ELECTRONIC SUPPLEMENTARY INFORMATION

Zirconium arene triple-decker sandwich complexes: Synthesis, electronic structure and bonding

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Table of contents

1. Experimental details

1.1. General procedures and instrumentation

All manipulations were carried out using standard Schlenk techniques under N_2,[1] or in an MBraun UNIlab glovebox under N_2. All glassware was dried at 160 °C overnight prior to use. Benzene and toluene were dried and degassed using an MBraun SPS-800 solvent purification system.[2] Dried solvents were collected, degassed under partial vacuum and stored over N_2 in K mirrored ampoules. THF was distilled from purple Na/benzophenone, degassed under partial vacuum and stored over activated 4 Å molecular sieves. Deuterated solvents (C_6D_6, C_7D_8) were purchased from Goss Scientific, degassed by three freeze-pump-thaw cycles, dried by refluxing over K for 3 days, vacuum distilled into ampoules and stored under N_2.

Cumene, *o*-xylene and *m*-xylene were purchased from Sigma-Aldrich, stored over activated 4 Å molecular sieves and degassed by three freeze-pump-thaw cycles before use. Reference complexes Cp_2ZrCl_2 and $Cp^*_2ZrCl_2$ were purchased from Sigma-Aldrich and used as received. The following compounds were synthesised according to the literature procedures: KC_8,[3,4] $[ZrPn^*(\mu\text{–}Cl)_{3/2}]_2(\mu\text{–}Cl)_2Li.THF_x$,[5] Pn*ZrCpCl,[6] $Cp_2Zr(CO)_2$[7] and $Cp^*_2Zr(CO)_2$.[7] The permethylpentalene ligand precursor, $Li_2Pn^*(TMEDA)_x$,[8] was kindly donated by Dr S. C. Binding.

Solution samples for NMR spectroscopy were prepared in the glovebox, using 5 mm J. Young tap NMR tubes. Spectra were recorded either on a Bruker Avance III HD nanobay 400 MHz NMR spectrometer, or a Bruker Avance III 500 MHz NMR spectrometer and were referenced internally to the residual protic solvent (^1H) or the signals of the solvent (^{13}C). Spin simulations of ^1H NMR spectra were carried out using MestReNova[9] and gNMR.[10]

Mass spectrometry measurements were carried out by Dr A. Abdul-Sada at the University of Sussex using a VG Autospec Fisons instrument (electron impact at 70 eV).

Elemental analyses for were carried out by Mr. S. Boyer at the Elemental Analysis Service, London Metropolitan University.

Electrochemical studies were carried out using a Princeton Applied Research AMETEK VersaSTAT 3 potentiostat under computer control. CV experiments were performed in a Saffron Omega Scientific glovebox under N_2 using a three-electrode configuration with a Au disc (2.0 mm^2) or glassy carbon disc (7.0 mm^2) as the working electrode, a Pt wire as the counter electrode and a Ag wire as the pseudo-reference electrode. Sample solutions were prepared by dissolving the analyte (*ca.* 5 mM) in THF (5.0 cm^3) followed by addition of a supporting electrolyte $[^nBu_4N][PF_6]$. The reported mid-peak potentials are referenced internally to that of the $FeCp_2^{+/0}$ redox couple, which was measured by adding ferrocene (*ca*. 1 mg) to the sample solution.

Single crystal X-ray diffraction data for **1**–**5** were collected at Chemical Crystallography (University of Oxford) on a Bruker-Nonius Kappa CCD area detector diffractometer with a sealed-tube source ($\lambda_{Mo\ K\alpha}$), in ω scanning mode with ψ and ω scans to fill the Ewald sphere. The data were collected at 150 K using an Oxford Cryosystems low temperature device. Data were processed using Collect,[11] Scalepack, and Denzo,[12] and unit cell parameters were refined against all data. Absorption was corrected for by Multi-Scan methods from symmetry-related measurements using *SORTAV*.[13] The structure was solved using SUPERFLIP[14] and refined on F_o^2 by full-

matrix least-squares refinements using SHELXL-2013.[15] Solutions and refinements were performed using the OLEX2[16] and WinGX[17] software packages. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms treated by a mixture of independent and constrained refinement.

Zr K-edge (17.998 keV) X-ray Absorption Near-Edge Structure (XANES) spectroscopy data were collected on the B18 beamline of the Diamond Light Source, Didcot, UK, with the assistance of beamline scientists Dr G. Cibin, Dr S. Parry and Mr D. Gianolio.

Measurements were performed using a QEXAFS set up with a fast-scanning Si (111) double crystal monochromator. The resolution of the spectra reported herein was 186.74 s/spectrum (k_{max} = 18, step size 1.0 eV), on average 10 scans were acquired to improve the signal to noise level of the data for transmission measurements.

Complex samples (*ca.* 15 mg) were mixed with dry boron nitride (*ca.* 65 mg) pressed into a cylindrical pellet of 8 mm diameter with a thickness (*ca.* 4 mm) chosen to give a total absorbance (μx) of about 2.0. Pellets were positioned vertically in a Nalgene vial under Ar sealed with Parafilm, before being measured in transmission mode using ion chamber detectors. All XANES spectra were acquired concurrently with a Zr foil placed between I_t and I_{ref}. XANES data processing was performed using IFEFFIT[18] with the Horae package (Athena).[19] The edge energy in the Zr K-edge energy was determined from the first peak of the 1st derivative of the XANES, which was fit with a Gaussian curve using OriginPro2017 software.[19]

1.2. Synthesis and characterisation of [(η⁸-Pn)Zr]₂(μ:η⁶,η⁶-C₆H₆) (**1**).*

To an ampule charged with $[\eta^8\text{-Pn*Zr}(\mu\text{-Cl})_{3/2}]_2\text{Li.THF}_x$ (331 mg, 0.405 mmol) in benzene (10 mL) was added KC_8 (241 mg, 1.78 mmol). A color change from light brown to dark red was observed and the mixture was allowed to stir for 48 h at room temperature. The resultant suspension was filtered and dried *in vacuo*. The red filtrate was concentrated to *ca.* 1 mL and after cooling to 5 °C, deposited dark red crystals that were isolated by decantation and dried *in vacuo*. Total yield: 84 mg (33% with respect to $[\eta^8\text{-Pn*Zr}(\mu\text{-Cl})_{3/2}]_2\text{Li.THF}_x$)).

^{1}H NMR (C_6D_6, 400.2 MHz, 298 K): δ_H 2.82 (6H, s, C_6H_6), 2.19 (24H, s, Pn* NWT CH_3), 1.58 (12H, s, Pn* WT CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.6 MHz, 298 K): δ_C 133.06 (Pn* ring *C*), 132.39 (Pn* ring *C*), 68.13 (C_6H_6), 12.46 (Pn* NWT CH_3), 10.21 (Pn* WT CH_3), Pn* bridgehead *C* signals were not observed. ^{13}C NMR (C_6D_6, 100.6 MHz, 298 K): δ_C 68.10 (d, $^1J_{CH}$ = 171.15 Hz, C_6H_6). ^2H NMR (C_6H_6, 61.43 MHz, 298 K): (for **1-*d*₆**) δ_D 2.79 (C_6D_6). EI-MS: *m/z* = 627–637 (principal peak 629, 60%), $[M]^+$; 462–465 (principal peak 462, 30%), $[M - Zr - C_6H_6]^+$. Anal. found (calcd. for $C_{34}H_{42}Zr_2$): C, 64.63 (64.50); H, 6.72 (6.69) %.

1.3. Synthesis and characterisation of [(η⁸-Pn)Zr]₂(μ:η⁶,η⁶-C₆H₅CH₃) (**2**).*

To an ampule charged with $[\eta^8\text{-Pn*Zr}(\mu\text{-Cl})_{3/2}]_2\text{Li.THF}_x$ (297 mg, 0.363 mmol) in toluene (20 mL) was added KC_8 (216 mg, 1.60 mmol). A color change from light brown to dark red was observed and the mixture was allowed to stir for 48 h at room temperature. The resultant suspension was filtered and dried *in vacuo*. The red filtrate was concentrated to *ca.* 1 mL and after cooling to −35 °C, deposited dark red crystals that were isolated by decantation and dried *in vacuo*. Total yield: 71 mg (30% with respect to $[\eta^8\text{-Pn*Zr}(\mu\text{-Cl})_{3/2}]_2\text{Li.THF}_x$)).

^{1}H NMR (C_6D_6, 400.2 MHz, 298 K): δ_H 3.13 (1H, m, Ph *p-H*), 2.58 (4H, apparent d, Ph *o*/*m-H*), 2.18 (24H, s, Pn* NWT CH_3), 1.59 (12H, s, Pn* WT CH_3), 1.49 (3H, s, Ph-CH_3). ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz, 298 K): δ_C 132.75 (Pn* NWT *C*), 132.10 (Pn* WT *C*), 77.65 (Ph *i-C*), 72.48 (Ph *o*/*m-C*H), 68.90 (Ph *o*/*m-C*H), 68.57 (Ph *p-C*H), 19.42 (Ph-*C*H_3), 12.39 (Pn* NWT *C*H_3), 10.25 (Pn* WT *C*H_3). ^{2}H NMR (C_6H_6, 61.43 MHz, 298 K): (for **2-*d*$_8$**) δ_D 3.51 (Ph *p-D*), 2.52 (Ph *o*/*m-D*), 1.40 (Ph-CD_3). EI-MS: *m/z* = 637–644 (principal peak 641, 25%), $[M - 2H]^+$; 602–610 (principal peak 604, 30%), $[M - H - C_3H_3]^+$; 587–594 (principal peak 590, 20%), $[M - H - C_4H_5]^+$. Anal. found (calcd. for $C_{35}H_{44}Zr_2$): C, 64.96 (64.68); H, 6.85 (6.99) %.

1.4. Synthesis and characterisation of [(η^8-Pn)Zr]$_2$(μ:η^6,η^6-C$_6$H$_5$ ^{i}Pr) (**3**).*

To an ampoule charged with [η^8-Pn*Zr(μ-Cl)$_{3/2}$]$_2$Li.THF$_x$ (100 mg, 0.122 mmol) in cumene (1 mL) was added KC_8 (132 mg, 0.978 mmol). A colour change from light brown to dark red was observed and the mixture was allowed to stir for 48 h at room temperature. The resultant suspension was filtered and dried *in vacuo*. The red residue was dissolved in benzene (*ca.* 1 mL) and concentrated by slow evaporation at room temperature to afford the product as dark red crystals that were isolated by decantation and dried *in vacuo*. Total yield: 29 mg (35% with respect to [η^8-Pn*Zr(μ-Cl)$_{3/2}$]$_2$Li.THF$_x$)).
^{1}H NMR (C_6D_6, 400.2 MHz, 298 K, selected data): δ_H 3.07 (1H, m, Ph *p-H*), 2.88 (4H, m, Ph *o/m-H*), 2.33 (1H, m, ^{i}Pr-C*H*), 2.20 (24H, s, Pn* NWT CH_3), 1.59 (12H, s, Pn* WT CH_3), 1.30 (1H, br s, ^{i}Pr-CH_3), 0.92 (1H, br s, ^{i}Pr-CH_3). ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz, 298 K, selected data): δ_C 132.40 (Pn* WT *C*), 132.16 (Pn* NWT *C*), 100.69 (Pn* bridgehead *C*), 99.93 (Pn* bridgehead *C*), 94.03 (Ph *i-C*), 70.19 (Ph *o*/*m-C*H), 69.10 (Ph *p-C*H), 67.15 (Ph *o*/*m-C*H), 23.14 (^{i}Pr *C*H), 14.39 (^{i}Pr *C*H_3), 13.63 (^{i}Pr *C*H_3), 12.80 (Pn* NWT *C*H_3), 10.18 (Pn* WT *C*H_3). EI-MS: *m/z* = 668–678 (principal peak 672, 35%), $[M]^+$; 462–466 (principal peak 462, 55%), $[M - Zr - Ph^iPr]^+$.

*1.5. Synthesis and characterisation of [(η^8-Pn*)Zr]$_2$(μ:η^6,η^6-C$_6$H$_4${1,2-CH$_3$}$_2$) (**4**).*

To an ampoule charged with [η^8-Pn*Zr(μ-Cl)$_{3/2}$]$_2$Li.THF$_x$ (100 mg, 0.122 mmol) in *o*-xylene (1 mL) was added KC_8 (132 mg, 0.976 mmol). The mixture was allowed to stir for 48 h at room temperature, and then filtered. The filtrate was stripped to dryness and the red residue dissolved in benzene (5 mL). This solution was frozen at −78 °C, exposed to dynamic vacuum, then removed from the cold bath to allow the benzene to sublime over 3 h to afford the product as a red powder. Single crystals suitable for X-ray diffraction were grown from slow evaporation at ambient temperature of a saturated *o*-xylene solution. Total yield: 15 mg (31% with respect to [η^8-Pn*Zr(μ-Cl)$_{3/2}$]$_2$Li.THF$_x$)).
^{1}H NMR (C_6D_6, 400.2 MHz, 298 K, selected data): δ_H 2.99 (2H, m, Ar-*H*), 2.17 (24 H, br s, Pn* NWT CH_3), 2.99 (2H, m, Ar-*H*), 1.59 (12 H, s, Pn* WT CH_3), 1.51 (6H, s, Ar-CH_3). ^{13}C{^{1}H} NMR (C_6D_6, 400.2 MHz, 298 K, selected data): δ_C 132.46 (Pn* ring *C*), 131.85 (Pn* ring *C*), 73.91 (Ar-*C*H), 69.97 (Ar-*C*H), 17.45 (Ar-*C*H_3), 12.32 (br s, Pn* NWT *C*H_3), 10.34 (Pn* WT *C*H_3). EI-MS: *m/z* = 627-637 (principal peak 629, 60%), $[M]^+$; 462-465 (principal peak 462, 30%), $[M - Zr - C_6H_6]^+$.

1.6. Synthesis and characterisation of [(η^8-Pn)Zr]$_2$(μ:η^6,η^6-C_6H_4{1,3-CH_3}$_2$) (**5**).*

To an ampoule charged with [η^8-Pn*Zr(μ-Cl)$_{3/2}$]$_2$Li.THF$_x$ (113 mg, 0.138 mmol) in *m*-xylene (2 mL) was added KC_8 (130 mg, 0.962 mmol) and the mixture was allowed to stir for 48 h at room temperature. The mixture was allowed to stir for 48 h at room temperature, and then filtered. The filtrate was stripped to dryness and the red residue dissolved in benzene (5 mL). This solution was frozen at −78 °C, exposed to dynamic vacuum, then removed from the cold bath to allow the benzene to sublime over 3 h to afford the product as a red powder. Single crystals suitable for X-ray diffraction were grown from slow evaporation at ambient temperature of a saturated *m*-xylene solution. Total yield: 23 mg (25% with respect to [η^8-Pn*Zr(μ-Cl)$_{3/2}$]$_2$-Li.THF$_x$)). ^{1}H NMR (C_6D_6, 400.2 MHz, 298 K, selected data): δ_H 3.13 (2H, m, Ar-*H*), 2.17 (24 H, br s, Pn* NWT C*H*$_3$), 2.04 (1H, m, Ar-*H*), 1.80 (1H, br s, Ar-*H*), 1.59 (12 H, s, Pn* WT C*H*$_3$), 1.44 (6H, s, Ar-C*H*$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 400.2 MHz, 298 K, selected data): δ_C 133.32 (Pn* ring *C*), 131.79 (Pn* ring *C*), 100.71 (Ar-*C*), 98.83 (Pn* ring *C*), 77.05 (Ar-*C*H), 73.06 (Ar-*C*H), 70.12 (Ar-*C*H), 19.16 (Ar-*C*H$_3$), 12.31 (br s, Pn* NWT *C*H$_3$), 10.32 (Pn* WT *C*H$_3$). EI-MS: *m/z* = 657-667 (principal peak 662, 30%), [M]$^+$; 462-465 (principal peak 464, 30%), [M – Zr – $C_6H_2Me_2$]$^+$.

Note: Compounds **1–5** are highly air and moisture sensitive and solid state samples were unstable to prolonged (*ca.* 10 h) dynamic vacuum. **1–5** are very soluble in aromatic hydrocarbon solvents, each giving dark red solutions that were stable for *ca.* 7 days. However, aliphatic hydrocarbon (methylcyclohexane-d_{14}) and ethereal (tetrahydrofuran-d_8) solutions of **1–2** showed decomposition by ^{1}H NMR spectroscopy after *ca.* 24 h.

2. Additional characterising data

2.1. Cyclic voltammetry data

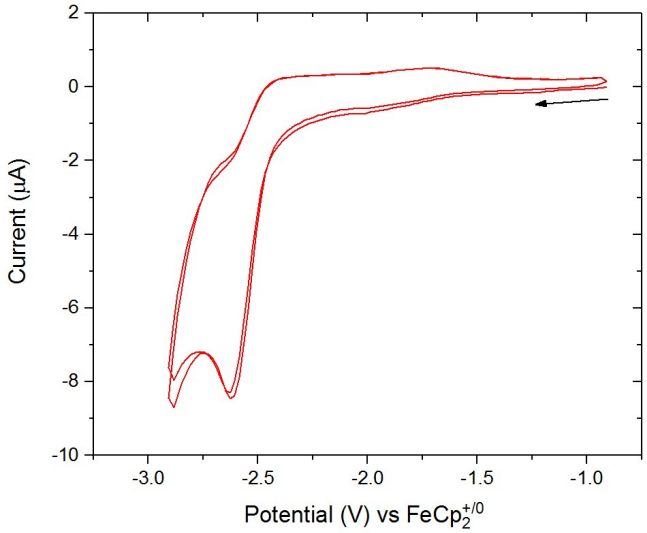

Figure S1 CV scans (2 cycles) of $[\eta^8\text{-Pn*Zr}(\mu\text{-Cl})_{3/2}]_2(\mu\text{-Cl})_2\text{Li}\cdot\text{THF}_x$ in THF/0.1 M $[^n\text{Bu}_4\text{N}][\text{PF}_6]$, scan rate 100 mV s^{-1}.

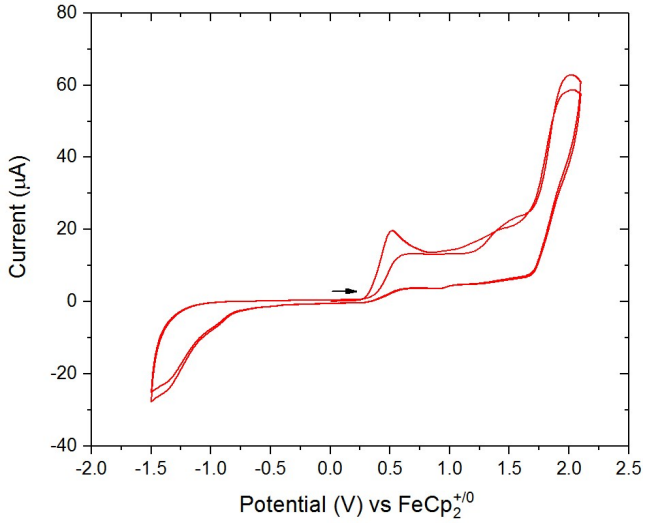

Figure S2 CV scans (1 cycle) of **1** in THF/0.1 M $[^n\text{Bu}_4\text{N}][\text{PF}_6]$, scan rate 100 mV s^{-1}.

Table S1 Peak potentials (E_p vs $FeCp_2^{+/0}$) and limiting currents (i_p) for CV scans in THF / 0.1 M $[^n\text{Bu}_4\text{N}][\text{PF}_6]$ at scan rate 100 mV s^{-1}.

Complex	E_{pa} / V	E_{pc} / V	ΔE_{pp} / mV	i_{pa} / μA	i_{pc} / μA	$\lvert i_{pa}/i_{pc} \rvert$
$[\text{Pn*}_2\text{Zr}_2\text{Cl}_5]\text{Li}\cdot\text{THF}_x$	−2.444	−2.627	183	1.019	−3.871	0.263
1	−1.335	n/a	n/a	7.660	n/a	n/a

2.2. NMR spectroscopic data

[(η⁸-Pn*)Zr]₂(μ:η⁶,η⁶-C₆H₆) (1)

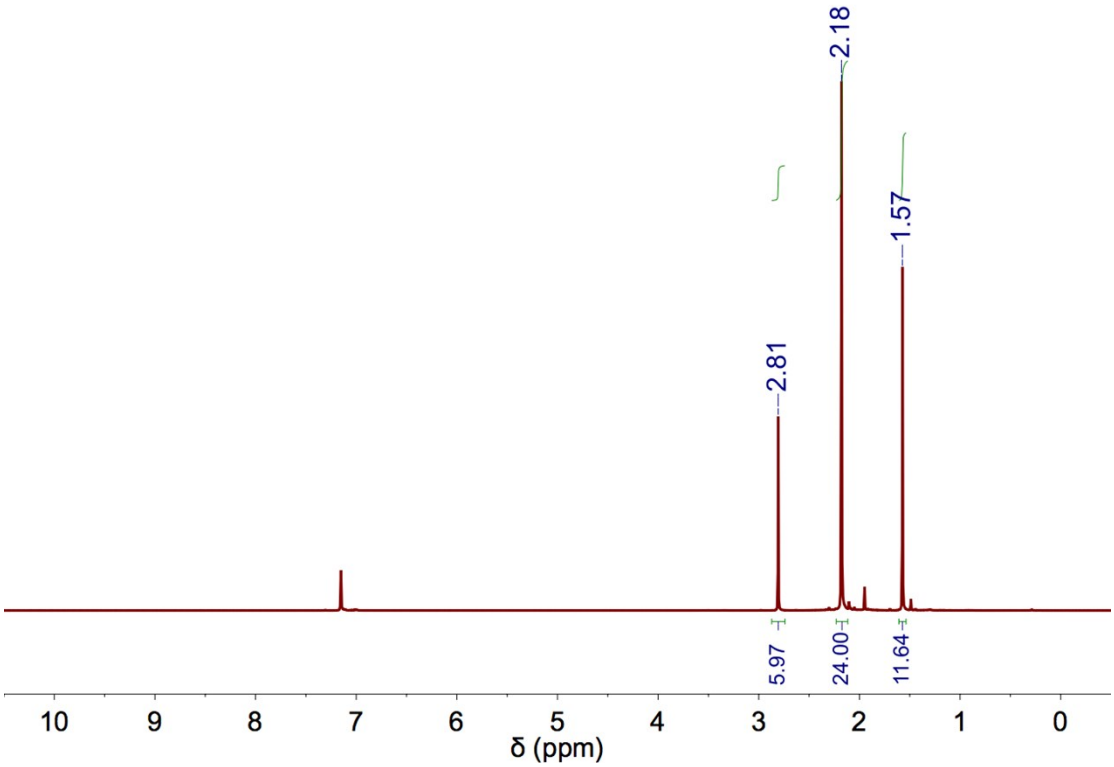

Figure S3 ^{1}H NMR spectrum (C_6D_6, 500 MHz, 298 K) of **1**.

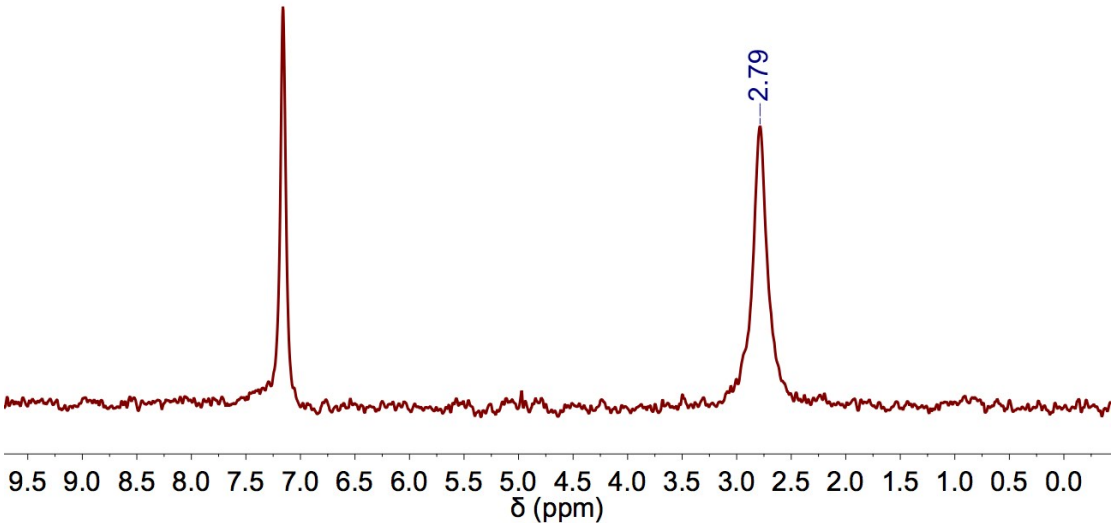

Figure S4 ^{2}H NMR spectrum (C_6H_6, 61.43 MHz, 298 K) of **1-*d*₆**.

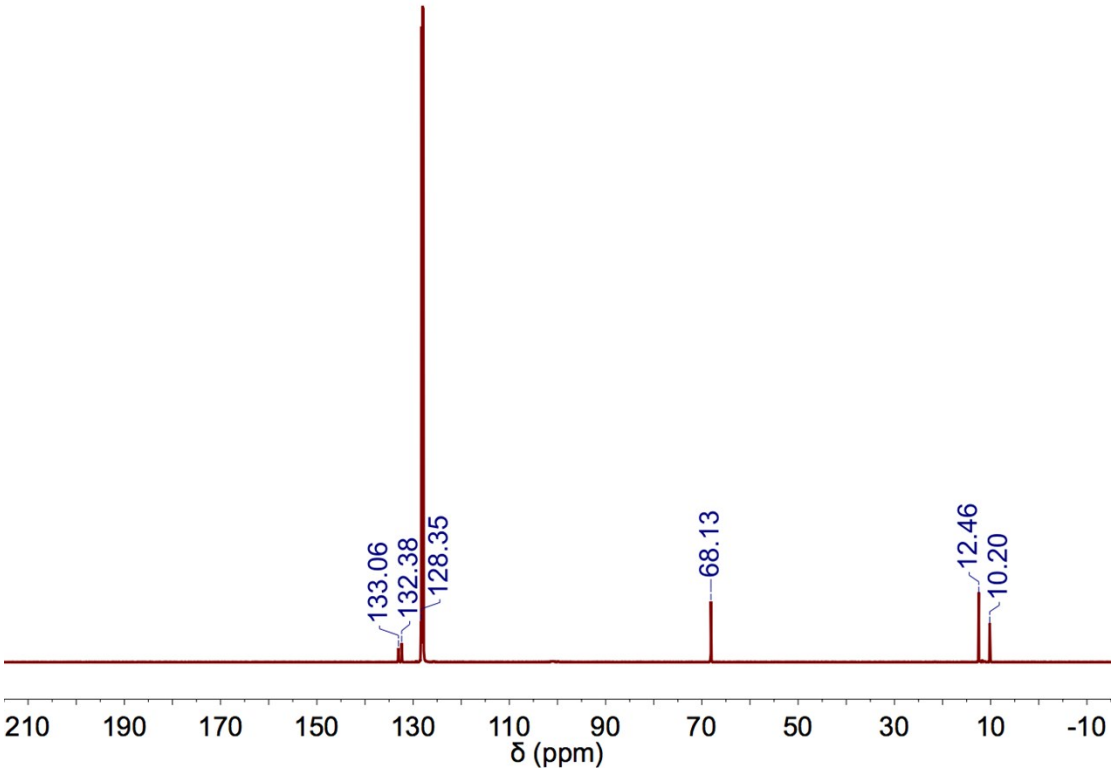

Figure S5 $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 125.7 MHz, 298 K) of **1**.

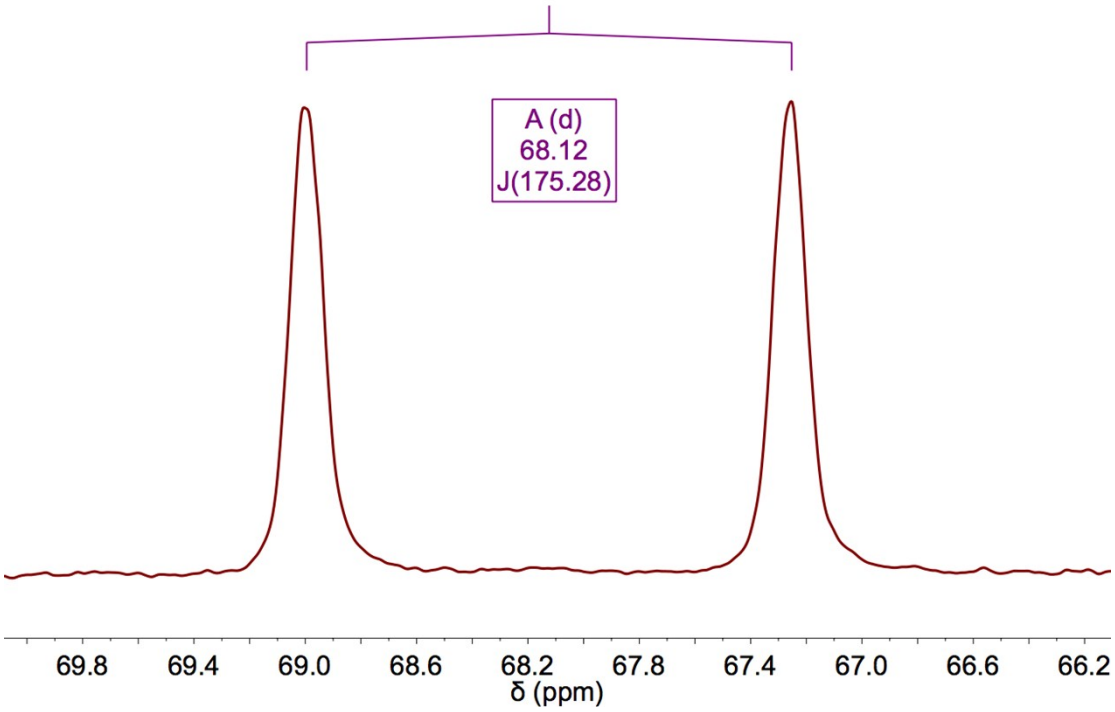

Figure S6 Selected region of ^{13}C NMR spectrum (C_6D_6, 100.6 MHz, 298 K) of **1**.

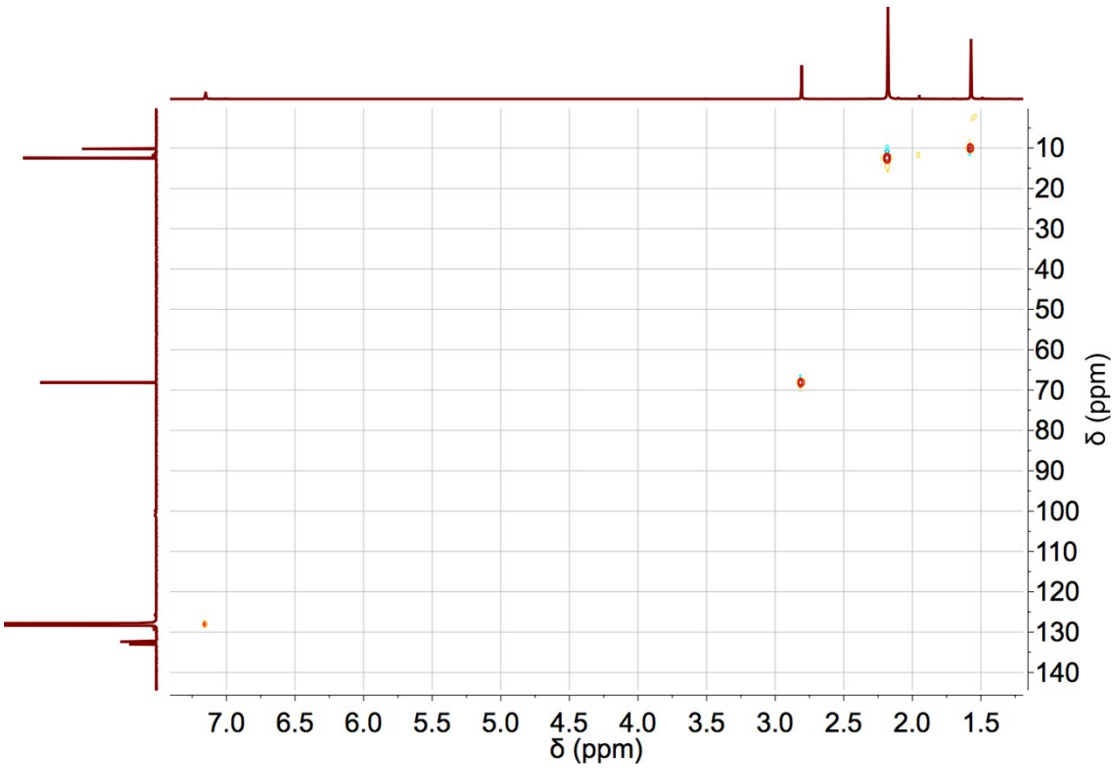

Figure S7 ^{13}C–^{1}H HSQC NMR spectrum (C_6D_6, 298 K) of **1**.

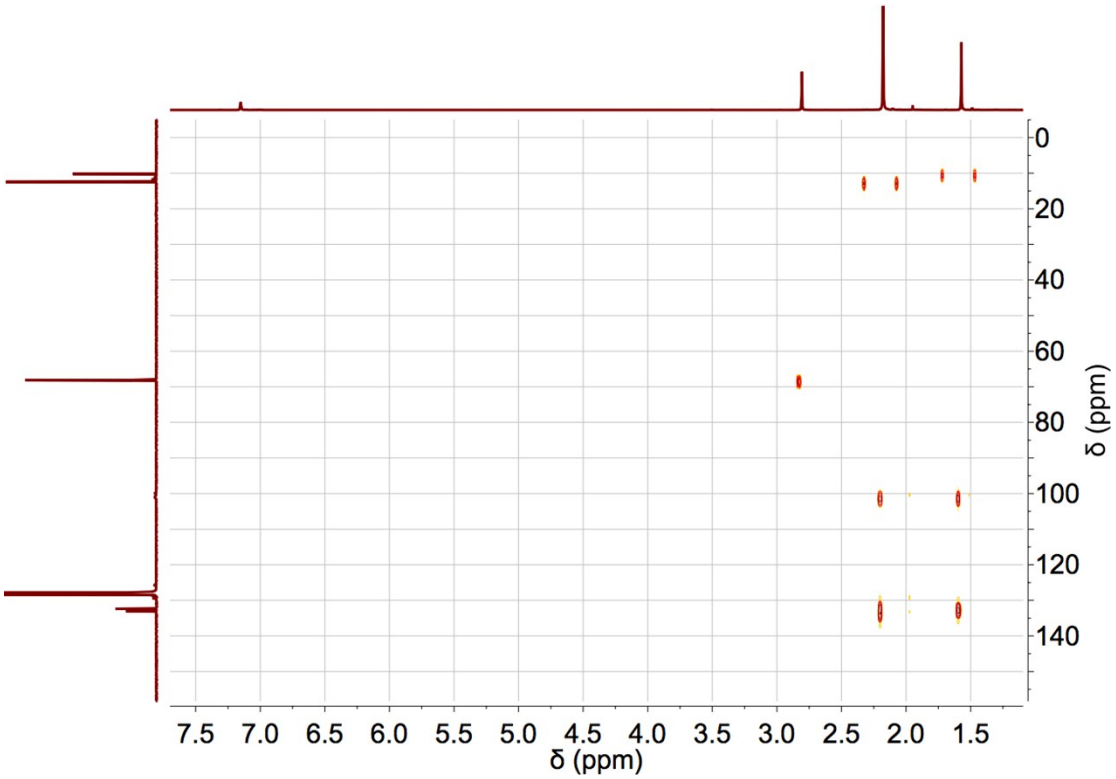

Figure S8 ^{13}C–^{1}H HMBC NMR spectrum (C_6D_6, 298 K) of **1**.

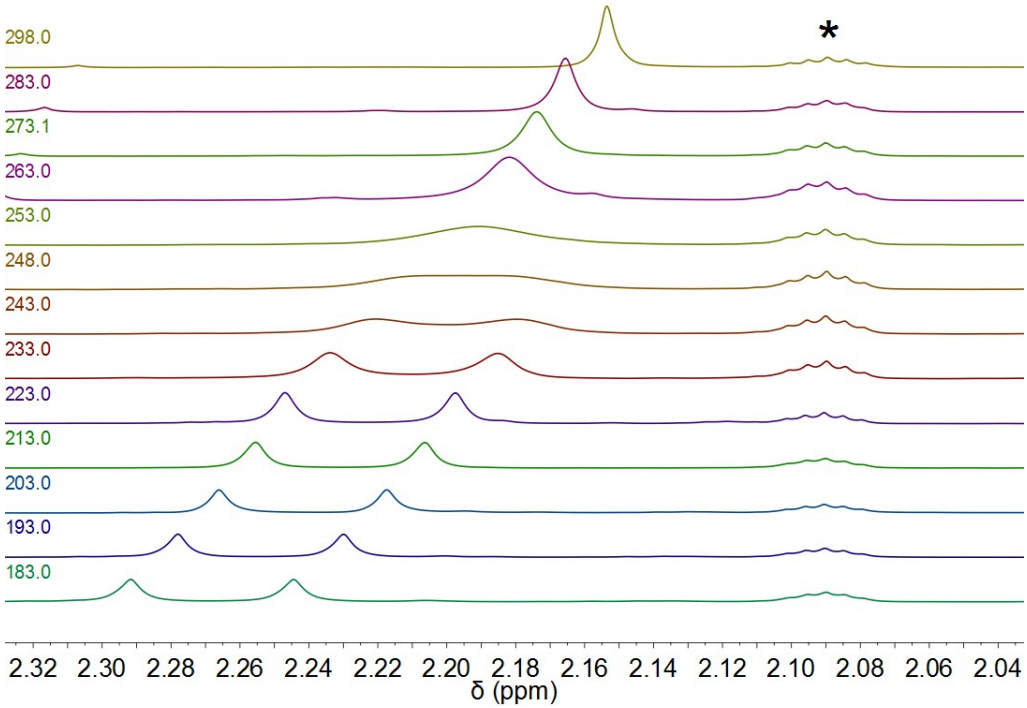

Figure S9 Selected region of variable-temperature ^{1}H NMR spectra (C_7D_8) of **1** from 183 to 298 K. Asterisk denotes residual protio solvent.

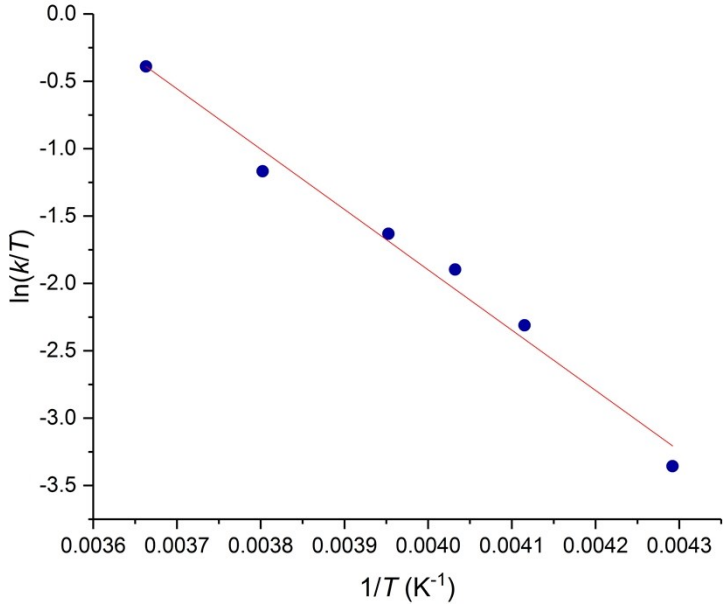

Figure S10 Eyring plot of the exchange rate for the Pn* ligand twisting process in **1**, as determined from VT ^{1}H NMR spectra in C_7D_8.

Table S2 Activation parameters for Pn* ligand twisting process in **1**, calculated from fitting the exchange rate for VT ^{1}H NMR spectra in C_7D_8.[a]

Compound	$\Delta H^{\ddagger}$ / kJ mol^{-1}	$\Delta S^{\ddagger}$ / J K^{-1} mol^{-1}	$\Delta G^{\ddagger}_{285}$ / kJ mol^{-1}
1	37(2)	−65(9)	56(3)

[a] Errors in parentheses.

[(η^8-Pn*)Zr]$_2$(μ:η^6,η^6-$C_6H_5CH_3$) (2).

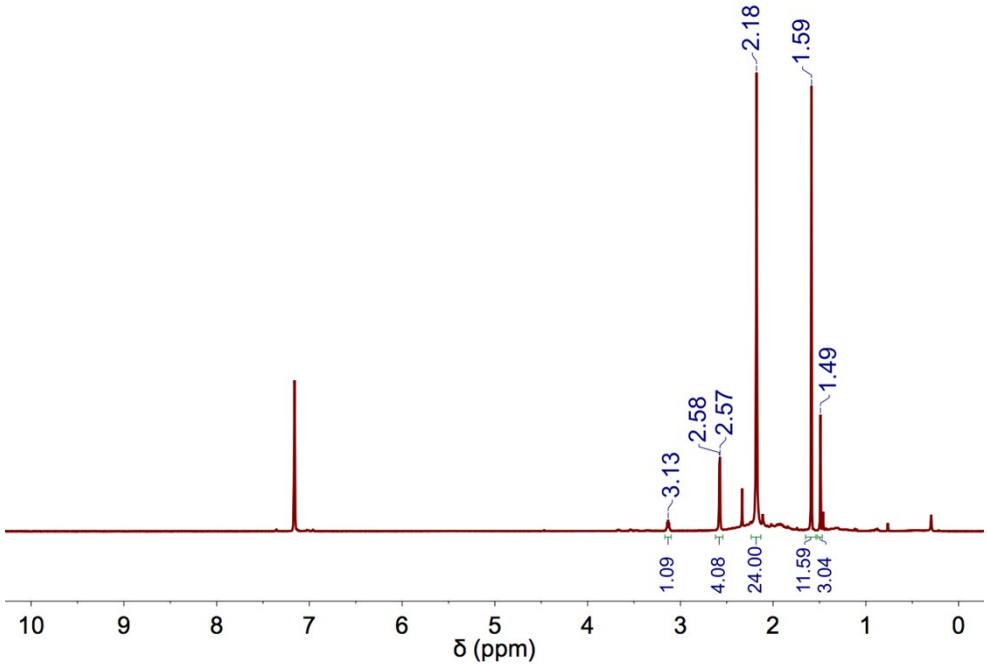

Figure S11 ^{1}H NMR spectrum (C_6D_6, 400.2 MHz, 298 K) of **2**.

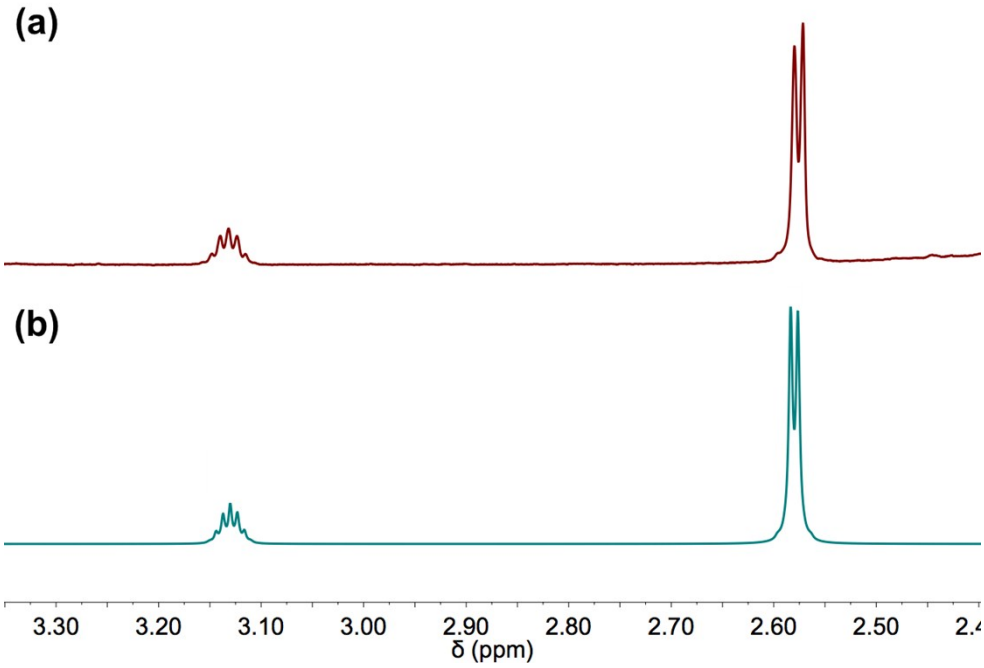

Figure S12 Selected region of the ^{1}H NMR spectrum (C_6D_6, 400.2 MHz, 298 K) of **2**: a) experimental spectrum; b) AA'BB'X spectrum simulated using typical aromatic *J* coupling values.[20]

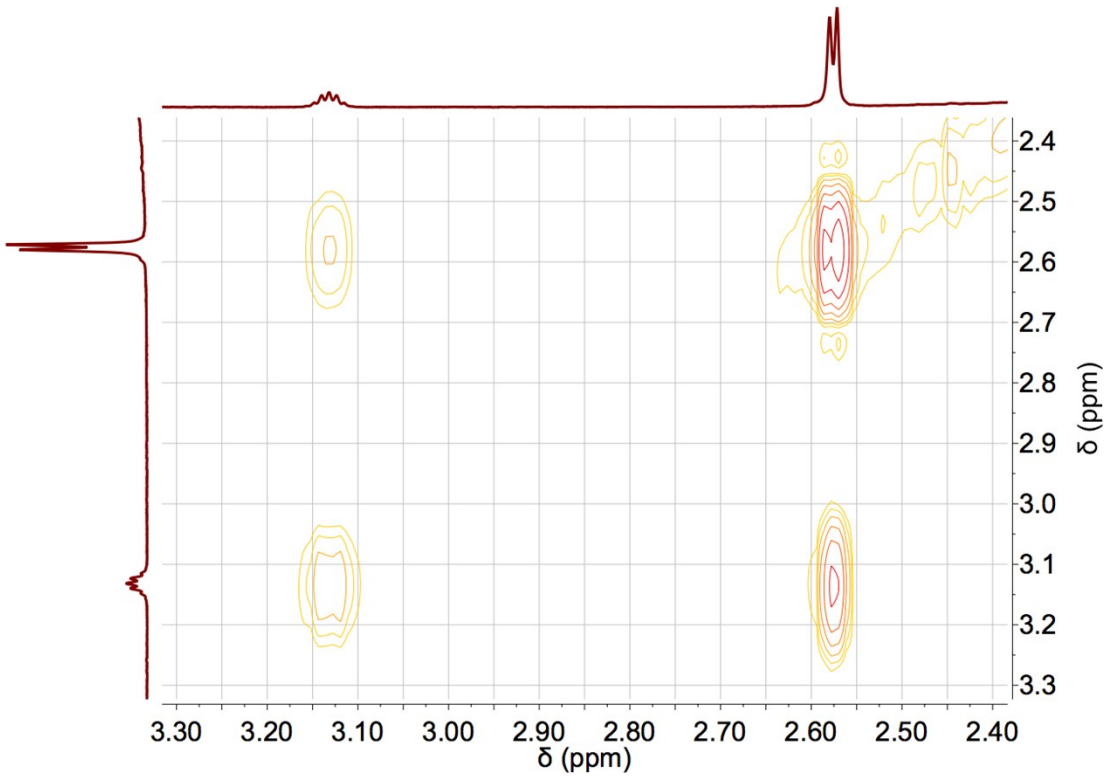

Figure S13 Selected region of the ^{1}H–^{1}H COSY NMR spectrum (C_6D_6, 298 K) of **2**.

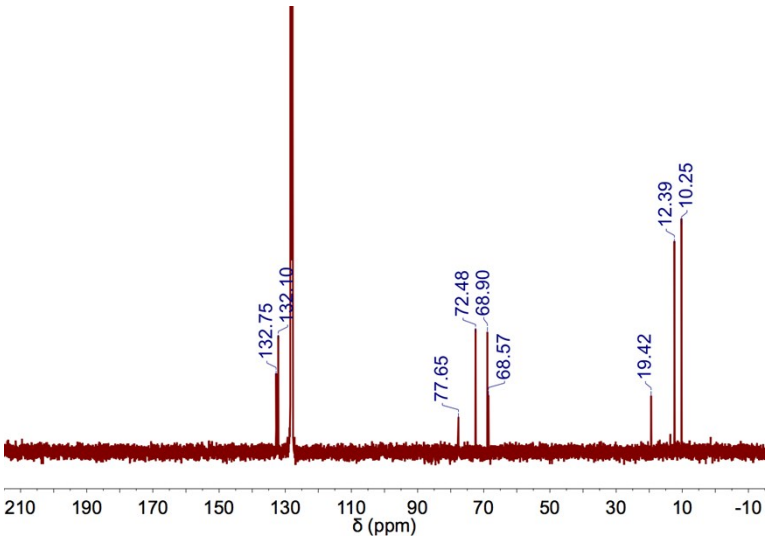

Figure S14 $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 100.6 MHz, 298 K) of **2**.

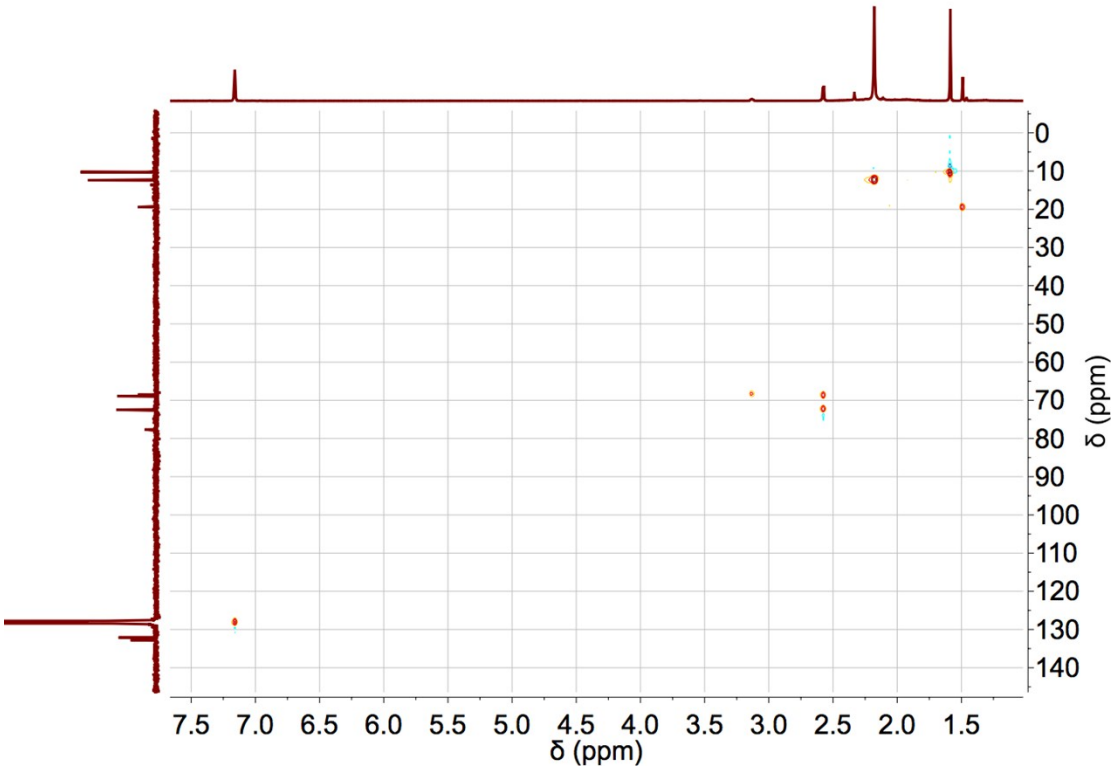

Figure S15 ^{13}C–^{1}H HSQC NMR spectrum (C_6D_6, 298 K) of **2**.

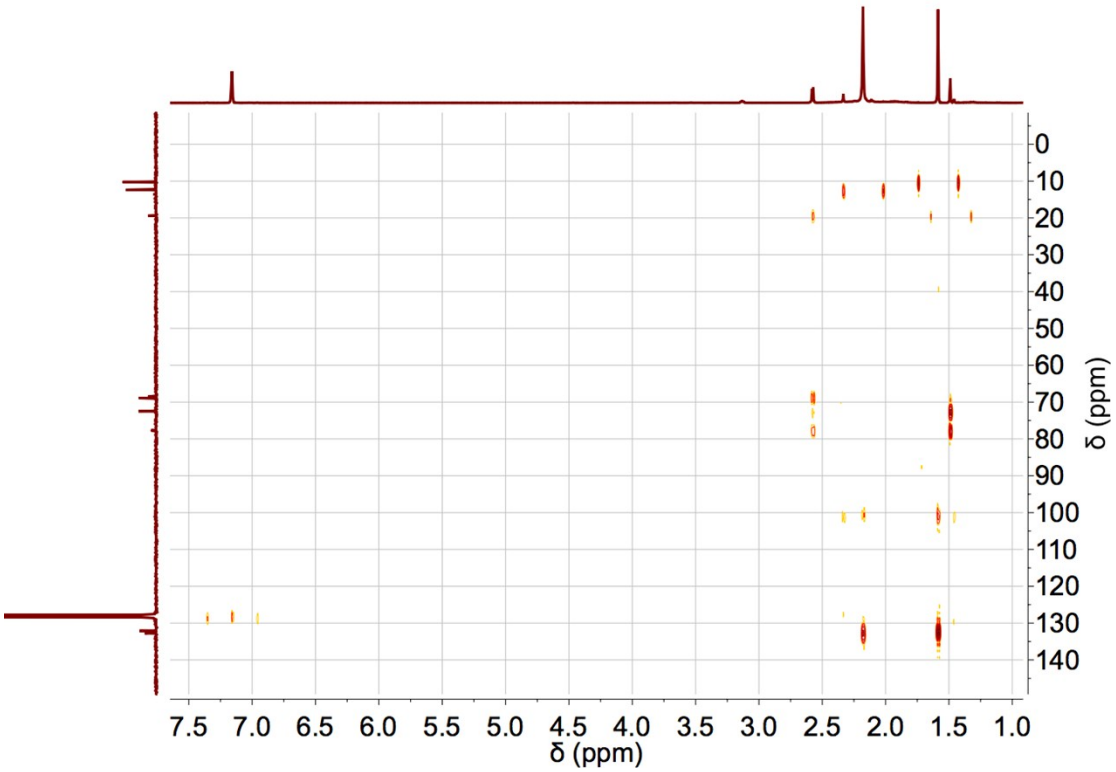

Figure S16 ^{13}C–^{1}H HMBC NMR spectrum (C_6D_6, 298 K) of **2**.

2.3. Additional X-ray crystallographic data

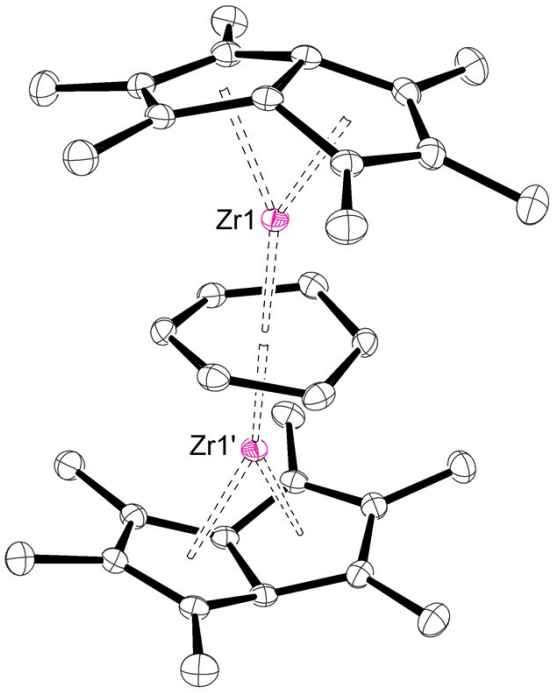

Figure S17 Thermal displacement ellipsoid drawing (50% probability) of **1**. Hydrogen atoms are omitted for clarity. Primed atoms are generated by symmetry.

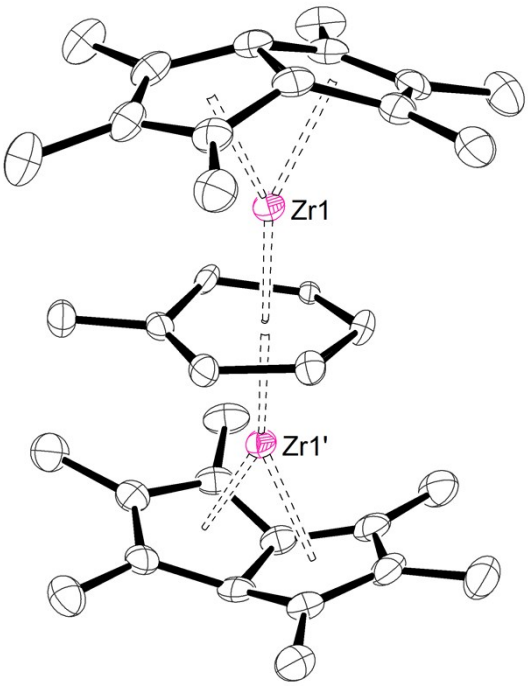

Figure S18 Thermal displacement ellipsoid drawing (50% probability) of **2**. Hydrogen atoms are omitted for clarity. Primed atoms are generated by symmetry.

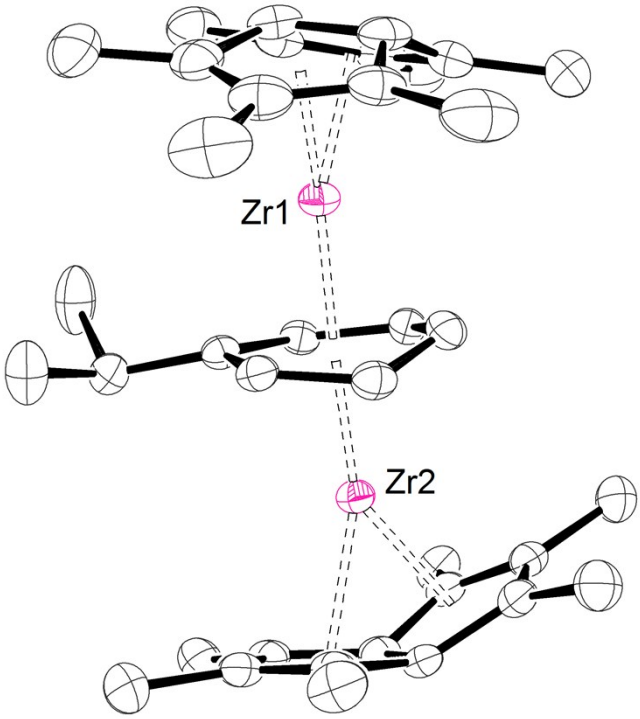

Figure S19 Thermal displacement ellipsoid drawing (50% probability) of **3**. Hydrogen atoms are omitted for clarity.

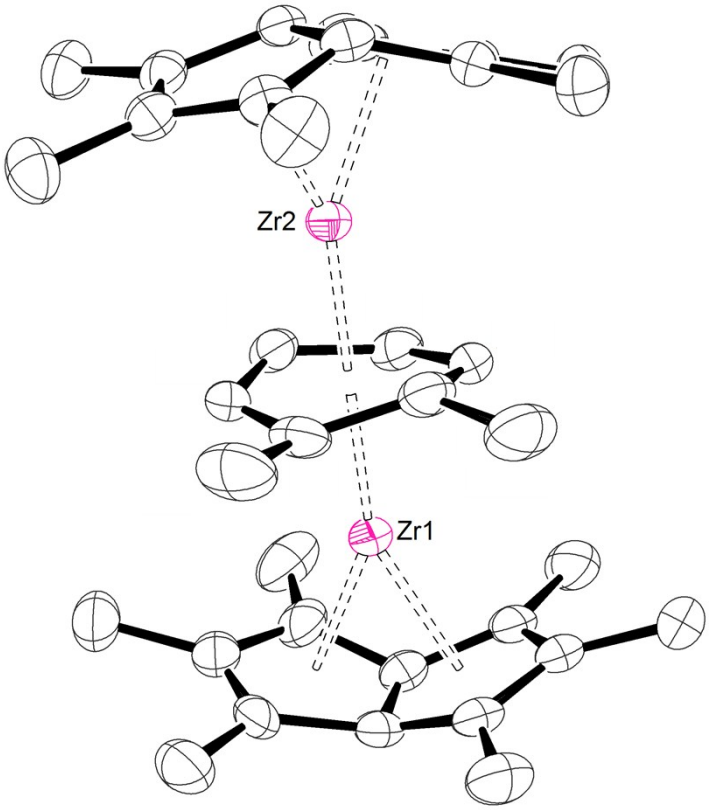

Figure S20 Thermal displacement ellipsoid drawing (50% probability) of **4**. Hydrogen atoms are omitted for clarity.

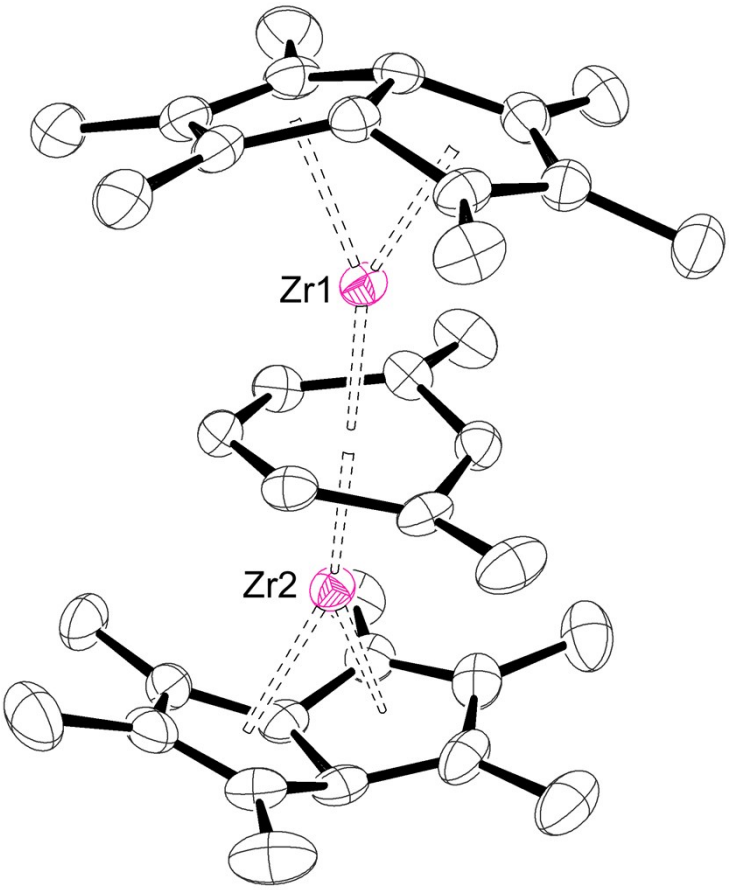

Figure S21 Thermal displacement ellipsoid drawing (50% probability) of **5**. Hydrogen atoms are omitted for clarity.

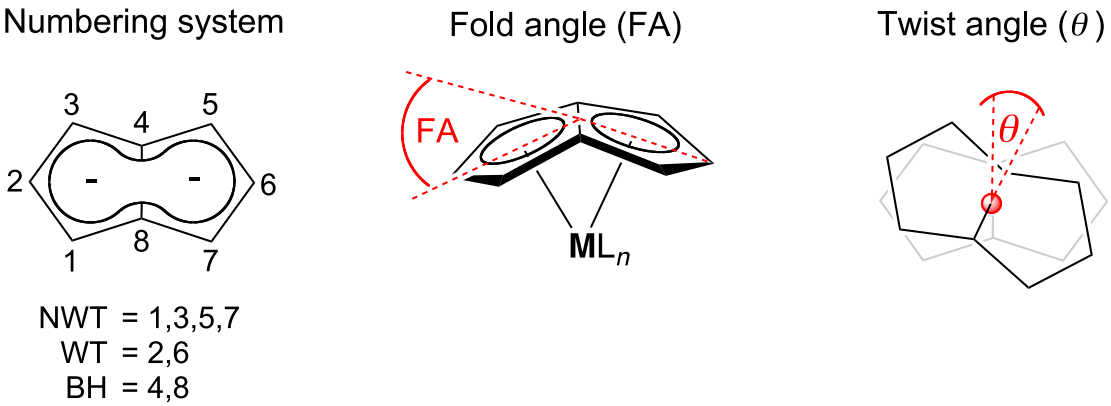

Figure S22 Pentalene numbering scheme and definition of structural parameters. The Pn* fold angle (FA) is defined as the angle between the wing-tip carbons (C2, C6) and the bridgehead (C4, C8) centroid. The twist angle (θ) for inverted sandwich structures is defined as the average torsion angle between the two opposite bridgehead carbon atoms and two zirconium atoms.

Table S3 Selected mean distances (Å), angles (°) and parameters (defined in Fig. S22) for molecular structures **1**–**5** determined by X-ray crystallography. Ct denotes the η^6-centroid of the bridging arene ring.

Parameter	**1**	**2**	**3**	**4**	**5**
Zr–Zr	3.8437(6)	3.84765(12)	3.8648(6)	3.8478(4)	3.8427(4)
$Zr–Ct_{arene}$	1.9219(3)	1.90667(6)	1.9328(5)	1.9241(3)	1.9216(17)
$Zr–C_{arene}$	2.4013	2.4043	2.419(4)	2.4168(3)	2.4140(3)
$C–C_{arene}$	1.4640(20)	1.4680(17)	1.4629(26)	1.4713(16)	1.4701(21)
Puckering Q_{arene}	0.226(4)	0.210(3)	0.220(5)	0.241(3)	0.236(4)
Puckering φ_{arene}	330.0(10)	17.0(10)	148.4(13)	29.2(7)	331.4(10)
Pn* twist angle	45.3(4)	47.199(2)	49.6(8)	47.5597(8)	47.8(8)
Pn* fold angle	33.08(13)	31.2133(3)	31.58(16)	32.7895(6)	33.3(2)

Table S4 Selected experimental crystallographic data.

Complex	**1**	**2**	**3**	**4**	**5**
			Crystal data		
CCDC	1573277	1573278	1573279	1573280	1573281
Chemical formula	$C_{34}H_{42}Zr_2$	$C_{35}H_{44}Zr_2$	$C_{37}H_{48}Zr_2$	$C_{36}H_{46}Zr_2$	$C_{36}H_{46}Zr_2$
M_r	633.11	647.14	675.19	661.17	661.17
Crystal system, space group	Orthorhombic, *Pbnb*	Orthorhombic, *Pbnb*	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$
a, *b*, *c* (Å)	13.4361(3), 14.4172(4), 14.9673(4)	13.1736(5), 14.3455(6), 15.6258(8)	9.4522(1), 15.4296(2), 23.2350(3)	13.3867(2), 14.8682(2), 16.7564(2)	14.4103(3), 13.6833(3), 16.5470(4)
α, β, γ (°)	90, 90, 90	90, 90, 90	89.097(1), 88.321(1), 72.418(1)	96.391(1), 109.561(1), 90.021(1)	90, 107.418(1), 90
V (Å^3)	2899.33(13)	2953.0(2)	3228.91(7)	3120.59(8)	3113.14(12)
Z	4	4	4	4	4
μ (mm^{-1})	0.74	0.73	0.67	0.69	0.69
Crystal size (mm)	0.20 × 0.20 × 0.10	0.1 × 0.1 × 0.05	0.24 × 0.20 × 0.10	0.30 × 0.20 × 0.10	0.15 × 0.10 × 0.10
			Data collection		
T_{min}, T_{max}	0.951, 1.000	0.849, 1.000	0.914, 1.000	0.849, 1.000	0.900, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3305, 3305, 2213	6359, 3379, 1932	26410, 14721, 9962	25997, 14243, 10296	13842, 7076, 5151
R_{int}	0.035	0.071	0.046	0.035	0.039
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.649	0.650	0.650	0.651	0.649
			Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.038, 0.097, 0.99	0.054, 0.131, 1.06	0.048, 0.114, 1.04	0.038, 0.095, 1.04	0.038, 0.100, 0.96
No. of reflections	3305	3379	14721	14243	7076
No. of parameters	169	206	762	745	369
No. of restraints	0	132	0	0	0
H-atom treatment	Constrained	Constrained	Mixed	Mixed	Mixed
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.94, -0.57	0.98, -0.54	0.91, -0.65	0.74, -0.56	0.66, -0.65

All experiments were carried out at 150 K with Mo *K*α radiation using a KappaCCD diffractometer. Absorption was corrected for by multi-scan methods from symmetry-related measurements using *SORTAV*.[13]

2.4. Additional XANES data

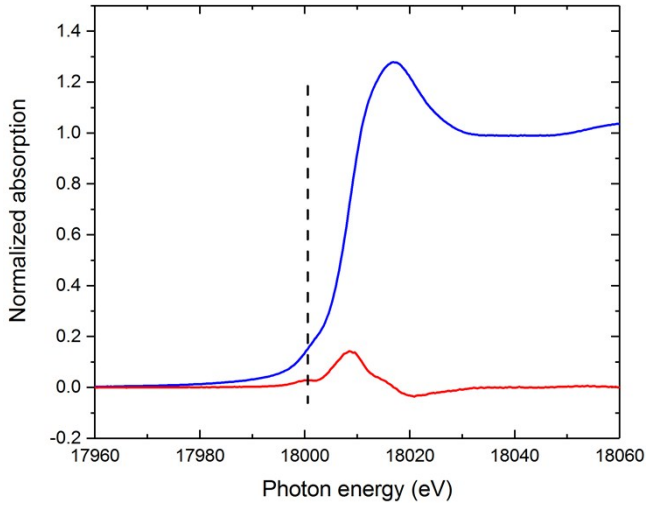

Figure S23 Solid state XANES Zr K-edge spectrum from 17960 eV to 18060 eV of Cp_2ZrCl_2 (blue) and its first derivative (red). The position of the edge energy is denoted by a vertical dotted line.

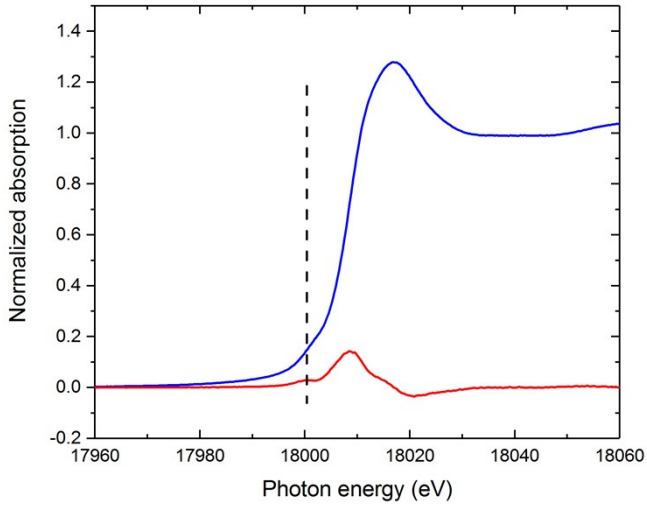

Figure S24 Solid state XANES Zr K-edge spectrum from 17960 eV to 18060 eV of $Cp_2Zr(CO)_2$ (blue) and its first derivative (red). The position of the edge energy is denoted by a vertical dotted line.

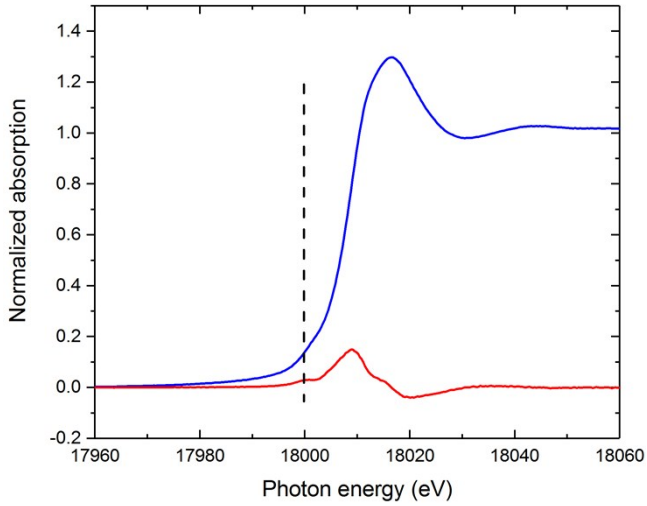

Figure S25 Solid state XANES Zr K-edge spectrum from 17960 eV to 18060 eV of $Cp^*_2ZrCl_2$ (blue) and its first derivative (red). The position of the edge energy is denoted by a vertical dotted line.

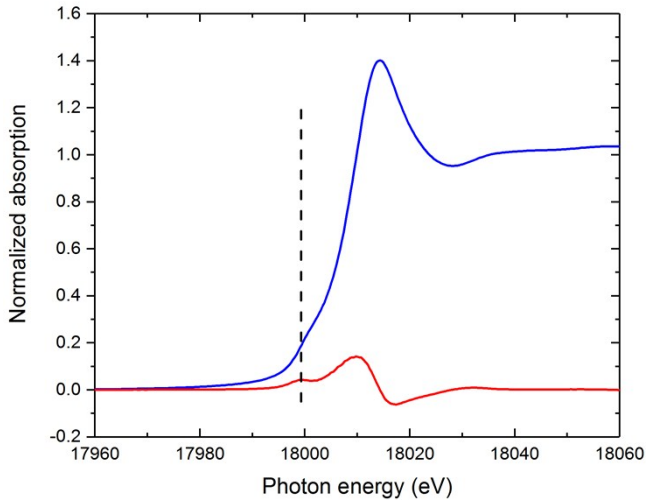

Figure S26 Solid state XANES Zr K-edge spectrum from 17960 eV to 18060 eV of $Cp^*_2Zr(CO)_2$ (blue) and its first derivative (red). The position of the edge energy is denoted by a vertical dotted line.

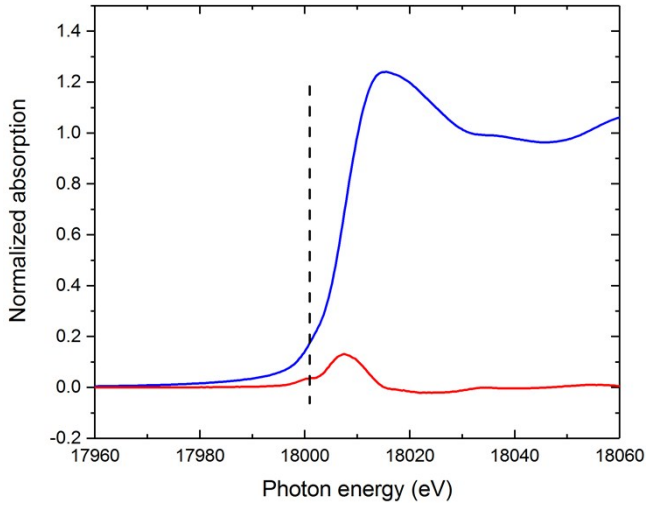

Figure S27 Solid state XANES Zr K-edge spectrum from 17960 eV to 18060 eV of $[\eta^8\text{-Pn*Zr}(\mu\text{-Cl})_{3/2}]_2(\mu\text{-Cl})_2\text{Li}\cdot\text{THF}_x$ (blue) and its first derivative (red). The position of the edge energy is denoted by a vertical dotted line.

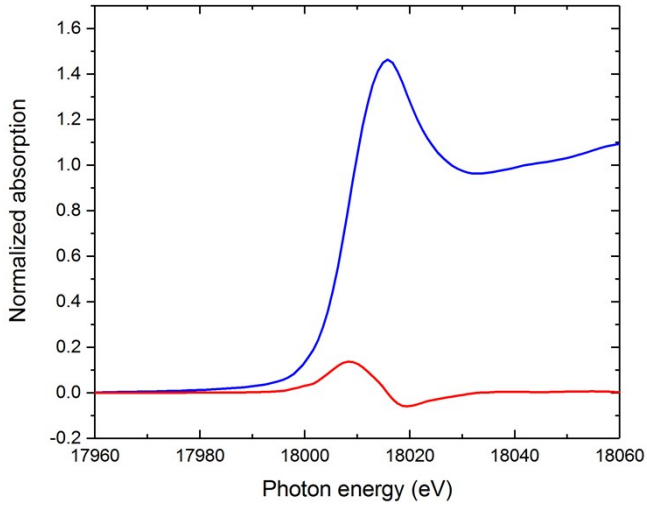

Figure S28 Solid state XANES Zr K-edge spectrum from 17960 eV to 18060 eV of Pn*ZrCpCl (blue) and its first derivative (red). The position of the edge energy could not be determined.

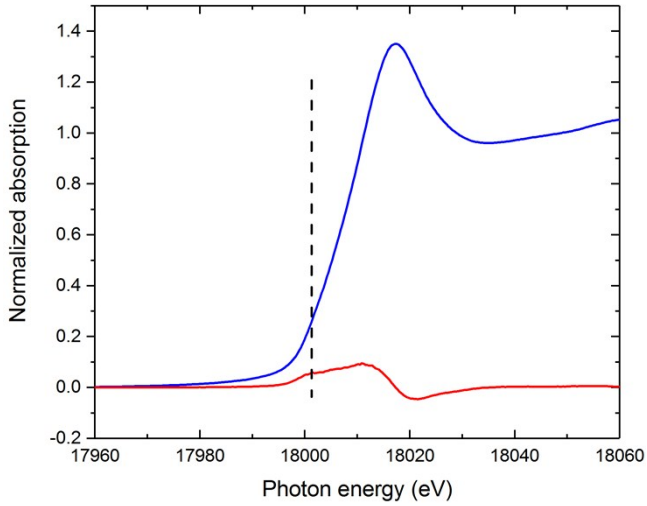

Figure S29 Solid state XANES Zr K-edge spectrum from 17960 eV to 18060 eV of **1** (blue) and its first derivative (red). The position of the edge energy is denoted by a vertical dotted line.

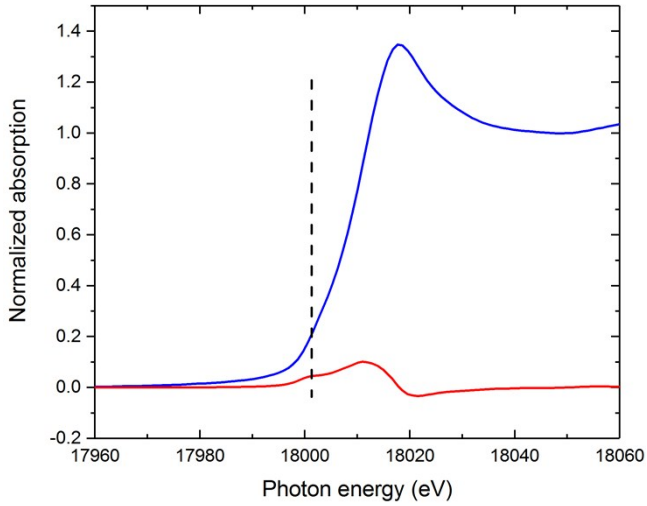

Figure S30 Solid state XANES Zr K-edge spectrum from 17960 eV to 18060 eV of **2** (blue) and its first derivative (red). The position of the edge energy is denoted by a vertical dotted line.

3. DFT calculations

3.1. Computational details

Density functional calculations were carried using the Amsterdam Density Functional package (version ADF2016.107).[21] The Slater-type orbital (STO) basis sets were of triple-ζ quality augmented with a one polarisation function (ADF basis TZP). Core electrons were frozen (C 1s; Zr 3d) in the model of the electronic configuration for each atom. The local density approximation (LDA) by Vosko, Wilk and Nusair (VWN)[22] was used together with the exchange correlation corrections of Becke and Perdew (BP86).[23,24] In addition to the calculations on the experimental compounds calculations the related model compounds with no methyl substituents on the penatene ligands were carried out. They are denoted by Roman numerals.

3.2. Additional computational data

Table S5 Selected distances (Å), angles (°) and parameters for DFT optimised structures (Roman numerals refer to the Pn structures; Arabic to the Pn*).

Parameter	**I**	**1**	**II**	**2**	**III**	**3**	**IV**	**4**	**V**	**5**
Zr–Zr	3.944	3.963	3.943	3.964	3.939	3.972	3.946	3.964	3.941	3.969
Zr–Ct_{arene}	1.972	1.982	1.972	1.987	1.920	1.987	1.973	1.982	1.971	1.985
av. Zr–C_{arene}	2.456	2.464	2.454	2.468	2.456	2.468	2.460	2.466	2.459	2.467
av. C–C_{arene}	1.474	1.474	1.476	1.475	1.478	1.476	1.476	1.477	1.476	1.475
Puckering Q_{arene}	0.252	0.253	0.257	0.258	0.254	0.260	0.264	0.264	0.250	0.253
Puckering φ_{arene}	90	90	88.128	86.941	86.994	88.035	90.096	90	85.752	83.274
Pn* twist angle	44.04	44.87	44.06	44.06	43.26	46.4	44.01	43.56	45.38	44.19
Pn* fold angle	29.91	29.41	29.77	29.01	29.63	28.98	29.70	28.88	29.60	28.63
Short C–C_{arene}	1.472	1.473	1.471	1.473	1.47	1.473	1.47	1.473	1.469	1.47
Long C–C_{arene}	1.477	1.477	1.483	1.478	1.488	1.479	1.484	1.483	1.483	1.478
Σ(C–C_{arene})	8.842	8.846	8.855	8.852	8.867	8.855	8.857	8.864	8.857	8.851
Δ(C–C_{arene})	0.005	0.004	0.012	0.005	0.018	0.006	0.014	0.010	0.014	0.008

Σ(C–C_{arene}) is the sum of the six C–C_{arene} bond distances, Δ(C–C_{arene}) is the difference between the longest and shortest C–C_{arene} distances.

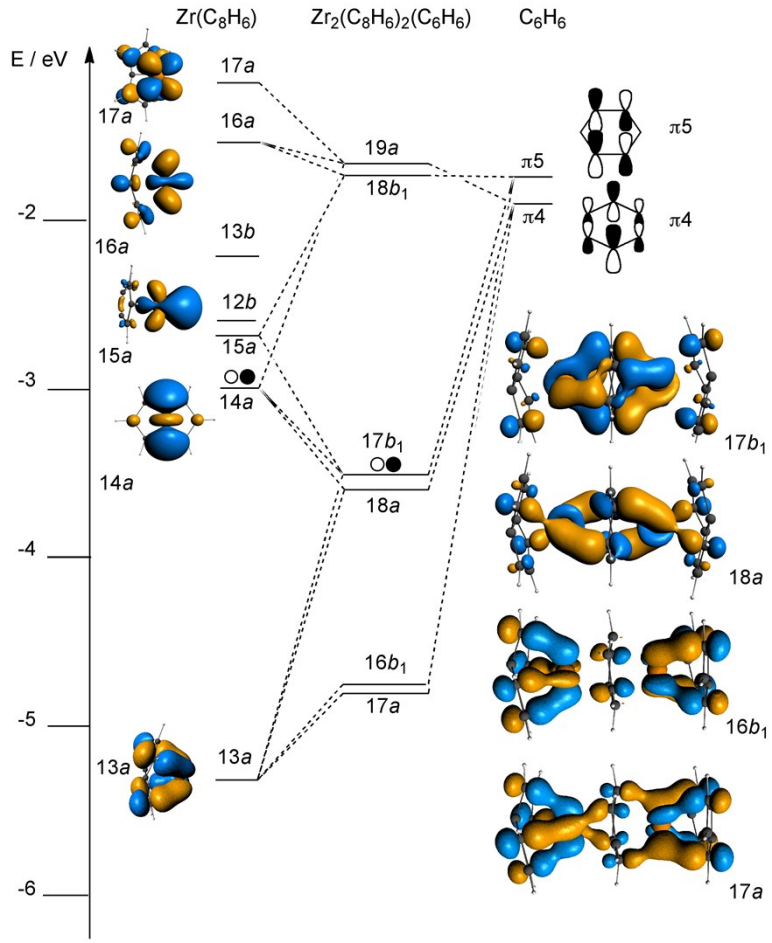

Figure S31 Energy levels and isosurfaces for the Kohn-Sham frontier orbitals of **I**.

Table S6 Hirshfeld charges on fragments and binding energies (kJ mol^{-1}) for calculated structures **1**/**I**, **2**/**II**, **3**/**III**, **4**/**IV** and **5**/**V** (Roman numerals refer to the Pn structures Arabic to the Pn*). The binding energies are for the fragments with *S*=0 and structures identical with those found for the optimised compound.

Structure	ZrPn	Arene	Binding energy
1	0.09	−0.18	−723
I	0.15	−0.30	−766
2	0.08	−0.16	−719
II	0.14	−0.28	−766
3	0.07	−0.14	−723
III	0.12	−0.26	−769
	0.14		
4	0.07	−0.13	−713
IV	0.13	−0.25	−766
5	0.07	−0.14	−706
V	0.13	−0.26	−757
6	0.005	-0.005	-345
VI	0.039	-0.039	-374

3.3. Cartesian coordinates for optimised structures

1

78

C	-0.67405814	0.27472132	4.17512917
C	0.67405814	-0.27472132	4.17512917
C	1.58966073	0.78052287	3.78678583
C	0.79641007	1.96483406	3.61873704
C	-0.59120671	1.67554113	3.81072243
C	0.59120671	-1.67554113	3.81072243
C	-1.58966073	-0.78052287	3.78678583
C	-0.79641007	-1.96483406	3.61873704
H	3.47148447	-0.25236528	3.47485101
H	2.28924518	3.28046151	2.75963321
H	-1.47322233	3.54562756	3.16765110
H	2.65130250	-2.25658079	3.45220393
H	-3.50424262	-0.93232925	4.79076426
H	-0.64793230	-3.95786303	2.77905362
C	-0.67405814	-0.27472132	-4.17512917
C	0.67405814	0.27472132	-4.17512917
C	0.59120671	1.67554113	-3.81072243
C	-0.79641007	1.96483406	-3.61873704
C	-1.58966073	0.78052287	-3.78678583
C	1.58966073	-0.78052287	-3.78678583
C	-0.59120671	-1.67554113	-3.81072243
C	0.79641007	-1.96483406	-3.61873704
H	1.89203519	3.07902838	-4.82526511
H	-0.64793230	3.95786303	-2.77905362
H	-3.47148447	-0.25236528	-3.47485101
H	3.50424262	-0.93232925	-4.79076426
H	-1.47322233	-3.54562756	-3.16765110
H	1.58555832	-3.85887031	-4.27849229
Zr	0.00000000	0.00000000	-1.98160642
Zr	0.00000000	0.00000000	1.98160642
C	0.00000000	1.43089506	0.00000000
C	-1.28745692	0.72752169	0.12670811
C	-1.28745692	-0.72752169	-0.12670811
C	0.00000000	-1.43089506	0.00000000
C	1.28745692	-0.72752169	0.12670811
C	1.28745692	0.72752169	-0.12670811
H	-2.20831833	1.29073439	-0.01649025
H	-2.20831833	-1.29073439	0.01649025
H	0.00000000	-2.51825422	0.00000000
H	2.20831833	-1.29073439	-0.01649025
H	2.20831833	1.29073439	0.01649025
H	0.00000000	2.51825422	0.00000000
C	3.09336583	0.72955598	3.78602424
H	3.52510465	1.47577453	3.10422189
H	3.50424262	0.93232925	4.79076426
C	1.35650460	3.33146579	3.33734245
H	0.64793230	3.95786303	2.77905362
H	1.58555832	3.85887031	4.27849229
C	1.70592483	-2.68489705	3.81058577
H	1.89203519	-3.07902838	4.82526511
H	1.47322233	-3.54562756	3.16765110
C	-1.35650460	-3.33146579	3.33734245

H	-1.58555832	-3.85887031	4.27849229
H	-2.28924518	-3.28046151	2.75963321
C	-1.70592483	2.68489705	3.81058577
H	-2.65130250	2.25658079	3.45220393
H	-1.89203519	3.07902838	4.82526511
C	-3.09336583	-0.72955598	3.78602424
H	-3.47148447	0.25236528	3.47485101
H	-3.52510465	-1.47577453	3.10422189
C	1.70592483	2.68489705	-3.81058577
H	1.47322233	3.54562756	-3.16765110
H	2.65130250	2.25658079	-3.45220393
C	3.09336583	-0.72955598	-3.78602424
H	3.47148447	0.25236528	-3.47485101
H	3.52510465	-1.47577453	-3.10422189
C	1.35650460	-3.33146579	-3.33734245
H	2.28924518	-3.28046151	-2.75963321
H	0.64793230	-3.95786303	-2.77905362
C	-1.70592483	-2.68489705	-3.81058577
H	-2.65130250	-2.25658079	-3.45220393
H	-1.89203519	-3.07902838	-4.82526511
C	-1.35650460	3.33146579	-3.33734245
H	-1.58555832	3.85887031	-4.27849229
H	-2.28924518	3.28046151	-2.75963321
C	-3.09336583	0.72955598	-3.78602424
H	-3.52510465	1.47577453	-3.10422189
H	-3.50424262	0.93232925	-4.79076426

I

42

C	-0.80803288	0.29037100	4.15982859
C	0.41017694	-0.51523838	4.12224231
C	1.50299079	0.35871523	3.76828909
C	0.96043613	1.66912460	3.64102817
C	-0.44543720	1.65223034	3.84936237
C	0.04477554	-1.84927734	3.71316179
C	-1.90345246	-0.55450134	3.74527871
C	-1.36117854	-1.85236267	3.51591632
H	2.54962294	0.08967892	3.66157022
H	1.54158343	2.55906655	3.40365678
H	-1.10795758	2.51153776	3.79919956
H	0.70836404	-2.69971492	3.58655968
H	-2.95249595	-0.28162743	3.67536660
H	-1.94424047	-2.72245646	3.21678668
C	-0.58861092	-0.00633145	-4.24584938
C	0.84473313	0.22929579	-4.10658432
C	1.02841788	1.60225563	-3.70647713
C	-0.26345480	2.18554045	-3.61483166
C	-1.26982647	1.22312676	-3.90160618
C	1.45432312	-1.00966006	-3.68444131
C	-0.84017152	-1.39381992	-3.93712552
C	0.41450311	-1.98211786	-3.62506600
H	1.97104797	2.10748808	-3.51687158
H	-0.45963410	3.22311390	-3.34788664
H	-2.34019135	1.40766036	-3.91980588
H	2.50835166	-1.19262774	-3.49826481
H	-1.79880653	-1.90467519	-3.95048355
H	0.56052513	-3.02874029	-3.36165772

Zr	-0.08430255	0.06109938	-1.99207632
Zr	-0.21120594	-0.01477576	1.94750344
C	0.11373095	1.42657786	0.03169287
C	-1.28539092	0.97421100	0.06042005
C	-1.54562955	-0.45540446	-0.17090519
C	-0.40833581	-1.38286045	-0.08828217
C	0.97941207	-0.93027539	0.15179989
C	1.25310764	0.50036009	-0.11316305
H	-2.08341124	1.69963789	-0.08511019
H	-2.55821313	-0.84273755	-0.07719259
H	-0.61136951	-2.45060601	-0.10725949
H	1.78392583	-1.65110605	0.01583263
H	2.25498777	0.88532500	0.06883726
H	0.31138502	2.49547101	0.05179018

2

81

C	4.16276381	-0.28347534	-0.92157727
C	4.19058943	0.25710319	0.42979322
C	3.81129115	-0.80081417	1.34545839
C	3.61973830	-1.97881267	0.54794192
C	3.79009538	-1.68199809	-0.84082260
C	3.83944710	1.66177437	0.36224871
C	3.76620669	0.78039719	-1.82282476
C	3.62247737	1.96100687	-1.01931284
H	3.55549084	0.22290820	3.24100569
H	2.77134917	-3.29799357	2.04418022
H	3.10740175	-3.53567874	-1.72933113
H	3.52589234	2.23656890	2.43223011
H	4.73375682	0.92678476	-3.75668392
H	2.81277871	3.96373603	-0.83866289
C	-4.16307020	0.25431083	-0.91905267
C	-4.18800934	-0.28465154	0.43216490
C	-3.79973335	-1.67966491	0.37216131
C	-3.56212507	-1.97673748	-1.00528383
C	-3.72661189	-0.79944417	-1.81298997
C	-3.85218202	0.78518020	1.35086605
C	-3.83309383	1.66323120	-0.83625462
C	-3.69202020	1.96758843	0.55305877
H	-4.81233849	-3.09956589	1.65601525
H	-2.70685482	-3.95795442	-0.80794886
H	-3.36792069	0.22076975	-3.69323275
H	-4.97674215	0.81143964	3.19993927
H	-3.18795503	3.53046968	-1.72475395
H	-4.43314633	3.83893094	1.32282829
Zr	-1.98182542	0.01387817	-0.19441915
Zr	1.98237406	0.00243224	-0.20728495
C	-0.00851777	-1.40517928	-0.19704077
C	0.11693151	-0.69547949	-1.48153543
C	-0.12952870	0.76001355	-1.46265044
C	0.00176845	1.44880915	-0.16585081
C	0.15773708	0.74713873	1.12447057
C	-0.11094192	-0.70558539	1.09631298
H	-0.04096595	-1.24960356	-2.40547377
H	0.01181354	1.33416367	-2.37669980
H	0.01544898	2.53758953	-0.15971252
H	-1.07731875	1.70956162	2.65416157

H	0.49479991	2.48659929	2.36267960
H	-0.00705695	-2.49211771	-0.19991050
C	3.84371171	-0.76091384	2.84968265
H	3.16142642	-1.50110184	3.29088919
H	4.85432495	-0.98031084	3.23651636
C	3.33837820	-3.34702771	1.10472300
H	2.76920905	-3.96739364	0.39944527
H	4.27953427	-3.87993160	1.32051918
C	3.87422665	2.66404391	1.48264156
H	4.89810525	3.04000691	1.65382134
H	3.24285859	3.53731842	1.26584864
C	3.34118766	3.33325215	-1.56617944
H	4.28120549	3.84969719	-1.82279996
H	2.73401198	3.29282872	-2.48052321
C	3.76367222	-2.68488398	-1.96127839
H	3.40660031	-2.24438026	-2.90142217
H	4.76964635	-3.09560851	-2.15733745
C	3.73423784	0.73938717	-3.32674666
H	3.39746794	-0.23446181	-3.70449702
H	3.05720442	1.50065876	-3.73914437
C	-3.80558269	-2.67384529	1.50049564
H	-3.12551616	-3.51495161	1.30503558
H	-3.49767615	-2.21840898	2.45080061
C	-3.93058035	0.74552844	2.85336748
H	-3.50980974	-0.17963395	3.26846919
H	-3.38742961	1.58376388	3.31078182
C	-3.46991124	3.34663948	1.10841633
H	-2.90094919	3.32455460	2.04792047
H	-2.92667655	3.98901840	0.40265050
C	-3.82617389	2.66616950	-1.95715951
H	-3.45827165	2.23270152	-2.89629347
H	-4.84014098	3.05572499	-2.15542020
C	-3.23747419	-3.34166298	-1.54590464
H	-4.15984827	-3.88140371	-1.81806989
H	-2.61582818	-3.28696452	-2.44976624
C	-3.68123531	-0.76121696	-3.31657257
H	-2.97993581	-1.50481563	-3.72057910
H	-4.67147470	-0.97702007	-3.75463170
C	-0.01776093	1.51605108	2.41491921
H	0.41233110	0.95614041	3.25691774
H	0.04089089	-1.28174193	2.00936586

II

45

C	-0.66222730	0.26490186	4.17709971
C	0.69248307	-0.27909082	4.15918188
C	1.58754512	0.78431802	3.77052048
C	0.79182963	1.95397659	3.60244183
C	-0.58186698	1.66074078	3.81843477
C	0.60390929	-1.67304692	3.79642861
C	-1.56536054	-0.79589195	3.79908325
C	-0.77335232	-1.96521546	3.60908607
H	2.66765214	0.72938016	3.67165795
H	1.18244132	2.93444047	3.33333511
H	-1.40439813	2.36607185	3.74249365
H	1.42465440	-2.37761057	3.69824589
H	-2.64776969	-0.74144500	3.72649348

H	-1.16942765	-2.94456220	3.34358384
C	-0.66638324	-0.25966902	-4.17622303
C	0.69041722	0.27926911	-4.16157432
C	0.60817405	1.67342050	-3.79716276
C	-0.76630579	1.97062625	-3.60396405
C	-1.56323921	0.80286523	-3.79015826
C	1.58302582	-0.78913570	-3.77987020
C	-0.58974423	-1.65679696	-3.82323794
C	0.78291938	-1.95613775	-3.61499344
H	1.43276849	2.37319113	-3.69641071
H	-1.15786020	2.95075665	-3.33503878
H	-2.64550842	0.75268028	-3.71382982
H	2.66447442	-0.73968958	-3.69422576
H	-1.41470531	-2.35919227	-3.74612557
H	1.16948489	-2.93948192	-3.35084434
Zr	-0.01520692	0.00100257	-1.97226635
Zr	-0.01647510	0.00350730	1.97106375
C	-0.00493976	1.41929472	0.01028241
C	-1.29434403	0.71695071	0.10106482
C	-1.28286661	-0.74064437	-0.10816056
C	0.01212412	-1.43323218	-0.01310341
C	1.30652489	-0.73940657	0.16312326
C	1.28447027	0.71352810	-0.13296390
H	-2.21864109	1.27322215	-0.04200831
H	-2.20139169	-1.30774006	0.02752085
H	0.01280880	-2.52166753	0.00257968
H	2.84663759	-1.69043785	-1.06890404
H	2.51840858	-2.49815179	0.48157216
H	-0.00494922	2.50594073	0.00751308
C	2.59210827	-1.51810245	-0.00944679
H	3.43109222	-0.97750727	0.44940450
H	2.19987343	1.28591371	0.01705145

3

87

C	4.09926668	-0.33626091	-1.02873509
C	4.26506951	0.17166679	0.32462951
C	3.88286086	-0.87560880	1.25163923
C	3.55540639	-2.02246856	0.45078955
C	3.64405437	-1.70860398	-0.94095850
C	4.02864267	1.60168312	0.30619548
C	3.70500476	0.77099502	-1.87601443
C	3.71931563	1.94374458	-1.04541712
H	3.92347973	0.12139803	3.17593035
H	2.72591692	-3.30936778	1.98403315
H	2.76005251	-3.48449209	-1.81285269
H	3.96063761	2.18076614	2.40039160
H	4.52631148	0.90459783	-3.87729542
H	3.11548521	4.00761404	-0.76976115
C	-4.13235775	0.18856129	-0.97084663
C	-4.19014967	-0.32136603	0.39092610
C	-3.74723270	-1.70087921	0.37839950
C	-3.44437703	-2.01950391	-0.98172117
C	-3.62223303	-0.86747574	-1.82285914
C	-3.92980406	0.78048252	1.29617252
C	-3.86149321	1.61129888	-0.90767517
C	-3.78592721	1.95118679	0.47729018

H	-4.74976058	-3.11297548	1.67962590
H	-2.51392573	-3.95597744	-0.70234394
H	-3.21891995	0.12279696	-3.70962714
H	-5.13865887	0.86791919	3.09025776
H	-3.24807190	3.48005052	-1.81608637
H	-4.62608240	3.79230532	1.21962804
Zr	-1.97250036	0.03385826	-0.15871136
Zr	1.99971389	0.06483994	-0.14267067
C	0.00267024	-1.34602001	-0.13237068
C	0.17440863	-0.65051445	-1.41994997
C	-0.13589036	0.79507837	-1.41823876
C	0.01199510	1.50002235	-0.12981830
C	0.11062550	0.82710731	1.18130985
C	-0.08967755	-0.63613141	1.15485908
H	0.04135532	-1.21827982	-2.33963516
H	0.01371534	1.36447910	-2.33459585
H	0.00804176	2.58666651	-0.15399451
H	-1.26002436	1.69282906	2.59218692
H	1.48215104	3.03206478	2.27586931
H	0.03075534	-2.43258345	-0.11762953
C	4.05624770	-0.87938400	2.74622502
H	3.33669755	-1.54671072	3.24083840
H	5.06659739	-1.22169304	3.03250875
C	3.21912079	-3.37894816	1.00505107
H	2.55891372	-3.94415394	0.33351106
H	4.13308556	-3.98051288	1.14382768
C	4.28580522	2.57139207	1.42683585
H	5.36285901	2.79787166	1.51458250
H	3.76812896	3.52709684	1.26623528
C	3.50581656	3.34335703	-1.55205420
H	4.45543240	3.77783457	-1.90680130
H	2.80392350	3.36910512	-2.39660050
C	3.46491434	-2.68190474	-2.07349972
H	3.08438136	-2.19358394	-2.98003478
H	4.42081804	-3.16490993	-2.34108033
C	3.55372122	0.76917196	-3.37247286
H	3.12587760	-0.17168994	-3.74153870
H	2.89714122	1.58153855	-3.71459313
C	-3.75115530	-2.66596285	1.53193239
H	-3.04633439	-3.49388654	1.37153134
H	-3.47292997	-2.17896808	2.47605246
C	-4.07848387	0.77866224	2.79431575
H	-3.69291880	-0.14242974	3.24984804
H	-3.54453995	1.61999207	3.25750153
C	-3.63833855	3.34799037	1.01209641
H	-3.07072996	3.36894208	1.95287236
H	-3.12931587	4.00802163	0.29743944
C	-3.84897301	2.58981319	-2.05007344
H	-3.43445752	2.14869213	-2.96595176
H	-4.86780311	2.94007406	-2.29112146
C	-3.04133940	-3.38132153	-1.47539397
H	-3.92829151	-3.96725031	-1.76866916
H	-2.38708599	-3.32059744	-2.35546115
C	-3.51799664	-0.86005908	-3.32360436
H	-2.77881364	-1.59005993	-3.68243526
H	-4.48262897	-1.11590757	-3.79556635
C	-0.16289912	1.61140931	2.47052193
H	1.45519576	0.73722367	3.64517147

H	0.05440929	-1.21315622	2.06558297
C	0.39252692	3.04269852	2.42951335
H	-0.05946340	3.64512343	1.63026064
H	0.18422546	3.55479072	3.38072139
C	0.36747525	0.88911635	3.71814735
H	0.16112316	1.48794946	4.61763077
H	-0.10611488	-0.09133241	3.86225590

III

51

C	-0.73882839	0.31500158	4.15202535
C	0.61557340	-0.22758844	4.20923692
C	1.52726436	0.82543674	3.83046585
C	0.73922503	1.98834224	3.59336221
C	-0.64244383	1.69912004	3.75602040
C	0.54244471	-1.63318754	3.89183673
C	-1.62437947	-0.75832354	3.76950575
C	-0.82541016	-1.93223264	3.65162823
H	2.61088137	0.77237904	3.78804949
H	1.14083052	2.96142869	3.31369926
H	-1.46122704	2.39977547	3.62035587
H	1.36465290	-2.34172185	3.86506852
H	-2.70214215	-0.70658877	3.64489753
H	-1.21018890	-2.92033476	3.40236303
C	-0.69499214	-0.24797466	-4.15590307
C	0.66255741	0.28889657	-4.16226244
C	0.59028024	1.67874676	-3.77932953
C	-0.78007713	1.97538176	-3.55539186
C	-1.58257178	0.81149499	-3.74057553
C	1.56048022	-0.78517651	-3.80997589
C	-0.61364810	-1.64952223	-3.82140927
C	0.76203471	-1.95331510	-3.64408177
H	1.41793417	2.37604362	-3.68660273
H	-1.16450182	2.95253290	-3.26611629
H	-2.66298261	0.76144205	-3.64234629
H	2.64367102	-0.73885747	-3.74657529
H	-1.43818285	-2.35160319	-3.73698753
H	1.15275279	-2.94048457	-3.40127921
Zr	0.00171908	-0.00756275	-1.96251301
Zr	0.00752092	-0.00936906	1.98345951
C	0.00232734	1.40415709	0.00716507
C	-1.28067663	0.69865150	0.13441468
C	-1.26168170	-0.75390015	-0.10947665
C	0.03670227	-1.44151089	0.00364541
C	1.33964540	-0.75225130	0.15287221
C	1.29597556	0.70755053	-0.11023020
H	-2.20677633	1.25450965	0.00091466
H	-2.17294848	-1.33106197	0.03463971
H	0.02317425	-2.52766366	0.02013321
H	2.83820821	-1.56630262	-1.15821266
H	3.55377842	-3.46202856	0.29955034
H	0.00083846	2.49081454	0.01496224
C	2.64810304	-1.52185786	-0.06938285
H	4.76944912	-1.38133481	0.39437596
H	2.19781978	1.29779440	0.03665413
C	3.84846888	-0.80597252	0.56909201
H	4.00669155	0.19753799	0.15165351

H	3.70257414	-0.70657960	1.65566897
C	2.58185261	-2.96818171	0.44264752
H	2.34067147	-2.98969067	1.51651208
H	1.83162271	-3.56910204	-0.08886727

4

84

C	4.15531651	-0.26778962	-0.93804822
C	4.20021672	0.26580928	0.41481236
C	3.86023308	-0.80236757	1.33337494
C	3.67430458	-1.97968707	0.53364222
C	3.80529048	-1.67224099	-0.85657169
C	3.83548425	1.66708188	0.36334031
C	3.72795319	0.79583255	-1.82403780
C	3.58921924	1.97261748	-1.01084283
H	3.56904603	0.16655146	3.25719782
H	2.88305809	-3.33027463	2.03370887
H	3.13873476	-3.53417349	-1.74009319
H	3.54276356	2.21838106	2.44196816
H	4.65606972	0.96812196	-3.77448832
H	2.76018384	3.96456912	-0.80362173
C	-4.15531651	0.26778962	-0.93804822
C	-4.20021672	-0.26580928	0.41481236
C	-3.83548425	-1.66708188	0.36334031
C	-3.58921924	-1.97261748	-1.01084283
C	-3.72795319	-0.79583255	-1.82403780
C	-3.86023308	0.80236757	1.33337494
C	-3.80529048	1.67224099	-0.85657169
C	-3.67430458	1.97968707	0.53364222
H	-4.90280943	-3.03600131	1.65691057
H	-2.76018384	-3.96456912	-0.80362173
H	-3.33940249	0.21447937	-3.70336063
H	-5.00685582	0.86328343	3.16824635
H	-3.13873476	3.53417349	-1.74009319
H	-4.39901901	3.86372806	1.28809037
Zr	-1.98192315	0.00689962	-0.19167735
Zr	1.98192315	-0.00689962	-0.19167735
C	-0.00050743	-1.41833648	-0.15369791
C	0.12169547	-0.72733649	-1.44925345
C	-0.12169547	0.72733649	-1.44925345
C	0.00050743	1.41833648	-0.15369791
C	0.14165520	0.72766265	1.14792839
C	-0.14165520	-0.72766265	1.14792839
H	-0.03288087	-1.29588061	-2.36467173
H	0.03288087	1.29588061	-2.36467173
H	0.00773197	2.50664494	-0.14998475
H	-1.08746372	1.64987979	2.71060456
H	-0.51240048	-1.10385274	3.25404367
H	-0.00773197	-2.50664494	-0.14998475
C	3.95835837	-0.76905708	2.83498220
H	3.39974389	-1.59402769	3.29786060
H	5.00685582	-0.86328343	3.16824635
C	3.44007434	-3.35742799	1.08724897
H	2.87945081	-3.99018669	0.38633643
H	4.39901901	-3.86372806	1.28809037
C	3.87841620	2.65813148	1.49332890
H	4.90280943	3.03600131	1.65691057

H	3.24135427	3.53099826	1.29288407
C	3.28262236	3.34459707	-1.54444143
H	4.21179870	3.87357367	-1.81464950
H	2.65974427	3.30252024	-2.44810331
C	3.77604178	-2.67141308	-1.98044052
H	3.39414533	-2.23385168	-2.91219464
H	4.78516869	-3.06393567	-2.19646758
C	3.66781830	0.76283020	-3.32718016
H	3.33940249	-0.21447937	-3.70336063
H	2.97145127	1.51565627	-3.72281671
C	-3.87841620	-2.65813148	1.49332890
H	-3.24135427	-3.53099826	1.29288407
H	-3.54276356	-2.21838106	2.44196816
C	-3.95835837	0.76905708	2.83498220
H	-3.56904603	-0.16655146	3.25719782
H	-3.39974389	1.59402769	3.29786060
C	-3.44007434	3.35742799	1.08724897
H	-2.88305809	3.33027463	2.03370887
H	-2.87945081	3.99018669	0.38633643
C	-3.77604178	2.67141308	-1.98044052
H	-3.39414533	2.23385168	-2.91219464
H	-4.78516869	3.06393567	-2.19646758
C	-3.28262236	-3.34459707	-1.54444143
H	-4.21179870	-3.87357367	-1.81464950
H	-2.65974427	-3.30252024	-2.44810331
C	-3.66781830	-0.76283020	-3.32718016
H	-2.97145127	-1.51565627	-3.72281671
H	-4.65606972	-0.96812196	-3.77448832
C	0.02999117	-1.54939436	2.40944298
H	-0.37037936	-2.56133666	2.25792790
H	1.08746372	-1.64987979	2.71060456
C	-0.02999117	1.54939436	2.40944298
H	0.51240048	1.10385274	3.25404367
H	0.37037936	2.56133666	2.25792790

IV

48

C	-0.68011600	0.25913100	4.17001100
C	0.67953900	-0.27257100	4.16628500
C	1.56975200	0.80060600	3.79218100
C	0.76489100	1.96391600	3.62169400
C	-0.60774800	1.65700900	3.81801400
C	0.60803000	-1.66714700	3.80192300
C	-1.56803700	-0.80840700	3.77788800
C	-0.76342300	-1.97181200	3.59791400
H	2.65259100	0.75873100	3.72046100
H	1.14913600	2.94955800	3.36266800
H	-1.43596200	2.35483500	3.73484000
H	1.43686200	-2.36343100	3.71218100
H	-2.64986600	-0.76356300	3.69200600
H	-1.14763500	-2.95447200	3.32738700
C	-0.68090600	-0.25914600	-4.16968400
C	0.67856300	0.27323700	-4.16620600
C	0.60648600	1.66779700	-3.80178000
C	-0.76516200	1.97177000	-3.59770000
C	-1.56928400	0.80810500	-3.77774600
C	1.56927500	-0.79957100	-3.79220200

C	-0.60778600	-1.65703300	-3.81778700
C	0.76501800	-1.96326600	-3.62157400
H	1.43475700	2.36489600	-3.71258800
H	-1.14988800	2.95416400	-3.32694700
H	-2.65105400	0.76274200	-3.69171000
H	2.65206700	-0.75698500	-3.72072400
H	-1.43562900	-2.35532400	-3.73442700
H	1.14998000	-2.94868600	-3.36278000
Zr	-0.00897100	-0.00209100	-1.96939100
Zr	-0.00892800	0.00207300	1.96969300
C	0.01989900	1.41621300	0.00968100
C	-1.27714900	0.72747700	0.10581700
C	-1.27705200	-0.72794700	-0.10365000
C	0.01950600	-1.41676400	-0.00950100
C	1.32309600	-0.72817800	0.15271200
C	1.32340000	0.72765200	-0.15603300
H	-2.19326300	1.29692800	-0.03647500
H	-2.19298600	-1.29789600	0.03769900
H	0.02253400	-2.50469500	-0.00179100
H	2.90126500	-1.62890900	-1.07322100
H	3.42676000	1.10491900	-0.52431500
H	0.02294700	2.50414900	0.00120000
C	2.58313400	-1.55272800	-0.01907400
H	3.41856100	-1.12588600	0.55076900
H	2.41847700	-2.57302600	0.35353000
C	2.58305300	1.55208300	0.01702500
H	2.43091900	2.56199800	-0.38784400
H	2.88148900	1.65652700	1.07447900

5

84

C	4.18430152	-0.21788305	-0.90668137
C	4.17509253	0.33399229	0.44059084
C	3.85725178	-0.73792632	1.36158282
C	3.75155271	-1.93288457	0.57390512
C	3.90457691	-1.63735174	-0.81685450
C	3.74073919	1.71314122	0.36020226
C	3.73439469	0.81384169	-1.81965618
C	3.51494271	1.98933736	-1.02661964
H	3.53583285	0.27997006	3.24997582
H	2.98032700	-3.30440060	2.06562120
H	3.46864406	-3.58404159	-1.66119398
H	3.39858729	2.28402699	2.42623837
H	4.69771419	1.01766321	-3.74980328
H	2.57352582	3.93551277	-0.86749782
C	-4.14730830	0.32488481	-0.92614549
C	-4.21008323	-0.20903693	0.42543964
C	-3.92327056	-1.62776393	0.36878929
C	-3.70463411	-1.94237244	-1.00673844
C	-3.77408302	-0.75583443	-1.81566484
C	-3.81510760	0.83876841	1.34562593
C	-3.73477599	1.71103114	-0.84338638
C	-3.58272574	2.00883921	0.54683947
H	-5.06405899	-2.93151974	1.66711444
H	-3.07828825	-4.00970443	-0.81219192
H	-3.34692171	0.23076996	-3.69929609
H	-4.95221569	0.92174199	3.18549808

H	-2.96926460	3.52902853	-1.74005905
H	-4.21533186	3.92286750	1.30809421
Zr	-1.98440183	-0.03178976	-0.18913844
Zr	1.98516550	-0.03557222	-0.21133948
C	-0.01876589	-1.50484690	-0.22040096
C	0.10764363	-0.76001580	-1.48124557
C	-0.13559501	0.69757199	-1.44646830
C	-0.00499910	1.37164946	-0.14203234
C	0.17140934	0.64680976	1.13414680
C	-0.08806249	-0.80735890	1.07489034
H	-0.05386454	-1.29448673	-2.41774696
H	0.00682292	1.27778909	-2.35597358
H	0.00924795	2.45978099	-0.11817153
H	-1.06202987	1.56870985	2.68930315
H	0.50161883	2.36433359	2.40018964
H	1.03346414	-3.40543342	-0.42916808
C	3.87986604	-0.68849956	2.86541344
H	3.23702344	-1.46282465	3.30731404
H	4.89894076	-0.84992423	3.25892965
C	3.59065775	-3.31129496	1.15234737
H	3.12524123	-4.00739974	0.44201612
H	4.57356612	-3.73260582	1.42241728
C	3.71381341	2.72538800	1.47149339
H	4.71162873	3.16906740	1.63380413
H	3.02578015	3.55381521	1.25036024
C	3.15518911	3.33919965	-1.58318258
H	4.06414511	3.91550249	-1.82400402
H	2.56936041	3.25711033	-2.50856581
C	3.96963720	-2.64468936	-1.93259431
H	3.49508701	-2.27760004	-2.85272183
H	5.01497367	-2.89536897	-2.18407179
C	3.71396819	0.75443001	-3.32318270
H	3.46059767	-0.24852023	-3.68930371
H	2.97979621	1.45328724	-3.74843800
C	-4.01949882	-2.61604405	1.49859399
H	-3.43549193	-3.52443692	1.29577095
H	-3.65339686	-2.19608237	2.44495259
C	-3.90752928	0.80469297	2.84773994
H	-3.53567678	-0.13954841	3.26671774
H	-3.32843694	1.61630855	3.30901673
C	-3.28178538	3.37390129	1.09958037
H	-2.71909923	3.32117989	2.04150062
H	-2.69903346	3.98085986	0.39399823
C	-3.66605241	2.70928003	-1.96627924
H	-3.33432474	2.24914447	-2.90618146
H	-4.65251670	3.16623178	-2.15909445
C	-3.51642687	-3.32968731	-1.55429287
H	-4.48684616	-3.75864678	-1.85592247
H	-2.87242630	-3.33709162	-2.44441948
C	-3.72386997	-0.72734518	-3.31921676
H	-3.07032305	-1.51579604	-3.71820453
H	-4.72465859	-0.88125719	-3.75958968
C	-0.00286953	1.38891553	2.43933948
H	0.43846935	0.81807945	3.26809149
H	0.06156607	-1.39708123	1.98073613
C	0.01763842	-3.01733404	-0.25506445
H	-0.34094253	-3.43720193	0.69377310
H	-0.62088147	-3.41392657	-1.05666953

V

48

C	-0.65260776	0.24529262	4.18284479
C	0.69245607	-0.32352519	4.15200307
C	1.60633303	0.73118809	3.78825732
C	0.83321733	1.91817965	3.64645562
C	-0.54628587	1.64717137	3.85606473
C	0.57819108	-1.70651514	3.75910597
C	-1.57612712	-0.79189313	3.78869839
C	-0.80579645	-1.96985333	3.56991046
H	2.68499317	0.65786023	3.68499450
H	1.24467624	2.89696621	3.40329301
H	-1.35502766	2.37041738	3.80543327
H	1.38546605	-2.42382867	3.64410427
H	-2.65742308	-0.71571343	3.71851465
H	-1.22011832	-2.93602624	3.28518226
C	-0.66888881	-0.29676708	-4.16964562
C	0.68610252	0.24705716	-4.16929597
C	0.59993937	1.64882167	-3.83752231
C	-0.77536537	1.94510914	-3.64968763
C	-1.56847966	0.77095695	-3.80747193
C	1.58347401	-0.81049147	-3.76868457
C	-0.58692562	-1.68613435	-3.78840891
C	0.78757834	-1.97620920	-3.57769981
H	1.42200759	2.35435475	-3.75920792
H	-1.17133264	2.93087574	-3.40969788
H	-2.65041625	0.71875650	-3.72757618
H	2.66504449	-0.75612768	-3.68710246
H	-1.40913938	-2.38971001	-3.69570623
H	1.17815187	-2.95263547	-3.29482139
Zr	-0.01051676	0.00564080	-1.97183236
Zr	-0.01764898	0.00860463	1.96930846
C	-0.00945491	1.47552469	-0.00219512
C	-1.28471442	0.75276118	0.09501467
C	-1.27933607	-0.70688301	-0.11705644
C	0.01724267	-1.40170218	-0.01396346
C	1.30790153	-0.69972921	0.16831899
C	1.27269155	0.75531411	-0.11461366
H	-2.21116687	1.30855940	-0.04644752
H	-2.19619951	-1.27304806	0.03022509
H	0.01824917	-2.48967995	0.00267591
H	2.84798031	-1.63902060	-1.07357499
H	2.53933480	-2.44468745	0.48186910
H	0.93996928	3.39245119	-0.32072638
C	2.59982501	-1.46566824	-0.01296625
H	3.43638207	-0.91526981	0.43859489
H	2.19003264	1.32807971	0.02788612
C	-0.02281936	2.99029897	0.02062513
H	-0.80292784	3.39264604	-0.64145220
H	-0.21476873	3.38813737	1.02932879

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