Supporting Information

for

Synthesis, Structure, and Reactivity of Dicationic Bimetallic Tetrabenzyldihafnium Complexes Bearing a Chelating (2-Hydroxyethyl)amido Ligand

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1. **X-Ray Crystallographic Analysis**

2. **^{1}H and ^{13}C{^{1}H} NMR Spectra of (2-Hydoroxyethylene)amine**

3. **^{1}H and ^{13}C{^{1}H} NMR Spectra of Hafnium Complexes**

4. **Screening of Reaction Condition for Oligomerization of 1-Hexene; ^{1}H and ^{13}C{^{1}H} NMR Spectra of Oligomer of 1-hexene**

5. **^{1}H and ^{13}C{^{1}H} NMR Spectra of Alkene 3**

1. X-ray Crystallographic Analysis

The crystals were mounted on the CryoLoop (Hampton Reserch Corp) with a layer of light mineral oil and placed in a nitrogen stream at 113(1) K. All measurements were made on Rigaku Xtalab P200 diffractometer using multi-layer mirror monochromated Mo-Kα (0.71075 Å) radiation. The structure was solved by SIR92,[S1] SHELXT Version 2014/5[S2] in the CrystalClear program,[S3] and refined on F^2 by full-matrix least-squares method, using SHELXL-2016/4.[S4] Non-hydrogen atoms were anisotropically refined, except for one carbon atom of $B(C_6F_5)_4$ for **5a**. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. A bromine atom of the packing solvent in complex **2a** was disordered due to thermal motion, resulted in the remaining of large electron density around the bromine atom. Large residual electron density was found closed to the heavy hafnium atom for **1a** and **5a**. The function minimized was $[\Sigma w(F_o^2 - F_c^2)^2]$ ($w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$), where $P = (\max(F_o^2,0) + 2F_c^2)/3$ with $\sigma^2(F_o^2)$ from countin statistics. The functions $R1$ and $wR2$ were $(\Sigma \| F_o | - | F_c \|)/\Sigma | F_o |$ and $[\Sigma w(F_o^2 - F_c^2)^2 /\Sigma(wF_o^4)]^{1/2}$, respectively. The PLATON/SQUEEZE program[S5] was used for the refinement of **5a** and **6a**. Crystal data and structure refinement parameters are listed in Table S1 and S2. The ORTEP-3 program[S6] was used to draw the molecules.

Table S1. Crystal Data and Data Collection Parameters of Complexes **1a** and **2a**

	1a	2a
empirical formula	$C_{76}H_{94}Hf_2N_2O_2$	$C_{122}H_{90}B_2Br_2F_{40}Hf_2N_2O_2$
formula weight	1424.57	2914.41
crystal system	*monoclinic*	*triclinic*
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	13.8298(5)	12.6621(14)
b, Å	21.0139(8)	15.0147(13)
c, Å	11.6755(4)	15.5219(17)
α, deg.	–	79.207(7)
β, deg.	91.249(6)	88.564(8)
γ, deg.	–	74.747(7)
V, Å^3	3392.3(2)	2795.8(5)
Z	2	1
Dcalcd, g/cm^{-3}	1.395	1.731
μ [Mo-$K\alpha$], cm^{-1}	30.979	26.898
T, K	113	113
crystal size, mm	$0.17 \times 0.10 \times 0.07$	$0.36 \times 0.17 \times 0.16$
θ range for data collection (deg.)	3.00 to 27.60	3.10 to 27.50
no. of reflections measured	7413	52878
unique data (Rint)	7413 (0.0980)	12842 (0.0573)
data / restraints / parameters	7413 / 0 / 403	12842 / 0 / 770
$R1$ ($I > 2.0\sigma(I))$ [a]	0.0711	0.0664
$wR2$ ($I > 2.0\sigma(I))$ [b]	0.1864	0.1733
$R1$ (all data) [a]	0.1459	0.0798
$wR2$ (all data) [b]	0.2441	0.1827
GOF on F^2	1.159	1.049
$\Delta\rho$, e Å^{-3}	2.57, -2.08	8.53, -7.16

a) $R1 = (\Sigma||Fo| - |Fc||)/(\Sigma|Fo|)$ *b)* $wR2 = [\{\Sigma w(Fo^2 - Fc^2)^2\}/\{\Sigma w(Fo^4)\}]^{1/2}$

Table S2. Crystal Data and Data Collection Parameters of Complexes **5a** and **6a**

	5a	6a
empirical formula	$C_{126}H_{102}B_2F_{40}Hf_2N_2O_2P_2$	$C_{130}H_{100}B_2F_{40}Hf_2N_6O_2$
formula weight	2876.69	2916.79
crystal system	*triclinic*	*triclinic*
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	12.937(3)	13.6112(17)
b, Å	14.2819(18)	16.6645(15)
c, Å	19.054(4)	17.442(2)
α, deg.	71.294(18)	62.030(8)
β, deg.	74.826(19)	78.174(12)
γ, deg.	75.655(19)	71.120(10)
V, Å^3	3166(12)	3299.5(8)
Z	1	1
Dcalcd, g/cm^{-3}	1.509	1.468
μ [Mo-$K\alpha$], cm^{-1}	17.691	16.766
T, K	113	113
crystal size, mm	$0.20 \times 0.12 \times 0.08$	$0.15 \times 0.01 \times 0.01$
θ range for data collection (deg.)	3.10 to 27.30	3.00 to 25.20
no. of reflections measured	57659	28337
unique data (Rint)	14458 (0.2094)	14187 (0.1337)
data / restraints / parameters	14458 / 0 / 793	14187 / 0 / 820
$R1$ ($I > 2.0\sigma(I)$) ^{a}	0.0963	0.0754
$wR2$ ($I > 2.0\sigma(I)$) ^{b}	0.2241	0.1644
$R1$ (all data) ^{a}	0.1548	0.1227
$wR2$ (all data) ^{b}	0.2512	0.1954
GOF on F^2	0.951	1.064
$\Delta\rho$, e Å^{-3}	8.65, -2.71	1.74, -2.55

a) $R1 = (\Sigma||Fo| - |Fc||)/(\Sigma|Fo|)$ *b*) $wR2 = [\{\Sigma w(Fo^2 - Fc^2)^2\}/\{\Sigma w(Fo^4)\}]^{1/2}$

2. ¹H and ¹³C{¹H} NMR Spectra of (2-Hydoroxyethylene)amine
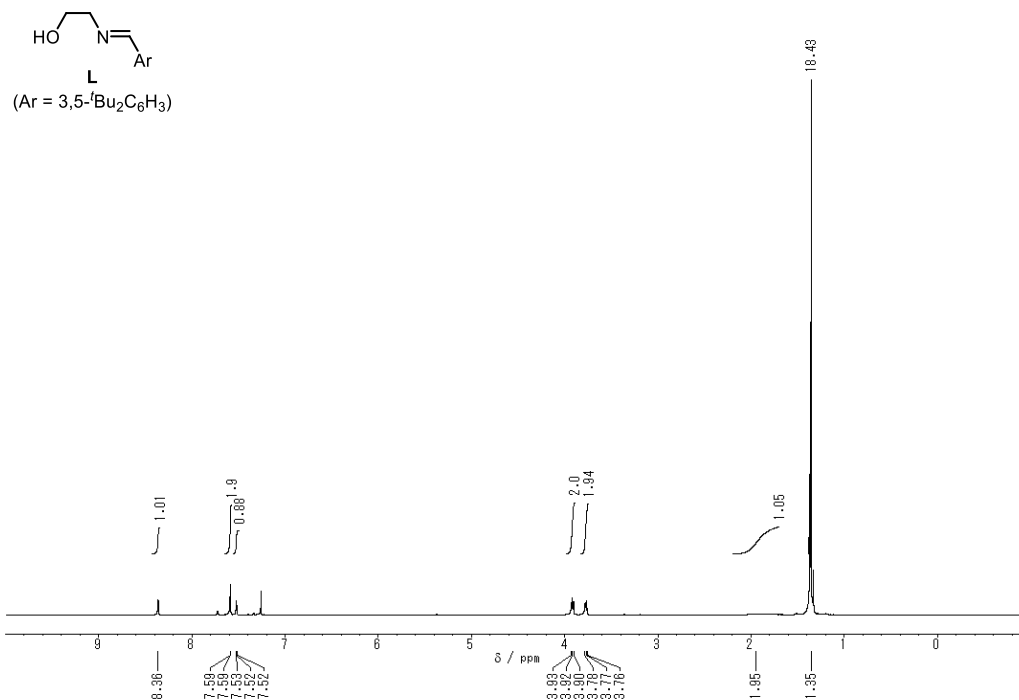
Figure S1. ¹H NMR spectrum of pro-ligand **L** in CDCl₃.
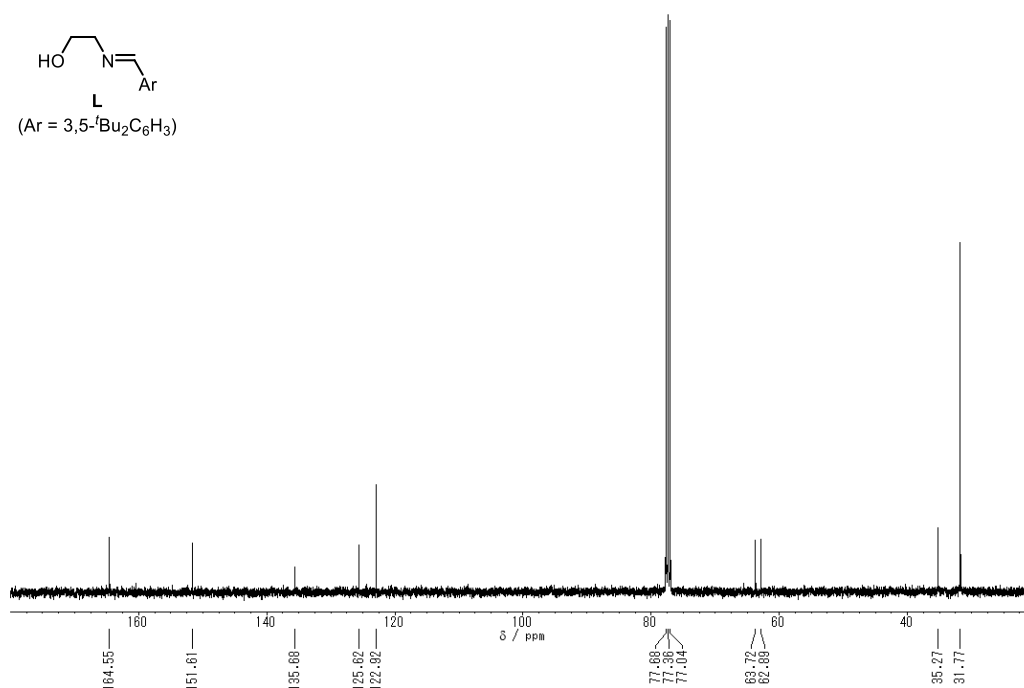
Figure S2. ¹³C{¹H} NMR spectrum of pro-ligand **L** in CDCl₃.

3. ^{1}H and ^{13}C{^{1}H} NMR Spectra of Hafnium Complexes

1:1 mixture of
1a (*SR* isomer) and **1b** (*RR* and *SS* isomers)
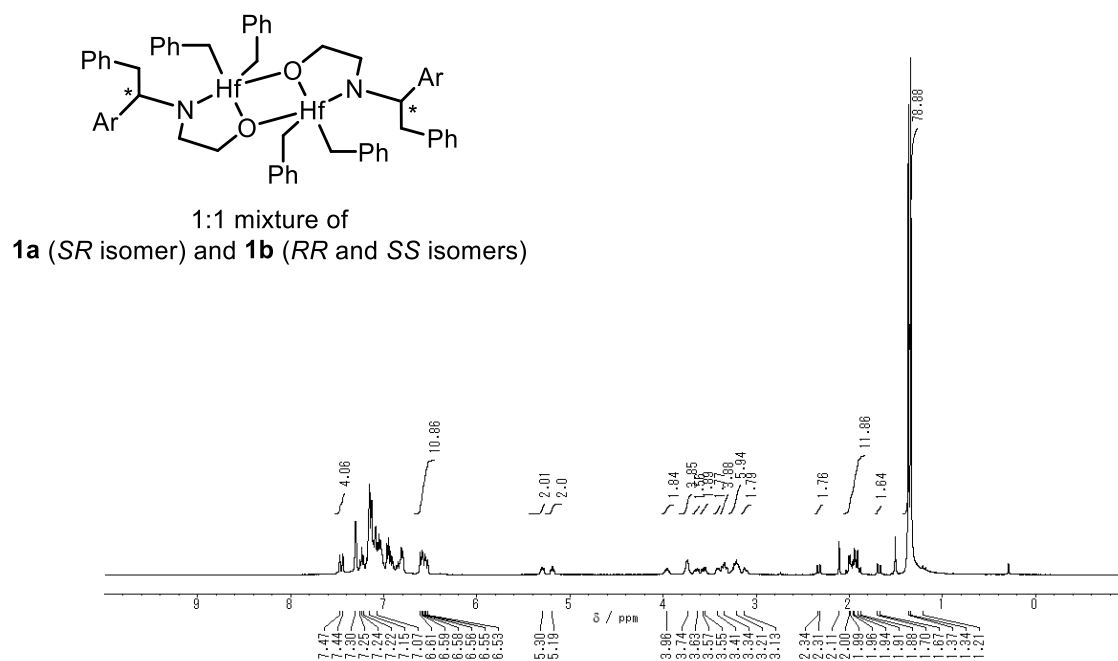
Figure S3. ^{1}H NMR spectrum of mixture of the mixture of **1a** and **1b** in C$_6$D$_6$.

1:1 mixture of
1a (*SR* isomer) and **1b** (*RR* and *SS* isomers)
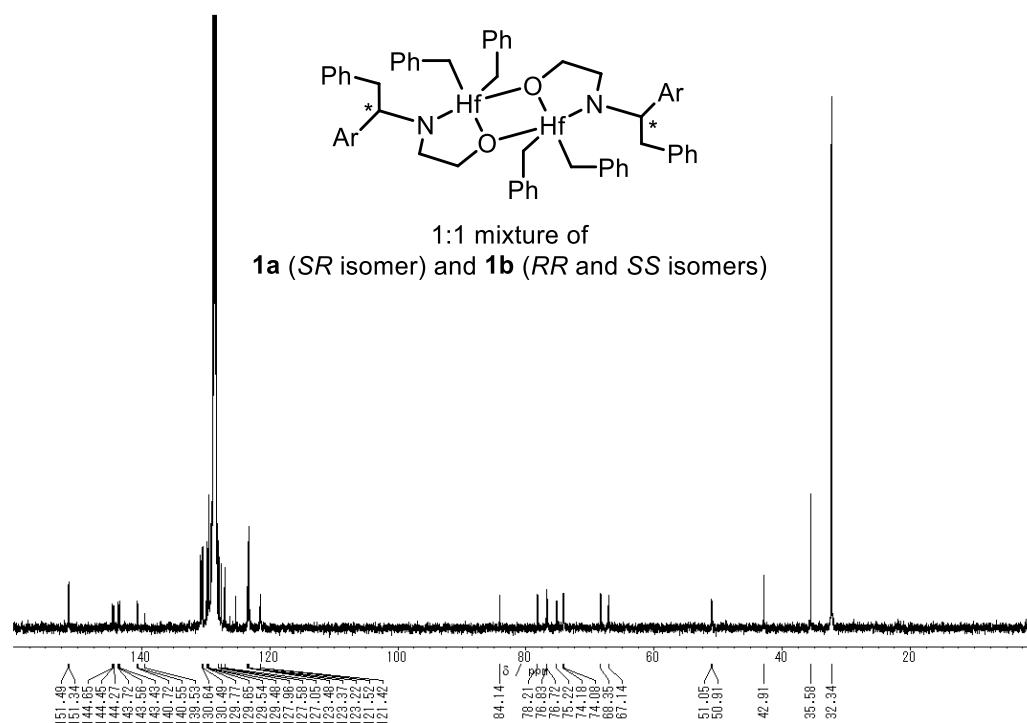
Figure S4. ^{13}C{^{1}H} NMR spectrum of the mixture of **1a** and **1b** in C$_6$D$_6$.

1a (*SR* isomer)
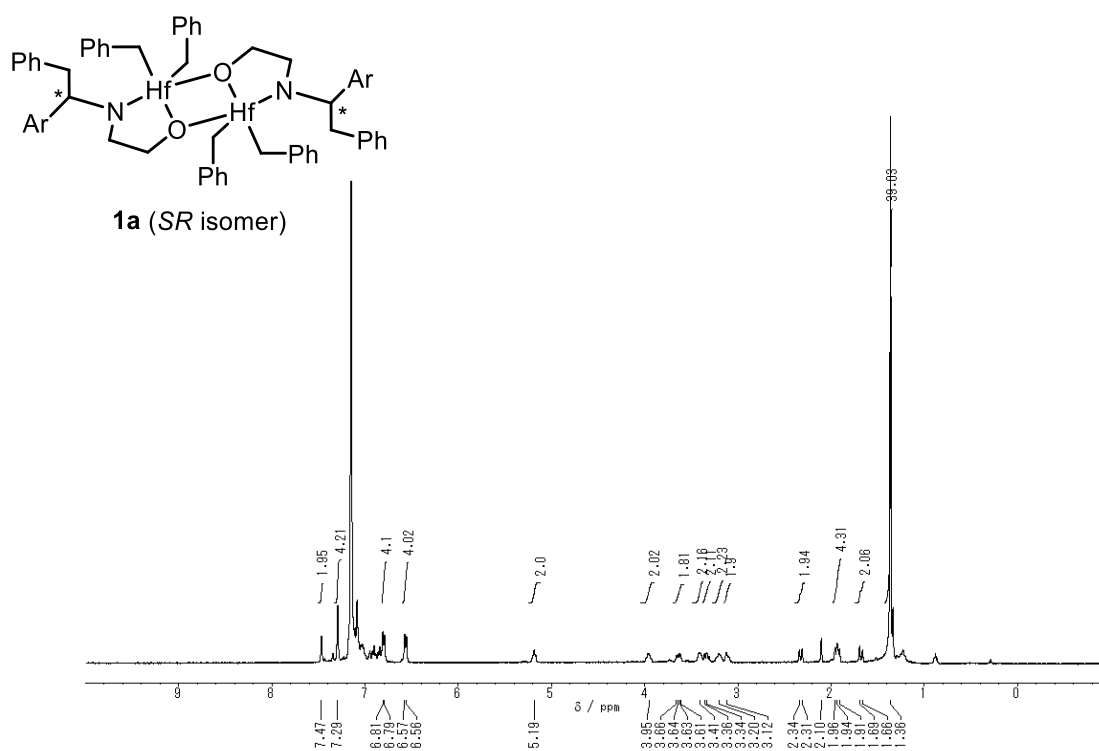
Figure S5. ^{1}H NMR spectrum of complex **1a** in C$_6$D$_6$.

1a (*SR* isomer)
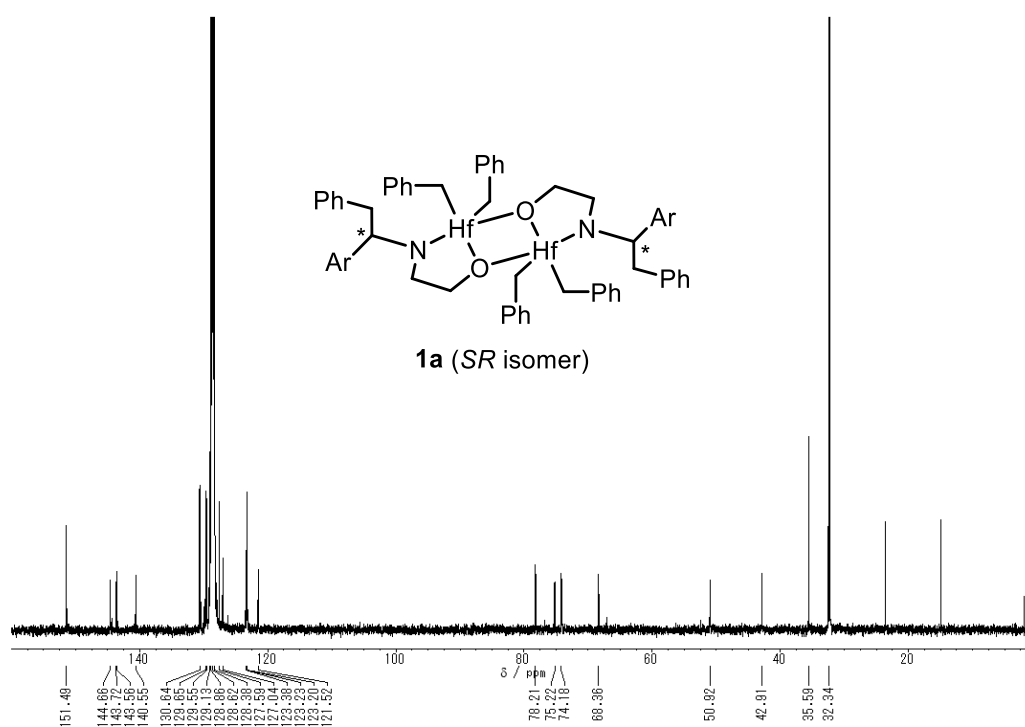
Figure S6. ^{13}C{^{1}H} NMR spectrum of complex **1a** in C$_6$D$_6$.

S7
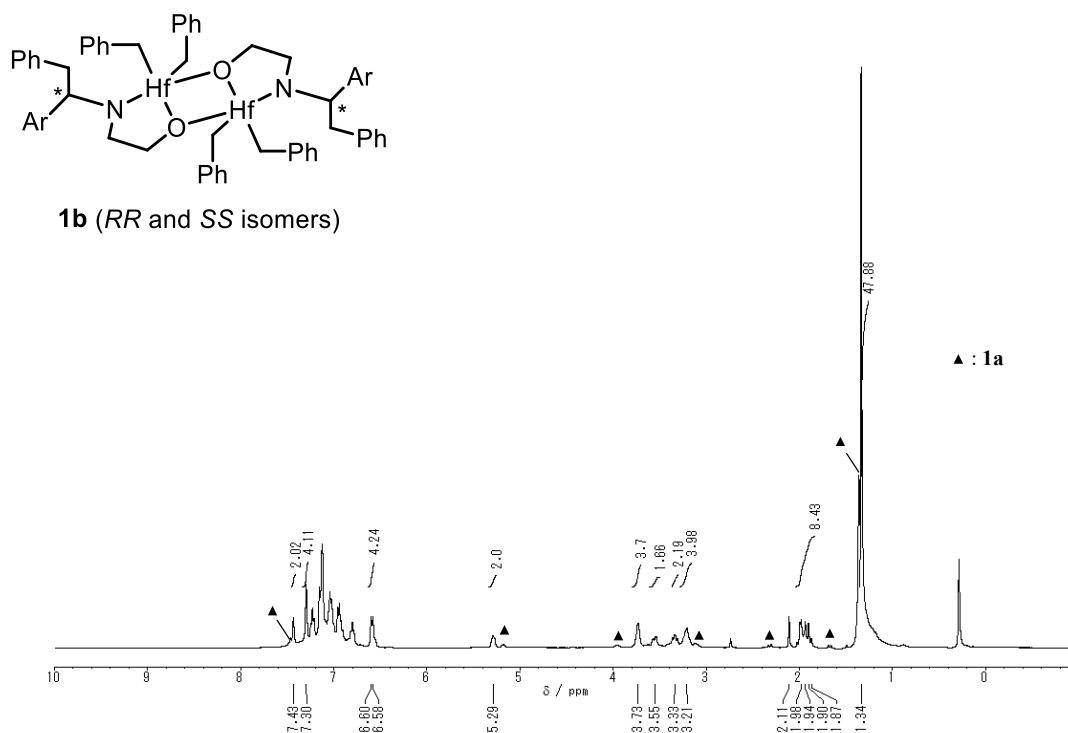
Figure S7. ¹H NMR spectrum of complex **1b** in C₆D₆.
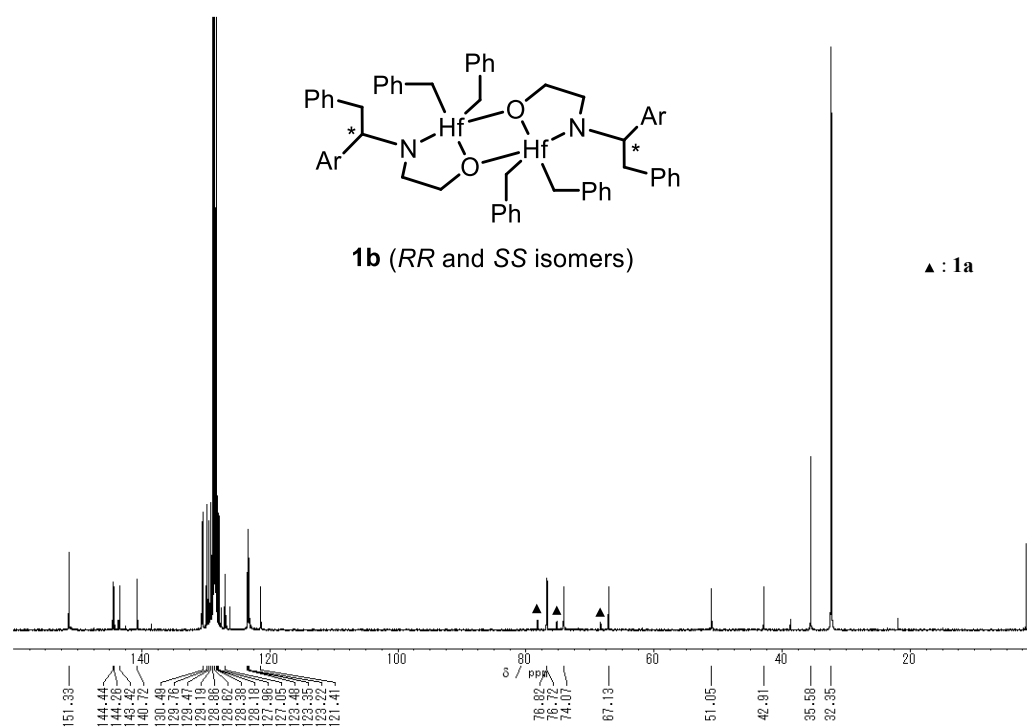
Figure S8. ¹³C{¹H} NMR spectrum of complex **1b** in C₆D₆.
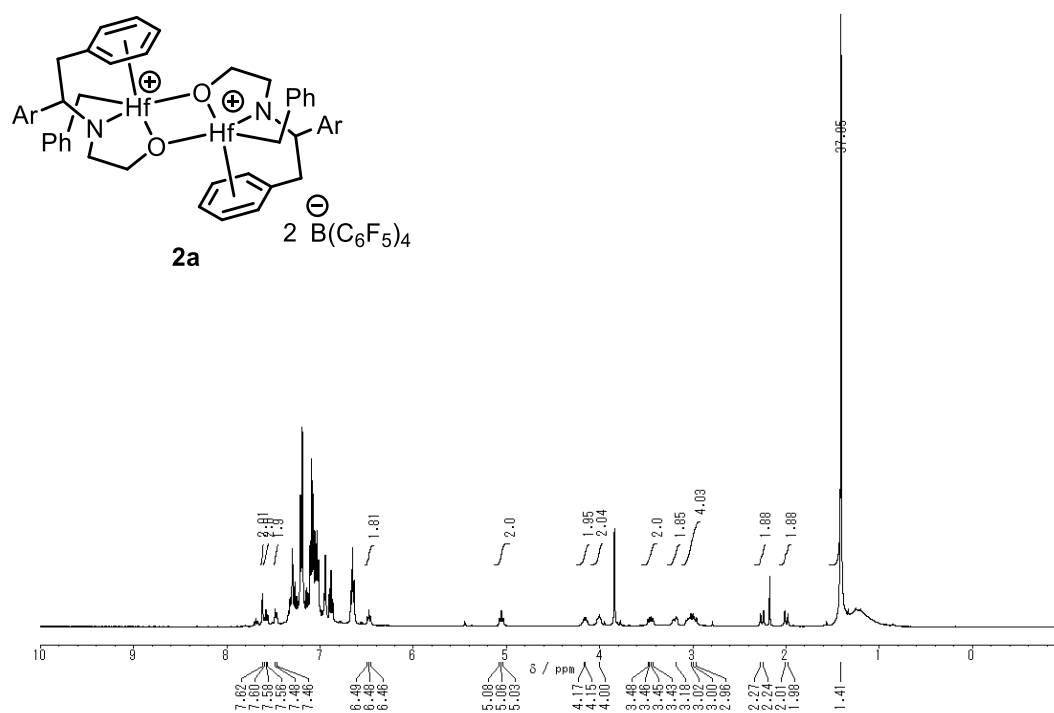
Figure S9. ^{1}H NMR spectrum of complex **2a** in C$_6$D$_5$Br.
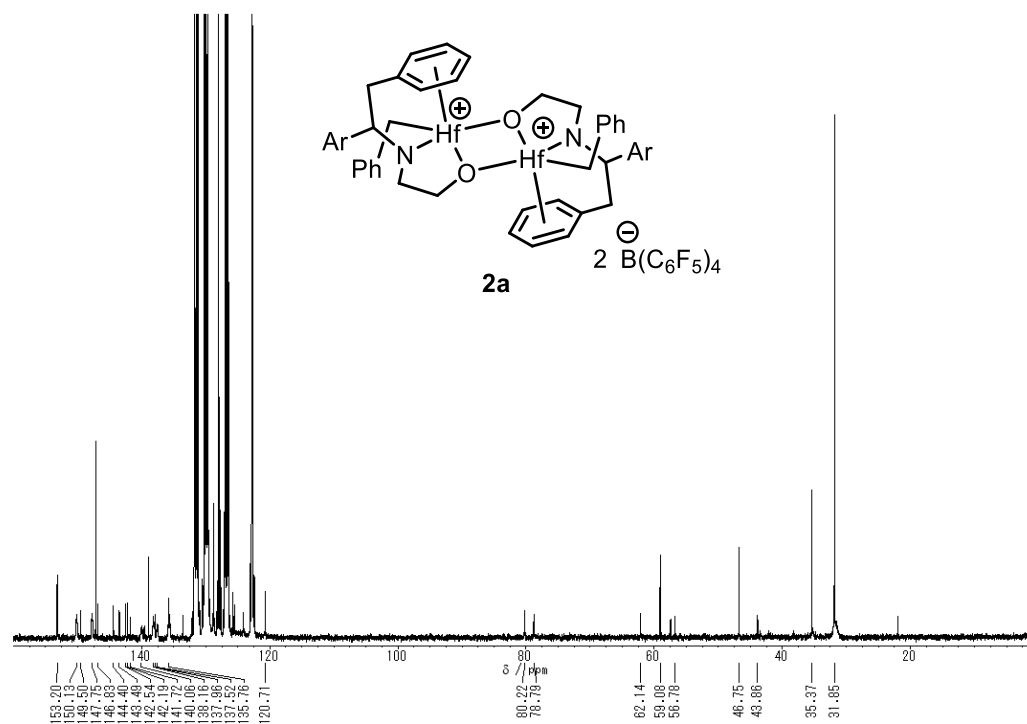
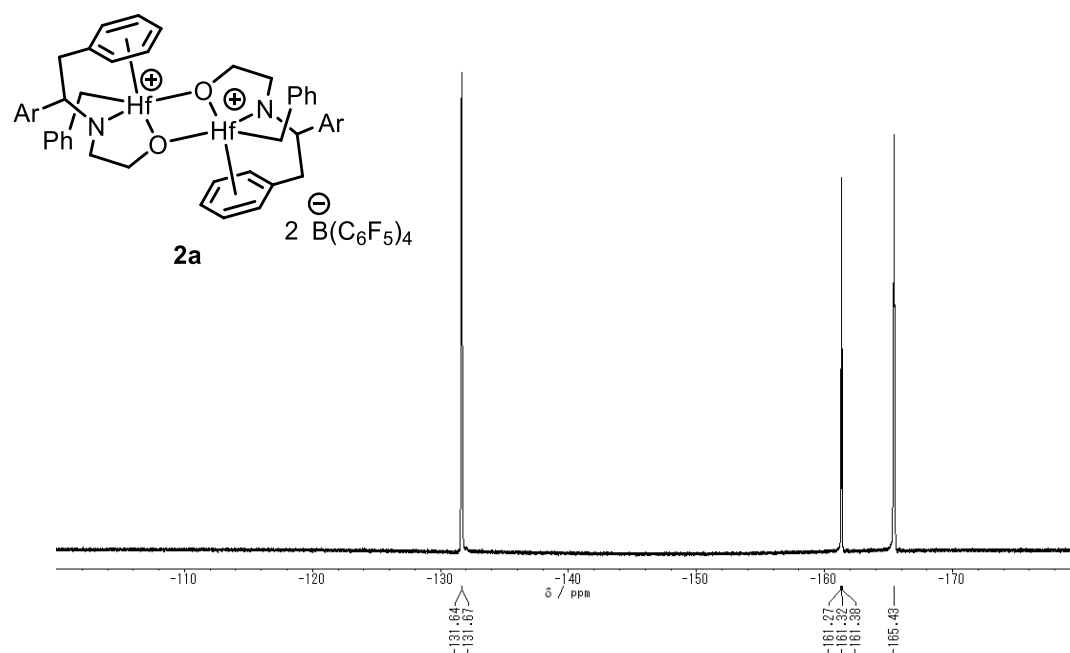**Figure S10.** ^{13}C{^{1}H} NMR spectrum of complex **2a** in C$_6$D$_5$Br.

Figure S11. ^{19}F NMR spectrum of complex **2a** in C_6D_5Br.

4. 1-Hexene Oligomerization

General Procedure for Oligomerization of 1-Hexene: Complex **1a** (7.1 mg, 5.0 μmol, 0.2 mol%) was dissolved in bromobenzene (0.3 mL), and 1-hexene (210.2 mg, 2.50 mmol) was added. [Ph$_3$C][B(C$_6$F$_5$)$_4$] (9.2 mg, 10.0 μmol, 0.4 mol%) was subsequently added. The reaction mixture was kept at designated temperature for the time period as shown the table. Methanol was added to quench the reaction mixture. After removing all the volatile, the residue was dissolved in hexane, and the solution was passed through pad of silica gel. Oligomer of 1-hexene was obtained by evaporating the solvent to dryness.

Table S3. Oligomerization of 1-Hexene Catalyzed by Complex **1a**

entry	cocatalyst	temp. [°C]	time [h]	yield[a] [%]	M_n[b] (×10³)	M_w[b] (×10³)	M_w/M_n
1	[Ph$_3$C][B(C$_6$F$_5$)$_4$]	rt	20	n.r.[c]	–	–	–
2	[Ph$_3$C][B(C$_6$F$_5$)$_4$]	80	20	47	1.02	1.21	1.19
3	[Ph$_3$C][B(C$_6$F$_5$)$_4$]	100	20	78	0.81	1.02	1.26
4	[Ph$_3$C][B(C$_6$F$_5$)$_4$]	100	10	48	0.82	0.98	1.20
5[d]	[Ph$_3$C][B(C$_6$F$_5$)$_4$]	100	20	trace	–	–	–
6	B(C$_6$F$_5$)$_3$	120	20	trace	–	–	–

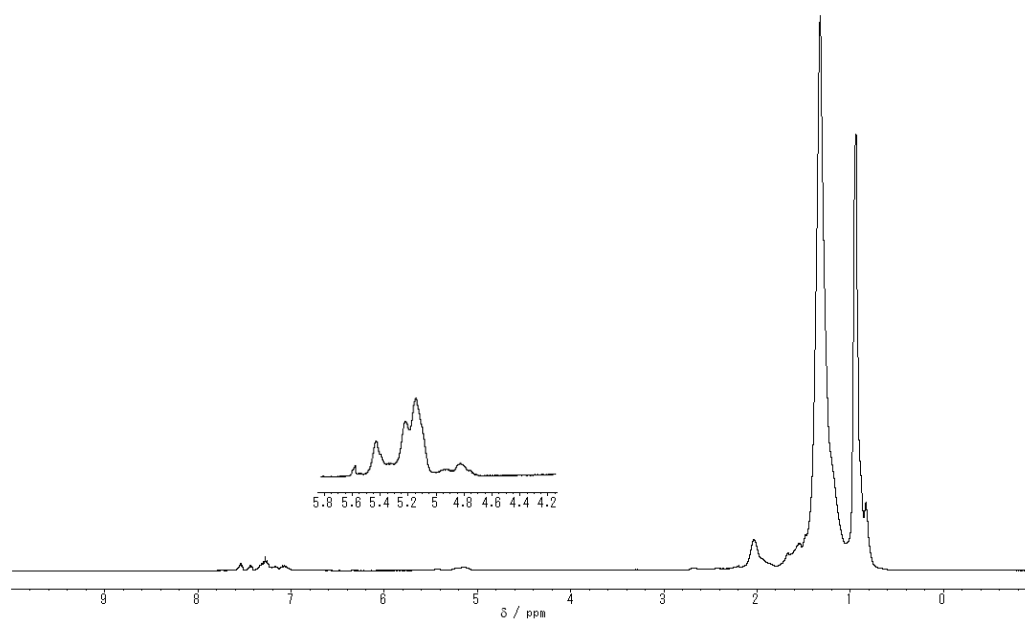[a] Isolated yield. [b] Determined by GPC. [c] No reaction. [d] Performed with 0.2 mol% of cocatalyst.

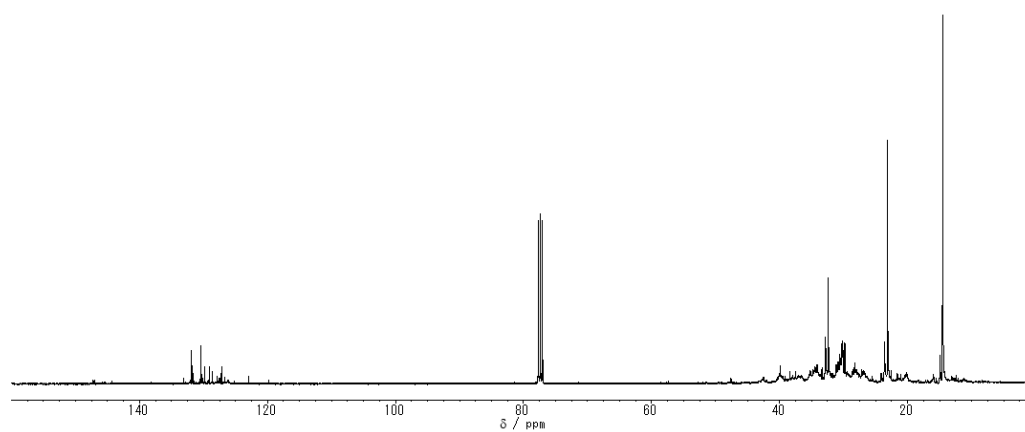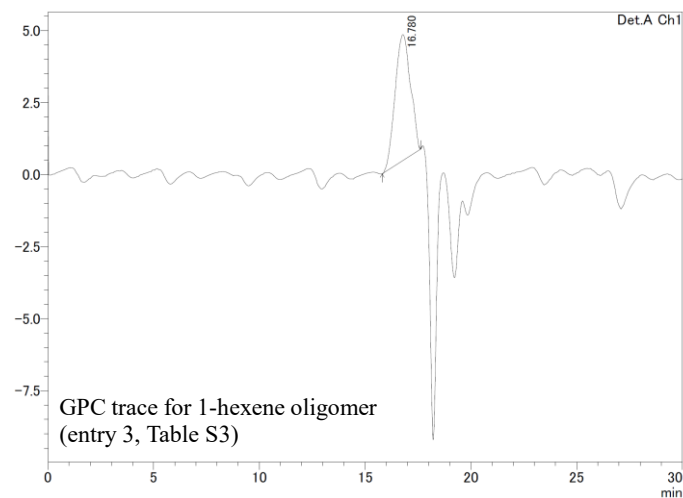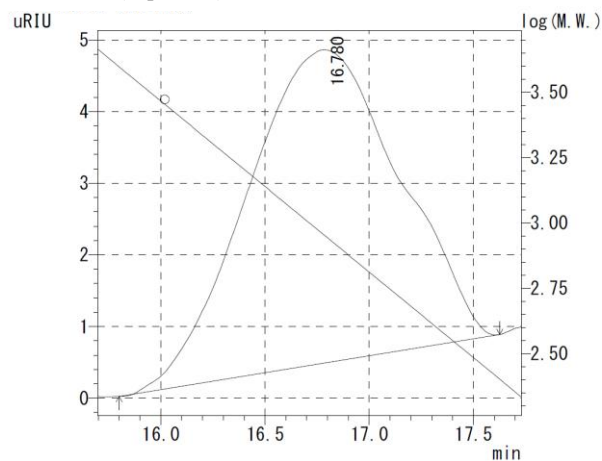**Figure S12.** ^{1}H NMR spectrum of 1-hexene oligomer in CDCl$_3$.

Figure S13. ^{13}C$\{^1$H$\}$ NMR spectrum of 1-hexene oligomer in CDCl$_3$.

GPC trace (expanded) with calibration line

Peak Information

	Retention time	Area	Height	Area%	Height%
1	16.780	220815	4375	100.000	100.000
Sum		220815	4375	100.000	100.000

Molecular weight calculation

Peak Information

	time (min)	flow (mL)	MW	hight
Start	15.800	12.640	3955	25
Peak top	16.780	13.424	901	4375
end	17.625	14.100	252	887

area : 220815
area % : 100.0000

Average molecular weight

Mn	811
Mw	1018
Mz	1265
Mw/Mn	1.25598
Mv/Mn	0.00000
Mz/Mw	1.24242

Figure S14. GPC trace of 1-hexene oligomer for entry 3 in Table S3.

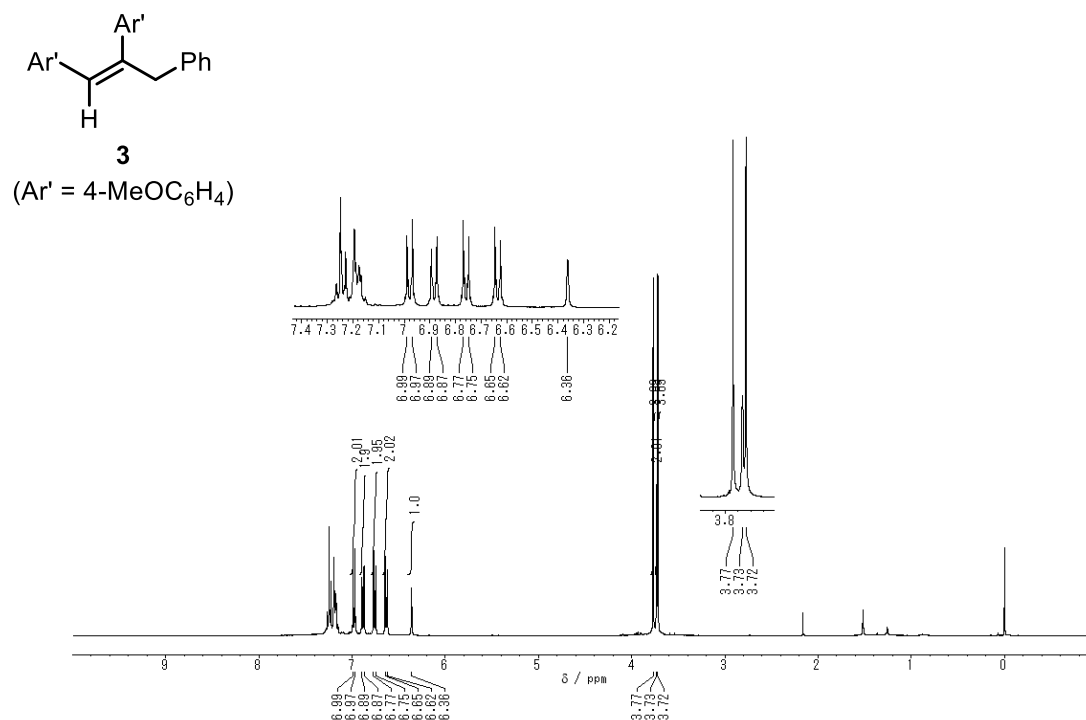## 5. ^{1}H and ^{13}C{^{1}H} NMR Spectra of Alkene 3

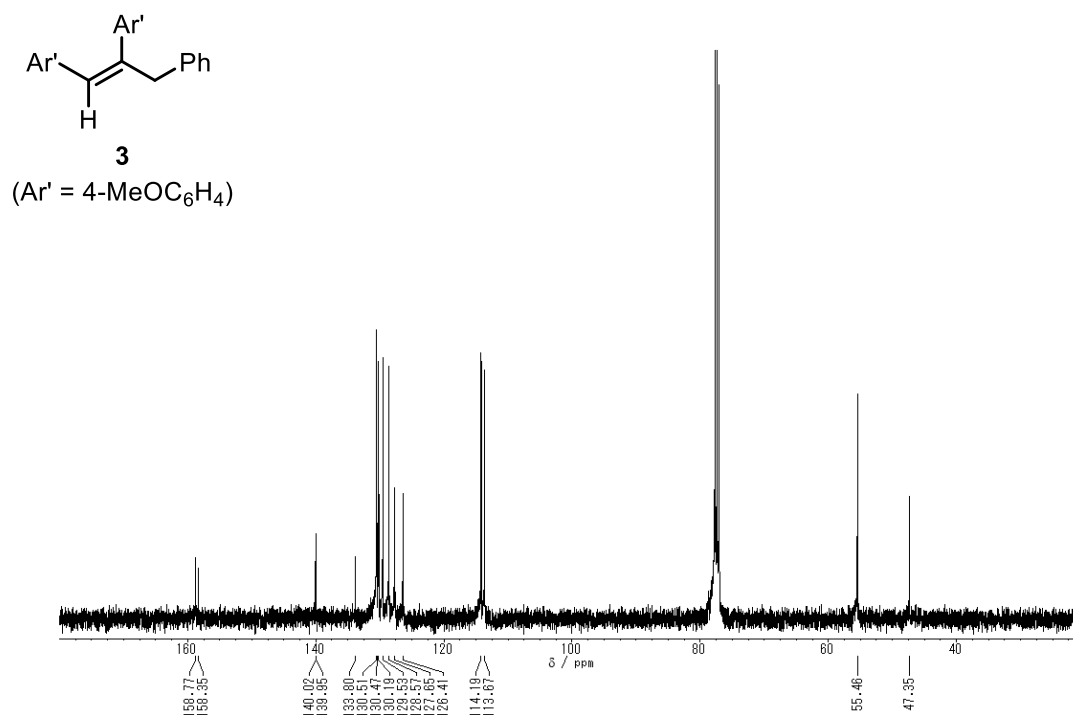**Figure S15.** ^{1}H NMR spectrum of trisubstituted alkene **3** in CDCl$_3$.

Figure S16. ^{13}C{^{1}H} NMR spectrum of trisubstituted alkene **3** in CDCl$_3$.

References

(S1) Altomare, A., Cascarano, G., Giacovazzo, C. and Guagliardi, A. Completion and refinement of crystal structures with SIR92. *J. Appl. Cryst.* **1993,** *26,* 343–350.

(S2) Sheldrick, G. M. *Acta Cryst.* **2014,** *A70,* C1437.

(S3) *CrystalClear: Data Collection and Processing Software,* Rigaku Corporation, 1998–2015, Tokyo 196–8666, Japan.

(S4) Sheldrick, G. M. A Short History of SHELX. *Acta Cryst.* **2008,** *A64,* 112–122.

(S5) van der Sluis, P.; Spek, A. L. BYPASS: an Effective Method for the Refinement of Crystal Structures Containing Disordered Solvent Regions. *Acta Cryst.* **1990,** *A46,* 194–201.

(S6) Farrugia, L. J. *ORTEP*-3 for Windows – a Version of *ORTEP*-III with a Graphical User Interface (GUI). *J. Appl. Crystallogr.* **1997,** *30,* 565.