Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary information for

Mononuclear complexes of Fe^{II}, Co^{II} and Co^{III} containing imine-based ligands of 8-aminoquinoline and 7-aminoindazole: spin state tuning of Fe^{II} complexes in solution

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1. NMR spectroscopy

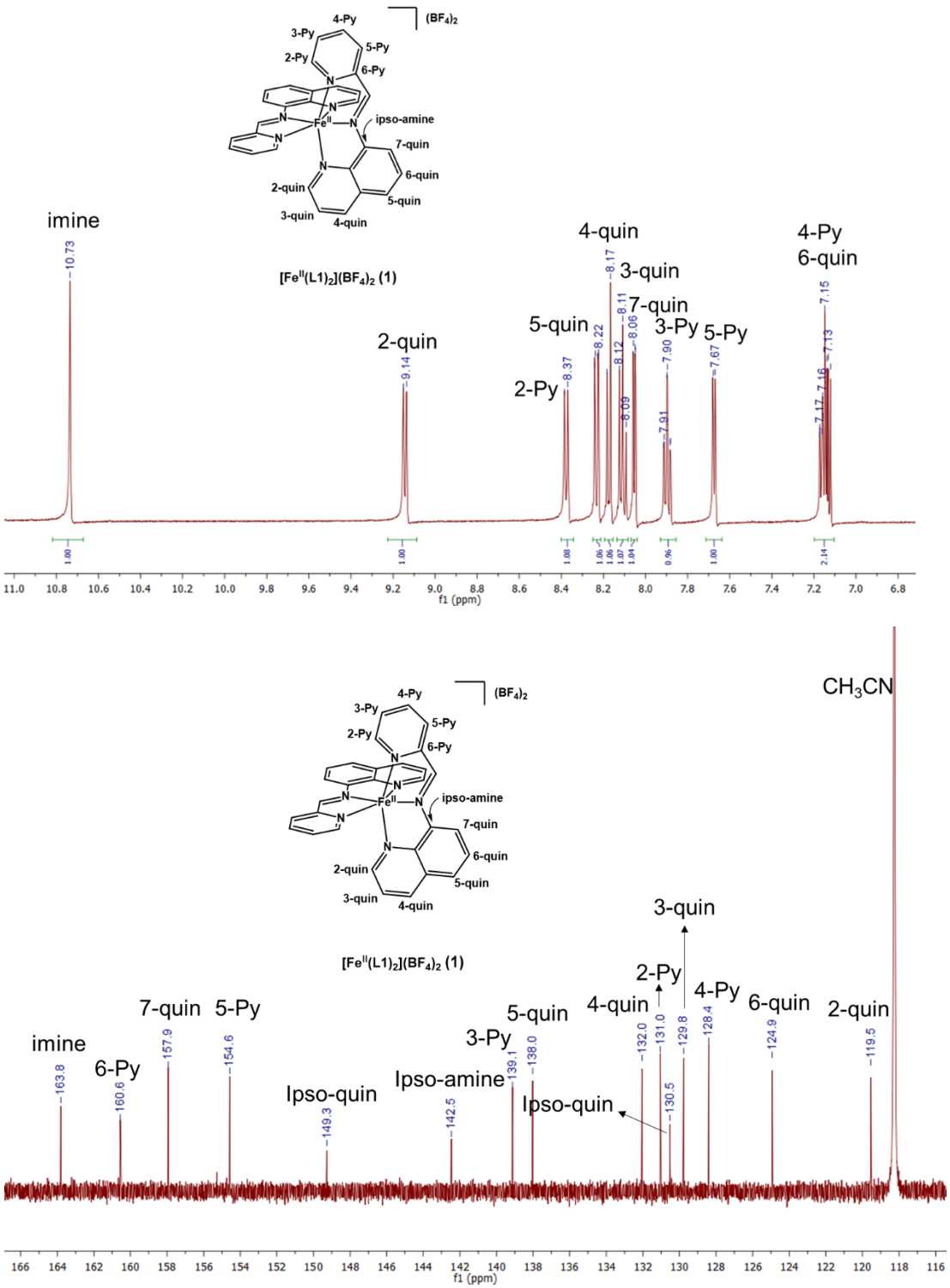

Fig S1. ^{1}H NMR and ^{13}C NMR of complex **1** in CD_3CN solution.

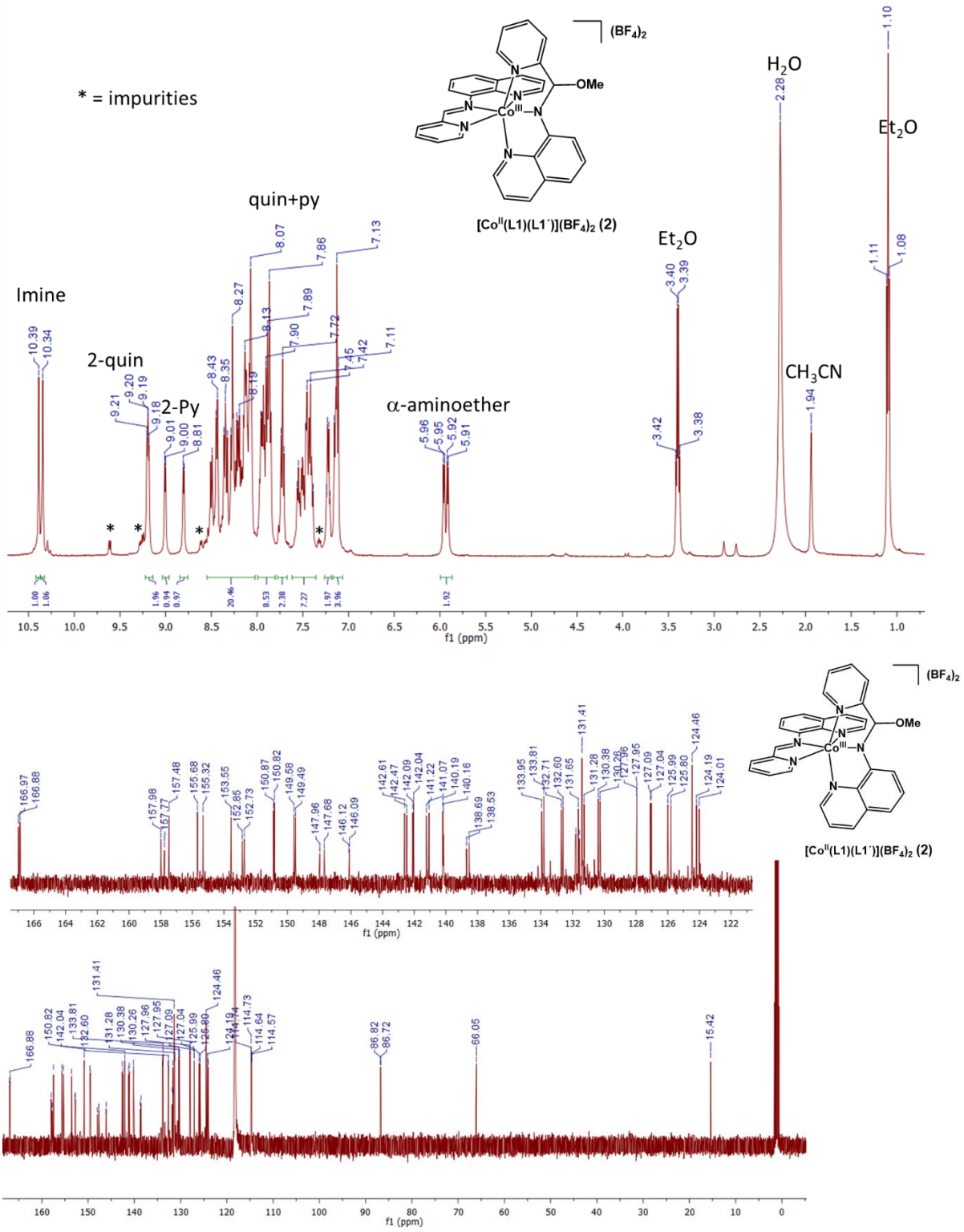

Fig S2. ^{1}H NMR and ^{13}C NMR of complex **2** in CD_3CN solution.

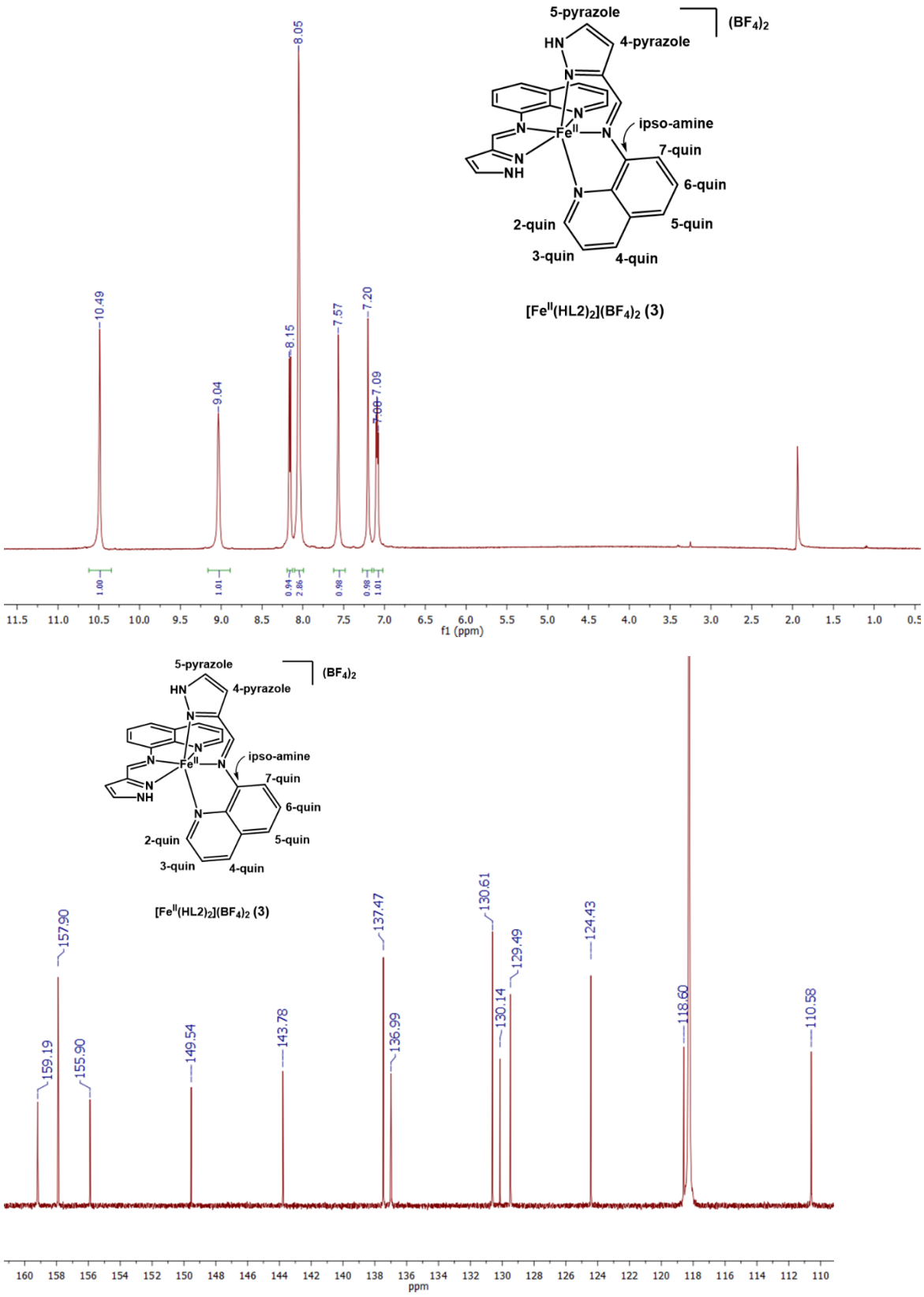

Fig S3. ^{1}H NMR and ^{13}C NMR of complex **3** in CD_3CN solution.

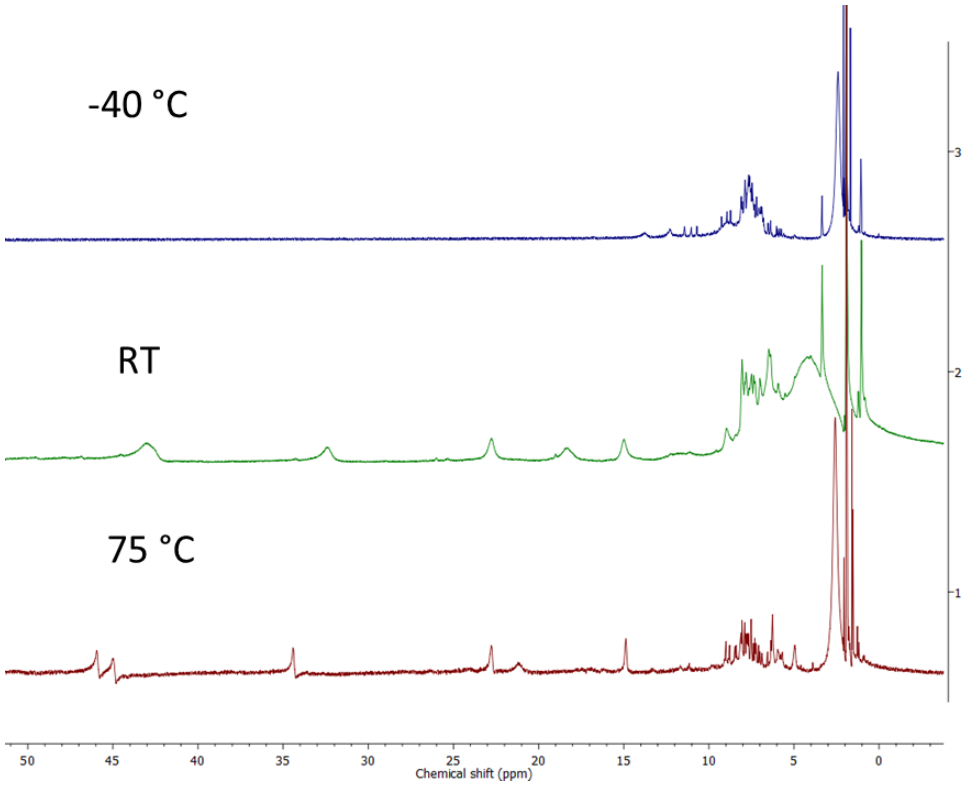

Figure S4. Paramagnetic VT-^{1}H NMR for complex **4** in CD_3CN solution.

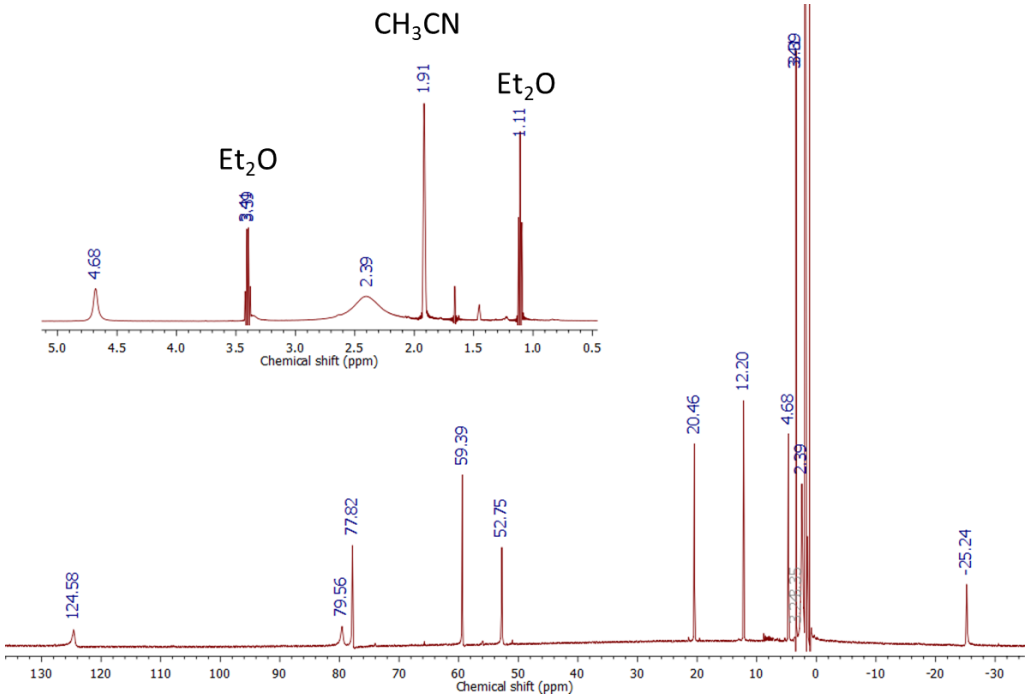

Figure S5. Paramagnetic ^{1}H NMR for complex **5·(MeOH)$_2$(Et$_2$O)$_{0.5}$** in CD_3CN solution. Inset shows an expansion of the 0.5-5.0 ppm range.

2. IR Spectroscopy

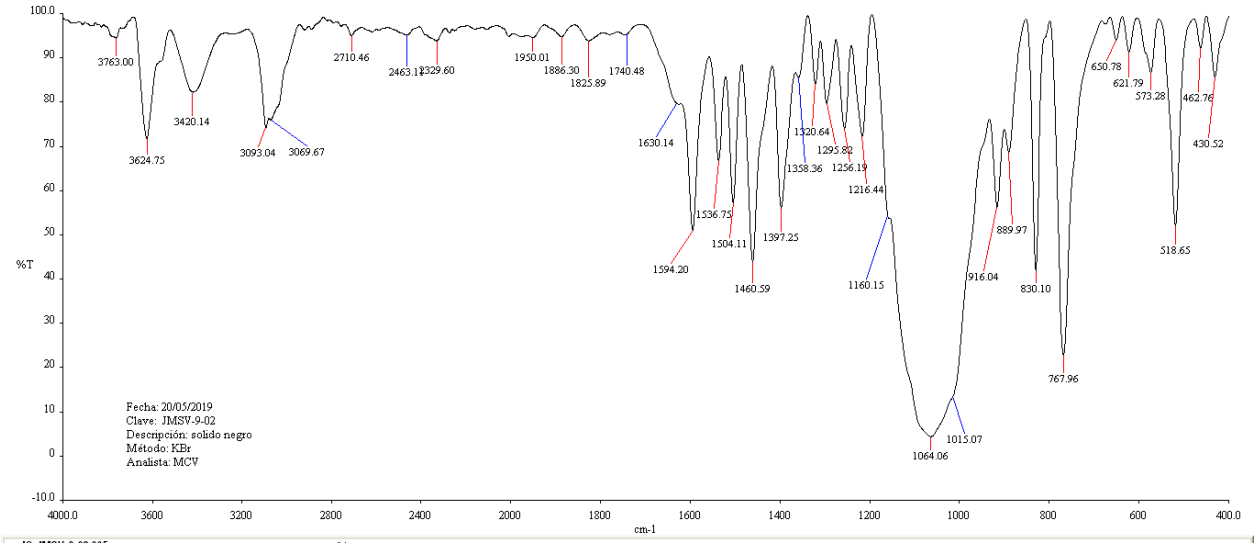

Figure S6. IR spectrum for complex **1**.

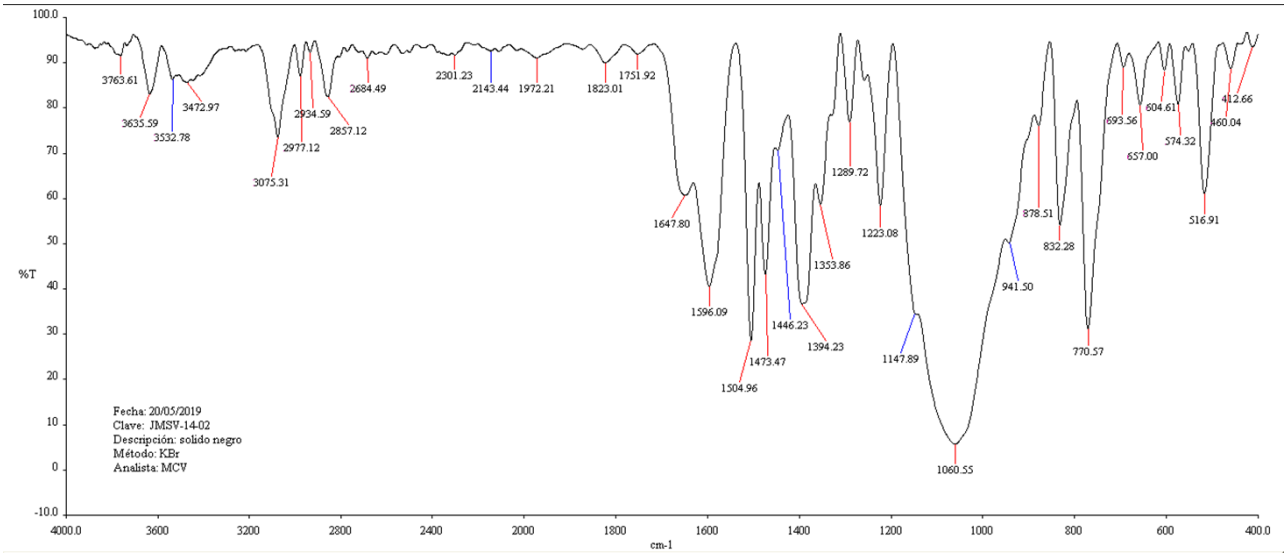

Figure S7. IR spectrum for complex **2**.

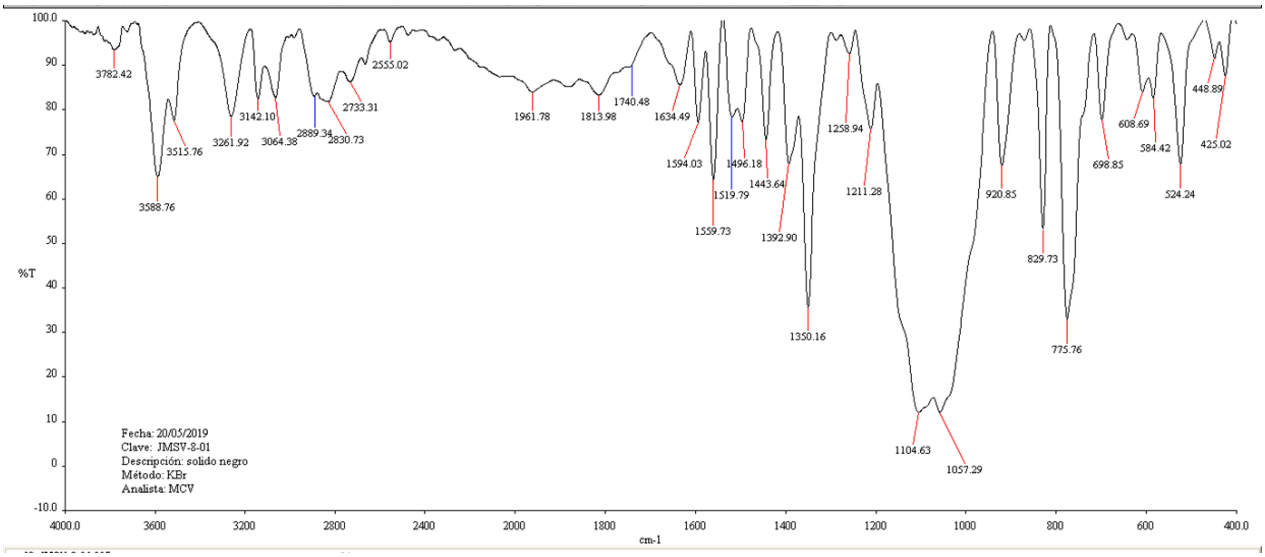

Figure S8. IR spectrum for complex **3**.

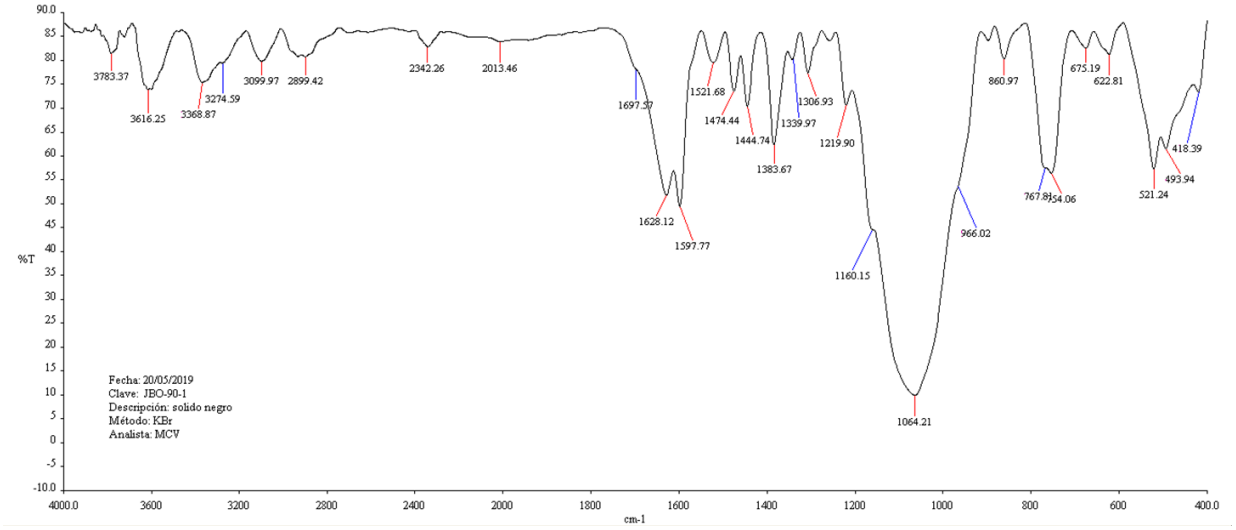

Figure S9. IR spectrum for complex **4**.

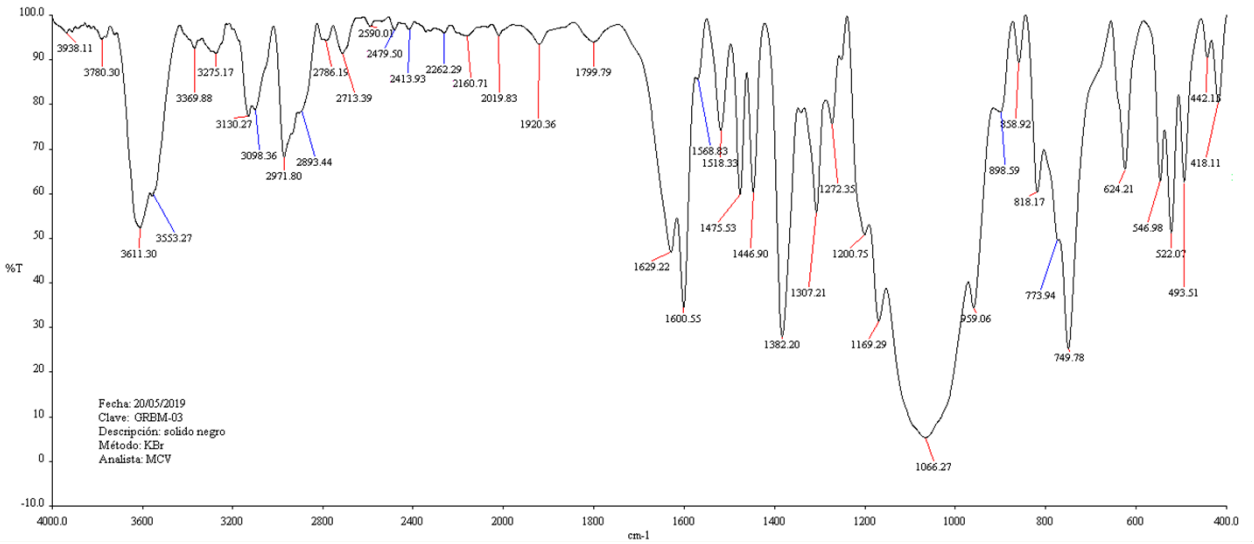

Figure S10. IR spectrum for complex **5**.

3. Comments on checkcif alert for complex 2

The following alert level B for complex **2** (JMSV14sq.cif) was not possible to remove. The alert in this file is:

```
Alert level B
PLAT230_ALERT_2_B Hirshfeld Test Diff for    O19      --C31      .        9.0 s.u.
```

O19 and C31 are the atoms corresponding to the methoxy group in the α-aminoether, which has some disorder. Attempts to model the disorder were not successful. Thus, this alert B is caused by vibration of the entire methoxy group and not due to wrong atom assignment.[S1]

S1. G. Valluru, S. Rahman, P. E. Georghiou, L. N. Dawe, A. N. Alodhayb and L. Y. Beaulieu, *N. J. Chem.*, 2014, **38**, 5868-5872.

Table S1. Crystal data and structure refinement for complexes **2**, **3** and **5**.

Compound	**2·solvents**	**3·solvents**	**5·(MeOH)(Et_2O)$_{0.5}$**
Identification code	JMSV14sq	JMSV01sq	ICQ02
Empirical formula	$C_{31}H_{25}B_2CoF_8N_6O$	$C_{26}H_{20}B_2F_8FeN_8$	$C_{60}H_{66}B_4Co_2F_{16}N_{16}O_5$
Formula weight	730.12	673.97	1556.38
Temperature	298(2) K	293(2) K	166(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	I2/a	C2/c
Unit cell dimensions	a = 12.1427(7) Å, α = 90° b = 15.5443(9) Å, β = 106.570(2)° c = 19.5164(12) Å, γ = 90°	a = 16.375(3) Å, α = 90° b =12.327(3) Å, β = 102.25(3)° c = 17.399(4), γ = 90°	a = 21.699(9) Å, α = 90° b = 12.540(4) Å, β = 119.63(2)° c = 15.873(8) Å, γ = 90°
Volume	3530.7(4) $Å^3$	3431.9(13) $Å^3$	3754(3) $Å^3$
Z	4	4	2
Density (calculated)	1.374 mg/m^3	1.304 mg/m^3	1.377 mg/m^3
Absorption coefficient	0.562 mm^{-1}	0.511 mm^{-1}	0.537 mm^{-1}
F(000)	1480	1360	1592
Crystal size	0.390 x 0.250 x 0.150 mm^3	0.320 x 0.290 x 0.180 mm^3	0.460 x 0.300 x 0.200 mm^3
Theta range for data collection	2.186 to 25.026°.	2.396 to 26.575°.	2.660 to 28.907°.
Index ranges	-14 ≤ h ≤ 14, -18 ≤ k ≤ 18, -23 ≤ l ≤ 23	-20 ≤ h ≤ 20, -15 ≤ k ≤ 15, -21 ≤ l ≤ 21	-29 ≤ h ≤ 29, -17 ≤ k ≤ 17, -21 ≤ l<=21
Reflections collected	113448	55537	136671
Independent reflections	6231 [R(int) = 0.0997]	3536 [R(int) = 0.1307]	4897 [R(int) = 0.0784]
Completeness to theta	99.8 %	99.8 %	99.6 %
Max. and min. transmission	0.7458 and 0.6496	0.7455 and 0.5768	0.7458 and 0.6754
Data / restraints / parameters	6231 / 306 / 516	3536 / 0 / 204	4897 / 21 / 279
Goodness-of-fit on F^2	0.971	1.037	1.222
Final R indices [I>2sigma(I)]	R1 = 0.0620, wR2 = 0.1709	R1 = 0.0587, wR2 = 0.1570	R1 = 0.0548, wR2 = 0.1578
R indices (all data)	R1 = 0.0840, wR2 = 0.1892	R1 = 0.1046, wR2 = 0.1812	R1 = 0.0701, wR2 = 0.1660
Largest diff. peak and hole	0.945 and -0.488 e.$Å^{-3}$	0.420 and -0.343 e.$Å^{-3}$	0.658d -0.541 e.$Å^{-3}$

4. Supramolecular interactions

Complex **3**

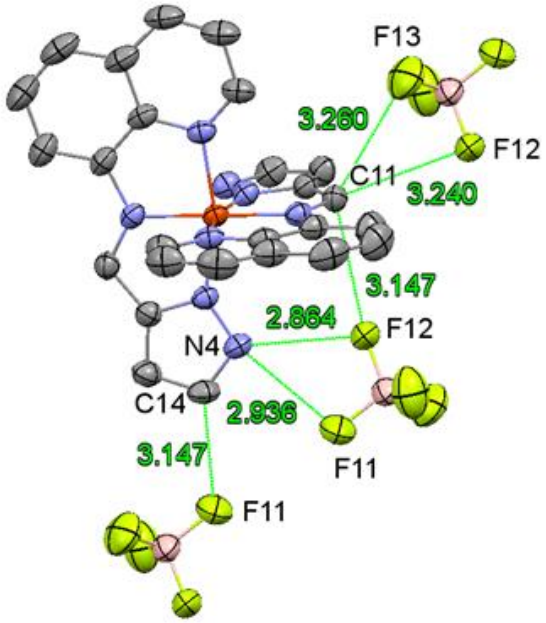

Figure S11. H-bonds of the type NH···F-BF_3, N=C-H···F-BF_3 and C-H···F-BF_3 found in the crystal structure of complex **3.**

Table S2. Hydrogen bonds for complex **3** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(2)-H(2)...N(2)#1	0.93	2.65	3.116(5)	111.3
N(4)-H(4A)...F(11)#1	0.86	2.31	2.936(4)	129.5
N(4)-H(4A)...F(12)#1	0.86	2.01	2.864(4)	169.9
C(3)-H(3)...F(14)#2	0.93	2.53	3.434(6)	164.9
C(11)-H(11)...F(12)#3	0.93	2.36	3.240(4)	157.4
C(14)-H(14)...F(11)#4	0.93	2.31	3.148(5)	149.6

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,y,-z+1 #2 -x+1,-y+1,-z+1 #3 -x+1/2,-y+1/2,-z+1/2

#4 x-1/2,-y,z

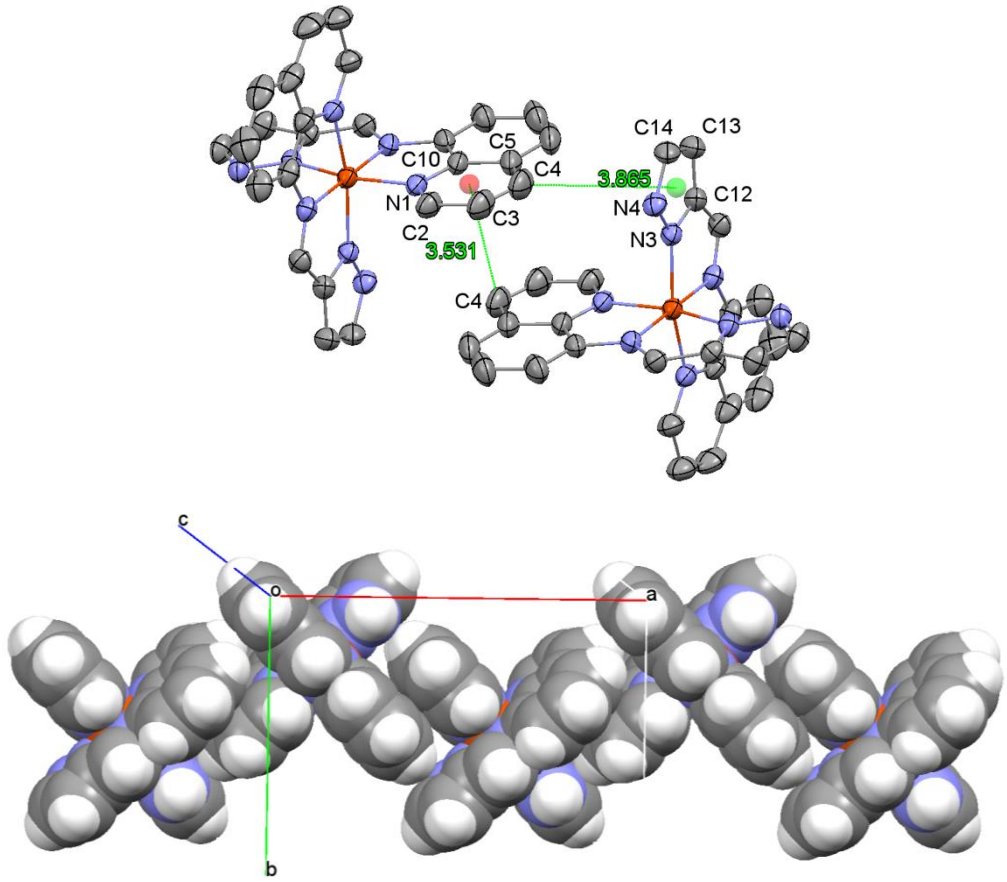

Figure S12. Embracing π-π and C-H-π interactions found in the crystal structure of complex **3** (top). Supramolecular zig-zag polymer running along a-axis (bottom).

Complex **2**

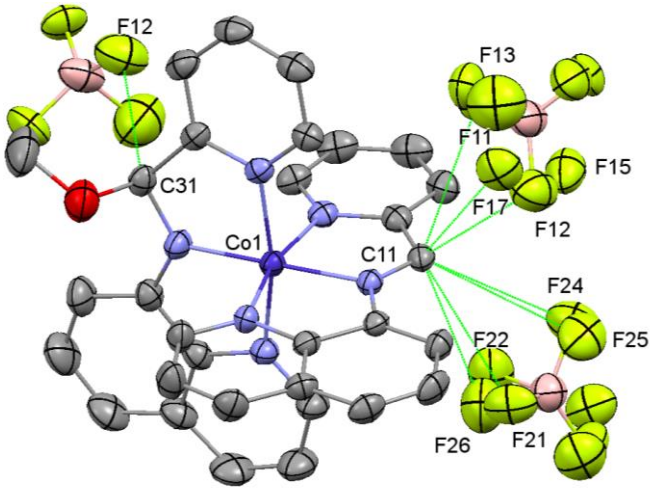

Figure S13. H-bonds interactions (green dotted lines) present in complex **2**.

Table S3. Hydrogen bonds for Complex **2** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(31)-H(31)...F(12)#3	0.98	2.36	3.279(10)	156.4
C(22)-H(22)...F(26)	0.93	2.45	3.144(14)	131.2
C(11)-H(11)...F(12)	0.93	2.34	2.939(10)	122.1
C(11)-H(11)...F(15)	0.93	2.48	3.142(10)	128.3
C(11)-H(11)...F(25)	0.93	2.56	3.330(13)	140.6

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,-y+1/2,z-1/2 #2 x+1,y,z #3 -x+1/2,y+1/2,-z+1/2

#4 -x+1,-y+1,-z+1

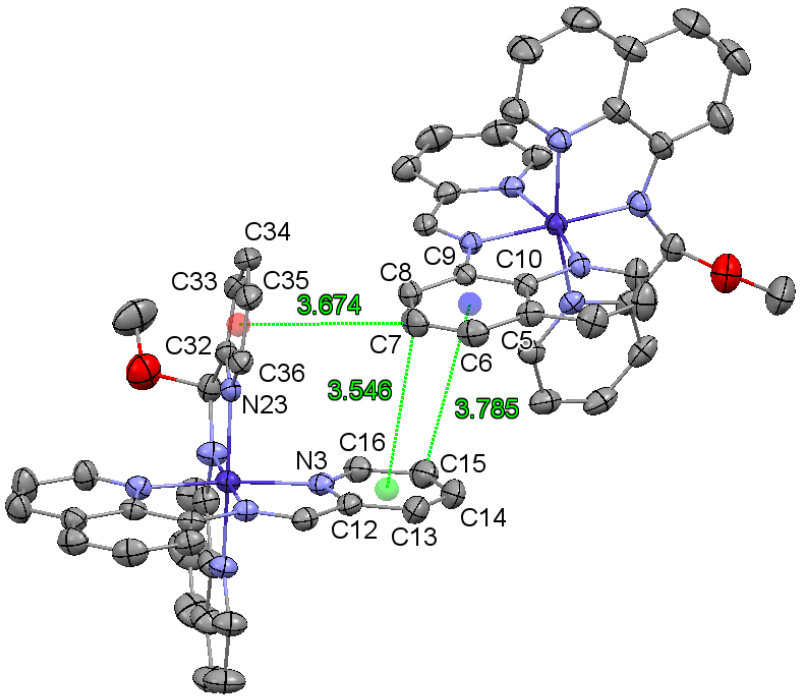

Figure S14. Perspective view of the dimers formed via π-π and C-H···π interactions observed in the crystal lattice of complex **2**.

Complex **5**

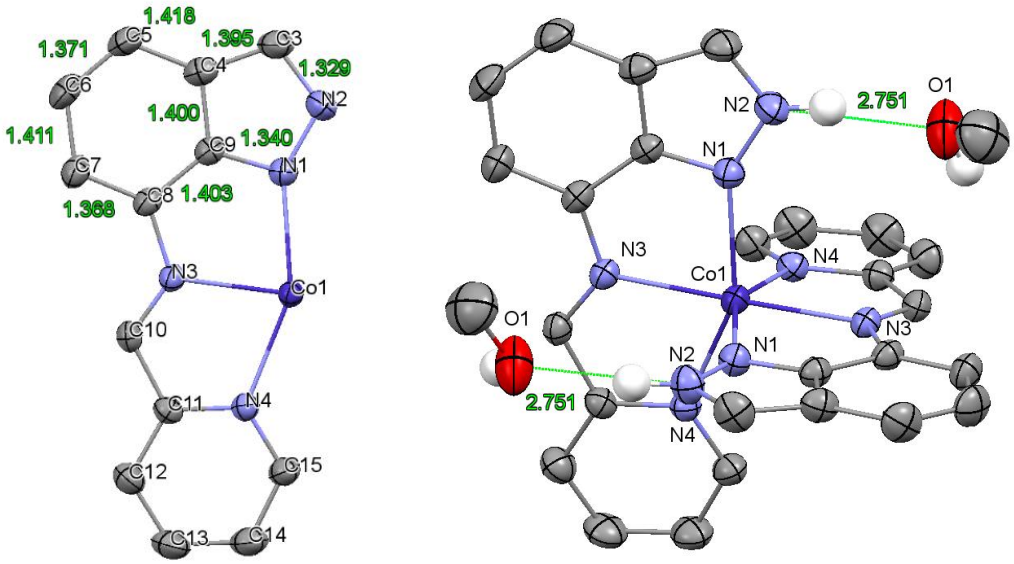

Figure S15. Perspective views of complex **5** showing the C-C bond lengths for the 7-amino-2*H*-indazole unit (left) and the hydrogen bonding of the $NH_{indazole}$ unit to the methanol solvent molecule (right).

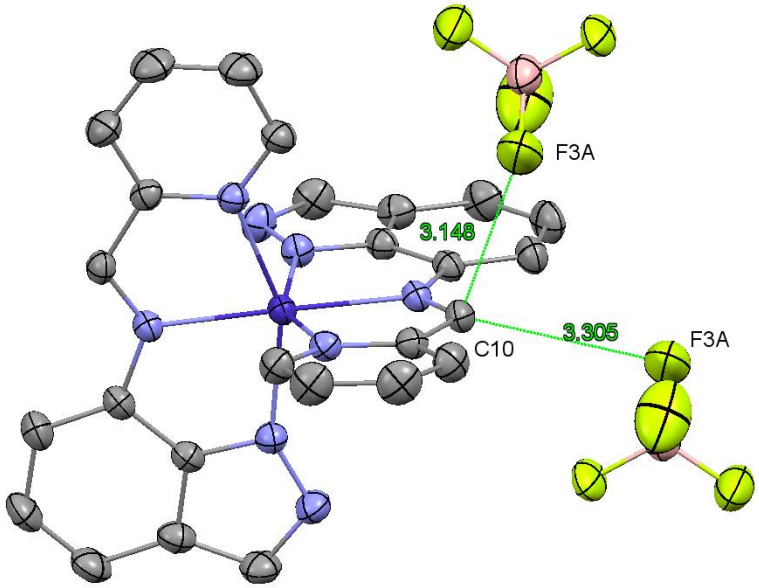

Figure S16. Perspective view of complex **5** showing the H-bond interactions between the imine C-H and the F-BF_3 anions.

Table S4. Hydrogen bonds for complex **5** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2)...O(1)	0.88	1.88	2.751(4)	168.3
C(3)-H(3)...F(4A^a)	0.95	2.53	3.277(9)	136.1
C(15)-H(15)...F(1)#2	0.95	2.52	3.225(4)	131.4
C(12)-H(12)...F(4A^a)#3	0.95	2.57	3.440(10)	151.8
C(10)-H(10)...F(3A^a)#3	0.95	2.40	3.305(5)	158.3
C(20)-H(1B)...F(4B^b)	0.98	2.63	3.58(3)	163.1
C(20)-H(1C)...F(3B^b)#4	0.98	2.64	3.152(18)	112.5
O(1)-H(1)...F(2A^a)#4	0.953(10)	2.08(8)	2.796(5)	131(8)
O(1)-H(1)...F(3B^b)#4	0.953(10)	2.19(8)	2.89(2)	129(8)
O(1)-H(1)...F(4B^b)#4	0.953(10)	2.61(8)	3.30(3)	130(8)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2 #2 x,-y+1,z-1/2 #3 x+1/2,y-1/2,z

#4 -x+1/2,y-1/2,-z+1/2

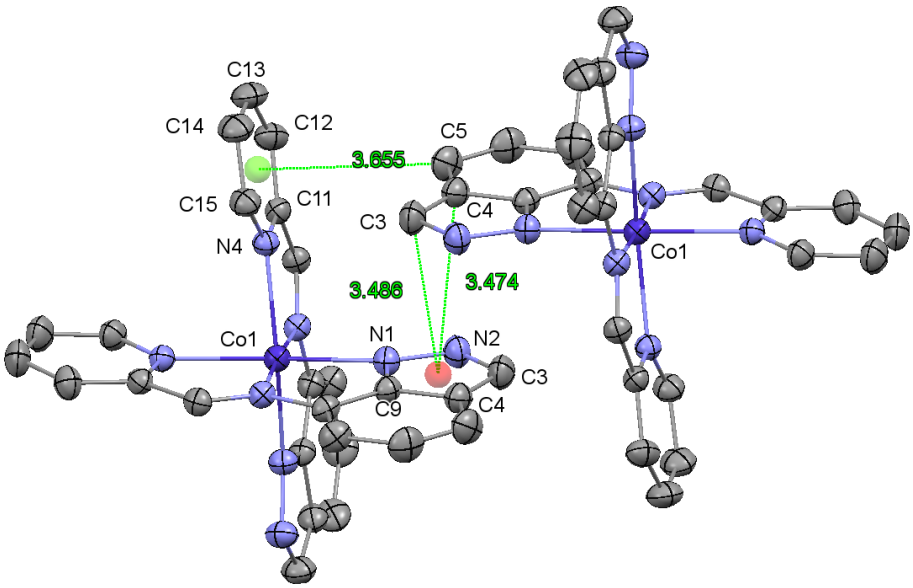

Figure S17. Perspective view of the dimers formed via π-π and C-H···π interactions observed in the crystal lattice of complex **5**.