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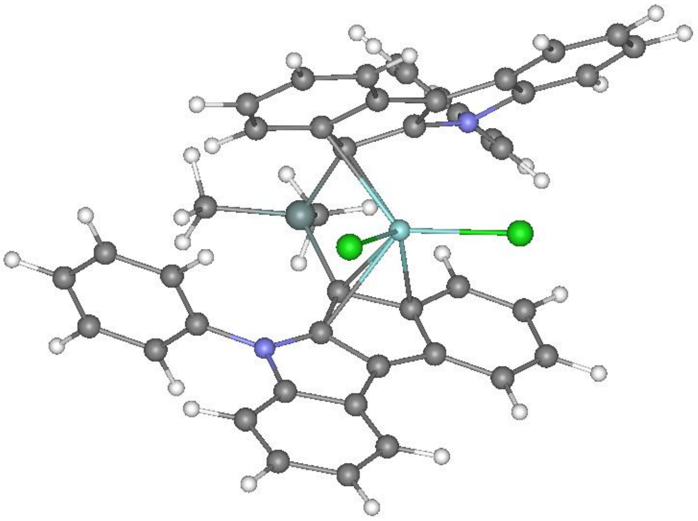
Racemo-selective formation of *ansa*-zirconocene in the reaction of dimethylbis(5-phenyl-5,6-dihydroindeno[2,1-*b*]indol-6-yl)silane dilithium salt with $ZrCl_4$: X-ray and DFT argumentation for stereocontrol

Ilya E. Nifant'ev, Alexander A. Vinogradov, Mikhail E. Minyaev, Konstantin A. Lyssenko and Pavel V. Ivchenko

1. DFT calculations

rac-**2**



Zero-point vibrational energy	1676797.4 (J mol^{-1})
	400.76421 (kcal mol^{-1})
Zero-point correction	0.638658 (Hartree/particle)
Thermal correction to Energy	0.680156
Thermal correction to Enthalpy	0.681100
Thermal correction to Gibbs Free Energy	0.567807
Sum of electronic and zero-point Energies	-6554.945082
Sum of electronic and thermal Energies	-6554.903584
Sum of electronic and thermal Enthalpies	-6554.902640
Sum of electronic and thermal Free Energies	-6555.015934

Cartesian

40	0.19258168	-1.27148533	-0.33746707	6	-5.11571836	-1.62078536	-0.46216705
17	-1.03631830	-3.35228539	-0.03126705	1	-5.70171833	-1.16758537	0.33073294
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14	-0.00281832	1.91011453	0.44763294	1	-6.58371830	-3.10848546	-0.93326706
7	-3.14561820	-0.05878535	-0.22626707	6	-4.85981846	-3.29938531	-2.21146703
7	3.32058167	-0.03998536	0.74263299	1	-5.26331854	-4.15768528	-2.73876691
6	-1.14301836	2.88111472	1.58103287	6	-3.60931826	-2.79928541	-2.55996704
1	-0.56331831	3.16131473	2.46883297	1	-3.02951837	-3.26088548	-3.35296702
1	-1.43121827	3.80771470	1.07133293	6	-3.10861826	-1.69748533	-1.86536705
1	-2.06291842	2.40331459	1.91883290	6	4.05438137	-1.22168529	0.90983295

6	1.17158175	3.22171474	-0.19176705	6	5.38428164	-1.46248543	0.57043296
1	1.49508166	3.84151483	0.65223294	1	5.99418163	-0.69538534	0.10283295
1	2.07028174	2.87411451	-0.70006704	6	5.89468193	-2.72698545	0.84733295
1	0.61658168	3.87011456	-0.88046706	1	6.92588186	-2.94928527	0.59163296
6	-0.81141829	0.93801463	-0.95366704	6	5.10218191	-3.72198534	1.44293296
6	-1.96241832	0.08031467	-0.94966704	1	5.53038168	-4.70058537	1.63423288
6	-1.89781833	-0.91358531	-1.95406711	6	3.77658176	-3.47138548	1.77993286
6	-0.73301828	-0.64998531	-2.74316692	1	3.16488171	-4.24738503	2.22913313
6	-0.21231832	-1.24588537	-3.91716695	6	3.24328160	-2.20698524	1.51813293
1	-0.69951832	-2.11398530	-4.34916735	6	-3.80691838	1.02761459	0.41083294
6	0.91198170	-0.70548534	-4.49386740	6	-3.85051823	2.27801466	-0.21126705
1	1.32338166	-1.15058529	-5.39386702	1	-3.37141824	2.40961456	-1.17746711
6	1.53798175	0.44111463	-3.93696690	6	-4.49661827	3.33921456	0.41803291
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6	0.66008168	-1.75808537	2.27863312	6	3.84408164	1.12711465	0.12323294
6	0.06178168	-2.83338547	2.97113299	6	4.07348156	1.12381458	-1.25356710
1	0.61528170	-3.75268531	3.13073301	1	3.81788158	0.23471466	-1.82666707
6	-1.23441827	-2.70278549	3.40943313	6	4.60558176	2.26331472	-1.85676706
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6	-1.96171832	-1.50848532	3.17583299	6	4.90628147	3.38981462	-1.08766711
1	-2.97961831	-1.43008542	3.54613304	1	5.31848192	4.27511501	-1.56156707
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6	-0.05771832	-0.53118533	2.04853296	6	4.15998173	2.24031472	0.90223294
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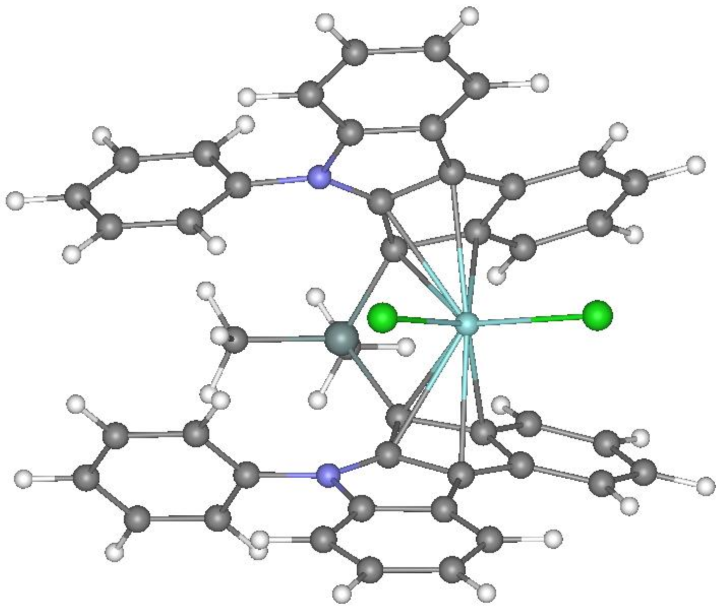
meso-**2**



Zero-point vibrational energy	1675814.9 (J mol^{-1})
	400.52936 (kcal mol^{-1})
Zero-point correction	0.638284 (Hartree/particle)
Thermal correction to Energy	0.679252
Thermal correction to Enthalpy	0.680196
Thermal correction to Gibbs Free Energy	0.567310
Sum of electronic and zero-point Energies	-6554.941788
Sum of electronic and thermal Energies	-6554.900820
Sum of electronic and thermal Enthalpies	-6554.899876
Sum of electronic and thermal Free Energies	-6555.012761

Cartesian

17	-3.59454274	-0.01639636	-1.98932433	6	-0.83404279	-3.26809645	-1.84462440
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6	-2.22324276	-1.72869647	1.26887560	6	1.44375718	-3.80069637	-2.58102441
6	-2.59994268	-2.39649653	0.05197567	6	-0.87274277	3.26480365	-1.83762431
6	-1.39444280	-2.60169649	-0.69212437	6	0.52995723	3.22610354	-1.66482437
6	-0.31224278	-2.16989636	0.12317565	6	2.15025711	2.49230361	0.07797566
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40	-1.62504280	-0.00749637	-0.53142434	6	-1.41574275	3.88200355	-2.96612430
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6	-0.33624279	2.16780353	0.12687564	1	-2.44214272	-3.91159654	-3.13552427
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6	-4.88884258	-2.50779653	0.76687562	6	0.83485723	4.44210386	-3.68872428
6	-3.94464278	-2.75749636	-0.19912435	1	2.47315717	3.80750370	-2.42572427
6	-3.22584271	-1.52779639	2.25327563	1	1.48735726	4.90980387	-4.41922474
1	-2.96164274	-1.12769639	3.22437572	1	-0.95834279	4.94340372	-4.77532482
1	-5.27754307	-1.77219641	2.76937556	6	3.15935731	1.83270359	-0.62442434
1	-5.92374325	-2.78519630	0.59477568	6	2.42405725	3.13360357	1.28687561
1	-4.21354294	-3.22649646	-1.13962436	6	3.18275714	-1.80119646	-0.61972433
6	-4.53994274	1.86190355	2.01237559	6	2.45355725	-3.11259651	1.28677571
6	-4.91524315	2.45390368	0.77817571	6	3.74225736	-3.06109643	1.81287575
6	-3.97564268	2.71560359	-0.18912435	1	1.65605724	-3.64259648	1.80027556
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6	1.84575725	0.00850363	2.25077558	1	1.62355721	3.65580368	1.80357575
6	-0.50314277	-0.00509637	4.06797600	1	5.24355698	1.30610359	-0.64682436
1	-0.07804278	0.88520366	4.54447556	6	4.72945690	2.42930365	1.11727560
1	-1.56864274	-0.01929636	4.29567528	1	5.26265717	-1.25779641	-0.63582432
1	-0.05424279	-0.88189638	4.54767609	6	4.75355721	-2.38949633	1.12417567
1	2.19485712	0.89330363	2.79247570	1	5.75915718	-2.35689640	1.53147566
1	2.20555711	-0.87369639	2.78957558	1	3.95935702	-3.55439639	2.75527573
1	2.31185722	0.01290363	1.26177561	1	5.73615742	2.40390348	1.52217567
6	0.56795722	-3.21479630	-1.66962433	1	3.92965722	3.58380365	2.75307560

2. Synthesis and X-ray diffraction study of compound 3

Synthesis and crystallization of compound 3

The suspension of dimethylbis(5-phenyl-5,6-dihydroindeno[2,1-*b*]indol-6-yl)silane **2** (310 mg, 0.50 mmol) in Et_2O (20 ml) was cooled to –60 °C. Then BuLi (0.42 ml, 2.5 M in hexane, 1.05 mmol) was added dropwise to the stirred suspension. The resulting mixture was allowed to warm to room temperature for 30 min, resulting in yellow solution. Then all the solvent was evaporated and dry residue was dissolved in a mixture of THF (25 ml) and diglyme (5 ml). The solution was divided into three equal parts. Hexane (30 ml) was layered on top of the solution in each portion. After one week, yellow-greenish crystals formed in each portion. The solution was decanted and the crystals were dried *in vacuo*. The combined yield was 0.43 g (76%).

NMR spectra of compound **3** are provided in Figures S1 and S2.

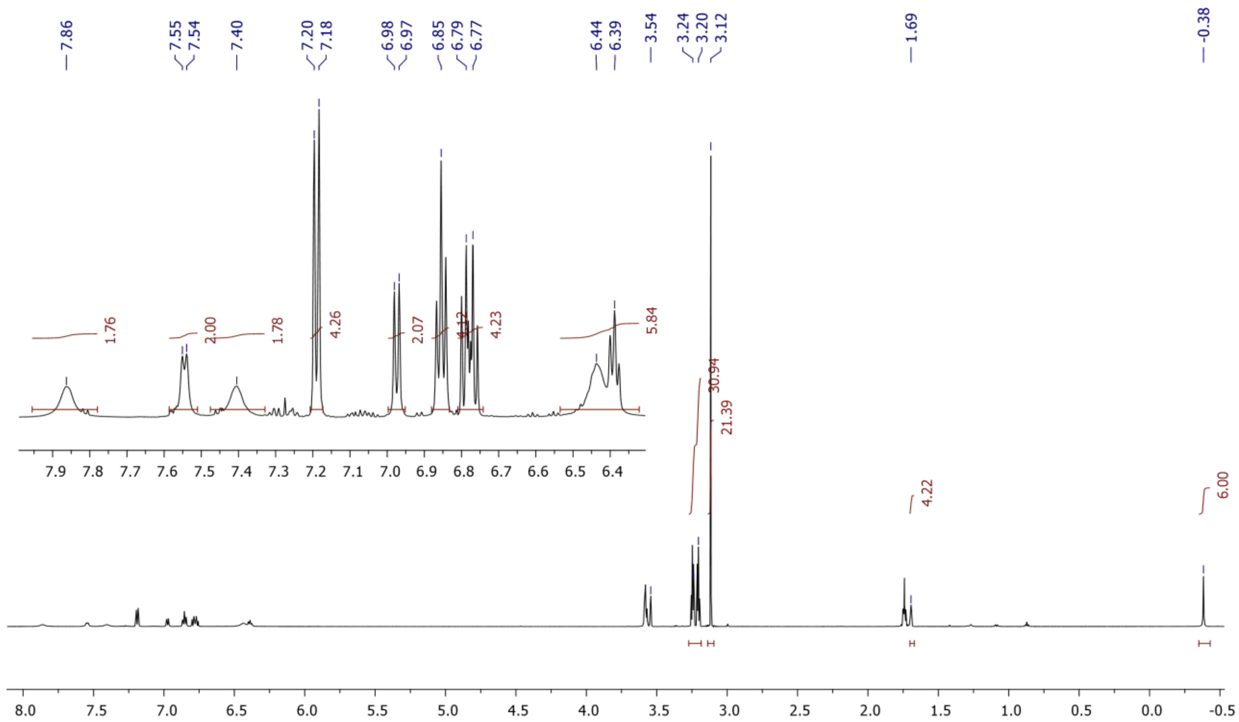

Figure S1 ^{1}H NMR spectrum (THF-d_8, 20 °C, 400 MHz) of compound **3**.

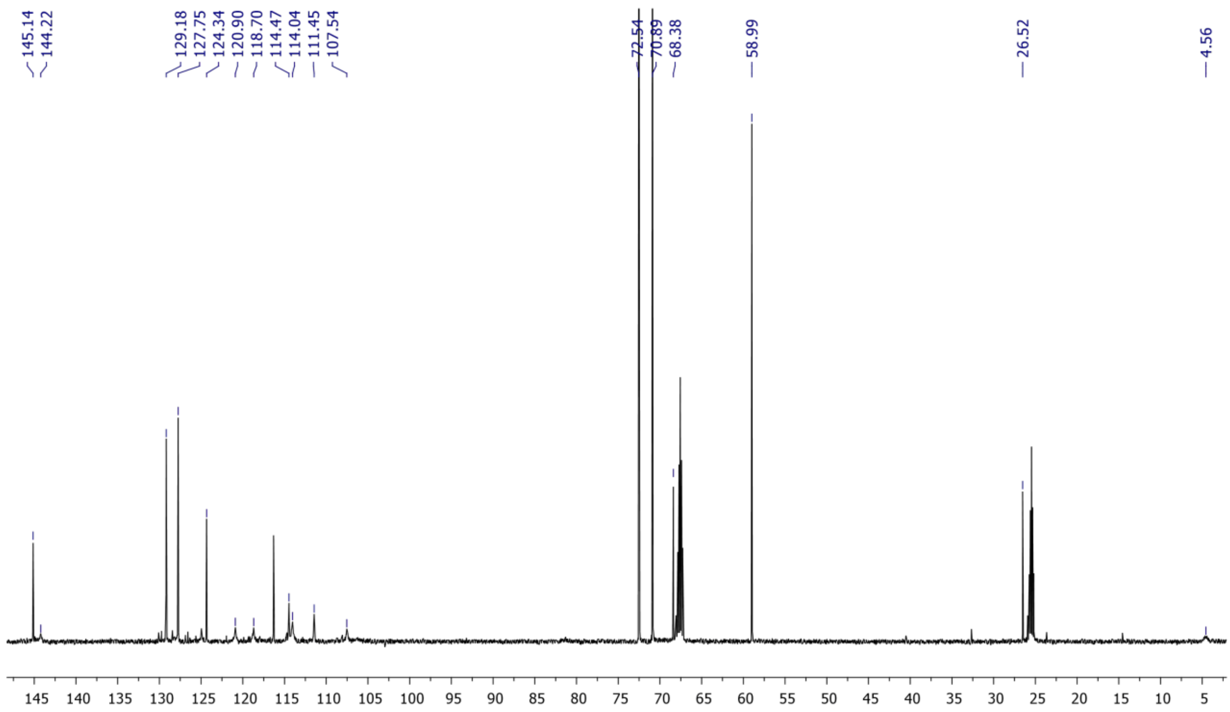

Figure S2 ^{13}C NMR spectrum (THF-d_8, 20 °C, 101 MHz) of compound **3**

X-ray diffraction studies. X-ray diffraction data were collected on a SMART APEX II area-detector diffractometer (graphite monochromator, ω-scan technique) using MoKα radiation. The intensity data were integrated by the SAINT program[1] and were corrected for absorption and decay using SADABS.[1] The structure was solved by direct method using SHELXS[2] and refined by full-matrix least squares on F^2 using SHELXL.[3] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in geometrically calculated positions (C–H distance 0.950 Å for aromatic, 0.980 Å for methyl and 0.990 Å for methylene hydrogen atoms) and refined using a riding model with relative isotropic displacement parameters $U_{iso}(H) = 1.5\ U_{eq}(C)$ for methyl hydrogen atoms and 1.2 $U_{eq}(C)$ otherwise. A rotating group model was applied for methyl groups. The structure of $[Li(diglyme)_2]^+[Li(THF)_2(diglyme)]^+[Me_2Si(PhNC_{15}H_8)]^{2-}\cdot(hexane)_{0.5}\cdot(thf)_{0.5}$ contained poorly resolved non-coordinating THF and hexane solvent molecules in the crystal channels. Since these molecules could not be reasonably resolved by conventional methods, they were removed by the SQUEEZE method[4] implemented in the PLATON program.[5,6] The $[Li(THF)_2(diglyme)]^+$ cation had disordered coordinated solvent molecules with the disorder ratios of 0.607(3) : 0.393(3) for diglyme, 0.698(4) : 0.302(4) and 0.783(7) : 0.217(7) for the two THF molecules. Relatively high peaks in the residual electron density map indicated the presence of some minor disorder within this cation. However, insufficient residual electron density did not allow to reasonably model the disorder. SHELXL[3] was used for molecular graphics. Crystal data, structure solution and refinement are provided in Table S1.

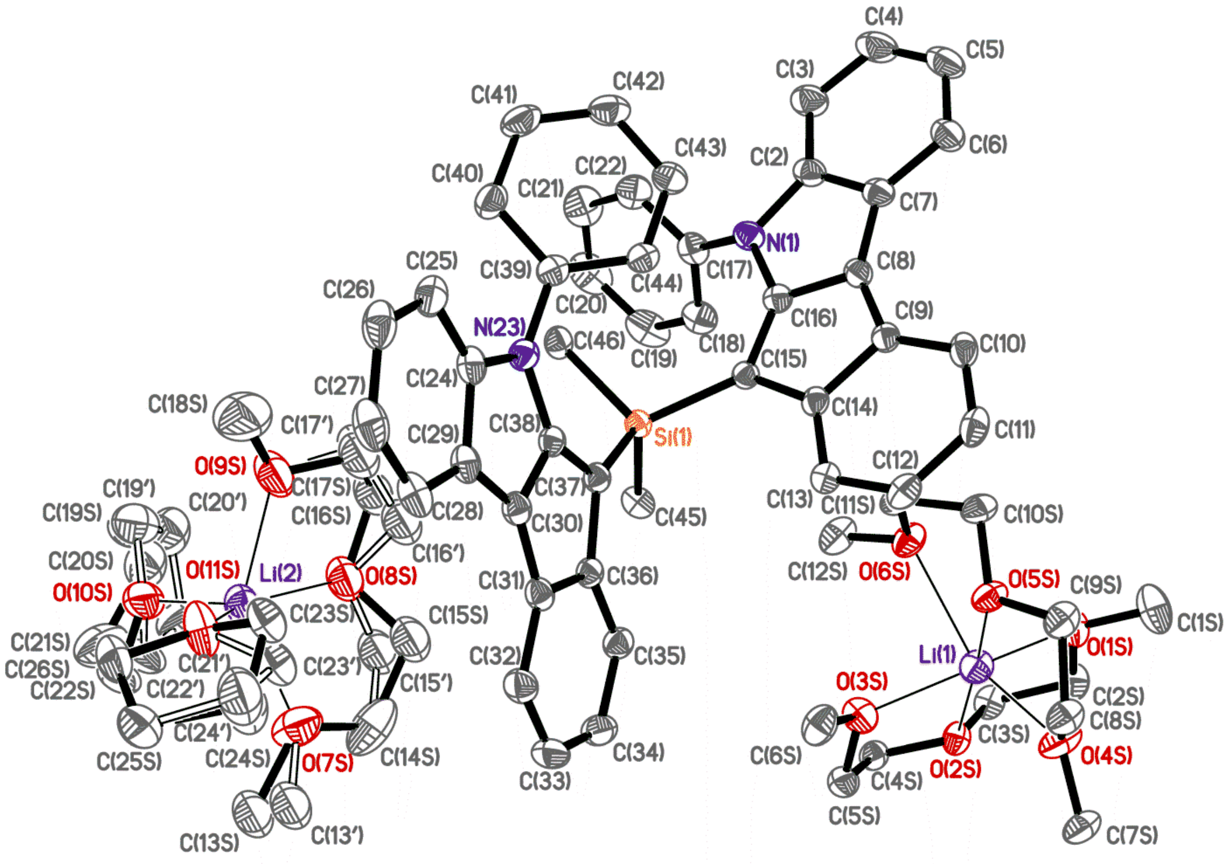

Figure S3 The structure of the cations and anion in complex **3** $[Li(diglyme)_2]^+[Li(THF)_2(diglyme)]^+[Me_2Si(PhNC_{15}H_8)]^{2-}\cdot(hexane)_{0.5}\cdot(thf)_{0.5}$. Displacement ellipsoids are drawn at the 50% probability level. All H atoms are omitted. The minor components of THF disorder are shown with open solid lines.

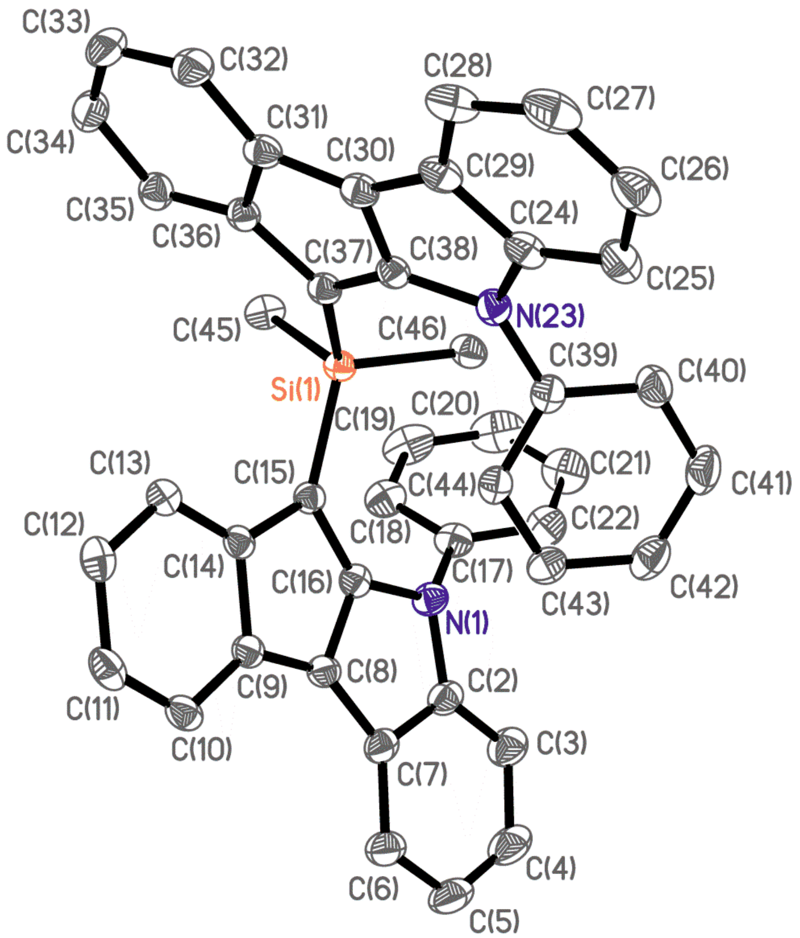

Figure S4 The structure of dianion $[Me_2Si(PhNC_{15}H_8)]^{2-}$. Displacement ellipsoids are drawn at the 50% probability level. All H atoms are omitted.

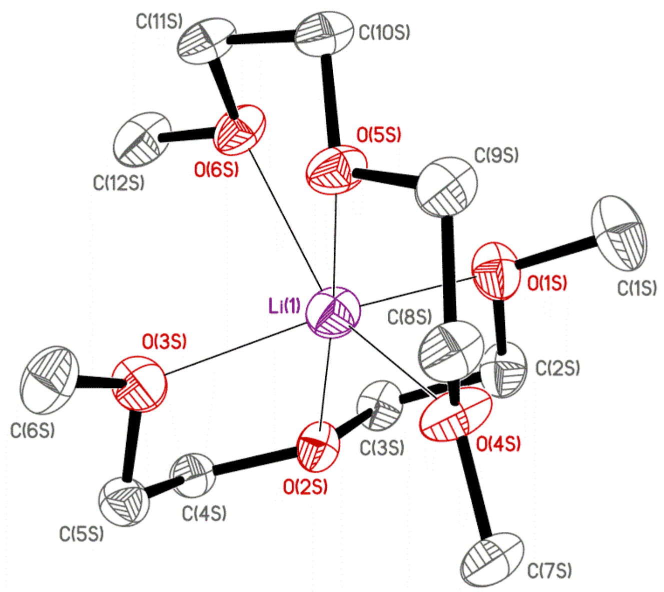

Figure S5 The structure of cation $[Li(diglyme)_2]^+$. Displacement ellipsoids are drawn at the 50% probability level. All H atoms are omitted.

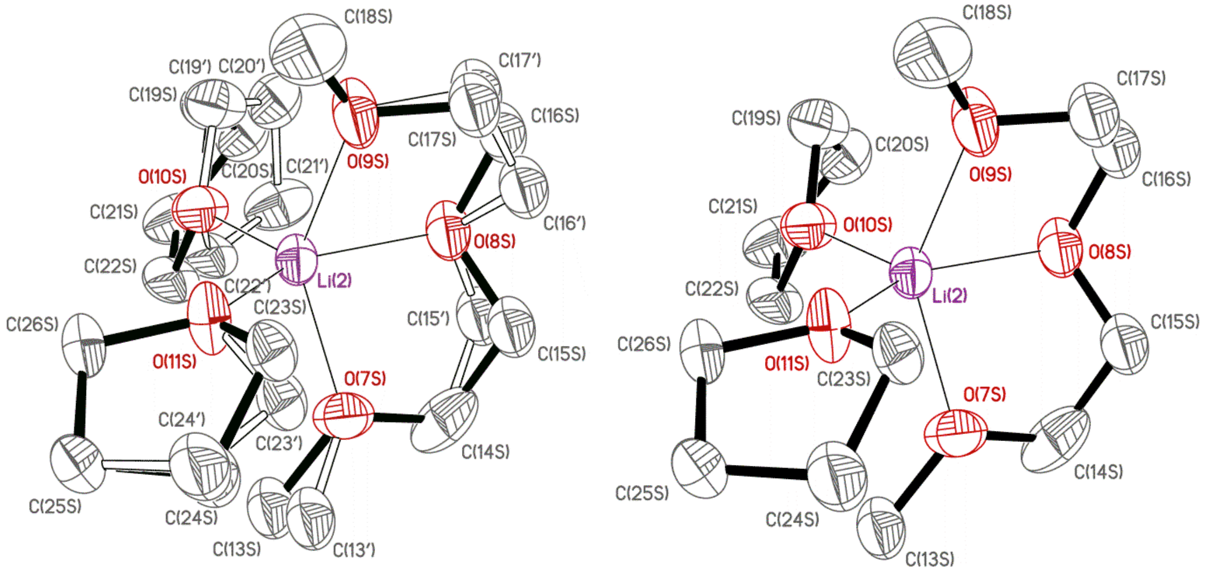

Figure S6 The structure of cation $[Li(THF)_2(diglyme)]^+$. Displacement ellipsoids are drawn at the 50% probability level. All H atoms are omitted. The minor components of THF disorder are shown with open solid lines on the left image.

Table S1 Crystal data, data collection, structure solution and refinement parameters for compound **3**.

Empirical formula	$C_{75}H_{101}Li_2N_2O_{11.5}Si$
Formula weight	1256.54
Colour, habit	yellow-greenish block
Crystal size	0.38 × 0.34 × 0.23 mm
Temperature, K	120(2)
Radiation wavelength, Å	0.71073 (MoKα, graphite monochromatized)
Crystal system, space group	Monoclinic, *C*2/*c*
Unit cell dimensions	
a, Å	47.412(3)
b, Å	11.6851(7)
c, Å	28.2569(16)
β, °	110.2852(12)
Volume, $Å^3$	14683.8(15)
Z	8
Calculated density, $g \cdot cm^{-3}$	1.137
Absorption coefficient, mm^{-1}	0.090
F(000)	5416
Theta range, °	0.916 to 27.499.
Index ranges	-61<=h<=61, -15<=k<=15, -36<=l<=36
Reflections collected	78499
Independent reflections	16866 [R_{int} = 0.0367]

Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents (SADABS)
Max. and min. transmission	0.7460 and 0.6994
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	16866 / 23 / 802
Goodness-of-fit on F^2	1.020
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0561, wR_2 = 0.1448
R indices (all data)	R_1 = 0.0730, wR_2 = 0.1573
Largest diff. peak and hole, e·Å^{-3}	1.334 and -0.619

Table S2 Bond lengths, Å.

Si(1)–C(15)	1.8556(17)	C(29)–C(30)	1.431(3)	C(10S)–C(11S)	1.497(3)
Si(1)–C(37)	1.8658(17)	C(30)–C(38)	1.412(2)	Li(2)–O(10S)	1.936(4)
Si(1)–C(45)	1.8962(19)	C(30)–C(31)	1.418(2)	Li(2)–O(11S)	1.960(4)
Si(1)–C(46)	1.8881(18)	C(31)–C(32)	1.404(2)	Li(2)–O(7S)	2.086(4)
N(1)–C(2)	1.413(2)	C(31)–C(36)	1.457(2)	Li(2)–O(9S)	2.094(4)
N(1)–C(16)	1.413(2)	C(32)–C(33)	1.386(3)	Li(2)–O(8S)	2.133(4)
N(1)–C(17)	1.421(2)	C(33)–C(34)	1.399(3)	O(7S)–C(13')	1.331(7)
C(2)–C(3)	1.390(3)	C(34)–C(35)	1.391(3)	O(7S)–C(14S)	1.388(3)
C(2)–C(7)	1.423(3)	C(35)–C(36)	1.405(2)	O(7S)–C(13S)	1.488(5)
C(3)–C(4)	1.394(3)	C(36)–C(37)	1.458(2)	O(8S)–C(15')	1.400(7)
C(4)–C(5)	1.389(3)	C(37)–C(38)	1.422(2)	O(8S)–C(16')	1.421(7)
C(5)–C(6)	1.389(3)	C(39)–C(44)	1.391(2)	O(8S)–C(16S)	1.436(2)
C(6)–C(7)	1.407(3)	C(39)–C(40)	1.397(2)	O(8S)–C(15S)	1.440(2)
C(7)–C(8)	1.430(2)	C(40)–C(41)	1.389(3)	O(9S)–C(17S)	1.373(5)
C(8)–C(16)	1.411(2)	C(41)–C(42)	1.382(3)	O(9S)–C(18S)	1.413(3)
C(8)–C(9)	1.421(2)	C(42)–C(43)	1.385(3)	O(9S)–C(17')	1.437(3)
C(9)–C(10)	1.399(2)	C(43)–C(44)	1.389(2)	O(10S)–C(19S)	1.437(2)
C(9)–C(14)	1.457(2)	Li(1)–O(5S)	1.966(3)	O(10S)–C(19')	1.438(3)
C(10)–C(11)	1.385(3)	Li(1)–O(2S)	2.014(3)	O(10S)–C(22S)	1.439(2)
C(11)–C(12)	1.408(3)	Li(1)–O(4S)	2.055(3)	O(10S)–C(22')	1.442(3)
C(12)–C(13)	1.388(2)	Li(1)–O(3S)	2.108(4)	O(11S)–C(23S)	1.436(2)
C(13)–C(14)	1.403(2)	Li(1)–O(1S)	2.179(4)	O(11S)–C(23')	1.441(3)
C(14)–C(15)	1.456(2)	Li(1)–O(6S)	2.444(4)	O(11S)–C(26S)	1.442(2)
C(15)–C(16)	1.416(2)	O(1S)–C(1S)	1.424(2)	C(14S)–C(15S)	1.489(3)
C(17)–C(18)	1.386(3)	O(1S)–C(2S)	1.430(2)	C(14S)–C(15')	1.493(3)
C(17)–C(22)	1.394(3)	O(2S)–C(4S)	1.425(2)	C(16S)–C(17S)	1.497(3)
C(18)–C(19)	1.389(3)	O(2S)–C(3S)	1.430(2)	C(16')–C(17')	1.465(13)

C(19)–C(20)	1.392(4)	O(3S)–C(6S)	1.419(2)	C(19S)–C(20S)	1.497(3)
C(20)–C(21)	1.377(4)	O(3S)–C(5S)	1.428(2)	C(20S)–C(21S)	1.498(3)
C(21)–C(22)	1.391(3)	O(4S)–C(7S)	1.418(2)	C(21S)–C(22S)	1.496(3)
N(23)–C(24)	1.408(2)	O(4S)–C(8S)	1.423(2)	C(19')–C(20')	1.497(3)
N(23)–C(38)	1.414(2)	O(5S)–C(9S)	1.425(2)	C(20')–C(21')	1.497(3)
N(23)–C(39)	1.415(2)	O(5S)–C(10S)	1.426(2)	C(21')–C(22')	1.497(3)
C(24)–C(25)	1.391(3)	O(6S)–C(12S)	1.420(2)	C(23S)–C(24S)	1.496(3)
C(24)–C(29)	1.429(3)	O(6S)–C(11S)	1.431(2)	C(24S)–C(25S)	1.505(3)
C(25)–C(26)	1.400(3)	C(2S)–C(3S)	1.499(3)	C(23')–C(24')	1.496(3)
C(26)–C(27)	1.389(3)	C(4S)–C(5S)	1.499(3)	C(24')–C(25S)	1.498(3)
C(27)–C(28)	1.390(3)	C(8S)–C(9S)	1.499(3)	C(25S)–C(26S)	1.527(3)
C(28)–C(29)	1.405(3)				

Table S3 Bond angles, °.

C(15)–Si(1)–C(37)	114.52(7)	O(4S)–Li(1)–O(1S)	90.82(14)
C(15)–Si(1)–C(46)	110.22(8)	O(3S)–Li(1)–O(1S)	157.65(17)
C(37)–Si(1)–C(46)	107.97(8)	O(5S)–Li(1)–O(6S)	76.91(12)
C(15)–Si(1)–C(45)	109.82(8)	O(2S)–Li(1)–O(6S)	103.84(14)
C(37)–Si(1)–C(45)	109.47(8)	O(4S)–Li(1)–O(6S)	154.99(16)
C(46)–Si(1)–C(45)	104.34(8)	O(3S)–Li(1)–O(6S)	89.20(13)
C(2)–N(1)–C(16)	107.67(14)	O(1S)–Li(1)–O(6S)	85.65(13)
C(2)–N(1)–C(17)	122.18(14)	C(1S)–O(1S)–C(2S)	111.55(16)
C(16)–N(1)–C(17)	125.26(15)	C(1S)–O(1S)–Li(1)	123.06(15)
C(3)–C(2)–N(1)	128.98(18)	C(2S)–O(1S)–Li(1)	107.00(14)
C(3)–C(2)–C(7)	121.97(17)	C(4S)–O(2S)–C(3S)	113.94(13)
N(1)–C(2)–C(7)	109.05(15)	C(4S)–O(2S)–Li(1)	110.35(14)
C(2)–C(3)–C(4)	118.0(2)	C(3S)–O(2S)–Li(1)	109.45(14)
C(5)–C(4)–C(3)	121.19(19)	C(6S)–O(3S)–C(5S)	112.55(15)
C(4)–C(5)–C(6)	120.92(19)	C(6S)–O(3S)–Li(1)	129.39(15)
C(5)–C(6)–C(7)	119.7(2)	C(5S)–O(3S)–Li(1)	109.15(14)
C(6)–C(7)–C(2)	118.22(17)	C(7S)–O(4S)–C(8S)	113.68(15)
C(6)–C(7)–C(8)	135.31(18)	C(7S)–O(4S)–Li(1)	128.66(15)
C(2)–C(7)–C(8)	106.48(15)	C(8S)–O(4S)–Li(1)	110.72(14)
C(16)–C(8)–C(9)	106.89(15)	C(9S)–O(5S)–C(10S)	115.28(14)
C(16)–C(8)–C(7)	108.51(15)	C(9S)–O(5S)–Li(1)	114.27(14)
C(9)–C(8)–C(7)	144.38(17)	C(10S)–O(5S)–Li(1)	115.36(15)
C(10)–C(9)–C(8)	133.58(16)	C(12S)–O(6S)–C(11S)	110.81(14)
C(10)–C(9)–C(14)	120.41(16)	C(12S)–O(6S)–Li(1)	125.21(14)
C(8)–C(9)–C(14)	105.99(14)	C(11S)–O(6S)–Li(1)	100.03(12)
C(11)–C(10)–C(9)	119.84(17)	O(1S)–C(2S)–C(3S)	107.57(15)

C(10)–C(11)–C(12)	120.09(16)	O(2S)–C(3S)–C(2S)	106.50(15)
C(13)–C(12)–C(11)	121.43(17)	O(2S)–C(4S)–C(5S)	106.44(14)
C(12)–C(13)–C(14)	120.14(17)	O(3S)–C(5S)–C(4S)	106.37(15)
C(13)–C(14)–C(15)	130.86(16)	O(4S)–C(8S)–C(9S)	106.83(15)
C(13)–C(14)–C(9)	118.08(15)	O(5S)–C(9S)–C(8S)	106.41(15)
C(15)–C(14)–C(9)	111.06(14)	O(5S)–C(10S)–C(11S)	106.60(15)
C(16)–C(15)–C(14)	102.04(14)	O(6S)–C(11S)–C(10S)	108.20(15)
C(16)–C(15)–Si(1)	131.61(13)	O(10S)–Li(2)–O(11S)	110.79(18)
C(14)–C(15)–Si(1)	125.20(12)	O(10S)–Li(2)–O(7S)	107.04(18)
C(8)–C(16)–N(1)	108.29(15)	O(11S)–Li(2)–O(7S)	92.57(17)
C(8)–C(16)–C(15)	114.00(15)	O(10S)–Li(2)–O(9S)	106.69(18)
N(1)–C(16)–C(15)	137.43(16)	O(11S)–Li(2)–O(9S)	92.05(16)
C(18)–C(17)–C(22)	119.96(18)	O(7S)–Li(2)–O(9S)	141.69(19)
C(18)–C(17)–N(1)	119.94(17)	O(10S)–Li(2)–O(8S)	101.74(17)
C(22)–C(17)–N(1)	120.10(18)	O(11S)–Li(2)–O(8S)	147.5(2)
C(17)–C(18)–C(19)	120.0(2)	O(7S)–Li(2)–O(8S)	78.16(14)
C(18)–C(19)–C(20)	120.1(2)	O(9S)–Li(2)–O(8S)	77.69(13)
C(21)–C(20)–C(19)	119.8(2)	C(13')–O(7S)–C(14S)	107.9(3)
C(20)–C(21)–C(22)	120.6(2)	C(14S)–O(7S)–C(13S)	116.5(2)
C(21)–C(22)–C(17)	119.5(2)	C(13')–O(7S)–Li(2)	134.9(3)
C(24)–N(23)–C(38)	108.23(14)	C(14S)–O(7S)–Li(2)	114.96(18)
C(24)–N(23)–C(39)	123.59(15)	C(13S)–O(7S)–Li(2)	126.4(2)
C(38)–N(23)–C(39)	127.23(14)	C(15')–O(8S)–C(16')	118.5(4)
C(25)–C(24)–N(23)	129.62(17)	C(16S)–O(8S)–C(15S)	113.6(3)
C(25)–C(24)–C(29)	121.43(17)	C(15')–O(8S)–Li(2)	112.7(2)
N(23)–C(24)–C(29)	108.87(15)	C(16')–O(8S)–Li(2)	105.2(3)
C(24)–C(25)–C(26)	118.49(19)	C(16S)–O(8S)–Li(2)	111.8(2)
C(27)–C(26)–C(25)	120.73(18)	C(15S)–O(8S)–Li(2)	105.1(2)
C(26)–C(27)–C(28)	121.22(19)	C(17S)–O(9S)–C(18S)	112.3(3)
C(27)–C(28)–C(29)	119.60(19)	C(18S)–O(9S)–C(17')	113.2(5)
C(28)–C(29)–C(24)	118.51(17)	C(17S)–O(9S)–Li(2)	111.6(3)
C(28)–C(29)–C(30)	135.25(18)	C(18S)–O(9S)–Li(2)	128.7(2)
C(24)–C(29)–C(30)	106.22(15)	C(17')–O(9S)–Li(2)	114.2(5)
C(38)–C(30)–C(31)	107.24(15)	C(19S)–O(10S)–C(22S)	111.3(6)
C(38)–C(30)–C(29)	108.85(15)	C(19')–O(10S)–C(22')	96.6(10)
C(31)–C(30)–C(29)	143.80(16)	C(19S)–O(10S)–Li(2)	120.1(9)
C(32)–C(31)–C(30)	133.26(17)	C(19')–O(10S)–Li(2)	116(2)
C(32)–C(31)–C(36)	120.57(16)	C(22S)–O(10S)–Li(2)	118.9(2)
C(30)–C(31)–C(36)	106.15(15)	C(22')–O(10S)–Li(2)	118.7(5)
C(33)–C(32)–C(31)	120.00(17)	C(23S)–O(11S)–C(26S)	105.48(18)

C(32)–C(33)–C(34)	120.09(17)	C(23')–O(11S)–C(26S)	108.1(5)
C(35)–C(34)–C(33)	121.13(18)	C(23S)–O(11S)–Li(2)	119.41(18)
C(34)–C(35)–C(36)	121.01(17)	C(23')–O(11S)–Li(2)	111.1(5)
C(35)–C(36)–C(31)	117.17(15)	C(26S)–O(11S)–Li(2)	135.10(16)
C(35)–C(36)–C(37)	132.00(16)	O(7S)–C(14S)–C(15S)	109.5(2)
C(31)–C(36)–C(37)	110.82(15)	O(7S)–C(14S)–C(15')	113.0(3)
C(38)–C(37)–C(36)	102.28(14)	O(8S)–C(15S)–C(14S)	109.2(2)
C(38)–C(37)–Si(1)	130.52(13)	O(8S)–C(16S)–C(17S)	109.2(4)
C(36)–C(37)–Si(1)	126.67(13)	O(9S)–C(17S)–C(16S)	108.7(4)
C(30)–C(38)–N(23)	107.81(15)	O(8S)–C(15')–C(14S)	111.2(4)
C(30)–C(38)–C(37)	113.50(15)	O(8S)–C(16')–C(17')	112.5(6)
N(23)–C(38)–C(37)	138.50(15)	O(9S)–C(17')–C(16')	110.1(7)
C(44)–C(39)–C(40)	119.89(16)	O(10S)–C(19S)–C(20S)	100.9(3)
C(44)–C(39)–N(23)	119.91(15)	C(19S)–C(20S)–C(21S)	101.9(7)
C(40)–C(39)–N(23)	120.21(16)	C(22S)–C(21S)–C(20S)	104.2(3)
C(41)–C(40)–C(39)	119.31(18)	O(10S)–C(22S)–C(21S)	103.8(2)
C(42)–C(41)–C(40)	120.72(18)	O(10S)–C(19')–C(20')	113.5(9)
C(41)–C(42)–C(43)	119.93(18)	C(21')–C(20')–C(19')	105.1(9)
C(42)–C(43)–C(44)	120.03(18)	C(20')–C(21')–C(22')	99.7(8)
C(43)–C(44)–C(39)	120.09(16)	O(10S)–C(22')–C(21')	115.0(6)
O(5S)–Li(1)–O(2S)	175.4(2)	O(11S)–C(23S)–C(24S)	103.1(3)
O(5S)–Li(1)–O(4S)	80.06(13)	C(23S)–C(24S)–C(25S)	106.2(3)
O(2S)–Li(1)–O(4S)	99.90(15)	O(11S)–C(23')–C(24')	109.1(9)
O(5S)–Li(1)–O(3S)	95.46(15)	C(23')–C(24')–C(25S)	100.7(7)
O(2S)–Li(1)–O(3S)	80.07(13)	C(24')–C(25S)–C(26S)	105.4(7)
O(4S)–Li(1)–O(3S)	102.64(16)	C(24S)–C(25S)–C(26S)	103.5(2)
O(5S)–Li(1)–O(1S)	104.48(15)	O(11S)–C(26S)–C(25S)	105.48(17)
O(2S)–Li(1)–O(1S)	80.09(12)		

3. Reaction of compound 3 with $ZrCl_4$

The suspension of dilithium salt **3** (0.42 g, 0.37 mmol) was suspended in Et_2O (20 ml). This suspension was cooled to –60 °C, and $ZrCl_4$ (86 mg, 0.37 mmol) was added. The mixture was allowed to warm to 0 °C and stirred for 24 h. The precipitate formed was washed by Et_2O (4×10 ml) and dried. Compound **2** was isolated as yellow crystalline powder, yield 245 mg (85%); after recrystallization from CH_2Cl_2 the yield was 185 mg (64%).

^{1}H NMR (CD_2Cl_2, 20 °C, 400 MHz) δ: 7.83 (d, 2H), 7.79 (d, 2H), 7.58 (br. m, 6H), 7.46 (d, 2H), 7.40 (dd, 2H), 7.22 (m, 4H), 7.03 (m, 4H), 0.16 (s, 6H). ^{13}C NMR (CD_2Cl_2, 20 °C, 101 MHz) δ: 147.22, 146.40, 139.79, 130.79, 129.63, 128.81, 127.70, 126.62, 126.60, 126.28, 124.84, 124.04, 124.02, 123.20, 122.89, 121.29, 120.77, 116.19, 110.50, 56.25, 2.22.

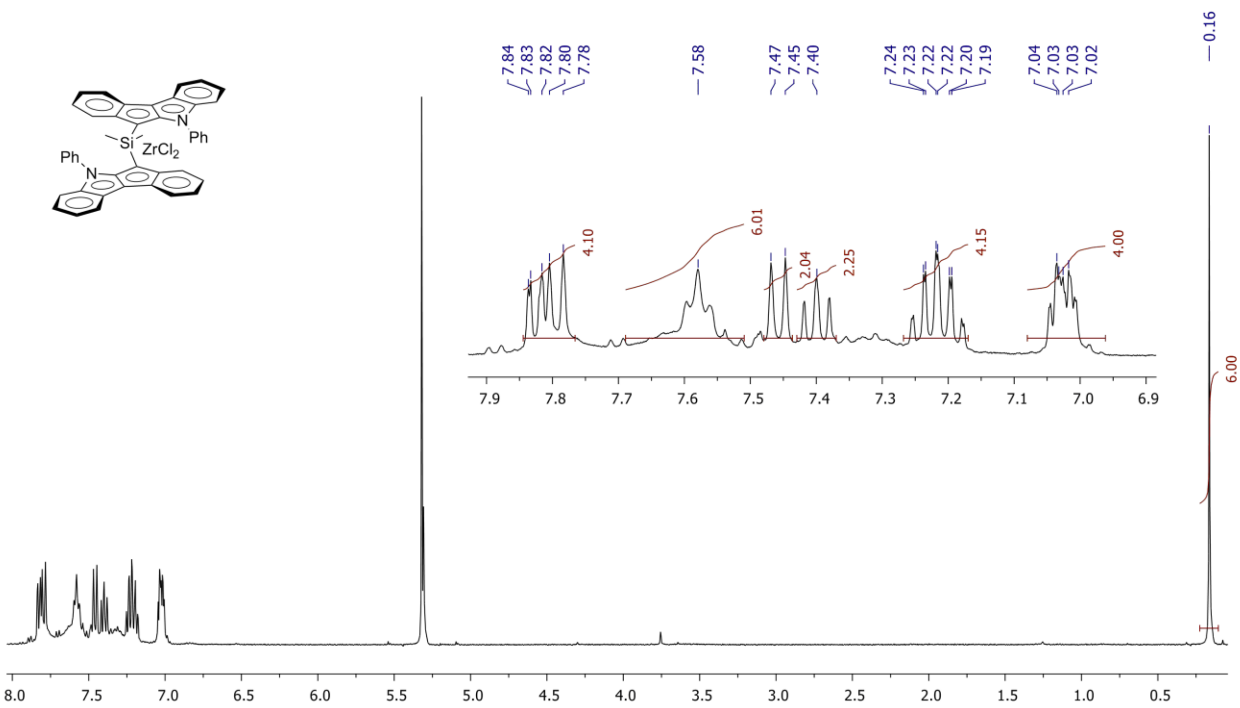

Figure S7 ^{1}H NMR spectrum (CD_2Cl_2, 20 °C, 400 MHz) of compound **2**.

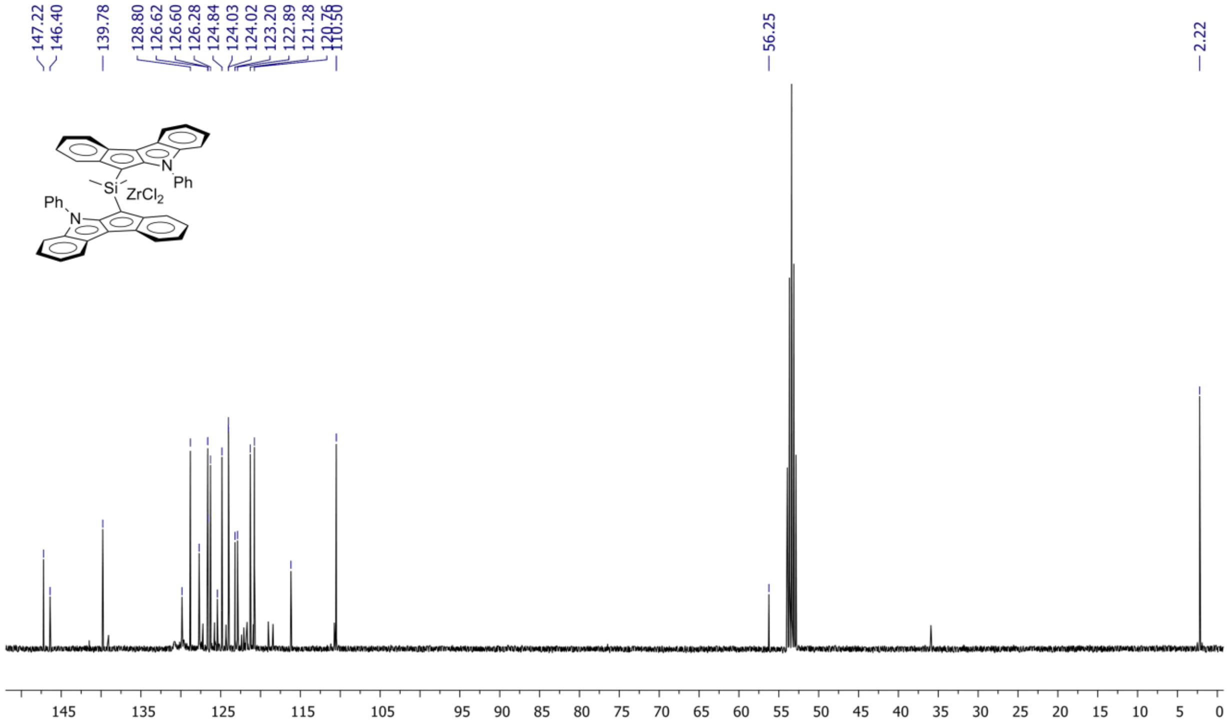

Figure S8 ^{13}C NMR spectrum (CD_2Cl_2, 20 °C, 101 MHz) of compound **2**.

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