Electronic Supplementary Material (ESI) for RSC Advances.


**Supporting Information**

**Title:** Mixed Amido-cyclopentadienyl Group 4 Metal Complexes

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**Contents:**

**Table S1.** Crystallographic data for **5**, **7**, **8**, **8'**

| Compound | 5 | 7 | 8 | 8' |
|---|---|---|---|---|
| **Formula** | $C_{22}H_{33}Cl_2HfN$ | $C_{19}H_{28}Cl_2N_2Ti$ | $C_{19}H_{28}Cl_2N_2Zr$ 1.5($C_7H_8$) | $C_{19}H_{28}Cl_2N_2Zr$ |
| **Cell setting** | orthorhombic | monoclinic | triclinic | triclinic |
| **Space group** | $P2_12_12_1$ | $P\,2_1/c$ | $P$ -1 | $P$ -1 |
| **a (Å)** | 7.5820(4) | 24.5850(16) | 9.0950(4) | 9.1900(4) |
| **b (Å)** | 15.3669(10) | 9.2920(7) | 9.8420(5) | 9.7300(5) |
| **c (Å)** | 20.4961(13) | 17.769(2) | 16.5011(16) | 14.4511(9) |
| **α (°)** | 90 | 90 | 102.455(5) | 88.286(4) |
| **β (°)** | 90 | 94.609(7) | 96.228(5) | 88.435(5) |
| **γ (°)** | 90 | 90 | 91.467(4) | 63.754(4) |
| **Z** | 4 | 8 | 2 | 2 |
| **Volume (Å$^3$)** | 2388.0(3) | 4046.1(6) | 1431.96(17) | 1158.32(11) |
| **Density (g.cm$^{-3}$)** | 1.560 | 1.324 | 1.356 | 1.280 |
| **Crystal size (mm)** | 0.34x0.21x0.19 | 0.26x0.20x0.15 | 0.29x0.20x0.08 | 0.41x0.34x0.24 |
| **Crystal description** | block | block | plate | block |
| **Crystal colour** | colourless | dark red | colourless | colourless |
| **μ (mm$^{-1}$)** | 4.598 | 0.690 | 0.591 | 0.708 |
| **F(000)** | 1112 | 1696 | 610 | 460 |
| **$T_{min}$; $T_{max}$** | 0.474; 0.589 | 0.879; 0.922 | 0.910; 0.967 | 0.805; 0.893 |
| **h; k; l min, max** | -8, 9; -16, 19; -25, 23 | -30, 31; -12, 11; -22, 20 | -10, 11; -12, 11; -20, 21 | -11, 11; -12, 12; -18, 18 |
| **$\theta_{min;\,max}$ (°)** | 4.10; 25.80 | 1.66; 27.50 | 2.26; 26.2 | 2.33; 27.50 |
| **Reflections nr.** | 11106 | 32497 | 10672 | 22110 |
| **- total ($R_{int}$) [a)]** | 10516 (0.0421) | 32411 (0.0692) | 10597 (0.0446) | 21916 (0.0232) |
| **- gt [I>2σ(I)]** | 4258 | 5985 | 4514 | 4750 |
| **Nr. of Parameters** | 248 | 433 | 284 | 232 |
| **Max/min τ/eÅ$^{-3}$** | 0.504; -0.585 | 0.326; -0.385 | 0.452; -0.538 | 0.918; -0.665 |
| **GOF [b)]** | 1.123 | 1.118 | 1.022 | 1.035 |
| **R [c)] / wR [c)]** | 0.0288/0.0530 | 0.0566/0.0958 | 0.0487/0.0972 | 0.0351/0.0829 |

[a)] $R_{int} = \sum |F_o^2 - F_{o,mean}^2| \,/\, \sum F_o^2$; [b)] $S = [\sum(w(F_o^2 - F_c^2)^2) \,/\, (N_{diffr.} - N_{param.})]^{½}$; [c)] Weighting scheme : $w = [\sigma^2(F_o^2) + (w_1P)^2 + w_2P]^{-1}$, where $P = [\max(F_o^2) + 2F_c^2]$, $R(F) = \sum ||F_o| - |F_c|| \,/\, \sum |F_o|$, $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2) \,/\, (\sum w(F_o^2)^2)]^{½}$

**Table S2.** Crystallographic data for **6**, **10, 11, 12, 14**

| Compound | 11 | 12 | 14 | 10 | 6 |
|---|---|---|---|---|---|
| **Formula** | $C_{42}H_{60}Cl_2N_2Zr_2$ | $C_{44}H_{64}Cl_2N_2Zr_2$ | $C_{44}H_{64}Cl_2Hf_2N_2$ | $C_{38}H_{54}Cl_2Hf_2N_4$ | $C_{46}H_{69}N_3Zr$ |
| **Cell setting** | triclinic | monoclinic | monoclinic | triclinic | triclinic |
| **Space group** | *P*-1 | *C*2/c | *C*2/c | *P*-1 | *P*-1 |
| **a (Å)** | 10.2009(5) | 21.2253(6) | 21.2660(3) | 9.2969(7) | 10.5520(9) |
| **b (Å)** | 10.5211(7) | 18.0580(3) | 18.0465(6) | 10.3570(5) | 11.3391(10) |
| **c (Å)** | 10.6140(7) | 11.1202(4) | 11.0391(3) | 11.6491(5) | 19.2680(15) |
| **α (°)** | 113.719(6) | 90 | 90 | 112.212(4) | 89.837(6) |
| **β (°)** | 103.394(5) | 96.141(3) | 95.851(4) | 102.671(6) | 85.731(5) |
| **γ (°)** | 98.566(5) | 90 | 90 | 104.562(4) | 70.379(7) |
| **Z** | 1 | 1 | 4 | 1 | 2 |
| **Volume (Å$^3$)** | 976.34(12) | 4237.8(2) | 4214.48(19) | 941.17(11) | 2164.9(3) |
| **Density (g.cm$^{-3}$)** | 1.439 | 1.370 | 1.653 | 1.755 | 1.159 |
| **Crystal size (mm)** | 0.29x0.19x0.05 | 0.40x0.32x0.28 | 0.33x0.24x0.17 | 0.33x0.25x0.15 | 0.26x0.23x0.08 |
| **Crystal description** | plate | block | block | block | plate |
| **Crystal colour** | orange | orange | yellow | yellow | colourless |
| **μ (mm$^{-1}$)** | 0.702 | 0.650 | 5.082 | 5.685 | 0.286 |
| **F(000)** | 440 | 1824 | 2080 | 488 | 812 |
| **$T_{min}$; $T_{max}$** | 0.877; 0.963 | 0.800; 0.872 | 0.347; 0.554 | 0.346; 0.644 | 0.939; 0.978 |
| **h; k; l min, max** | -13, 13; -13, 13; -13, 13 | -27, 26; -21, 23; -14, 14 | -27, 27; -23, 21; -14, 13 | -12, 12; -13, 13; -15, 15 | -13, 13; -14, 14; -24, 25 |
| **$\theta_{min;\ max}$ (°)** | 2.13; 27.50 | 2.44; 27.50 | 1.48; 27.50 | 2.25; 27.50 | 2.06; 27.50 |
| **Reflections nr.** | 20466 | 17975 | 19301 | 18255 | 43774 |
| **- total ($R_{int}$) [a)]** | 20373 (0.0323) | 17895 (0.0354) | 19227 (0.0458) | 18182 (0.0277) | 43669 (0.0357) |
| **- gt [I>2σ(I)]** | 3929 | 3584 | 3852 | 4076 | 8380 |
| **Nr. of Parameters** | 217 | 226 | 226 | 208 | 451 |
| **Max/min τ/eÅ$^{-3}$** | 0.401; -0.453 | 1.248; -0.678 | 2.622; -1.137 | 1.562; -1.883 | 0.383; -0.326 |
| **GOF [b)]** | 1.093 | 1.128 | 1.126 | 1.088 | 1.114 |
| **R [c)] / wR [c)]** | 0.0274/0.0591 | 0.0558/0.1289 | 0.0365/0.0820 | 0.0237/0.0582 | 0.0377/0.0780 |

[a)] $R_{int} = \sum |F_o^2 - F_{o,mean}^2| / \sum F_o^2$; [b)] $S = [\sum(w(F_o^2 - F_c^2)^2) / (N_{diffr.} - N_{param.})]^{½}$; [c)] Weighting scheme : $w = [\sigma^2(F_o^2) + (w_1P)^2 + w_2P]^{-1}$, where $P = [\max(F_o^2) + 2F_c^2]$, $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2) / (\sum w(F_o^2)^2)]^{½}$

**Table S3.** Crystallographic data for **13**, **15** - **17**

| Compound | 13 | 15 | 16 | 17 |
|---|---|---|---|---|
| **Formula** | $C_{42}H_{60}Cl_2Hf_2N_2$ | $C_{36}H_{50}Cl_2N_4Zr_2$ | $C_{38}H_{54}Cl_2N_4Zr_2$ | $C_{27}H_{38}ClHfN_3$ |
| **Cell setting** | triclinic | triclinic | triclinic | monoclinic |
| **Space group** | *P*-1 | *P*-1 | *P*-1 | $P2_1/c$ |
| **a (Å)** | 10.1859(5) | 10.7960(11) | 9.3661(7) | 10.7501(7) |
| **b (Å)** | 10.5241(9) | 11.405(2) | 10.4020(8) | 9.0630(6) |
| **c (Å)** | 10.6120(7) | 14.398(3) | 11.5359(7) | 27.246(2) |
| **α (°)** | 113.815(5) | 90.892(13) | 111.082(4) | 90 |
| **β (°)** | 103.680(4) | 90.032(11) | 103.324(5) | 102.570(6) |
| **γ (°)** | 98.356(5) | 105.131(12) | 105.615(5) | 90 |
| **Z** | 1 | 2 | 1 | 4 |
| **Volume (Å$^3$)** | 973.38(13) | 1711.1(5) | 940.61(13) | 2590.9(3) |
| **Density (g.cm$^{-3}$)** | 1.741 | 1.537 | 1.448 | 1.586 |
| **Crystal size (mm)** | 0.18x0.15x0.11 | 0.13x0.12x0.12 | 0.39x0.18x0.09 | 0.50x0.18x0.06 |
| **Crystal description** | block | block | block | plate |
| **Crystal colour** | yellow | orange | orange | colourless |
| **μ (mm$^{-1}$)** | 5.498 | 0.797 | 0.728 | 4.149 |
| **F(000)** | 504 | 816 | 424 | 1240 |
| **$T_{min}$; $T_{max}$** | 0.582; 0.764 | 0.937; 0.954 | 0.866; 0.950 | 0.416; 0.845 |
| **h; k; l min, max** | -13, 13; -13, 13; -13, 13 | -12, 13; -13, 13; -17, 17 | -12, 12; -12, 13; -14, 14 | -13, 12; -11, 10; -35, 32 |
| **$\theta_{min;\ max}$ (°)** | 2.14; 27.50 | 1.85; 25.60 | 2.03; 27.50 | 1.94; 27.50 |
| **Reflections nr.** | 19985 | 20105 | 20294 | 21236 |
| **- total ($R_{int}$) [a)]** | 4456 (0.0295) | 6396 (0.0985) | 4314 (0.0559) | 5822 (0.0749) |
| **- gt [I>2σ(I)]** | 4166 | 4748 | 3813 | 4760 |
| **Nr. of Parameters** | 217 | 397 | 208 | 289 |
| **Max/min τ/eÅ$^{-3}$** | 2.763; -2.064 | 2.265; -0.891 | 0.583; -0.608 | 0.978; -1.209 |
| **GOF [b)]** | 1.096 | 1.225 | 1.106 | 1.146 |
| **R [c)] / wR [c)]** | 0.0260/0.0632 | 0.0774/0.1587 | 0.0314/0.0707 | 0.0391/0.0648 |

[a)] $R_{int} = \sum |F_o^2 - F_{o,mean}^2| / \sum F_o^2$; [b)] $S = [\sum(w(F_o^2 - F_c^2)^2) / (N_{diffr.} - N_{param.})]^{½}$ ; [c)] Weighting scheme : $w = [\sigma^2(F_o^2) + (w_1P)^2 + w_2P]^{-1}$, where $P = [\max(F_o^2) + 2F_c^2]$, $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2) / (\sum w(F_o^2)^2)]^{½}$

**Table S4.** Crystallographic data for **3**, **4**

| Compound | 3 | 4 |
|---|---|---|
| **Formula** | $C_{22}H_{33}Cl_2NTi$ | $C_{22}H_{33}Cl_2NZr$ |
| **Cell setting** | Orthorhombic, | Orthorhombic, |
| **Space group** | $P2_12_12_1$ | $P2_12_12_1$ |
| **a (Å)** | 7.5530(4) | 7.607(5) |
| **b (Å)** | 15.4710(11) | 15.343(10) |
| **c (Å)** | 20.2441(14) | 20.501 (6) |
| **α (°)** | 90 | 90 |
| **β (°)** | 90 | 90 |
| **γ (°)** | 90 | 90 |
| **Z** | 4 | 4 |
| **Volume (Å$^3$)** | 2365.6(3) | 2393(2) |
| **Density (g.cm$^{-3}$)** | 1.208 | 1.315 |
| **Crystal size (mm)** | 0.25 × 0.25 × 0.19 | 0.65 × 0.19 × 0.11 |
| **Crystal description** | block | needle |
| **Crystal colour** | yellow | colourless |
| **μ (mm$^{-1}$)** | 0.593 | 0.689 |
| **F(000)** | 912 | 984 |
| **$T_{min}$; $T_{max}$** | 0.866; 0.898 | 0.665; 0.928 |
| **h; k; l min, max** | -9, 8; -19, 18; -21, 25 | -9, 8; -19, 16; -25, 25 |
| **$\theta_{min;\ max}$ (°)** | 4.08; 26.37 | 4.11; 26.37 |
| **Reflections nr.** | 14634 | 18852 |
| **- total ($R_{int}$) [a)]** | 4602 (0.0357) | 4809 (0.0587) |
| **- gt [I>2σ(I)]** | 3919 | 4139 |
| **Nr. of Parameters** | 263 | 224 |
| **Max/min τ/eÅ$^{-3}$** | 0.5218; -0.417 | 0.690; -0.508 |
| **GOF [b)]** | 1.1084 | 1.119 |
| **R [c)] / wR [c)]** | 0.0522/0.1261 | 0.0493/0.1033 |

[a)] $R_{int} = \sum |F_o^2 - F_{o,mean}^2| / \sum F_o^2$; [b)] $S = [\sum(w(F_o^2 - F_c^2)^2) / (N_{diffr.} - N_{param.})]^{½}$ ; [c)] Weighting scheme : $w = [\sigma^2(F_o^2) + (w_1P)^2 + w_2P]^{-1}$, where $P = [\max(F_o^2) + 2F_c^2]$, $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2) / (\sum w(F_o^2)^2)]^{½}$

**Figure S1.** Molecular structure of **3** (ORTEP view, 30% probability level). Hydrogen atoms are omitted (except of H1) for clarity. Selected interatomic distances [Å] and angles [°]: Ti1 N1 1.898(4), Ti1 Cl2 2.2657(18), Ti1 Cl1 2.2707(18), Ti1 Cg1 2.0204(8), N1 Ti1 Cl2 105.57(14), N1 Ti1 Cl1 106.27(15), Cl2 Ti1 Cl1 100.79(9), N1 Ti1 Cg1 112.5(2), Cl2 Ti1 Cg1 117.2(2), Cl1 Ti1 Cg1 113.3(2).

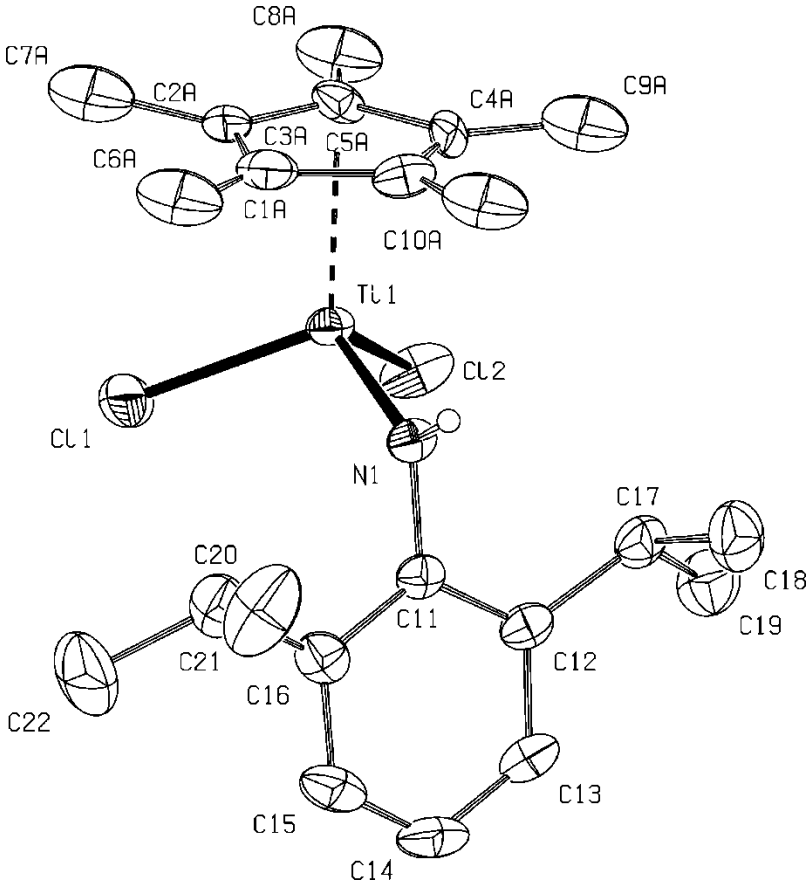

**Figure S2.** Molecular structure of **4** (ORTEP view, 30% probability level). Hydrogen atoms are omitted (except of H1) for clarity. Selected interatomic distances [Å] and angles [°]: Zr1 N1 2.027(6) Zr1 Cl2 2.400(3) Zr1 Cl1 2.404(2) Zr1 Cg1 2.173(3), N1 Zr1 Cl2 108.32(18) N1 Zr1 Cl1 106.91(18) Cl2 Zr1 Cl1 104.27(11) N1 Zr1 Cg1 109.7(5) Cl2 Zr1 C3B 114.6(4) Cl1 Zr1 C3B 112.7(4).

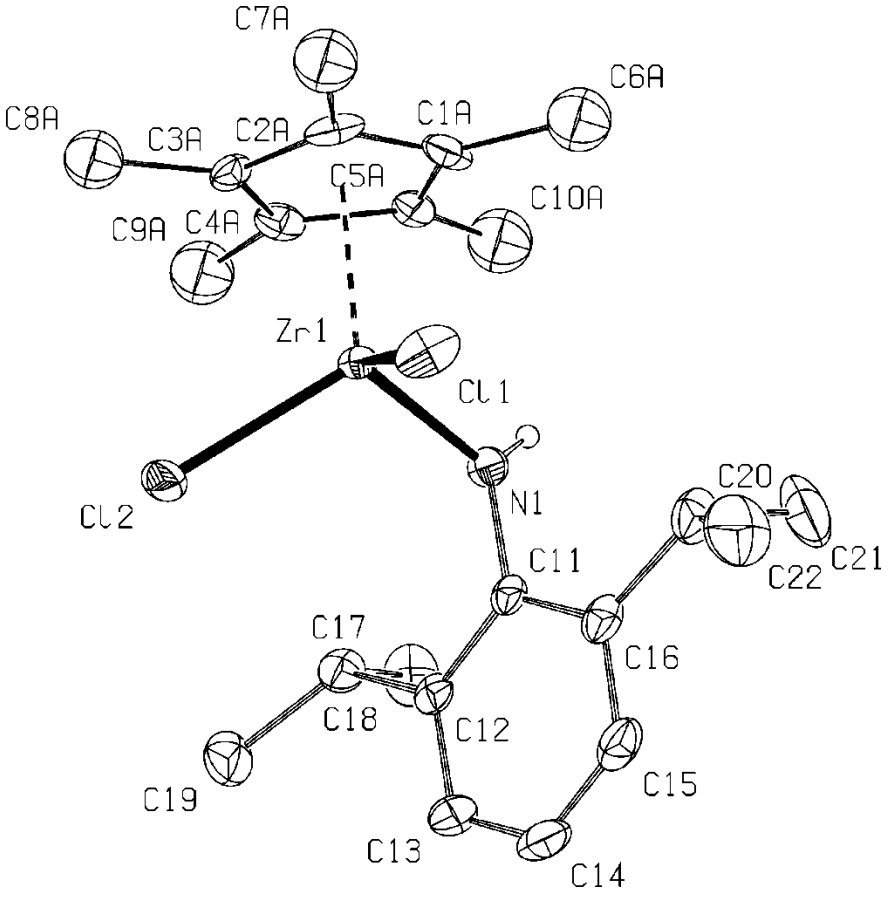

**Figure S3.** Molecular structure of **14** (ORTEP view, 30% probability level, Symmetry code: (a) −*x*+1/2, −*y*+1/2, −*z*). Hydrogen atoms are omitted (except of H1) for clarity. Selected interatomic distances [Å] and angles [°]: Hf1 N1 2.067(5), Hf1 N1a 2.100(5), Hf1 Cl1 2.4040(16), Hf1 Cg1 2.206(4), Hf1 Hf1a 3.070(4); Cg1 Hf1 Cl1 106.66(2), Cg1 Hf1 N1 122.79(3), Cg1 Hf1 N1a 124.58(3), Cg1 Hf1 Hf1a 138.84(3), N1 Hf1 N1a 85.12(18), N1 Hf1 Cl1 108.79(14), N1a Hf1 Cl1 106.80(13), Hf1 N1 Hf1a 94.88(18), C11 N1 Hf1 138.1(4), C11 N1 Hf1a 127.0(4).

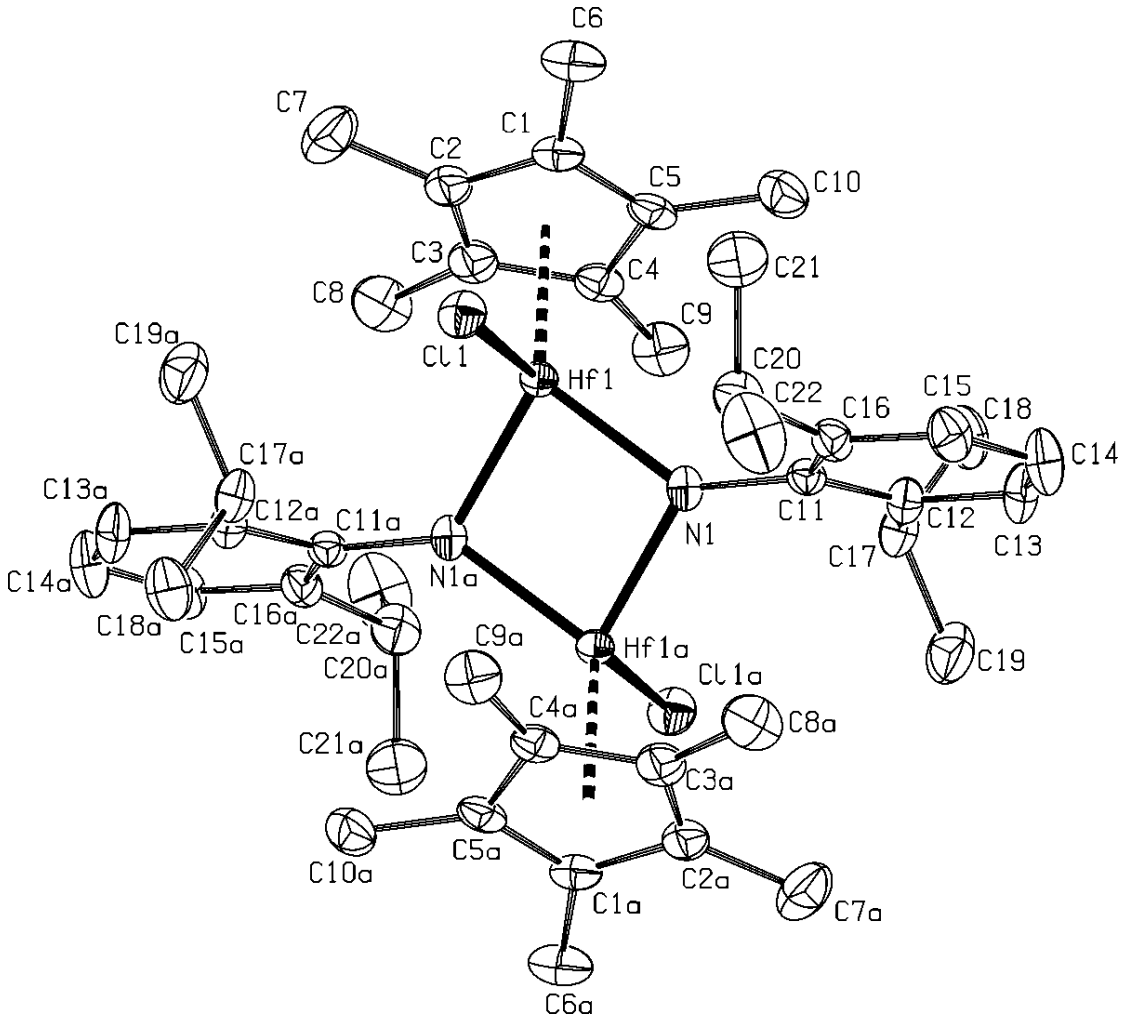

**Figure S4.** Eyring plot for **8**

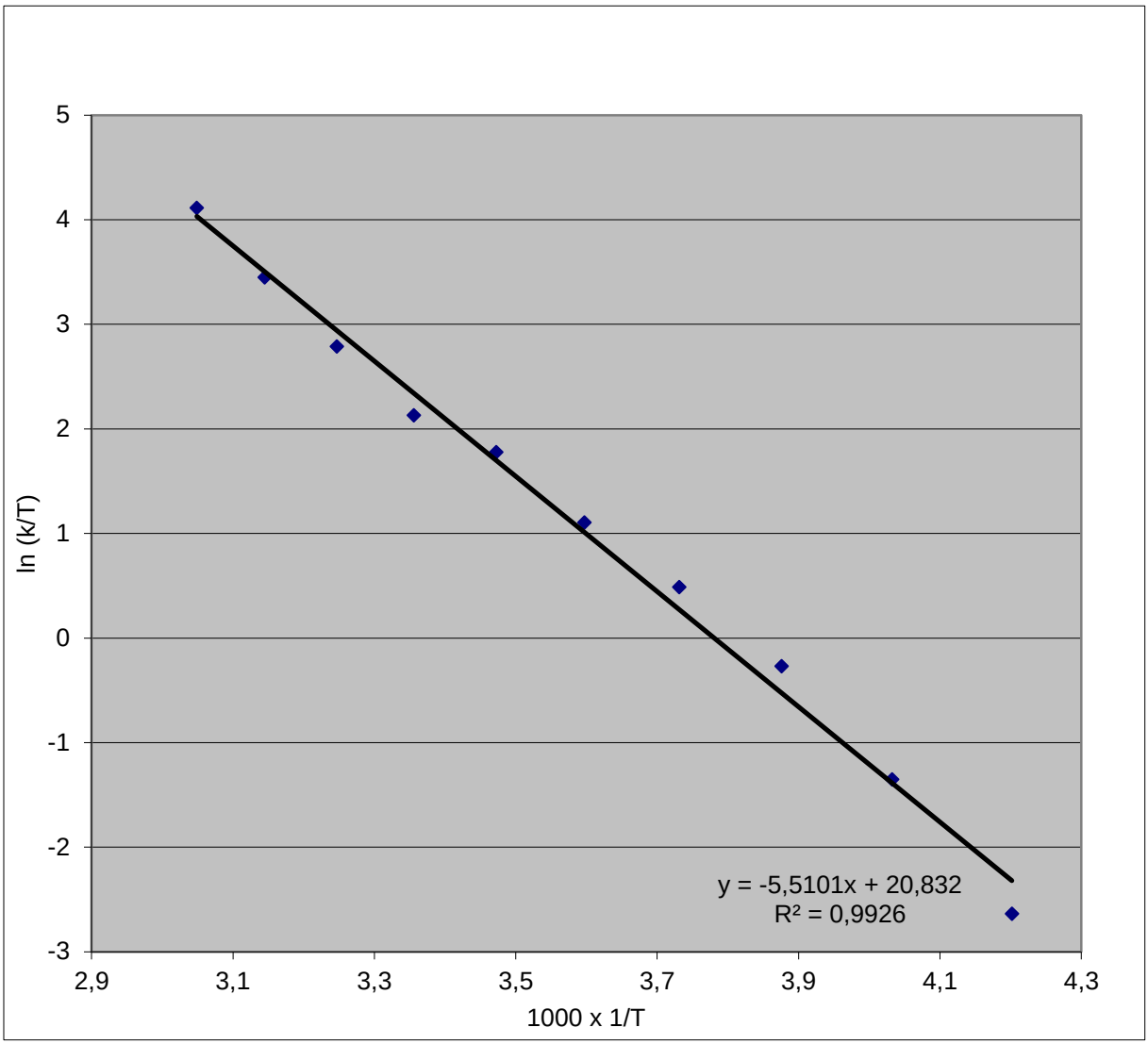

**Figure S5.** Eyring plot for **9**

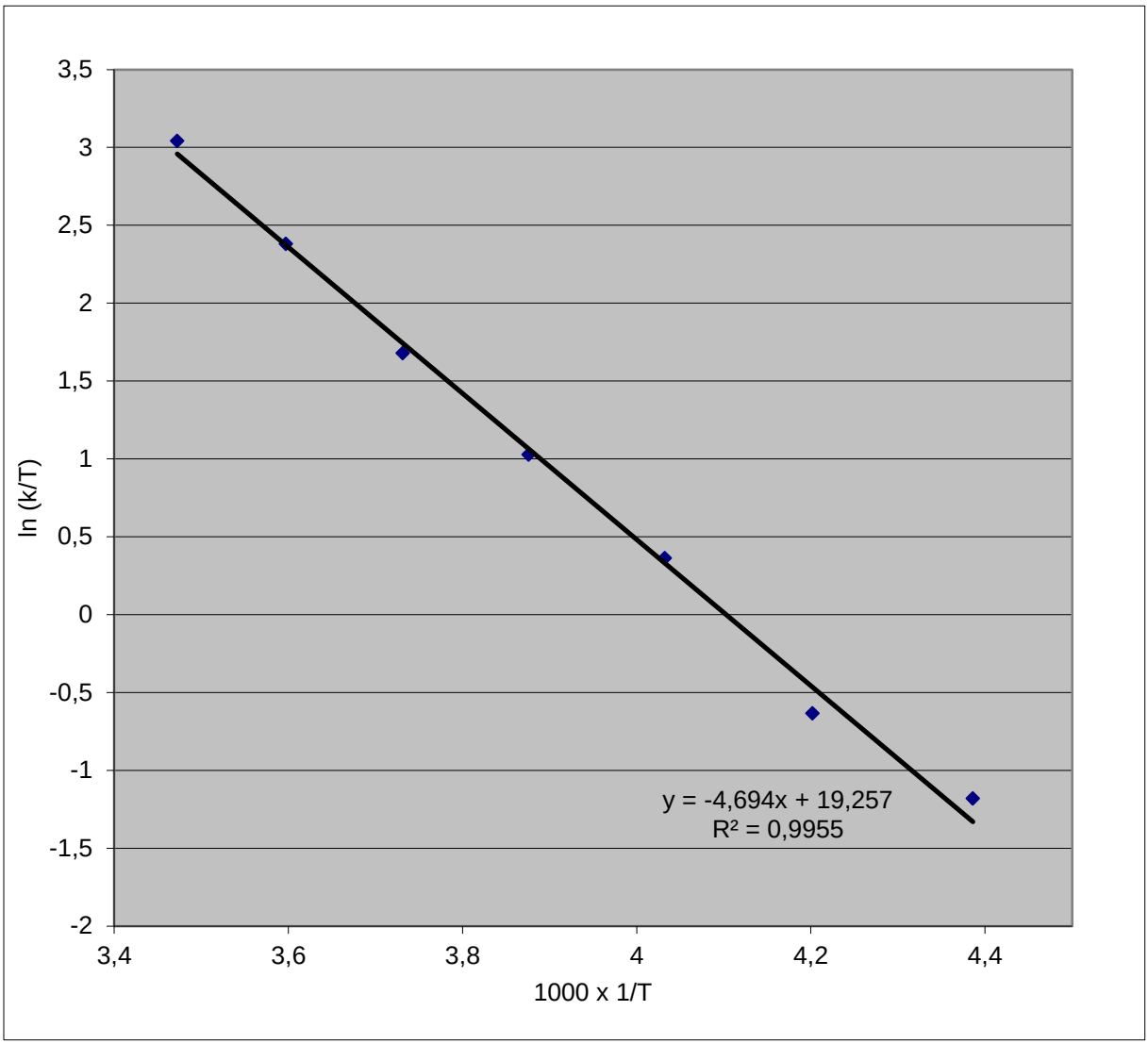

**Figure S6.** An expanded region of $^{1}$H NMR spectra of **8** in the temperature range from -35 °C to 55 °C