Supplementary Information for the manuscript entitled

Ligand and Metal-Centred Reactivity in 2,6-bis(imino)-1,4-dihydropyridinate Zn(II) alkyls: the dual behaviour of an intriguing type of complex.

Juan Manuel Delgado-Collado, Manuel Gallardo-Villagrán, Eleuterio Álvarez, Juan Cámpora,* and Antonio Rodríguez-Delgado.*

Instituto de Investigaciones Químicas, CSIC-Universidad de Sevilla, c/Américo Vespucio, 49, 41092 Sevilla, Spain

Table of Contents

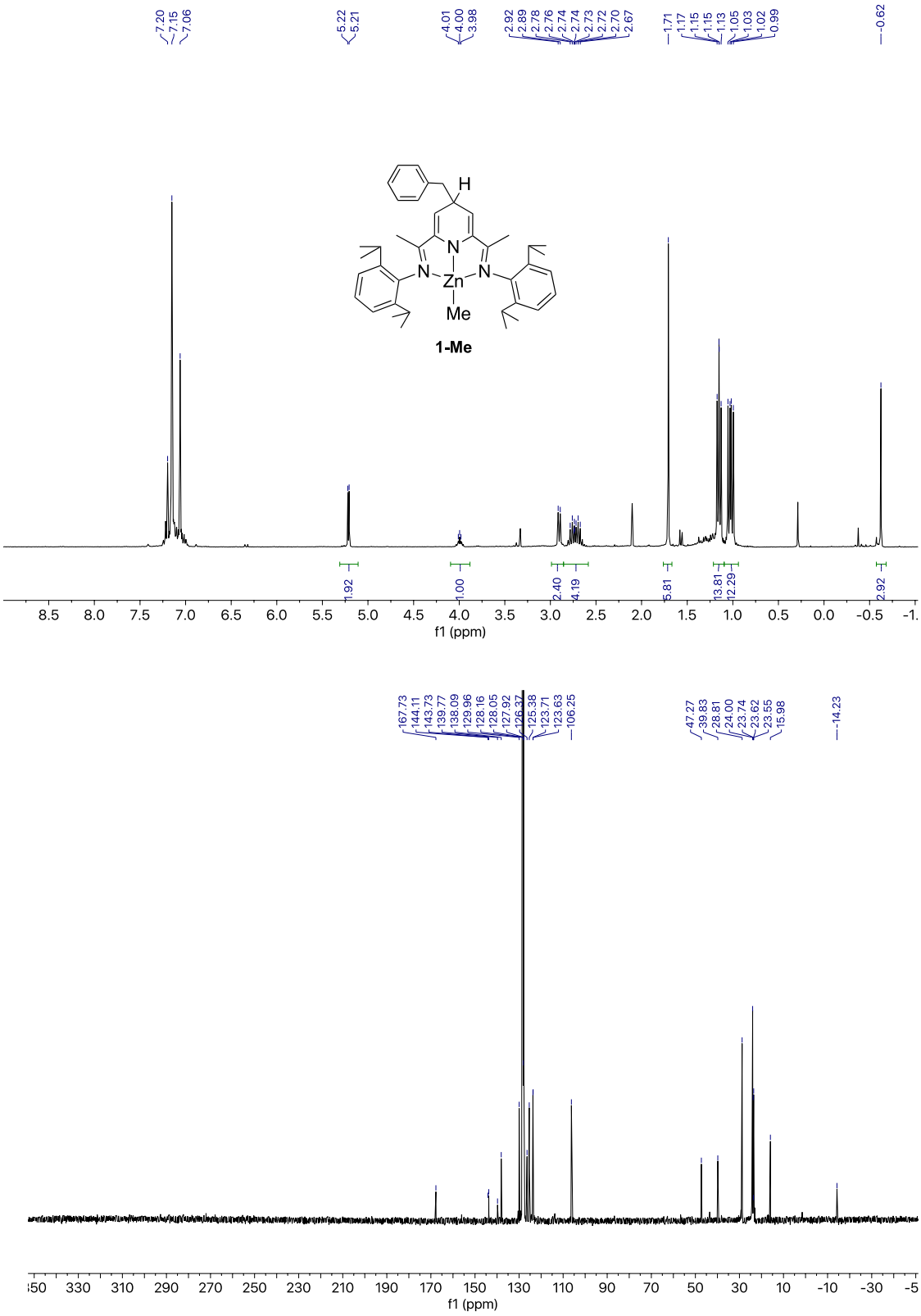


Figure S1. ^{1}H (C_6D_6, 25 °C, 400 MHz) and ^{13}C-NMR (C_6D_6, 25 °C, 100 MHz) spectra of **1-Me**

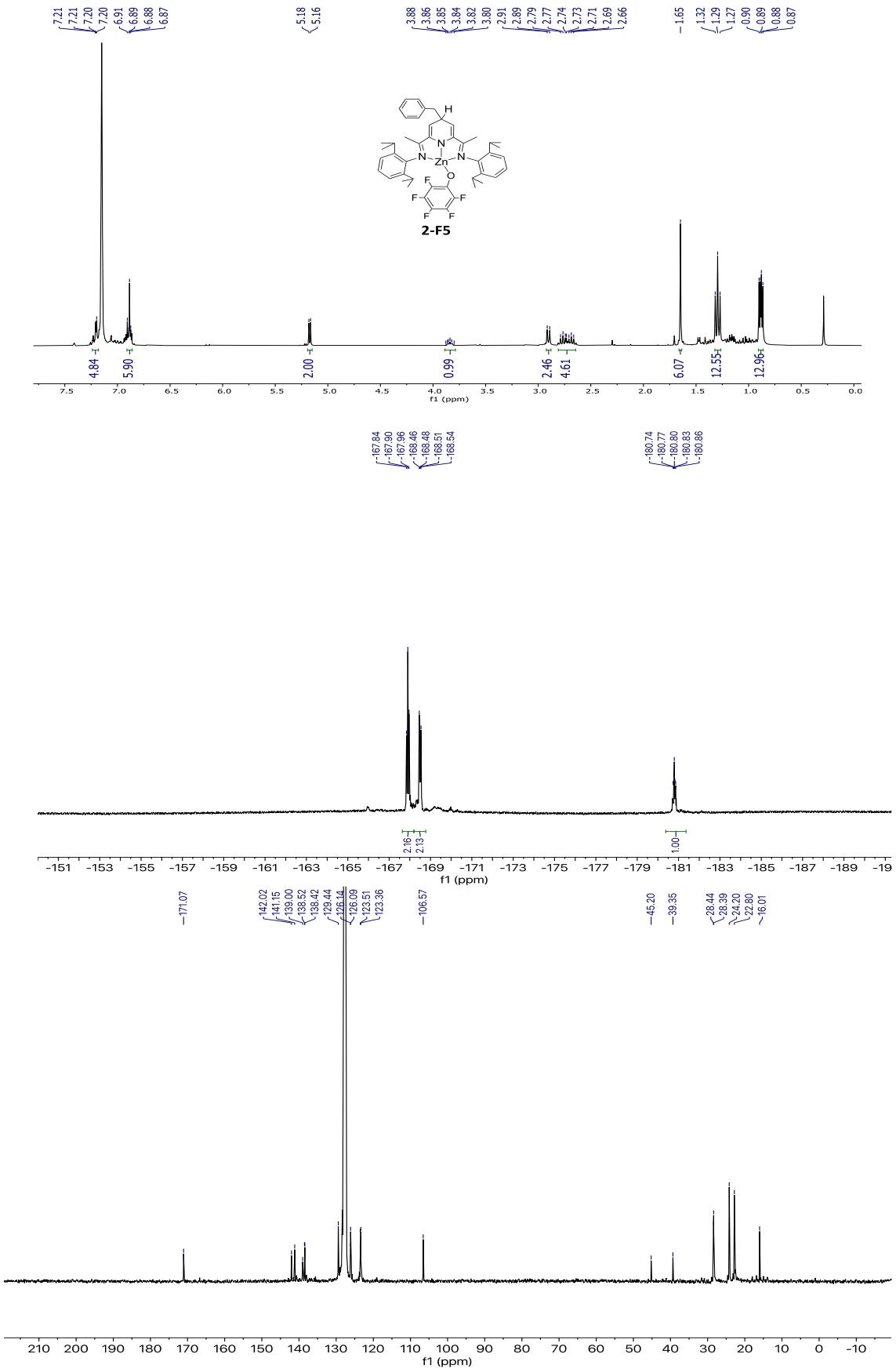
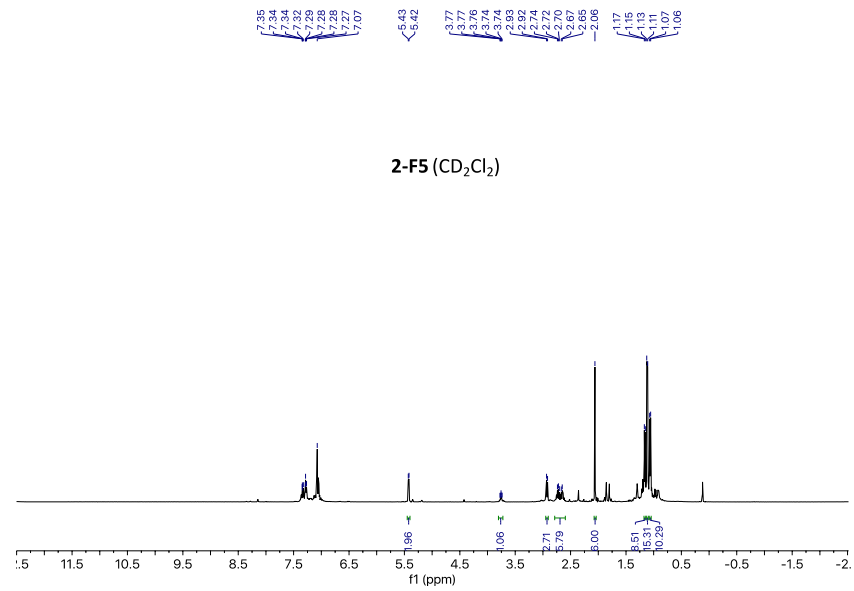
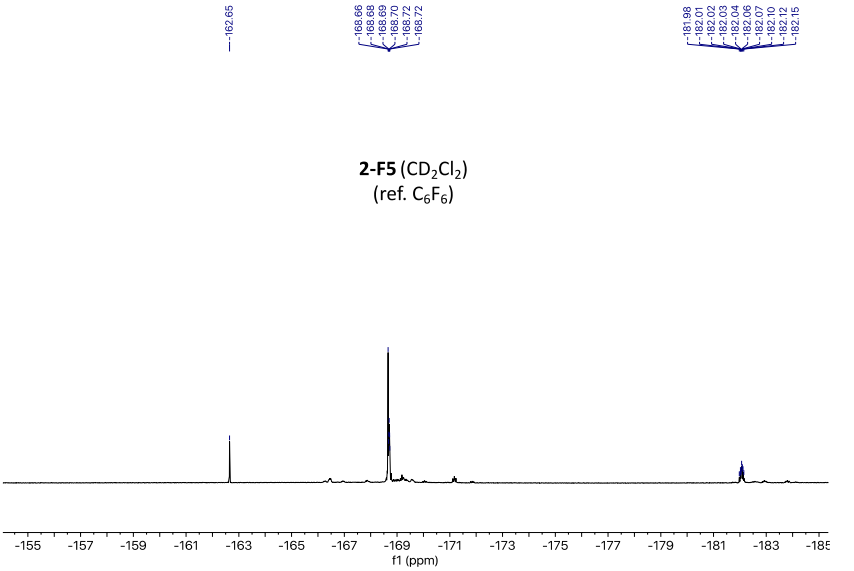


Figure S2. ^{1}H (C_6D_6, 25 °C, 400 MHz), ^{19}F (C_6D_6, 25 °C, 376 MHz) and ^{13}C-NMR (C_6D_6, 25 °C, 100 MHz) spectra of **2-F5**



2-F5 (CD_2Cl_2)



2-F5 (CD_2Cl_2)
(ref. C_6F_6)

Figure S3. ^{1}H (CD_2Cl_2, 25 °C, 400 MHz) and ^{19}F (CD_2Cl_2, 25 °C, 376 MHz) spectra of **2-F5**

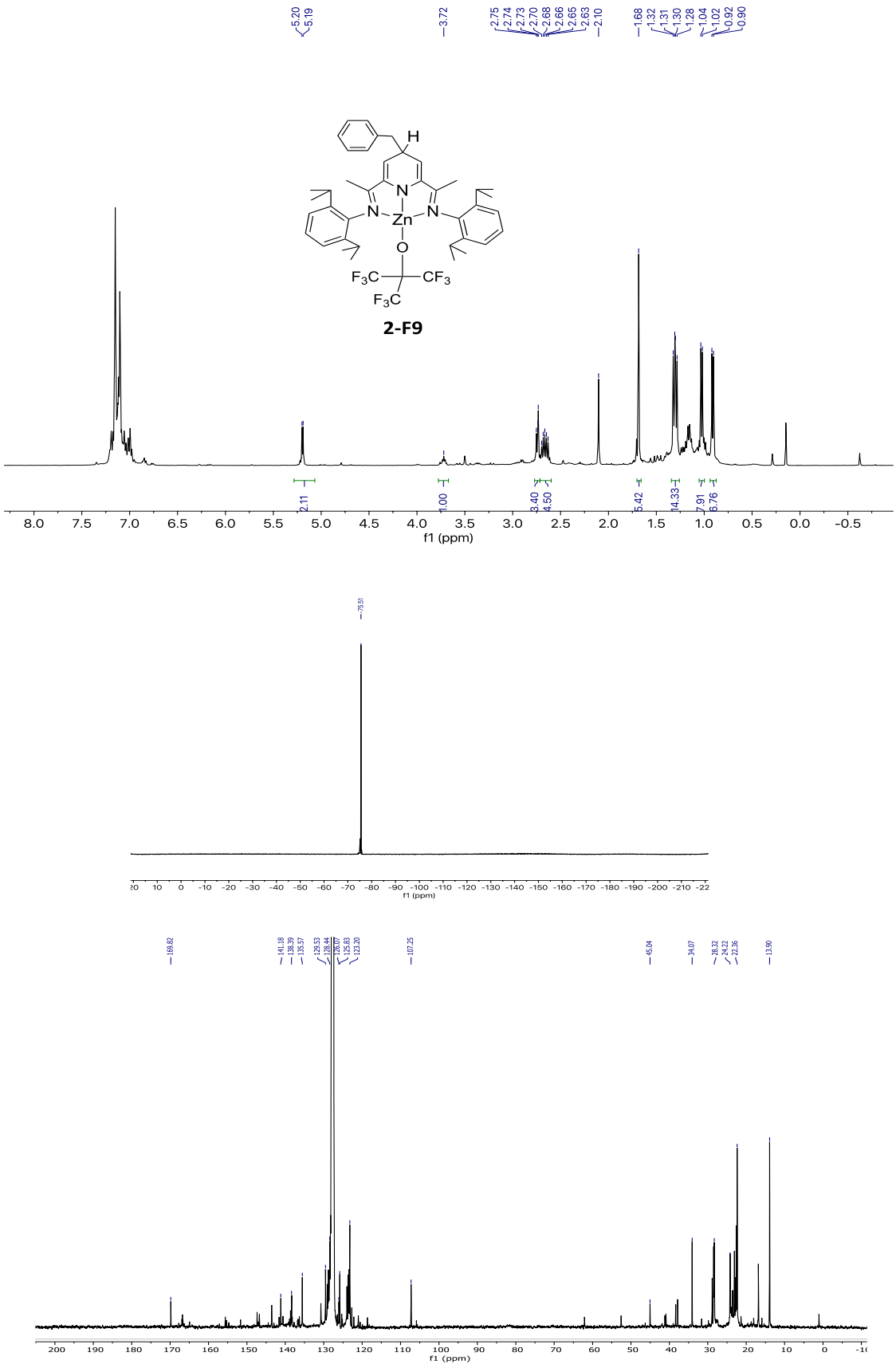


Figure S4. ^{1}H (C_6D_6, 25 °C, 400 MHz), ^{19}F (C_6D_6, 25 °C, 376 MHz) and ^{13}C-NMR (C_6D_6, 25 °C, 100 MHz) spectra of **2-F9**

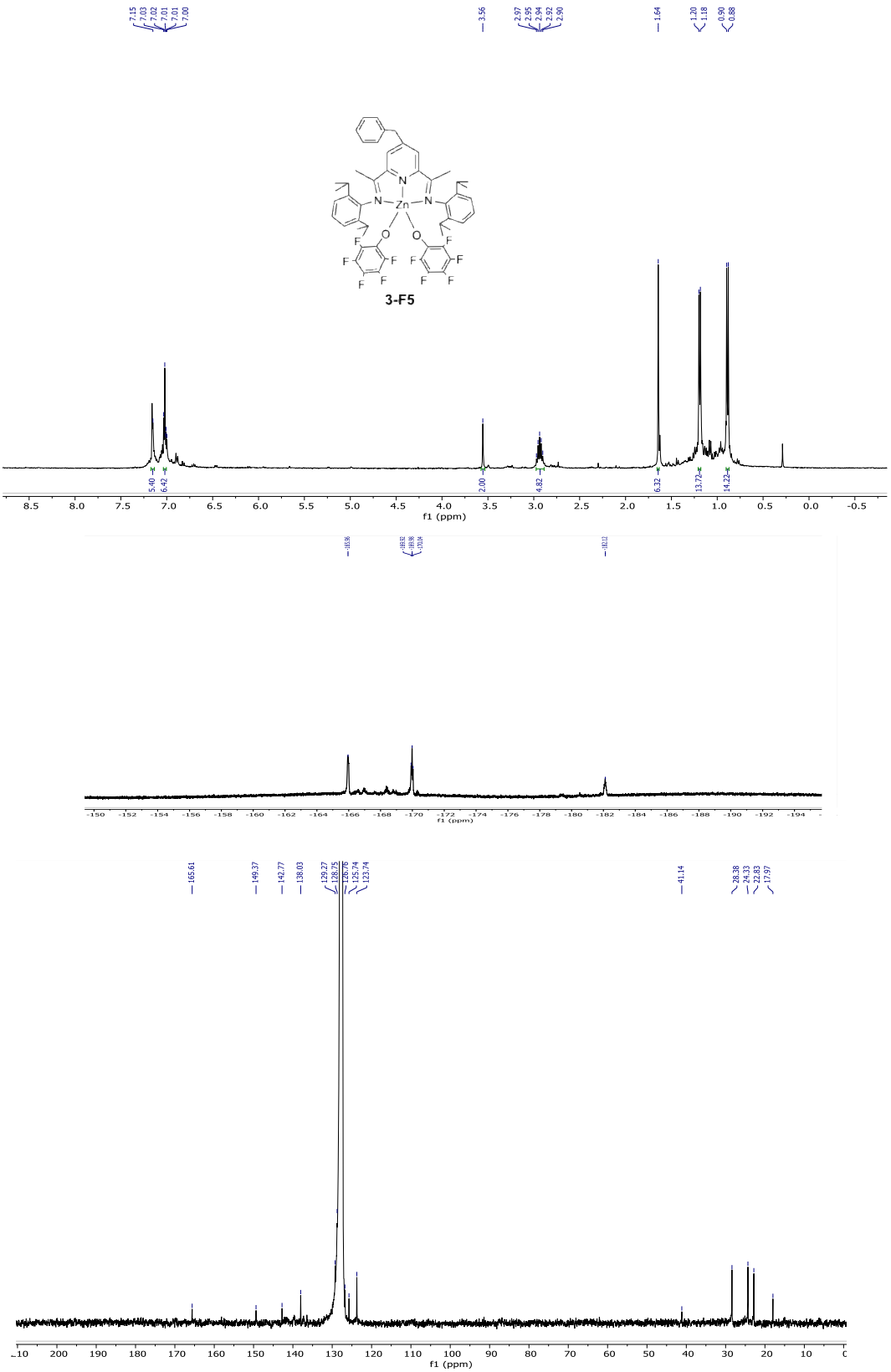


Figure S5. ^{1}H (C_6D_6, 25 °C, 400 MHz), ^{19}F (C_6D_6, 25 °C, 376 MHz) and ^{13}C-NMR (C_6D_6, 25 °C, 100 MHz) spectra of **3-F5**

Partial NMR characterization of **3-F9**

^{1}H NMR (C_6D_6, 25 °C, 400 MHz): δ 1.64 (s, 6H, *Me*(CN)), 3.50 (s, 2H, $CH_{2,\ Py-Bn}$). The remaining ^{1}H NMR signals appear overlapped with signals of other products or solvents; therefore, they cannot be unambiguously assigned.

$^{19}F\{^{1}H\}$ NMR (C_6D_6, 25 °C, 376 MHz): δ -75.43 (s, 9F, ($F_9C_4O^-$)).

VT-^{19}F NMR spectra and dynamic behavior of 2-F5

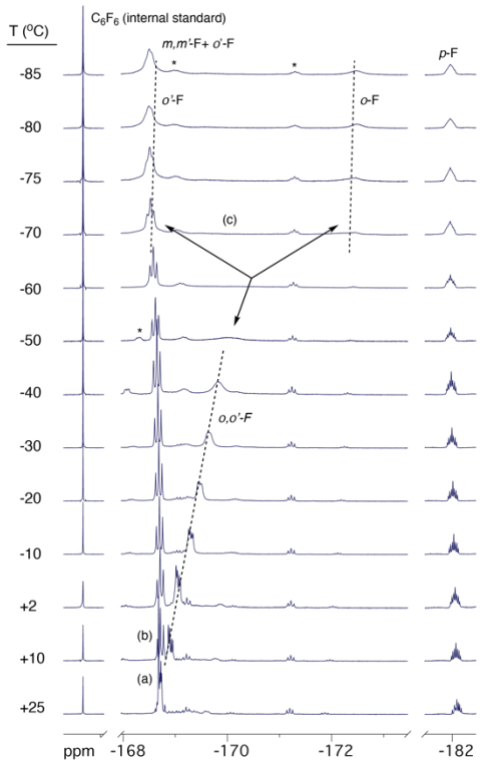


Figure S6. VT-^{19}F NMR spectra of complex **2-F5** between 298 K (25 ºC, bottom) and 188 K (-85 ºC, top) in CD_2Cl_2. For clarity, two empty spectral regions have been cut from the plots. The leftmost region shows the signal C_6F_6 for referencing (-166.7 ppm). The sharp resolution of this signal over the full temperature interval indicates that any line broadening is due to dynamic effects and not to poor spectral quality. Small amounts of **3-F5**, very difficult to avoid, are responsible for the small signal marked with an asterisk. Signal assignments are shown in the first and second spectra on the top, and the signal positions can be traced down in the series until the bottom spectrum at 25 ºC. The broad signal at -169.2 ppm is due to the accidental coincidence of one of the uncoordinated *o'*-F and the two *m*-F signals. The estimated position of the *o'*-F is marked with a dashed line; the signal for the coordinated *o'*-F is marked with a second dashed line at -172.5 ppm. The *o,o'*-F signals remain approximately in the same position as the temperature rises, but they become increasingly broadened as the temperature increases. The coalescence occurs at 213 K (-60 ºC), at which temperature the *o,o'*-F signals become too broad to be observed (solid arrows, marked c). As the temperature rises, a single signal emerges from the baseline (223 K, -50 ºC), for two *o*-F signals. This resonance is subject to evident temperature drift, shifting to the lower field as the temperature increases. The coincidence of the *m*- and -*o*-F signals at room temperature (298 K, 25 ºC) is accidental (a and b). We believe that the thermal drift of the *o*-F signal is caused by the decreasing fraction of time that the F atoms are in the vicinity of the Zn atom (notice that the *o*-F signal of the **3-F5** impurity, marked with an asterisk on the left side of the -50 ºC spectrum, is also subject to a similar thermal drift, exiting the spectral window above -30 ºC).

Computational details

For structure optimization and energy assessment, we used the commercial software Spartan'20.[i] Topological analyses of the electron density were performed with the AIMALL package (version 19.10.12).[ii] For the generation of suitably formatted (.wfx) electron density files, we used ORCA 5.0.3.[iii] The latter software was also applied for the estimate of ^{19}F NMR chemical shifts. XYZ coordinates for all optimized structures are listed below.

AIM analysis of the electron density wavefunction of **2-F5**. The purpose of these analyses is to confirm the existence of a chemical interaction between the atoms of Zn and F1, based on Bader's "Atoms in Molecules" (AIM) theory. Preliminary tests for the generation of an accurate description of the structure of this complex with different functionals using DFT methods gave significant overestimations of the Zn···F distance. Therefore, we decided to start from the experimental coordinates provided by the X-ray structure. Since the lengths of C-H bonds determined by X-ray diffraction are known to be subject to a systematic error, we refined the H atoms coordinates by performing a molecular mechanics calculation on the structural data while keeping fixed the positions of all heavy atoms. This previous step was executed using the fast molecular optimization method with the Merck Molecular Force Field (MMFF) provided by the Spartan software and the "freeze heavy atoms option". The resulting geometry was fed as an xyz coordinate file to the ORCA software. A single-point energy calculation was performed with ORCA, using the RSH-mGGA functional ω-B97M-V and the def2-TZVPP basis functions set. The TightSCF and AIM keywords were added in the input to provide a tighter SCF convergence criterion and to generate the required electron density wavefunction file (.wfx). The latter file was processed with the AIMALL software using standard parameters. The image shown in Figure 4 shows a slice of the contour plot of the Laplacian of the electron density in the plane defined by the atoms Zn, F1 and C42, superimposed on a 3-D plot of the molecular geometry. All hydrogen atoms with their associated BCP, RCP, and bond paths have been hidden (cloaked) to facilitate the interpretation.

Modeling the fluxional exchange of o-F *atoms in dihydropyridinate*. Full geometry optimizations of stationary points at ground and transition states were carried out in Spartan20, taking advantage of its excellent graphic user interface (GUI) for partial optimization and driving systematic variations of bond distances and angles. Geometry optimizations were computed at the ωB97X-D functional, which includes Grimme's empirical correction for dispersive forces, the 6-31G* basis function, and the CPCM implicit model for dichloromethane solvent. The energy gradient criterium was tightened from Spartan's default value 3 x 10^{-4} to 5 x 10^{-5} erg/bohr. Electronic (SCF) energies were refined with a single point calculation at the ωB97X-D/6-311++G(3df,2p) (with SCF convergence criterion set to "HIGH"). This is largest Pople-type triple-zeta quality basis function set available in Spartan. A finer grid than Spartan's default was used in all calculations to improve the accuracy of the electron density integration (keyword BIGGRID).

Single-point calculations were accelerated using the "dual" option, which specifies that SCF convergence is achieved at the 6–311G* level, and then corrected perturbatively for the effect of additional diffuse and polarization functions. Thermal Corrections (TC) were computed at 213 K (coalescence temperature), at the same level at which the vibrational data were available (namely, the double-zeta quality basis set used for geometry optimization), *i. e.:* TC = G°– E(SCF) (both at the ωB97X-D /6-31G*, CPCM level). To compute the solvent correction (SC), we performed an inexpensive additional gas phase single-point energy calculation on optimized geometries at the ωB97X-D /6-31G* level (i.e., omitting the solvent calculation), therefore SC = E(SCF, CPCM)-E(SCF, gas phase) (ωB97X-D /6-31G*). In addition to reducing the computational cost, this procedure has the advantage of computing the solvent effect at a level of the theory that is similar to that used for the parametrization of the CPCM model. Refined G° figures were computed for each molecule as G° = E(SCF, ωB97X-D/6-311++G(3df,2p) + TC + SC.

To facilitate the transition state search, the **2-F5** molecule used for the AIM analysis was edited, removing the phenyl fragment of the 4-benzyl group. This operation leads to the simplified model **2'-F5**. We believe that this change should have only minor consequences on the energy of the transition state relative to the ground state. In the search for a straightforward exchange of the *o*-F atoms between the coordinated and non-coordinated sites, the potential energy surface was swept by rotating the C_6F_5 ring 180 deg by regular 10 deg angles and fully optimizing the rest of the geometry at each step. During the calculation of the rotation energy profile, the approximately flat metal fragment spontaneously undergoes a similar rotation in the opposite direction, which causes the F(5) atom to approach the Zn atom *by the opposite face* (with regard to the stereogenic sp^3-carbon in the dihydropyridine ring). This leads to **2"-F5**, a complex showing a very similar but not identical configuration to **2'-F5,** and only 0.9 Kcal·mol^{-1} less stable. In the transition state (**TS-F5**), none of the *o*-F atoms interact with the Zn. However, locating the TS (with a single imaginary frequency) was a very difficult task due to the flat energy profile and low imaginary frequency (26 cm^{-1}), in the limit of DFT accuracy. The energy profile shows a smooth transition between **2'-F5** and **2"-F5** with **TS-F5** lying 5 Kcal·mol^{-1} over the ground state (at the theory level used for geometry optimization). After refining the SCF energy at the higher level of the theory, the computed energy barrier for the *o,o'*-F exchange lowered to ca. 2 Kcal·mol^{-1} at, a significant underestimate compared to the observed energy barrier (8.5 *vs.* 2 Kcal·mol^{-1} at the We have tested other high-level methods to refine the SCF energy (e. g. ωB97M-V/def2-TZVPP(D)) with essentially identical results. Table S2 shows the computed parameters and the estimate of relative energies for **2'-F5**, **TS-F5**, and **2"-F5,** and xyz coordinates for the geometries of these species are given at the end of this section. All energies are expressed in Kcal·mol^{-1}.

Table S1. ΔG° and energy barrier for the fluxional exchange between **2'-F5** and **2"-F5**

	ωB97X-D/6-31G*/CPCM(CH_2Cl_2)					ωB97M-V/6-311++G(3df,2p)		
Label	E SCF (CH_2Cl_2)	G°(213 K) (CH_2Cl_2)	E SCF (SP, gas)[a]	TC[b]	SC[c]	E SCF (SP, g)	G° (estim.)	ΔG°
2'-F5	-2553467.70	-2553022.69	-2553454.70	445.01	-13.00	-2554080.14	-2553648.10	0.00
TS- F5	-2553462.17	-2553017.77	-2553448.44	444.40	-13.73	-2554076.71	-2553646.00	2.09
2"-F5	-2553466.83	-2553021.99	-2553453.65	444.84	-13.18	-2554079.22	-2553647.60	0.57

DFT Estimation of the NMR chemical shifts. ^{19}F NMR chemical shifts were computed with ORCA, by applying a single-point high-level calculation (ωB97M-V/def2-TZVPP/CPCM(dichloromethane), TightSCF) to the Cartesian coordinates generated with the Spartan software. For **2-F5**, we used the same atomic coordinates as in the AIM. To ascertain whether the stereochemical configuration has a potential to significantly alter chemical shifts, the coordinates for the molecular models **2'-F5** or **2"-F5**, fully optimized ω-B97X-D/6-31G* geometry (which exhibits a somewhat longer Zn···F-C interaction). In addition, the chemical shifts of the internal standard actually used (C_6F_6) and the conventional ^{19}F reference ($FSiCl_3$, 0 ppm) were computed using the same methodology. To suppress the effect of temperature on the relative chemical shift scale, the signal of C_6F_6 was arbitrarily fixed at -162.669 ppm (chemical shift recorded directly in a sample of **2-F5** at 25 °C). The relative chemical shift of $FSiCl_3$ (0.0 ppm by definition) in this C_6F_6 reference framework was displaced by only +1.540 ppm.

Chemical shifts computed from the X-ray diffraction structure of **2-F5** resemble more the experimental data recorded at the lowest accessible temperature (-80 °C) than the calculations from the optimized **2'-F5** geometry. As expected, ^{19}F NMR chemical shift calculations place the **2'-F5** and **2"-F5** signals on very close positions, confirming that these could not have been possibly resolved even at -80° C.

Table S.2. Calculated ^{19}F NMR isotropic chemical shielding in dichloromethane

Species	**F1** (*o*)	**F5** (*o'*)	**F2**(*m*)	**F4**(*m'*)	**F3** (*p*)	Other
2-F5	367.076	359.269	356.619	361.816	380.504	
2'-F5	360.085	358.640	354.716	360.085	378.482	
2"-F5	358.846	359.906	360.407	354.885	378.694	
C_6F_6						359.623
$SiCl_3F$						195.414

Table S.3. Calculated ^{19}F NMR relative chemical shifts (C_6D_6 = -162.669 ppm)

Species	**F1** (*o*)	**F5** (*o'*)	**F2**(*m*)	**F4**(*m'*)	**F3** (*p*)	Other
2-F5	-170.122	-162.315	-159.665	-164.862	-183.55	
2-F5[a]	-166.218		-162.263		-183.55	
2'-F5	-166.509	-164.932	-161.008	-166.377	-184.754	
2"-F5	-165.138	-166.198	-166.699	-161.177	-184.986	
C_6F_6						-162.669
$SiCl_3F$						+1.577

(a) *averaged ortho and meta shifts to simulate dynamic exchange.*

Table S3. Experimental ^{19}F NMR relative chemical shifts (C_6D_6 = -162.669 ppm)

	F1 (*o*)	**F5** (*o'*)	**F2+F4** (*m,m'*)	**F3** (*p*)
2-F5 (-84 °C)	-172.46	-164.46	-164.26	-181.96
2-F5 (25 °C)	-168.74		-168.71	-182.04

XYZ coordinate files.

2-F5 (XYZ coordinates used for AIM studies)

106

C	-4.651469	0.643240	1.748845
C	-4.612728	-2.225321	-2.832534
C	-5.006051	-0.956888	-2.685947
C	-4.237097	-0.036814	-2.025270
F	-5.368046	-3.137061	-3.478759
F	-6.194548	-0.548522	-3.202100
F	-4.685772	1.216619	-1.880747
H	-4.925276	-4.085223	3.373378
H	-5.251943	-1.677909	3.438892
H	-5.621638	0.281562	2.107629
H	-4.479312	0.194734	0.769835
H	-4.741899	1.726441	1.611379
C	-0.791165	-4.835529	0.764024
H	-2.813606	-5.017486	2.629970
H	-1.259016	-5.727921	1.193370
H	0.162651	-5.157669	0.330024
H	-0.289774	-5.064093	3.484876
C	1.967505	1.113277	0.278840
C	3.012290	1.671655	0.964291
C	2.956740	1.885005	2.436362
C	1.858277	1.049940	3.026841
C	0.883176	0.533232	2.260870
C	1.958109	0.833256	-1.154003
C	3.144024	1.248288	-1.979848
C	2.845794	3.285116	2.861672
C	4.053430	4.213524	2.506559
C	3.762349	5.550297	2.411587
C	4.727042	6.478704	2.072990
C	6.018014	6.050337	1.829365
C	6.290555	4.730232	1.978018
C	5.302235	3.828493	2.287710
C	-0.211341	-0.346839	2.787346
C	-0.290657	-0.575190	4.267675
C	0.799966	-0.008478	-3.038996
C	0.307053	0.993268	-3.858648
C	0.238134	0.743248	-5.223358
C	0.595207	-0.468515	-5.741576
C	1.002228	-1.468594	-4.907472
C	1.117014	-1.278579	-3.546891
C	-0.118665	2.363377	-3.321848
C	0.724805	3.496800	-3.864841
C	-1.573150	2.613397	-3.643928
C	1.623511	-2.405336	-2.644654
C	3.117950	-2.558681	-2.787113
C	0.901478	-3.720440	-2.937830
C	-2.063579	-1.735282	2.333131
C	-1.866962	-3.122060	2.244353
C	-2.917654	-3.933790	2.644887
C	-4.119978	-3.418749	3.076392
C	-4.287612	-2.065309	3.113555
C	-3.269885	-1.181905	2.729537
C	-0.562039	-3.740442	1.783944
C	0.234569	-4.262150	2.952515
C	-3.522627	0.323215	2.715084
C	-3.829880	0.819921	4.110764
C	-2.995557	-0.401843	-1.465760
C	-2.612513	-1.698613	-1.641252
C	-3.379547	-2.630354	-2.310187
F	-1.426188	-2.103645	-1.120969
F	-2.972589	-3.883786	-2.442322
H	3.906462	1.995614	0.441934
H	3.879899	1.446974	2.840379
H	1.883821	0.895696	4.100657
H	2.751110	5.911319	2.595115
H	4.473395	7.531649	1.990350

H	6.793644	6.759828	1.559797
H	7.306257	4.372762	1.818550
H	5.598934	2.785751	2.374069
H	-0.107825	1.513203	-5.910606
H	0.530003	-0.645055	-6.812601
H	1.266400	-2.424942	-5.355272
H	-0.029006	2.384511	-2.231594
H	1.405765	-2.168487	-1.598186
H	0.047069	-2.983330	1.279320
H	-2.637125	0.859436	2.361595
H	-1.120141	-1.212800	4.573464
H	-0.405551	0.385118	4.779837
H	0.629711	-1.057111	4.612029
H	0.617560	3.615102	-4.948797
H	1.787702	3.334089	-3.659288
H	0.441622	4.448913	-3.402221
H	-1.924846	3.531046	-3.158551
H	-2.206801	1.794623	-3.290879
H	-1.755698	2.727797	-4.718304
H	3.408220	-2.838986	-3.806146
H	3.494644	-3.335630	-2.112647
H	3.642604	-1.629732	-2.541755
H	1.167790	-4.138898	-3.914052
H	-0.185766	-3.593614	-2.910247
H	1.166108	-4.472031	-2.185393
H	-1.423942	-4.491066	-0.061211
H	0.442370	-3.470444	3.680082
H	1.198929	-4.663079	2.620976
H	-3.027014	0.569087	4.811962
H	-4.759313	0.400864	4.511794
H	-3.939789	1.910232	4.113633
H	3.063580	0.991398	-3.036016
H	4.043610	0.755468	-1.597413
H	3.275739	2.332429	-1.909357
H	2.737608	3.352347	3.953765
H	1.938563	3.734817	2.431591
N	0.845198	0.673243	0.935387
N	0.924099	0.218206	-1.635058
N	-0.969475	-0.875214	1.918144
O	-2.280548	0.488228	-0.823665
Zn	-0.549918	-0.127488	-0.074829

2’-F5

96

C	-1.655487	-3.900867	1.944919
C	1.896920	-3.748234	-2.605077
C	0.616031	-4.272950	-2.481118
C	-0.368917	-3.576790	-1.798566
F	2.847341	-4.420929	-3.264219
F	0.335631	-5.459234	-3.027018
F	-1.594051	-4.114389	-1.700644
H	3.315046	-4.594562	2.521347
H	0.889382	-4.787437	2.929821
H	-1.218732	-4.895276	2.091181
H	-1.538653	-3.617385	0.896474
H	-2.727507	-3.974742	2.160662
C	4.262750	-0.061494	0.792032
H	4.307390	-2.407991	1.964248
H	5.127880	-0.514663	1.289090
H	4.557200	0.945806	0.480067
H	4.188709	0.216926	3.571131
C	-1.738270	2.613974	0.593901
C	-2.009628	3.770239	1.239855
C	-2.249408	3.720159	2.734919
C	-1.339471	2.653325	3.308618
C	-1.099424	1.547840	2.568271
C	-1.465908	2.529319	-0.867564
C	-1.937989	3.619936	-1.778302
C	-3.728916	3.429510	3.057925

C	-0.214588	0.433897	3.008290
C	0.076057	0.244532	4.464815
C	-0.518389	1.197645	-2.623196
C	-1.472188	0.584386	-3.452507
C	-1.077801	0.223308	-4.743646
C	0.215128	0.451922	-5.192570
C	1.145360	1.050450	-4.349088
C	0.802847	1.427625	-3.051410
C	-2.902510	0.323889	-3.002937
C	-3.889375	1.190454	-3.799545
C	-3.279366	-1.159657	-3.108455
C	1.810731	2.100621	-2.132004
C	1.735387	3.628936	-2.266422
C	3.246851	1.620220	-2.357537
C	1.066548	-1.465176	2.293906
C	2.447136	-1.335117	2.049324
C	3.239323	-2.478329	2.143810
C	2.682627	-3.713937	2.457898
C	1.317884	-3.819180	2.685379
C	0.480121	-2.703505	2.604549
C	3.052189	0.022611	1.725660
C	3.427720	0.773819	3.011740
C	-1.009807	-2.861925	2.870963
C	-1.263130	-3.220170	4.343114
C	-0.130856	-2.325853	-1.203695
C	1.176256	-1.838198	-1.356756
C	2.173416	-2.514947	-2.032766
F	1.453579	-0.634383	-0.803057
F	3.398956	-1.989457	-2.139668
H	-2.057194	4.722086	0.722173
H	-1.993556	4.690482	3.175921
H	-0.901617	2.795056	4.290743
H	-1.799262	-0.245908	-5.407176
H	0.501801	0.161356	-6.199004
H	2.155101	1.220600	-4.708985
H	-2.990406	0.603252	-1.948463
H	1.537863	1.846866	-1.101566
H	2.283313	0.611592	1.213223
H	-1.501368	-1.904568	2.672067
H	0.794933	-0.559274	4.629665
H	-0.855260	0.007616	4.989568
H	0.469097	1.168047	4.899501
H	-3.888681	0.907374	-4.858689
H	-3.634679	2.253055	-3.735112
H	-4.907010	1.057475	-3.416051
H	-4.308295	-1.307221	-2.761016
H	-2.620539	-1.775924	-2.491950
H	-3.224750	-1.513811	-4.144031
H	1.981398	3.935405	-3.289936
H	2.448367	4.106856	-1.585315
H	0.736855	4.008888	-2.031835
H	3.643500	1.964097	-3.319521
H	3.311522	0.529565	-2.327779
H	3.897218	2.023653	-1.574712
H	4.034824	-0.644649	-0.103885
H	2.563752	0.915018	3.667225
H	3.835494	1.761884	2.770768
H	-0.816663	-2.484458	5.019460
H	-0.835719	-4.200838	4.582579
H	-2.339216	-3.262968	4.544300
H	-1.603678	3.458375	-2.803984
H	-1.572289	4.591418	-1.433844
H	-3.032083	3.656742	-1.757795
H	-3.889167	3.391772	4.141774
H	-4.024989	2.464756	2.631973
N	-1.535617	1.427565	1.266018
N	-0.836102	1.475697	-1.263726
N	0.240388	-0.327559	2.072216
O	-1.062868	-1.676862	-0.561430
Zn	-0.688217	0.026912	0.233574
H	-4.378230	4.206011	2.636915

TS-F5

96

C	-1.966098	-3.704467	0.197682
C	3.044565	-3.958368	-1.484354
C	1.813162	-4.141803	-2.096799
C	0.868755	-3.127891	-2.093884
F	3.958124	-4.937255	-1.483623
F	1.543148	-5.300876	-2.704908
F	-0.311629	-3.353940	-2.697787
H	2.292919	-5.464432	1.956775
H	-0.001821	-5.039625	1.162064
H	-2.101512	-4.668341	0.701370
H	-1.339118	-3.857278	-0.682996
H	-2.951812	-3.374584	-0.146367
C	4.365534	-0.856254	2.453507
H	3.643389	-3.622797	2.882639
H	4.963635	-1.772284	2.510513
H	4.940536	-0.051458	2.924995
H	3.885029	-2.197553	4.797537
C	-0.914417	2.960862	0.644597
C	-1.399763	3.942018	1.433230
C	-1.225329	3.911097	2.936761
C	-0.840903	2.509624	3.361011
C	-0.377835	1.603787	2.474130
C	-1.124635	2.934367	-0.829674
C	-1.750334	4.110721	-1.520033
C	-2.501066	4.379990	3.654780
C	0.010634	0.220148	2.862112
C	-0.038720	-0.190314	4.303833
C	-0.921060	1.632873	-2.814547
C	-1.968443	0.786661	-3.213844
C	-2.111724	0.516439	-4.574928
C	-1.224325	1.044210	-5.505421
C	-0.168338	1.844191	-5.082726
C	0.008787	2.151511	-3.732658
C	-2.923807	0.207022	-2.183113
C	-4.168270	1.093746	-2.040111
C	-3.306790	-1.247536	-2.468338
C	1.212047	2.946663	-3.249135
C	1.732342	3.964151	-4.267863
C	2.333061	1.982985	-2.826575
C	0.851793	-1.881217	2.072326
C	2.148403	-2.112234	2.569193
C	2.640719	-3.420041	2.516243
C	1.882319	-4.460057	2.000839
C	0.588736	-4.216177	1.549351
C	0.050204	-2.932477	1.578022
C	3.022322	-1.021883	3.177118
C	3.271802	-1.298165	4.669072
C	-1.379620	-2.651445	1.138585
C	-2.297087	-2.479600	2.359460
C	1.078771	-1.908965	-1.429626
C	2.354036	-1.750484	-0.864849
C	3.311284	-2.747679	-0.860167
F	2.614995	-0.572090	-0.255080
F	4.496254	-2.552664	-0.276554
H	-1.947522	4.776566	1.006595
H	-0.423444	4.613975	3.228288
H	-0.955558	2.253964	4.409528
H	-2.923758	-0.120427	-4.913004
H	-1.348115	0.822719	-6.561432
H	0.530044	2.232635	-5.817413
H	-2.402742	0.210796	-1.220324
H	0.913912	3.511592	-2.359597
H	2.497197	-0.065947	3.096092
H	-1.368855	-1.702120	0.591352
H	0.165376	-1.255811	4.414757
H	-1.027848	0.023638	4.718319
H	0.695102	0.376090	4.885805

H	-4.727413	1.126366	-2.982741
H	-3.897278	2.121206	-1.773959
H	-4.833589	0.703374	-1.261756
H	-3.909215	-1.637862	-1.640515
H	-2.413690	-1.871520	-2.564810
H	-3.903350	-1.346173	-3.382046
H	2.184813	3.474789	-5.137620
H	2.505637	4.585740	-3.804550
H	0.930898	4.620987	-4.622776
H	2.680212	1.402774	-3.689828
H	1.990333	1.275816	-2.065650
H	3.186136	2.536998	-2.419275
H	4.223734	-0.611416	1.400694
H	2.338810	-1.448042	5.219933
H	3.808659	-0.458985	5.125081
H	-1.954576	-1.680741	3.022981
H	-2.333113	-3.408396	2.940794
H	-3.316310	-2.237302	2.038467
H	-1.841329	3.936814	-2.592811
H	-1.142725	5.005516	-1.352971
H	-2.744993	4.305304	-1.107770
H	-2.363862	4.364699	4.741732
H	-3.344390	3.726064	3.405566
N	-0.259932	1.850775	1.126548
N	-0.751435	1.856333	-1.423562
N	0.362753	-0.558078	1.898407
O	0.166441	-0.976710	-1.377915
Zn	0.102669	0.390511	-0.059281
H	-2.760531	5.402655	3.358883

2”-F5

96

C	-2.283266	-3.550284	0.533515
C	2.141515	-3.514725	-2.798828
C	0.960335	-3.069763	-2.222621
C	0.961844	-1.909804	-1.471490
F	2.161660	-4.635782	-3.529182
F	-0.169705	-3.764273	-2.396346
F	-0.194869	-1.484306	-0.911297
H	1.928198	-5.453800	2.288061
H	-0.419246	-4.989644	1.698245
H	-2.411628	-4.547981	0.968314
H	-1.651796	-3.639126	-0.354025
H	-3.272491	-3.203810	0.217094
C	4.217651	-0.961184	1.970674
H	3.465614	-3.596061	2.813190
H	4.784051	-1.890361	2.099389
H	4.880568	-0.129522	2.235167
H	3.928445	-1.910305	4.563971
C	-1.054978	2.909530	0.720683
C	-1.867971	3.752636	1.392621
C	-1.768612	3.826470	2.904354
C	-1.382110	2.447784	3.404319
C	-0.591355	1.668005	2.636069
C	-1.111969	2.718733	-0.755020
C	-1.718429	3.778354	-1.621976
C	-3.069619	4.325203	3.540153
C	-0.196435	0.281670	3.010264
C	-0.248413	-0.146055	4.444355
C	-0.528204	1.272547	-2.578697
C	-1.472008	0.353802	-3.075629
C	-1.331622	-0.080705	-4.392792
C	-0.283153	0.367512	-5.189537
C	0.641982	1.264211	-4.673798
C	0.545203	1.731456	-3.360479
C	-2.627389	-0.119313	-2.206324
C	-3.830071	0.827514	-2.334256
C	-3.055121	-1.559337	-2.503482
C	1.573335	2.722850	-2.835215
C	1.437358	4.075856	-3.549878

C	3.006166	2.189120	-2.957996
C	0.651943	-1.812117	2.200662
C	1.997091	-2.054431	2.526725
C	2.431662	-3.381984	2.556301
C	1.569546	-4.428987	2.262564
C	0.245061	-4.163409	1.930822
C	-0.238175	-2.856375	1.885932
C	2.971102	-0.935318	2.864570
C	3.370349	-0.991872	4.346934
C	-1.691232	-2.562874	1.543255
C	-2.553799	-2.525190	2.813811
C	2.106579	-1.129158	-1.247062
C	3.280791	-1.614912	-1.847753
C	3.302285	-2.775874	-2.604321
F	4.421412	-0.928485	-1.681865
F	4.446918	-3.191922	-3.152584
H	-2.612906	4.358081	0.885788
H	-0.970818	4.542186	3.176381
H	-1.772922	2.106559	4.357853
H	-2.047511	-0.784966	-4.804700
H	-0.187932	0.013831	-6.211957
H	1.459170	1.610065	-5.301098
H	-2.291096	-0.085699	-1.164001
H	1.381449	2.888210	-1.770479
H	2.470271	0.022107	2.691168
H	-1.729354	-1.566681	1.088732
H	0.017099	-1.197674	4.559941
H	-1.249402	0.013987	4.855079
H	0.445245	0.467146	5.028561
H	-4.196068	0.842349	-3.367639
H	-3.572536	1.852782	-2.053582
H	-4.648535	0.494238	-1.686400
H	-3.777168	-1.891282	-1.750399
H	-2.200911	-2.240859	-2.482739
H	-3.542396	-1.645200	-3.481245
H	1.670010	3.976753	-4.616671
H	2.133057	4.804856	-3.119747
H	0.422797	4.477314	-3.462950
H	3.277560	2.005473	-4.003643
H	3.126387	1.260166	-2.395881
H	3.712668	2.924475	-2.556249
H	3.947046	-0.858276	0.917301
H	2.493479	-0.968815	5.001614
H	4.010962	-0.140153	4.601128
H	-2.199212	-1.772484	3.523820
H	-2.535185	-3.499103	3.316858
H	-3.594013	-2.290047	2.561897
H	-1.745568	3.472866	-2.668780
H	-1.130447	4.697363	-1.530773
H	-2.735571	4.008384	-1.292403
H	-2.976516	4.374779	4.630343
H	-3.900241	3.652176	3.298258
N	-0.201640	2.036546	1.364454
N	-0.598423	1.623051	-1.200902
N	0.196203	-0.473008	2.041119
O	2.096941	-0.034456	-0.537538
Zn	0.474311	0.592870	0.265554
H	-3.323278	5.325889	3.174366

[i] Spartan'20. Wavefunction, Inc. Irvine, CA. (Version 1.1.2, 2021).

[ii] AIMAll (Version 19.10.12), Todd A. Keith, TK Gristmill Software, Overland Park KS, USA, 2019 (aim.tkgristmill.com).

[iii] F. Neese, F. Wennmohs, U. Becker and C. Riplinger, *J. Chem. Phys.*, 2020, **152**, 224108. DOI: 10.1063/5.0004608.