Table S1. Data for hydrogen bonds present in **3**, **4** and **5**.

Complex	Axis	Hydrogen bonds				
		D–H···A	**d(D–H) /Å**	**d(D···H) /Å**	**α(DHA) /º**	**d(D···A) /Å**
3	***a***	C–H(21A)···F(8)B(2)F_3	0.971	3.207	109.35	2.752
		C–H(23B)···F(7)B(2)F_3	0.970	3.203	101.21	2.870
		C–H(6B)···F(2)B(1)F_3	0.969	3.275	124.24	2.630
		C–H(8B)···F(1)B(1)F_3	0.970	3.271	107.09	2.852
	b	C–H(7B)···F(7)B(2)F_3	0.960	3.216	100.96	2.892
		C–H(8A)···F(8)B(2)F_3	0.970	3.408	151.22	2.526
		C–H(18C)···F(3)B(1)F_3	0.959	3.201	152.13	2.321
		C–H(23A)···F(1)B(1)F_3	0.970	3.249	133.44	2.543
	c	C–H(26)···F(7)B(2)F_3	0.930	3.265	168.20	2.349
		C–H(26)···F(5)B(2)F_3	0.930	3.388	136.14	2.656
		C–H(28A)···F(5)B(2)F_3	0.959	3.410	153.89	2.522
	a/b	C–H(14C)···F(5)B(2)F_3	0.961	3.308	115.82	2.775
	a/b/c	C–H(14A)···F(6)B(2)F_3	0.960	3.144	132.63	2.413
5	***a***	C–H(29B)···F(3)B(1)F_3	0.960	3.500	135.54	2.750
	b	C–H(11A)···F(2)B(1)F_3	0.971	3.447	123.32	2.817
		C–H(12B)···F(2)B(1)F_3	0.960	3.152	111.97	2.665
		C–H(28A)···F(6)B(2)F_3	0.971	3.178	125.05	2.519
		C–H(29A)···F(6)B(2)F_3	0.961	3.094	121.06	2.487
	c	C–H(14A)···F(6)B(2)F_3	0.930	3.944	171.27	3.023
		C–H(17A)···F(8)B(2)F_3	0.961	3.298	155.34	2.401
		C–H(4A)···F(5)B(2)F_3	0.960	3.624	148.38	2.772
		C–H(4A)···F(7)B(2)F_3	0.960	3.344	148.11	2.490
	a/b	C–H(5C)···F(4)B(1)F_3	0.960	3.224	144.78	2.392
		C–H(9B)···F(7)B(2)F_3	0.971	3.256	132.55	2.520

		C–H(29C)···F(2)B(1)F_3	0.960	3.483	116.01	2.750
	a/c	C–H(10A)···F(6)B(2)F_3	0.961	3.541	114.68	3.039
		C–H(10C)···F(5)B(2)F_3	0.959	3.534	139.01	2.754
		C–H(22A)···F(5)B(2)F_3	0.960	3.137	124.80	2.488
		C–H(22C)···F(7)B(2)F_3	0.961	3.270	107.00	2.857
4	***a***	C–H(11C)···F(5)B(2)F_3	0.980	3.412	125.06	2.753
		C–H(9)···F(8)B(2)F_3	0.949	3.220	141.14	2.426
		C–H(25)···F(6)B(2)F_3	0.950	3.249	140.75	2.457
		C–H(27C)···F(7)B(2)F_3	0.980	3.308	130.78	2.583
	b	C–H(17)···F(2)B(1)F_3	0.951	3.922	148.21	3.082
		C–H(31A)···F(1)B(1)F_3	0.989	3.160	134.20	2.390
		C–H(31B)···F(2)B(1)F_3	0.992	3.357	132.36	2.607
	c	C–H(17)···F(3)B(1)F_3	0.951	3.411	162.18	2.493
		C–H(23)···F(3)B(1)F_3	0.950	3.228	121.68	2.626
		C–H(18)···F(7)B(2)F_3	0.949	3.136	115.45	2.609
		C–H(19)···F(5)B(2)F_3	0.950	3.335	145.71	2.507
		C–H(9)···F(5)B(2)F_3	0.949	3.570	162.47	2.653
		C–H(2)···F(5)B(2)F_3	0.949	3.203	123.32	2.582
		C–H(25)···F(6)B(2)F_3	0.950	3.249	140.75	2.457
		C–H(19)···F(7)B(2)F_3	0.950	3.578	161.12	2.666

Table S2. CH-π interactions present in **3** and **5**, not indicated in Table 2 of the manuscript.

Complex	Axis	CH-π interactions				
		CH-π	$d_{CH\text{-}centr}$ /Å	$d_{CH\text{-}atom}$ /Å	β /°	D_{offset} /Å
3	***a***	C(11)H-pz(N5)	2.574	2.746 (N5)	3.91	0.176
	c	C(28)H-pz(N7)	2.682	2.829(C)	8.43	0.393
5	***a***	C(21)H-pz(N15)	2.850	2.991(N15)	4.55	0.226
	c	C(17)H-pz(N7)	2.780	2.852(C15)	9.73	0.470

RI-MP2 and CCSD(T) Energies (in Hartree) and XYZ coordinates (in angstrom) of CH_4, BF_4^- and compounds 6-20

CH_4

RI-MP2/AVTZ Energy -40.432967
CCSD(T)/AVTZ' Energy -40.440161 -40.440404 -40.440627
CCSD(T)/AVTZ Energy -40.440845

XYZ coordinates

C 0.0000 0.0000 0.0000
H -0.6259 -0.6259 -0.6259
H 0.6259 0.6259 -0.6259
H -0.6259 0.6259 0.6259
H 0.6259 -0.6259 0.6259

BF_4^-

RI-MP2/AVTZ Energy -424.140222
CCSD(T)/AVTZ' Energy -424.073420 -424.081870 -424.089670
CCSD(T)/AVTZ Energy -424.096654

XYZ coordinates
B 0.0000 0.0000 0.0000
F -0.8114 0.8114 0.8114
F 0.8114 -0.8114 0.8114
F -0.8114 -0.8114 -0.8114

F 0.8114 0.8114 -0.8114

Compound 6

RI-MP2/AVTZ Energy -279.954671
CCSD(T)/AVTZ' Energy -279.913842
CCSD(T)/AVTZ Energy -279.915141

XYZ coordinates
C -0.6928 -1.2005 0.2450
N -1.3862 -0.0001 -0.2447
C -0.6931 1.2007 0.2446
N 0.6932 1.2007 -0.2453
C 1.3865 0.0003 0.2443
N 0.6934 -1.2005 -0.2449
H -0.6930 1.2011 1.3346
H -0.6927 -1.2006 1.3350
H 1.3871 0.0005 1.3343

Compound 7

RI-MP2/AVTZ Energy -1426.506274
CCSD(T)/AVTZ' Energy -2977.861766

XYZ coordinates
C 0.0000 0.0000 -3.6024
N 1.1850 0.0000 -2.9967
C 1.1354 0.0000 -1.6745
N 0.0000 0.0000 -0.9731
C -1.1354 0.0000 -1.6745
N -1.1850 0.0000 -2.9967
H 0.0000 0.0000 -4.6810
H 2.0534 0.0000 -1.1062
H -2.0534 0.0000 -1.1062
Zn 0.0000 0.0000 1.0966
Cl -2.0326 0.0000 1.6407
Cl 2.0326 0.0000 1.6407

Compound 8

RI-MP2/AVTZ Energy -320.391910 BSSE corrected -320.389235
CCSD(T)/AVTZ' Energy -320.356102 BSSE corrected -320.355036
CCSD(T)/AVTZ Energy -320.358882 BSSE corrected -320.357043

XYZ coordinates
C 0.6453 1.1176 -0.5781
N 1.3660 0.0000 -0.5793
C 0.6453 -1.1176 -0.5781

N -0.6830 -1.1830 -0.5793
C -1.2905 0.0000 -0.5781
N -0.6830 1.1830 -0.5793
H 1.1850 2.0526 -0.5792
H 1.1850 -2.0526 -0.5792
H -2.3701 0.0000 -0.5792
H 0.5117 0.8863 3.2840
C 0.0000 0.0000 2.9252
H 0.0000 0.0000 1.8422
H -1.0234 0.0000 3.2840
H 0.5117 -0.8863 3.2840

Compound 9

RI-MP2/AVTZ Energy -320.392706 BSSE corrected -320.390354
CCSD(T)/AVTZ' Energy -320.357532 BSSE corrected -320.356595

XYZ coordinates
C 0.6784 -1.2533 0.0000
N 0.6155 -0.6492 1.1828
C 0.4775 0.6716 1.1173
N 0.4030 1.3885 0.0000
C 0.4775 0.6716 -1.1173
N 0.6155 -0.6492 -1.1828
H 0.7909 -2.3270 0.0000
H 0.4208 1.2084 2.0521
H 0.4208 1.2084 -2.0521
H -2.3012 -0.5856 0.8860
C -2.7518 -0.1515 0.0000
H -2.3012 -0.5856 -0.8860
H -3.8163 -0.3590 0.0000
H -2.5922 0.9213 0.0000

Compound 10

RI-MP2/AVTZ Energy -320.392180 BSSE corrected -320.389916
CCSD(T)/AVTZ' Energy -320.357094 BSSE corrected -320.356202

XYZ coordinates
C 1.2899 -0.5526 0.0000
N 0.6828 -0.5528 1.1828
C -0.6452 -0.5517 1.1173
N -1.3659 -0.5517 0.0000
C -0.6452 -0.5517 -1.1173
N 0.6828 -0.5528 -1.1828
H 2.3696 -0.5553 0.0000
H -1.1850 -0.5536 2.0522
H -1.1850 -0.5536 -2.0522
H -0.5108 2.4313 0.8859

C 0.0007 2.7909 0.0000
H 1.0235 2.4308 0.0000
H 0.0010 3.8754 0.0000
H -0.5108 2.4313 -0.8859

Compound 11

RI-MP2/AVTZ Energy -320.392709 BSSE corrected -320.390352
CCSD(T)/AVTZ' Energy -320.357529 BSSE corrected -320.356590

XYZ coordinates
C 0.6451 1.1174 -0.5439
N 1.3658 0.0000 -0.5440
C 0.6451 -1.1174 -0.5439
N -0.6829 -1.1828 -0.5440
C -1.2902 0.0000 -0.5439
N -0.6829 1.1828 -0.5440
H 1.1849 2.0522 -0.5435
H 1.1849 -2.0522 -0.5435
H -2.3697 0.0000 -0.5435
H 1.0231 0.0000 2.3883
C 0.0000 0.0000 2.7487
H -0.5115 0.8860 2.3883
H 0.0000 0.0000 3.8332
H -0.5115 -0.8860 2.3883

Compound 12

RI-MP2/AVTZ Energy -704.106053 BSSE corrected -704.103363
CCSD(T)/AVTZ' Energy -703.997517 BSSE corrected -703.995598
CCSD(T)/AVTZ Energy -704.021317 BSSE corrected -704.020043

XYZ coordinates
C -0.6458 2.1303 1.1185
N -1.3725 2.1382 0.0000
C -0.6458 2.1303 -1.1185
N 0.6862 2.1385 -1.1887
C 1.2915 2.1303 0.0000
N 0.6862 2.1385 1.1887
H -1.1872 2.1193 2.0562
H -1.1872 2.1193 -2.0562
H 2.3743 2.1192 0.0000
F 1.3295 -2.4613 0.0000
F -0.6646 -2.4617 1.1513
F -0.6646 -2.4617 -1.1513
F -0.0003 -0.5835 0.0000
B 0.0000 -2.0018 0.0000

Compound 13

RI-MP2/AVTZ Energy -704.108164 BSSE corrected -704.104355

CCSD(T)/AVTZ' Energy -704.007736 BSSE corrected -704.005205

XYZ coordinates
C -1.7104 0.6857 1.1152
N -1.5464 1.3868 0.0000
C -1.7104 0.6857 -1.1152
N -2.0702 -0.5925 -1.1835
C -2.2360 -1.1717 0.0000
N -2.0702 -0.5925 1.1835
H -1.5439 1.1997 2.0484
H -1.5439 1.1997 -2.0484
H -2.5359 -2.2094 0.0000
F 0.9531 -0.0428 -1.1456
F 0.9531 -0.0428 1.1456
F 2.5472 -1.2293 0.0000
F 2.6040 1.0652 0.0000
B 1.7748 -0.0621 0.0000

Compound 14
RI-MP2/AVTZ Energy -704.109782 BSSE corrected -704.105206
CCSD(T)/AVTZ' Energy -704.016542 BSSE corrected -704.013795

XYZ coordinates
C -0.6436 1.1148 -1.7194
N -1.3657 0.0000 -1.7300
C -0.6436 -1.1148 -1.7194
N 0.6828 -1.1827 -1.7300
C 1.2873 0.0000 -1.7194
N 0.6828 1.1827 -1.7300
H -1.1830 2.0490 -1.7042
H -1.1830 -2.0490 -1.7042
H 2.3660 0.0000 -1.7042
F -0.6617 1.1461 1.1404
F -0.6617 -1.1461 1.1404
F 0.0000 0.0000 3.0165
F 1.3234 0.0000 1.1404
B 0.0000 0.0000 1.6186

Compound 15
RI-MP2/AVTZ Energy -704.106016 BSSE corrected -704.102732
CCSD(T)/AVTZ' Energy -704.013064 BSSE corrected -704.011025

XYZ coordinates
C 1.2880 1.8609 0.0000
N 0.6832 1.8687 -1.1830
C -0.6437 1.8624 -1.1153
N -1.3658 1.8701 0.0000

C -0.6437 1.8624 1.1153
N 0.6832 1.8687 1.1830
H 2.3671 1.8500 0.0000
H -1.1833 1.8527 -2.0498
H -1.1833 1.8527 2.0498
F 0.6615 -1.2725 1.1454
F 0.6615 -1.2725 -1.1454
F -0.0014 -3.1493 0.0000
F -1.3224 -1.2708 0.0000
B -0.0001 -1.7487 0.0000

Compound 16

RI-MP2/AVTZ Energy -744.544187 BSSE corrected -744.538222
CCSD(T)/AVTZ' Energy -744.440447 BSSE corrected -744.437100

XYZ coordinates
C -0.6520 1.5796 1.1147
N -1.3742 1.5819 0.0000
C -0.6520 1.5796 -1.1147
N 0.6744 1.6000 -1.1827
C 1.2787 1.5967 0.0000
N 0.6744 1.6000 1.1827
H -1.1917 1.5645 2.0500
H -1.1917 1.5645 -2.0500
H 2.3588 1.5960 0.0000
F -0.6608 -2.8934 1.1475
F 0.0136 -1.0273 0.0000
F -0.6608 -2.8934 -1.1475
F 1.3268 -2.9062 0.0000
B 0.0047 -2.4411 0.0000
H -0.9888 5.5305 0.0000
C 0.0171 5.1238 0.0000
H 0.5453 5.4583 -0.8866
H -0.0329 4.0422 0.0000
H 0.5453 5.4583 0.8866

Compound 17

RI-MP2/AVTZ Energy -744.548355 BSSE corrected -744.541148
CCSD(T)/AVTZ' Energy -744.460702 BSSE corrected -744.456996

XYZ coordinates
C -0.6434 1.1144 0.0244
N -1.3655 0.0000 0.0140
C -0.6434 -1.1144 0.0244
N 0.6828 -1.1826 0.0140
C 1.2868 0.0000 0.0244
N 0.6828 1.1826 0.0140
H -1.1831 2.0492 0.0401

H -1.1831 -2.0492 0.0401
H 2.3662 0.0000 0.0401
B 0.0000 0.0000 3.3596
F 1.3232 0.0000 2.8809
F -0.6616 1.1459 2.8809
F -0.6616 -1.1459 2.8809
F 0.0000 0.0000 4.7571
H -1.0203 0.0000 -3.0359
C 0.0000 0.0000 -3.4034
H 0.5101 0.8836 -3.0359
H 0.0000 0.0000 -4.4891
H 0.5101 -0.8836 -3.0359

Compound 18

RI-MP2/AVTZ Energy -1466.944461 BSSE corrected -1466.941188

CCSD(T)/AVTZ' Energy -3018.304810 BSSE corrected -3018.303195

XYZ coordinates
C 0.8112 -3.3537 0.0000
N 0.7098 -2.7567 -1.1851
C 0.4883 -1.4531 -1.1356
N 0.3710 -0.7623 0.0000
C 0.4883 -1.4531 1.1356
N 0.7098 -2.7567 1.1851
H 0.9920 -4.4176 0.0000
H 0.3931 -0.8924 -2.0539
H 0.3931 -0.8924 2.0539
Zn 0.0248 1.2754 0.0000
Cl -0.0666 1.8132 2.0325
Cl -0.0666 1.8132 -2.0325
H -3.2581 -2.2095 -0.8868
C -2.8208 -2.6550 0.0000
H -3.2581 -2.2095 0.8868
H -1.7526 -2.4772 0.0000
H -3.0045 -3.7237 0.0000

Compound 19

RI-MP2/AVTZ Energy -1850.675334 BSSE corrected -1850.671291
CCSD(T)/AVTZ' Energy -3401.963607 BSSE corrected -3401.960507

XYZ coordinates
C 1.5622 -2.7430 0.0000
N 1.0948 -2.3645 -1.1851
C 0.0829 -1.5190 -1.1342
N -0.4493 -1.0634 0.0000
C 0.0829 -1.5190 1.1342
N 1.0948 -2.3645 1.1851

H 2.3902 -3.4345 0.0000
H -0.3570 -1.1608 -2.0524
H -0.3570 -1.1608 2.0524
Zn -1.9914 0.2244 0.0000
Cl -2.5244 0.6891 1.9997
Cl -2.5244 0.6891 -1.9997
F 2.2818 2.2622 0.0000
B 3.0380 1.0866 0.0000
F 3.8309 1.0118 1.1468
F 2.1370 -0.0175 0.0000
F 3.8309 1.0118 -1.1468

Compound 20

RI-MP2/AVTZ Energy -1891.113982 BSSE corrected -1891.106082
CCSD(T)/AVTZ' Energy -3442.406818 BSSE corrected -3442.401916

XYZ coordinates
C 1.2878 -2.7113 0.0000
N 0.8768 -2.2725 -1.1854
C -0.0102 -1.2962 -1.1344
N -0.4746 -0.7726 0.0000
C -0.0102 -1.2962 1.1344
N 0.8768 -2.2725 1.1854
H 2.0140 -3.5101 0.0000
H -0.3970 -0.8812 -2.0532
H -0.3970 -0.8812 2.0532
Zn -1.8255 0.7135 0.0000
Cl -2.2878 1.2444 2.0007
Cl -2.2878 1.2444 -2.0007
H -2.7760 -3.9807 -0.8868
C -2.1675 -4.1221 0.0000
H -2.7760 -3.9807 0.8868
H -1.3618 -3.3993 0.0000
H -1.7489 -5.1228 0.0000
F 2.6840 2.1469 0.0000
B 3.2665 0.8758 0.0000
F 4.0403 0.6890 1.1470
F 2.2175 -0.0887 0.0000
F 4.0403 0.6890 -1.1470