Electronic Supplementary Information for

Versatile reactivities of rare-earth metal dialkyl complexes supported by a neutral pyrrolyl functionalized *β*-diketiminato ligand

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Table of contents

Table S1. Crystallographic data for complexes **1a-d**

	1a (CCDC:1568349)	**1b** (CCDC:1568350)	**1c** (CCDC:1568351)	**1d** (CCDC:1568352)
Formula	$C_{37}H_{66}N_3OSi_2Y$	$C_{37}H_{66}N_3OSi_2Dy$	$C_{37}H_{66}N_3OSi_2Er$	$C_{37}H_{66}N_3OSi_2Yb$
FW	714.01	787.60	792.36	798.14
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
T (K)	293(2)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
a (Å)	23.3415(14)	23.352(2)	23.3174(16)	23.2648(19)
b (Å)	19.3496(11)	19.347(2)	19.3447(13)	19.3033(16)
c (Å)	21.0787(13)	21.045(2)	21.0762(14)	21.0600 (18)
α (deg)	90	90	90	90
β (deg)	116.3900(10)	116.3780(10)	116.3480(10)	116.2920(10)
γ(deg)	90	90	90	90
Z	8	8	8	8
V ($Å^3$)	8528.1(9)	8517.9(15)	8519.2(10)	8479.4(12)
D_c (Mgm^{-3})	1.112	1.228	1.236	1.250
μ (mm^{-1})	1.452	1.839	2.504	2.291
F (000)	3072	3288	3304	3320
Reflns collected	74119	64770	65245	64308
Unique reflns	19928	16689	16729	16631
Parameters	906	906	906	906
Goodness of fit	0.923	1.029	0.999	1.046
θ range (deg)	1.434 to 27.683	1.434 to 26.000	1.434 to 26.000	1.509 to 25.998
R_1 ($I > 2\sigma(I)$)	0.0529	0.0312	0.0373	0.0306
wR_2 ($I > 2\sigma(I)$)	0.1007	0.0688	0.0688	0.0644
R(int)	0.1024	0.0351	0.0611	0.0372
Largest diff. peak	0.333	1.206	1.378	0.903
and hole (e. $Å^{-3}$)	-0.312	-0.488	-0.564	-0.738

Table S2. Crystallographic data for complexes **2-4c**

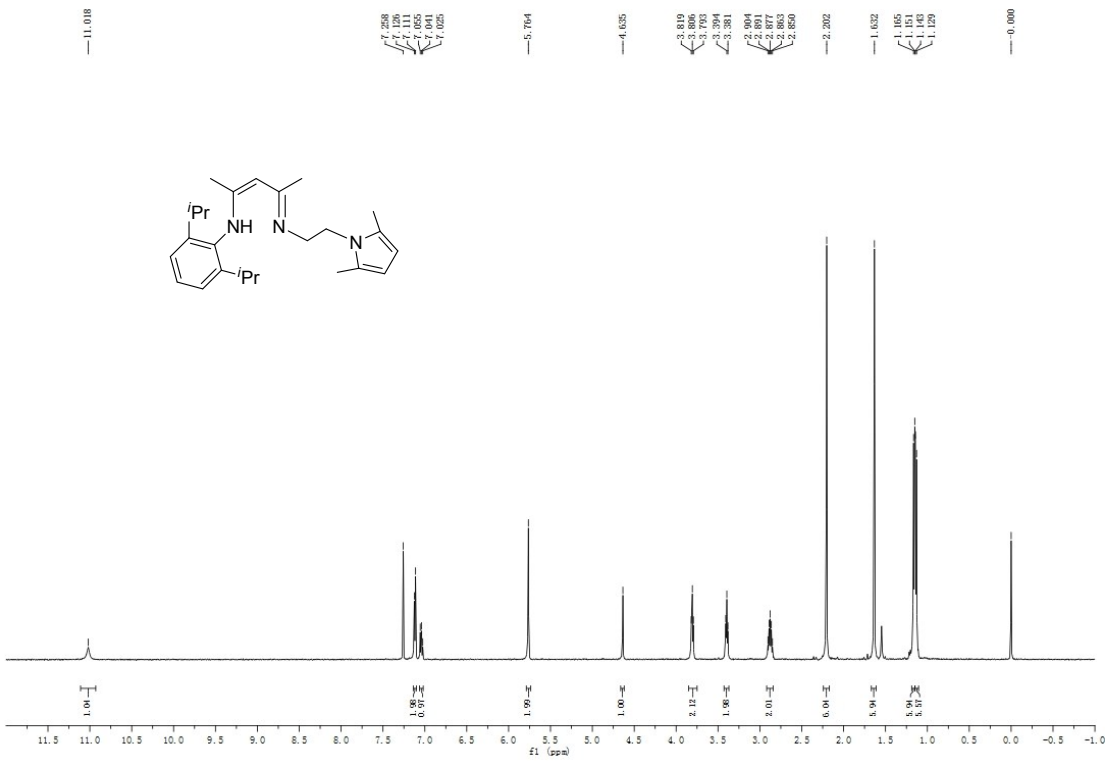
	2c (CCDC:1568353)	**3a** (CCDC:1568354)	**3c** (CCDC:1568355)	**4c**(CCDC:1568356)
Formula	$C_{38}H_{63}ErN_4Si_2$	$C_{41}H_{56}YN_5$	$C_{41}H_{56}ErN_5$	$C_{40}H_{55}ErN_4Si$
FW	799.36	707.81	786.16	787.23
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
T (K)	293(2)	293(2)	293(2)	291(2)
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
a (Å)	11.6567(8)	11.7518(16)	11.7631(9)	15.441(3)
b (Å)	19.5163(13)	17.743(2)	17.7324(13)	19.768(4)
c (Å)	18.9209(13)	19.507(3)	19.4789(15)	27.157(6)
α (deg)	90	72.717(2)	72.719010)	90
β (deg)	96.4370(10)	85.830(2)	85.7370(10)	101.637 (2)
γ(deg)	90	86.011(2)	85.9280(10)	90
Z	4	4	4	8
V ($Å^3$)	4277.3(5)	3868.6(9)	3863.8(5)	8119(3)
D_c (Mgm^{-3})	1.242	1.215	1.351	1.288
μ (mm^{-1})	2.046	1.541	2.206	2.127
F (000)	1661	1504	1620	3240
Reflns collected	32065	39430	44410	89264
Unique reflns	7835	14116	17289	17713
Parameters	448	871	871	851
Goodness of fit	1.029	0.912	0.988	1.083
θ range (deg)	1.504 to 25.371	1.095 to 25.359	1.096 to 27.545	1.283 to 26.999
R_1 ($I > 2\sigma(I)$)	0.0288	0.0600	0.0422	0.0414
wR_2 ($I > 2\sigma(I)$)	0.0656	0.1404	0.0699	0.0696
R(int)	0.0322	0.0810	0.0497	0.0707
Largest diff. peak	0.763	1.537	1.353	1.856
and hole (e. $Å^{-3}$)	-0.376	-0.462	-0.877	-0.742

Table S3. Crystallographic data for complexes **4d-7**

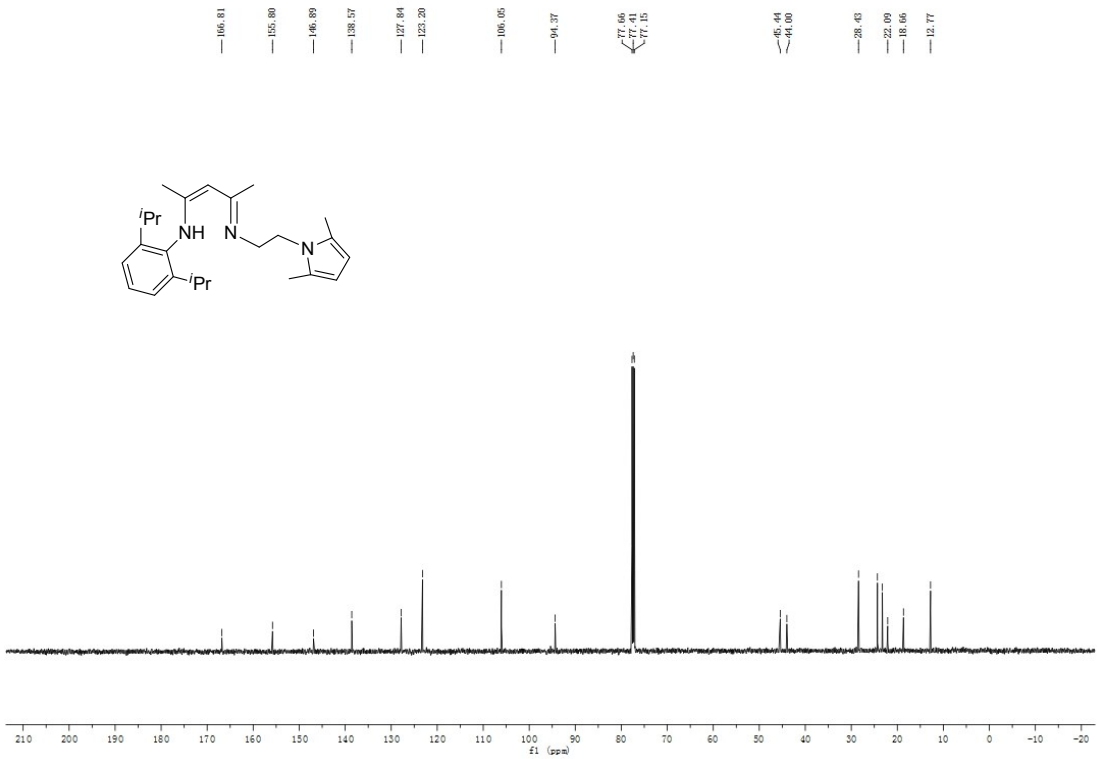
	4d (CCDC:1568357)	**5c** (CCDC:1568358)	**6d** (CCDC:1568359)	**7c** (CCDC:1568360)
Formula	$C_{40}H_{55}YbN_4Si$	$C_{74}H_{104}Er_2N_6Si_2$	$C_{58}H_{92}YbN_5Si_2$	$C_{54}H_{82}ErN_5Si$
FW	793.01	1468.33	1088.58	996.59
Space group	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$	$P\bar{1}$
T (K)	293(2)	293(2)	293(2)	293(2)
Crystal system	Triclinic	Triclinic	Orthorhombic	Triclinic
a (Å)	11.0943(11)	11.8774(14)	12.0511(9)	12.637(3)
b (Å)	11.3822(12)	13.9863(17)	20.7963(15)	12.882(3)
c (Å)	17.1060(17)	15.4143(19)	23.9256(17)	17.262(3)
α (deg)	103.6830(10)	88.1770(10)	90	84.376(2)
β (deg)	97.066010)	68.3690(10)	90	87.531(2)
γ(deg)	100.4450 (10)	76.2840(10)	90	76.720(9)
Z	2	1	4	2
V ($Å^3$)	2032.7(4)	2308.0(5)	5996.2(8)	2721.2(10)
D_c (Mgm^{-3})	1.296	1.056	1.206	1.216
μ (mm^{-1})	2.360	1.865	1.637	1.601
F (000)	814	754	2292	1046
Reflns collected	23378	8088	49979	31341
Unique reflns	9136	8088	13560	12238
Parameters	426	378	617	569
Goodness of fit	1.119	1.018	0.922	1.024
θ range (deg)	1.244 to 27.595	1.424 to 25.000	1.297 to 27.530	1.186 to 27.594
R_1 ($I > 2\sigma(I)$)	0.0277	0.0435	0.0429	0.0282
wR_2 ($I > 2\sigma(I)$)	0.0603	0.1042	0.0710	0.0635
R(int)	0.0240	0.0000	0.0690	0.0269
Largest diff. peak	0.788	1.379	2.036	0.961
and hole (e. $Å^{-3}$)	-0.343	-0.861	-0.959	-0.330

Table S4. Crystallographic data for complexes **8a** and **8c**

	8a (CCDC:1568361)	**8c** (CCDC:1568362)
Formula	$C_{83}H_{129}Y_2N_9Si_2S_3$	$C_{83}H_{129}Er_2N_9Si_2S_3$
FW	1583.12	1739.82
Space group	$P2_1/c$	$P2_1/c$
T (K)	293(2)	293(2)
Crystal system	Monolinic	Monolinic
a (Å)	25.5309(16)	25.4738(17)
b (Å)	13.4806(9)	13.4820(9)
c (Å)	27.6008(18)	27.6081(19)
α (deg)	90	90
β (deg)	93.8570(10)	93.7220(10)
γ(deg)	90	90
Z	4	4
V ($Å^3$)	9477.9 (11)	9461.7 (11)
D_c (Mgm^{-3})	1.109	1.221
μ (mm^{-1})	1.352	1.895
F (000)	3376	3608
Reflns collected	21515	21466
Unique reflns	21515	21466
Parameters	922	922
Goodness of fit	1.028	1.085
θ range (deg)	1.479 to 27.487	1.602 to 27.471
R_1 ($I > 2\sigma(I)$)	0.0656	0.0431
wR_2 ($I > 2\sigma(I)$)	0.1801	0.1157
R(int)	0.0000	0.0000
Largest diff. peak	1.165	1.973
and hole (e. $Å^{-3}$)	-1.502	-1.815



^{1}H NMR spectrum of compound H**L** (500 MHz, $CDCl_3$)



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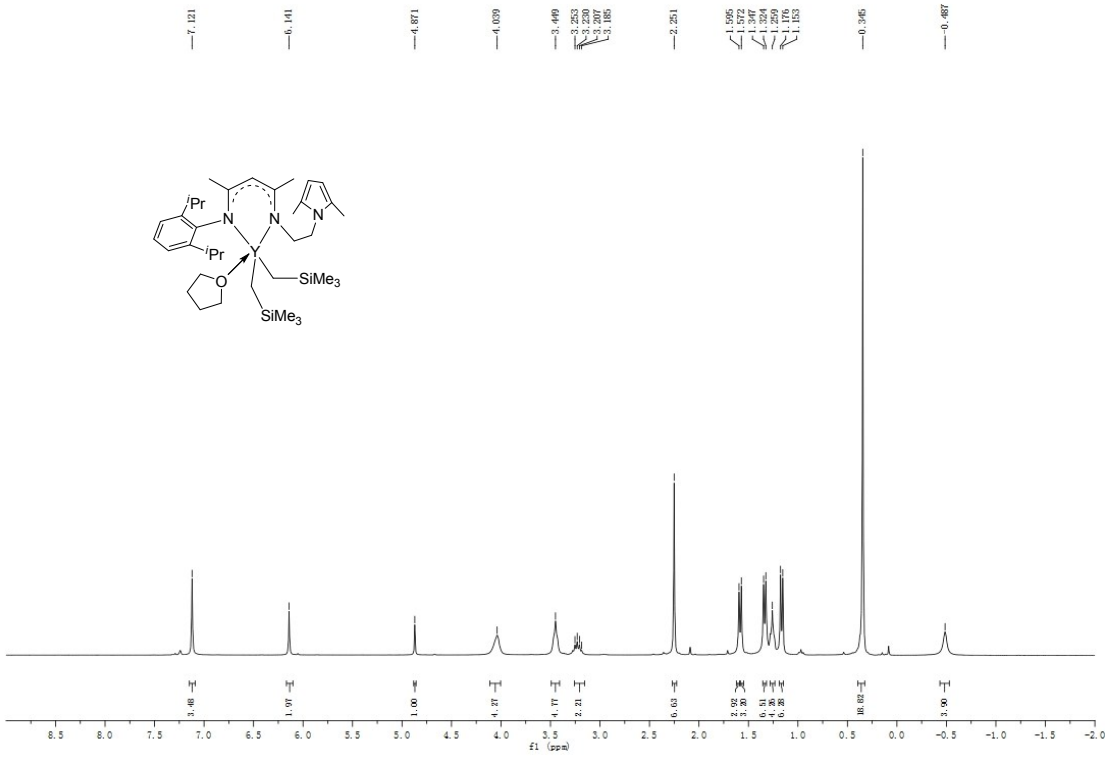
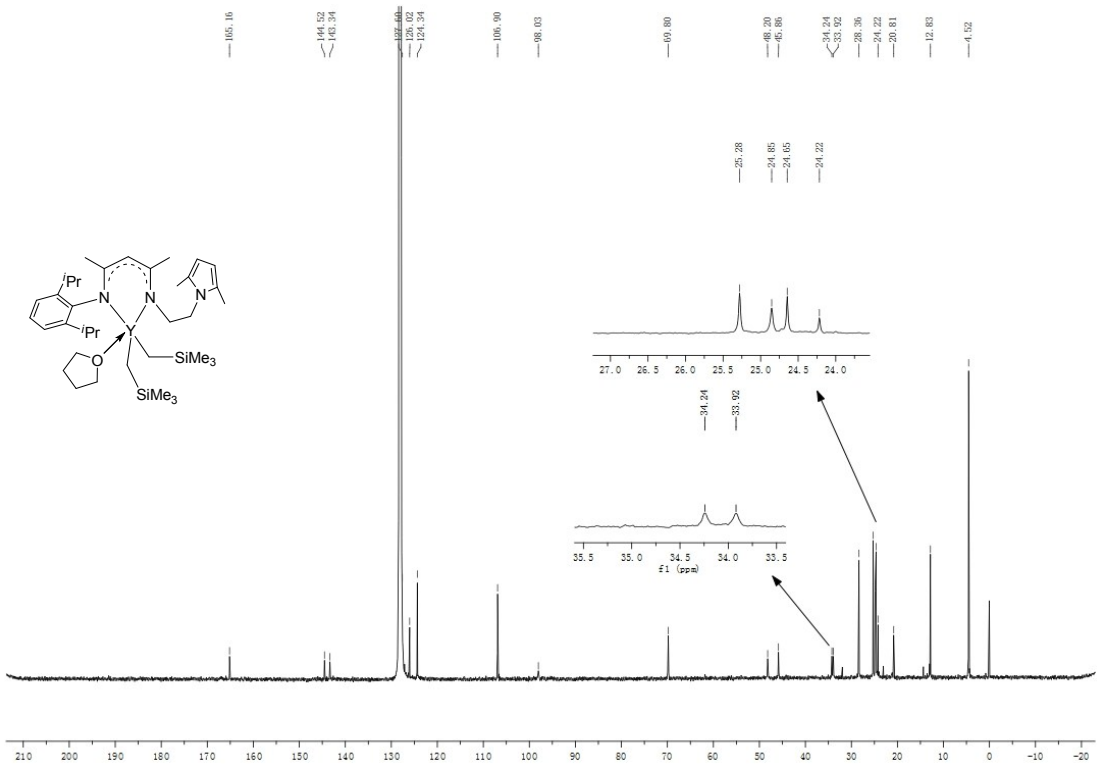
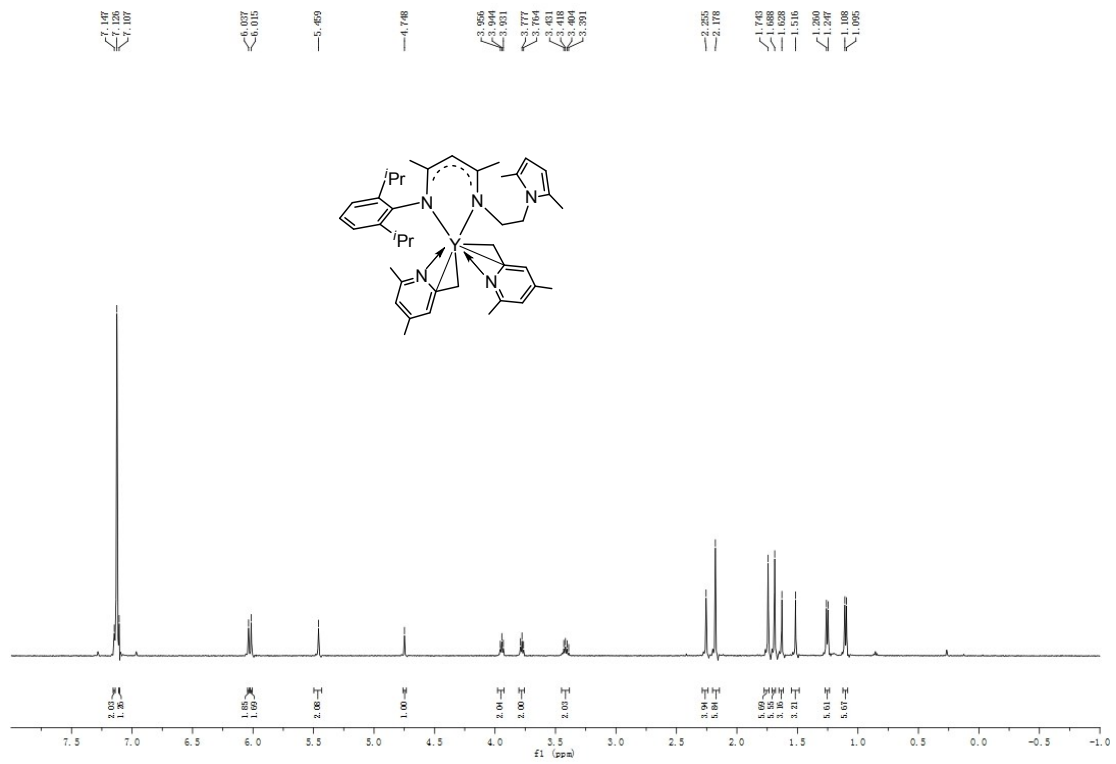


^{1}H NMR spectrum of complex **1a** (500 MHz, C_6D_6)



^{13}C NMR spectrum of complex **1a** (500 MHz, C_6D_6)



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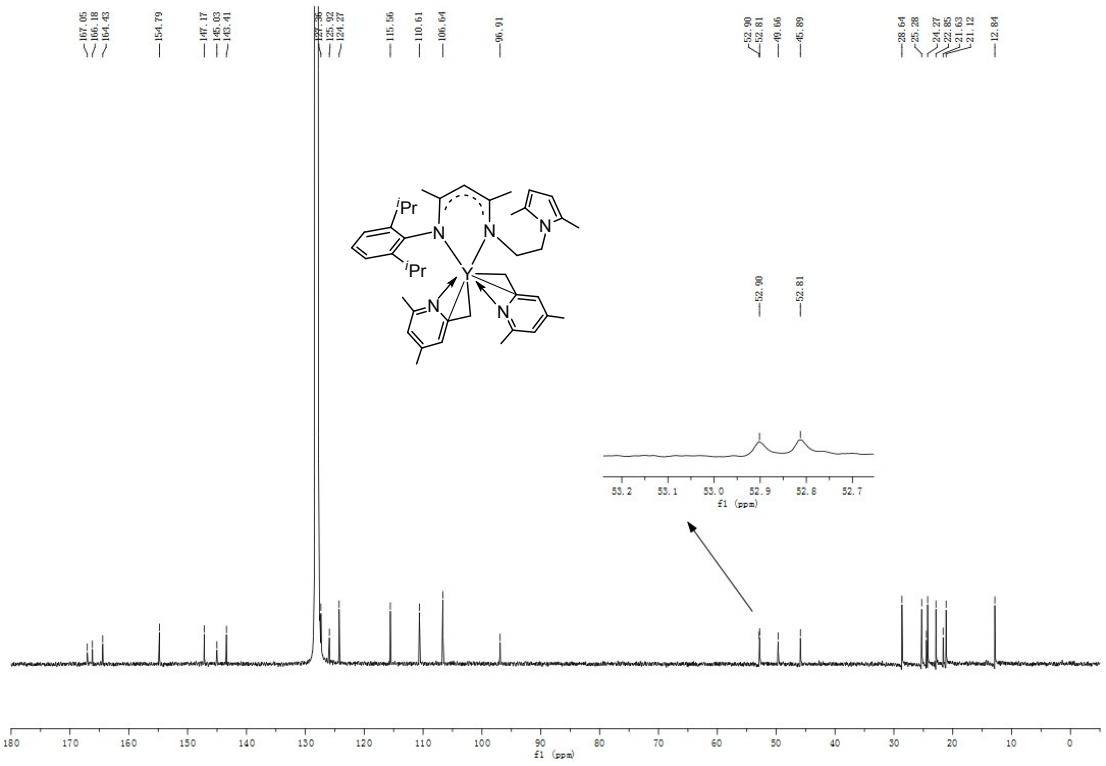

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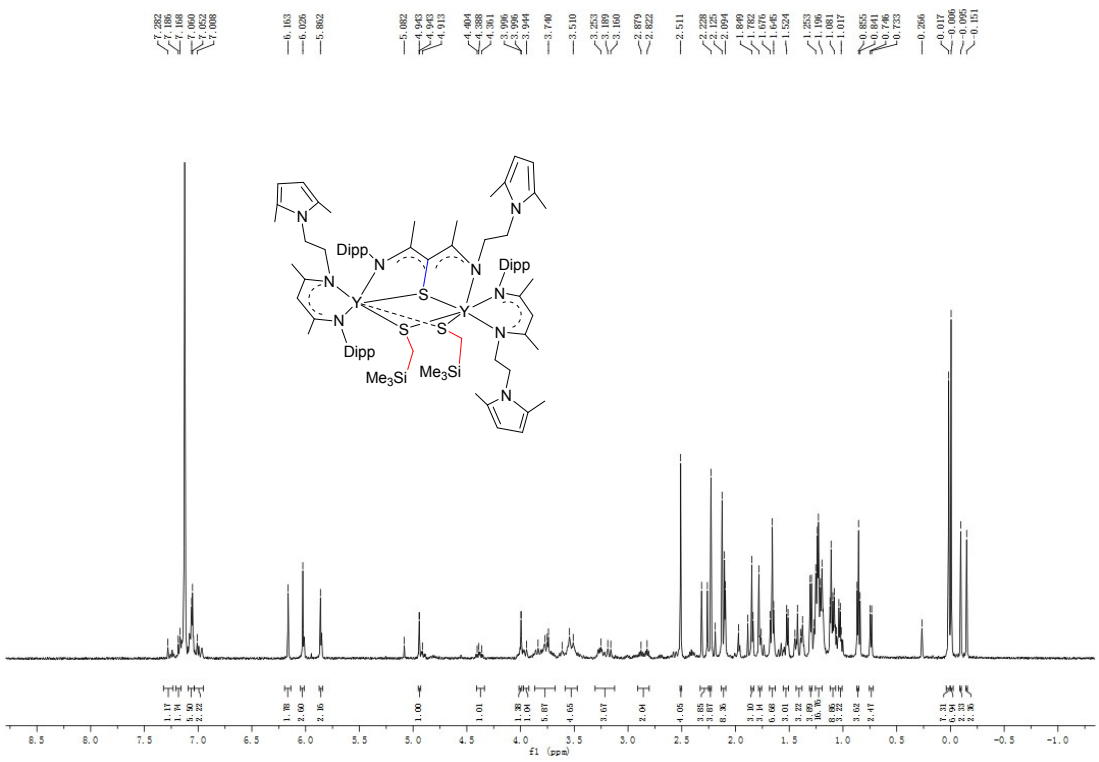
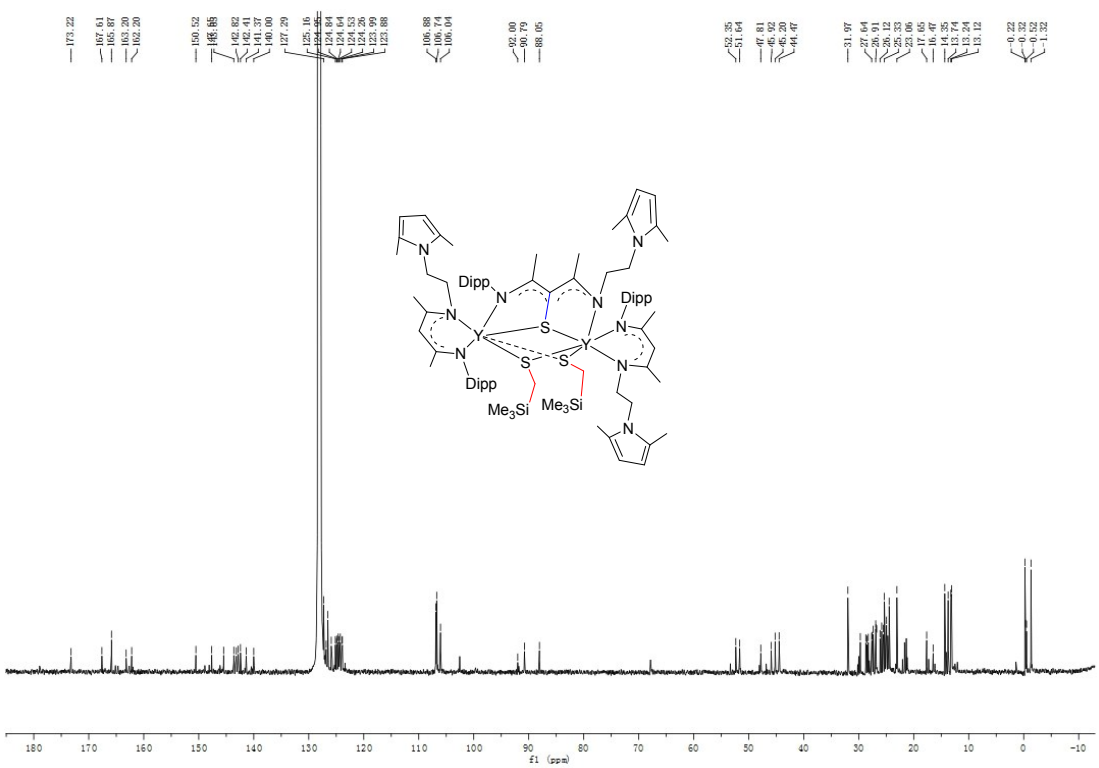


^{1}H NMR spectrum of complex **8a** (500 MHz, C_6D_6)



^{13}C NMR spectrum of complex **8a** (500 MHz, C_6D_6)