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SUPPORTING INFORMATION:

Structural, Kinetic, and DFT Studies of the Transfer Hydrogenation of Ketones Mediated by (Pyrazole)pyridine Iron(II) and Nickel(II) Complexes

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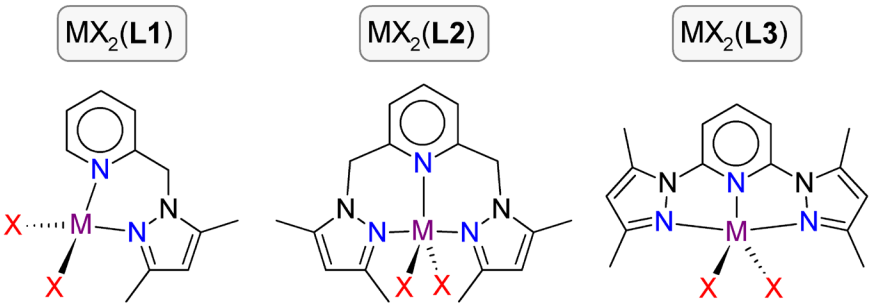
The supporting information contained herein relates to the following compounds:



M = Ni, X = Br (**1**)
M = Ni, X = Cl (**2**)
M = Fe, X = Cl (**3**)

M = Ni, X = Br (**4**)
M = Ni, X = Cl (**5**)
M = Fe, X = Cl (**6**)

M = Ni, X = Br (**7**)
M = Ni, X = Cl (**8**)
M = Fe, X = Cl (**9**)

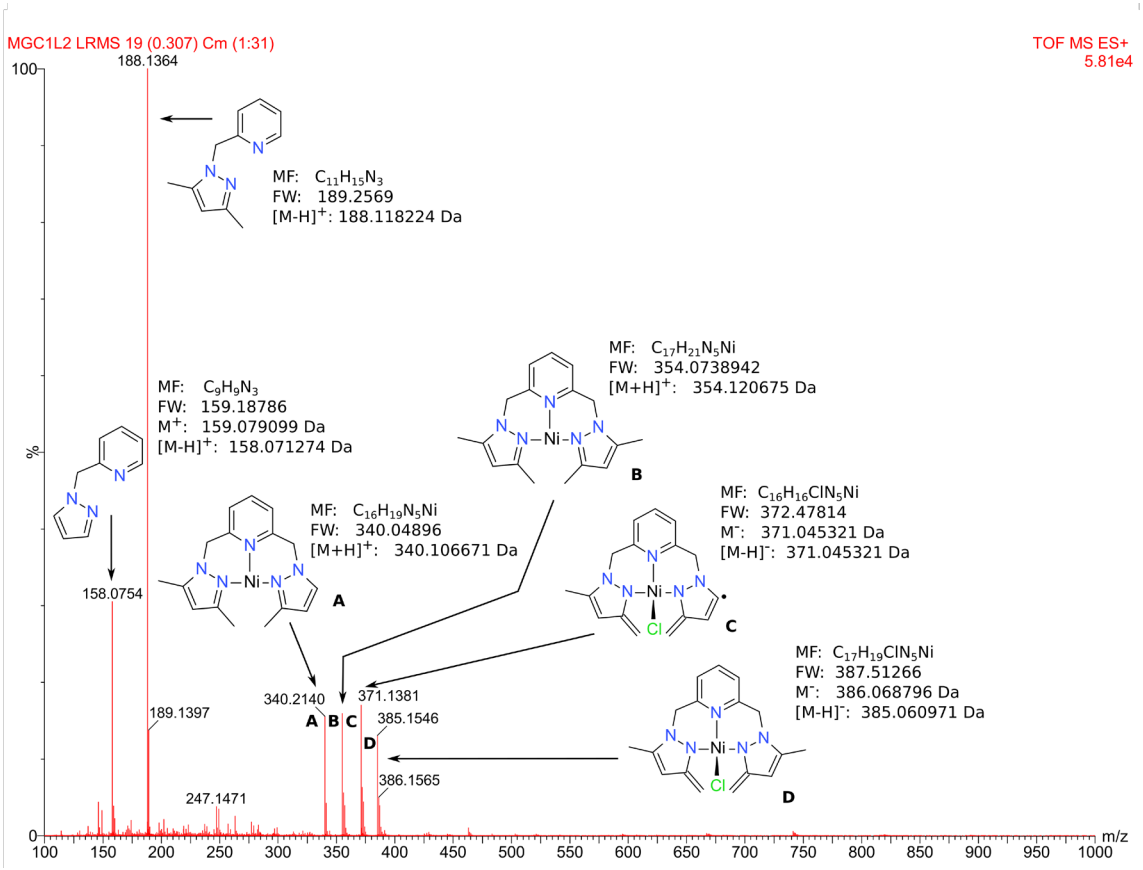
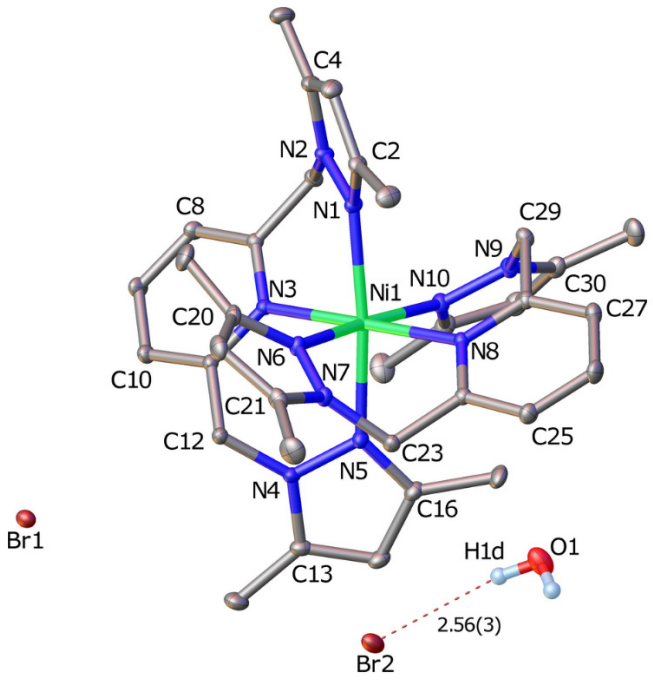
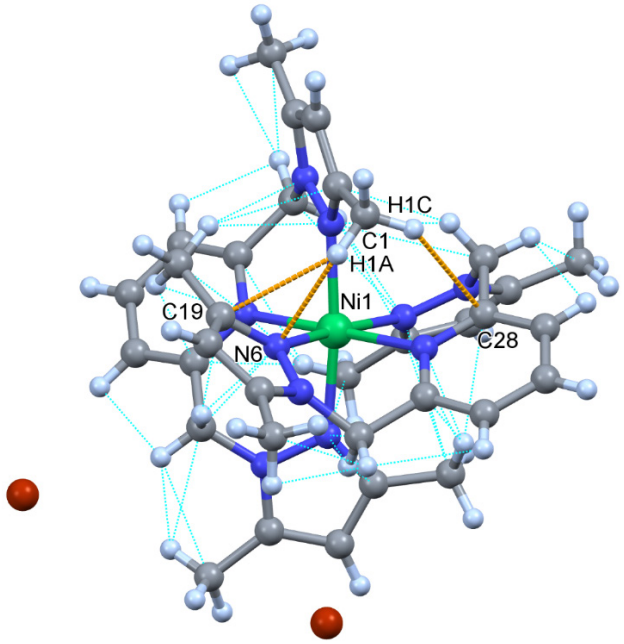


Figure S1: Low-resolution ESI-MS spectrum for complex **5.** Fragment assignments are indicated for the major peaks in the spectrum. The parent ion (MF, $C_{17}H_{21}Cl_2N_5Ni$; FW, 424.9809914; M^+, 423.051653 Da, and $[M+H]^+$, 424.059478 Da) is absent due to the loss of one chloride ligand during ionization.



(a)



(b)

Figure S2. (a) Molecular structure of **4a·H$_2$O** drawn with 50% probability ellipsoids and selected atom labels. H atoms on the cation are omitted for clarity; the classical H-bond (and distance in Å) involving the bromide ion and solvate water is indicated by a dashed line. Bond lengths (Å): Ni1–N1, 2.1300(10); Ni1–N3, 2.1284(10); Ni1–N5, 2.1162(10); Ni1–N6, 2.1129(10); Ni1–N8, 2.1350(10); Ni1–N10, 2.1364(10). Bond angles (°): N1–Ni1-N3, 87.06(4); N5–Ni1–N3, 86.51(4); N6–Ni1–N8, 86.46(4); N8–Ni1–N10, 86.85(4); N1–Ni1–N6, 86.48(4); N6–Ni1–N10, 173.29(4); N3–Ni1–N8, 179.47(4). (b) Illustration of the short intramolecular contacts in the structure of **4a·H$_2$O** (thin blue dashed lines). The short intramolecular contacts discussed in the main text are highlighted in thick orange dashed lines: H1C···C28, 2.81 Å; H1A···N6, 2.56 Å; H1A···C19, 2.70 Å.

Comments on the Structure of 4a·H_2O. From the molecular structure of **4a·H_2O**, the geometry around the Ni metal centre may be regarded as distorted octahedral since the bond angles for N1-Ni-N3 of 87.06° and N6–Ni–N8 of 86.46° deviate significantly from 90°. Similarly, the angle for N1–Ni–N5 of 173.53° is markedly less than 180° (expected for octahedral structures). The Ni–$N_{pyrazole}$ distances Ni–N1 [2.1300(10) Å] and Ni–N5 [2.1162(10) Å] are, within experimental error, equivalent, confirming the symmetrical nature of **L2**. The average Ni–$N_{pyrazole}$ (Ni–N_{pz}) bond distance determined here for **4a**, 2.13(1) Å, is somewhat longer than the equivalent mean distance reported elsewhere for the related complexes coordinated by the methyl-free analogue of **L2**, **L2′**: [NiCl(**L2′**)$(OH_2)_2$]Cl·H_2O, Ni–N_{pz} = 2.026(1) Å, and [Ni(**L2′**)$_2$]$(ClO_4)_2$, Ni–N_{pz} = 2.076(1) Å, where **L2′** = 2,6-bis(1*H*-pyrazol-1-ylmethyl)pyridine.[1] The elongation of the Ni–N_{pz} bonds in **4a** reflects adjustment of the coordination geometry to compensate for short intramolecular contacts between the inwardly-directed pyrazolyl methyl groups on one ligand with the pyridine and pyrazole rings of the counterpart ligand in the complex (Figure S2). For example, the contact distances between the H atoms attached to C1 and the neighbouring ligand's pyridine and pyrazole rings measure 2.81 (C1–H1C···C28), 2.56 (C1–H1A···N6), and 2.70 Å (C1–H1A···C19); these are between 0.1 and 0.2 Å shorter than the sum of the van der Waals radii of carbon and hydrogen. In effect, short intramolecular nonbonded interactions push the pyrazole moieties of **L2** out from the metal centre relative to the interaction geometry observed for the un-substituted parent ligand, **L2′**. The conformation of the complex, particularly the manner in which the twisted nonplanar ligands chelate and enwrap the metal ion is concerned, is such that it has approximate molecular C_2 symmetry. Consequently, **4a** is conformationally similar to the simpler derivative [Ni(**L2′**)$_2$]$(ClO_4)_2$ reported by Watson *et al.* in 1987.[1] (This perchlorate salt has exact C_2 molecular symmetry by virtue of the cation's location on a crystallographic twofold axis in the space group $P2_12_12$; in contrast, the cation of **4a** has no imposed molecular symmetry.)

The crystal packing in **4a** is such that the cations lie in planes parallel to [1, 1, 0]; the anions are sandwiched roughly between these planes and, in the case of the anion "layer" repeating at half the length of the *c*-axis, the bromide ions form hydrogen-bonded centrosymmetric 4-membered rings involving pairs of water molecules and bromide ions (Figures S3 and S4; Table S1). No intermolecular π–π stacking interactions involving the pyridine or pyrazole rings of the cations exist in the structure of **4a**.

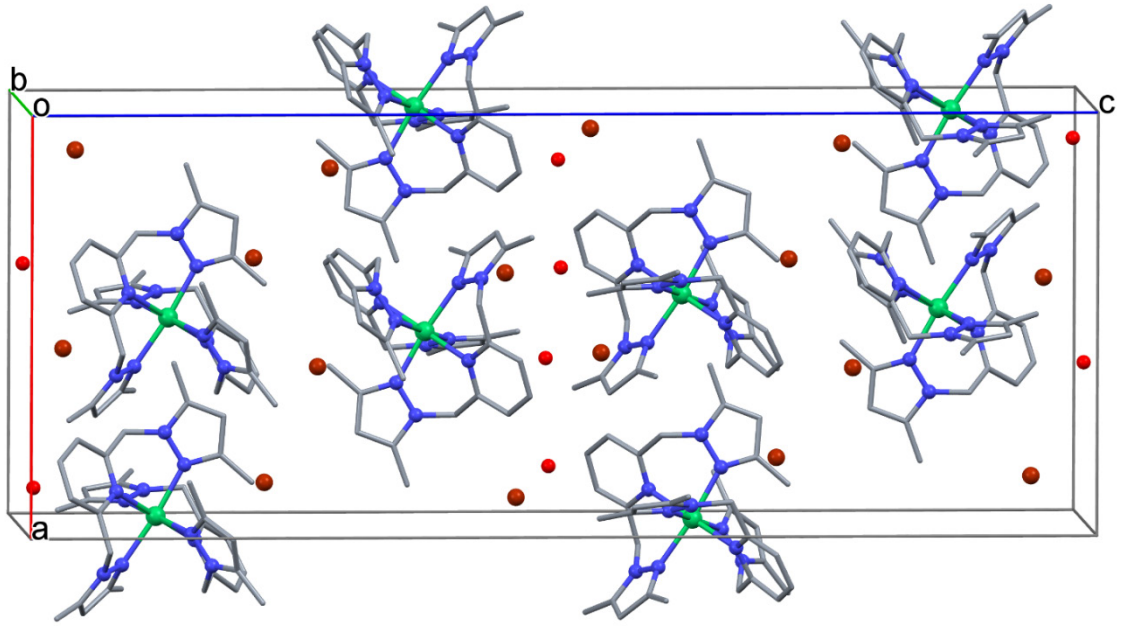


Figure S3: Unit cell packing diagram for **4a·H_2O** viewed approximately down the *b*-axis. H atoms have been omitted for clarity. Brown and red spheres correspond to the bromide ions and water molecules in the lattice, respectively.

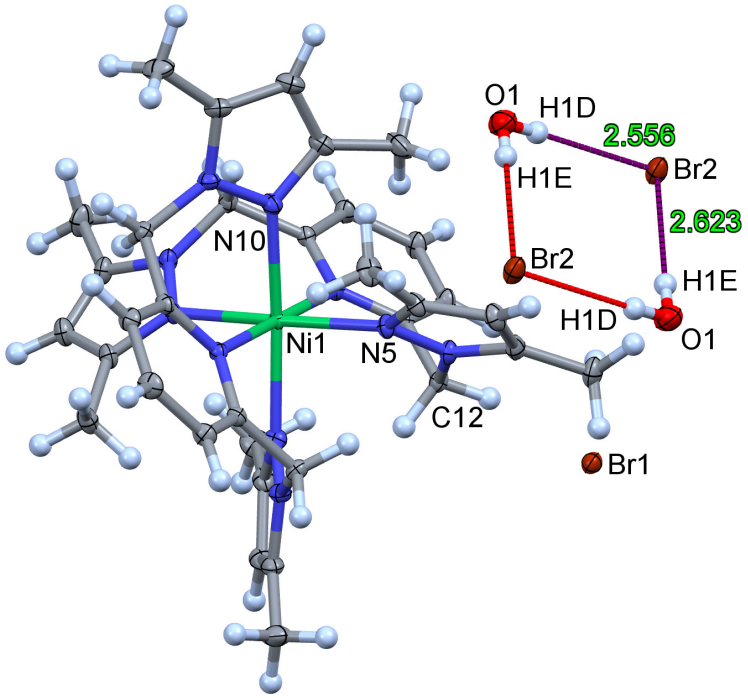


Figure S4: Hydrogen bonding between Br2 and lattice water in the structure of **4a·H_2O**. The symmetry unique interaction distances (Å) are indicated.

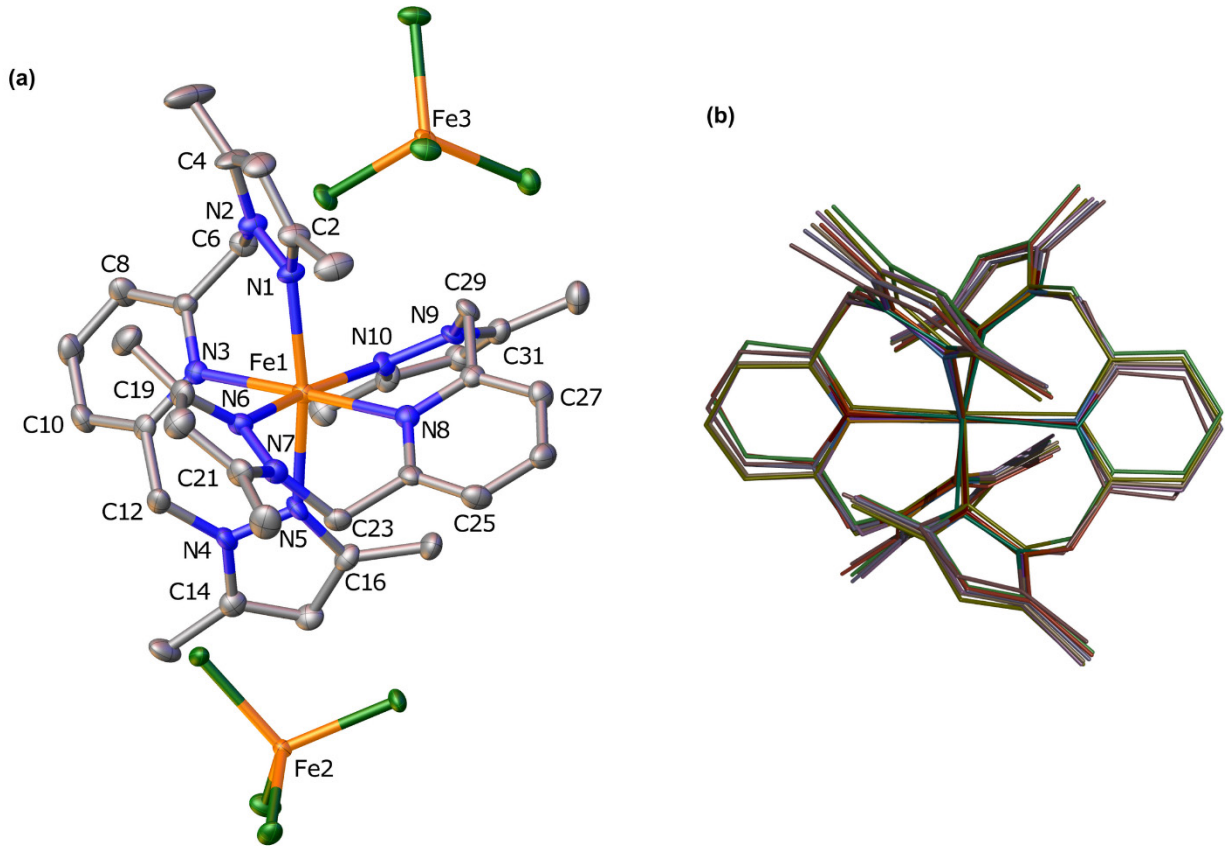


Figure S5: (a) Molecular structure of **6a** drawn with 50% probability ellipsoids and selected atom labels. Two solvent molecules (CH_2Cl_2) and all of the H atoms are omitted for clarity; only the major components of the two disordered $[FeCl_4]^-$ counter-ions are shown. Bond lengths (Å): Fe–N1, 2.211(8); Fe–N5, 2.208(8); Fe–N3, 2.273(7); Fe–N8, 2.255(8); Fe–N6, 2.226(8); Fe–N10, 2.198(8). Bond angles (°): N1–Fe1–N3, 84.9(3); N5–Fe1–N3, 84.3(3); N6–Fe1–N8, 83.8(3); N8–Fe1–N10 85.6(3); N1–Fe1–N6, 87.9(3); N6–Fe1–N10, 169.3(3); N1–Fe1–N5, 169.2(3); N3–Fe1–N8, 178.0(3). (b) Overlay of the X-ray structure of the cation in **6** with the six available X-ray structures of the same cation from different salts in the literature (CSD[2] reference codes: NIJMAU, NIJLOH, NIJLIB, ETONOR, ETONIL, and ETONEH). The similarity indices range from 0.94–0.98 for all non-H atoms. (Atomic coordinates were transformed by inversion where necessary to give the same enantiomorph for least-squares fitting.)

Comment on Figure S5. The crystal structure of **6a** (Figure S5a), formulated as $[Fe(\mathbf{L2})_2][FeCl_4]_2{\cdot}CH_2Cl_2$, is the only tetrachloroferrate(III) salt of the $[Fe(\mathbf{L2})_2]^{2+}$ cation that has been structurally elucidated. As noted in the Experimental Methods section, the presence of the $[Fe^{III}Cl_4]^-$ anions reflects partial oxidation of ferrous chloride during chelation of Fe(II) by the tridentate ligand and, presumably, a more favourable lattice energy for crystallization of $[Fe(\mathbf{L2})_2][FeCl_4]_2$ relative to the simpler, alternative salt from this system, namely $[Fe(\mathbf{L2})_2]Cl_2$. The latter salt has not yet been reported despite the fact that several perchlorates,[3] a tetraphenylborate,[3a] and a hexafluorophosphate[3a] salt of the $[Fe(\mathbf{L2})_2]^{2+}$ cation are known. The molecular structure of **6a** is similar to that of the Ni(II) derivative **4a**; the two tridentate ligands adopt the same wave-like conformation about the distorted octahedral metal centre. However, the distortion from a regular octahedral coordination geometry is more pronounced in **6a**, as evidenced by the rather acute mean N_{pz}–Fe–N_{py} bond angle of 84.7(8)° in the complex (where pz = pyrazole and py = pyridine). The mean Fe–N_{pz} and Fe–N_{py} bond distances measure 2.210(12) and 2.264(12) Å, respectively, and are in agreement with the ranges (2.131–2.245, Fe–N_{pz}; 2.191–2.251, Fe–N_{py}) observed

for each bond class from the known X-ray structures of the cation present in six different salts (Figure S5b). The Fe–N_{pz} bond to the metal ion is slightly shorter than the Fe–N_{py} bond, in contrast to the bonding about the Ni(II) ion of **4a**, and likely reflects the fact that the ionic radius of high-spin Fe(II) at 92 pm is 11% larger than that of Ni(II) (83 pm)[4] such that the intrinsic geometric differences of the two N-donor atom types is somewhat amplified for the iron chelate. It is noteworthy in this regard that the C–N_{py}–C bond angle (ca. 117°) is significantly wider than the N–N_{pz}–C bond angle (ca. 105°) and would account for a substantial part of the observed elongation of the Fe–N_{py} bond relative to the Fe–N_{pz} bond (all other factors being equivalent).

Figure S5b shows a least-squares superposition of the six known X-ray structures of $[Fe(L_2)_2]^{2+}$ in the literature with that of **6a**. The wave-like conformation of the tridentate ligand is essentially constant for all of the crystallographically characterized salts. The two chelating ligands are clearly relatively inflexible with minor conformational perturbations in the pyrazole ring orientations caused by minor rotations about the Fe-N_{pz} bonds and crystal packing interactions involving the methyl substituents on the rings. Interestingly, the chelate ring arrangements and spiral-like ligand conformations of **6a** yield a chiral molecular structure for the cation (the enantiomers are non-superimposable). However, the synthesis of the compound is not enantioselective and therefore the reaction affords a racemic mixture. Crystals of **6a** (and **4a** for similar reasons) are solid racemates comprising an equal number of enantiomorphs related by centres of inversion in the lattice. (It would be interesting from a crystallographic perspective to see whether use of an enantiopure chiral anion could permit resolution of the enantiomorphs upon crystallization of the racemate.)

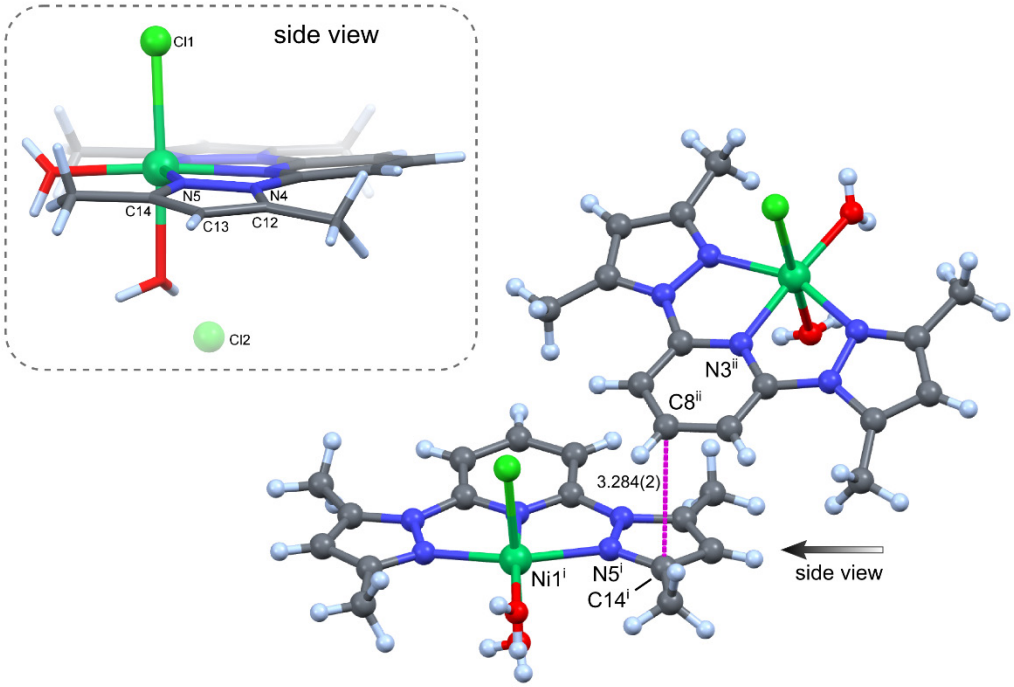


Figure S6: Short nonbonded contact between the pyrazole ring of one cation and the pyridine ring of the neighbouring cation in **8·2H₂O**. The interaction evidently tips the pyrazole ring below the mean plane of the chelating ligand and is at least partly responsible for the nonplanar conformation of the ligand. Symmetry codes: [i] x, y, z; [ii] $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

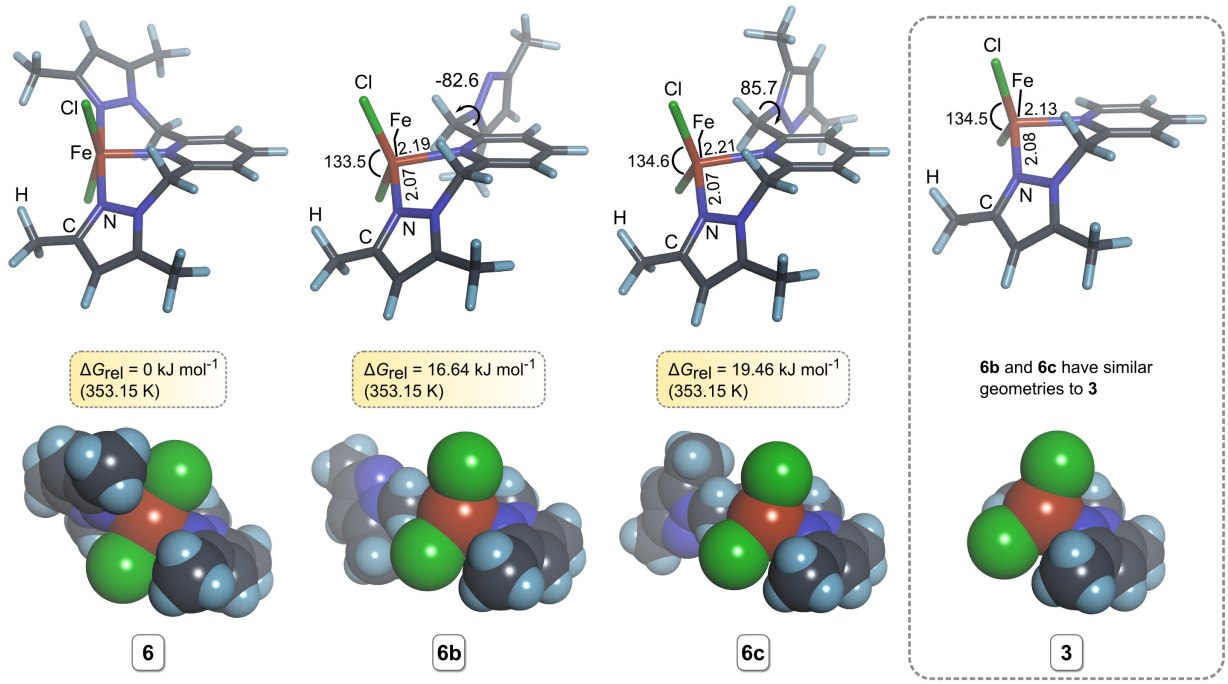


Figure S7: Comparison of the DFT-calculated structures (UHSEH1PBE[5]/6-311G(d,p)[6]) of **6**, **6b**, **6c**, and **3** in a 2-propanol solvent continuum (SCRF-PCM method)[7]. Complexes **6b** and **6c** are configurational isomers of **6** in which one pyrazole ring is dissociated from the metal ion to give a more open Fe(II) coordination sphere similar to that of **3**. Thermochemical analysis of **6**–**6c** at 80 °C indicates that the ΔG_{rel} values for isomers **6b** and **6c** are 16.64 and 19.46 kJ mol^{-1} relative to **6**, respectively, despite positive increases in entropy, ΔS_{rel}, of 35.38 and 31.74 J K^{-1} mol^{-1} for the respective complexes. From the molecular partition function (Boltzmann distribution) at 353.15 K, the solution populations of isomers **6b** and **6c** in equilibrium with **6** would amount to only 0.68% and 0.26% of the distribution, excluding either of these configurational isomers as being alternative solution species for **6** that might account for the similar k_{obs} values measured for **3** and **6** (Table 3, main text). Selected bond distances (Å) and angles (°) are indicated.

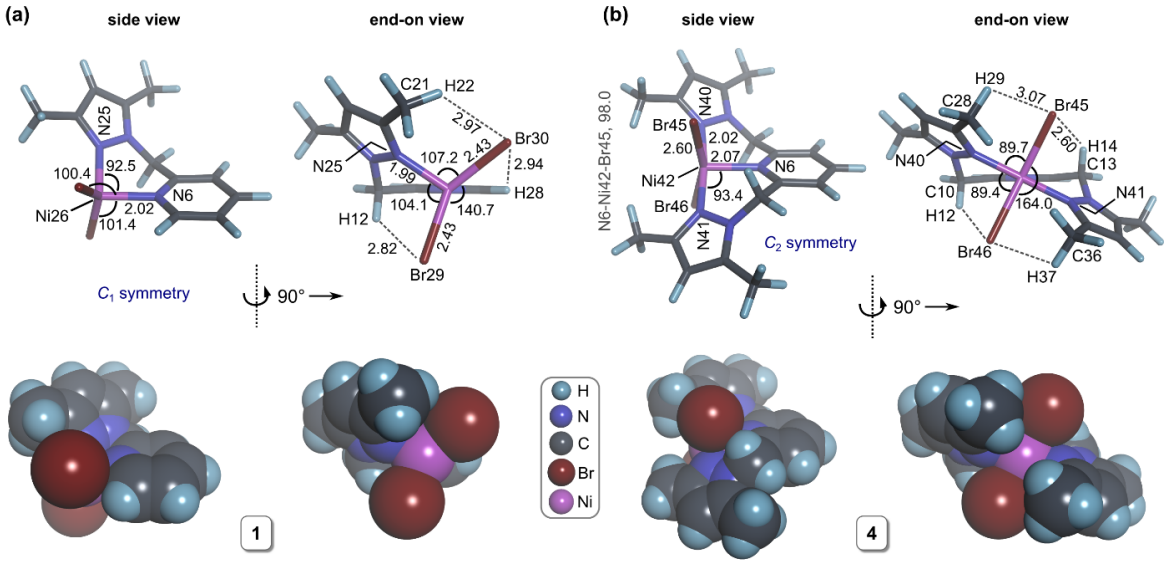
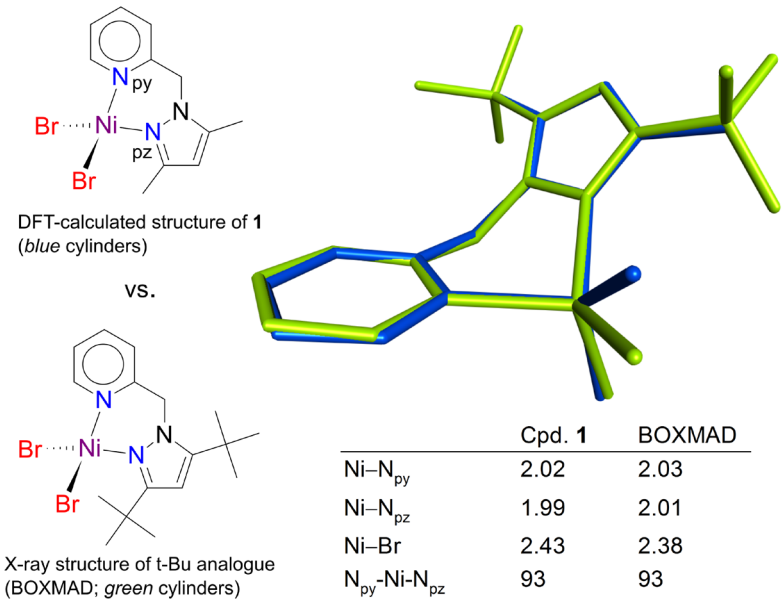
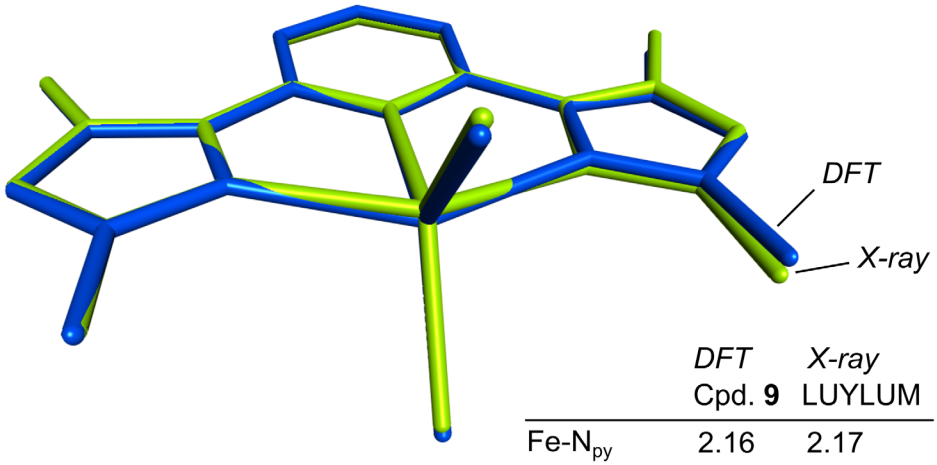


Figure S8: DFT-calculated geometries [UHSEH1PBE/6-311G(d,p) level of theory; 2-propanol solvent continuum] of the active Ni(II) precatalysts **1** (C_1 symmetry) and **4** (C_2 symmetry) illustrating the different degrees of steric hindrance about the metal centre. The upper views show the optimized geometries as bond cylinder models with selected atom labels, bond distances (Å) and bond angles (°); the lower views depict the structures rendered with van der Waals radii for the atoms.



	Cpd. **1**	BOXMAD
Ni–N_{py}	2.02	2.03
Ni–N_{pz}	1.99	2.01
Ni–Br	2.43	2.38
N_{py}-Ni-N_{pz}	93	93

Figure S9: Comparison (least-squares fit overlay) of the DFT-calculated geometry of **1** with the X-ray structure of the *t*-butyl substituted analogue (CSD code BOXMAD;[8] molecule 1 in the asymmetric unit). The similarity index of the fit is 0.914; selected bond lengths (Å) and bond angles (°) are listed. H atoms have been omitted from the fit and for clarity. Note how the closest *t*-Bu group of the X-ray structure distorts the coordination geometry of the metal ion (especially the closest bromide ion) due to steric repulsion. The remainder of the structure reflects good agreement between the DFT-calculated and experimental geometries.



	DFT Cpd. **9**	*X-ray* LUYLUM
Fe-N_{py}	2.16	2.17
Fe-N_{pz}	2.16	2.16
Fe-Cl	2.39	2.30
Cl-Fe-Cl	109	111
N_{py}-Fe-Cl	126	124
N_{py}-Fe-N_{pz}	73	72

Figure S10: Comparison (least-squares fit overlay) of the DFT-calculated geometry of **9** [UHSEH1PBE/6-311G(d,p) level of theory (C_1 symmetry); 2-propanol solvent continuum] with the X-ray structure of the complex (CSD code LUYLUM)[9]. The root mean square (RMS) difference of the fit is 0.0792 Å; selected bond lengths (Å) and bond angles (°) are listed. H atoms have been omitted from the fit and for clarity. Note: the Fe–Cl bonds in the C_1-symmetry DFT-calculated structure are inequivalent, measuring 2.33 and 2.44 Å; the mean distance is thus 2.39(5) Å.

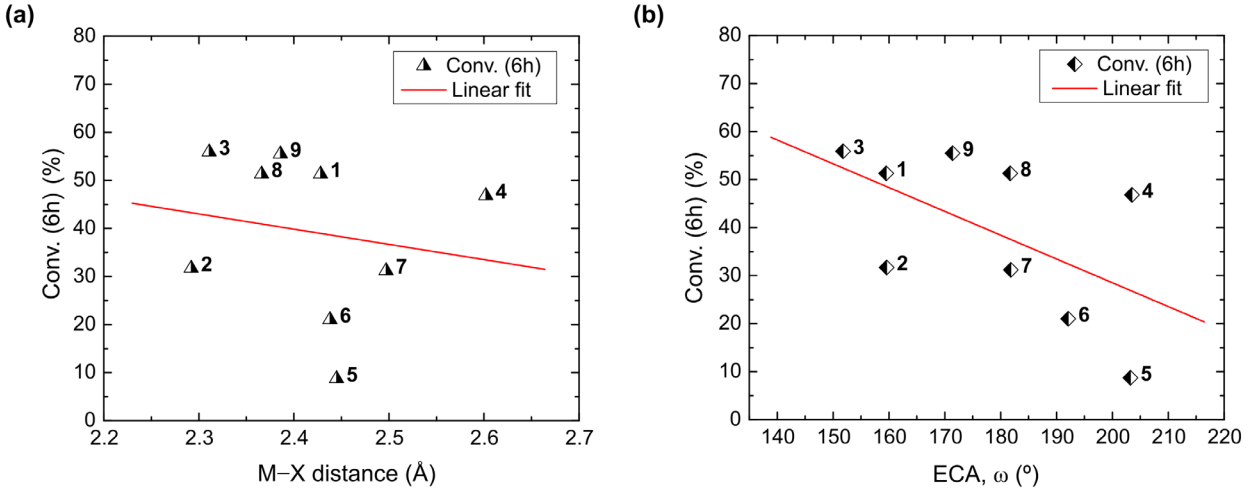
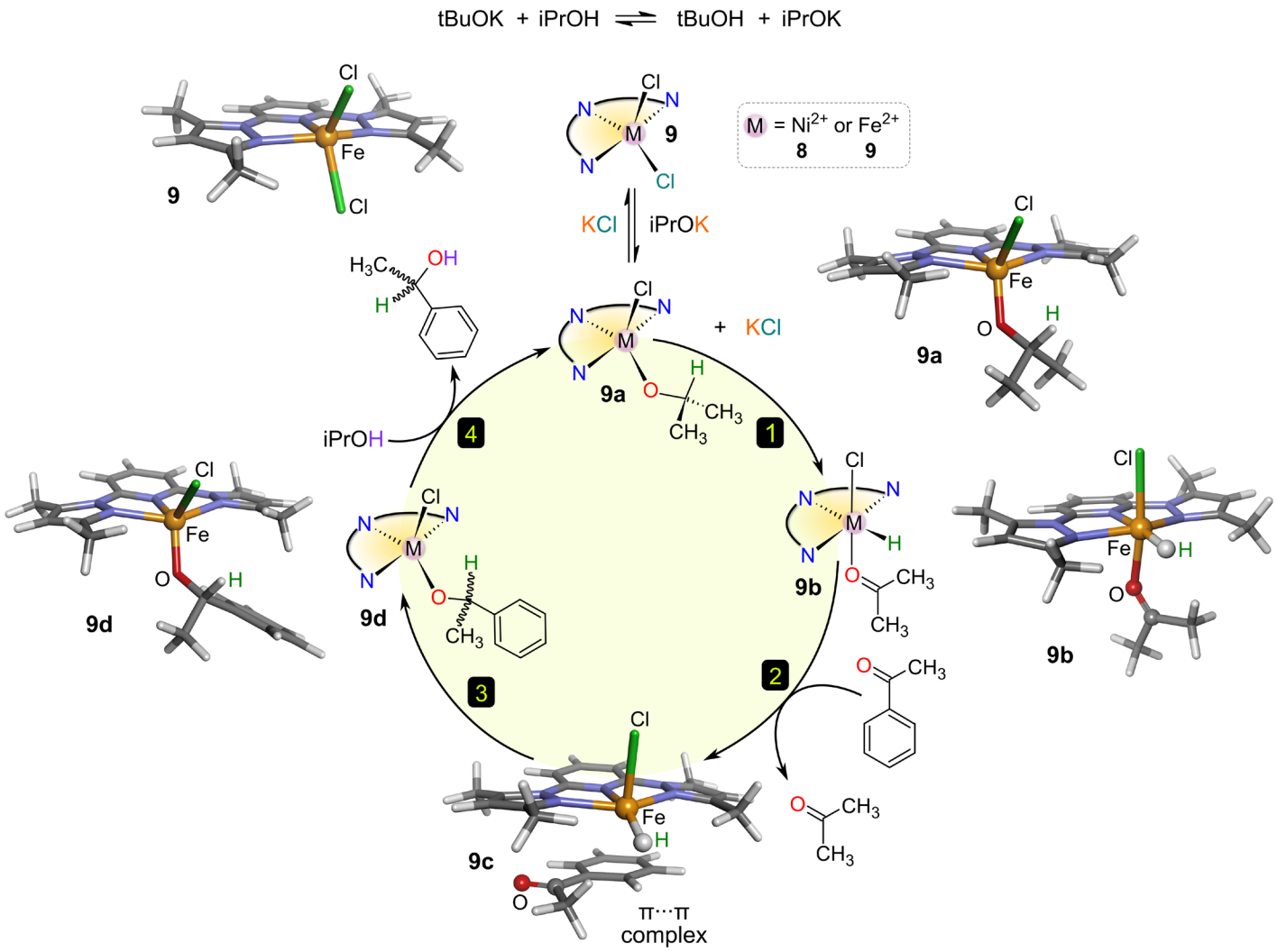


Figure S11: Plots of the percentage conversion to product after 6 h for the TH of acetophenone as a function of (a) the M–X distance and (b) the equivalent cone angle, ECA, of the ligand in complexes **1**–**9**. The straight line is the best-fit linear regression curve in each graph. Notably, no significant linear correlation exists in either case.



Compound	Fe–N_{py} (Å)	Fe–N_{pz} (Å)	Fe–Cl (Å)	Fe–O (Å)	Fe–H (Å)	N_{py}–Fe–Cl (°)	N_{py}–Fe–X (°)*
9	2.16	2.16	2.39(5)	-	-	126.5	124.7
9a	2.16	2.18	2.49	1.86	-	126.8	117.3
9b	2.22	2.20	2.55	2.34	1.72	89.7	79.1
9c	2.22	2.19	2.50	-	1.69	97.6	158.6
9d	2.18	2.16	2.49	1.87	-	130.5	118.9

*X = Cl, O, or H.

Figure S12: *Postulated* catalytic cycle for compound **9** in isopropyl alcohol. DFT-calculated structures at the UHSE1HPBE[5]/6-311G(d,p)[6] level of theory in a 2-propanol solvent continuum (PCM method)[7] for each intermediate are shown along with a list of selected geometrical parameters for key bond distances and angles at the metal centre. The DFT-calculated structures were all true minima (zero imaginary frequencies) on the potential energy surface. The structure of **9c** was modelled by augmenting the UHSE1HPBE functional with the empirical dispersion scheme from the APFD functional.[10]

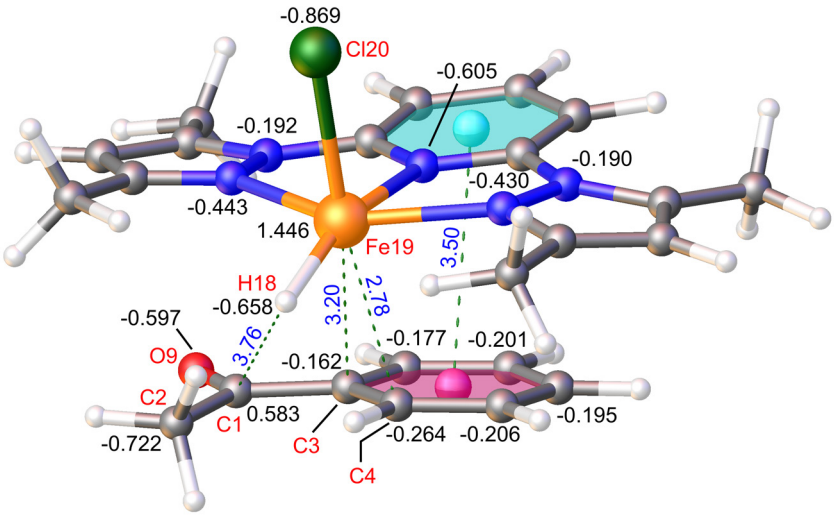


Figure S13: Structure of **9c** with selected NBO[11]-calculated partial atomic charges (in units of electrons) and intermolecular nonbonded distances (in Å). Selected atom labels are shown. The electrostatic complementarity of the Fe19···C4, Fe19···C3, and H18···C1 interactions is particularly noteworthy as these attractive forces contribute to the stability of the π-adduct.

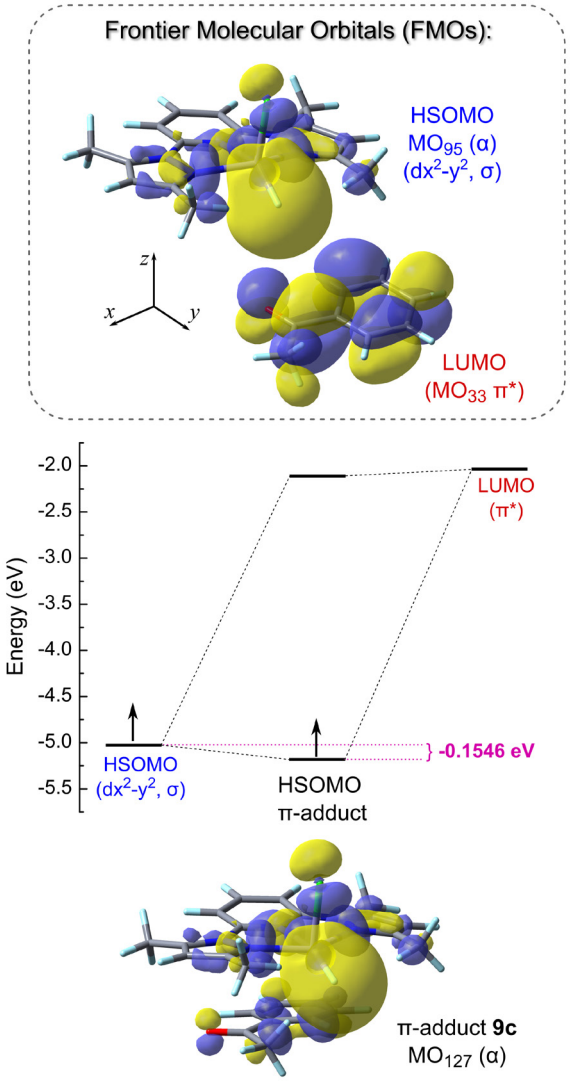


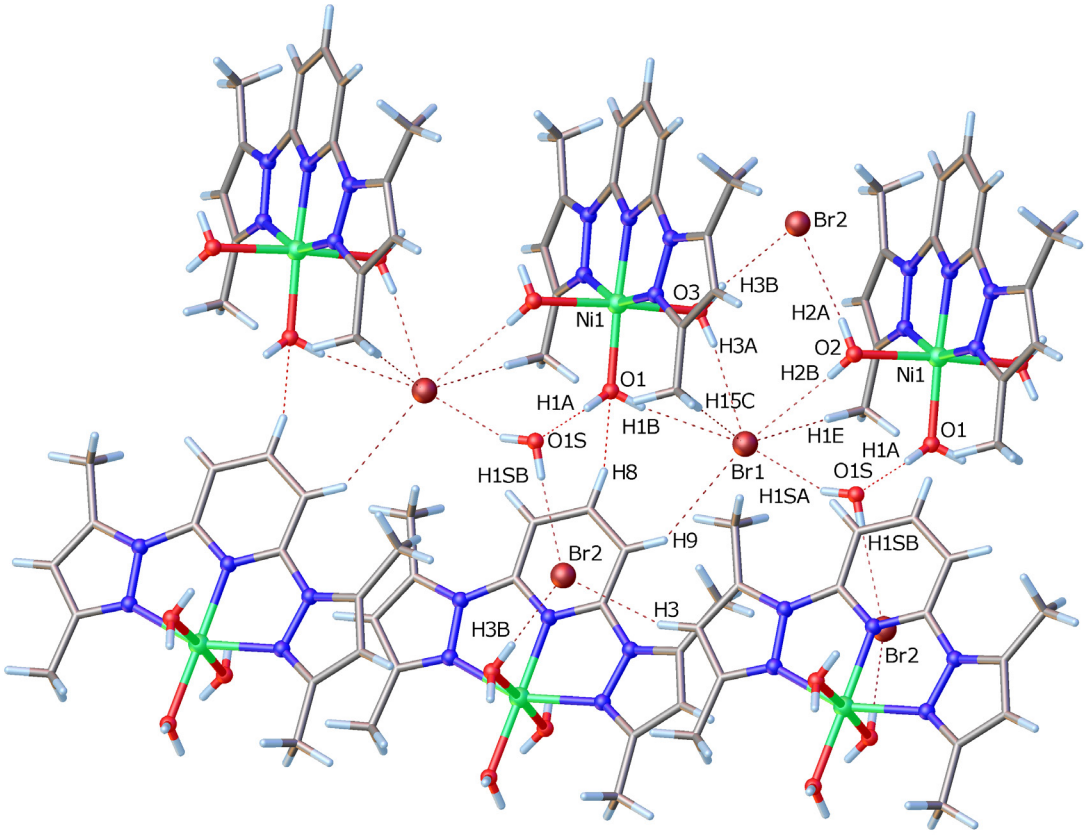
Figure S14: Depiction of the frontier molecular orbital (FMO) interaction for acetophenone and FeCl(H)(**L3**) leading to formation of the favourable π-adduct **9c**.

Table S1. Hydrogen-bond geometry (Å, º) for **4a•H$_2$O**.

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
C1—H1*A*···N6	0.98	2.55	3.2742 (17)	130
C1—H1*B*···Br1^{i}	0.98	3.10	4.0268 (14)	159
C3—H3···Br1^{i}	0.95	3.02	3.8569 (13)	148
C5—H5*B*···Br1^{ii}	0.98	3.14	4.0986 (14)	167
C6—H6*A*···N10	0.99	2.36	3.1110 (16)	132
C6—H6*B*···Br1^{iii}	0.99	2.77	3.7151 (12)	159
C8—H8···Br1^{iii}	0.95	2.82	3.6987 (12)	155
C10—H10···Br1	0.95	2.92	3.7728 (12)	150
C12—H12*A*···N6	0.99	2.33	3.0753 (16)	131
C12—H12*B*···Br1	0.99	2.77	3.6986 (12)	157
C17—H17*B*···Br2^{iv}	0.98	3.07	4.0029 (13)	159
C17—H17*C*···N8	0.98	2.45	3.2909 (17)	144
C18—H18*A*···N1	0.98	2.51	3.2509 (18)	132
C20—H20···Br1^{v}	0.95	2.87	3.8127 (13)	173
C23—H23*A*···N5	0.99	2.37	3.0951 (16)	129
C23—H23*B*···Br2^{vi}	0.99	2.80	3.7241 (12)	156
C25—H25···Br2^{vi}	0.95	2.87	3.7371 (13)	153
C27—H27···Br2^{i}	0.95	2.95	3.7597 (13)	144
C29—H29*A*···N1	0.99	2.33	3.1006 (16)	134
C29—H29*B*···Br2^{i}	0.99	2.72	3.6490 (12)	156
C31—H31···O1^{vii}	0.95	2.60	3.4356 (17)	147
C33—H33*C*···N3	0.98	2.44	3.3223 (17)	149
O1—H1*D*···Br2	0.80 (3)	2.56 (3)	3.3492 (12)	171 (2)
O1—H1*E*···Br2^{iv}	0.78 (3)	2.62 (3)	3.4005 (12)	179 (3)

Symmetry codes: (i) *x*, *y*-1, *z*; (ii) -*x*+1, *y*-1, -*z*+1/2; (iii) *x*-1/2, *y*-1/2, *z*; (iv) -*x*+1, -*y*+1, -*z*+1; (v) -*x*+3/2, *y*-1/2, -*z*+1/2; (vi) *x*+1/2, *y*-1/2, *z*; (vii) -*x*+1/2, -*y*+1/2, -*z*+1.

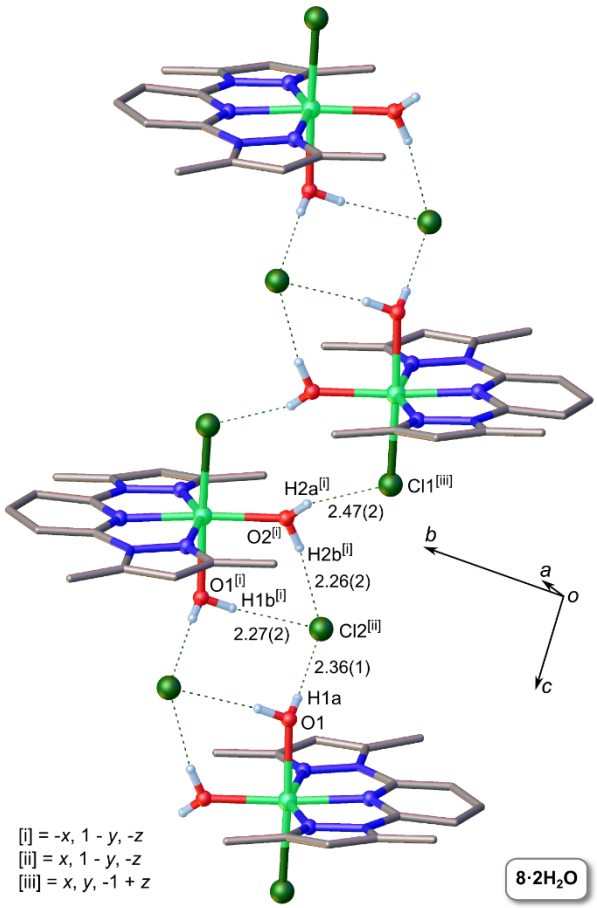
Table S2. Hydrogen-bond geometry (Å, º) for **7•4H₂O**.



D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
O1—H1*A*···O1*S*	0.82 (2)	1.85 (2)	2.664 (3)	176 (3)
O1—H1*B*···Br1	0.81 (2)	2.61 (2)	3.4077 (17)	170 (3)
O2—H2*A*···Br2^{i}	0.81 (2)	2.52 (2)	3.3278 (16)	176 (4)
O2—H2*B*···Br1^{i}	0.79 (2)	2.70 (2)	3.4824 (15)	173 (4)
O3—H3*A*···Br1	0.83 (2)	2.45 (2)	3.2695 (16)	168 (3)
O3—H3*B*···Br2	0.83 (2)	2.38 (2)	3.2067 (15)	172 (3)
C1—H1*E*···Br1^{i}	0.98	3.07	4.001 (2)	158
C3—H3···Br2^{ii}	0.95	2.89	3.795 (2)	161
C9—H9···Br1^{iii}	0.95	2.96	3.769 (2)	144
C13—H13···O3^{iv}	0.95	2.61	3.121 (3)	114
C15—H15*C*···Br1	0.98	3.07	4.031 (2)	166
O1*S*—H1*SA*···Br1^{i}	0.82 (2)	2.60 (2)	3.3642 (19)	157 (4)
O1*S*—H1*SB*···Br2^{v}	0.83 (2)	2.50 (2)	3.3030 (18)	164 (4)

Symmetry codes: (i) *x*-1/2, *y*+1/2, *z*; (ii) *x*-1, *y*, *z*; (iii) *x*, -*y*+1, *z*-1/2; (iv) *x*+1/2, *y*+1/2, *z*; (v) *x*, -*y*+1, *z*+1/2.

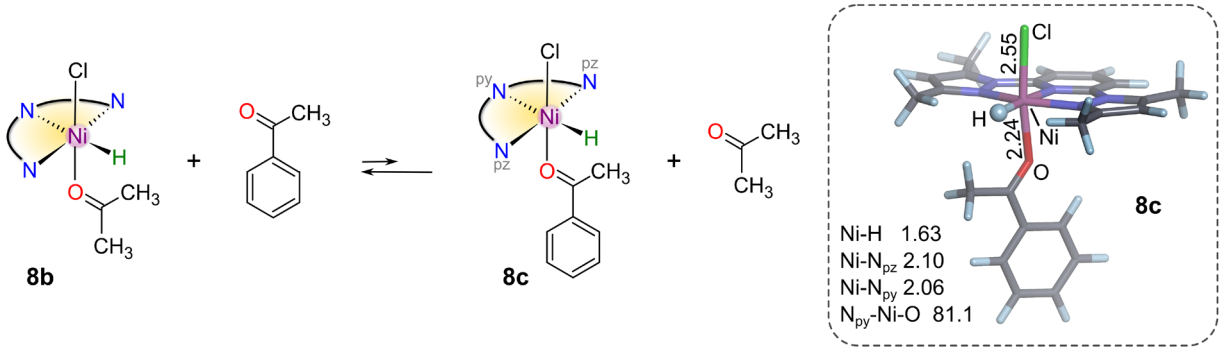
Table S3. Hydrogen-bond geometry (Å, º) for **8•2H₂O**.



D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
C1—H1*D*···Cl2^{i}	0.98	2.94	3.8022 (11)	148
C1—H1*E*···Cl1^{ii}	0.98	2.99	3.7136 (10)	132
C3—H3···Cl2^{i}	0.95	2.76	3.5642 (10)	142
C9—H9···Cl2^{iii}	0.95	2.85	3.7346 (10)	155
C7—H7···Cl1^{iv}	0.95	2.94	3.5723 (10)	125
C11—H11*C*···Cl2^{iii}	0.98	2.61	3.4592 (10)	145
C15—H15*C*···O2	0.98	2.54	3.3710 (13)	142
O2—H2*A*···Cl1^{ii}	0.80 (2)	2.47 (2)	3.2409 (8)	161.4 (18)
O1—H1*A*···Cl2	0.801 (19)	2.357 (19)	3.1535 (8)	173.0 (18)
O1—H1*B*···Cl2^{v}	0.830 (19)	2.274 (19)	3.0962 (8)	170.9 (17)
O2—H2*B*···Cl2^{v}	0.833 (19)	2.26 (2)	3.0863 (8)	170.3 (17)

Symmetry codes: (i) -*x*, -*y*, -*z*+1; (ii) -*x*+1, -*y*, -*z*+2; (iii) *x*+1/2, -*y*+1/2, *z*+1/2; (iv) *x*-1/2, -*y*+1/2, *z*-1/2; (v) -*x*+1, -*y*, -*z*+1.

Table S4. Thermochemical analysis (P = 1.0 atm; T = 298.15 K) for ketones and their complexes with the mono(hydrido) adduct of **8**. The DFT-calculated free energies of formation, ΔG_f, of various complexes such as **8c** are given in the second part of the table. Unless otherwise stated, energies are in Hartrees, bond distances in Å, and bond angles in degrees. The relevant reaction scheme pertinent to the free energy calculations is depicted below for the formation of the acetophenone complex **8c**.[a,b]



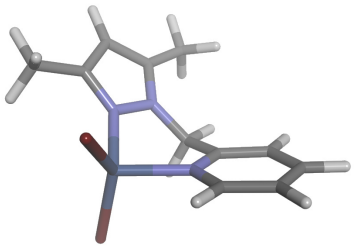
	acetophenone	2-MeCyHx	pentan-3-one	propanone
Zero-point correction	0.140135	0.18144	0.142772	0.084872
Thermal correction to energy	0.14785	0.189277	0.150575	0.090135
Thermal correction to enthalpy	0.148794	0.190221	0.151519	0.091079
Thermal correction to Gibbs free energy	0.10746	0.149366	0.110869	0.057681
Sum of electronic and zero-point energies	-384.288516	-348.59622	-271.304871	-192.838807
Sum of electronic and thermal energies	-384.280801	-348.588384	-271.297068	-192.833545
Sum of electronic and thermal enthalpies	-384.279857	-348.58744	-271.296124	-192.8326
Sum of electronic and thermal free energies	-384.321191	-348.628295	-271.336774	-192.865998

	[NiClH(L3)(AcPh)], 8c	[NiClH(L3)(2-MeCyHx)]*	[NiClH(L3)(pent)]	[NiClH(L3)(prop)]
Zero-point correction	0.459611	0.500569	0.462271	0.404192
Thermal correction to energy	0.490479	0.531698	0.493153	0.432524
Thermal correction to enthalpy	0.491423	0.532642	0.494097	0.433468
Thermal correction to Gibbs free energy	0.394164	0.43517	0.396512	0.342902
Sum of electronic and zero-point energies	-1870.119809	-1834.428174	-1757.135162	-1678.67072
Sum of electronic and thermal energies	-1870.088941	-1834.397046	-1757.10428	-1678.642388
Sum of electronic and thermal enthalpies	-1870.087996	-1834.396102	-1757.103336	-1678.641444
Sum of electronic and thermal free energies	-1870.185256	-1834.493574	-1757.200921	-1678.732011
ΔG_f / Hartrees	**0.001948**	**0.000734**	**0.001866**	**0**
ΔG_f / kJ mol^{-1}	**5.11**	**(1.93)**	**4.90**	**0**

[a]Abbreviations: 2-MeCyHx, 2-methylcyclohexanone; AcPh, acetophenone; pent, pentan-3-one; prop, propanone. [b]DFT simulations were performed at the HSE1HPBE/SDD level of theory in an *i*PrOH solvent continuum. *Structure failed to converge; ΔG_f is an estimate based on a near-converged geometry for the complex.

Cartesian Coordinates for DFT-Optimized Structures

Compound 1 (HSEH1PBE/6-311g**; 2-propanol PCM):



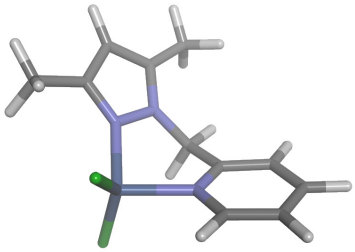
Gaussian 09 Job keywords:

```
# opt freq=vcd uhseh1pbe/6-311g(d,p)/auto
scrf=(solvent=2-Propanol) pop=npa geom=connectivity
```

Cartesian Coordinates (.xyz):

```
C -1.2458  1.4514  0.2169
C -2.1266  2.4754 -0.0969
C -3.3300  2.1675 -0.7171
C -3.6141  0.8426 -1.0110
C -2.6801 -0.1246 -0.6814
N -1.5242  0.1716 -0.0765
H -4.0328  2.9533 -0.9685
H -1.8704  3.4993  0.1462
H -4.5393  0.5547 -1.4934
C  0.0432  1.7193  0.9469
H  0.1668  2.7887  1.1034
H  0.0106  1.2321  1.9269
C  2.5496 -0.2438 -0.5711
C  3.1639  1.0054 -0.7192
H  4.1294  1.2085 -1.1544
C  2.2852  1.9361 -0.1933
C  2.4062  3.4117 -0.0724
H  2.4285  3.7314  0.9734
H  3.3336  3.7367 -0.5427
H  1.5775  3.9257 -0.5667
C  3.0555 -1.5859 -0.9633
H  2.3994 -2.0503 -1.7036
H  4.0574 -1.5015 -1.3843
H  3.1006 -2.2537 -0.0990
N  1.3616 -0.0831  0.0150
Ni -0.1857 -1.2920  0.3194
Cl -0.3280 -1.4442  2.6057
Cl -0.4429 -2.5614 -1.5667
N  1.2121  1.2384  0.2383
H -2.8451 -1.1710 -0.9092
```

Compound 2 (HSEH1PBE/6-311g**; 2-propanol PCM):



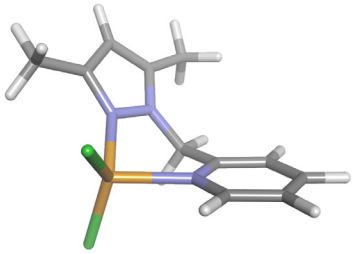
Gaussian 09 Job keywords:

```
# opt freq=vcd uhseh1pbe/6-311g(d,p)/auto
scrf=(solvent=2-Propanol) pop=npa geom=connectivity
```

Cartesian Coordinates (.xyz):

```
C -1.2458  1.4514  0.2169
C -2.1266  2.4754 -0.0969
C -3.3300  2.1675 -0.7171
C -3.6141  0.8426 -1.0110
C -2.6801 -0.1246 -0.6814
N -1.5242  0.1716 -0.0765
H -4.0328  2.9533 -0.9685
H -1.8704  3.4993  0.1462
H -4.5393  0.5547 -1.4934
C  0.0432  1.7193  0.9469
H  0.1668  2.7887  1.1034
H  0.0106  1.2321  1.9269
C  2.5496 -0.2438 -0.5711
C  3.1639  1.0054 -0.7192
H  4.1294  1.2085 -1.1544
C  2.2852  1.9361 -0.1933
C  2.4062  3.4117 -0.0724
H  2.4285  3.7314  0.9734
H  3.3336  3.7367 -0.5427
H  1.5775  3.9257 -0.5667
C  3.0555 -1.5859 -0.9633
H  2.3994 -2.0503 -1.7036
H  4.0574 -1.5015 -1.3843
H  3.1006 -2.2537 -0.0990
N  1.3616 -0.0831  0.0150
Ni -0.1857 -1.2920  0.3194
Cl -0.3280 -1.4442  2.6057
Cl -0.4429 -2.5614 -1.5667
N  1.2121  1.2384  0.2383
H -2.8451 -1.1710 -0.9092
```

Compound 3 (HSEH1PBE/6-311g; 2-propanol PCM):**



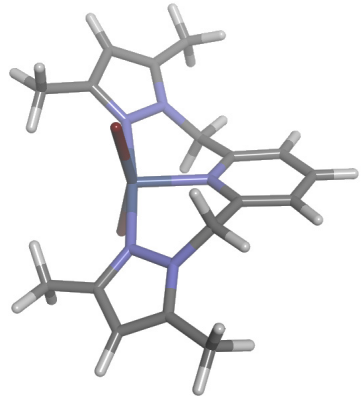
Gaussian 09 Job keywords:

```
# opt freq=vcd uhseh1pbe/6-311g(d,p)/auto
scrf=(solvent=2-Propanol) pop=npa geom=connectivity
```

Cartesian Coordinates (.xyz):

```
C -1.2185  1.4998  0.2571
C -2.0530  2.5728 -0.0190
C -3.2538  2.3435 -0.6780
C -3.5813  1.0466 -1.0438
C -2.6940  0.0285 -0.7351
N -1.5388  0.2453 -0.0971
H -3.9207  3.1677 -0.9030
H -1.7642  3.5729  0.2807
H -4.5061  0.8199 -1.5588
C  0.0729  1.6869  1.0123
H  0.2169  2.7396  1.2471
H  0.0256  1.1365  1.9576
C  2.5773 -0.2138 -0.5832
C  3.1758  1.0440 -0.7148
H  4.1317  1.2700 -1.1601
C  2.2956  1.9514 -0.1497
C  2.4089  3.4233  0.0169
H  2.4455  3.7071  1.0729
H  3.3268  3.7713 -0.4556
H  1.5689  3.9480 -0.4458
C  3.0812 -1.5395 -1.0308
H  2.5414 -1.8842 -1.9172
H  4.1416 -1.4780 -1.2772
H  2.9479 -2.2923 -0.2509
N  1.3955 -0.0868  0.0278
Fe -0.1984 -1.3877  0.2955
Cl -0.3905 -1.6570  2.5852
Cl -0.5283 -2.7071 -1.5689
N  1.2371  1.2318  0.2792
H -2.9010 -1.0001 -1.0091
```

Compound 4 (HSEH1PBE/6-311g; 2-propanol PCM):**



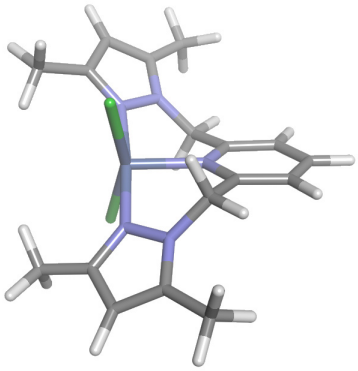
Gaussian 09 Job keywords:

```
# opt freq=vcd uhseh1pbe/6-311g(d,p)/auto
scrf=(solvent=2-Propanol) pop=npa geom=connectivity
```

Cartesian Coordinates (.xyz; C2 symmetry):

```
C  1.0628  2.2164  0.4559
C  1.0986  3.6043  0.4572
C -0.0003  4.3116 -0.0001
C -1.0990  3.6042 -0.4574
C -1.0631  2.2163 -0.4561
N -0.0001  1.5316 -0.0001
H -0.0003  5.3953 -0.0001
H  1.9797  4.1165  0.8230
H -1.9802  4.1163 -0.8233
C  2.2022  1.4512  1.0667
H  3.0058  2.1413  1.3138
H  1.8443  0.9831  1.9924
C -2.2024  1.4509 -1.0667
H -1.8445  0.9827 -1.9924
H -3.0061  2.1408 -1.3139
C  2.8483 -1.5555 -0.6348
C  4.1548 -1.0449 -0.6220
H  5.0486 -1.5316 -0.9794
C -2.8482 -1.5557  0.6350
C -4.1546 -1.0450  0.6229
H -5.0482 -1.5316  0.9806
C  4.0731  0.2108 -0.0542
C -4.0731  0.2106  0.0549
C  5.1382  1.2037  0.2423
H  5.2645  1.3531  1.3189
H  6.0860  0.8458 -0.1588
H  4.9233  2.1750 -0.2113
C  2.3898 -2.8784 -1.1350
H  2.2040 -2.8455 -2.2113
H  3.1524 -3.6347 -0.9382
H  1.4613 -3.1852 -0.6519
C -5.1381  1.2036 -0.2412
H -6.0858  0.8459  0.1607
H -4.9228  2.1751  0.2120
H -5.2651  1.3527 -1.3178
C -2.3896 -2.8788  1.1349
H -2.2048 -2.8463  2.2113
H -3.1517 -3.6353  0.9370
H -1.4605 -3.1850  0.6525
N  2.0165 -0.6571 -0.1089
N -2.0165 -0.6575  0.1087
Ni -0.0000 -0.5364 -0.0000
N -2.7654  0.4099 -0.2343
N  2.7653  0.4102  0.2344
Br -0.1449 -0.8974 -2.5725
Br  0.1450 -0.8975  2.5720
```

Compound 5 (HSEH1PBE/6-311g; 2-propanol PCM):**



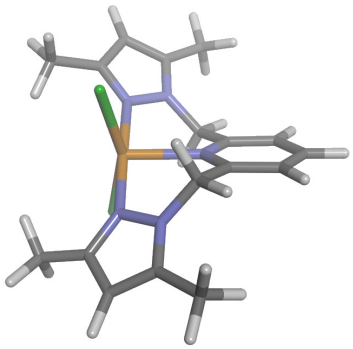
Gaussian 09 Job keywords:

```
# opt freq=vcd uhseh1pbe/6-311g(d,p)/auto
scrf=(solvent=2-Propanol) pop=npa geom=connectivity
```

Cartesian Coordinates (.xyz; C2 symmetry):

```
C -0.4964  1.0446 -2.0520
C -0.5015  1.0800 -3.4397
C  0.0000  0.0000 -4.1466
C  0.5015 -1.0800 -3.4397
C  0.4964 -1.0446 -2.0520
N  0.0000  0.0000 -1.3684
H  0.0000  0.0000 -5.2303
H -0.9023  1.9458 -3.9521
H  0.9023 -1.9458 -3.9521
C -1.1314  2.1646 -1.2772
H -1.4253  2.9558 -1.9631
H -2.0292  1.7809 -0.7794
C  1.1314 -2.1646 -1.2772
H  2.0292 -1.7809 -0.7794
H  1.4253 -2.9558 -1.9631
C  0.6843  2.8751  1.6496
C  0.6289  4.1751  1.1263
H  0.9962  5.0791  1.5861
C -0.6843 -2.8751  1.6496
C -0.6289 -4.1751  1.1263
H -0.9962 -5.0791  1.5861
C  0.0000  4.0717 -0.0989
C  0.0000 -4.0717 -0.0989
C -0.3585  5.1207 -1.0885
H -1.4427  5.2285 -1.1898
H  0.0434  6.0787 -0.7596
H  0.0537  4.9023 -2.0774
C  1.2455  2.4355  2.9542
H  2.2827  2.1107  2.8452
H  1.2077  3.2572  3.6714
H  0.6803  1.5934  3.3573
C  0.3585 -5.1207 -1.0885
H -0.0434 -6.0787 -0.7596
H -0.0537 -4.9023 -2.0774
H  1.4427 -5.2285 -1.1898
C -1.2455 -2.4355  2.9542
H -2.2827 -2.1107  2.8452
H -1.2077 -3.2572  3.6714
H -0.6803 -1.5934  3.3573
N  0.1259  2.0255  0.7880
N -0.1259 -2.0255  0.7880
Ni  0.0000  0.0000  0.7037
Cl -2.4039  0.1781  1.1156
Cl  2.4039 -0.1781  1.1156
N  0.2823 -2.7589 -0.2671
N -0.2823  2.7589 -0.2671
```

Compound 6 (HSEH1PBE/6-311g; 2-propanol PCM):**



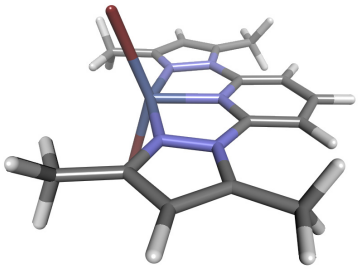
Gaussian 09 Job keywords:

```
# opt freq=vcd uhseh1pbe/6-311g(d,p)/auto
scrf=(solvent=2-Propanol) pop=npa geom=connectivity
```

Cartesian Coordinates (.xyz; C2 symmetry):

```
C -0.5228  1.0306 -2.0455
C -0.5310  1.0671 -3.4337
C  0.0000 -0.0000 -4.1399
C  0.5310 -1.0671 -3.4337
C  0.5228 -1.0306 -2.0455
N  0.0000 -0.0000 -1.3618
H  0.0000 -0.0000 -5.2238
H -0.9545  1.9212 -3.9479
H  0.9545 -1.9212 -3.9479
C -1.1789  2.1375 -1.2634
H -1.5420  2.8987 -1.9508
H -2.0390  1.7273 -0.7229
C  1.1789 -2.1375 -1.2634
H  2.0390 -1.7273 -0.7229
H  1.5420 -2.8987 -1.9508
C  0.6273  3.0405  1.6135
C  0.6217  4.2937  0.9832
H  1.0138  5.2219  1.3685
C -0.6273 -3.0405  1.6135
C -0.6217 -4.2937  0.9832
H -1.0138 -5.2219  1.3685
C  0.0000  4.1067 -0.2366
C -0.0000 -4.1067 -0.2366
C -0.3162  5.0804 -1.3139
H -1.3955  5.2156 -1.4336
H  0.1156  6.0491 -1.0634
H  0.0939  4.7655 -2.2772
C  1.1618  2.6859  2.9554
H  2.2046  2.3653  2.8895
H  1.1047  3.5478  3.6226
H  0.5931  1.8640  3.3949
C  0.3162 -5.0804 -1.3139
H -0.1156 -6.0491 -1.0634
H -0.0939 -4.7655 -2.2772
H  1.3955 -5.2156 -1.4336
C -1.1618 -2.6859  2.9554
H -2.2046 -2.3653  2.8895
H -1.1047 -3.5478  3.6226
H -0.5931 -1.8640  3.3949
N  0.0514  2.1361  0.8213
N -0.0514 -2.1361  0.8213
Fe -0.0000  0.0000  0.8366
Cl -2.3955  0.0816  1.2836
Cl  2.3955 -0.0816  1.2836
N  0.3222 -2.7937 -0.2975
N -0.3222  2.7937 -0.2975
```

Compound 7 (HSEH1PBE/6-311g; 2-propanol PCM):**



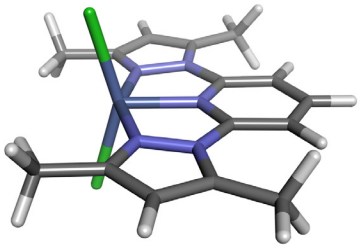
Gaussian 09 Job keywords:

```
# opt freq=vcd uhseh1pbe/6-311g(d,p)/auto
scrf=(solvent=2-Propanol) pop=npa geom=connectivity
```

Cartesian Coordinates (.xyz; C2 symmetry):

```
C  0.0002  1.1624 -1.8933
C -0.0009  1.2127 -3.2812
C  0.0000  0.0000 -3.9553
C  0.0009 -1.2127 -3.2812
C -0.0002 -1.1624 -1.8933
N  0.0000  0.0000 -1.2432
H  0.0000  0.0000 -5.0387
H -0.0028  2.1408 -3.8277
H  0.0028 -2.1408 -3.8277
C -0.0139  3.1792  0.9186
C  0.0000  4.2194 -0.0356
H  0.0027  5.2808  0.1553
C  0.0139 -3.1792  0.9186
C  0.0000 -4.2194 -0.0356
H -0.0027 -5.2808  0.1553
C  0.0091  3.6233 -1.2702
C -0.0091 -3.6233 -1.2702
C  0.0256  4.2763 -2.6030
H -0.8635  4.0314 -3.1904
H  0.0416  5.3559 -2.4566
H  0.9120  4.0036 -3.1821
C -0.0218  3.2737  2.3992
H  0.9089  3.7207  2.7587
H -0.8463  3.9051  2.7385
H -0.1292  2.2845  2.8428
C -0.0256 -4.2763 -2.6030
H -0.0416 -5.3559 -2.4566
H -0.9120 -4.0036 -3.1821
H  0.8635 -4.0314 -3.1904
C  0.0218 -3.2737  2.3992
H -0.9089 -3.7207  2.7587
H  0.8463 -3.9051  2.7385
H  0.1292 -2.2845  2.8428
N -0.0138  2.0126  0.3053
N  0.0138 -2.0126  0.3053
Ni  0.0000  0.0000  0.7451
N -0.0001 -2.2679 -1.0342
N  0.0001  2.2679 -1.0342
Br  2.3827  0.0188  1.4904
Br -2.3827 -0.0188  1.4904
```

Compound 8 (HSEH1PBE/6-311g; 2-propanol PCM):**



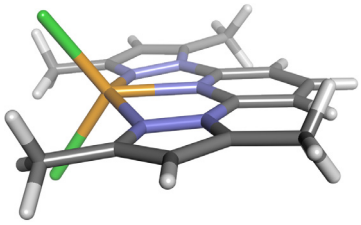
Gaussian 09 Job keywords:

```
# opt freq=vcd uhseh1pbe/6-311g(d,p)/auto
scrf=(solvent=2-Propanol) pop=npa geom=connectivity
```

Cartesian Coordinates (.xyz; C2 symmetry):

```
C -0.0046  1.1626 -1.6127
C -0.0089  1.2129 -3.0007
C  0.0000  0.0000 -3.6745
C  0.0089 -1.2129 -3.0007
C  0.0046 -1.1626 -1.6127
N  0.0000  0.0000 -0.9637
H  0.0000  0.0000 -4.7579
H -0.0207  2.1408 -3.5474
H  0.0207 -2.1408 -3.5474
C -0.0518  3.1798  1.1992
C  0.0000  4.2197  0.2460
H  0.0180  5.2810  0.4372
C  0.0518 -3.1798  1.1992
C  0.0000 -4.2197  0.2460
H -0.0180 -5.2810  0.4372
C  0.0275  3.6229 -0.9880
C -0.0275 -3.6229 -0.9880
C  0.0913  4.2745 -2.3202
H -0.7992  4.0681 -2.9203
H  0.1515  5.3524 -2.1733
H  0.9733  3.9634 -2.8863
C -0.0895  3.2712  2.6796
H  0.8233  3.7385  3.0580
H -0.9346  3.8823  3.0055
H -0.1829  2.2781  3.1185
C -0.0913 -4.2745 -2.3202
H -0.1515 -5.3524 -2.1733
H -0.9733 -3.9634 -2.8863
H  0.7992 -4.0681 -2.9203
C  0.0895 -3.2712  2.6796
H -0.8233 -3.7385  3.0580
H  0.9346 -3.8823  3.0055
H  0.1829 -2.2781  3.1185
N -0.0562  2.0133  0.5862
N  0.0562 -2.0133  0.5862
Ni  0.0000  0.0000  1.0260
Cl -2.2768 -0.0975  1.6627
Cl  2.2768  0.0975  1.6627
N  0.0103 -2.2681 -0.7527
N -0.0103  2.2681 -0.7527
```

Compound 9 (HSEH1PBE/6-311g; 2-propanol PCM):**



Gaussian 09 Job keywords:

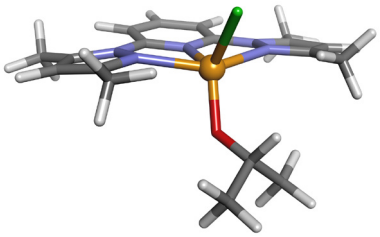
```
# opt freq=vcd uhseh1pbe/6-311g(d,p)/auto
scrf=(solvent=2-Propanol) pop=npa geom=connectivity
```

Cartesian Coordinates (.xyz; C1 symmetry):

Note: the C2 symmetry structure is a saddle point whereas the C1 symmetry structure (coordinates below) is a true minimum.

```
C -1.1579  1.7584 -0.0418
C -1.2098  3.1438 -0.1311
C  0.0002  3.8197 -0.1674
C  1.2101  3.1438 -0.1305
C  1.1581  1.7583 -0.0414
N  0.0001  1.1012  0.0116
H  0.0003  4.9003 -0.2463
H -2.1380  3.6861 -0.1913
H  2.1384  3.6859 -0.1901
C -3.2400 -1.0075 -0.0898
C -4.2539 -0.0325  0.0098
H -5.3188 -0.1990  0.0495
C  3.2399 -1.0079 -0.0882
C  4.2540 -0.0328  0.0095
H  5.3189 -0.1994  0.0484
C -3.6264  1.1864  0.0499
C  3.6266  1.1861  0.0492
C -4.2521  2.5285  0.1606
H -4.1096  3.1231 -0.7462
H -5.3242  2.3961  0.3034
H -3.8658  3.0936  1.0125
C -3.3817 -2.4846 -0.1425
H -3.5729 -2.8820  0.8589
H -4.2252 -2.7641 -0.7767
H -2.4721 -2.9441 -0.5305
C  4.2527  2.5282  0.1579
H  5.3249  2.3957  0.2994
H  4.1090  3.1222 -0.7491
H  3.8677  3.0941  1.0099
C  3.3812 -2.4851 -0.1393
H  4.2272 -2.7655 -0.7698
H  3.5678 -2.8820  0.8631
H  2.4729 -2.9443 -0.5308
N -2.0542 -0.4226 -0.1098
N  2.0541 -0.4229 -0.1076
Fe -0.0001 -1.0557  0.0949
Cl  0.0007 -2.5202 -1.8572
Cl -0.0009 -2.3701  2.0206
N  2.2796  0.9183 -0.0215
N -2.2795  0.9185 -0.0224
```

Compound 9a (HSEH1PBE/6-311g; 2-propanol PCM):**



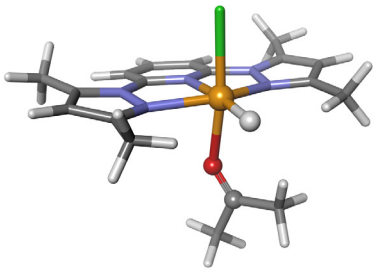
Gaussian 09 Job keywords:

```
# opt freq=vcd uhseh1pbe/6-311g(d,p)/auto
scrf=(solvent=2-Propanol) pop=npa geom=connectivity
```

Cartesian Coordinates (.xyz; C1 symmetry):

```
C  1.4365  1.8864  0.1144
C  1.6401  3.2515  0.2748
C  0.5114  4.0534  0.3487
C -0.7635  3.5185  0.2451
C -0.8618  2.1419  0.0799
N  0.2154  1.3605  0.0307
H  0.6285  5.1244  0.4635
H  2.6242  3.6879  0.3140
H -1.6269  4.1617  0.2665
C  3.2233 -1.0264 -0.4228
C  4.3166 -0.2297 -0.0196
H  5.3480 -0.5311  0.0757
C -3.2398 -0.2870 -0.5795
C -4.1395  0.7491 -0.2522
H -5.2172  0.7023 -0.2439
C  3.8146  1.0189  0.2452
C -3.3779  1.8455  0.0613
C  4.5494  2.2138  0.7337
H  4.0950  2.6361  1.6334
H  5.5677  1.9136  0.9797
H  4.6106  2.9989 -0.0252
C  3.2059 -2.4600 -0.8079
H  3.9060 -2.6494 -1.6254
H  3.5075 -3.0849  0.0374
H  2.2029 -2.7460 -1.1233
C -3.8496  3.1874  0.4891
H -4.9268  3.1374  0.6464
H -3.3860  3.5084  1.4251
H -3.6620  3.9502 -0.2719
C -3.5478 -1.6791 -0.9940
H -3.9697 -2.2450 -0.1584
H -4.2868 -1.6818 -1.7988
H -2.6418 -2.1762 -1.3412
N  2.1127 -0.3118 -0.4092
N -1.9939  0.1414 -0.4685
Cl -0.1403 -1.9302 -2.4871
N -2.0694  1.4472 -0.0812
N  2.4644  0.9407 -0.0041
Fe -0.0176 -0.7586 -0.2899
O -0.0456 -1.8526  1.2174
C -0.7765 -3.0126  1.4544
H -1.2162 -3.4048  0.5166
C  0.1355 -4.1012  2.0132
H -0.4101 -5.0305  2.2103
H  0.9432 -4.3177  1.3083
H  0.5864 -3.7587  2.9513
C -1.9304 -2.7282  2.4136
H -1.5345 -2.3778  3.3735
H -2.5731 -1.9415  2.0080
H -2.5436 -3.6176  2.5962
```

Compound 9b (HSEH1PBE/6-311g; 2-propanol PCM):**



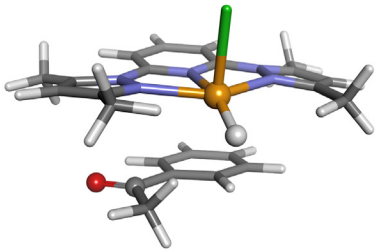
Gaussian 09 Job keywords:

```
# opt freq=vcd uhseh1pbe/6-311g(d,p)/auto
scrf=(solvent=2-Propanol) pop=npa geom=connectivity
```

Cartesian Coordinates (.xyz; C1 symmetry):

```
Fe  0.0057 -1.0013 -0.7469
Cl -0.1008 -0.0229 -3.1014
N -0.1384  1.0425  0.0955
N  2.0391 -0.2463 -0.3842
N -2.1039 -0.5725 -0.3027
N -2.4025  0.6970  0.0845
C  3.2557 -0.6455 -0.7092
C -0.3081  3.4762  1.3172
H -0.3751  4.4372  1.8134
C -3.2548 -1.1743 -0.5397
C  0.9705  1.7178  0.3784
C -1.3294  1.5397  0.4126
C  3.5076 -2.0228 -1.2055
H  2.5639 -2.5629 -1.2936
H  4.1727 -2.5656 -0.5282
H  3.9903 -1.9921 -2.1858
C -3.7625  0.9063  0.0841
C  4.1757  0.4087 -0.5260
H  5.2377  0.3933 -0.7151
C  3.4537  1.4826 -0.0717
C -4.3235 -0.2807 -0.3120
H -5.3779 -0.4750 -0.4310
C -1.4701  2.7761  1.0338
H -2.4300  3.1768  1.3129
C  3.9524  2.8466  0.2406
H  3.4004  3.6200 -0.2994
H  4.9977  2.9064 -0.0619
H  3.9050  3.0692  1.3104
C  0.9394  2.9597  1.0030
H  1.8338  3.5012  1.2616
C -4.4614  2.1746  0.4173
H -4.3926  2.4169  1.4817
H -5.5174  2.0571  0.1746
H -4.0760  3.0208 -0.1568
C -3.3032 -2.5915 -0.9820
H -3.7796 -2.6732 -1.9627
H -3.8863 -3.1948 -0.2810
H -2.2899 -2.9906 -1.0478
H  0.1017 -2.6542 -1.1984
C  0.5066 -2.3317  2.2477
O  0.0202 -1.4629  1.5424
C  1.3994 -3.3939  1.6865
H  1.2772 -4.3420  2.2138
H  1.2105 -3.5043  0.6179
H  2.4371 -3.0716  1.8314
N  2.1499  1.0518  0.0084
C  0.2344 -2.3615  3.7206
H -0.3886 -3.2335  3.9473
H  1.1659 -2.4872  4.2794
H -0.2805 -1.4547  4.0349
```

Compound 9c (HSEH1PBE/6-311g; 2-propanol PCM):**



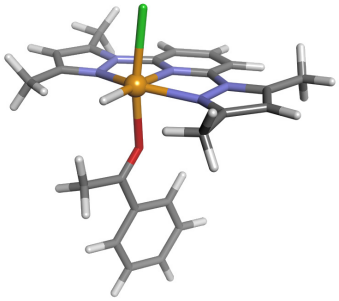
Gaussian 09 Job keywords:

```
# opt freq=vcd uhseh1pbe/6-311g(d,p)/auto
scrf=(solvent=2-Propanol) pop=npa geom=connectivity
empiricaldispersion(pfd)
```

Cartesian Coordinates (.xyz; C1 symmetry):

```
C -2.1998 -0.2093  2.2216
C -2.4102  1.1964  2.6990
C -0.7984 -0.7083  2.1271
C  0.3076  0.1103  2.3746
C -0.5979 -2.0585  1.8242
C  1.5920 -0.4269  2.3514
C  0.6818 -2.5874  1.7858
C  1.7800 -1.7707  2.0595
O -3.1326 -0.9377  1.9376
H -1.8166  1.8941  2.0967
H -3.4678  1.4483  2.6402
H -2.0682  1.2969  3.7341
H  0.1743  1.1502  2.6440
H -1.4668 -2.6787  1.6331
H  2.4460  0.2102  2.5534
H  0.8304 -3.6357  1.5492
H  2.7827 -2.1860  2.0478
H -0.1431  2.7285  1.1051
Fe  0.0692  1.4973 -0.0254
Cl  0.1731  2.7105 -2.2127
N  0.2659 -0.5665 -0.8240
N -1.9131  0.7503 -0.5776
N  2.1953  1.0045 -0.2307
N  2.5178 -0.2519 -0.6022
C -3.1332  1.2431 -0.5458
C  0.5084 -3.0523 -1.9100
H  0.6041 -4.0366 -2.3538
C  3.2950  1.5787  0.2044
C -0.8251 -1.2462 -1.1565
C  1.4716 -1.0847 -1.0151
C -3.3606  2.6745 -0.2291
H -2.4268  3.1413  0.0878
H -4.1056  2.7879  0.5620
H -3.7318  3.2036 -1.1112
C  3.8530 -0.4983 -0.3821
C -4.0629  0.2315 -0.8568
H -5.1383  0.3127 -0.8804
C -3.3358 -0.9072 -1.0885
C  4.3687  0.6666  0.1288
H  5.3949  0.8327  0.4175
C  1.6523 -2.3414 -1.5806
H  2.6289 -2.7511 -1.7782
C -3.8489 -2.2688 -1.3833
H -3.6187 -2.5916 -2.4027
H -4.9334 -2.2575 -1.2773
H -3.4489 -3.0076 -0.6839
C -0.7562 -2.5222 -1.7024
H -1.6345 -3.0795 -1.9824
C  4.5650 -1.7787 -0.6297
H  4.0868 -2.6199 -0.1204
H  5.5815 -1.6873 -0.2477
H  4.6300 -2.0142 -1.6958
C  3.2631  2.9800  0.6907
H  3.7022  3.6576 -0.0474
H  3.8337  3.0829  1.6164
H  2.2298  3.2844  0.8707
N -2.0174 -0.5525 -0.9262
```

Compound 9c AXIAL (HSEH1PBE/6-311g; 2-propanol PCM):**



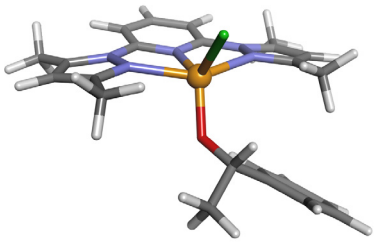
Gaussian 09 Job keywords:

```
# opt freq=vcd uhseh1pbe/6-311g(d,p)/auto
scrf=(solvent=2-Propanol) pop=npa geom=connectivity
```

Cartesian Coordinates (.xyz; C1 symmetry):

```
Fe  0.8235 -0.0812 -1.3924
Cl  3.3531  0.0109 -1.7950
N  1.2726  0.0919  0.7730
N  0.8549 -2.0901 -0.5134
N  0.7212  2.0302 -0.8160
N  1.1536  2.3525  0.4326
C  0.7720 -3.3209 -0.9855
C  1.8349  0.3086  3.4320
H  2.0508  0.3946  4.4903
C  0.5532  3.1682 -1.4635
C  1.4359 -1.0059  1.5030
C  1.3754  1.2946  1.3285
C  0.3362 -3.5809 -2.3815
H  0.2152 -2.6346 -2.9111
H -0.6125 -4.1251 -2.3954
H  1.0740 -4.1922 -2.9072
C  1.2717  3.7159  0.5757
C  1.1489 -4.2469  0.0101
H  1.1913 -5.3215 -0.0754
C  1.4675 -3.5142  1.1246
C  0.8914  4.2536 -0.6273
H  0.8685  5.3039 -0.8726
C  1.6599  1.4596  2.6796
H  1.7302  2.4285  3.1439
C  1.9429 -4.0227  2.4370
H  2.8992 -3.5805  2.7276
H  2.0828 -5.1003  2.3555
H  1.2187 -3.8421  3.2364
C  1.7225 -0.9502  2.8630
H  1.8412 -1.8332  3.4677
C  1.7409  4.4412  1.7843
H  1.0369  4.3566  2.6170
H  1.8303  5.4983  1.5347
H  2.7204  4.0911  2.1199
C  0.0725  3.1834 -2.8688
H  0.8021  3.6688 -3.5224
H -0.8648  3.7405 -2.9495
H -0.0839  2.1599 -3.2132
H  0.3823 -0.2526 -3.0425
C -2.4734 -0.3683 -0.9609
O -1.3531 -0.0469 -0.5848
C -2.6826 -0.9999 -2.3029
H -3.4351 -0.4552 -2.8789
H -1.7322 -1.0006 -2.8363
H -3.0443 -2.0259 -2.1819
C -3.6396 -0.1310 -0.0713
C -4.9333 -0.5226 -0.4282
C -3.4308  0.5006  1.1595
C -5.9980 -0.2865  0.4318
H -5.1154 -1.0152 -1.3763
C -4.4940  0.7388  2.0150
H -2.4233  0.8000  1.4241
C -5.7801  0.3447  1.6518
H -6.9986 -0.5942  0.1495
H -4.3252  1.2318  2.9661
H -6.6132  0.5306  2.3212
N  1.2765 -2.1969  0.7762
```

Compound 9d (HSEH1PBE/6-311g; 2-propanol PCM):**



Gaussian 09 Job keywords:

```
# opt freq=vcd uhseh1pbe/6-311g(d,p)/auto
scrf=(solvent=2-Propanol) pop=npa geom=connectivity
```

Cartesian Coordinates (.xyz; C1 symmetry):

```
Fe -0.3761 -0.5353  0.6430
Cl -0.2397 -1.5394  2.9204
N -1.4461  1.1998 -0.0593
N -2.4225 -1.1562  0.2254
N  0.8566  1.2015  1.0915
N  0.4418  2.3612  0.5023
C -3.0442 -2.3152  0.1009
C -2.8505  3.4220 -0.7893
H -3.4123  4.3062 -1.0661
C  2.1026  1.4093  1.4828
C -2.7116  1.0814 -0.4587
C -0.8683  2.3979  0.0068
C -2.4723 -3.5603  0.6725
H -2.1202 -4.2167 -0.1287
H -3.2288 -4.1077  1.2396
H -1.6334 -3.3226  1.3268
C  1.4384  3.3072  0.5150
C -4.2339 -2.1486 -0.6402
H -4.9487 -2.9097 -0.9115
C -4.3086 -0.8189 -0.9681
C  2.5070  2.7166  1.1391
H  3.4684  3.1715  1.3188
C -1.5403  3.5591 -0.3563
H -1.0899  4.5348 -0.2812
C -5.3516 -0.1316 -1.7714
H -5.9669  0.5366 -1.1621
H -6.0102 -0.8874 -2.1986
H -4.9218  0.4464 -2.5932
C -3.4690  2.1819 -0.8403
H -4.5015  2.0974 -1.1361
C  1.3582  4.6723 -0.0653
H  0.9993  4.6594 -1.0972
H  2.3574  5.1069 -0.0606
H  0.7092  5.3305  0.5195
C  2.8950  0.3512  2.1573
H  3.4636  0.7721  2.9895
H  3.6059 -0.0915  1.4526
H  2.2377 -0.4358  2.5292
C  1.7168 -2.3004 -0.4399
O  0.5350 -1.6009 -0.5981
C  1.6166 -3.6545 -1.1494
H  2.5306 -4.2466 -1.0427
H  0.7810 -4.2243 -0.7332
H  1.4286 -3.4950 -2.2159
C  2.9251 -1.5298 -0.9580
C  2.7540 -0.3772 -1.7197
C  4.2261 -1.9595 -0.6824
C  3.8525  0.3292 -2.2023
H  1.7400 -0.0430 -1.9086
C  5.3264 -1.2568 -1.1593
H  4.3795 -2.8488 -0.0760
C  5.1432 -0.1075 -1.9250
H  3.7000  1.2271 -2.7936
H  6.3296 -1.6027 -0.9304
H  6.0007  0.4438 -2.2967
N -3.1890 -0.2355 -0.4235
H  1.9203 -2.5082  0.6285
```

Table S5. Thermochemical analysis (P = 1.0 atm; T = 298.15 K) for compounds involved in the catalytic cycle of **9** (Figure S12) calculated at the HSEH1PBE/6-311G(d,p) level of theory in a 2-propanol solvent continuum.[a]

Parameter	ACP	Acetone	iPrOH	iPrOK	KCl	Cpd 9	Cpd 9a	Cpd 9b	π-adduct 9c	Axial 9c	Cpd 9d	1-PhEtOH
Zero-point correction	0.1382	0.0837	0.1081	0.0949	0.0004	0.3076	0.4038	0.3969	0.4537	0.4577	0.4574	0.1616
Thermal correction to Energy	0.1461	0.0890	0.1135	0.1020	0.0034	0.3297	0.4319	0.4263	0.4845	0.4892	0.4884	0.1700
Thermal correction to Enthalpy	0.1470	0.0899	0.1144	0.1029	0.0043	0.3307	0.4329	0.4273	0.4855	0.4901	0.4894	0.1709
Thermal correction to Gibbs Free Energy	0.1055	0.0566	0.0807	0.0629	-0.0234	0.2554	0.3421	0.3327	0.3915	0.3892	0.3914	0.1281
Sum of electronic and zero-point Energies	-384.4354	-192.9171	-194.0933	-793.3257	-1059.9147	-3038.3719	-2771.7492	-2771.7056	-2963.2008	-1823.1226	-2963.2692	-385.6089
Sum of electronic and thermal Energies	-384.4276	-192.9118	-194.0879	-793.3187	-1059.9117	-3038.3497	-2771.7210	-2771.6762	-2963.1700	-1823.0911	-2963.2381	-385.6005
Sum of electronic and thermal Enthalpies	-384.4267	-192.9109	-194.0869	-793.3177	-1059.9108	-3038.3488	-2771.7201	-2771.6752	-2963.1690	-1823.0901	-2963.2372	-385.5995
Sum of electronic and thermal Free Energies	-384.4682	-192.9442	-194.1207	-793.3577	-1059.9385	-3038.4241	-2771.8108	-2771.7699	-2963.2631	-1823.1910	-2963.3351	-385.6423

[a] Abbreviations: ACP, acetophenone; iPrOH, 2-propanol; iPrOK, potassium isopropoxide; 1-PhEtOH, 1-phenylethanol.

Table S6. State energy levels from the thermochemical data listed in Table S5 for the catalytic cycle of **9** depicted in Figure S12.

State	Gibbs energy (Hartree)	Gibbs rel. energy (Hartree)	Gibbs rel. energy (kJ mol^{-1})	ΔG (reaction step) (kJ mol^{-1})	
9 + iPrOK + Acetophenone + iPrOH	-4410.370679	0	0	/	/
9a + KCl + Acetophenone + iPrOH	-4410.338178	0.032501	85.33	**9** → **9a**, activation	85.33
9b + KCl + Acetophenone + iPrOH	-4410.297208	0.073471	192.90	**9a** → **9b**, step 1	107.57
9c + KCl + Acetone + iPrOH	-4410.266464	0.104215	273.62	**9b** → **9c**, step 2	80.72
9d + KCl + Acetone + iPrOH	-4410.338542	0.032137	84.38	**9c** → **9d**, step 3	-189.24
9a + KCl + Acetone + 1-PhEtOH	-4410.335886	0.034793	91.35	**9d** → **9a** + **prod**, step 4	6.97

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