Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Manuscript Title:

N-Aryloxide-Amidinate Group 4 Metal Complexes

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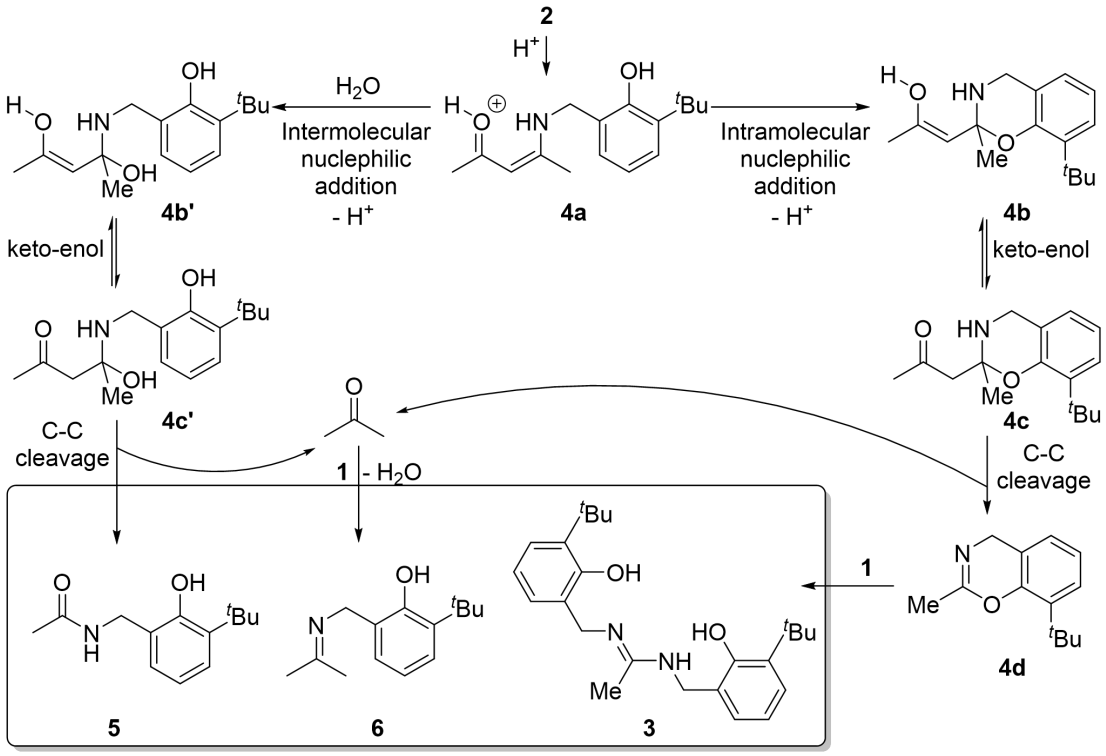
Content

Experimental Methods

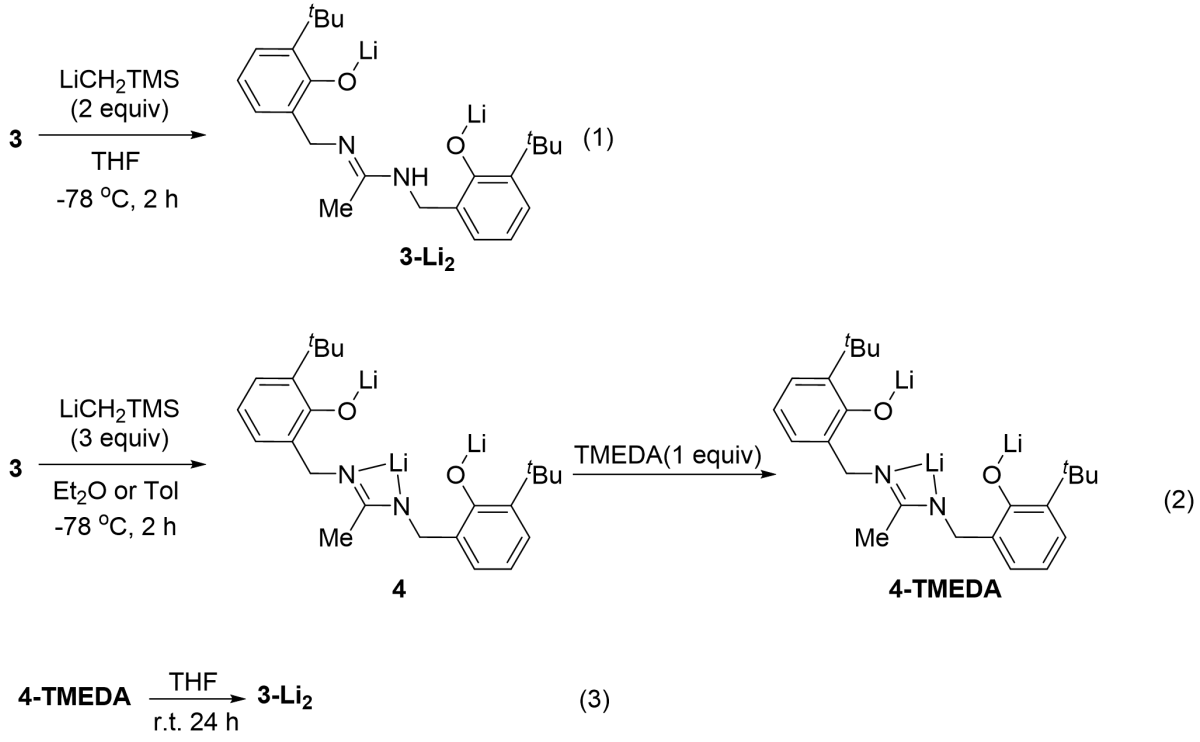
Scheme S1 Proposed mechanism for the conversion of 2 to 3:



The aryloxy group in compound 2 has nucleophilic character on the oxygen atom, which can attack the activated C=C bond generating the benzoxazine intermediate.[S3, S4] The benzoxazine will react with one equivalent of **1** to produce ligand **3**. However, in preliminary attempts, we could only get a trace amount of ligand **3**. The amide and imide derivatives were main products at almost 1 : 1 ratio. We hypothesized that acetone, the byproduct of C-C bond cleavage, would react with **1** readily to produce imide in the presence of Lewis acid, which inhibited the nucleophilic substitution step. Moreover, H_2O from the react and condensation of acetone with **1** would also react with the benzoxazine intermediate to produce the amide. After understanding these side reactions, we achieved our goal by adding two equivalents of **1** and strictly drying the implementation of the substrate. A simple mechanistic model is proposed in Scheme S2. Protonation of the carbonyl group by TsOH (p-toluene sulfonic acid) enhances the

electrophilicity of the enamineketone fragment in **2**. Then the intramolecular nucleophilic addition of intermediate **4a** would produce adduct **4b**. Next, C-C bond cleavage would generate the intermediate **4d** in a series of equilibria involving keto-enol tautomerism and prototropy. Finally, the nucleophilic substitution would proceed smoothly to afford ligand **3** in moderate yield. In addition, the intermolecular nucleophilic addition of **4a** with H_2O would produce an adduct **4b'**. Byproduct **5** would finally be generated along with **6**.

Scheme S2 Deprotonation of 3:



Initial deprotonation of **3** was conducted in THF and only 3-Li_2 can be observed in ^{1}H NMR in spite of three or excess equivalents of based added. However, when the solvent is Et_2O and Tol, the deprotonation reaction went sweetly to afford desired lithium salt, **4**.

4 was prepared by deprotonation of **3** (191.3 mg, 1.0 equiv, 0.5 mmol) with $LiCH_2TMS$ (141.3 mg, 3.0 equiv, 1.5 mmol) in Et_2O and Tol. After stirring in a low temperature (-78 ^{o}C) for two hours, the solvent was removed under vacuum to provide a white solid, **4** (> 95 %). The ^{1}H NMR spectrum of **4** was confused. However, the spectrum of **4-TMEDA**

was identifiable in the presence of 1 equivalent of TMEDA. The crystal of **4-TMEDA** was obtained in Et_2O at room temperature. ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 1.61 (s, 18H, ^{t}Bu), 1.89 (br s, 16H, TMEDA), 1.92 (s, 3H, CH_3), 3.80 (d, J = 11 Hz, 2H, CH_2), 3.36 (d, J = 11 Hz, 2H, CH_2), 6.53 (t, J = 15 Hz, 2H, *Ph*), 6.81 (dd, J = 7 Hz, J = 2 Hz, 2H, *Ph*), 7.30 (dd, J = 7 Hz, J = 2 Hz, 2H, *Ph*). ^{13}C NMR (125 MHz, C_6D_6): δ 13.2, 31.0, 35.5, 46.4, 51.8, 57.0, 114.5, 126.9, 128.0, 129.5, 138.5, 164.9, 175.7. FT-IR (KBr pellet, cm^{-1}): 2953 (s), 2909 (w), 1422 (s), 1226 (s), 870 (s), 746 (s), 682 (s), 620 (s).

X-Ray Crystallography

Figure S1. ORTEP drawing of **4-TMEDA** with 30% thermal ellipsoids. H atoms are omitted for clarity. Selected atom distances (Å) and angles (deg): C1-N1 1.3284(17); C1-N2 1.3286(17); C1-C2 1.5177(17); N1-C1-N2 116.81(11).

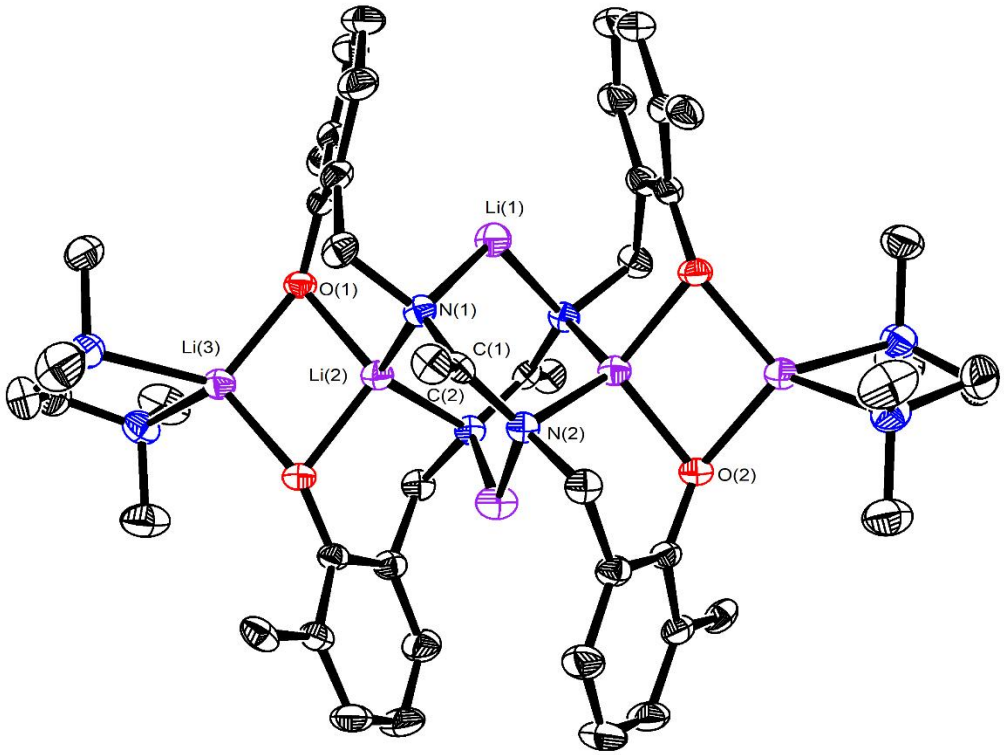


Table S1. Crystal data and structure refinement for **4-TMEDA**.

	4-TMEDA
CCDC No.	2222930
Formula	$C_{30}H_{47}Li_3N_4O_2$
Formula weight	516.53
Temp. (K)	180.00(10)
Crystal system	monoclinic
Space group	C2/c
***a* (Å)**	25.2159(6)
***b* (Å)**	14.3624(4)
***c* (Å)**	17.5594(4)
***α*(°)**	90
***β*(°)**	91.260(2)
***γ*(°)**	90
***V* [Å^3]**	6357.8(3)
Z	8
ρ_{calcd}(g·cm^{-3})	1.079
μ(mm^{-1})	0.066
***F*(000)**	2240.0
Collected data	43781
Unique data	7292 [R_{int} = 0.0252]
GOF on F^2	1.052
Final *R* indexes [I > 2σ(I)]	R_1 = 0.0489, wR_2 = 0.1498
***R* indexes (all data)**	R_1 = 0.0571, wR_2 = 0.1554
Completeness	0.999

Figure S2. ORTEP drawing of **5-Ti** with 30% thermal ellipsoids. H atoms, CH_3 groups of the ^{t}Bu substituents and solvents have been omitted for clarity. Selected atom distances (Å) and angles (deg): C1-N1 1.391(3); C1-N2 1.290(3); C1-C2 1.494(3); Ti1'-N1 2.208(2); Ti1'-N2 2.0692(18); Ti1'-Cl1' 2.3131(7); Ti1'- O2 1.8192(18); Ti1-O1' 1.8150(15); Ti1'-Ti1 3.3905(8); N1-C1-N2 110.37(19); N1'-Ti1'-Cl1' 164.32(5).

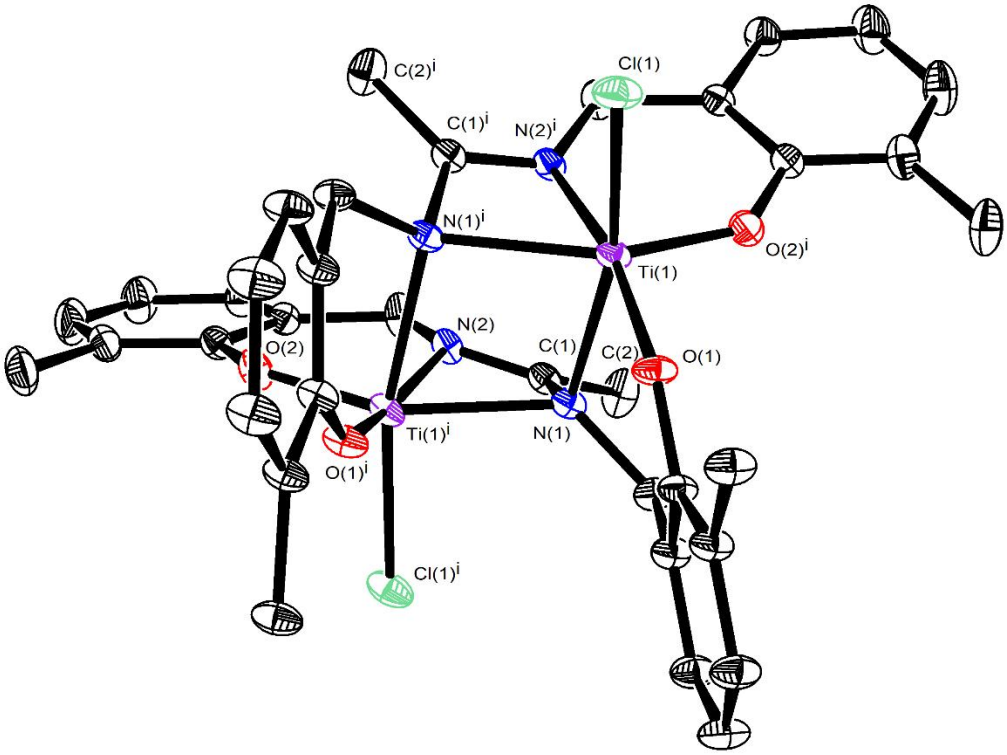


Table S2. Crystal data and structure refinement for **5-Ti**.

	5-Ti
CCDC No.	2222254
Formula	$C_{55}H_{73}Cl_2N_4O_5Ti_2$
Formula weight	1036.87
Temp. (K)	180.00(10)
Crystal system	orthorhombic
Space group	Pcca
***a* (Å)**	27.7408(8)
***b* (Å)**	16.6115(4)
***c* (Å)**	24.3585(7)
***α*(°)**	90
***β*(°)**	90
***γ*(°)**	90
***V* [Å^3]**	11224.8(5)
Z	8
ρ_{calcd}(g·cm^{-3})	1.227
μ(mm^{-1})	0.427
***F*(000)**	4392.0
Collected data	49340
Unique data	12844 [R_{int} = 0.0289]
GOF on F^2	1.025
Final *R* indexes [I > 2σ(I)]	R_1 = 0.0525, wR_2 = 0.1506
***R* indexes (all data)**	R_1 = 0.0662, wR_2 = 0.1588
Completeness	0.997

Figure S3. ORTEP drawing of **5-Zr** with 30% thermal ellipsoids. H atoms, CH_3 groups of the ^{t}Bu substituents and solvents have been omitted for clarity. Selected atom distances (Å) and angles (deg): C1-N1 1.336(2); C1-N2 1.337(2); C1-C2 1.489(2); Zr1-N1 2.3887(12); Zr1-N2 2.3200(12); Zr1-Cl1 2.4689(4); Zr1-O1 1. 970(1); Zr1-O2 1.9711(10); Zr1-Zr1' 3.2231(3); O1-Zr1-O2 103.01(5).

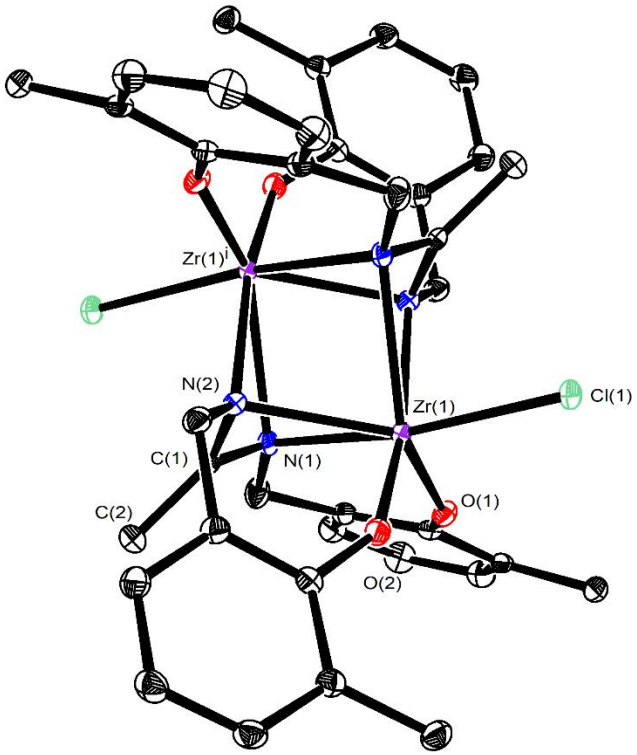


Table S3. Crystal data and structure refinement for **5-Zr**.

	5-Zr
CCDC No.	2222931
Formula	$C_{48}H_{62}Cl_2N_4O_4Zr_2$
Formula weight	1012.35
Temp. (K)	179.99(10)
Crystal system	triclinic
Space group	P-1
***a* (Å)**	12.3616(3)
***b* (Å)**	13.1320(3)
***c* (Å)**	16.7306(4)
***α*(°)**	101.875(2)
***β*(°)**	109.119(2)
***γ*(°)**	104.700(2)
***V* [Å^3]**	2354.84(10)
Z	2
ρ_{calcd}**(g·cm^{-3})**	1.428
***μ*(mm^{-1})**	0.603
***F*(000)**	1048.0
Collected data	41430
Unique data	10762 [R_{int} = 0.0281]
GOF on F^2	1.063
Final *R* indexes [I > 2σ(I)]	R_1 = 0.0240, wR_2 = 0.0638
***R* indexes (all data)**	R_1 = 0.0273, wR_2 = 0.0649
Completeness	0.998

Figure S4. ORTEP drawing of **5-Hf** with 30% thermal ellipsoids. H atoms, CH_3 groups of the ^{t}Bu substituents and solvents have been omitted for clarity. Selected atom distances (Å) and angles (deg): C1-N1 1.385(4); C1-N2 1.2984(2); C1-C2 1.497(4); Hf1-N1 2.340(2); Hf1-N2 2.224(2); Hf1-Cl1 2.4489(7); Hf1-O1 1. 952(2); Hf1-O2 1.9515(19); Hf1- Hf1' 3.4620(2); O1-Hf1-O2
104.64(9).

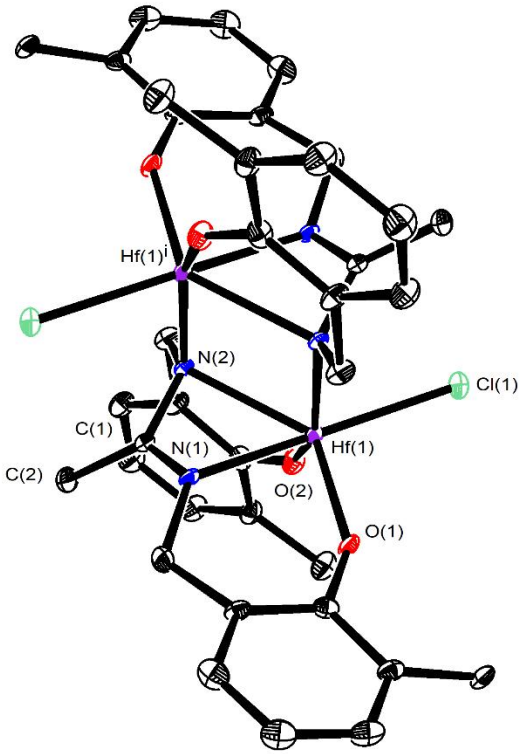


Table S4. Crystal data and structure refinement for **5-Hf**.

	5-Hf
CCDC No.	2222935
Formula	$C_{48}H_{62}Cl_2Hf_2N_4O_4$
Formula weight	1186.89
Temp. (K)	180.00(10)
Crystal system	triclinic
Space group	P-1
***a* (Å)**	12.2507(2)
***b* (Å)**	13.1833(2)
***c* (Å)**	16.8154(2)
***α*(°)**	100.1710(10)
***β*(°)**	109.6060(10)
***γ*(°)**	103.6480(10)
***V* [Å^3]**	2387.07(6)
Z	2
ρ_{calcd}**(g·cm^{-3})**	1.651
***μ*(mm^{-1})**	4.504
***F*(000)**	1176.0
Collected data	62891
Unique data	10906 [R_{int} = 0.0742]
GOF on F^2	1.025
Final *R* indexes [I > 2σ(I)]	R_1 = 0.0296, wR_2 = 0.0711
***R* indexes (all data)**	R_1 = 0.0325, wR_2 = 0.0724
Completeness	0.999

Figure S5 ORTEP drawing of **6** with 30% thermal ellipsoids. Hydrogen atoms, lithium and solvents have been omitted for clarity. Selected atom distances (Å) and angles (deg): C1-N1 1.335(4); C1-N2 1.337(4); Hf1-N1 2.219(3); Hf1-N3 2.236(3); Hf1-N6 2.255(3); Hf2-N2 2.223(3); Hf2-N3 2.245(3); Hf2-N6 2.259(3); Hf1-O1 1.939(2); Hf2-O2 1.945(2); Hf1-Cl1 2.425(18); Hf1-Cl2 2.4153(8); Hf2-Cl3 2.4203(9); Hf2-Cl4 2.4022(9); N3-N4 1.221(4); N4-N5 1.127(4); N6-N7 1.225(4); N7-N8 1.130(4); Hf1-Hf2 3.57762(19); N1-C1-N2 120.5(3); Hf1-N3-Hf2 104.82(10); Hf1-N6-Hf2
105.95(11).

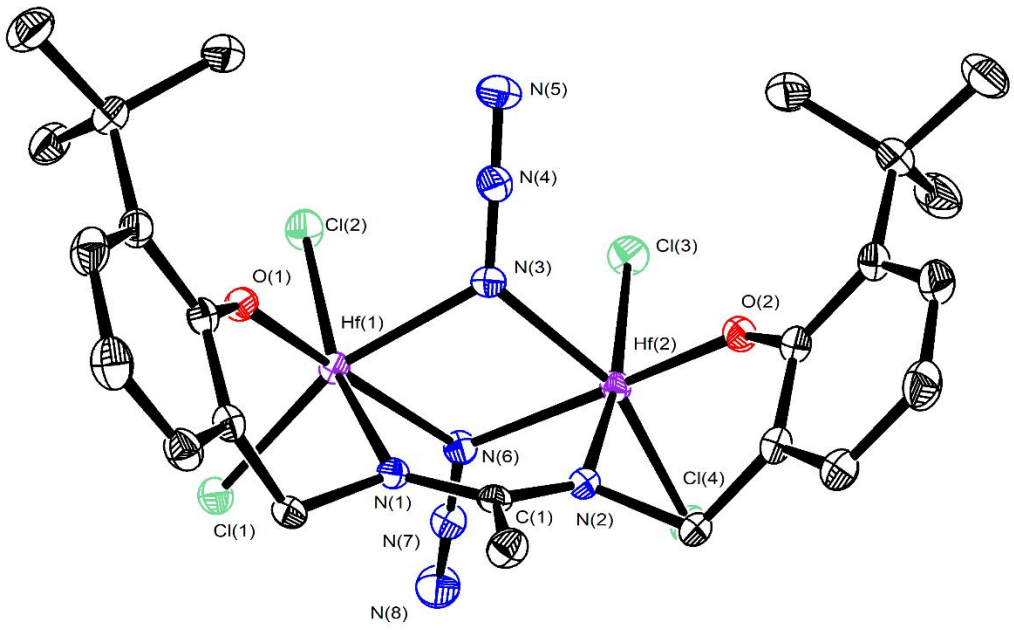


Table S5. Crystal data and structure refinement for **6**.

	6
CCDC No.	2249134
Formula	$C_{40}H_{62}Cl_4Hf_2LiN_8O_6$
Formula weight	1256.709
Temp. (K)	179.99(10)
Crystal system	triclinic
Space group	P-1
***a* (Å)**	12.5852(2)
***b* (Å)**	12.8869(2)
***c* (Å)**	17.0743(2)
***α*(°)**	89.129(1)
***β*(°)**	71.984(1)
***γ*(°)**	72.209(1)
***V* [Å^3]**	2497.84(7)
Z	2
ρ_{calcd}**(g·cm^{-3})**	1.671
***μ*(mm^{-1})**	4.417
***F*(000)**	1243.1
Collected data	60063
Unique data	9843 [R_{int} = 0.0522]
GOF on F^2	1.052
Final *R* indexes [I > 2σ(I)]	R_1 = 0.0231, wR_2 = 0.0538
***R* indexes (all data)**	R_1 = 0.0281, wR_2 = 0.0568
Completeness	1

NMR spectra

Figure S6. ^{1}H NMR spectrum of **1** in $CDCl_3$.

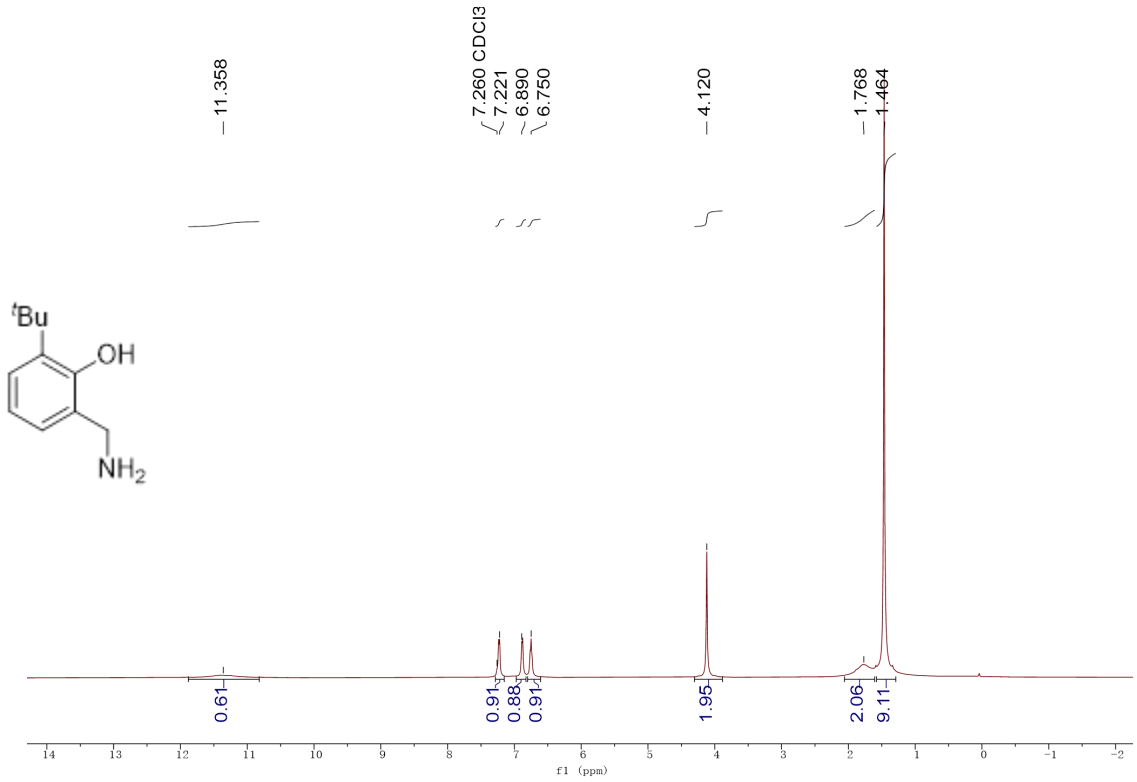


Figure S7. ^{13}C NMR spectrum of **1** in $CDCl_3$.

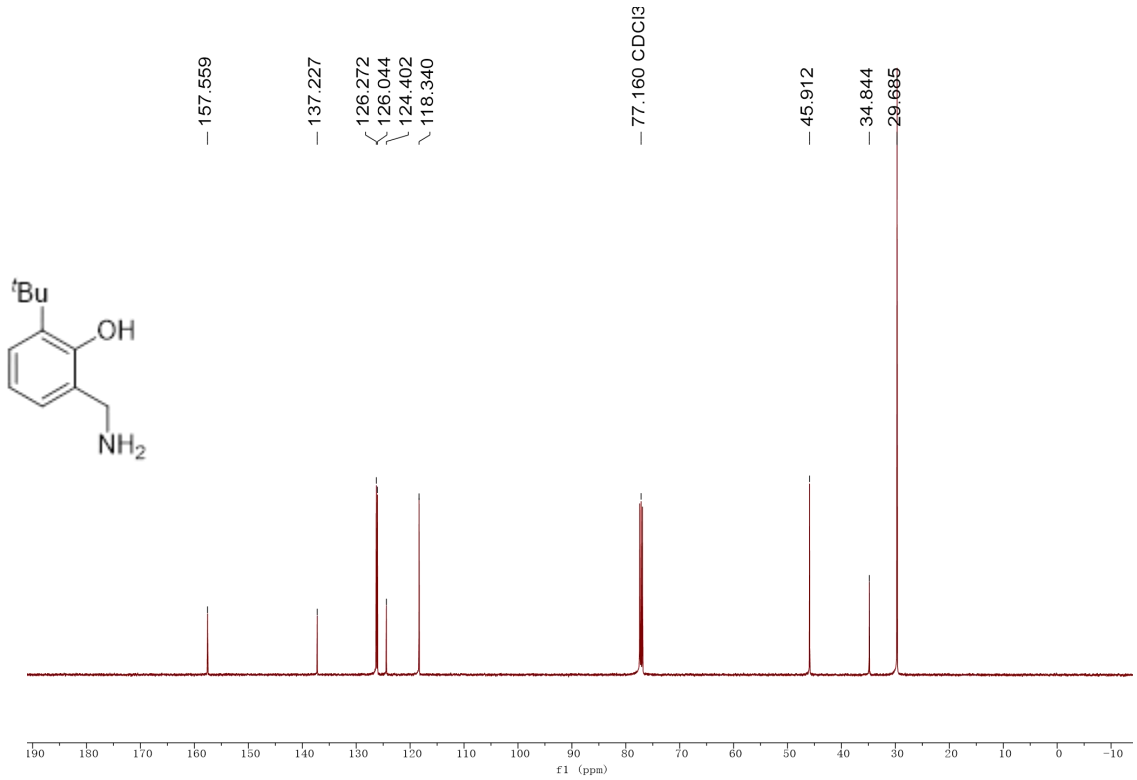


Figure S8. ^{1}H NMR spectrum of **2** in $CDCl_3$.

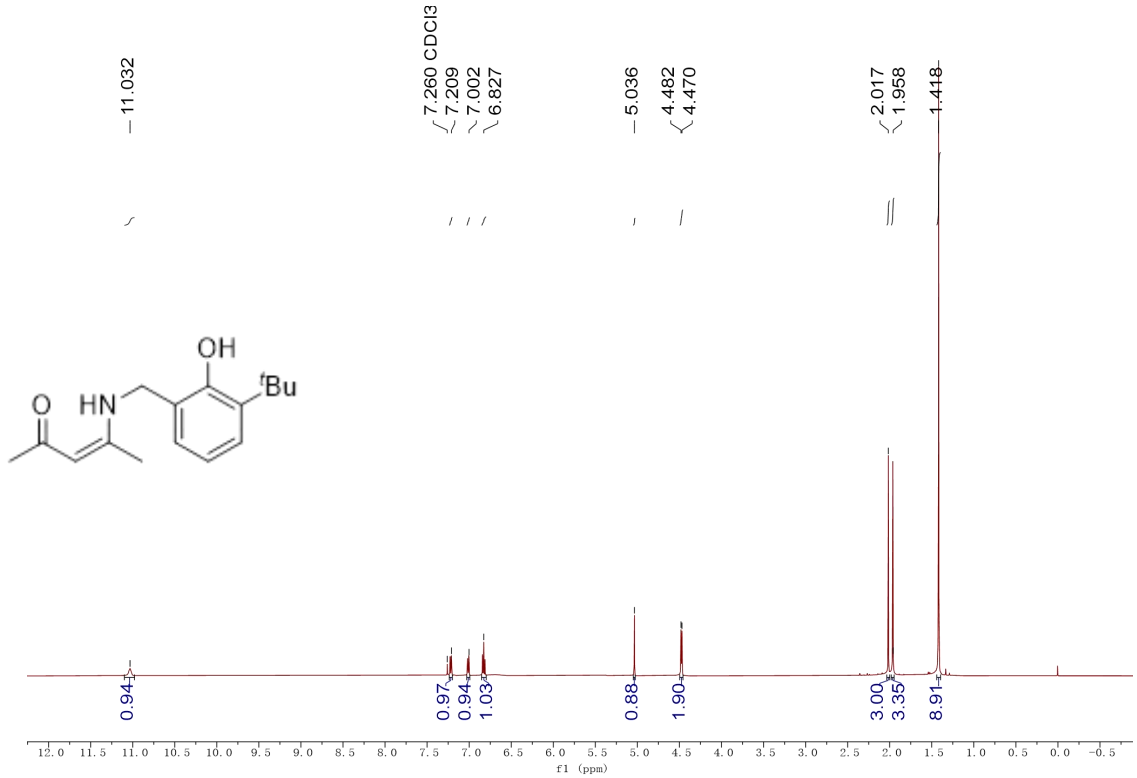


Figure S9. ^{13}C NMR spectrum of **2** in $CDCl_3$.

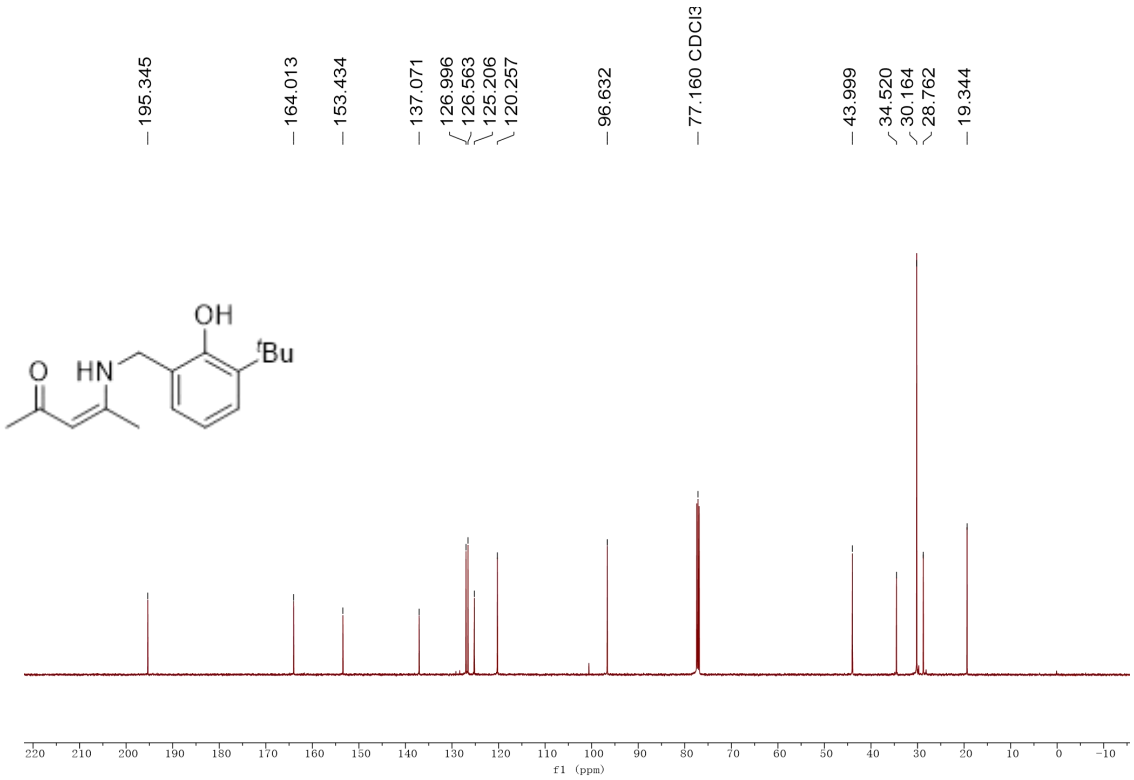


Figure S10. ^{1}H NMR spectrum of ligand **3** in DMSO-d_6.

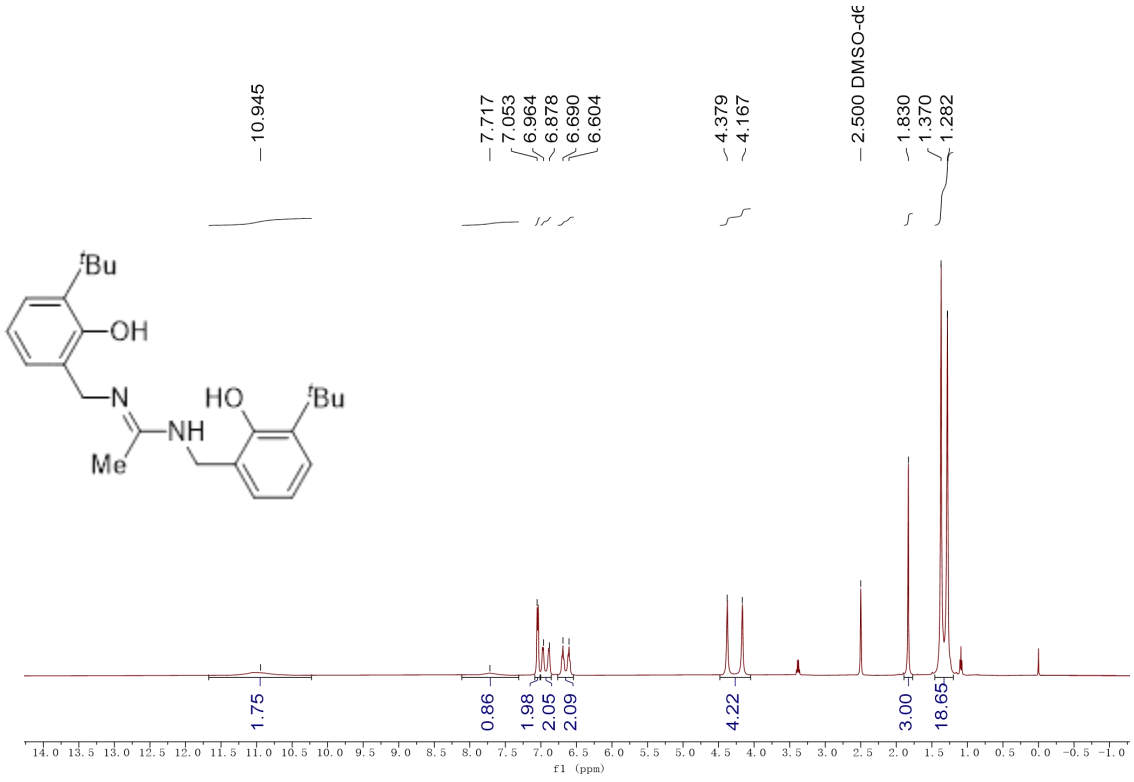


Figure S11. ^{13}C NMR spectrum of ligand **3** in DMSO-d_6.

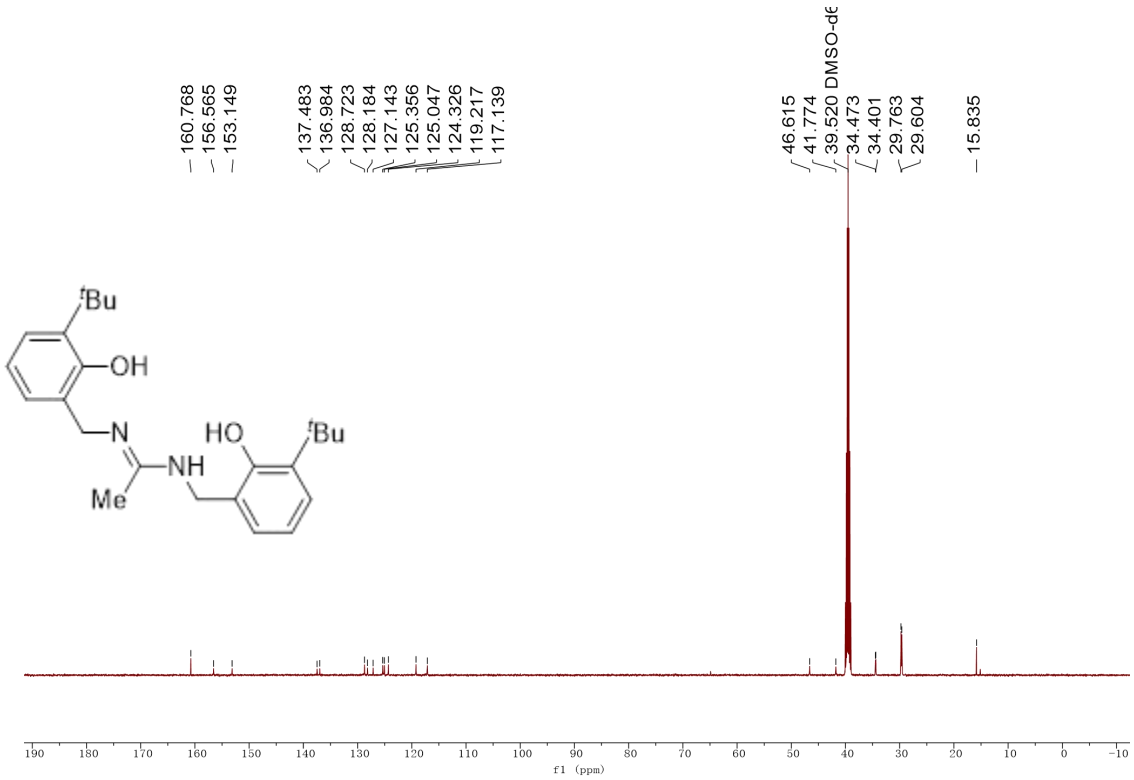


Figure S12. ^{1}H NMR spectrum of complex **4-TMEDA** in C_6D_6.

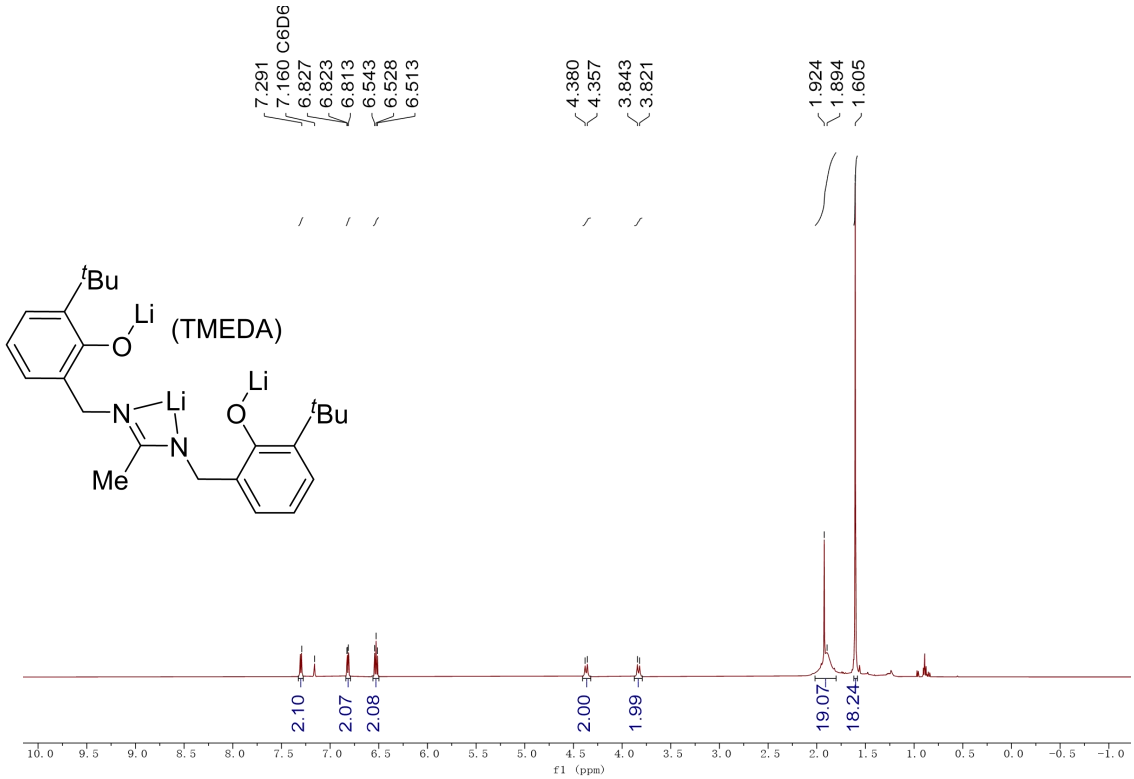


Figure S13. ^{13}C NMR spectrum of complex **4-TMEDA** in C_6D_6.

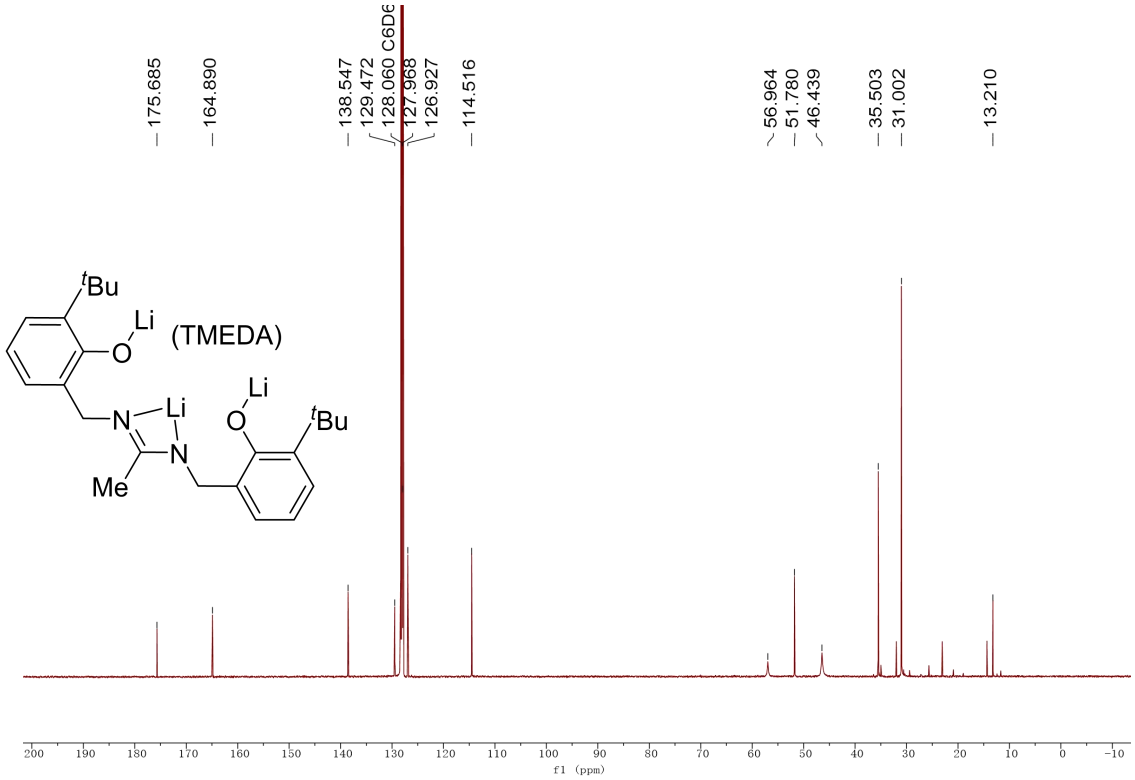


Figure S14. ^{1}H NMR spectrum of complex **3-Li$_2$** in THF-d$_8$.

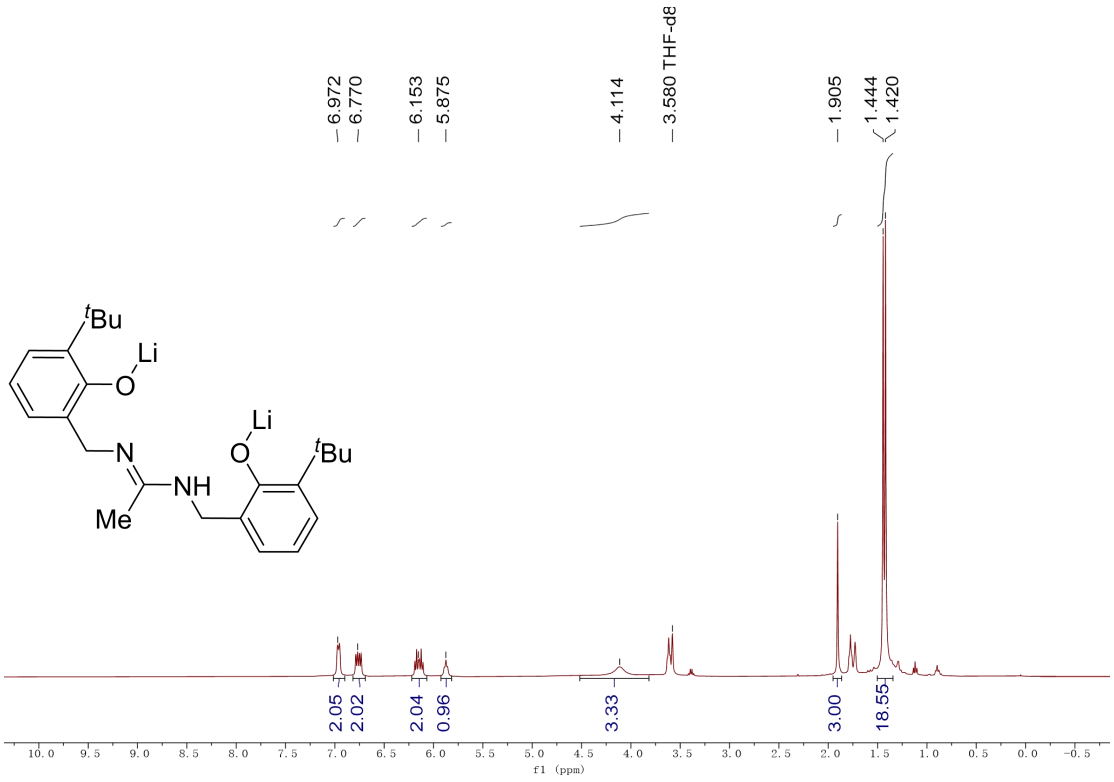


Figure S15. ^{1}H NMR spectrum of complex **4** to **3-Li$_2$** in THF-d$_8$.

(Half of **4** transformed to **3-Li$_2$** after 12 h)

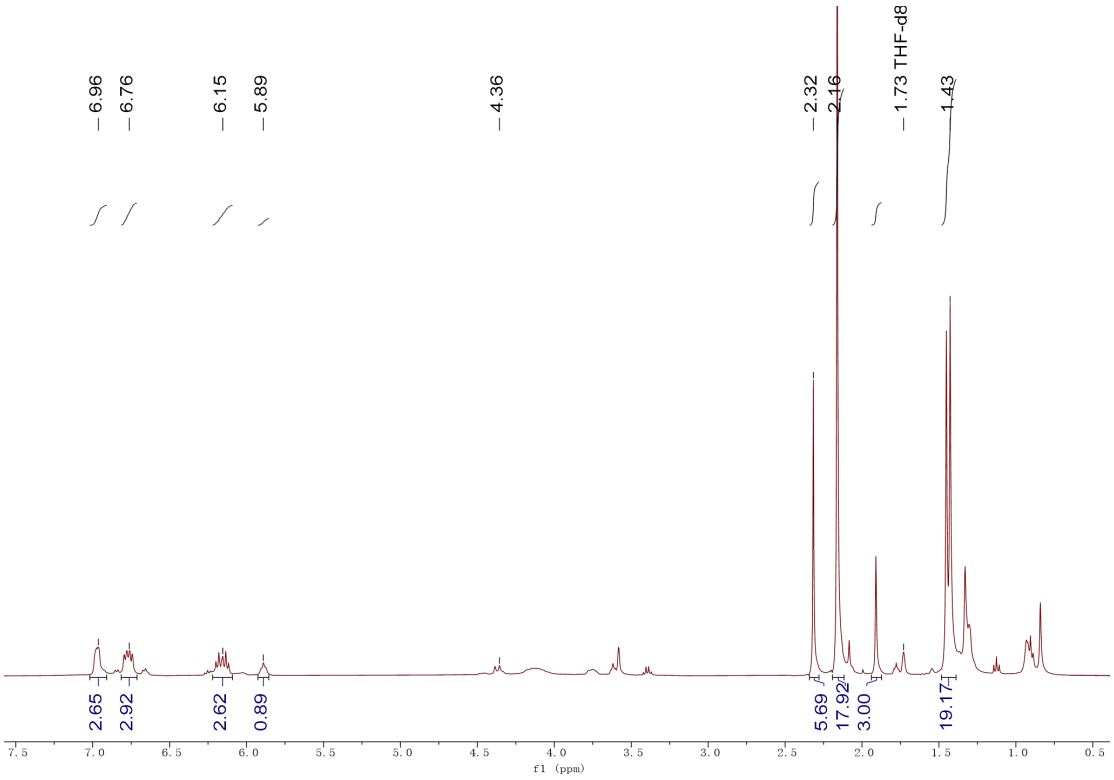


Figure S16. ^{1}H NMR spectrum of complex **5-Ti** in C_6D_6.

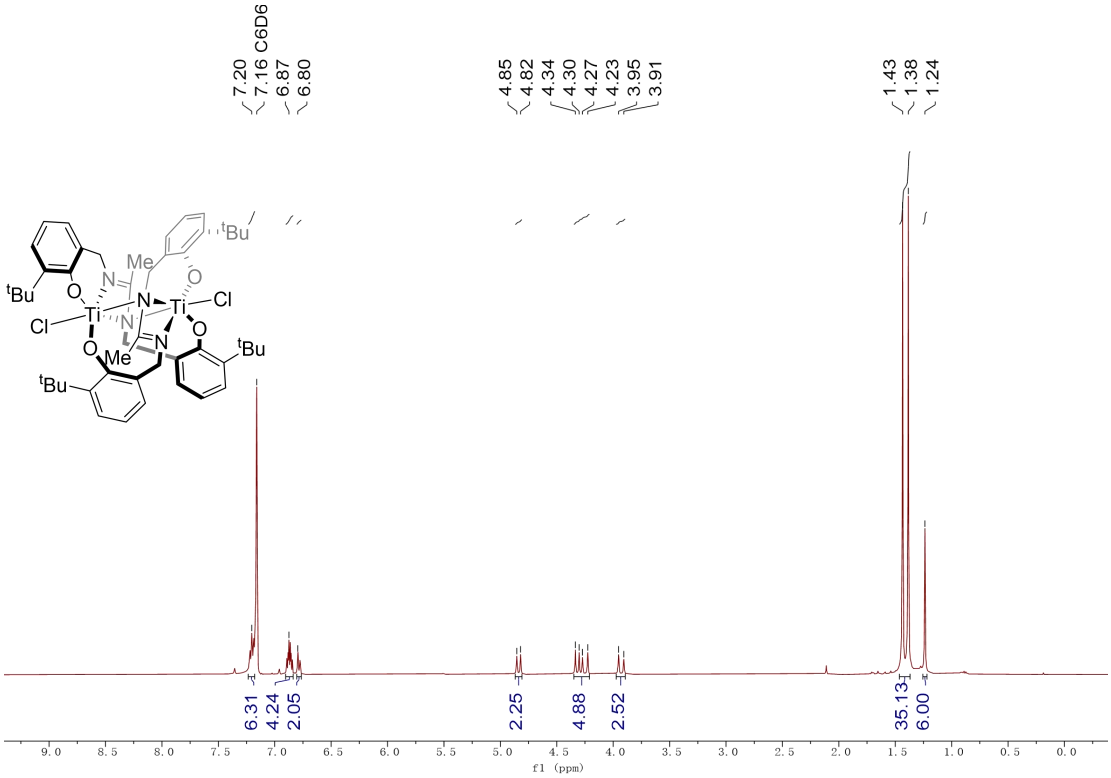


Figure S17. ^{13}C NMR spectrum of complex **5-Ti** in C_6D_6.

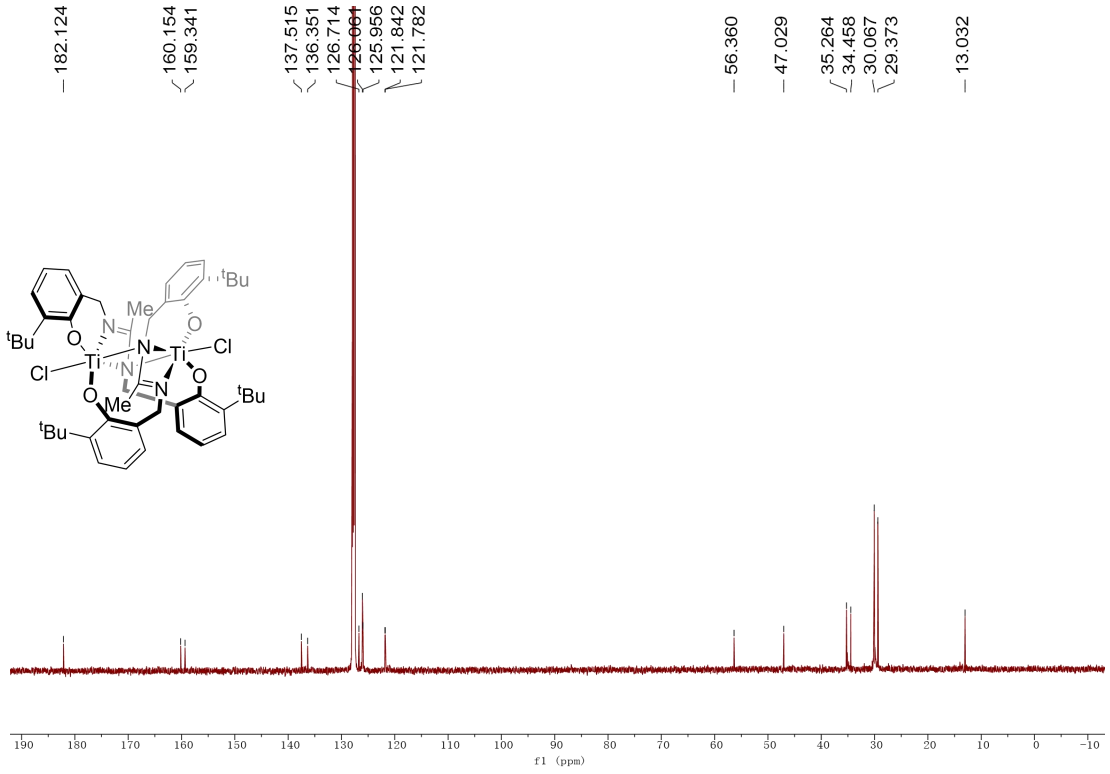


Figure S18. ^{1}H NMR spectrum of complex **5-Zr** in C_6D_6.

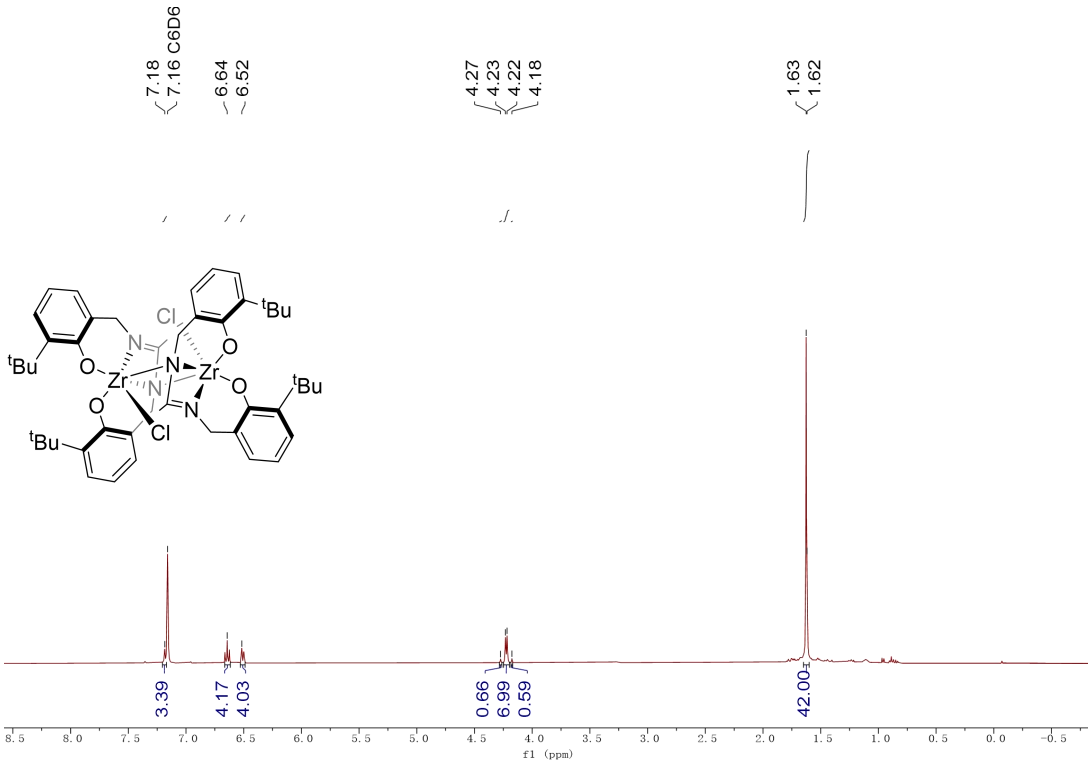


Figure S19. ^{13}C NMR spectrum of complex **5-Zr** in $CDCl_3$.

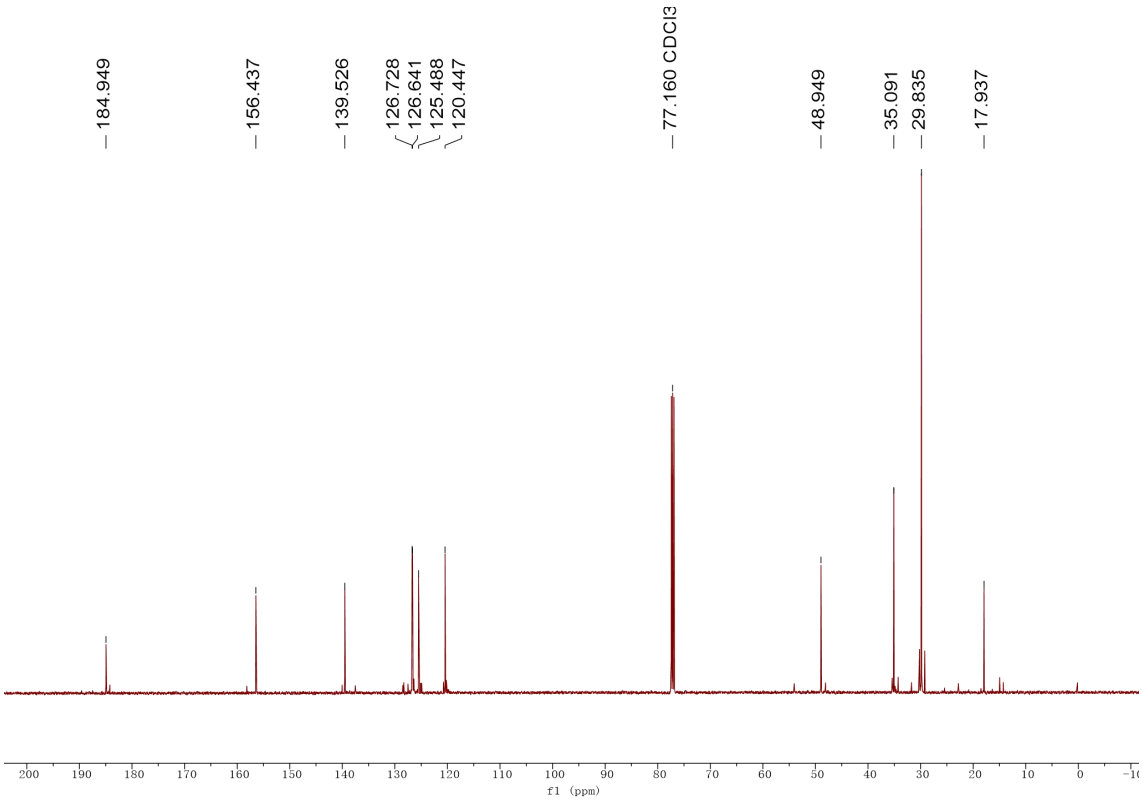


Figure S20. ^{1}H NMR spectrum of complex **5-Hf** in C_6D_6.

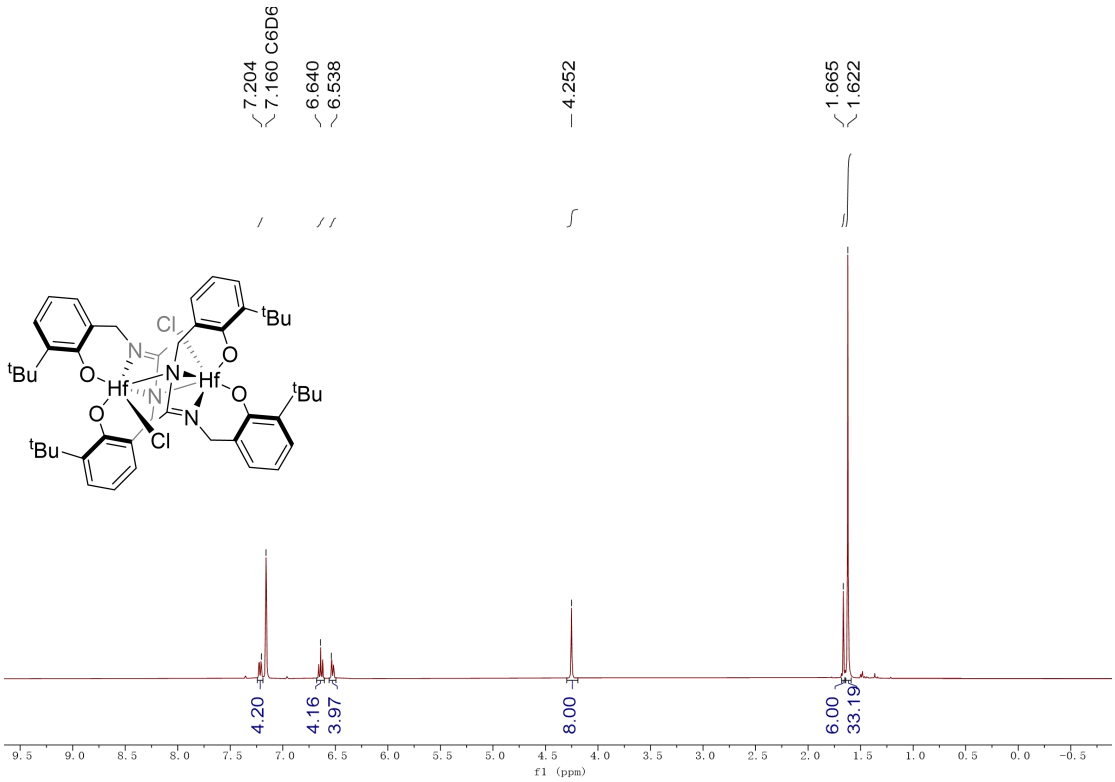


Figure S21. ^{13}C NMR spectrum of complex **5-Hf** in C_6D_6.

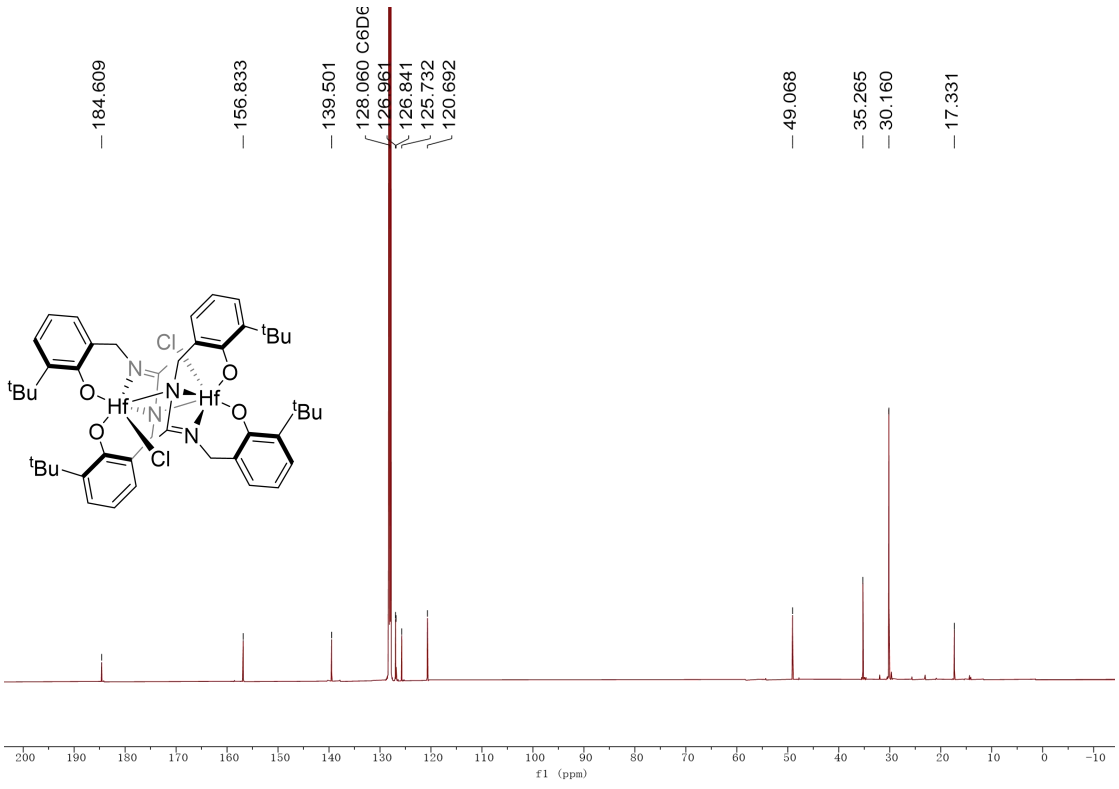


Figure S22. ^{1}H NMR spectrum of complex **6** in THF-d$_8$.

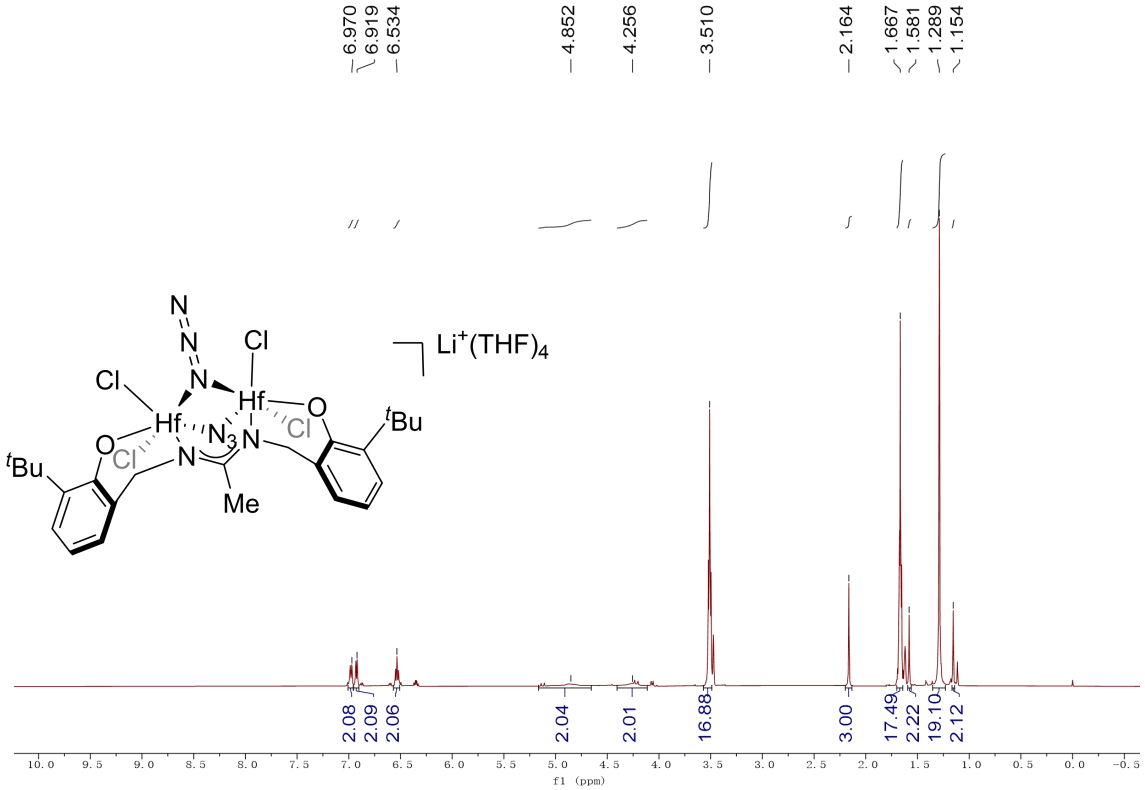


Figure S23. ^{1}H NMR spectrum of complex **6** in $CDCl_3$.

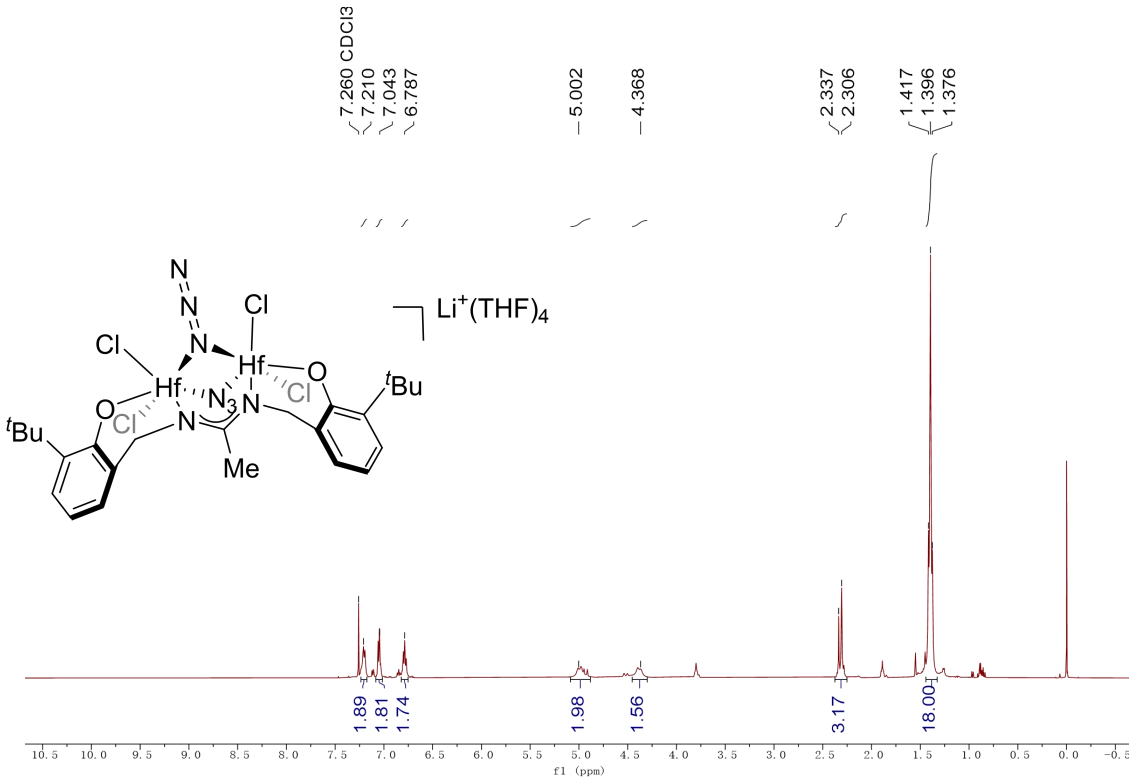


Figure S24. ^{13}C NMR spectrum of complex **6** in $CDCl_3$.

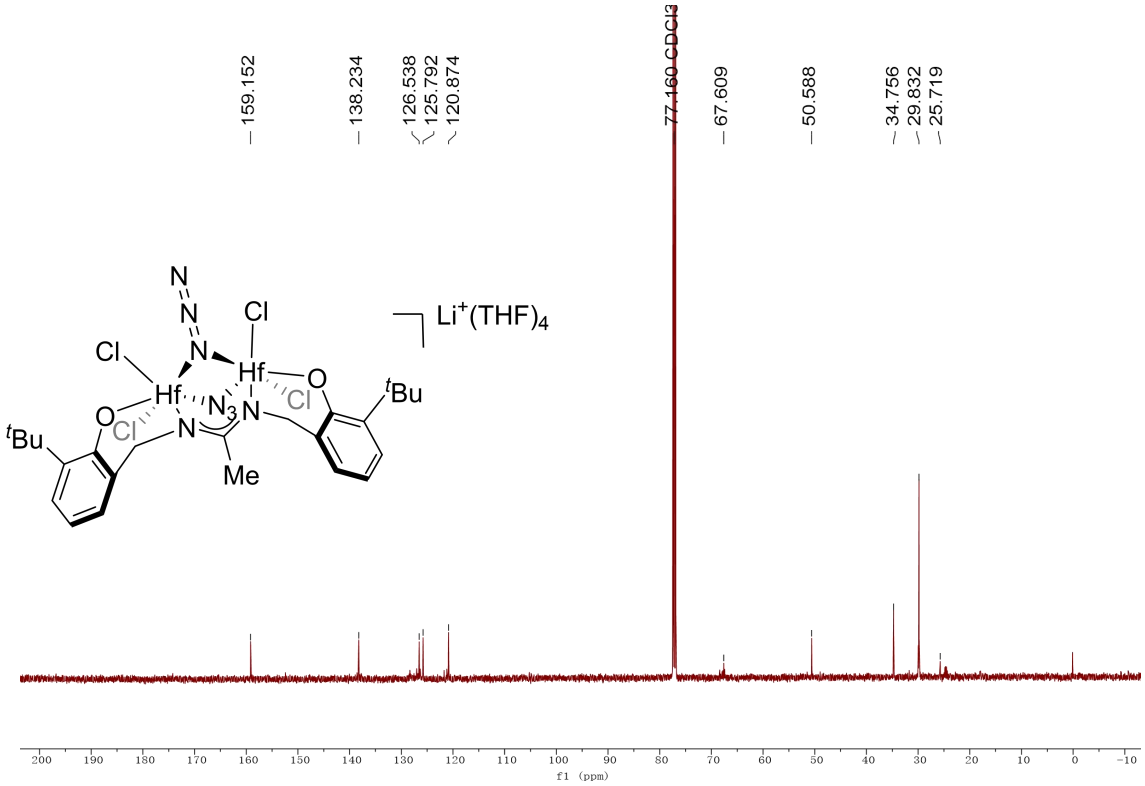


Figure S25. HSQC spectrum of complex **6** in $CDCl_3$.

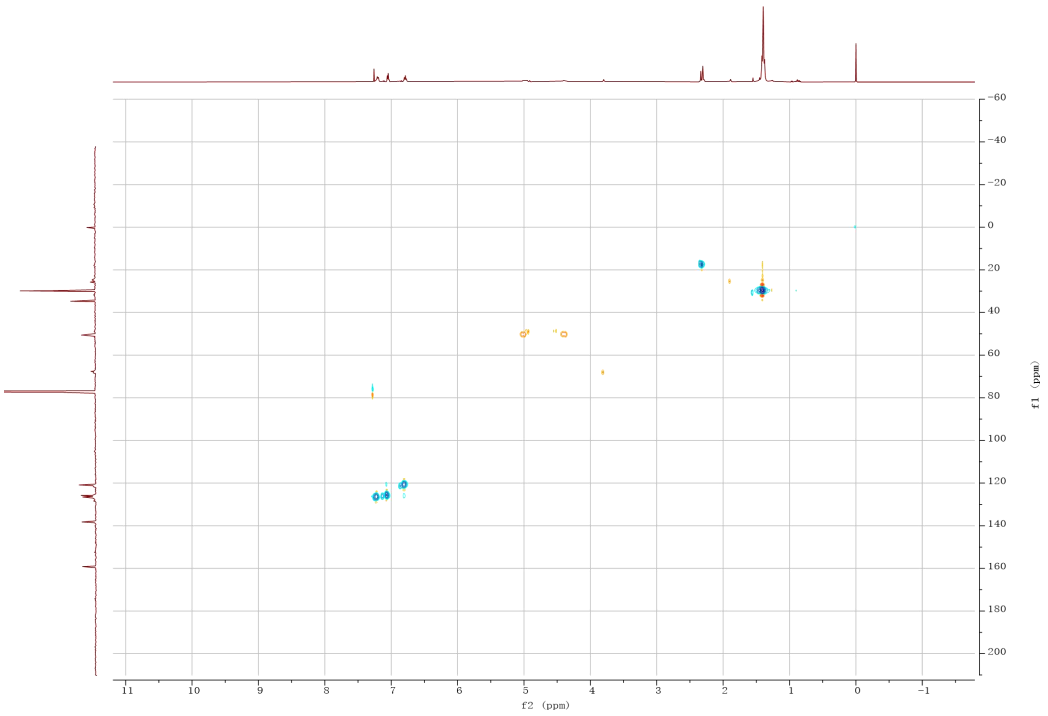
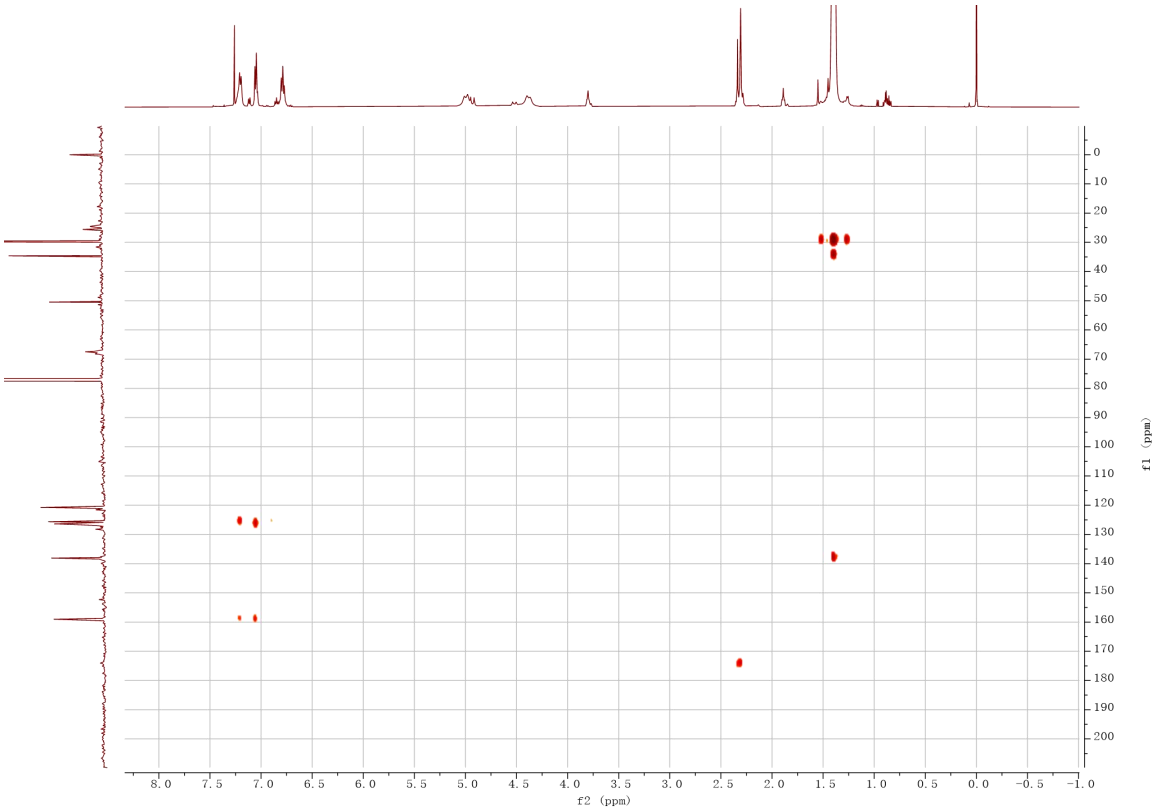


Figure S26. HSBC spectrum of complex **6** in $CDCl_3$.



IR spectra

Figure S27. IR spectrum of **4-TMEDA**.

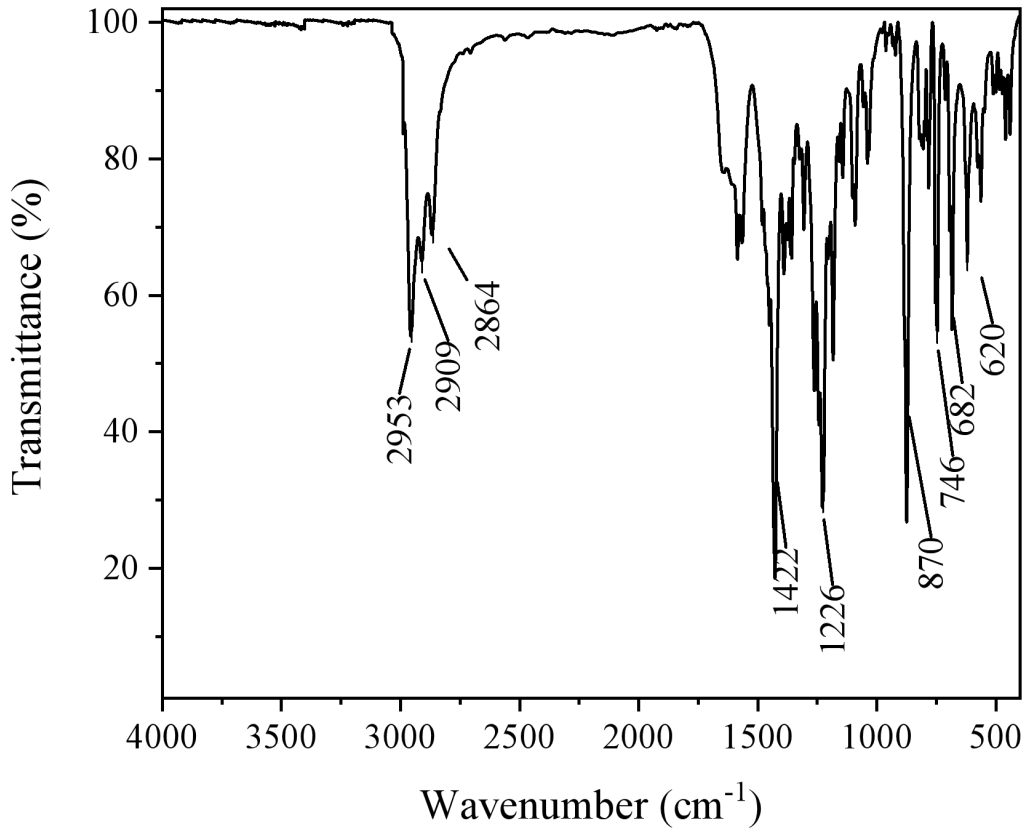


Figure S28. IR spectrum of **5-Ti**.

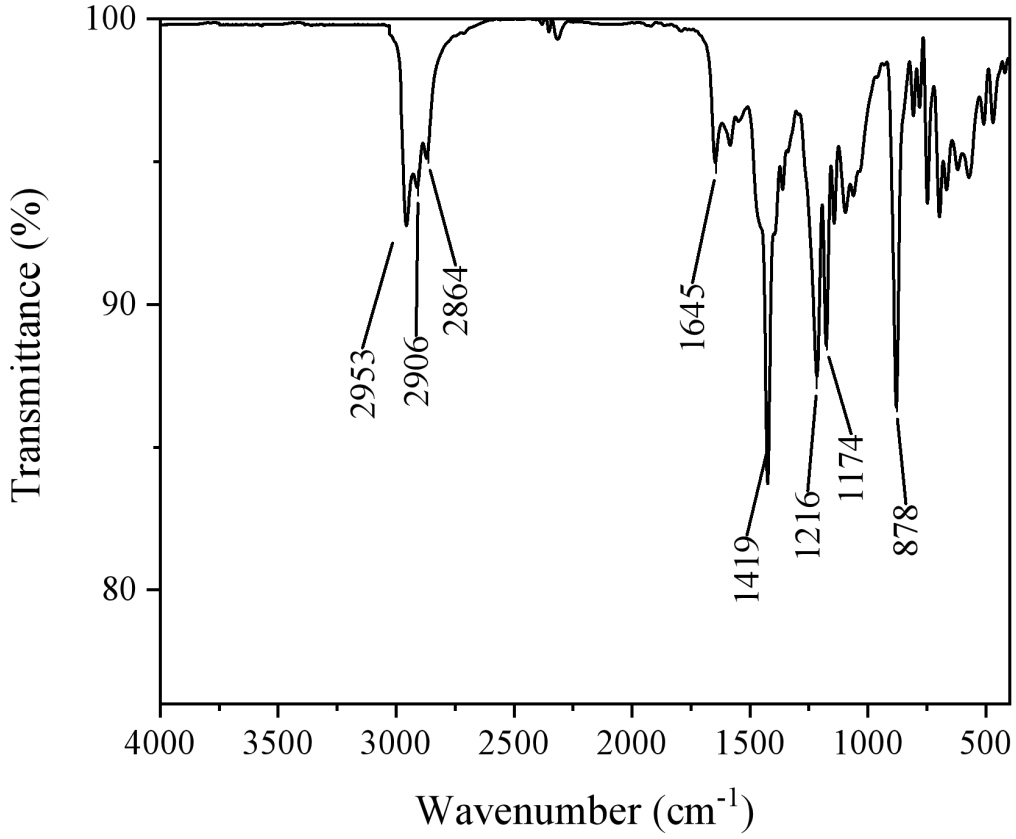


Figure S29. IR spectrum of **5-Zr**.

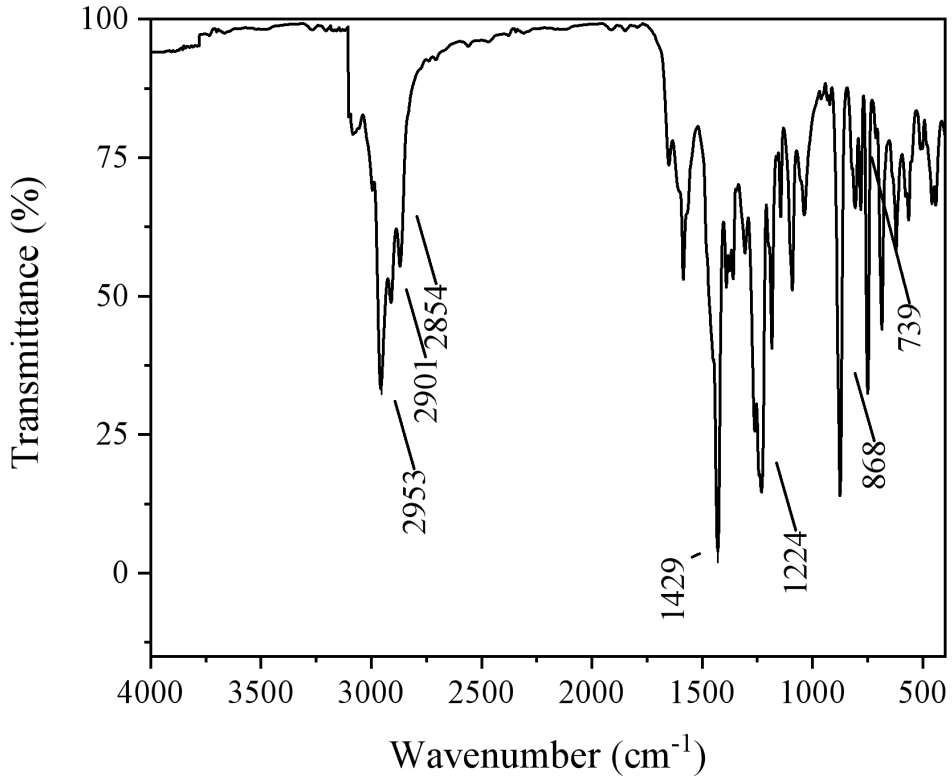


Figure S30. IR spectrum of **5-Hf**.

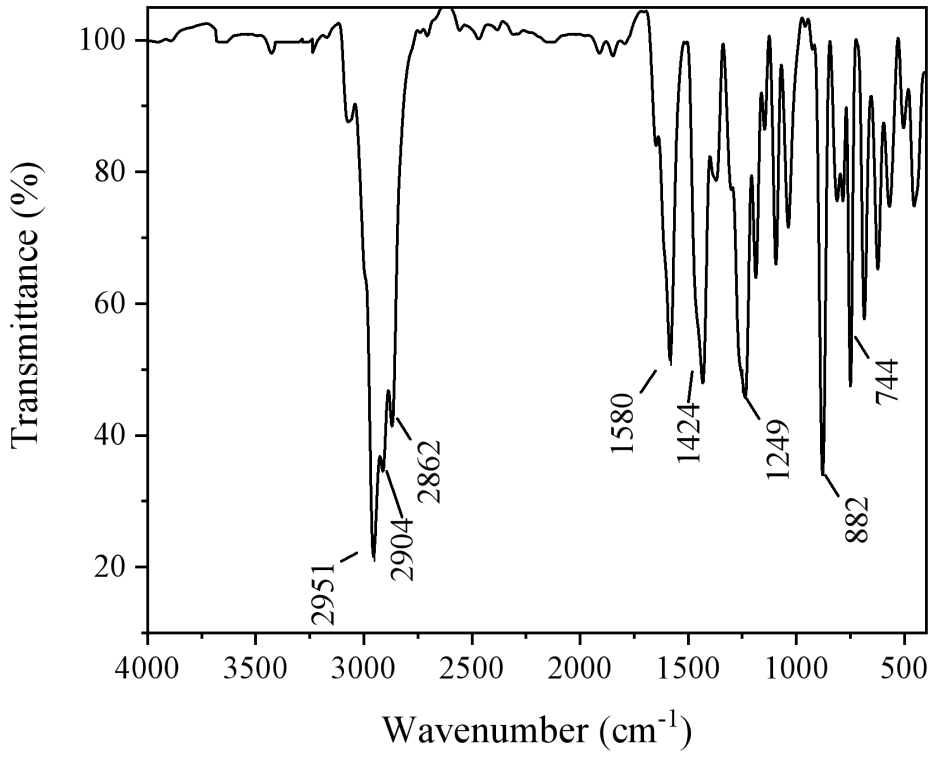
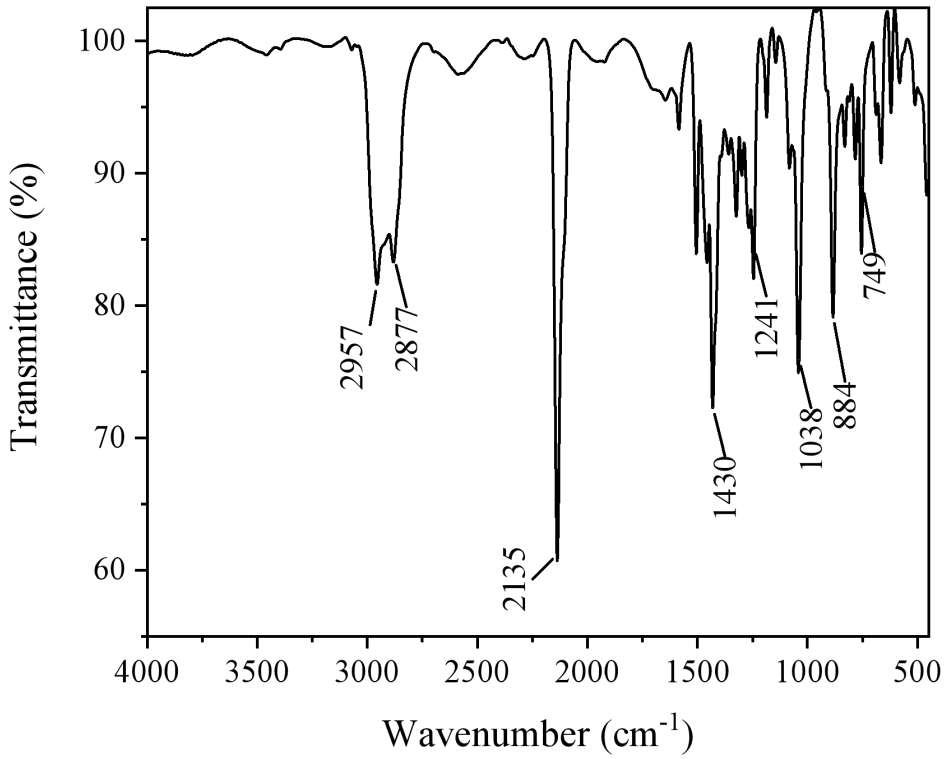


Figure S31. IR spectrum of **6**.



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