SUPPLEMENTARY MATERIAL

Syntheses of Unprecedented Heteroleptic Amidinate Strontium Complexes Using a Superbulky Ligand

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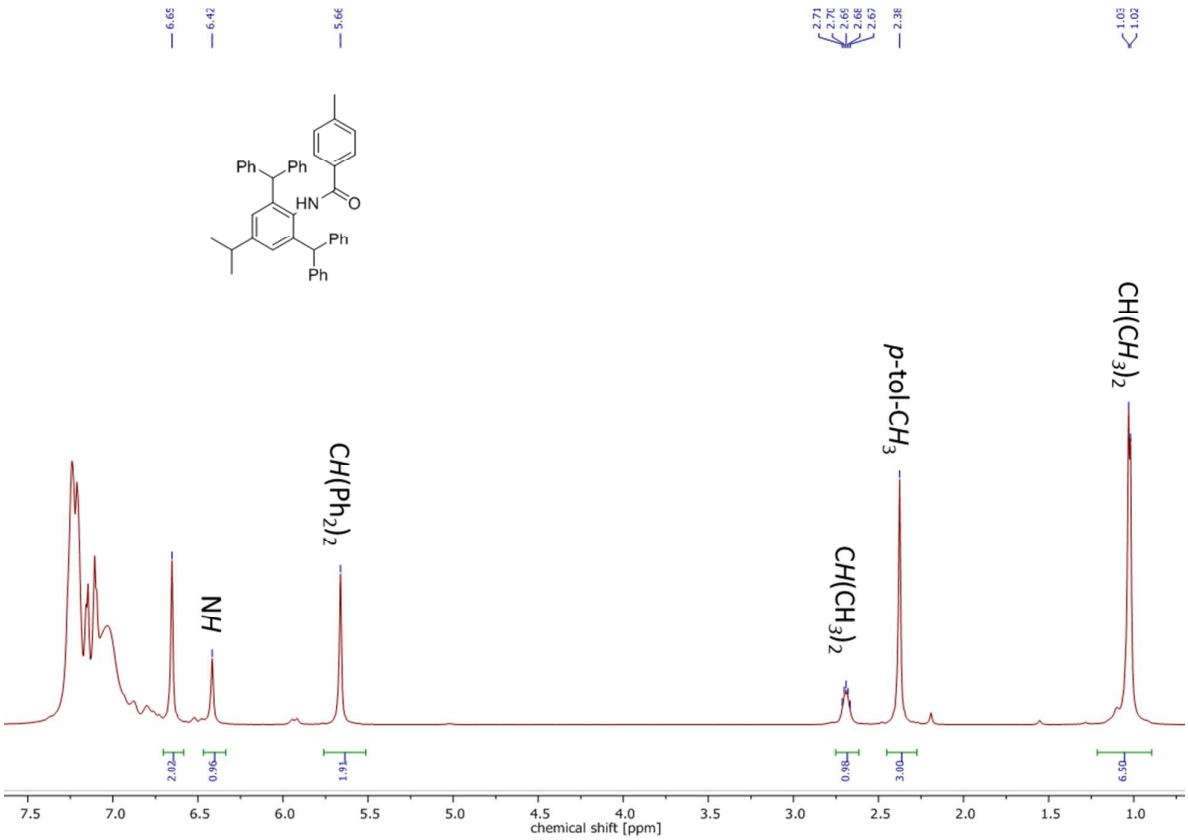
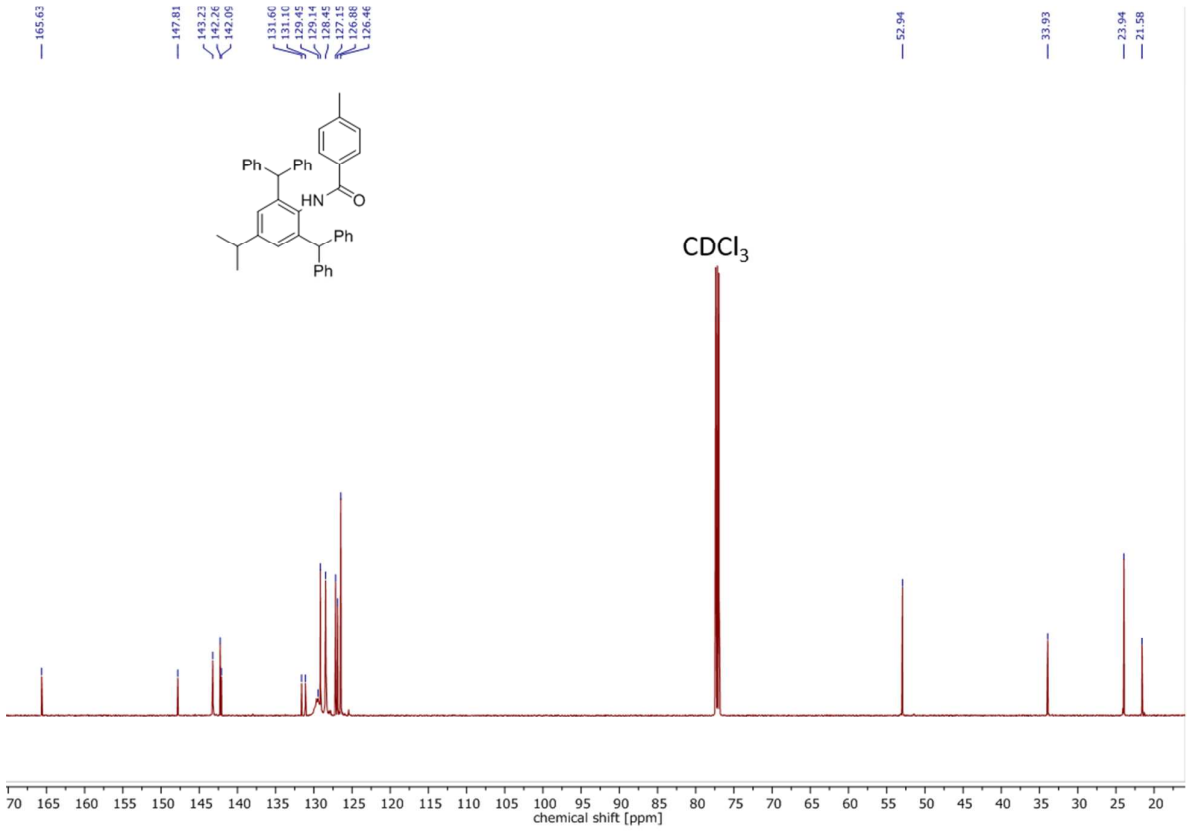
1) Selected NMR spectra

Figure S1. From top to bottom: ^{1}H, ^{13}C and DEPT-135 NMR spectra of *p*TolC(O)N(H)Ar‡ in $CDCl_3$ (600 MHz / 151 MHz)




165.63
147.81
143.23
142.26
142.09
131.60
131.10
129.45
129.14
128.45
127.15
126.88
126.46
52.94
33.93
23.94
21.58
Ph
Ph
HN
O
Ph
Ph
CDCl3
70 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
chemical shift [ppm]

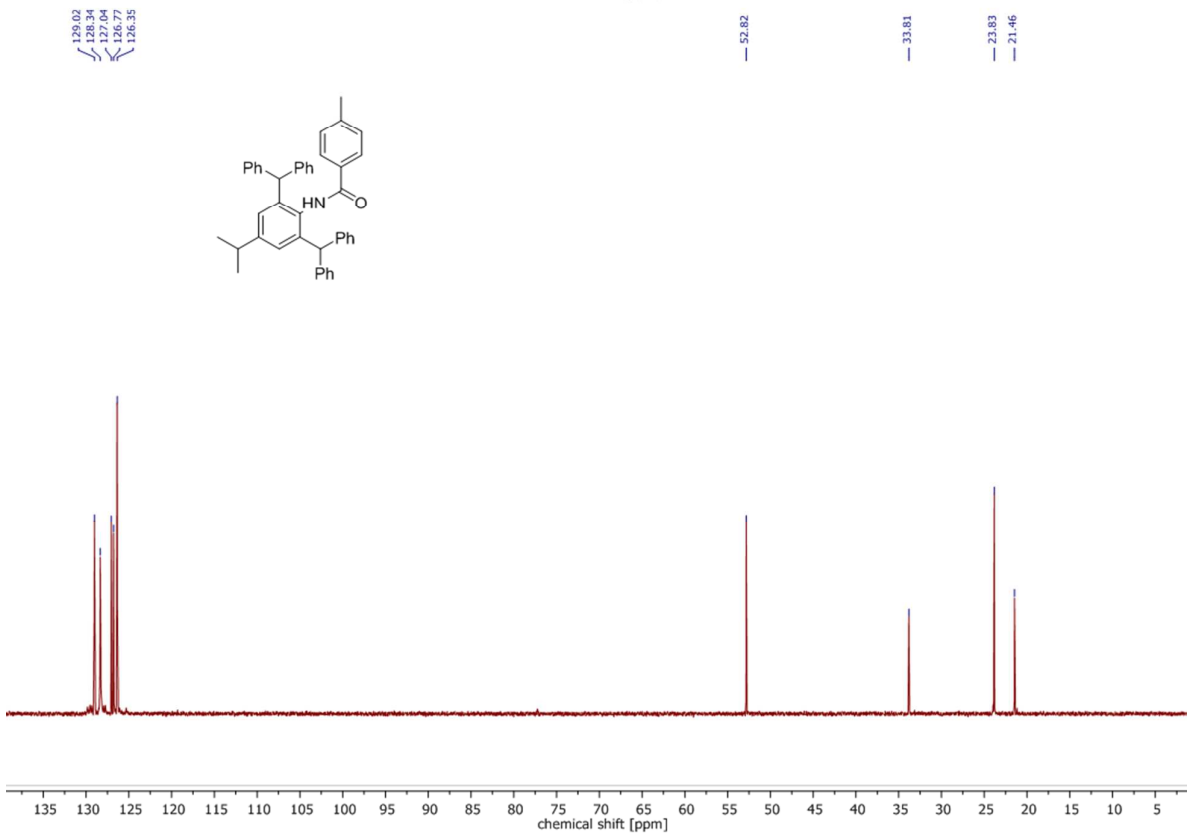
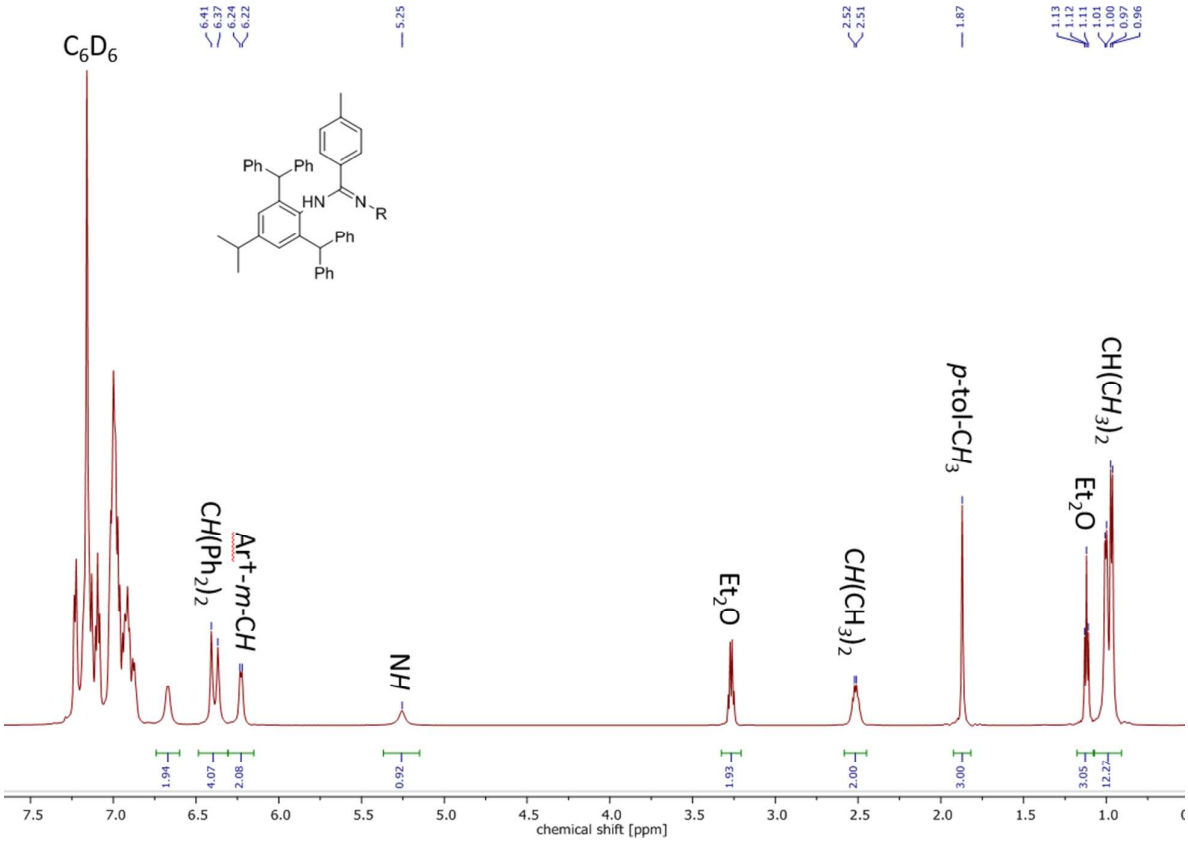
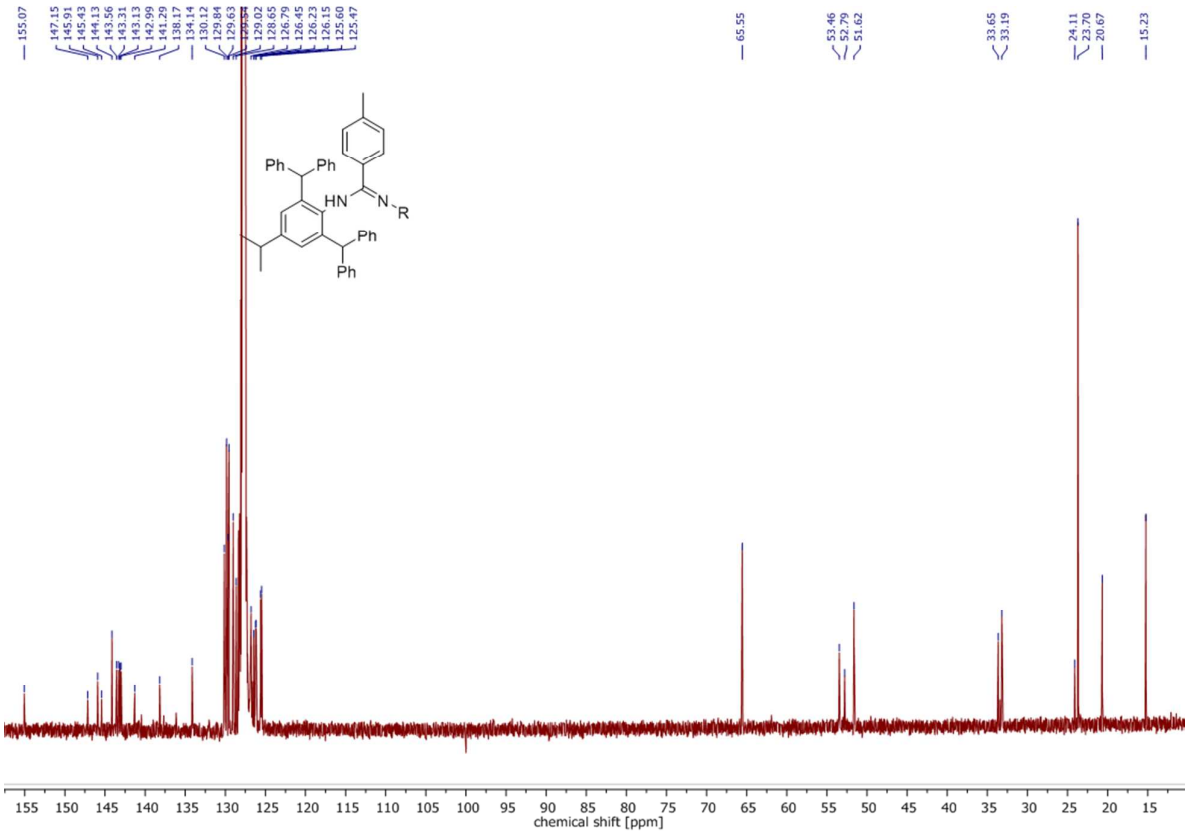

129.02
128.34
127.04
126.77
126.35
52.82
33.81
23.83
21.46
Ph
Ph
HN
O
Ph
Ph
135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
chemical shift [ppm]

Figure S2. From top to bottom: ^{1}H, ^{13}C and DEPT-135 NMR spectra of *p*TolAm^{Ar‡}-H ·$(Et_2O)_{0.5}$ in C_6D_6 (600 MHz / 151 MHz)




155.07
147.15
145.91
145.43
144.13
143.56
143.31
143.13
142.99
141.29
138.17
134.14
130.12
129.84
129.63
129.02
128.65
126.79
126.45
126.23
126.15
125.60
125.47
65.55
53.46
52.79
51.62
33.65
33.19
24.11
23.70
20.67
15.23
Ph
Ph
HN
N
R
Ph
Ph
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
chemical shift [ppm]

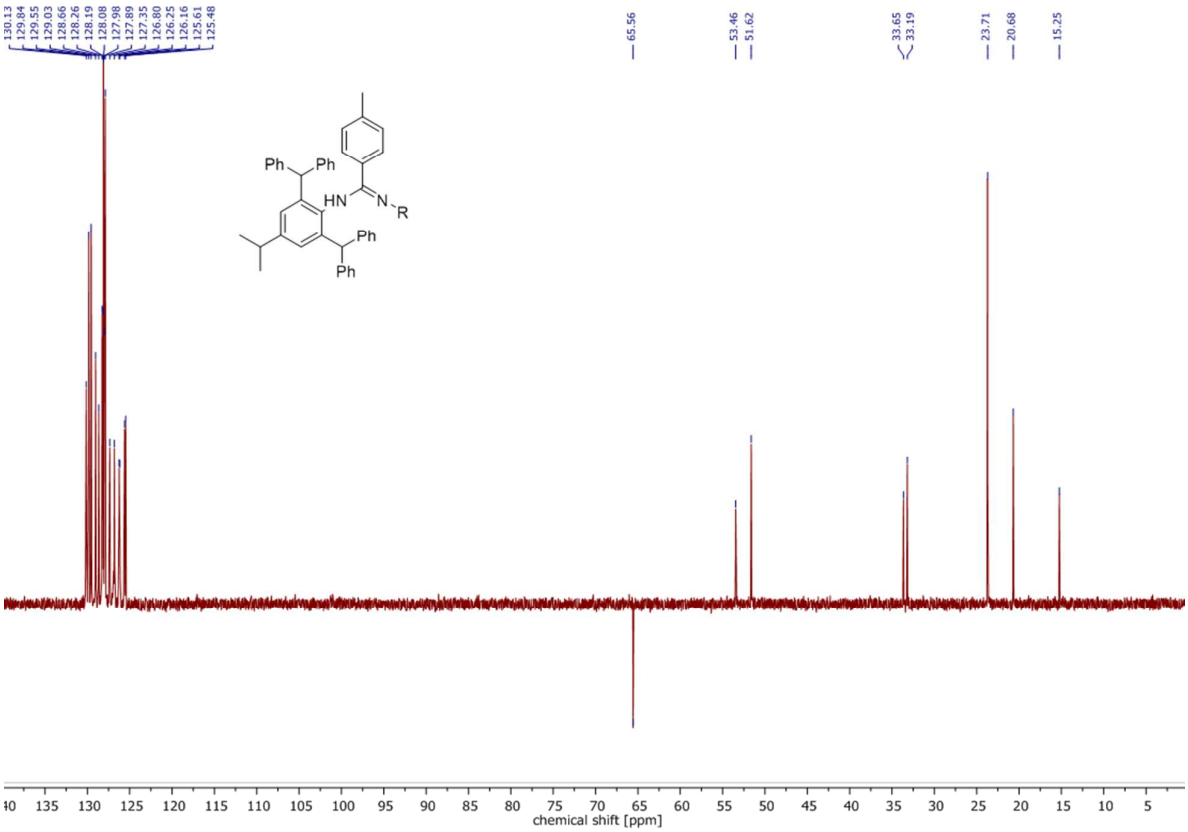
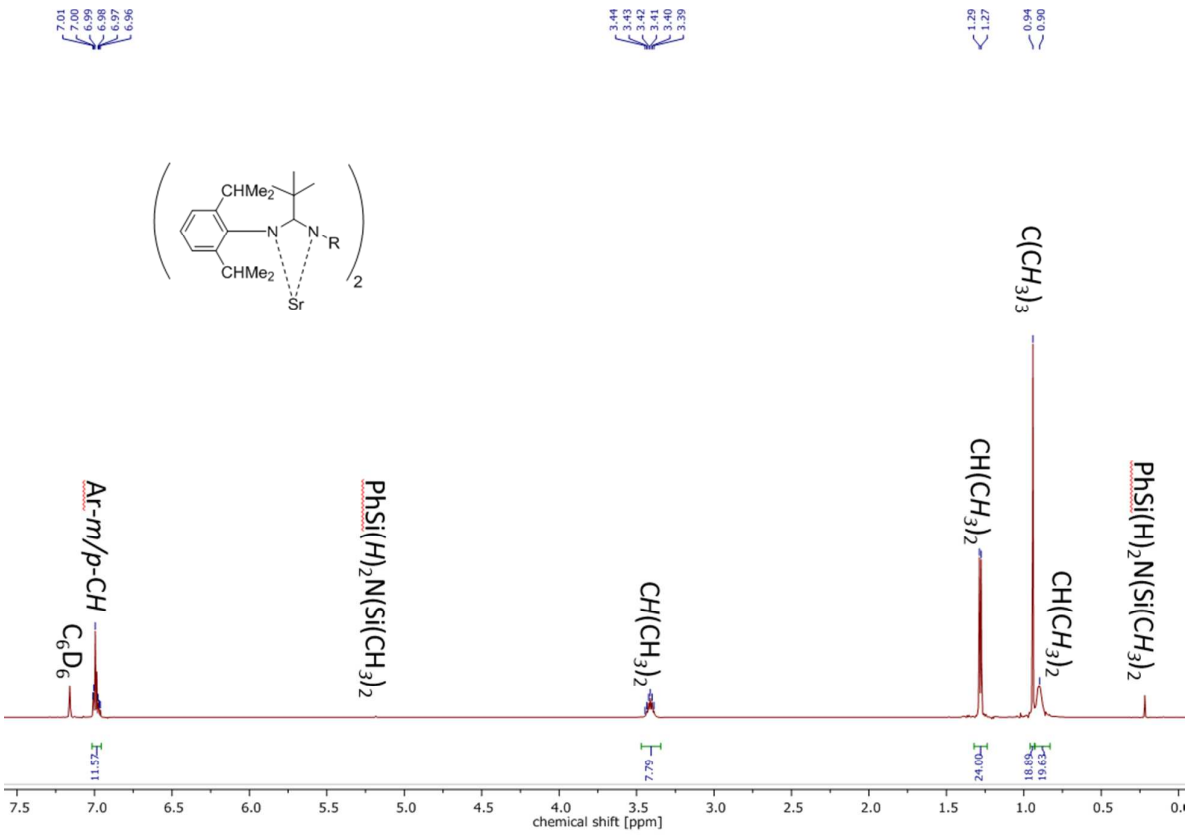
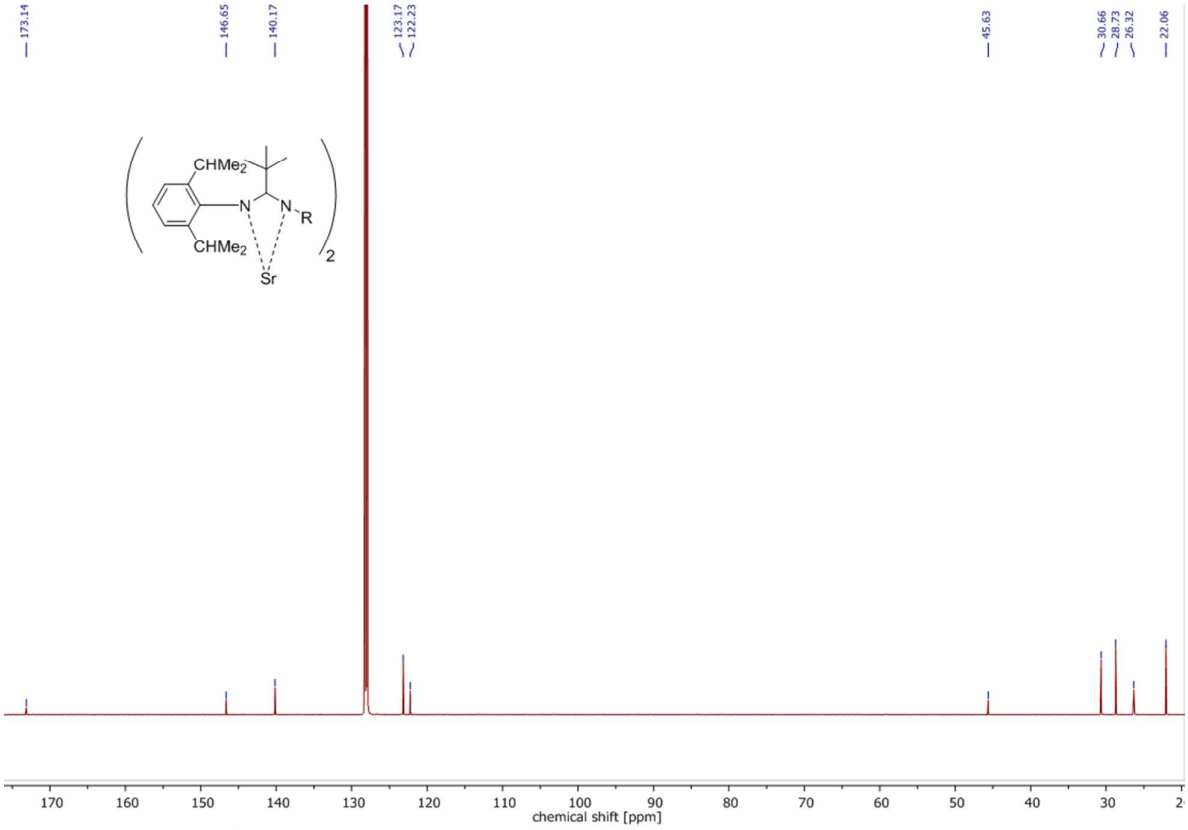

130.13
129.84
129.55
129.03
128.66
128.26
128.19
128.08
127.98
127.89
127.35
126.80
126.25
126.16
125.61
125.48
65.56
53.46
51.62
33.65
33.19
23.71
20.68
15.25
Ph
Ph
HN
N
R
Ph
Ph
40 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
chemical shift [ppm]

Figure S3. From top to bottom: ^{1}H, ^{13}C and DEPT-135 NMR spectra of (tBuAmDIPP)$_2$Sr in C_6D_6 (600 MHz / 151 MHz)




173.14
146.65
140.17
123.17
122.23
45.63
30.66
28.73
26.32
22.06
CHMe2
N
N
R
CHMe2
Sr
2
chemical shift [ppm]

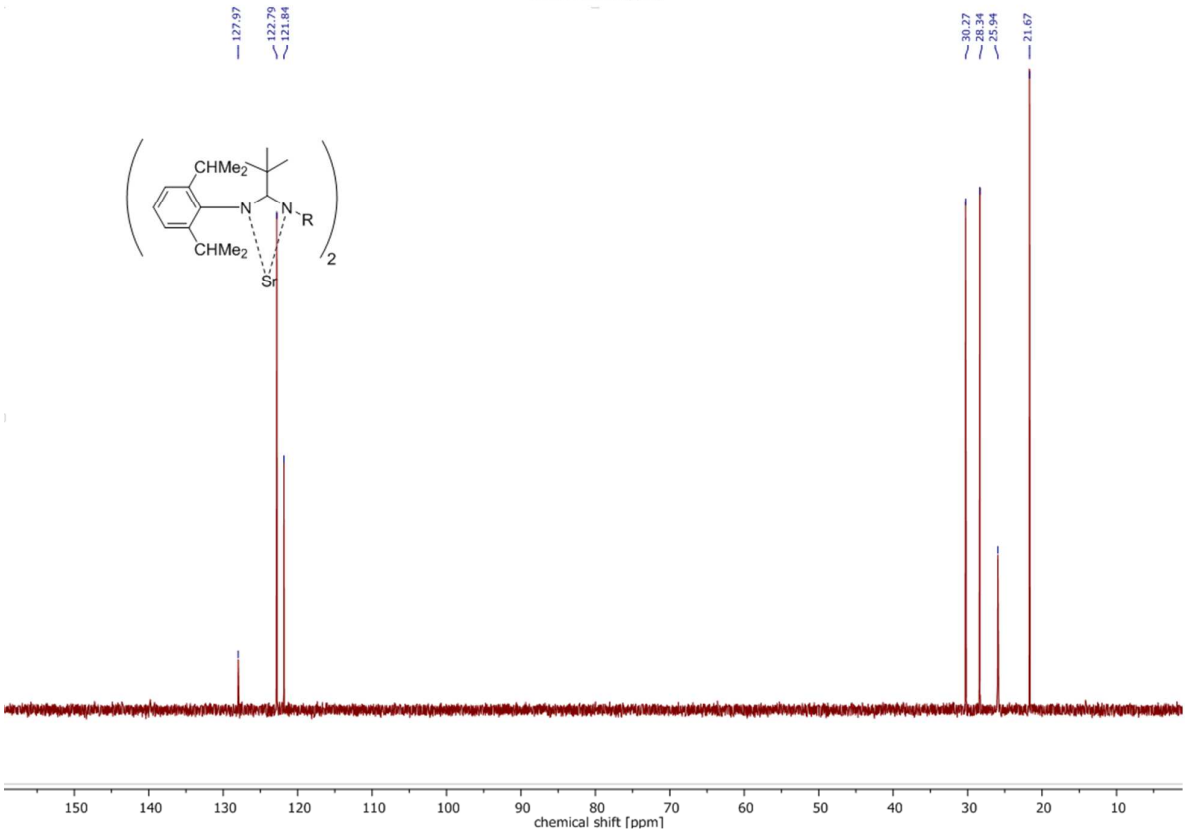
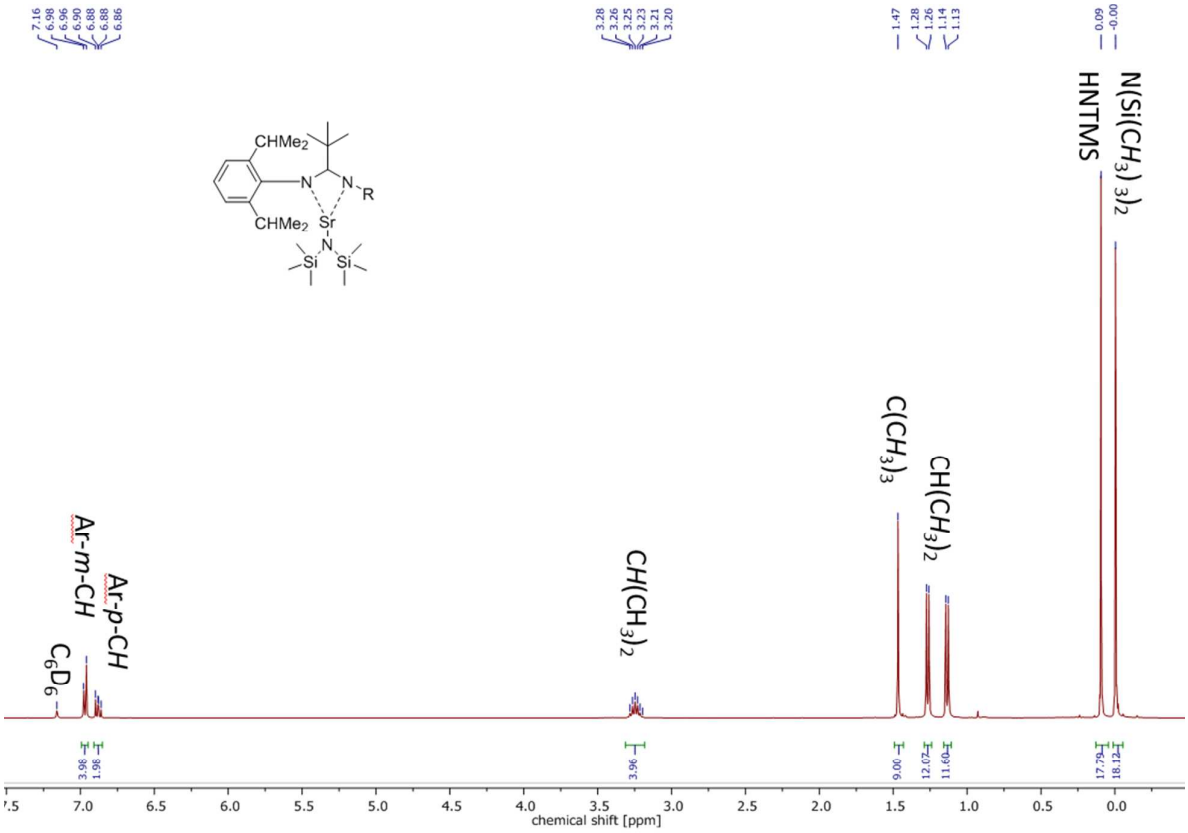
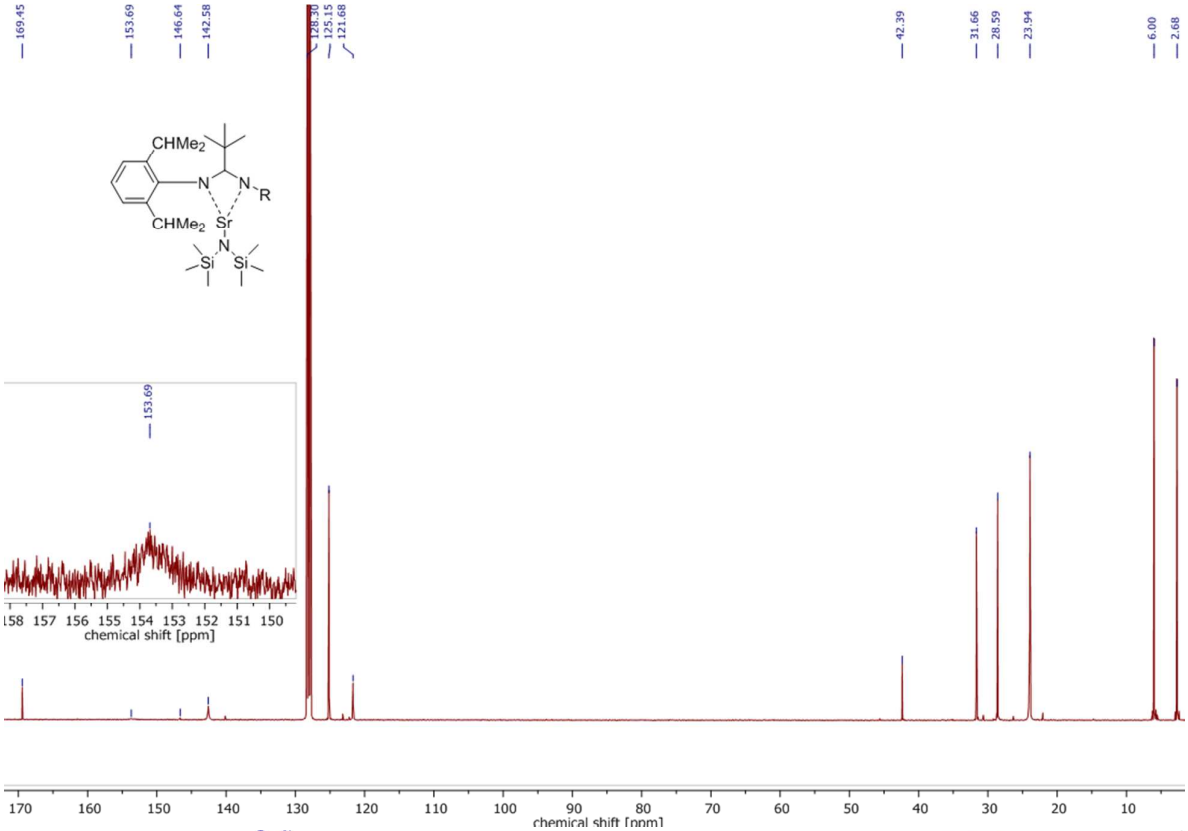

127.97
122.79
121.84
30.27
28.34
25.94
21.67
CHMe2
N
N
R
CHMe2
Sr
2
chemical shift [ppm]

Figure S4. From top to bottom: ^{1}H, ^{13}C and DEPT-135 NMR spectra of *in situ* generated *t*BuAm^{DIPP}SrN(SiMe$_3$)$_2$ in C_6D_6 (400 MHz / 151 MHz)




169.45
153.69
146.64
142.58
128.30
125.15
121.68
42.39
31.66
28.59
23.94
6.00
2.68
CHMe2
N
N
R
CHMe2
Sr
N
Si
Si
153.69
158 157 156 155 154 153 152 151 150
chemical shift [ppm]
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
chemical shift [ppm]

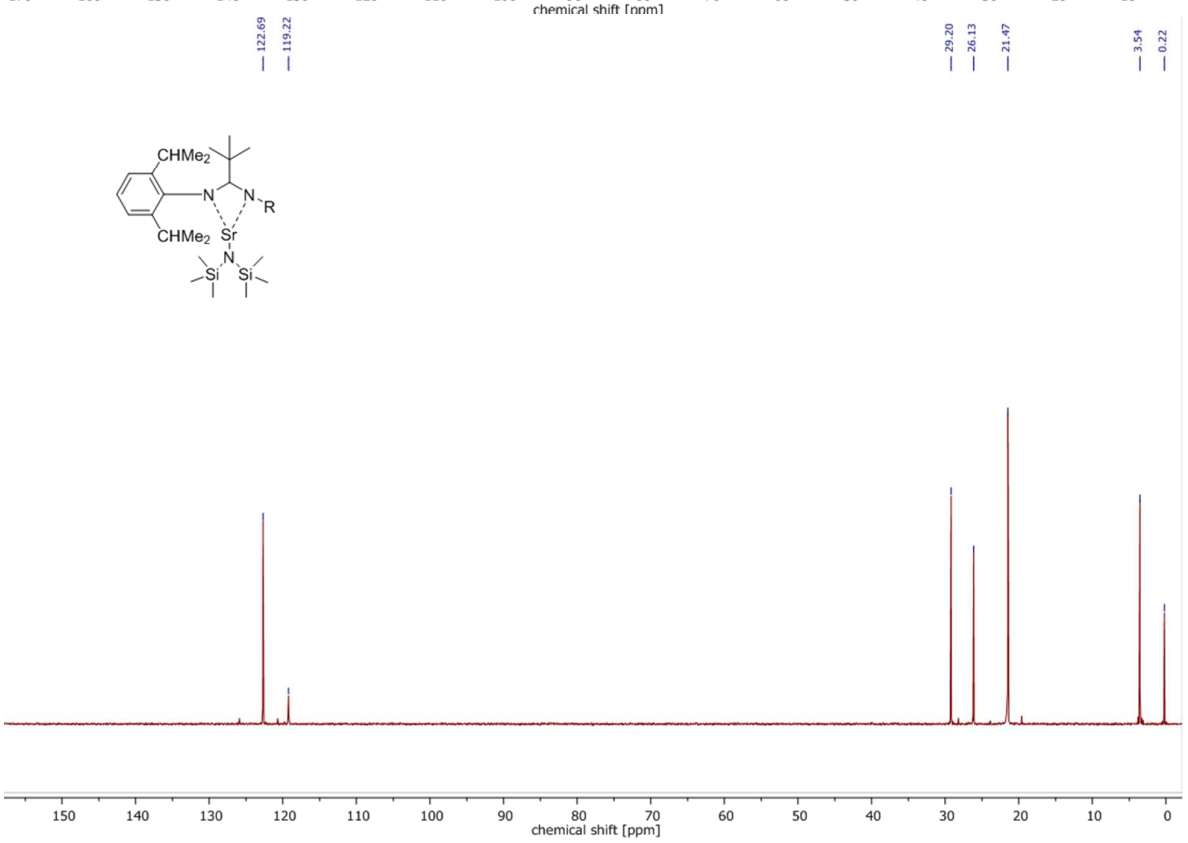
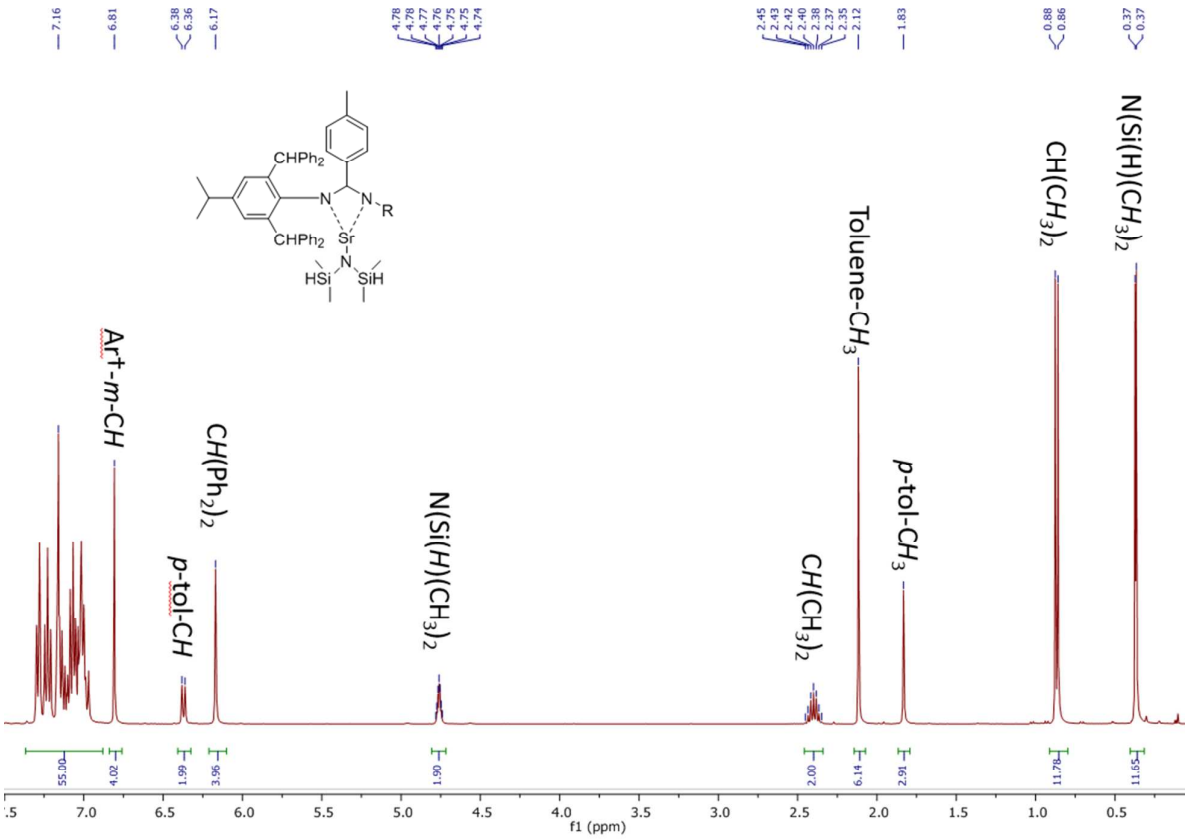
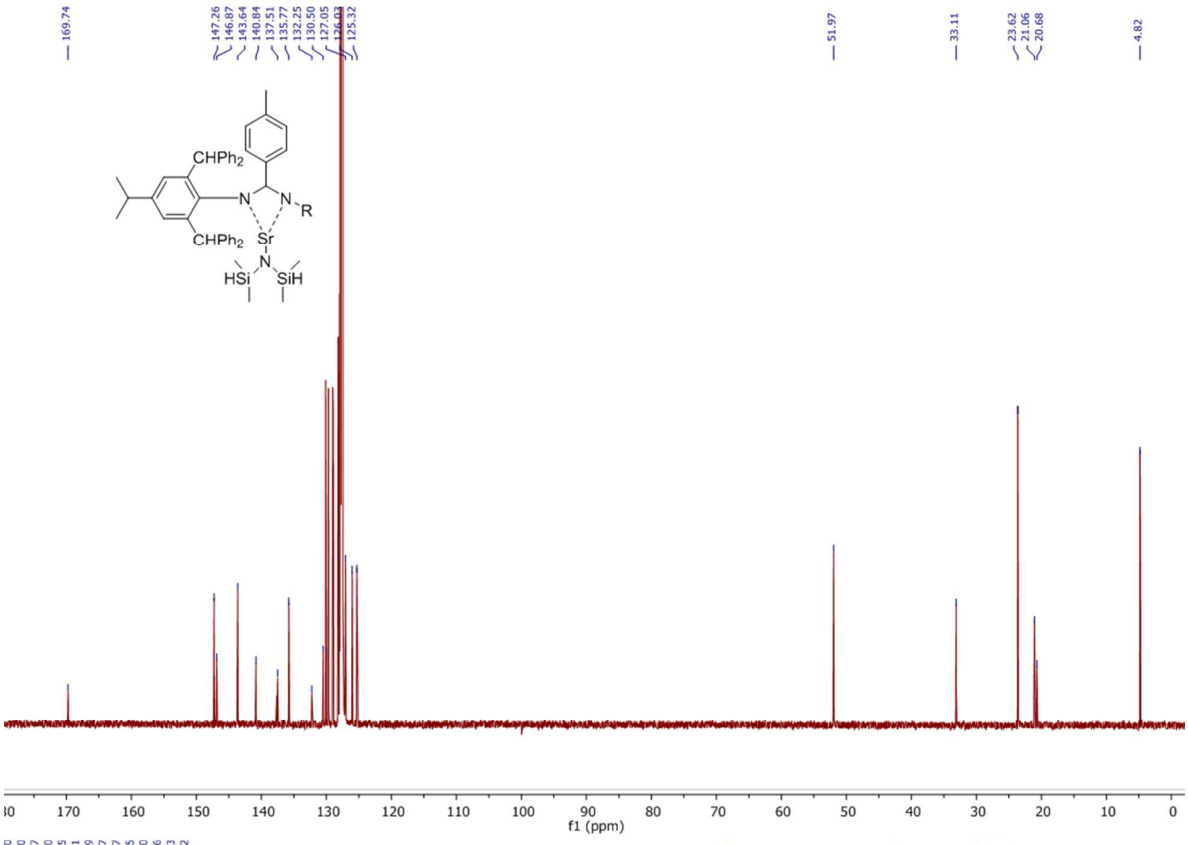

122.69
119.22
29.20
26.13
21.47
3.54
0.22
CHMe2
N
N
R
CHMe2
Sr
N
Si
Si
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift [ppm]

Figure S5. From top to bottom: ^{1}H, ^{13}C and DEPT-135 NMR spectra of *p*TolAm^{Ar‡}SrN(SiHMe$_2$)$_2$·(toluene)$_2$ in C_6D_6 (400 MHz / 151 MHz)




169.74
147.26
146.87
143.64
140.84
137.51
135.77
132.25
130.50
127.05
126.03
125.32
51.97
33.11
23.62
21.06
20.68
4.82
CHPh2
CHPh2
N
N
R
Sr
N
HSi
SiH
f1 (ppm)

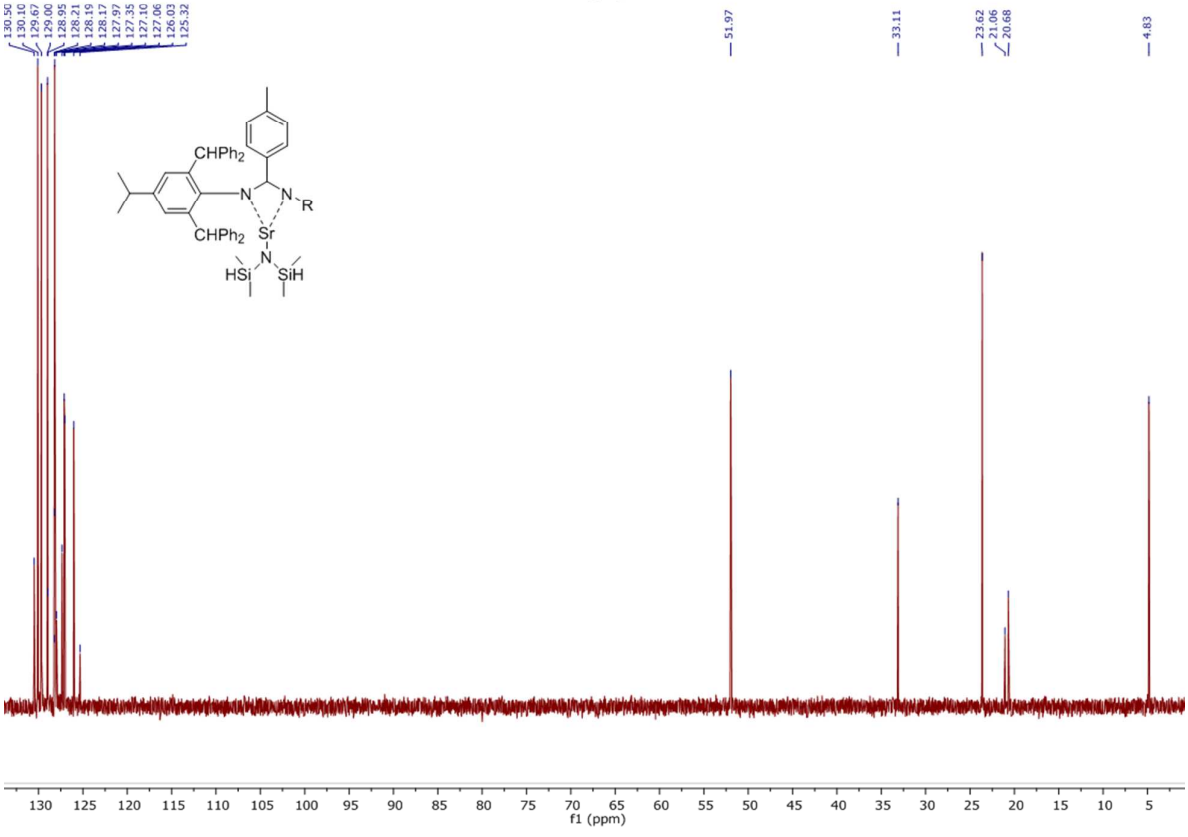
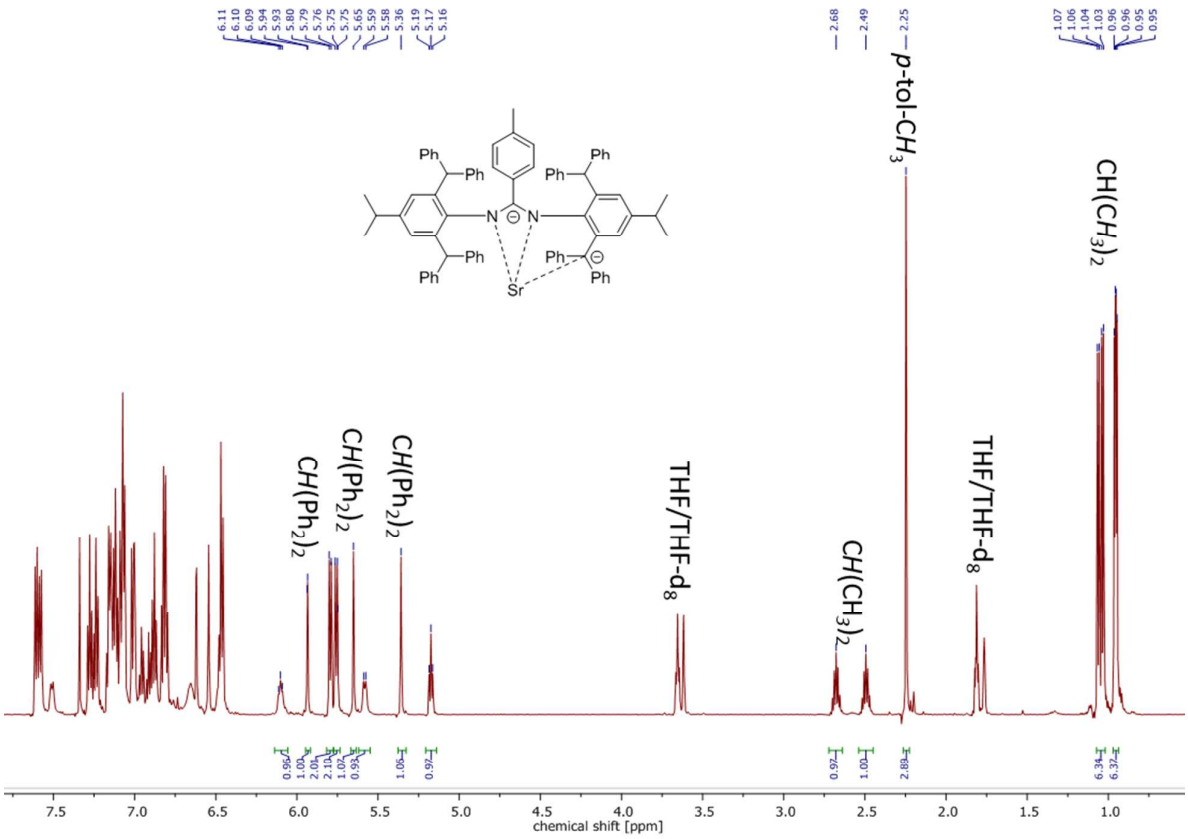
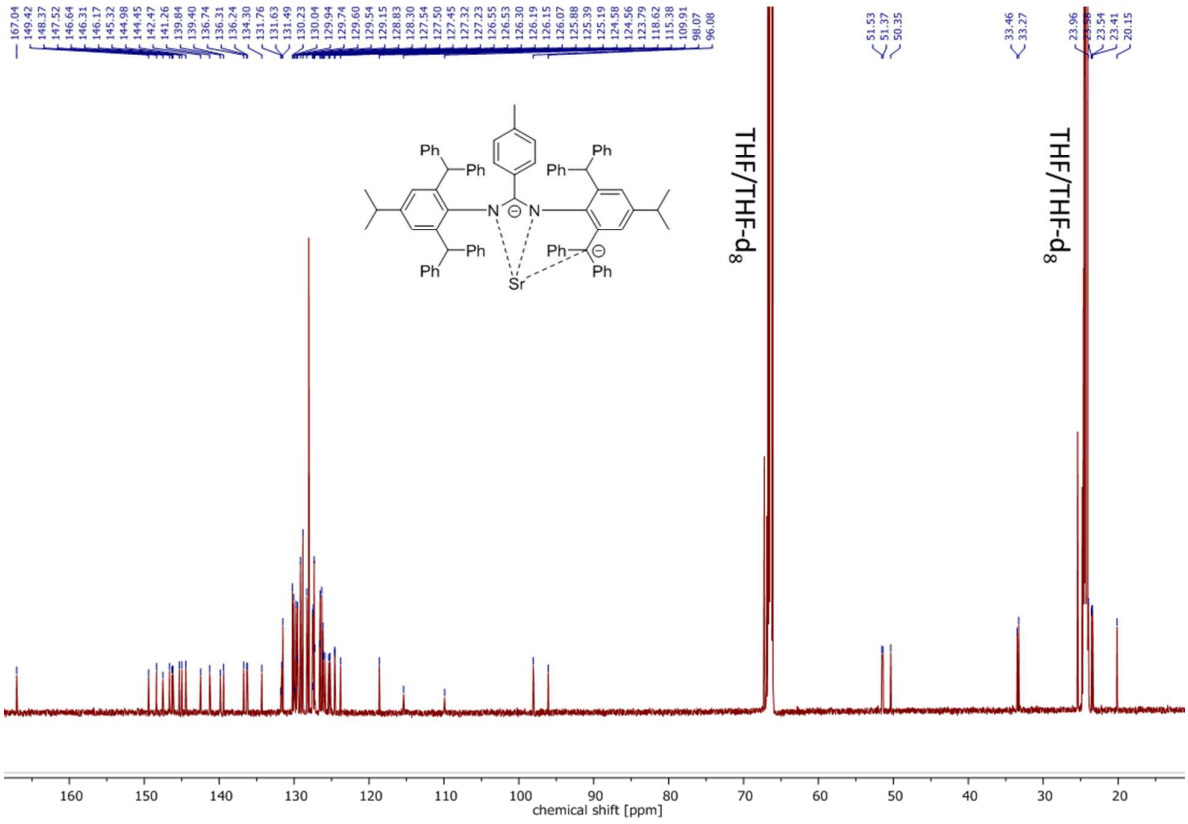
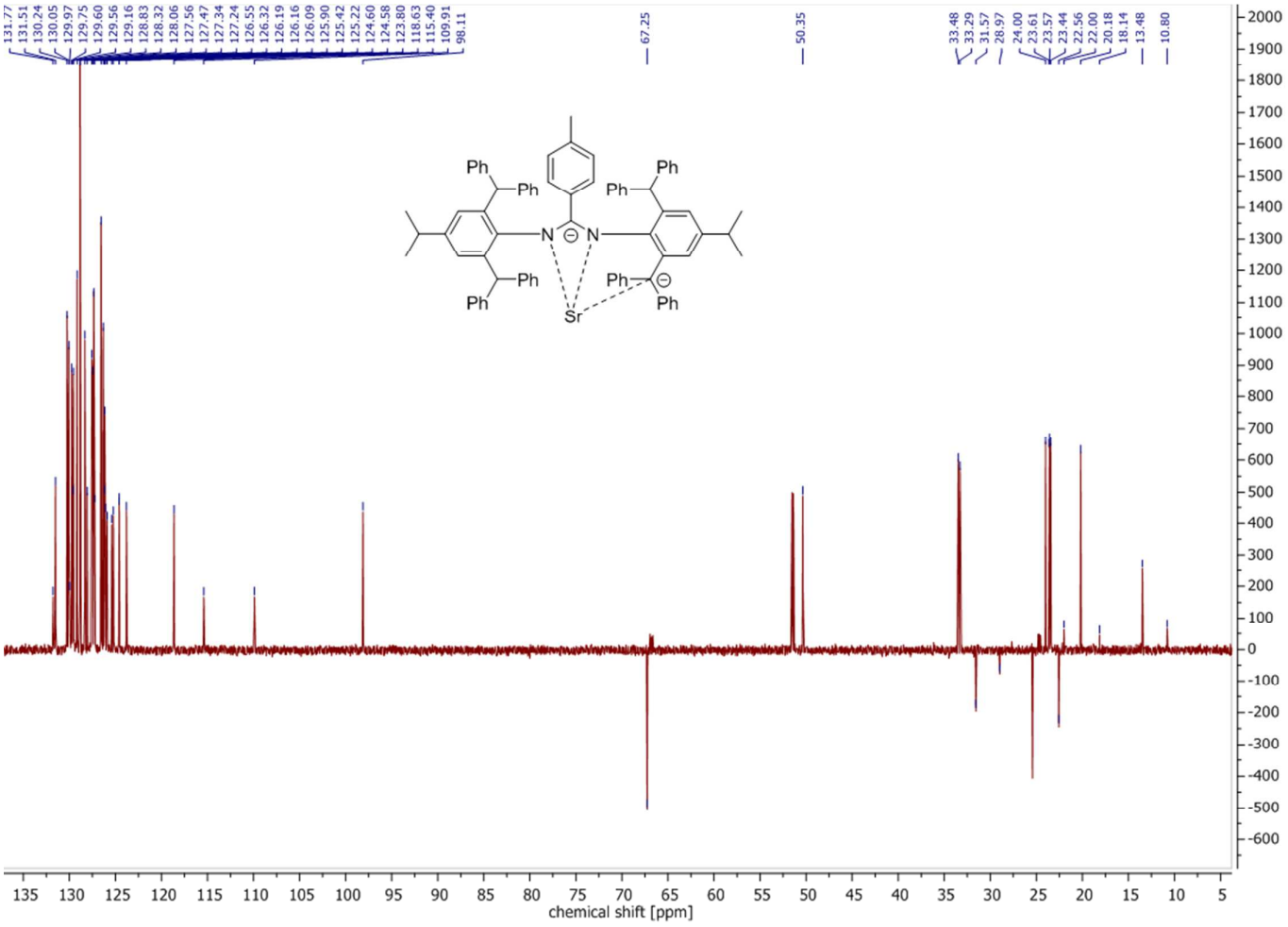
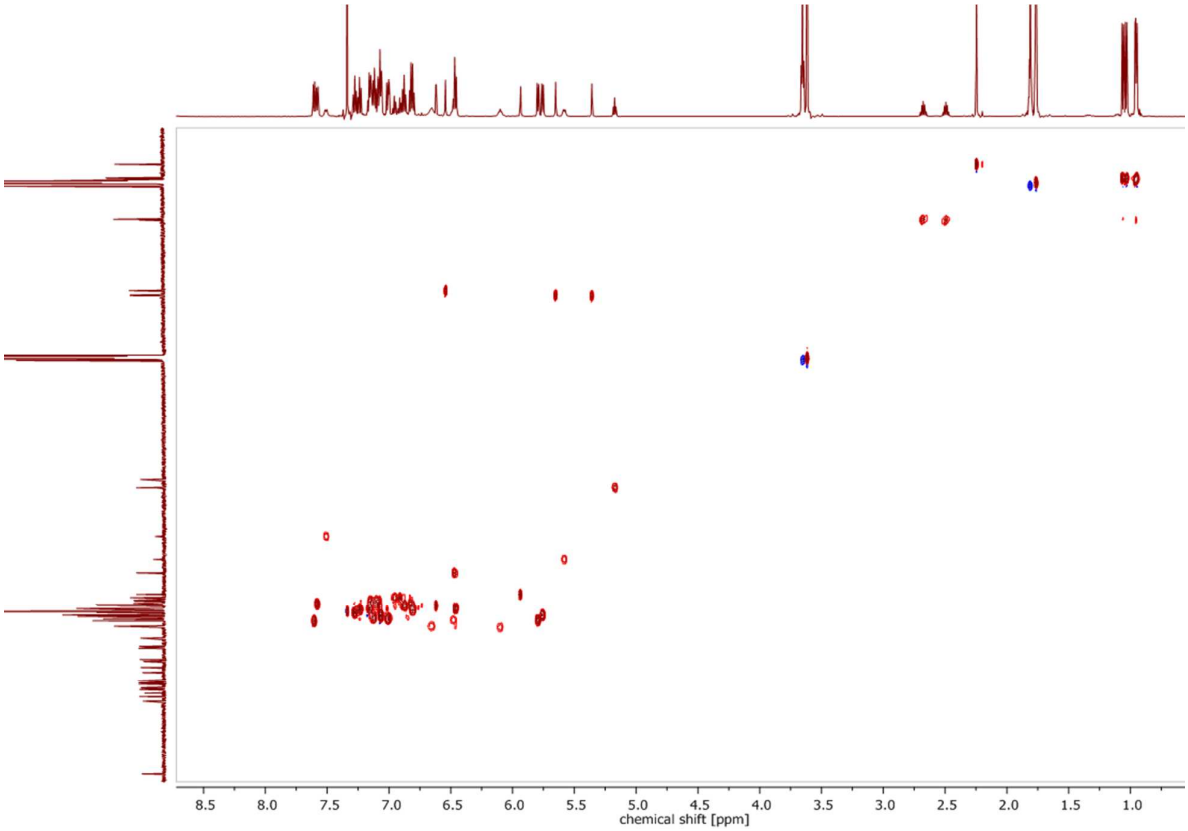

130.50
130.10
129.67
129.00
128.95
128.21
128.19
128.17
127.97
127.35
127.10
127.06
126.03
125.32
51.97
33.11
23.62
21.06
20.68
4.83
CHPh2
CHPh2
N
N
R
Sr
N
HSi
SiH
f1 (ppm)

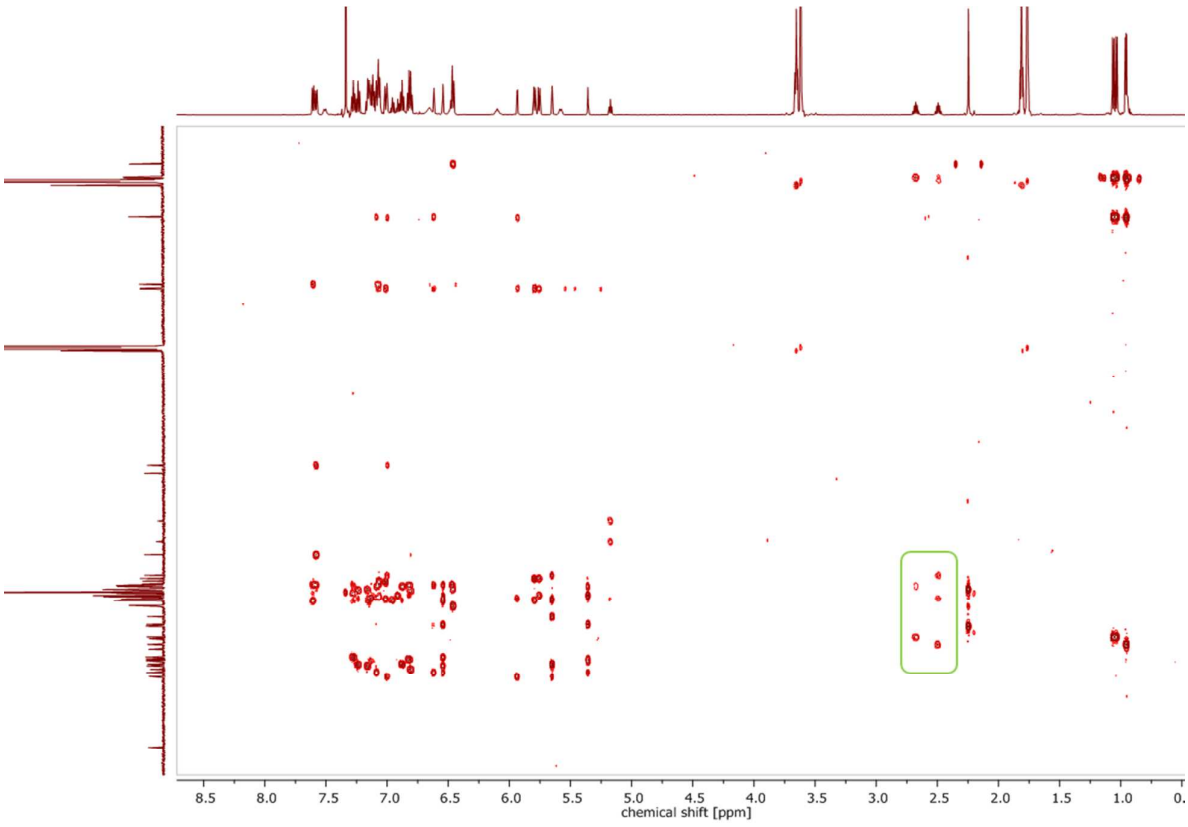
Figure S6. From top to bottom: ^{1}H, ^{13}C and DEPT-135, HSQC, HMBC and DOSY NMR spectra of **7** in THF-d_8 (600 MHz / 151 MHz)

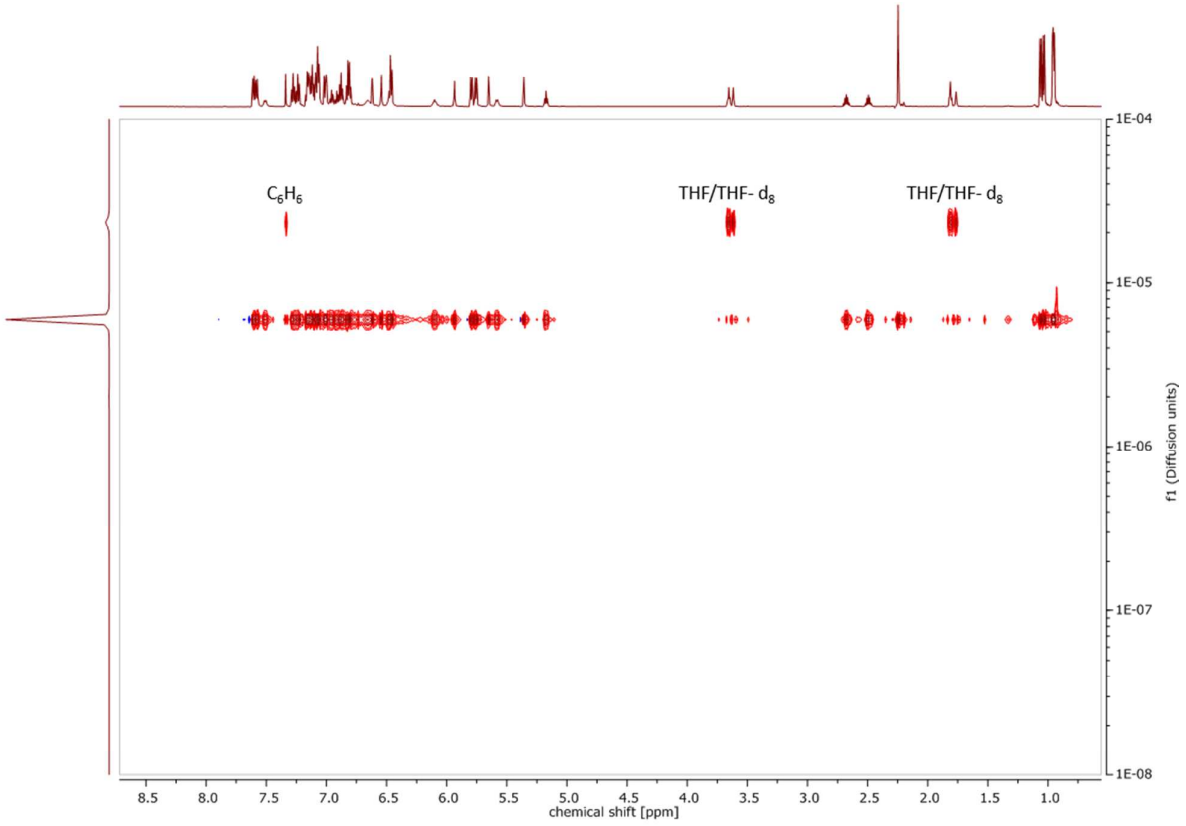



THF/THF-d8
THF/THF-d8
chemical shift [ppm]


131.77
131.51
130.24
130.05
129.97
129.75
129.60
129.56
129.16
128.83
128.32
128.06
127.56
127.47
127.34
127.24
126.55
126.32
126.19
126.16
126.09
125.90
125.42
125.22
124.60
124.58
123.80
118.63
115.40
109.91
98.11
67.25
50.35
33.48
33.29
31.57
28.97
24.00
23.61
23.57
23.44
22.56
22.00
20.18
18.14
13.48
10.80
Ph
Ph
Ph
Ph
Ph
Ph
Ph
Ph
N
N
Sr
chemical shift [ppm]


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
chemical shift [ppm]


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.
chemical shift [ppm]


C6H6
THF/THF- d8
THF/THF- d8
1E-04
1E-05
1E-06
1E-07
1E-08
f1 (Diffusion units)
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
chemical shift [ppm]

2) Crystallographic data

All crystal structures have been measured on a SuperNova (Agilent) diffractometer with dual Cu and Mo microfocus sources and an Atlas S2 detector. For geometry calculations and design of the figures in the main manuscript the program PLATON has been used.[S1] Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1586616 (*t*BuAm^{DIPP})$_2$Sr, 1586617 *p*TolAm^{Ar‡}SrN(SiHMe$_2$)$_2$ and 1586618 complex **7**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

Crystal structure of (*t*BuAm^{DIPP})$_2$Sr. Using Olex2,[S2] the structure was solved by Direct Methods (ShelXT)[S3] and refined with ShelXL[S4] using Least Squares minimisation. The hydrogen atoms have been placed on calculated positions and were refined isotropically in a riding model. One of the *t*-butyl-groups was refined over two positions (ratio ~ 60:40) as well as two carbon atoms of the cocrystalized pentane molecule (ratio ~ 55:45).

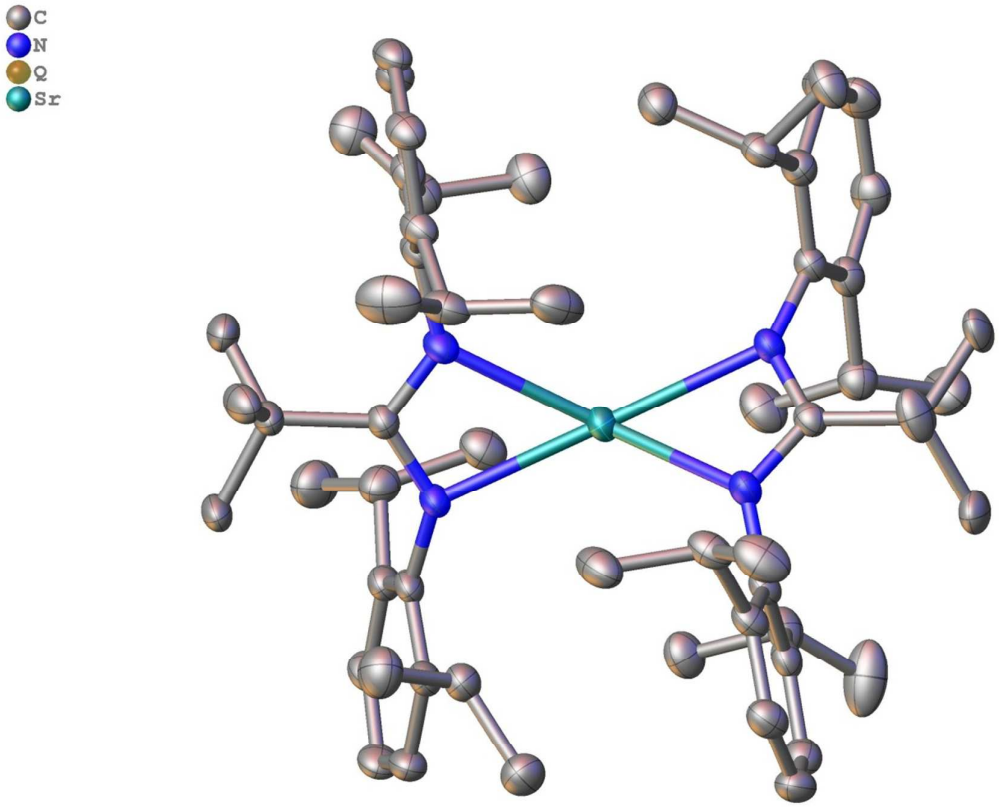


Figure S7. ORTEP plot[S2] (50% probability) for (*t*BuAm^{DIPP})$_2$Sr.

Table S1. Crystal data and structure refinement for (*t*BuAm^{DIPP})$_2$Sr	
Identification code	hasj150401b
Empirical formula	$C_{63}H_{98}N_4Sr$
Formula weight	999.07
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	12.9470(6)
b/Å	13.7245(7)
c/Å	17.1647(7)
α/°	79.485(4)
β/°	85.549(4)
γ/°	82.161(4)
Volume/Å^3	2966.4(2)
Z	2
ρ_{calc}g/cm^3	1.119
μ/mm^{-1}	1.545
F(000)	1084.0
Crystal size/mm^3	0.252 × 0.204 × 0.1
Crystal color	colorless
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.602 to 146.918
Index ranges	-15 ≤ h ≤ 11, -15 ≤ k ≤ 16, -21 ≤ l ≤ 20
Reflections collected	18130
Independent reflections	11362 [R_{int} = 0.0372, R_{sigma} = 0.0476]
Data/restraints/parameters	11362/0/688
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0514, wR_2 = 0.1348
Final R indexes [all data]	R_1 = 0.0562, wR_2 = 0.1415
Largest diff. peak/hole / e Å^{-3}	0.84/-0.86

Crystal structure of *p*TolAm^{Ar‡}SrN(SiHMe$_2$)$_2$. Using Olex2,[S2] the structure was solved by Direct Methods (ShelXT)[S3] and refined with ShelXL[S4] using Least Squares minimisation. The hydrogen atoms have been placed on calculated positions and were refined isotropically in a riding model. Three of the four molecules of toluene cocrystalized around a center of symmetry and were refined with occupancies of approximate ratios of 0.5, 0.7 and 0.3 resulting in total to 1.5 equivalents of toluene. The two toluene molecules with occupancies of 0.3 and 0.7 were additionally modeled using Rigid Bond (RIGU) Restraints and additionally equal displacement parameters (EADP) were used for 6 carbon atoms occupying almost the same coordinates.[S5] The geometry of the lesser occupied 6 membered ring was idealized using AFIX 66 as well.

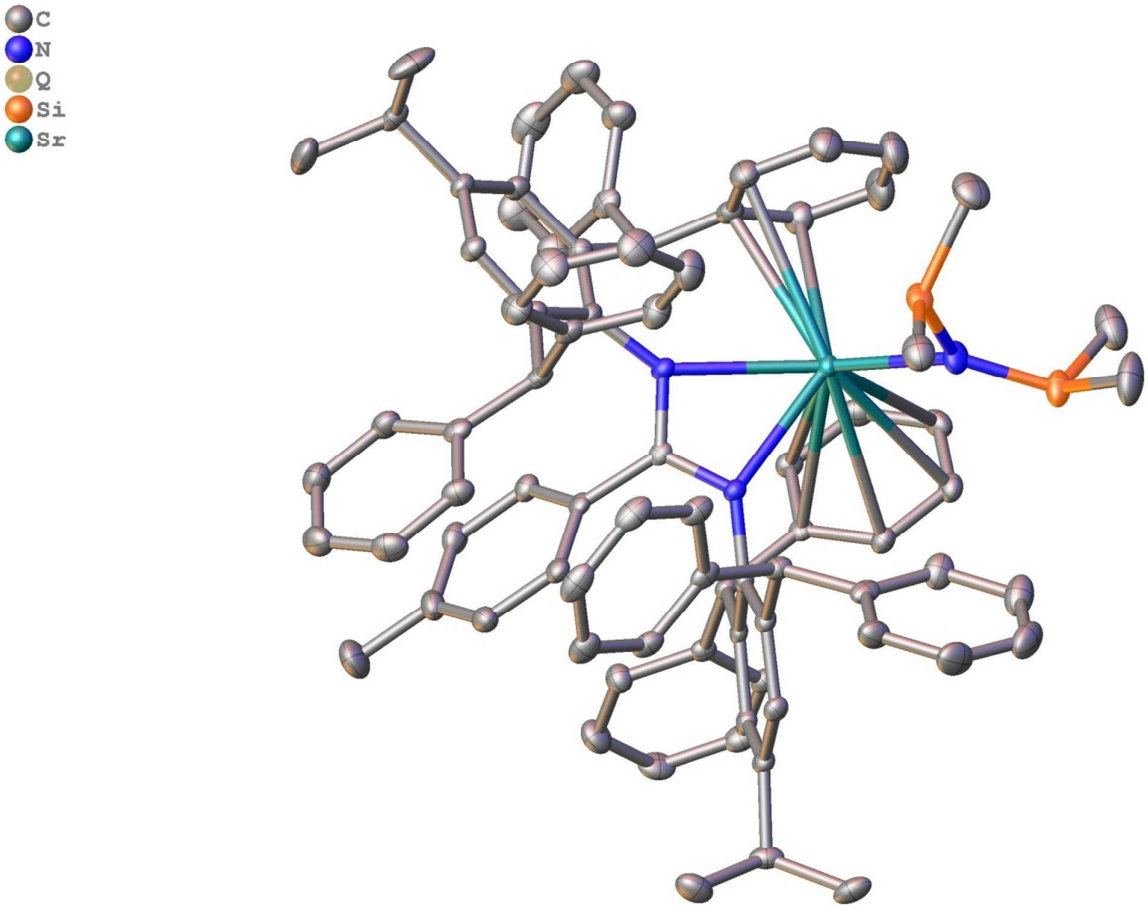


Figure S8. ORTEP plot[S2] (50% probability) for *p*TolAm^{Ar‡}SrN(SiHMe$_2$)$_2$.

Table S2. Crystal data and structure refinement for *p*TolAm^{Ar‡}SrN(SiHMe$_2$)$_2$	
Identification code	hasj150416b
Empirical formula	$C_{99.5}H_{103}N_3Si_2Sr$
Formula weight	1484.64
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.57635(7)
b/Å	21.20842(12)
c/Å	28.76613(14)
α/°	90
β/°	96.7436(5)
γ/°	90
Volume/Å^3	8225.41(7)
Z	4
ρ_{calc}g/cm^3	1.199
μ/mm^{-1}	1.555
F(000)	3148.0
Crystal size/mm^3	0.2251 × 0.118 × 0.1037
Crystal color	colorless
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.188 to 136.226
Index ranges	-16 ≤ h ≤ 16, -25 ≤ k ≤ 23, -34 ≤ l ≤ 34
Reflections collected	73487
Independent reflections	15035 [R_{int} = 0.0284, R_{sigma} = 0.0201]
Data/restraints/parameters	15035/37/1007
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0402, wR_2 = 0.1036
Final R indexes [all data]	R_1 = 0.0437, wR_2 = 0.1059
Largest diff. peak/hole / e Å^{-3}	1.17/-0.68

Crystal structure of 7. Using Olex2,[S2] the structure was solved by Direct Methods (ShelXT)[S3] and refined with ShelXL[S4] using Least Squares minimisation. The hydrogen atoms have been placed on calculated positions and were refined isotropically in a riding model. The voids (569Å³) contain disordered solvent molecules. However, a satisfactory disorder model for the solvent could not found, and therefore the OLEX2 Solvent Mask routine (similar to PLATON/SQUEEZE) was used to mask out the disordered electron density (130e⁻).[S6] Additionally one *i*Pr-group was refined over two positions with an approximate ratio of 80:20. The C-C distances of this *i*Pr-group were idealized against each other using the SADI command and the Uij components of the carbon atoms were restrained as well (SIMU s[0.01] st[0.02]).

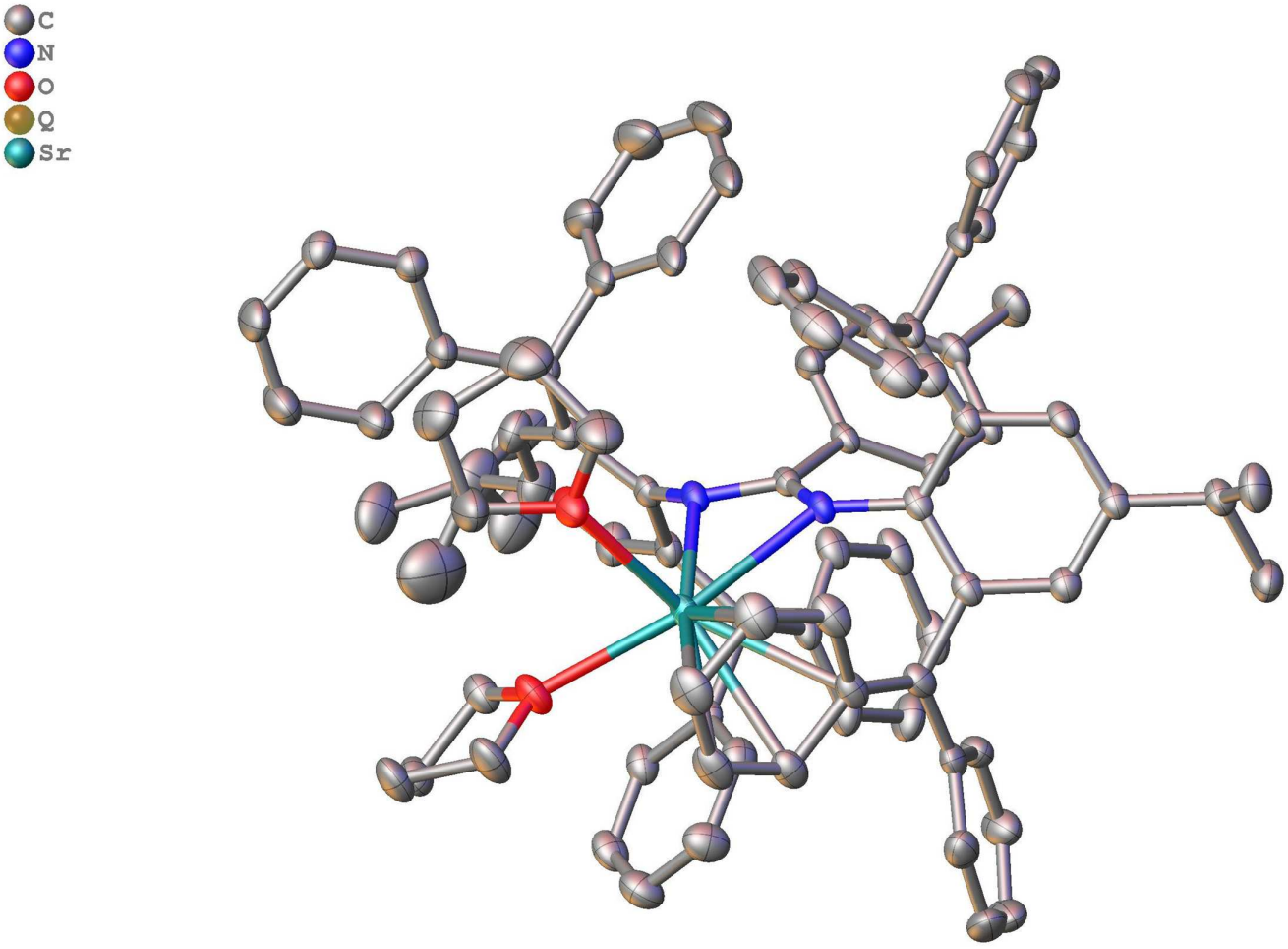


Figure S9. ORTEP plot[S2] (50% probability) for **7**.

Table S3. Crystal data and structure refinement for **7**	
Identification code	hasj150615a
Empirical formula	$C_{86}H_{84}N_2O_2Sr$
Formula weight	1265.17
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	14.3676(4)
b/Å	14.4992(3)
c/Å	18.6406(3)
α/°	91.0705(16)
β/°	103.8726(19)
γ/°	99.512(2)
Volume/Å^3	3711.20(15)
Z	2
ρ_{calc}g/cm^3	1.132
μ/mm^{-1}	1.360
F(000)	1336.0
Crystal size/mm^3	0.1695 × 0.134 × 0.0981
Crystal color	red
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.192 to 136.226
Index ranges	-17 ≤ h ≤ 17, -17 ≤ k ≤ 17, -22 ≤ l ≤ 22
Reflections collected	53999
Independent reflections	13514 [R_{int} = 0.0374, R_{sigma} = 0.0334]
Data/restraints/parameters	13514/62/846
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0450, wR_2 = 0.1169
Final R indexes [all data]	R_1 = 0.0529, wR_2 = 0.1207
Largest diff. peak/hole / e Å^{-3}	0.70/-0.47

3) References

(S1) *Program PLATON: Multipurpose Crystallographic Tool.* A. L. Spek, *Acta Cryst*. **2009**, *D65*, 148-155.

(S2) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339-341.

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(S4) G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122.

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