Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Rare-Earth Alkyl Complexes Supported by Formamidinate Ligands: Synthesis, Structure, and Catalytic Activity for Isoprene Polymerization

Table ESI 1. Crystallographic data for complexes 1, 2, 3

	1	**2**	**3**
Formula	$C_{42}H_{57}N_4OSiY$	$C_{58}H_{89}N_4OSiY$	$C_{58}H_{89}ErN_4OSi$
FW	750.92	975.33	1053.68
Space group	$P\bar{1}$	*P2(1)/n*	$P\bar{1}$
T (K)	173 (2)	173 (2)	173 (2)
Crystal system	Triclinic	Monoclinic	Triclinic
a (Å)	11.983(4)	13.795(2)	13.826(2)
b (Å)	12.232(4)	16.625(3)	21.926(3)
c (Å)	17.139(5)	28.098(5)	23.051(3)
α (deg)	97.761(4)	90	100.028(2)
β (deg)	91.453(4)	92.476(3)	100.543(2)
γ(deg)	114.960(4)	90	106.367(2)
Z	2	4	4
V ($Å^3$)	2247.2(12)	6437.7(19)	6399.9(16)
D_c (Mgm^{-3})	1.110	1.006	1.094
μ (mm^{-1})	1.356	0.960	1.365
F (000)	796	2104	2220
Reflns collected	17986	54427	52344
Unique reflns	9810	14817	28877
Parameters	453	605	1209
Goodness of fit	1.011	1.069	0.983
θ range (deg)	1.86 - 27.42	1.42 - 27.55	1.51 - 27.69
R_1 ($I > 2\sigma(I)$)	0.1140	0.1146	0.0770
wR_2 ($I > 2\sigma(I)$)	0.1094	0.1189	0.2197
Largest diff.peak	0.925	1.182	4.815
and hole (e. $Å^{-3}$)	-1.117	-0.592	-3.865

Table ESI 2. Crystallographic data for complexes 4, 5, 6

	4	**5**	**6**
Formula	C_{58} $H_{89}N_4OSiDy$	C_{58} $H_{89}N_4OSiSm$	$C_{58}H_{89}N_4OSiNd$
FW	1048.92	1036.77	1030.66
Space group	*P*2(1)/n	*P*2(1)/n	*P*2(1)/n
T (K)	173 (2)	173 (2)	293 (2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
a (Å)	13.7985(13)	13.841(3)	13.9414(9)
b (Å)	16.6154(16)	16.677(3)	16.8128(12)
c (Å)	28.071(3)	28.081(6)	28.3865(19)
α (deg)	90	90	90
β (deg)	92.5970(10)	92.483(3)	92.1740(10)
γ(deg)	90	90	90
Z	4	4	4
V ($Å^3$)	6429.2(11)	6476(2)	6648.8(8)
D_c (Mgm^{-3})	1.084	1.063	1.030
μ (mm^{-1})	1.216	0.960	0.833
F (000)	2212	2196	2188
Reflns collected	14894	54434	57150
Unique reflns	14894	14885	15309
Parameters	605	606	605
Goodness of fit	1.050	0.998	0.970
θ range (deg)	1.42-27.70	1.42-27.57	1.41-27.58
R_1 ($I > 2\sigma(I)$)	0.0294	0.0542	0.0489
wR_2 ($I > 2\sigma(I)$)	0.0751	0.1833	0.0845
Largest diff.peak and hole (e. $Å^{-3}$)	1.306	2.260	0.640
	-0.810	-0.535	-0.615

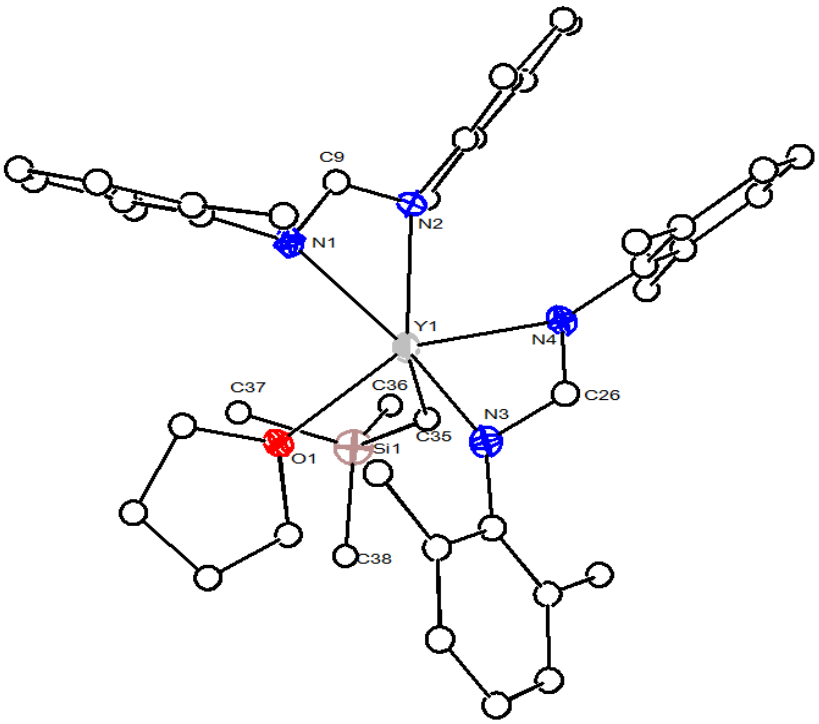


Figure 1. Molecular structure of the compound **1**, hydrogen atoms and disorder are omitted for clarity. Selected bond lengths (Å) and angles (°): Y(1)-N(1) 2.388(3), Y(1)-N(2) 2.411(3), Y(1)-N(3) 2.400(3), Y(1)-N(4) 2.378(3), Y(1)-C(35) 2.371(4), Y(1)-O(1) 2.396(2), C(9)-N(1) 1.330(4), C(9)-N(2) 1.309(4), C(26)-N(3) 1.321(4), C(26)-N(4) 1.302(4), N(1)-Y(1)-N(2) 56.44(10), N(3)-Y(1)-N(4) 56.40(10).

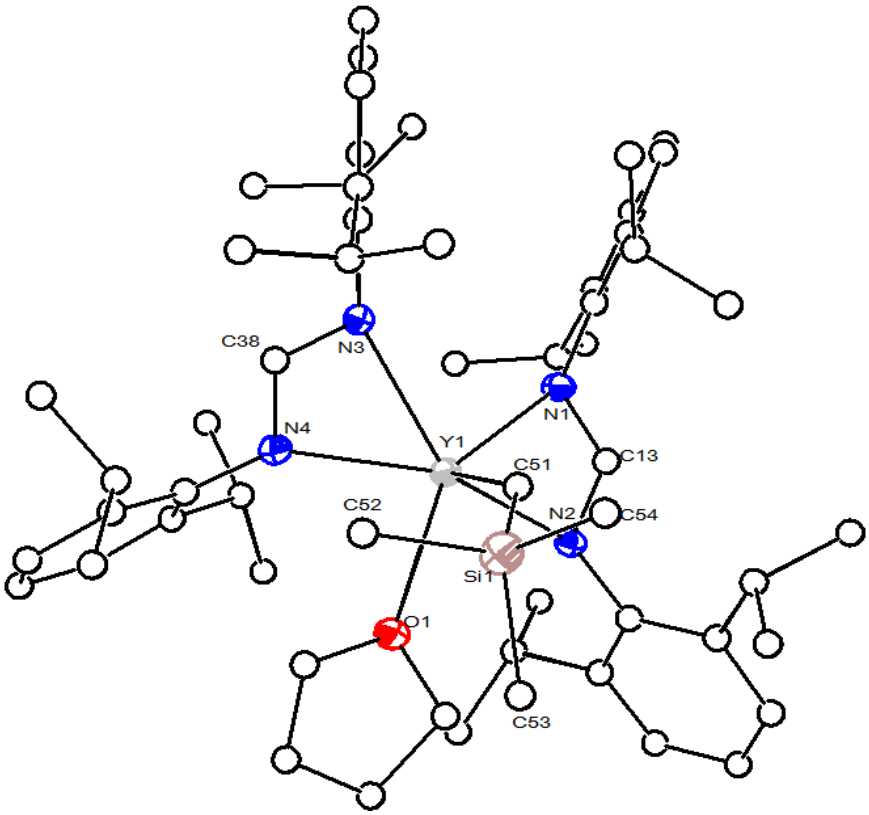


Figure 2. Molecular structure of the compound **2**, hydrogen atoms and disorder are omitted for clarity. Selected bond lengths (Å) and angles (°): Y(1)-N(1) 2.390(2), Y(1)-N(2) 2.443(2), Y(1)-N(3) 2.475(3), Y(1)-N(4) 2.391(3), Y(1)-C(51) 2.376(3), Y(1)-O(1) 2.406(2), C(13)-N(1) 1.313(4), C(13)-N(2) 1.323(4), C(38)-N(3) 1.303(4) , C(38)-N(4) 1.319(4) , N(1)-Y(1)-N(2) 56.18(8), N(3)-Y(1)-N(4) 55.51(9).

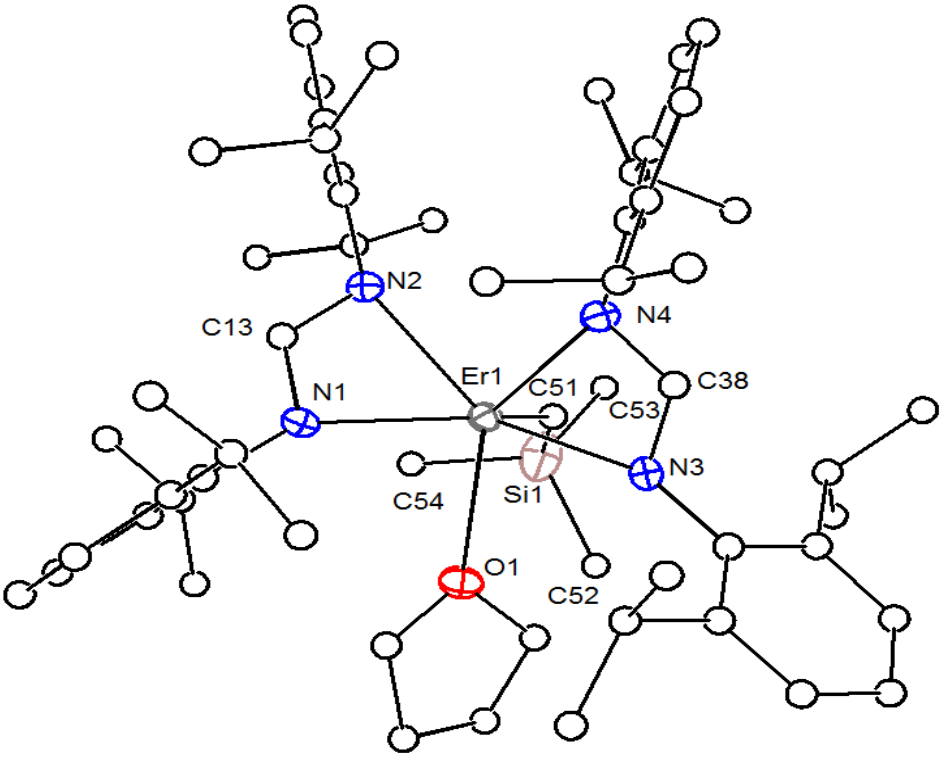


Figure 3. Molecular structure of the compound **3**, hydrogen atoms and disorder are omitted for clarity. Selected bond lengths (Å) and angles (°): Er(1)-N(1) 2.365(6), Er(1)-N(2) 2.439(6), Er(1)-N(3) 2.423(6), Er(1)-N(4) 2.367(5), Er(1)-C(51) 2.365(8), Er(1)-O(1) 2.402(5), C(13)-N(1) 1.323(9), C(13)-N(2) 1.332(9), C(38)-N(3) 1.322(8) , C(38)-N(4) 1.335(9) , N(1)-Er(1)-N(2) 56.5(2), N(3)-Er(1)-N(4) 56.65(19).

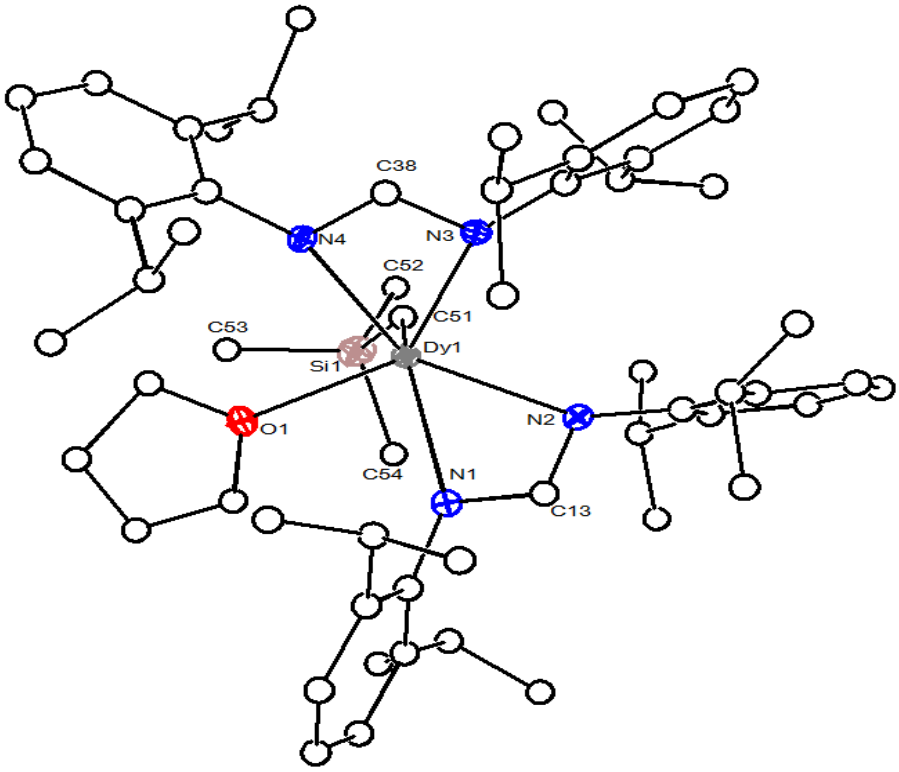


Figure 4. Molecular structure of the compound **4**, hydrogen atoms and disorder are omitted for clarity. Selected bond lengths (Å) and angles (°): Dy(1)-N(1) 2.4051(19), Dy(1)-N(2) 2.4776(17), Dy(1)-N(3) 2.3936(19), Dy(1)-N(4) 2.4539(17), Dy(1)-C(51) 2.375(2), Dy(1)-O(1) 2.4224(17), C(13)-N(1) 1.326(3), C(13)-N(2) 1.306(3), C(38)-N(3) 1.324(3) , C(38)-N(4) 1.318(3) , N(1)-Dy(1)-N(2) 55.39(6), N(3)-Dy(1)-N(4) 56.02(6).

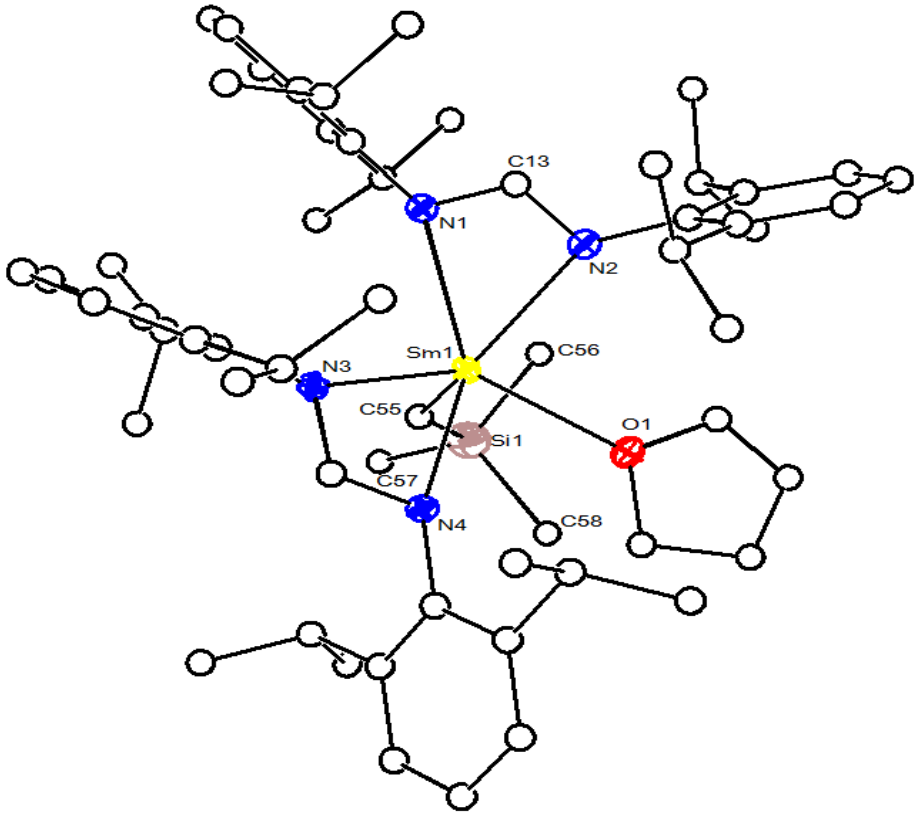


Figure 5. Molecular structure of the compound **5**, hydrogen atoms and disorder are omitted for clarity. Selected bond lengths (Å) and angles (°): Sm(1)-N(1) 2.519(4), Sm(1)-N(2) 2.456(4), Sm(1)-N(3) 2.437(4), Sm(1)-N(4) 2.494(4), Sm(1)-C(51) 2.388(6), Sm(1)-O(1) 2.482(4), C(13)-N(1) 1.305(6), C(13)-N(2) 1.321(7), C(38)-N(3) 1.321(6) , C(38)-N(4) 1.316(6) , N(1)-Sm(1)-N(2) 54.39(14), N(3)-Sm(1)-N(4) 54.94(13).

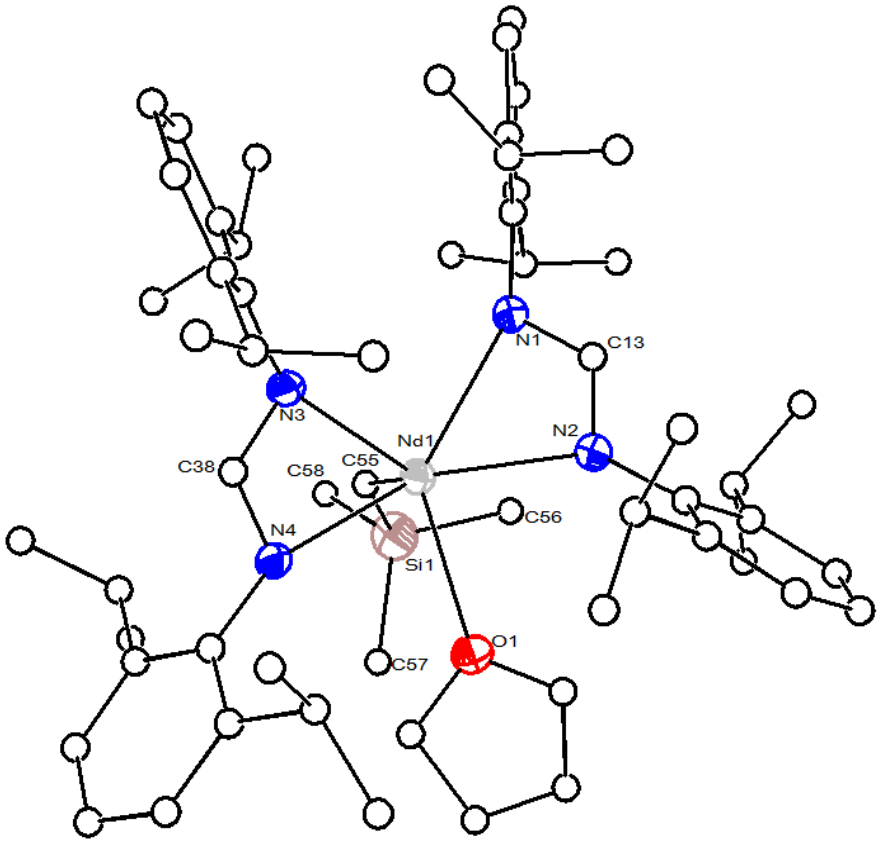
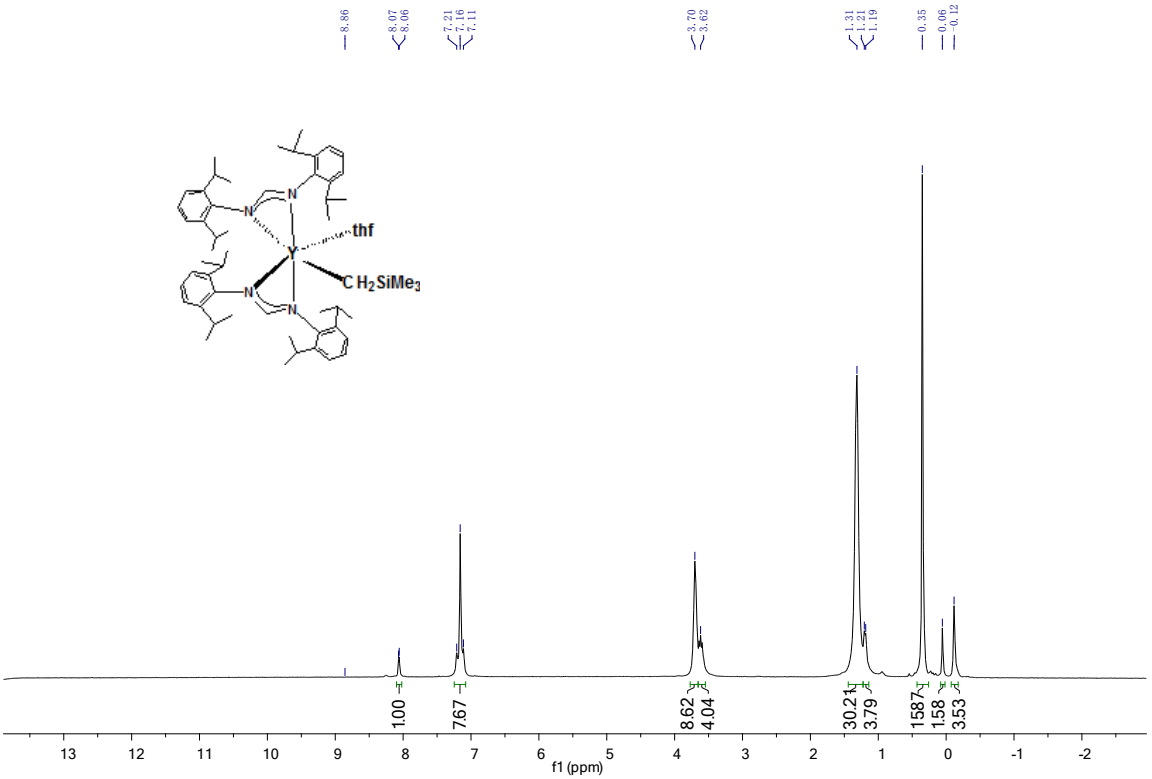
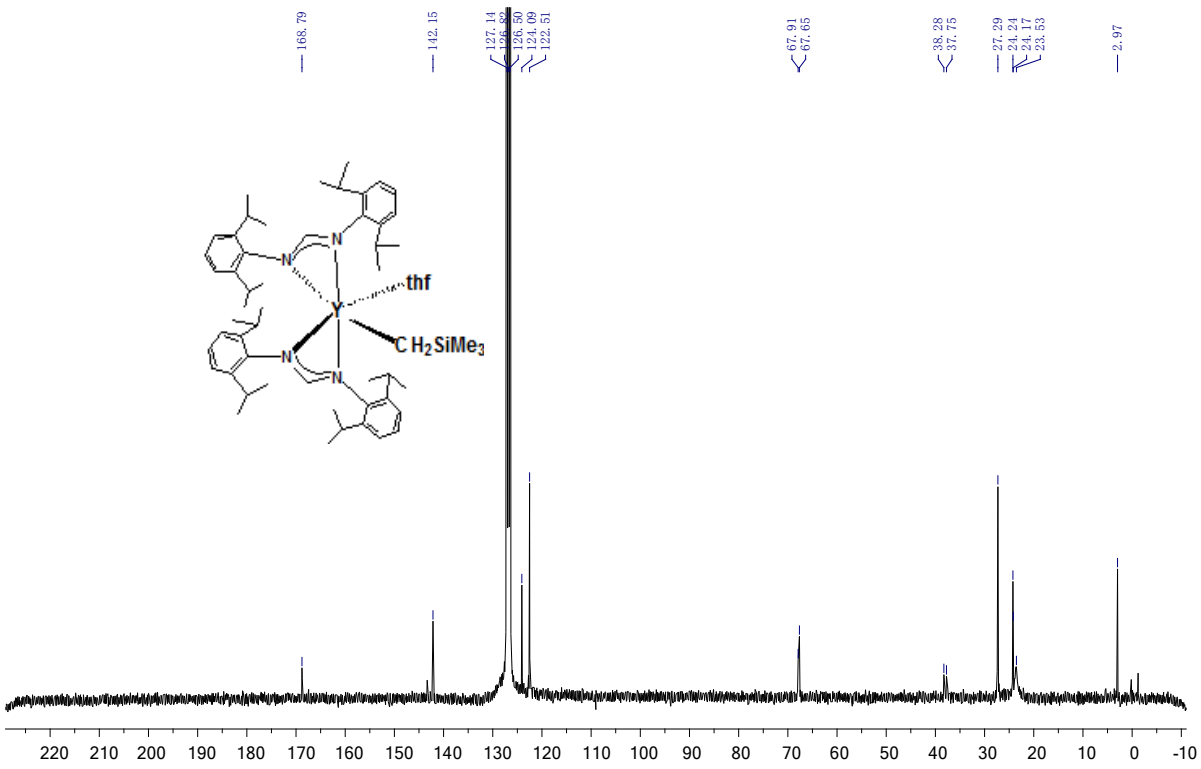


Figure 6. Molecular structure of the compound **6**, hydrogen atoms and disorder are omitted for clarity. Selected bond lengths (Å) and angles (°): Nd(1)-N(1) 2.550(3), Nd(1)-N(2) 2.482(3), Nd(1)-N(3) 2.467(3), Nd(1)-N(4) 2.519(3), Nd(1)-C(51) 2.440(4), Nd(1)-O(1) 2.519(3), C(13)-N(1) 1.307(4), C(13)-N(2) 1.319(4), C(38)-N(3) 1.315(4) , C(38)-N(4) 1.314(4) , N(1)-Nd(1)-N(2) 53.74(9), N(3)-Nd(1)-N(4) 54.33(9).

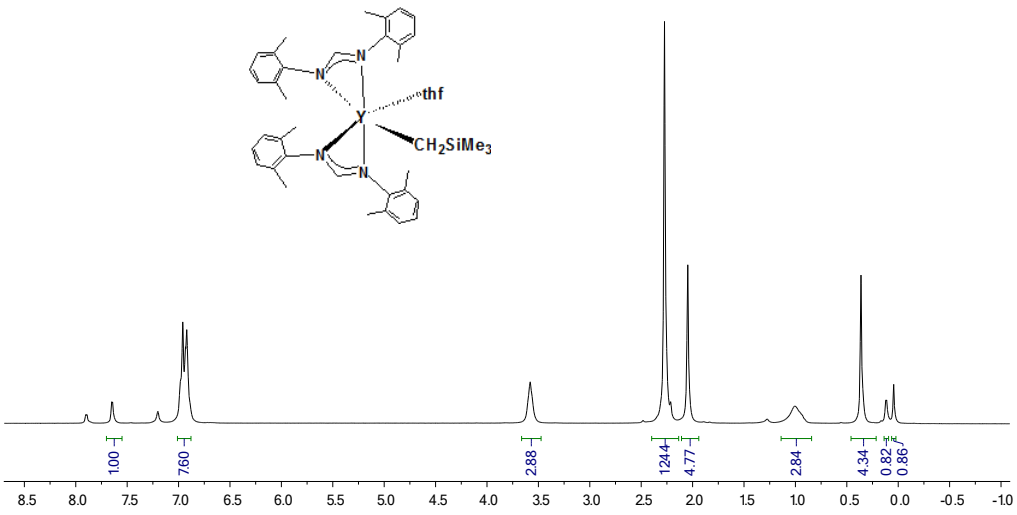
Copy of ^{1}H and ^{13}C NMR spectra



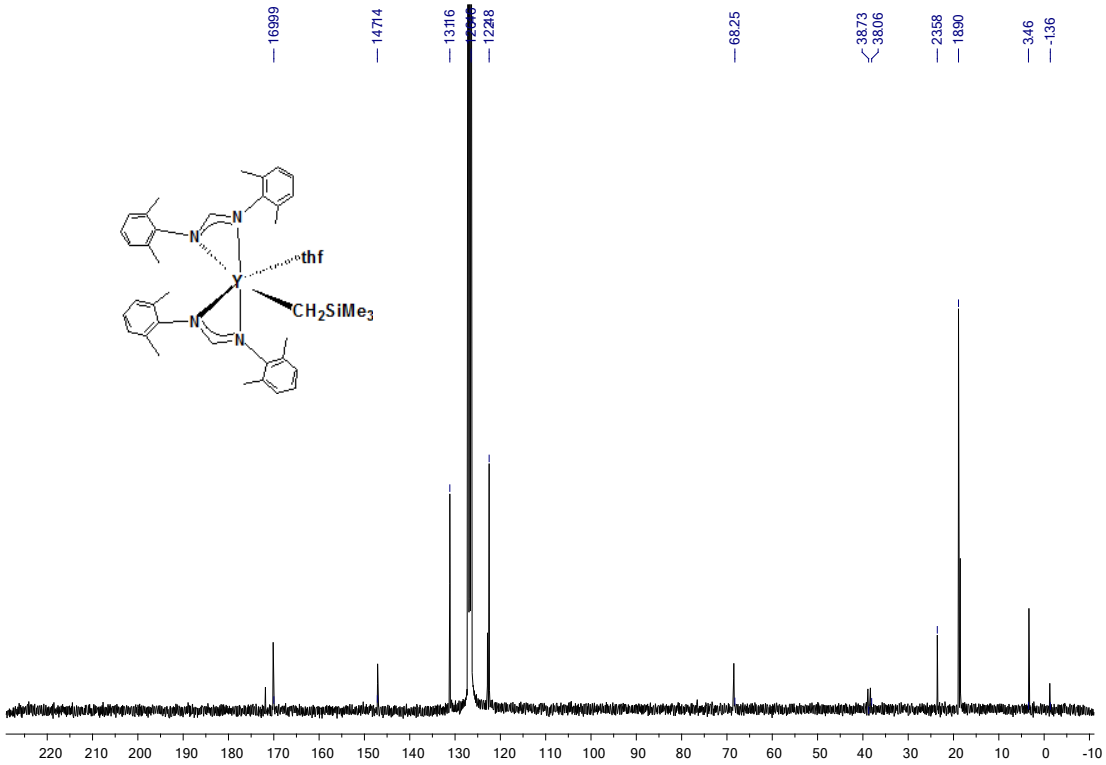
^{1}H NMR spectrum of compound **1**



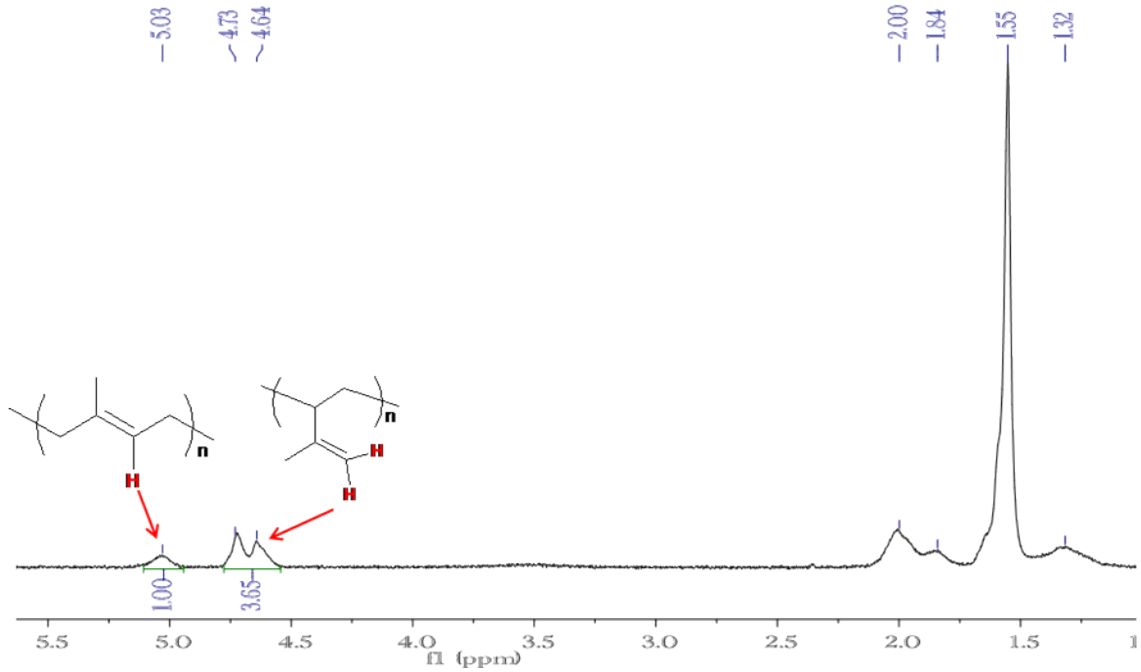
^{13}C NMR spectrum of compound **1**



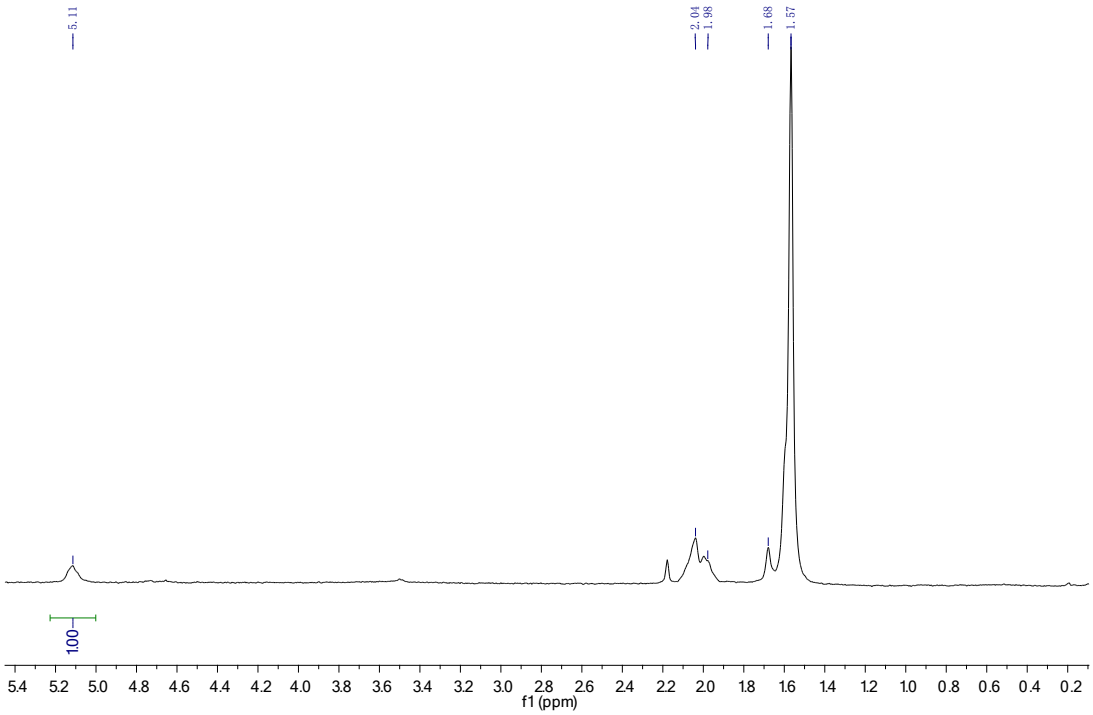
^{1}H NMR spectrum of compound **2**



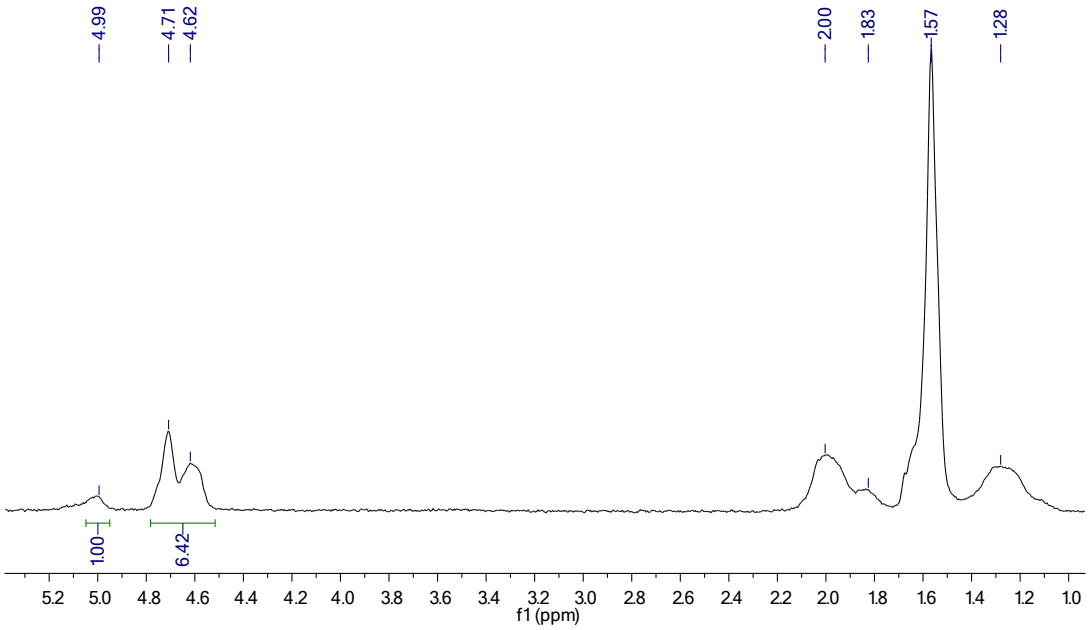
^{13}C NMR spectrum of compound **2**



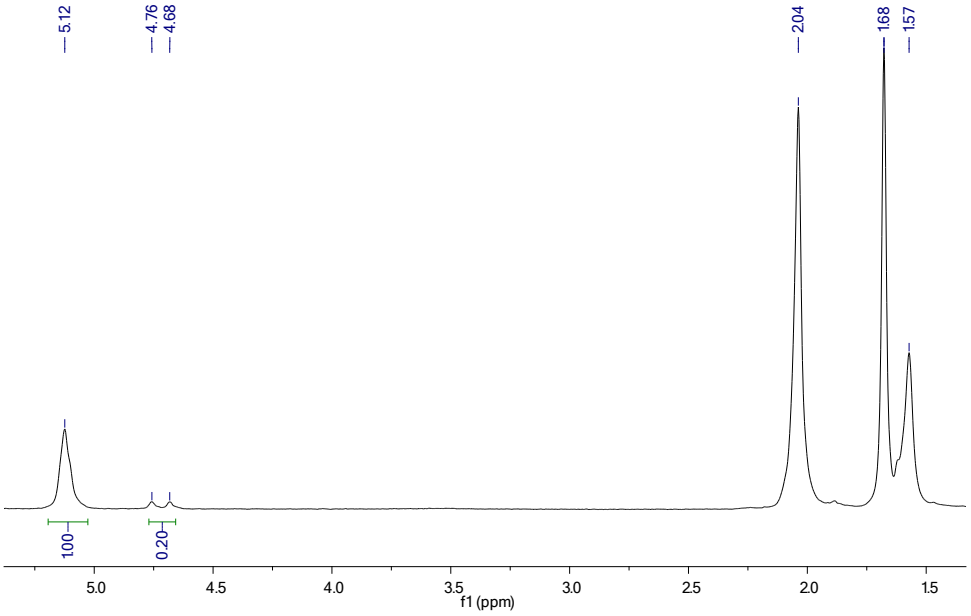
^{1}H NMR spectrum of polyisoprene from Entry 2(Table 2)



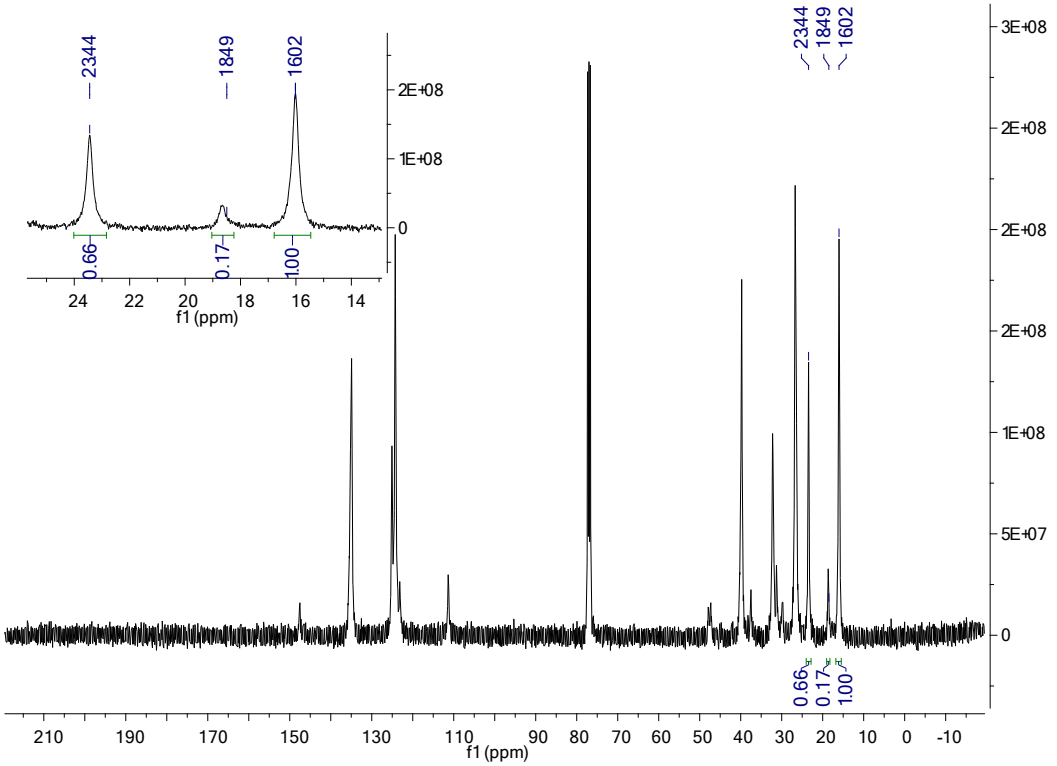
^{1}H NMR spectrum of polyisoprene from Entry 1(Table 3)



^{1}H NMR spectrum of polyisoprene from Entry 2(Table 3)



^{1}H NMR spectrum of polyisoprene from Entry 12(Table 3)



^{13}C NMR spectrum of polyisoprene from Entry 12(Table 3)