Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFORMATION

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I. Synthesis and characterization

I.1 General procedures

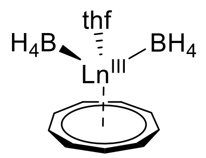
All air- and moisture-sensitive manipulations were performed under a dry N_2 or Ar atmosphere using standard Schlenk techniques or in an argon-filled MBraun glovebox. Et_2O, *n*-pentane, and toluene were dried using an MBraun solvent purification system (SPS-800) and degassed. THF, benzene and *n*-hexane were distilled under nitrogen from potassium benzophenone ketyl. C_6D_6, and THF-d_8 were dried over Na-K alloy and degassed by freeze-pump-thaw cycles. [K(Cnt)] was prepared according to a modified procedure by Katz *et al.*[1] $[Ln^{III}(BH_4)_3(thf)_3]$ was synthesized according to literature procedure.[2] All other chemicals were obtained from commercial sources and used without further purification.

Elemental analyses were carried out with an Elementar vario MICRO cube.

NMR spectra were recorded on Bruker spectrometers (Avance Neo 300 MHz, Avance Neo 400 MHz or Avance III 400 MHz). Chemical shifts are referenced internally using signals of the residual protio solvent (^{1}H) or the solvent ($^{13}C\{^{1}H\}$) and are reported relative to tetramethylsilane (^{1}H, $^{13}C\{^{1}H\}$), or $BF_3{\cdot}Et_2O$(^{11}B). All NMR spectra were measured at 298 K, unless otherwise specified. The multiplicity of the signals is indicated as s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet and br = broad. Assignments were determined based on unambiguous chemical shifts and coupling patterns

Raman spectra were obtained on a Bruker MultiRam spectrometer in flame sealed glass tubes. In terms of their intensity, the signals were classified into different categories (vs = very strong, s = strong, m = medium, w = weak, and sh = shoulder).

I.2 Synthesis of [Ln^{III}(η^9-Cnt)(η^3-BH$_4$)$_2$(thf)] (Ln = La (1), Ce (2))[3]



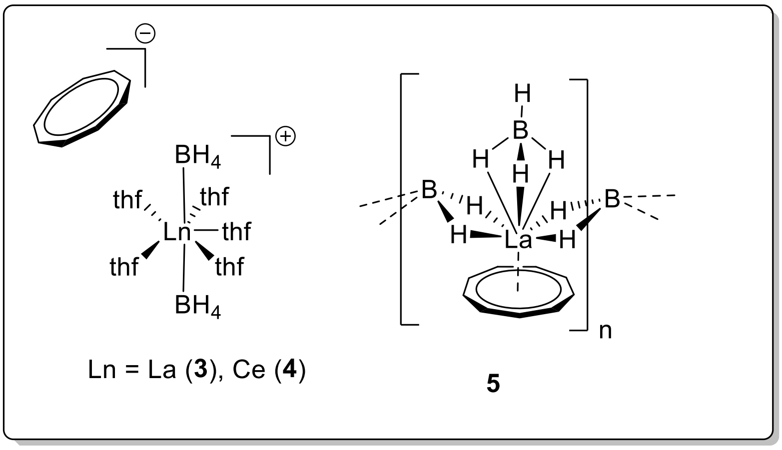
Ln = La (**1**), Ce (**2**)

To a mixture of 40 mg of [K(Cnt)] (0.26 mmol, 1.00 eq) and the respective borohydide [Ln^{III}(BH$_4$)$_3$(thf)$_3$] (La: 104 mg, Ce: 104 mg, 0.26 mmol, 1.00 eq), about 10 mL of toluene is condensed at -78 °C. The obtained suspension is stirred at 60 °C for twelve hours, during which a slow orange coloration of the reaction mixture and the formation of a colorless precipitate is observed. The reaction mixture is then filtered through a glass frit and the remaining residue is extracted with 20 mL of toluene. The filtrate is concentrated under reduced pressure until the formation of a nearly colorless precipitate occurs. This is dissolved by carefully heating the suspension, avoiding excessive temperature increases to prevent thermal decomposition reactions of the products. If the formation of insoluble decomposition products occurs, these can be removed by filtering the warm suspension through a PTFE filter. Storage of the saturated toluene solution at -30 °C for two days finally yields the target compounds (**1** and **2**) in the form of light-yellow crystalline solids, which are isolated after decantation of the mother liquor and drying under high vacuum. Single crystals suitable for single crystal X-ray diffraction studies can be obtained by slowly evaporating a toluene solution of the products at room temperature.

1: Yield: 65 % (60 mg, 0.17 mmol). Elemental analysis [%] calcd. for [$C_{13}H_{25}B_2LaO$] ([La(Cnt)(BH$_4$)$_2$(thf)], 356.86 g·mol^{-1}): C 43.63, H 7.04, found: C 43.08, H 7.57. It should be noted here that in some cases the resonances in the proton spectra of the diamagnetic compound **1** did not exhibit the expected integral ratio. **^{1}H NMR** (THF-d_8, 400.30 MHz): δ [ppm] = 7.01 (s, 9 H, C*H*-Cnt), 3.60-3.56 (m, 4 H, C*H$_2$*-thf), 1.09-1.06 (m, 4 H, C*H$_2$*-thf), 1.26-0.61 (br q, 8 H, $^1J_{HB}$ = 86 Hz). **^{1}H NMR** (400.30 MHz, C_6D_6): δ [ppm] = 7.43 (s, C*H*-Cnt), 3.48-3.45 (m, C*H$_2$*-thf), 1.09-1.06 (m, C*H$_2$*-thf), 1.49-0.85 (br q, $^1J_{HB}$ = 83 Hz). **^{13}C{^{1}H} NMR** (100.67 MHz, C_6D_6): δ [ppm] = 112.2 (*C*-Cnt), 70.5 (*C*-THF), 25.4 (*C*-THF). **^{11}B NMR** (128.43 MHz, C_6D_6): δ [ppm] = -19.8 (qui, $^1J_{HB}$ = 85 Hz, *B*H$_4$). **Raman**: $\tilde{\nu}$ [cm^{-1}] = 3053 (w), 3012 (w), 2982 (w), 2954 (w), 2937 (w), 2903 (w), 2814 (w), 2453 (w), 2311 (w), 2231 (w), 2125 (w), 1520 (w), 1484 (w), 1461 (w), 1372 (w), 1235 (w), 1168 (w), 1041 (w), 920 (w), 859 (w), 810 (w), 678 (vs), 374 (w), 285 (m), 145 (s).

2: Yield: 71 % (66 mg, 0.18 mmol). Elemental analysis [%] calcd. for [$C_{13}H_{25}B_2CeO$] ([Ce(Cnt)(BH$_4$)$_2$(thf)], 358.07 g·mol^{-1}): C 43.48, H 7.02, found: C 43.55, H 6.73. **^{1}H NMR** (400.30 MHz, C_6D_6): δ [ppm] = 39.44 (br s, 8 H, B*H$_4$*), 5.41 (s, 9 H, C*H*-Cnt), 1.24 (s, 5 H, C*H$_2$*-THF), 0.12 (s, 5 H, C*H$_2$*-THF). **^{13}C{^{1}H} NMR** (100.67 MHz, C_6D_6): δ [ppm] = 113.3 (*C*-Cnt), 61.9 (*C*-THF), 24.2 (*C*-THF). **^{11}B NMR** (128.43 MHz, C_6D_6): δ [ppm] = 35.2 (s, *B*H$_4$). **Raman**: $\tilde{\nu}$ [cm^{-1}] = 3053 (w), 3012 (w), 2990 (w), 2936 (w), 2902 (w), 2452 (w), 2315 (w), 2234 (w), 2127 (w), 1522 (w), 1486 (w), 1460 (w), 1368 (w), 1235 (w), 1175 (w), 1040 (w), 1015 (w), 924 (w), 862 (w), 783 (w), 679 (vs), 373 (w), 282 (m), 262 (m), 140 (s).

I.3 Synthesis of $[\mathrm{Ln}^{\mathrm{III}}(\eta^3\text{-}\mathrm{BH_4})_2(\mathrm{thf})_5][\mathrm{Cnt}]$ (Ln = La (3), Ce (4)) and $[\mathrm{La}^{\mathrm{III}}(\mu\text{-}\eta^2{:}\eta^2\text{-}\mathrm{BH_4})_2(\eta^3\text{-}\mathrm{BH_4})(\eta^9\text{-}\mathrm{Cnt})]_n$ (5)[3]



Ln = La (**3**), Ce (**4**)

5

Single crystals of the THF solvates **3** and **4** can be obtained by recrystallization of compounds **1** or **2** from hot THF. Drying of **3** and **4** under high vacuum returns them to the starting compounds **1** or **2**. Thus no further characterization besides SCXRD is feasible. Single crystals of the polymeric compound **5** can be obtained after drying **1** for 36 hours at 60 °C in high vacuum, extraction of the dried material with toluene, filtration, and slow evaporation of the solvent.

5: Yield: 14 % (20 mg, 0.70 mmol). Elemental analysis [%] calcd. for $[\mathrm{C_9H_{17}B_2La}]$ 285.76 $\mathrm{g{\cdot}mol^{-1}}$): C 37.83, H 6.00, found: C 36.63, H 5.90. It should be noted here that in some cases the resonances in the proton spectra of the diamagnetic compound **5** did not exhibit the expected integral ratio. **^{1}H NMR** (400.30 MHz, $\mathrm{C_6D_6}$): δ [ppm] = 7.44 (s, C*H*-Cnt), 0.96-0.38 (br q, $^1J_{\mathrm{HB}}$ = 81 Hz). **^{13}C{^{1}H} NMR** (100.67 MHz, $\mathrm{C_6D_6}$): δ [ppm] = 113.4 (*C*-Cnt). **^{11}B NMR** (128.43 MHz, $\mathrm{C_6D_6}$): δ [ppm] = -19.1 (qui, $^1J_{\mathrm{HB}}$ = 86 Hz, *B*H$_4$). **Raman**: $\tilde{\nu}$ [cm^{-1}] = 3053 (w), 3012 (w), 2985 (w), 2936 (w), 2903 (w), 2452 (w), 2320 (w), 2229 (w), 2126 (w), 1521 (w), 1234 (w), 1041 (w), 920 (w), 859 (w), 678 (vs), 373 (w), 285 (m), 145 (m).

II. NMR spectra

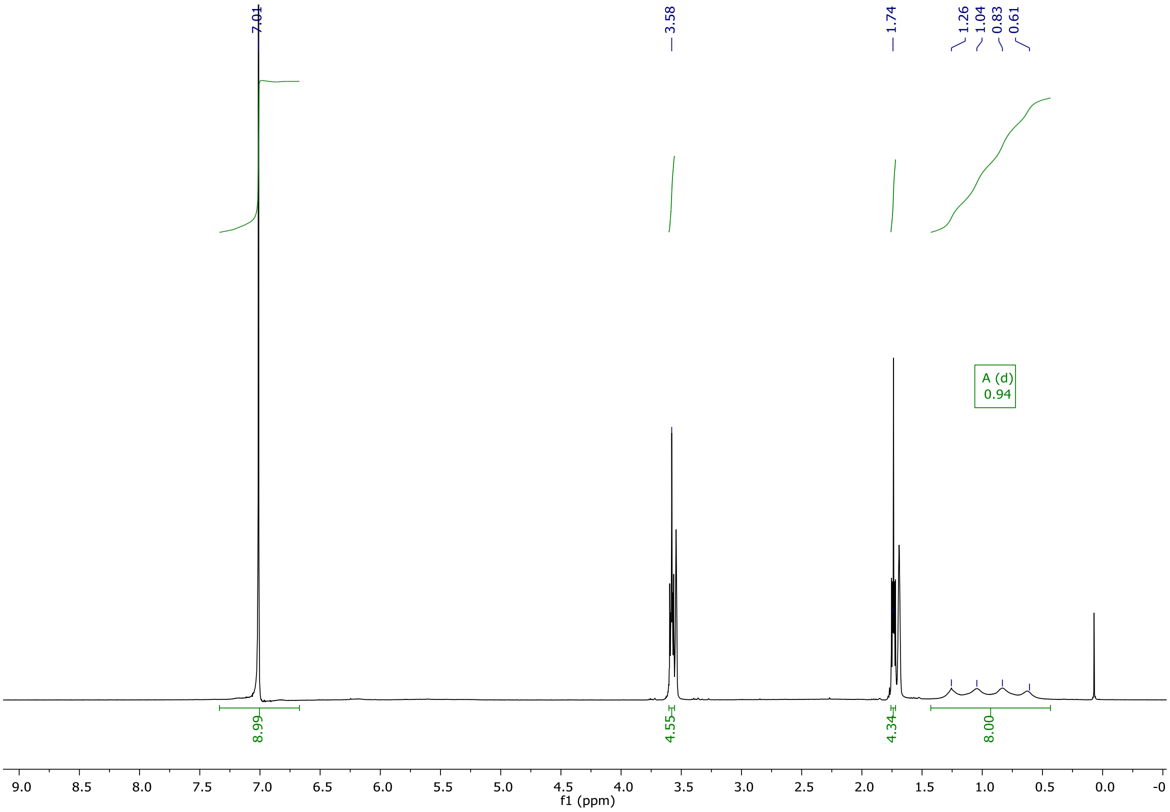


Figure S1. ^{1}H NMR (400 MHz) spectrum of compound **1** in THF-d_8 at room temperature.

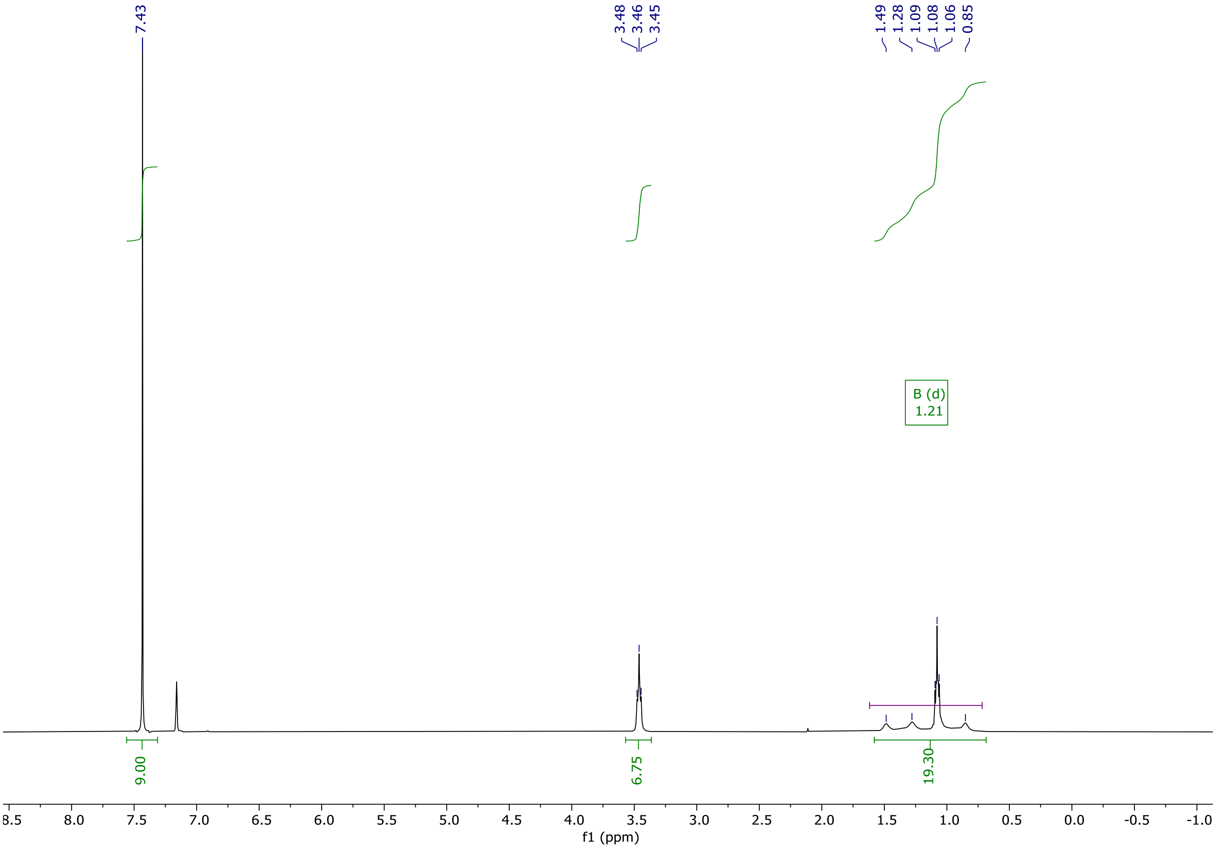


Figure S2. ^{1}H NMR (400 MHz) spectrum of compound **1** in C_6D_6 at room temperature. Note the BH_4 integrals are larger than expected.

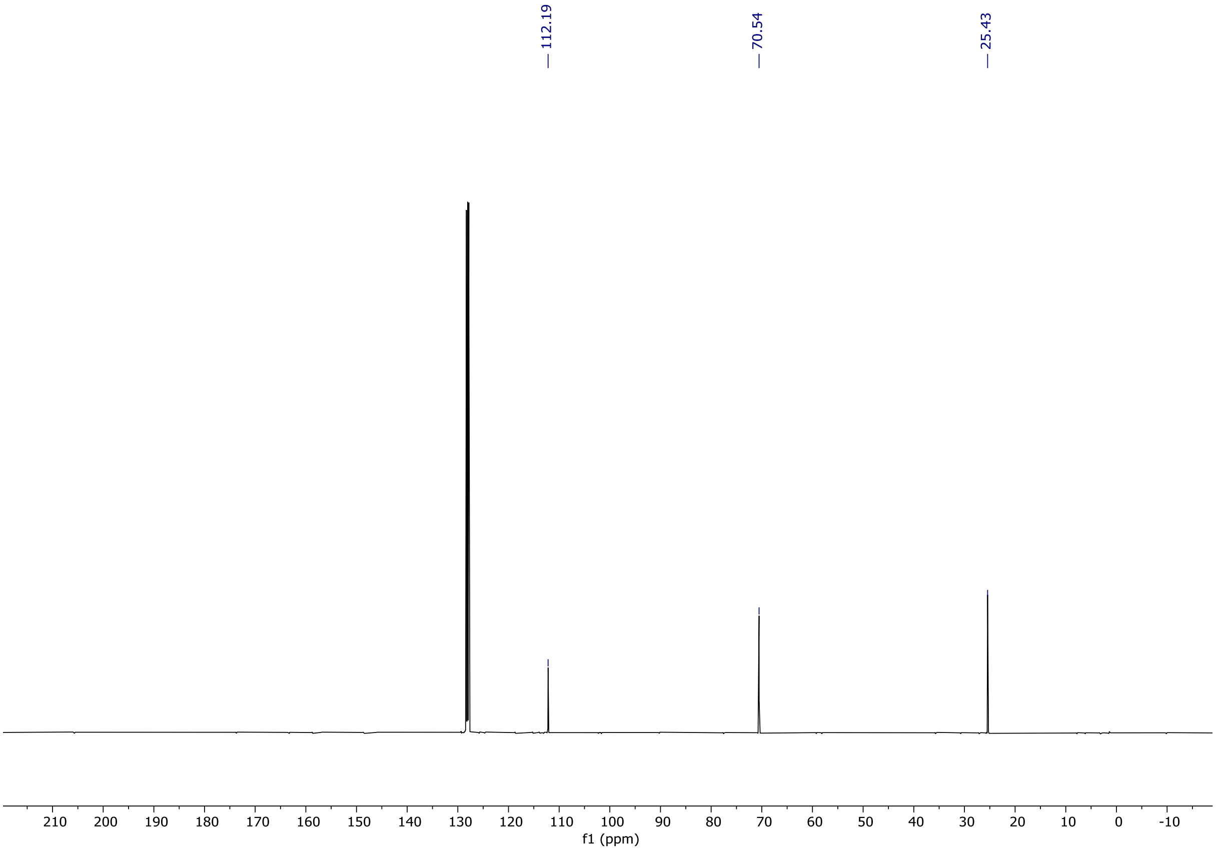


Figure S3. $^{13}C\{^1H\}$ NMR (101 MHz) spectrum of compound **1** in C_6D_6 at room temperature.

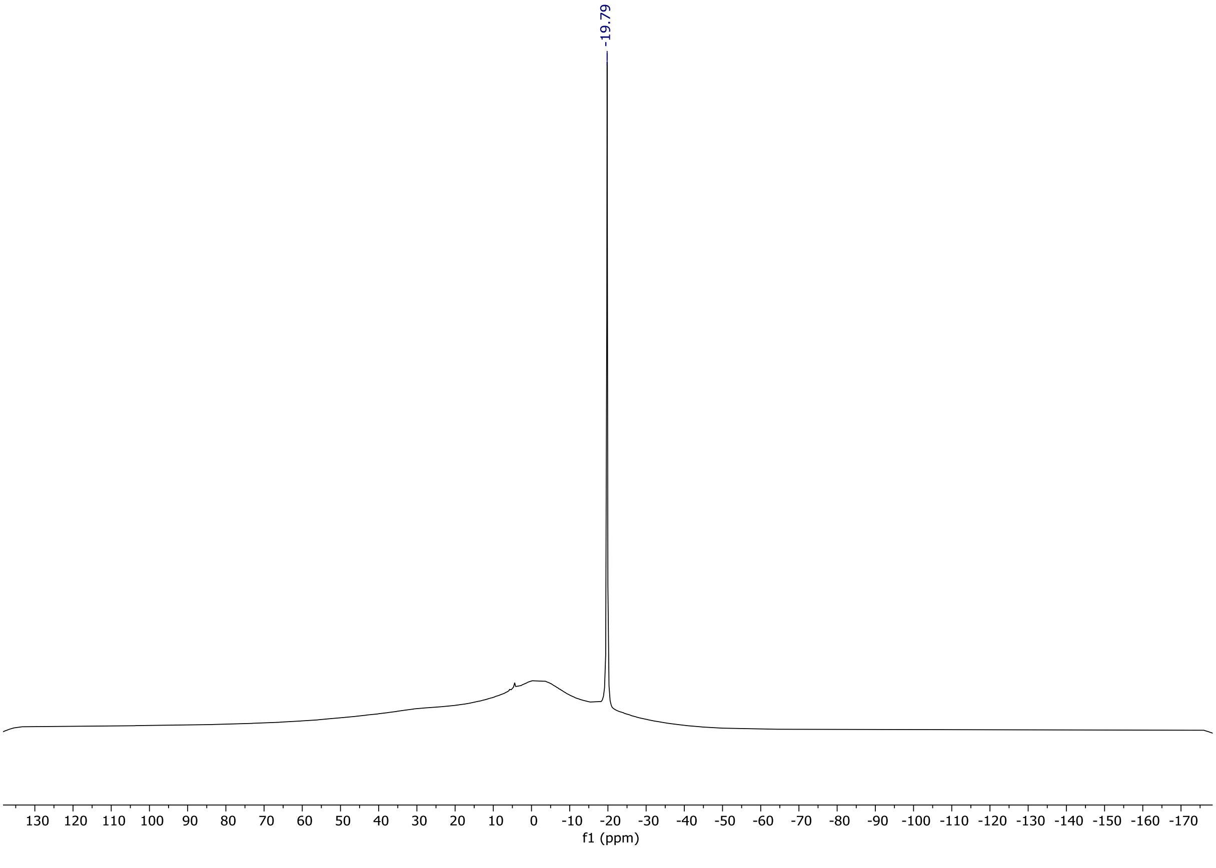


Figure S4. $^{11}B\{^1H\}$ NMR (128 MHz) spectrum of compound **1** in C_6D_6 at room temperature.

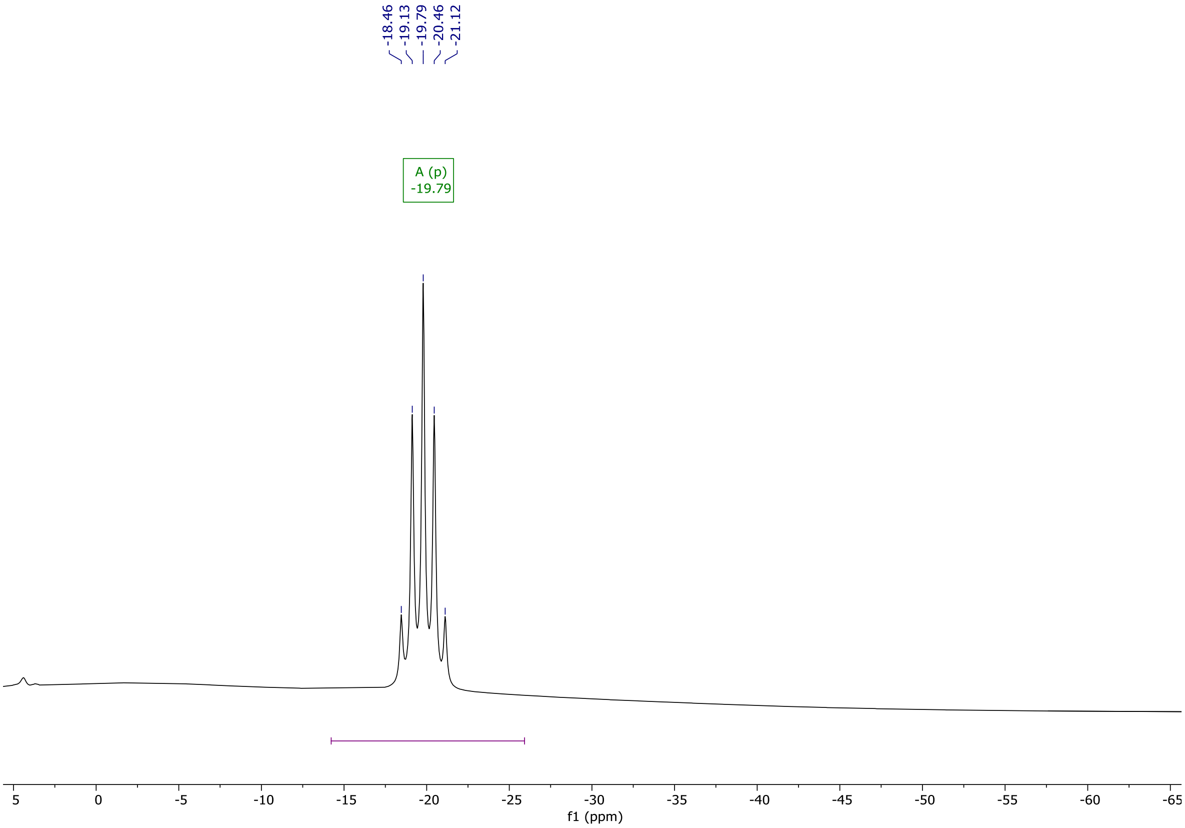


Figure S5. ^{11}B NMR (128 MHz) spectrum of compound **1** in C_6D_6 at room temperature.

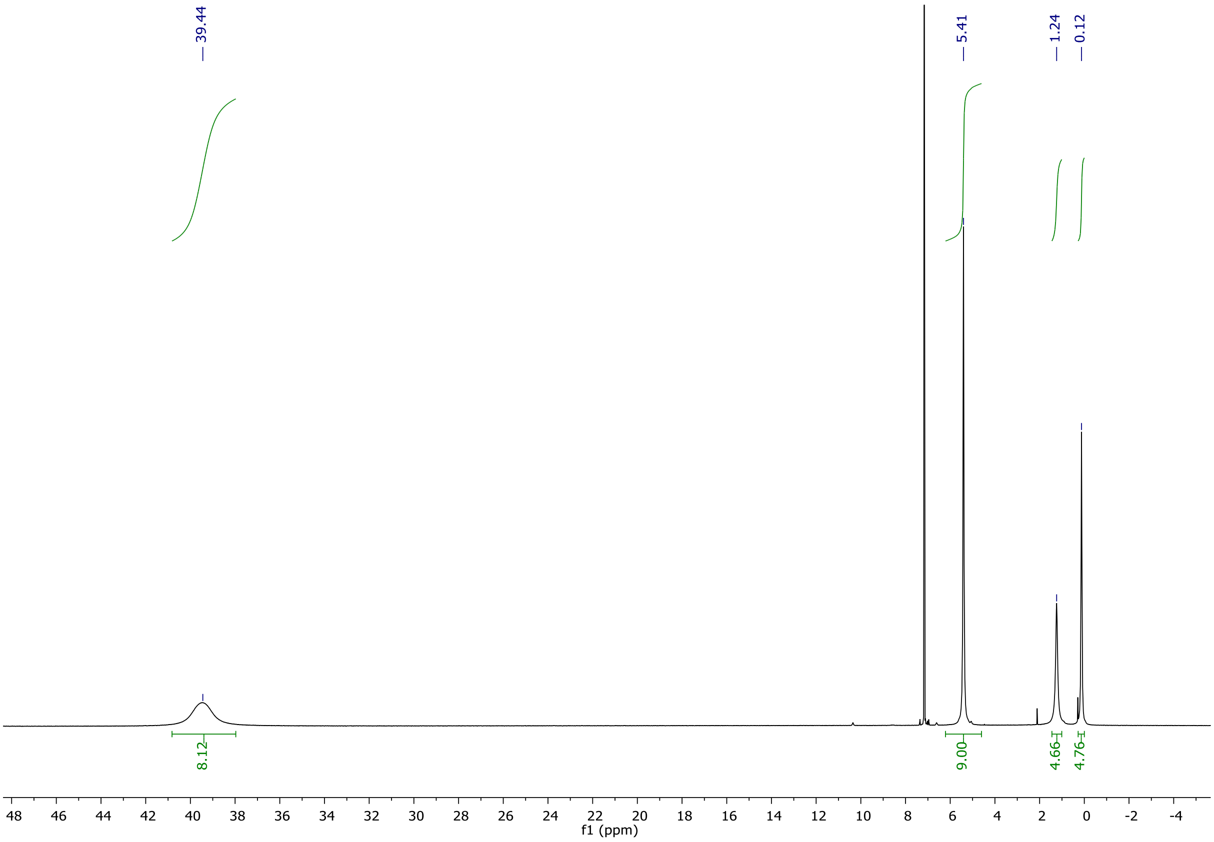


Figure S6. ^{1}H NMR (400 MHz) spectrum of compound **2** in C_6D_6 at room temperature.

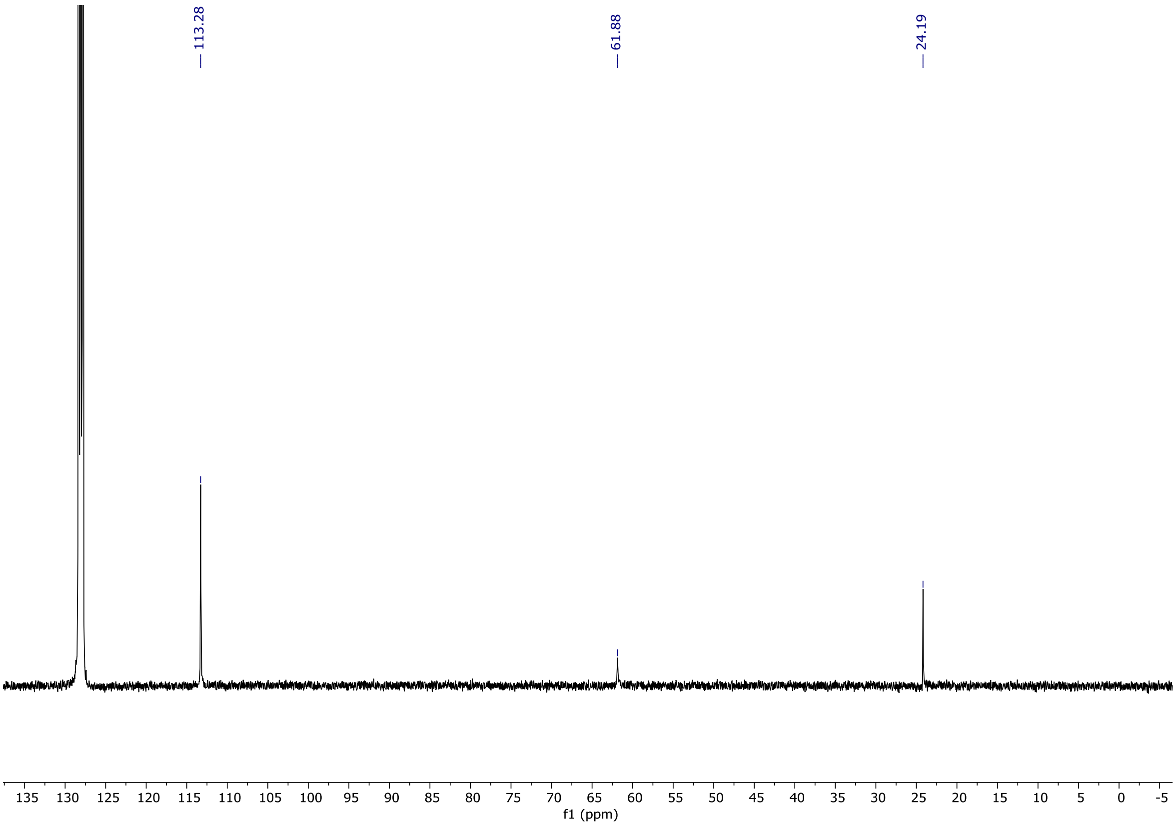


Figure S7. $^{13}C\{^1H\}$ NMR (101 MHz) spectrum of compound **2** in C_6D_6 at room temperature.

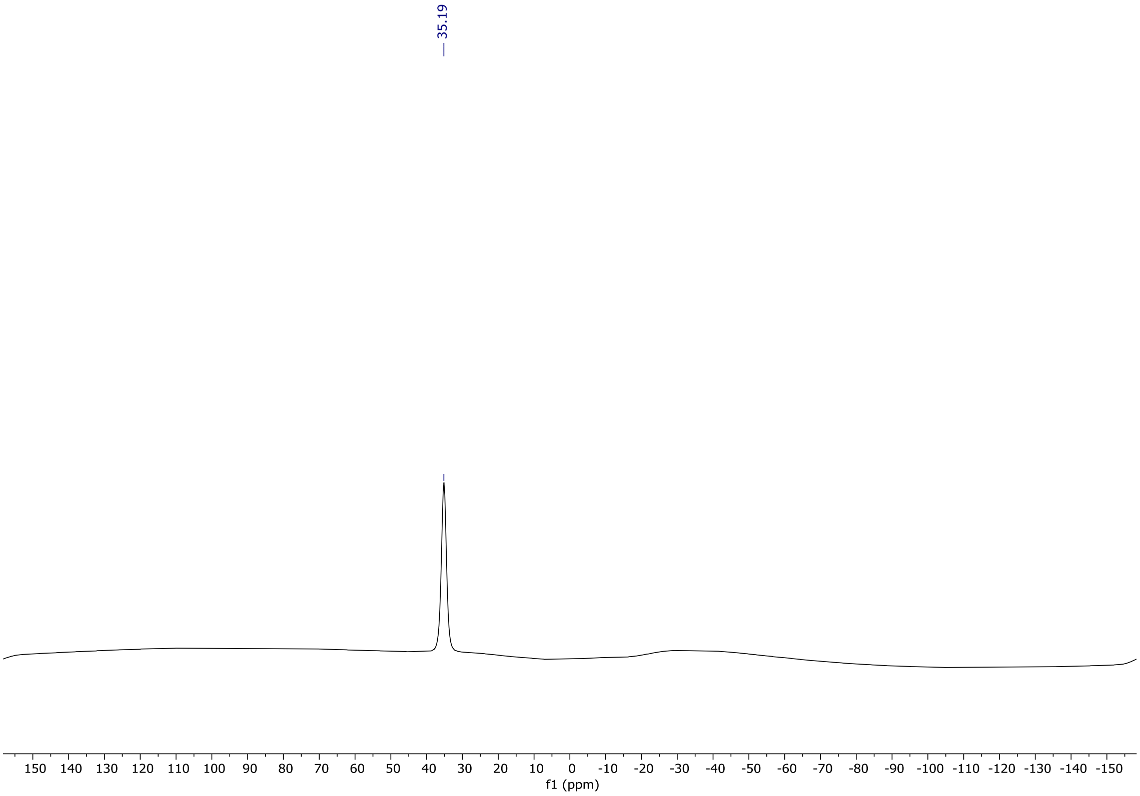


Figure S8. ^{11}B NMR (128 MHz) spectrum of compound **2** in C_6D_6 at room temperature.

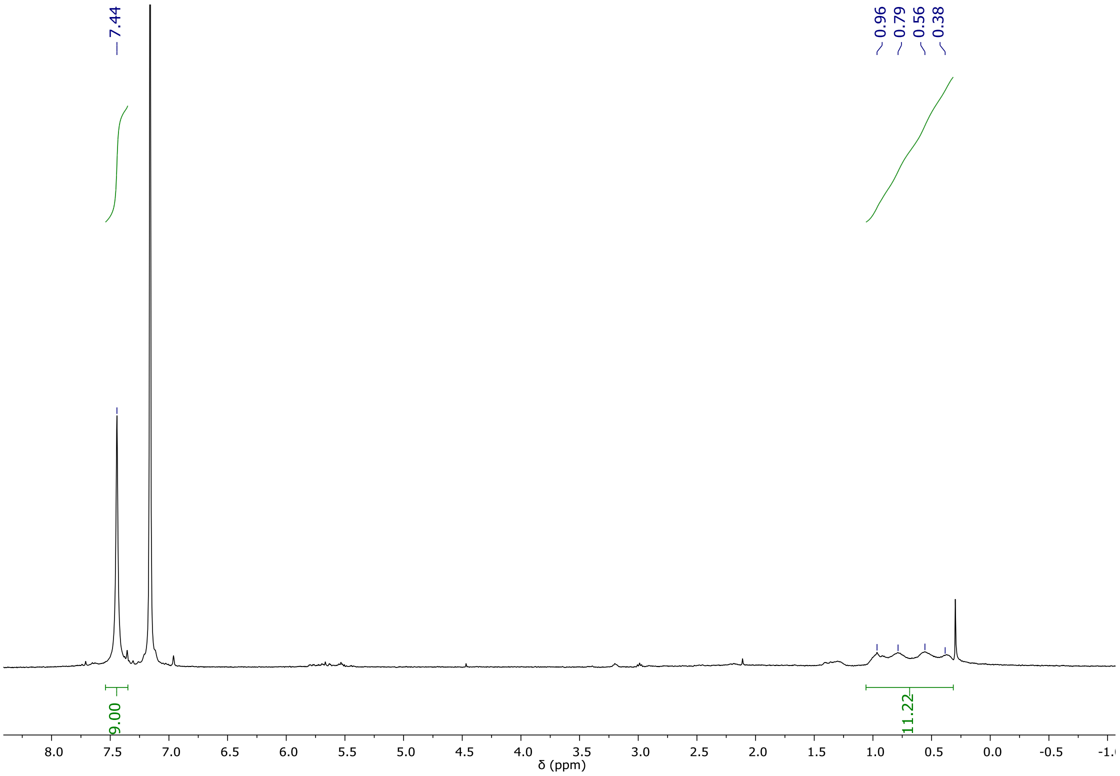


Figure S9. ^1H NMR (400 MHz) spectrum of compound **5** in C_6D_6 at room temperature. Due to poor solubility of compound **5** in C_6D_6, the NMR spectrum could not be obtained in better quality. Note the BH_4 integrals are larger than expected.

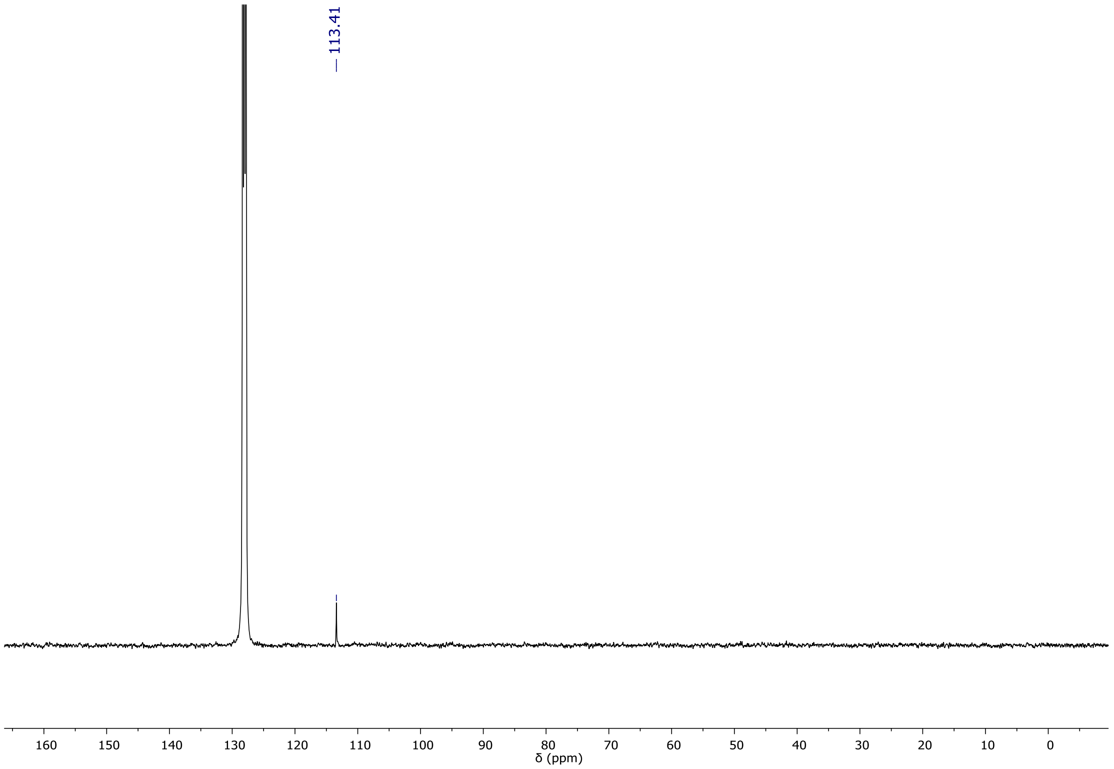


Figure S10: $^{13}C\{^1H\}$ NMR (101 MHz) spectrum of compound **5** in C_6D_6 at room temperature. Due to poor solubility of compound **5** in C_6D_6, the NMR spectra could not be obtained in better quality.

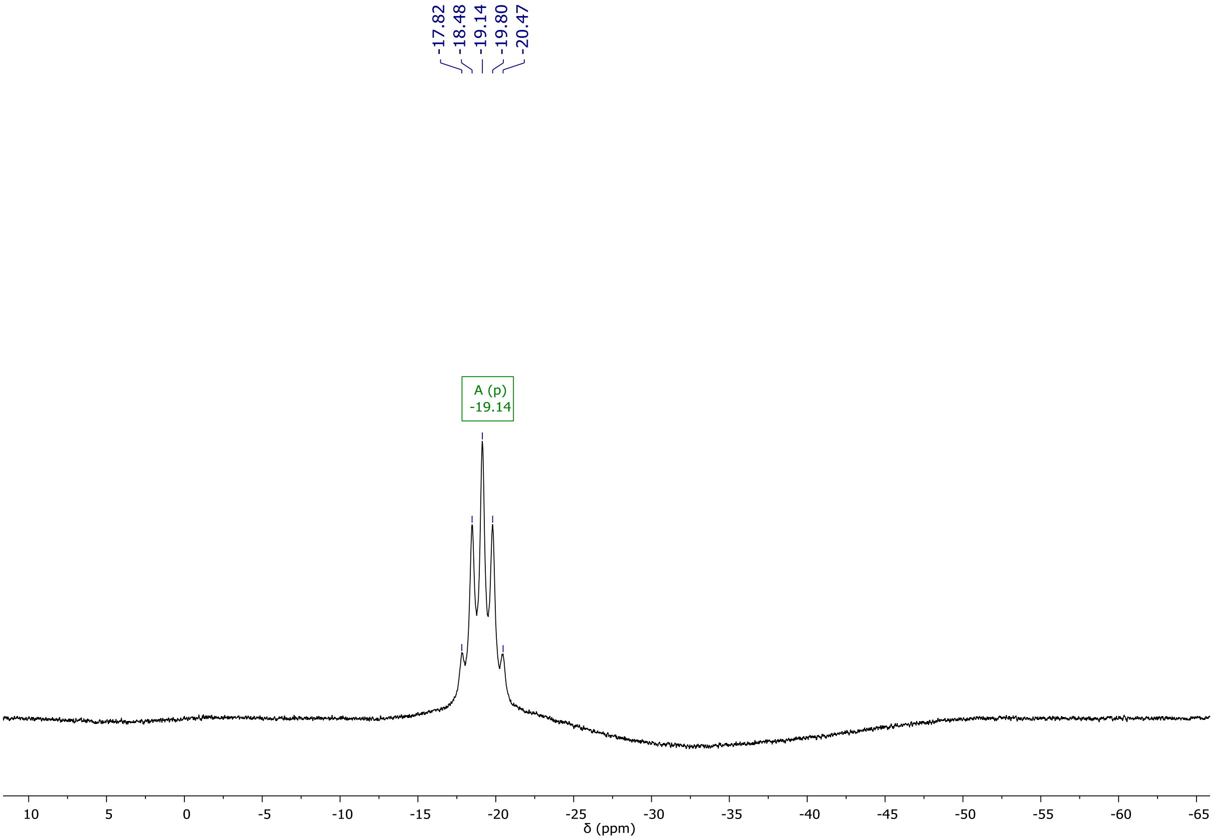


Figure S11. ^{11}B NMR (128 MHz) spectrum of compound **5** in C_6D_6 at room temperature.

III. Raman spectra

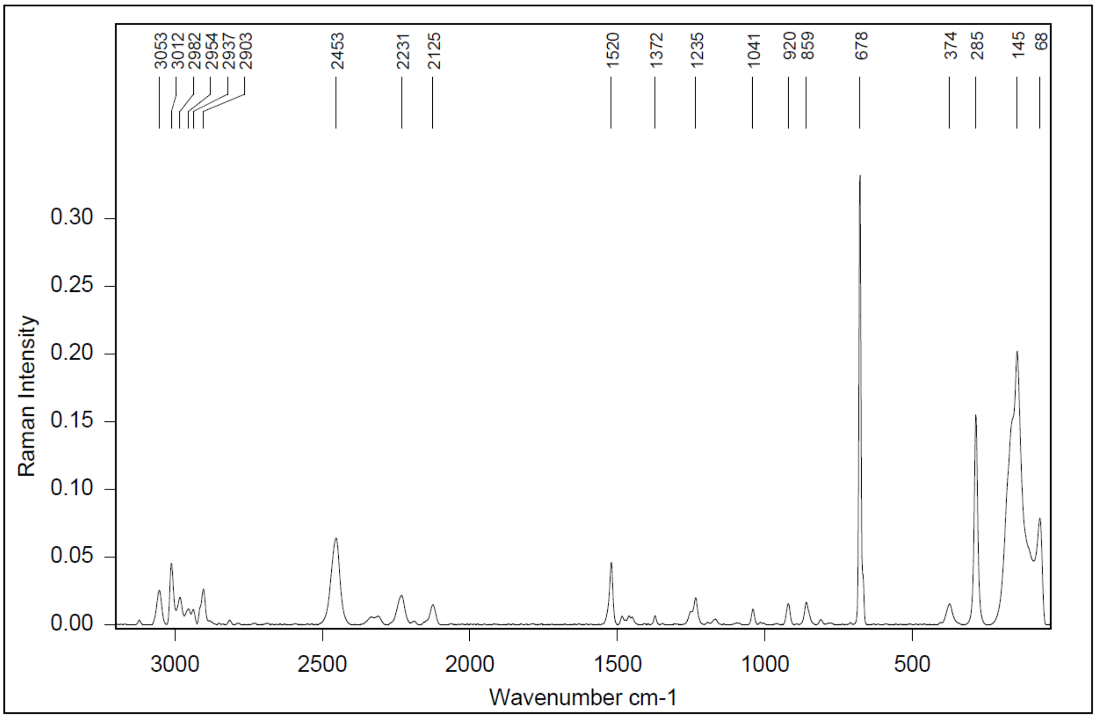


Figure S12. Raman spectrum of complex **1**.

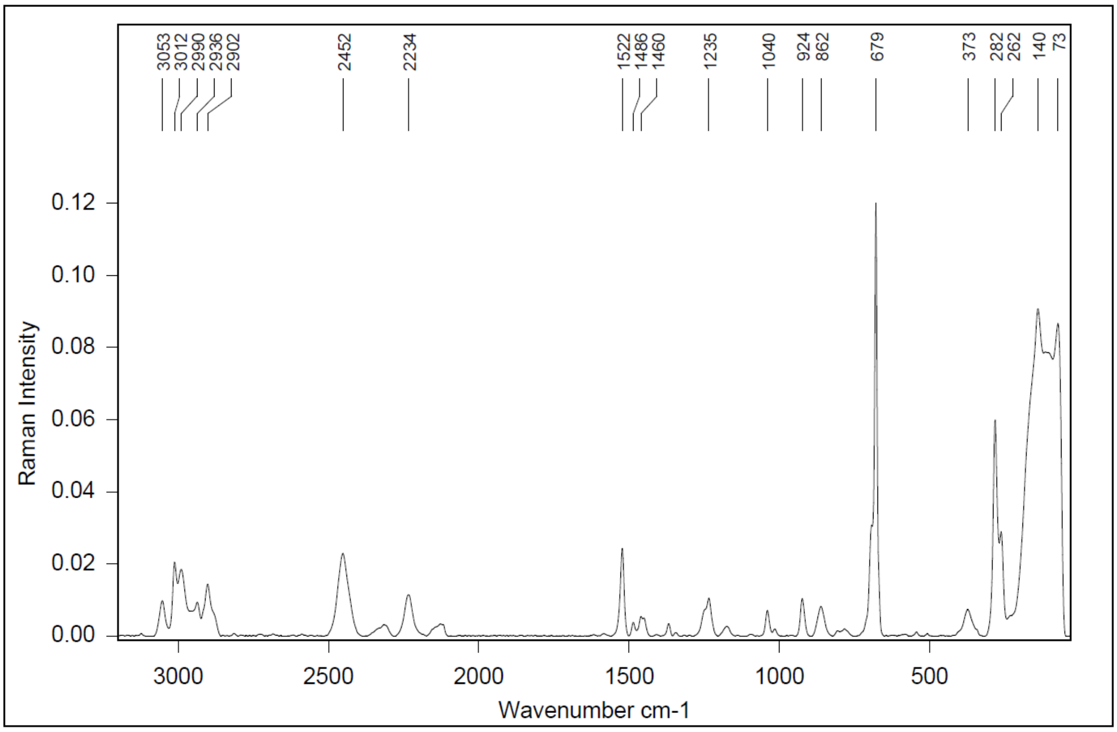


Figure S13. Raman spectrum of complex **2**.

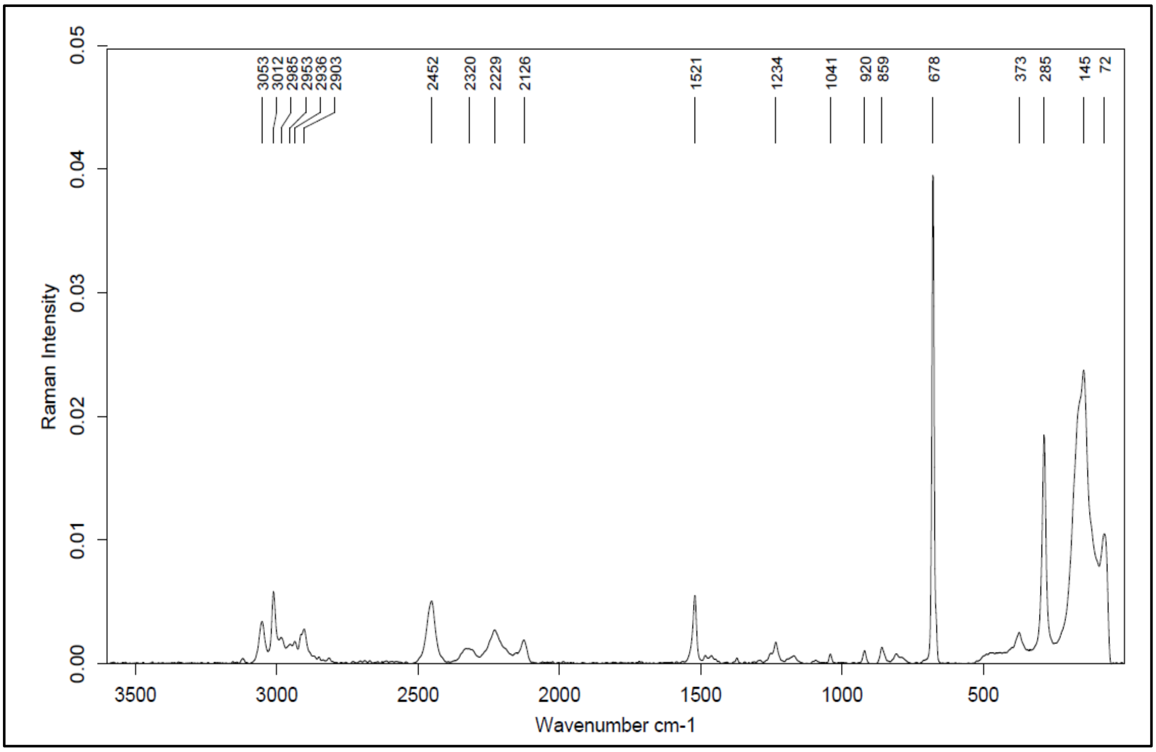


Figure S14. Raman spectrum of complex **5**.

IV. X-ray crystallography

IV.1 General methods

Suitable crystals for the X-ray analysis of all compounds were obtained as described above. A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fibre. The crystal was transferred directly to the cold stream of a STOE StadiVari diffractometer. All structures were solved using the programs SHELXS/T and Olex2 1.3.[4,5,6] The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F_o^2 by using the program SHELXL.[7,8] The H-atoms were introduced into the geometrically calculated positions (SHELXL procedures) unless otherwise stated and refined riding on the corresponding parent atoms. In each case, the locations of the largest peaks in the final difference Fourier map calculations, as well as the magnitude of the residual electron densities, were of no chemical significance. Specific comments for each data set are given below. Summary of the crystal data, data collection and refinement for compounds are given in Table S1.

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC 2267628-2267632. 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; email: deposit@ccdc.cam.ac.uk).

IV.2 Summary of crystal data

Table S1: Crystallographic Details of compounds **1-5**.

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Compound	**1**	**2**	**3**	**4**	**5**
Formula	$C_{13}H_{25}B_2LaO$	$C_{13}H_{25}B_2CeO$	$C_{33}H_{65}B_2LaO_6$	$C_{33}H_{65}B_2CeO_6$	$C_{13.67}H_{22.33}B_2La$
$D_{calc.}$/ g cm^{-3}	1.500	1.544	1.275	1.296	1.537
µ/mm^{-1}	2.679	2.930	1.178	1.273	2.821
Formula Weight	357.86	359.07	718.38	719.59	347.18
Color	colorless	colorless	colorless	colorless	yellow
Shape	fragment	fragment	rod	irregular	fragment
Size/mm^3	0.64×0.55×0.47	0.27×0.14×0.05	0.39×0.24×0.11	0.40×0.20×0.05	0.20×0.16×0.10
T/K	100	100	150	100	100
Crystal System	monoclinic	monoclinic	triclinic	triclinic	triclinic
Space Group	$P2_1/n$	$P2_1/c$	*P*-1	*P*-1	*P*-1
a/Å	8.4353(5)	7.3380(6)	8.4435(3)	8.3963(4)	8.2510(12)
b/Å	7.2384(3)	8.7957(4)	9.0953(4)	9.0379(4)	14.037(3)
c/Å	25.986(2)	23.948(2)	24.5660(9)	24.4820(11)	20.177(2)
α/°	-	-	94.126(3)	94.106(4)	85.128(12)
β/°	93.184(5)	92.499(6)	93.934(3)	93.801(4)	86.013(11)
γ/°	-	-	94.032(3)	94.191(4)	75.462(13)
V/Å^3	1584.2(2)	1544.2(2)	1871.88(13)	1843.3(2)	2251.1(6)
Z	4	4	2	2	6
Z'	1	1	1	1	3
Wavelength/Å	0.71073	0.71073	0.71073	0.71073	0.71073
Radiation type	Mo K_α	Mo K_α	Mo K_α	Mo K_α	Mo K_α
Q_{min}/°	2.501	2.467	2.251	2.266	2.439
Q_{max}/°	29.410	29.576	26.994	29.731	31.575
Measured Refl.	9000	12240	87186	48567	25783
Independent Refl.	3948	3955	87186	48567	11930
Reflections with I≥2 *s*(I)	3242	3030	65071	33495	10250
R_{int}	0.0243	0.0442	0.0360	0.0570	0.0696
Parameters	186	186	538	556	661
Restraints	0	18	187	207	128
Largest Peak	0.777	1.514	0.496	2.193	1.330
Deepest Hole	-1.872	-1.509	-0.428	-2.070	-0.988
GooF	0.952	1.106	0.872	1.023	1.004
wR_2 (all data)	0.0783	0.1400	0.0580	0.1483	0.0831
wR_2	0.0769	0.1297	0.0541	0.1340	0.0794
R_1 (all data)	0.0401	0.0731	0.0507	0.0875	0.0391
R_1	0.0331	0.0522	0.0301	0.0571	0.0320

IV.3 Crystal structures

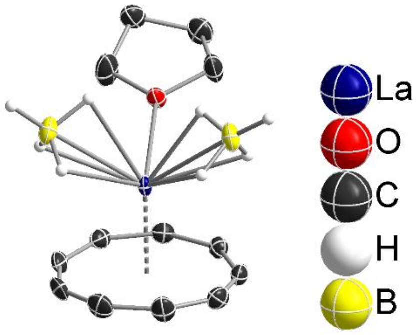

Figure S15. Molecular structure of the complex **1** in the solid state with thermal ellipsoids at 30% level. Hydrogen atoms, except the freely refined hydric ones, are omitted. For selected bond lengths and angles see Table S2.

Table S2: Selected bond lengths and angles of compound **1** (Ct = centroid of the aromatic ring system).

Length/ Å			**Angle/°**			
Ct	La	2.1149(2)	Ct	La	B1	126.7(1)
La	B1	2.675(4)	Ct	La	B2	126.5(1)
La	B2	2.684(4)	Ct	La	O	116.28(4)
La	O	2.468(2)				
La	H1B	2.45(5)				
La	H1C	2.52(4)				
La	H1D	2.52(4)				
La	H2A	2.49(5)				
La	H2C	2.34(4)				
La	H2D	2.30(5)				

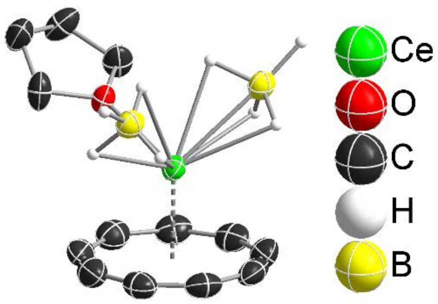

Figure S16. Molecular structure of the complex **2** in the solid state with thermal ellipsoids at 30% level. Hydrogen atoms, except the freely refined hydric ones, are omitted. For selected bond lengths and angles see Table S3.

Table S3: Selected bond lengths and angles of compound **2** (Ct = centroid of the aromatic ring system).

Length/ Å			**Angle/°**			
Ct	Ce	2.0739(4)	Ct	Ce	B1	127.8(2)
Ce	B1	2.659(8)	Ct	Ce	B2	128.2(2)
Ce	B2	2.669(9)	Ct	Ce	O	115.1(1)
Ce	O	2.447(5)				
Ce	H1A	2.27(6)				
Ce	H1B	2.45(7)				
Ce	H1C	2.35(6)				
Ce	H2B	2.39(8)				
Ce	H2C	2.44(7)				
Ce	H2D	2.41(6)				

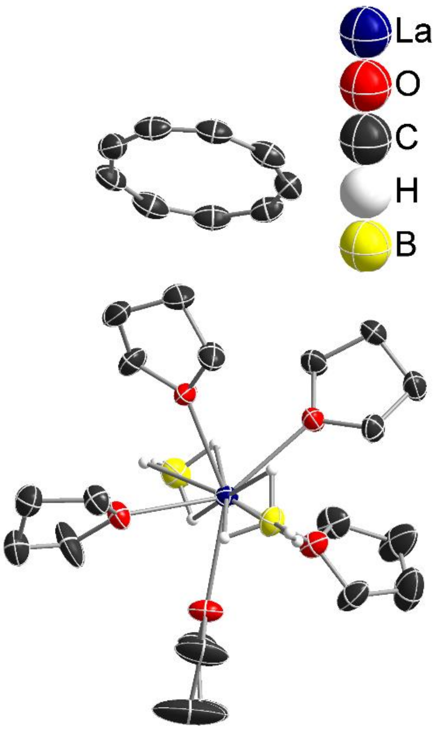

Figure S17. Molecular structure of the complex **3** in the solid state with thermal ellipsoids at 30% level. Two molecules are found in the asymmetric unit, only one of them is depicted here. Hydrogen atoms, except the freely refined hydric ones, are omitted. For selected bond lengths and angles see Table S4.

Table S4: Selected bond lengths and angles of compound **3** (Ct = centroid of the aromatic ring system).

Length/ Å			**Angle/°**			
La	B1	2.721(4)	B1	La	B2	177.15(2)
La	B2	2.717(5)				
La	H1A	2.49(3)				
La	H1B	2.43(2)				
La	H1D	2.51(3)				
La	H2A	2.47(3)				
La	H2B	2.51(3)				
La	H2D	2.45(3)				

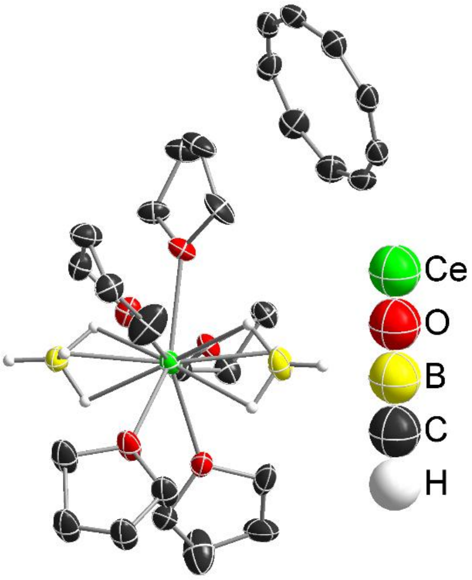

Figure S18. Molecular structure of the complex **4** in the solid state with thermal ellipsoids at 30% level. Two molecules are found in the asymmetric unit, only one of them is depicted here. Hydrogen atoms, except the freely refined hydric ones, are omitted. For selected bond lengths and angles see Table S5.

Table S5: Selected bond lengths and angles of compound **4** (Ct = centroid of the aromatic ring system).

Length/ Å			**Angle/°**			
Ce	B1	2.696(7)	B1	Ce	B2	177.5(3)
Ce	B2	2.697(8)				
Ce	H1B	2.32(3)				
Ce	H1C	2.34(3)				
Ce	H1D	2.33(3)				
Ce	H2B	2.41(3)				
Ce	H2C	2.42(3)				
Ce	H2D	2.41(3)				

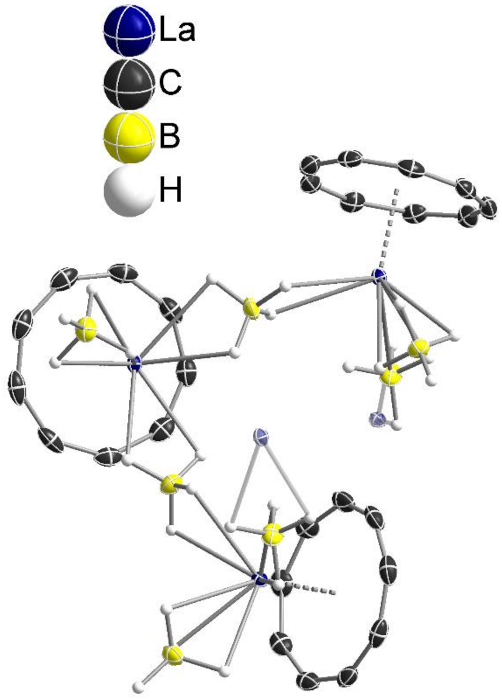

Figure S19. Molecular structure of the complex **5** in the solid state with thermal ellipsoids at 30% level. Hydrogen atoms, except the freely refined hydric ones, are omitted. For selected bond lengths and angles see Table S6.

Table S6: Selected bond lengths and angles of compound **5** (Ct = centroid of the aromatic ring system).

Length/ Å			**Angle/°**			
La1	Ct	2.0242(4)	La1	B3	La2	147.91(14)
La2	Ct	2.0237(4)	La1	B2	La3	153.2(2)
La3	Ct	2.0388(4)	Ct	La1	B1	131.47(9)
La1	B1	2.655(4)	Ct	La2	B4	132.46(8)
La1	B2	3.010(4)	Ct	La3	B5	121.04(8)
La1	B3	2.888(3)	Ct	La3	B6	131.28(9)
La2	B3	3.030(3)				
La2	B4	2.641(3)				
La2	B5	2.942(4)				
La3	B5	3.022(4)				
La3	B6	2.644(4)				

V. References

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