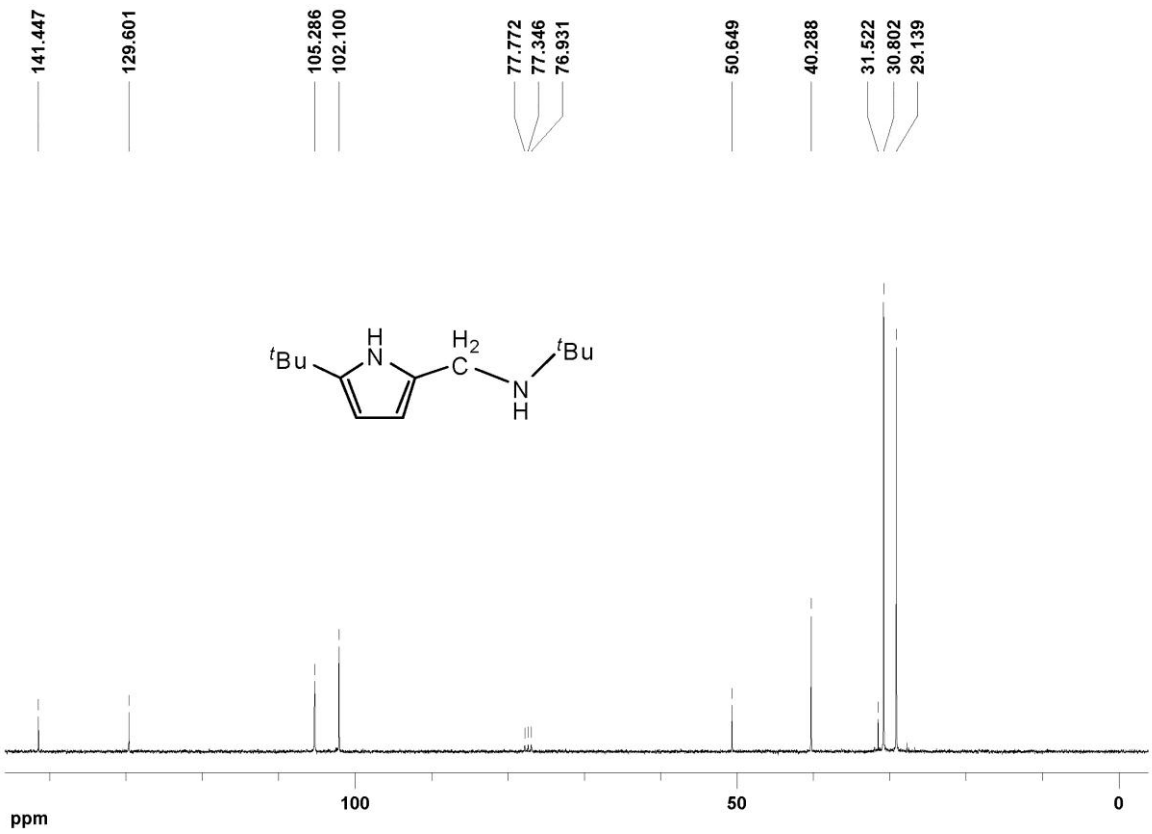
^{1}H NMR spectrum of compound **1a**



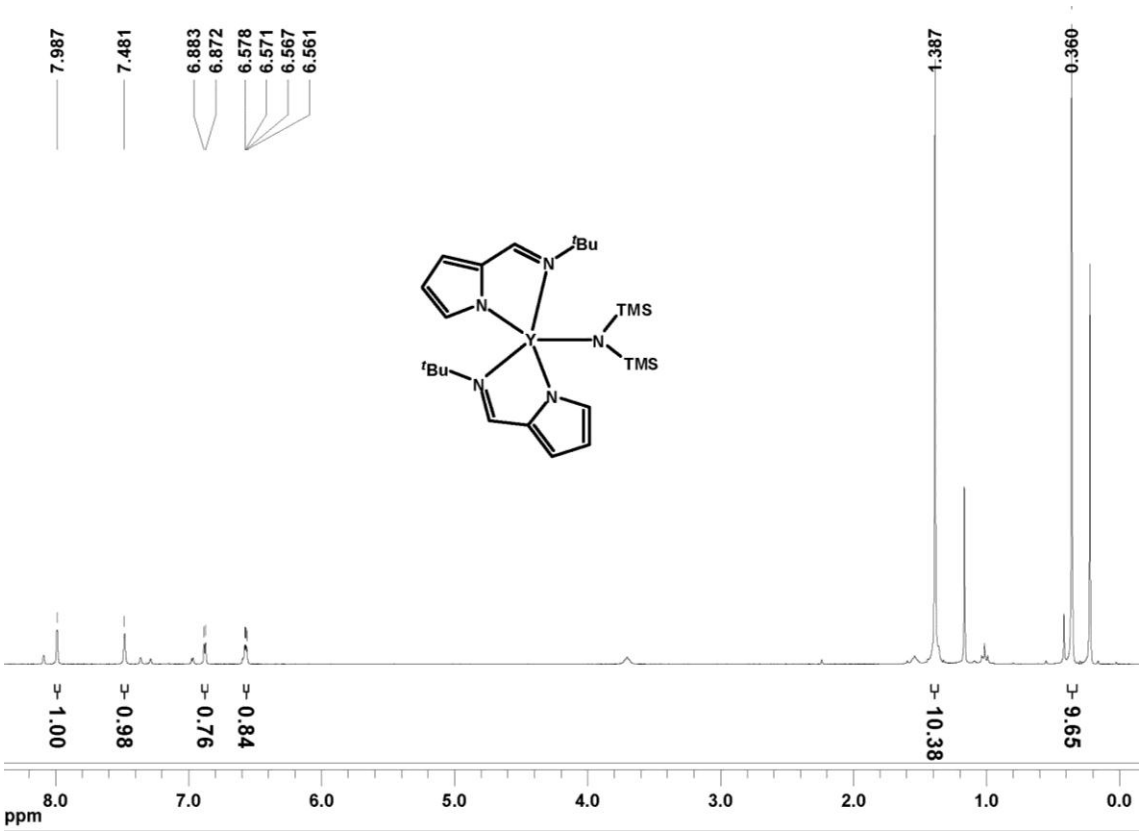
^{13}C NMR spectrum of compound **1a**



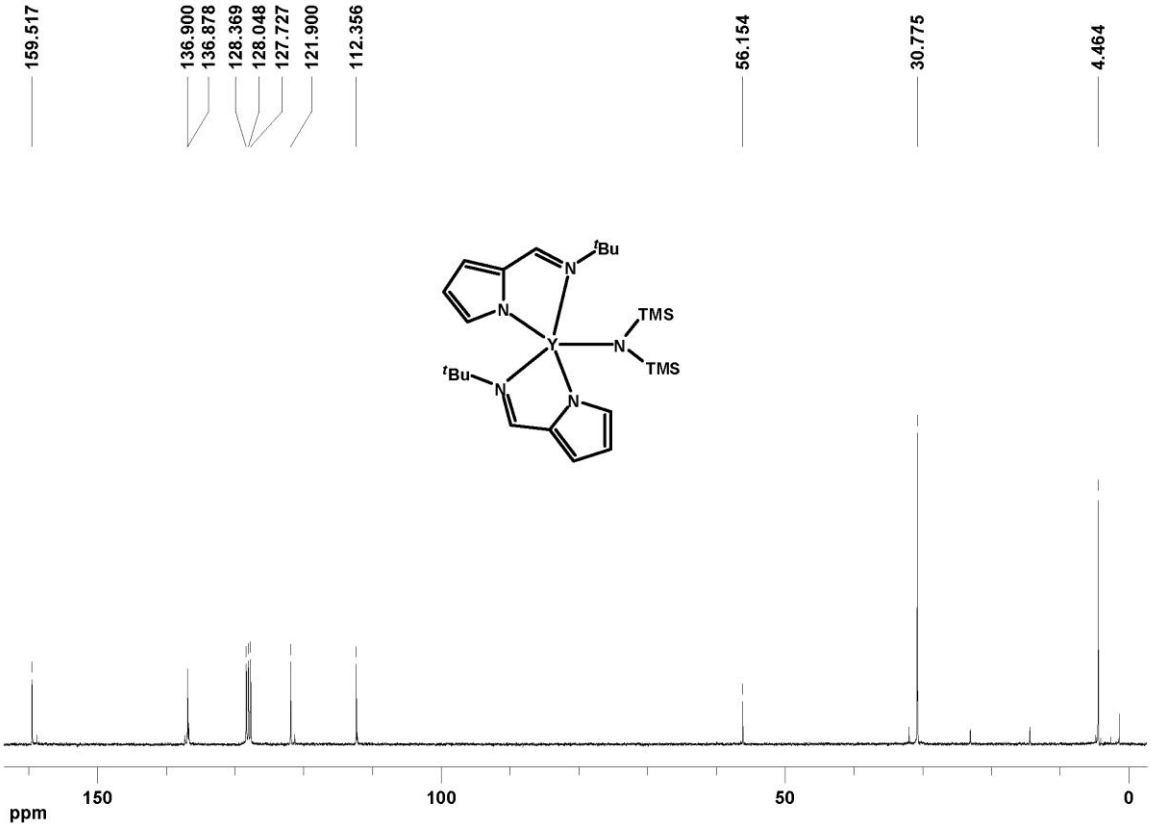
^{1}H NMR spectrum of compound **2**



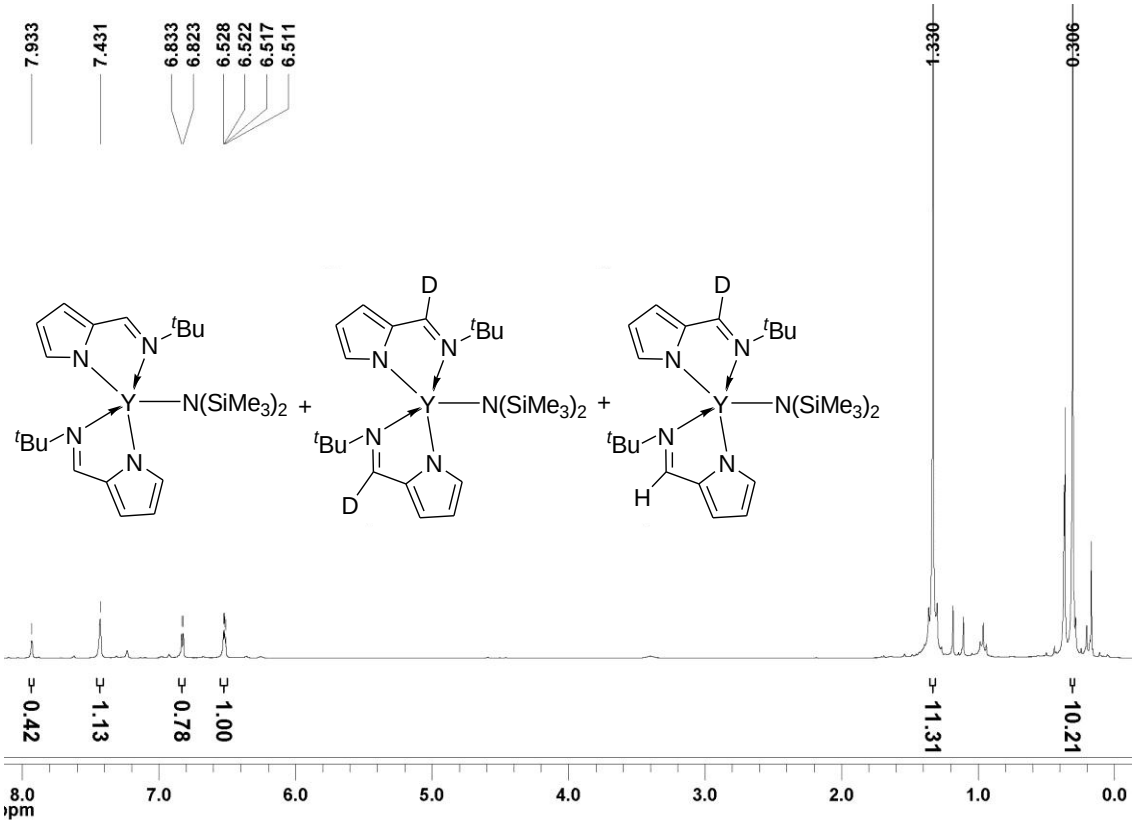
^{13}C NMR spectrum of compound **2**



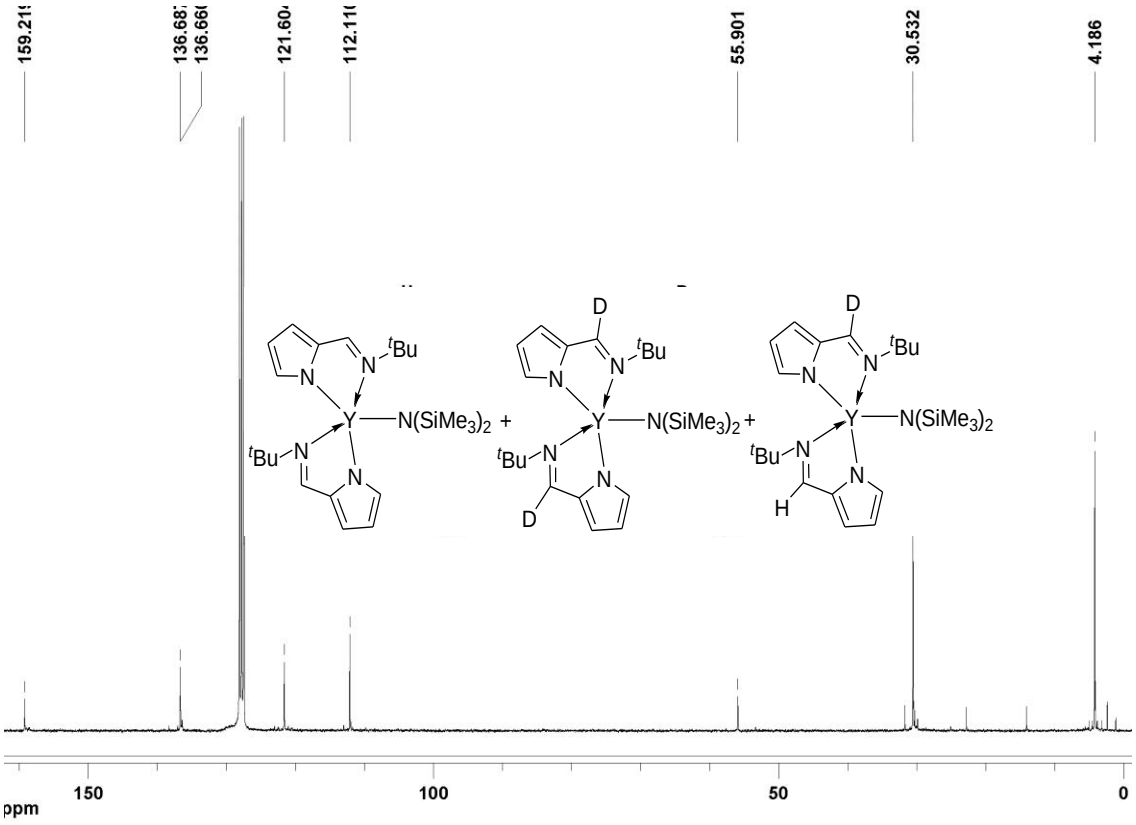
^{1}H NMR spectrum of compound **3a**



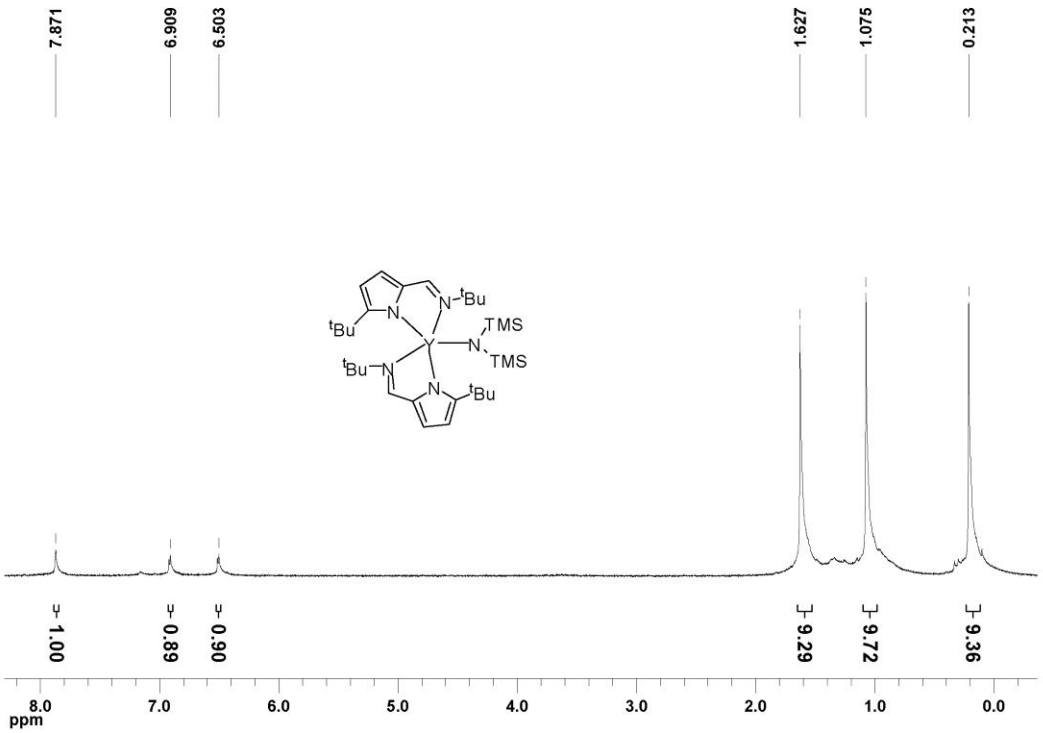
^{13}C NMR spectrum of compound **3a**



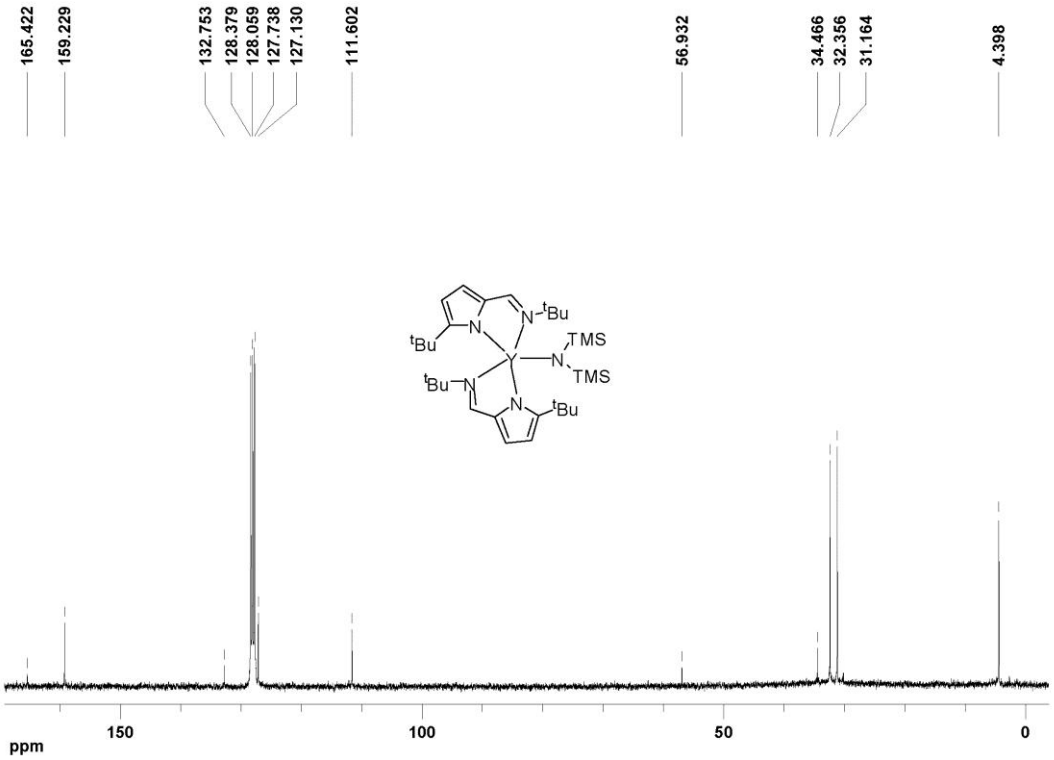
^{1}H NMR spectra of compounds **3a and 3a'**



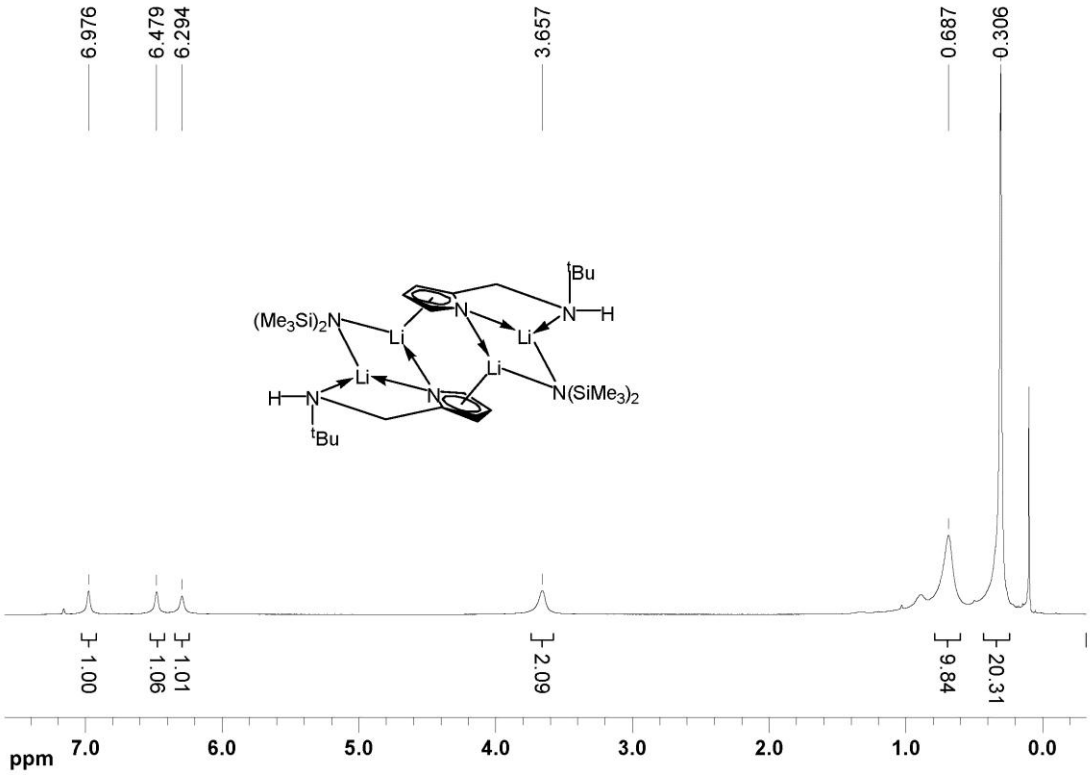
^{13}C NMR spectra of compounds **3a and 3a'**



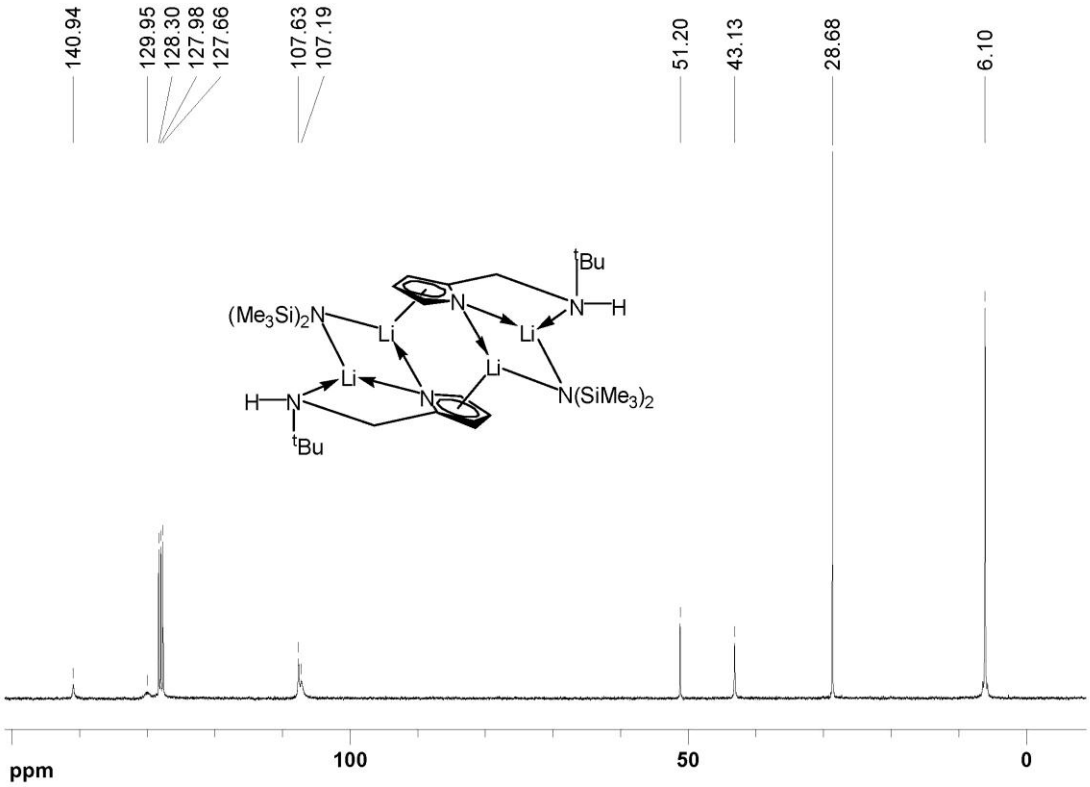
^{1}H NMR spectrum of compound **4a**



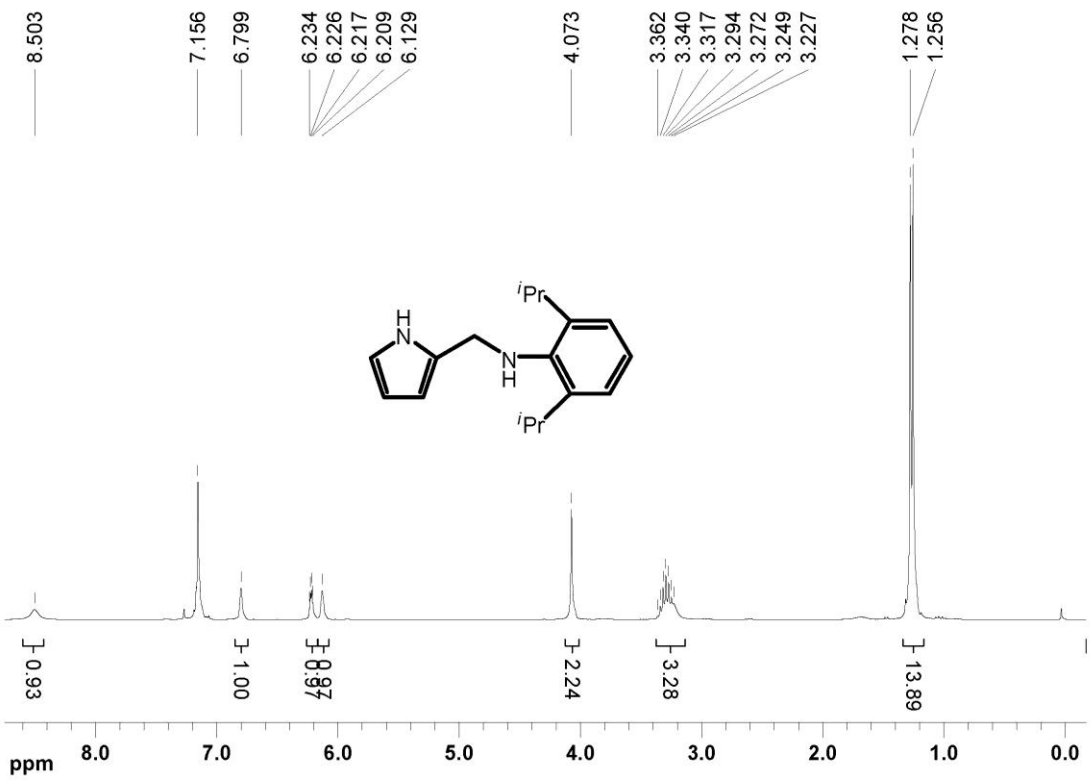
^{13}C NMR spectrum of compound **4a**



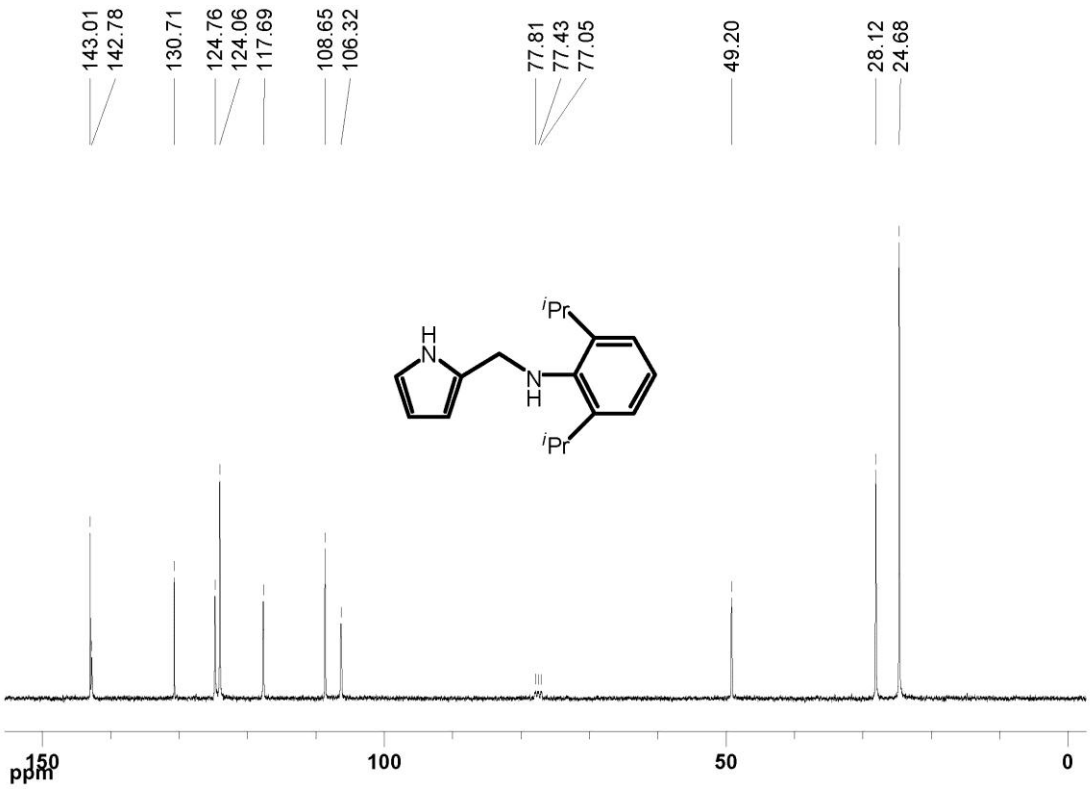
^{1}H NMR spectrum of compound **5**



^{13}C NMR spectrum of compound **5**



^{1}H NMR spectrum of compound **6**



^{13}C NMR spectrum of compound **6**