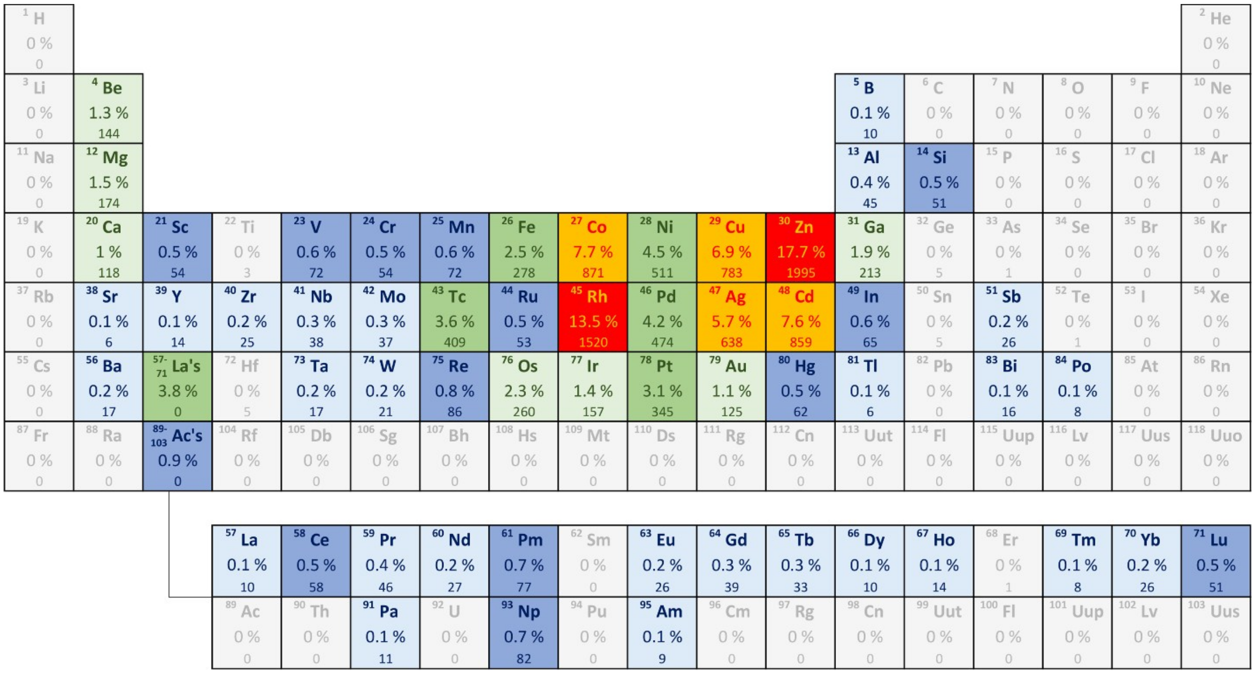
Supporting information for:

π-hole / *n*→π* interactions with acetonitrile in crystal structures

Figure S1 Schematic representation of the distribution of metals η^1-coordinated by an acetonitrile ligand................................ 2
Figure S2 IsoStar plots with acetonitrile as central unit and various possibly interacting units... 3
Figure S3 Directionality plot of ***P*** vs α of data involving a nitrile-N, nitro-O or covalently bound halogen atom......................... 4
Figure S4 Distribution plot of data with 90° ≤ α ≥ 110° for ElR = nitrile-N, nitro-O or covalently bound halogen atom.............. 4
Figure S5 Perspective views of (aligned) examples and of crystal structures displaying short N≡C···ElR distances...................... 5

Table S1 Cartesian coordinates of optimized structures with dimethylether (dme) shown in Figure 1....................................... 6
Table S2 Cartesian coordinates of the geometry optimized structures involving fluoromethyl... 7
Table S3 Cartesian coordinates of the geometry optimized structures involving dimethylthioether... 8
Table S4 Cartesian coordinates of the geometry optimized structures involving trimethylamine... 9
Table S5 Cartesian coordinates of the geometry optimized structures involving trimethylphosphine..10
Table S6 Numerical overview of the nature of ElR of the data used in Figure 2...11
Table S7 Overview of data in the IsoStar database (version 2.2.5).. 12
Table S8 Energies of the complexes highlighted in Figure 5 (DFT/B3LYP-D3/def2-TZVP)...13



1 H 0 % 0																	2 He 0 % 0
3 Li 0 % 0	4 Be 1.3 % 144											5 B 0.1 % 10	6 C 0 % 0	7 N 0 % 0	8 O 0 % 0	9 F 0 % 0	10 Ne 0 % 0
11 Na 0 % 0	12 Mg 1.5 % 174											13 Al 0.4 % 45	14 Si 0.5 % 51	15 P 0 % 0	16 S 0 % 0	17 Cl 0 % 0	18 Ar 0 % 0
19 K 0 % 0	20 Ca 1 % 118	21 Sc 0.5 % 54	22 Ti 0 % 3	23 V 0.6 % 72	24 Cr 0.5 % 54	25 Mn 0.6 % 72	26 Fe 2.5 % 278	27 Co 7.7 % 871	28 Ni 4.5 % 511	29 Cu 6.9 % 783	30 Zn 17.7 % 1995	31 Ga 1.9 % 213	32 Ge 0 % 5	33 As 0 % 1	34 Se 0 % 0	35 Br 0 % 0	36 Kr 0 % 0
37 Rb 0 % 0	38 Sr 0.1 % 6	39 Y 0.1 % 14	40 Zr 0.2 % 25	41 Nb 0.3 % 38	42 Mo 0.3 % 37	43 Tc 3.6 % 409	44 Ru 0.5 % 53	45 Rh 13.5 % 1520	46 Pd 4.2 % 474	47 Ag 5.7 % 638	48 Cd 7.6 % 859	49 In 0.6 % 65	50 Sn 0 % 5	51 Sb 0.2 % 26	52 Te 0 % 1	53 I 0 % 0	54 Xe 0 % 0
55 Cs 0 % 0	56 Ba 0.2 % 17	57-71 La's 3.8 % 0	72 Hf 0 % 5	73 Ta 0.2 % 17	74 W 0.2 % 21	75 Re 0.8 % 86	76 Os 2.3 % 260	77 Ir 1.4 % 157	78 Pt 3.1 % 345	79 Au 1.1 % 125	80 Hg 0.5 % 62	81 Tl 0.1 % 6	82 Pb 0 % 0	83 Bi 0.1 % 16	84 Po 0.1 % 8	85 At 0 % 0	86 Rn 0 % 0
87 Fr 0 % 0	88 Ra 0 % 0	89-103 Ac's 0.9 % 0	104 Rf 0 % 0	105 Db 0 % 0	106 Sg 0 % 0	107 Bh 0 % 0	108 Hs 0 % 0	109 Mt 0 % 0	110 Ds 0 % 0	111 Rg 0 % 0	112 Cn 0 % 0	113 Uut 0 % 0	114 Fl 0 % 0	115 Uup 0 % 0	116 Lv 0 % 0	117 Uus 0 % 0	118 Uuo 0 % 0
			57 La 0.1 % 10	58 Ce 0.5 % 58	59 Pr 0.4 % 46	60 Nd 0.2 % 27	61 Pm 0.7 % 77	62 Sm 0 % 0	63 Eu 0.2 % 26	64 Gd 0.3 % 39	65 Tb 0.3 % 33	66 Dy 0.1 % 10	67 Ho 0.1 % 14	68 Er 0 % 1	69 Tm 0.1 % 8	70 Yb 0.2 % 26	71 Lu 0.5 % 51
			89 Ac 0 % 0	90 Th 0 % 0	91 Pa 0.1 % 11	92 U 0 % 0	93 Np 0.7 % 82	94 Pu 0 % 0	95 Am 0.1 % 9	96 Cm 0 % 0	97 Rg 0 % 0	98 Cn 0 % 0	99 Uut 0 % 0	100 Fl 0 % 0	101 Uup 0 % 0	102 Lv 0 % 0	103 Uus 0 % 0

Figure S1. Schematic representation of the distribution of metals η^1-coordinated by an acetonitrile ligand. The data represents 11,277 M---N≡C–CH_3 structures found within 6,298 CIFs. The color code is meant as a guide to the eye, where red is the highest percentage of data, then green and light blue the lowest. NB: nine CIFs involve η^2-coordinated acetonitrile (HARTID, HOVSOA, KIJXIK, KOHBIS, KOHBIS10, NUFWEQ, TEQHAY, TEQHAY01 and WEQRAL), two are protonated (ELIJAM and ELIJEQ) and two are alkylated (MPACNB and LEFDEI).

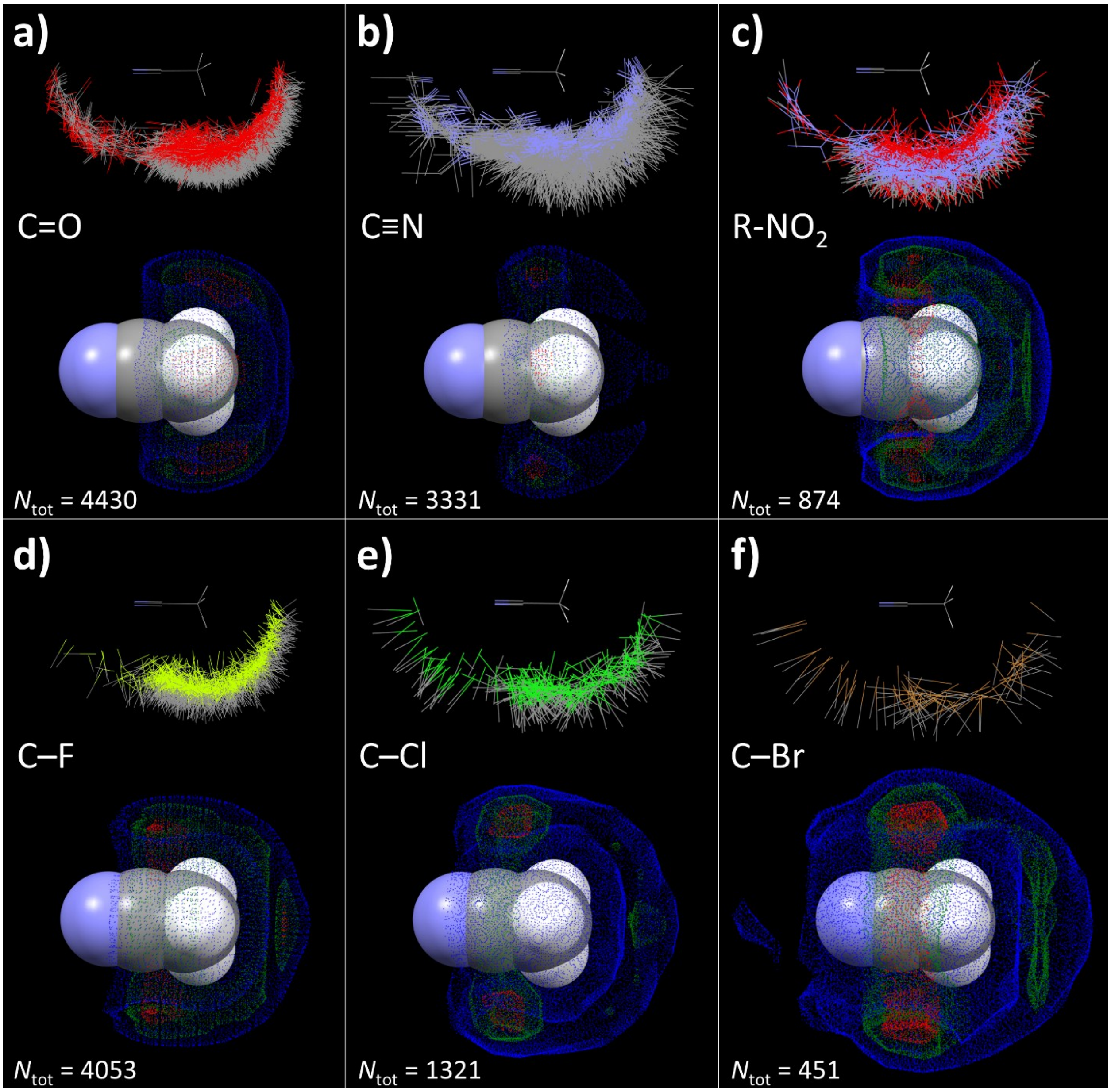


Figure S2. IsoStar plots with acetonitrile as central unit and various possibly interacting units: any carbonyl C=O (a) ; any nitrile C≡N (b); any nitro NO_2 (c); any C–F (d); any C–Cl (e); and any C–Br (f). See also Table S7. The top of each figure represents the asymmetric unit with the data displaying van der Waals overlap and the bottom represents an indication of the density (after symmetry expansion) where red is most dense and blue is least dense. These plots suggest that the H-bonded geometry is most prevalent for carbonyls (a, a typical example for many other such instances in Table S7), while the π-hole geometry is most prevalent for the nitrile, nitro and C-Halogen moieties. NB: it is not specified in the IsoStar database whether the acetonitrile is coordinated or not and the maximum amount of data that is used for these plots is about 5000; in case of more data the IsoStar software randomly compresses the data to a dataset with less than 5000 data points.

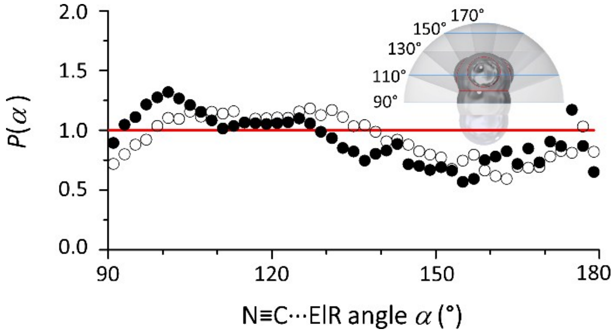


Figure S3. Directionality plot of ***P*** vs α of data where an electron rich atom (ElR, see Figure 2) of a nitrile-N, nitro-O or covalently bound halogen atom is potentially interacting with uncoordinated (○; N_{total} = 40,753) and η^1-coordinated (●; N_{total} = 27,209). The solid red line indicates a random distribution and the inset figure is a guide to the eye. Note that the amount of data used in these plots is about 40% of the amount of data used for Figure 3 and that the distributions are nearly identical in both figures.

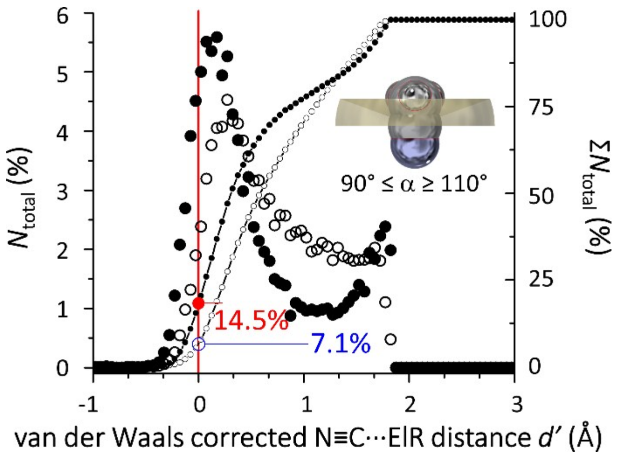


Figure S4. Distribution of data characterized by 90° ≤ α ≥ 110°, i.e. the gold transparent body around the model acetonitrile in the inset figure (from the subset used for Figure S3, i.e.: ElR = of a nitrile-N, nitro-O or covalently bound halogen). The distribution is given as percentages (large circles, left axis) and the cumulative percentage (small circles, right axis) and plotted as a function of the van der Waals corrected N≡C···ElR distance, d′ (i.e. d – {vdWC + vdWElR}). Uncoordinated acetonitrile = ○ with N_{total} = 14,743; η^1-coordinated acetonitrile = ●; N_{total} = 11,441. The solid red line is a guide to the eye for the van der Waals benchmark.

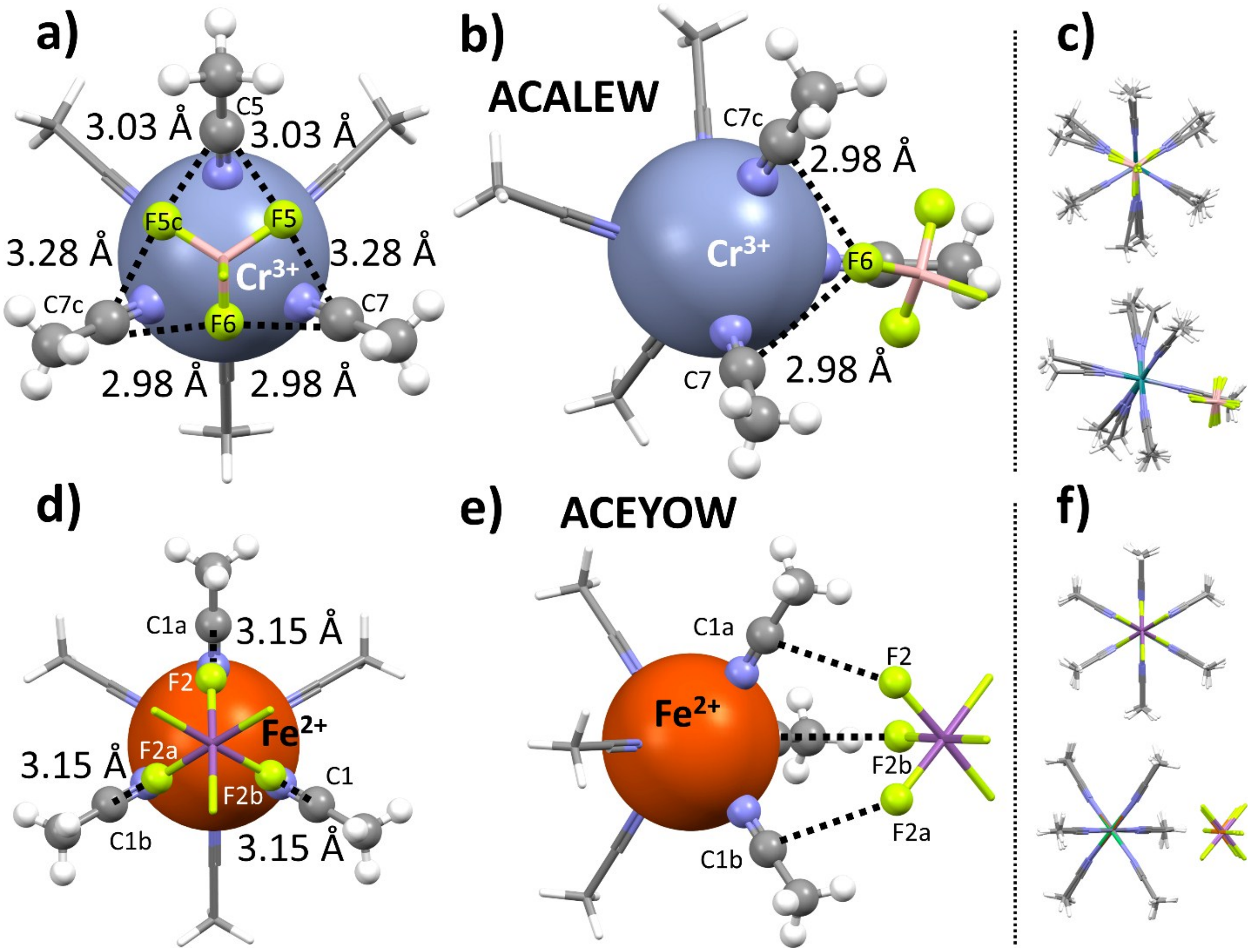


Figure S5. Perspective views of examples of crystal structures displaying short $N{\equiv}C\cdots ElR$ distances where ElR belongs to the tetrahedral anion BF_4^- (a-c) or octahedral anions (d-f) like SbF_6^-, AsF_6^- and PF_6^-. Top left (a) and middle (b) are close-ups of structure ACELEW also shown in Figure 5d and top right (c) shows two perspectives of aligned structures $[Cr^{3+}(N{\equiv}CCH_3)_6][BF_4]_3$ (ACELEW), $[Ru^{2+}(N{\equiv}CCH_3)_6][BF_4]_2$ (FILDEL), $[Rh^{3+}(N{\equiv}CCH_3)_6][BF_4]_3$ (VENYAO), and $[Tc^{2+}(N{\equiv}CCH_3)_6][BF_4]_2$ (TEQNAE). Bottom left (d) and middle (e) are close-ups of structure ECEYOW also shown in Figure 5e and bottom right (f) shows two perspectives of aligned structures $[Fe^{2+}(N{\equiv}CCH_3)_6]SbF_6]_2$ (ECEYOW and ACEYOW01), $[Ni^{2+}(N{\equiv}CCH_3)_6][SbF_6]_2$ (FUJVAH), $[Zn^{3+}(N{\equiv}CCH_3)_6][AsF_6]_3$ (JEPKEV), $[Fe^{2+}(N{\equiv}CCH_3)_6][PF_6]_2$ (RAPXOY). The alignments were done using the pair fitting option in PyMole (fitting on the atoms involved in close contacts). Color code of non-metals: white (H), grey (C), red (O), blue (N), bright green (Cl), pale green (F), pink (B), purple (Sb). All distances are in Angstroms (Å).

Table S1. Cartesian coordinates of the geometry optimized structures shown in Figure 1. Computations were done with the density functional theorem at the B3LYP-D3/def2-TZVP level of theory. The basis set superposition errors (BSSE's) were obtained from single point energy computations of the isolated molecular fragments extracted from the optimized structures. For references purposes, a methane dimer was computed with $\Delta E = -0.570$ kcal/mol.

$[O{=}C(CH_3)_2\cdots O(CH_3)_2]$ (Figure 1a)
$\Delta E = -5.830$ kcal/mol
BSSE = -0.0095 o kcal/mol

	X	Y	Z
C	-0.2448	-1.1768	-1.7583
C	-0.2463	1.1735	-1.7587
C	0.4042	-1.2810	1.6416
C	-0.3670	0.0023	1.4326
C	0.4064	1.2837	1.6457
H	0.7970	-1.3242	2.6608
H	-0.4346	-1.2189	-2.8389
H	-1.2004	-1.2368	-1.2239
H	0.3769	-2.0263	-1.4772
H	0.3736	2.0238	-1.4763
H	-1.2027	1.2317	-1.2257
H	-0.4345	1.2159	-2.8396
H	-0.2382	-2.1393	1.4584
H	1.2575	-1.3009	0.9609
H	-0.2369	2.1440	1.4751
H	1.2536	1.3083	0.9576
H	0.8084	1.3183	2.6616
O	-1.5348	0.0038	1.1128
O	0.4625	-0.0011	-1.4088

$[N{\equiv}CCH_3\cdots O(CH_3)_2]$ (Figure 1b)
$\Delta E = -4.701$ kcal/mol
BSSE = -0.0075 kcal/mol

	X	Y	Z
C	-1.0680	0.0026	2.0131
C	0.3473	-1.1767	-1.3083
C	0.3843	0.0002	1.9457
C	0.3442	1.1742	-1.3057
H	0.5973	1.2349	-2.3725
H	1.2683	1.2200	-0.7175
H	-0.2830	-2.0279	-1.0505
H	1.2713	-1.2214	-0.7199
H	0.6008	-1.2345	-2.3752
H	-1.4624	-0.8748	1.5022
H	-1.4596	0.8858	1.5102
H	-1.3969	-0.0012	3.0528
H	-0.2882	2.0231	-1.0459
N	1.5327	-0.0018	1.8898
O	-0.3881	-0.0025	-1.0182

$[H^+{-}N{\equiv}CCH_3\cdots O(CH_3)_2]^+$ (Figure 1c)
$\Delta E = -13.596$ kcal/mol
BSSE = -0.0227 kcal/mol

	X	Y	Z
C	1.4415	-1.0073	1.3161
C	-1.3453	-0.5518	-1.2206
C	1.9246	-0.1960	0.2355
C	-1.3462	1.2983	0.2656
H	-0.6714	1.9079	0.8662
H	-2.1108	0.8567	0.9130
H	-1.8344	1.9380	-0.4760
H	-0.6757	-1.2913	-1.6594
H	-1.8062	0.0305	-2.0241
H	-2.1315	-1.0660	-0.6575
H	2.2972	-1.4207	1.8566
H	0.8218	-1.8065	0.9068
H	0.8314	-0.3884	1.9758
H	2.7512	0.9905	-1.3442
N	2.4196	0.4197	-0.5848
O	-0.5656	0.2864	-0.3690

Table S2. Cartesian coordinates of the geometry optimized structures of acetone, acetonitrile and protonated acetonitrile with fluoromethyl. Computations were done with the density functional theorem at the B3LYP-D3/def2-TZVP level of theory. For references purposes, a methane dimer was computed with ΔE = – 0.570 kcal/mol.

$[O{=}C(CH_3)_2{\cdot}{\cdot}FCH_3]$ (complex) ΔE = –4.821 kcal/mol				$[N{\equiv}CCH_3{\cdots}FCH_3]$ (complex) ΔE = –4.211 kcal/mol				$[H^+{–}N{\equiv}CCH_3{\cdots}FCH_3]^+$ (complex) ΔE = –11.06 kcal/mol			
	X	**Y**	**Z**		**X**	**Y**	**Z**		**X**	**Y**	**Z**
C	0.1880	-1.5510	0.9200	C	-0.9210	0.6660	1.5950	C	-0.6310	1.1610	1.3910
C	-0.4210	-0.1700	0.9970	C	0.4900	0.3300	1.4920	C	-1.5530	0.6160	0.4390
C	0.4660	0.9260	1.5390	C	0.5980	-0.6830	-1.8980	C	1.7920	-1.1720	-1.1200
C	-0.4260	0.5810	-2.3960	F	-0.5990	-0.2650	-1.3030	F	0.7030	-0.5090	-0.4970
F	0.7260	0.2910	-1.6530	H	-1.5130	-0.2430	1.6960	H	-1.1830	1.7460	2.1300
H	0.5190	-1.8780	1.9090	H	-1.2380	1.1820	0.6890	H	0.0870	1.7890	0.8600
H	-0.5370	-2.2580	0.5210	H	-1.0940	1.3050	2.4610	H	-0.0980	0.3360	1.8690
H	1.0680	-1.5210	0.2730	H	0.4600	-1.6990	-2.2710	H	-2.9520	-0.1850	-0.9760
H	-0.0960	1.8530	1.6260	H	1.3840	-0.6530	-1.1450	H	2.6890	-0.9550	-0.5430
H	1.3080	1.0700	0.8570	H	0.8270	-0.0060	-2.7210	H	1.8790	-0.7900	-2.1350
H	0.8790	0.6450	2.5120	N	1.6060	0.0650	1.4030	H	1.5770	-2.2390	-1.1190
H	-0.4360	1.6500	-2.6090					N	-2.3110	0.2020	-0.3020
H	-1.2960	0.3020	-1.8030					C	-0.6310	1.1610	1.3910
H	-0.3860	0.0100	-3.3250					C	-1.5530	0.6160	0.4390
O	-1.5540	0.0490	0.6300					C	1.7920	-1.1720	-1.1200
C	0.1880	-1.5510	0.9200					F	0.7030	-0.5090	-0.4970
C	-0.4210	-0.1700	0.9970								
C	0.4660	0.9260	1.5390								
C	-0.4260	0.5810	-2.3960								
F	0.7260	0.2910	-1.6530								

Table S3. Cartesian coordinates of the geometry optimized structures of acetone, acetonitrile and protonated acetonitrile with dimethylthioether. Computations were done with the density functional theorem at the B3LYP-D3/def2-TZVP level of theory. For references purposes, a methane dimer was computed with ΔE = – 0.570 kcal/mol.

$[O{=}C(CH_3)_2{\cdot\cdot}S(CH_3)_2]$ (complex) ΔE = –6.383 kcal/mol				$[N{\equiv}CCH_3{\cdots}S(CH_3)_2]$ (complex) ΔE = –4.996 kcal/mol				$[H^+{-}N{\equiv}CCH_3{\cdots}S(CH_3)_2]^+$ (Nu attack) ΔE = –20.67 kcal/mol			
	X	**Y**	**Z**		**X**	**Y**	**Z**		**X**	**Y**	**Z**
C	-0.3930	1.2880	1.7800	C	-1.0930	0.0020	2.2760	C	1.0720	-0.8000	1.2860
C	0.3360	0.0030	1.4610	C	0.3290	0.0010	1.9690	C	1.3700	-0.0600	0.0290
C	-0.3990	-1.2800	1.7710	C	0.3890	1.3790	-1.4450	C	-1.2210	1.3740	0.4900
C	0.2580	1.3770	-1.9010	C	0.3930	-1.3810	-1.4460	C	-1.0770	-0.6890	-1.4290
C	0.2690	-1.3850	-1.9040	H	-1.5650	-0.8770	1.8410	H	1.9820	-1.3050	1.6060
H	-0.6600	1.3160	2.8400	H	-1.5630	0.8860	1.8460	H	0.2820	-1.5390	1.1430
H	0.2310	2.1450	1.5350	H	-1.2430	-0.0010	3.3560	H	0.7570	-0.1120	2.0740
H	-1.3230	1.3300	1.2090	H	-0.1860	2.3020	-1.3770	H	2.5480	0.6340	-1.3620
H	0.2090	-2.1380	1.4890	H	0.9420	1.3770	-2.3850	H	-0.6760	2.1670	0.9990
H	-1.3460	-1.3020	1.2280	H	1.0820	1.3220	-0.6060	H	-1.4880	0.5740	1.1770
H	-0.6320	-1.3300	2.8380	H	-0.1820	-2.3050	-1.3830	H	-2.1110	1.7870	0.0160
H	0.7770	1.3780	-2.8610	H	1.0820	-1.3240	-0.6040	H	-0.4340	-1.2130	-2.1330
H	0.9790	1.3190	-1.0860	H	0.9490	-1.3760	-2.3840	H	-1.9620	-0.3180	-1.9440
H	-0.3190	2.2970	-1.8120	N	1.4540	0.0000	1.7340	H	-1.3570	-1.3340	-0.5990
H	-0.3020	-2.3090	-1.8110	S	-0.7890	-0.0030	-1.3910	N	2.4730	0.0780	-0.5130
H	0.9920	-1.3200	-1.0910					S	-0.1580	0.7560	-0.8390
H	0.7840	-1.3840	-2.8650								
O	1.4510	0.0030	0.9860								
S	-0.9130	-0.0090	-1.8050								

Table S4. Cartesian coordinates of the geometry optimized structures of acetone, acetonitrile and protonated acetonitrile with trimethylamine. Computations were done with the density functional theorem at the B3LYP-D3/def2-TZVP level of theory. For references purposes, a methane dimer was computed with ΔE = – 0.570 kcal/mol.

$[O{=}C(CH_3)_2{\cdot\cdot}N(CH_3)_3]$ (complex) ΔE = –6.355 kcal/mol				$[N{\equiv}CCH_3{\cdots}N(CH_3)_3]$ (complex) ΔE = –4.814 kcal/mol				$[H^+{-}N{\equiv}CCH_3{\cdots}N(CH_3)_3]^+$ (Nu attack) ΔE = –-36.32 kcal/mol			
	X	**Y**	**Z**		**X**	**Y**	**Z**		**X**	**Y**	**Z**
C	0.0950	-1.1940	2.0890	C	0.4590	-0.1840	2.5510	C	-1.2760	0.3470	1.7200
C	-0.7200	0.0510	1.8220	C	1.7180	-0.2280	1.8250	C	-1.1610	0.2480	0.2320
C	-0.0070	1.3690	2.0230	C	0.3710	1.2420	-1.0340	C	1.3020	0.7900	0.4280
C	-0.5230	-1.2930	-1.3310	C	-1.7720	0.1710	-0.8170	C	0.4130	0.1970	-1.7650
C	1.4590	0.0150	-1.7330	C	0.2020	-1.1490	-1.2170	C	0.5750	-1.5260	-0.0370
C	-0.6740	1.1010	-1.4620	H	-0.2180	-0.9410	2.1560	H	-2.3320	0.2930	1.9710
H	0.3340	-1.2530	3.1550	H	-0.0110	0.7900	2.4180	H	-0.8910	1.3050	2.0740
H	-0.4670	-2.0780	1.7970	H	0.6310	-0.3600	3.6140	H	-0.7450	-0.4450	2.2470
H	1.0380	-1.1510	1.5420	H	1.4310	1.1420	-0.8010	H	-1.9770	0.3300	-1.5360
H	-0.6970	2.1950	1.8650	H	-0.0160	2.1170	-0.5080	H	1.2940	0.5540	1.4860
H	0.8210	1.4370	1.3160	H	0.2650	1.4220	-2.1190	H	1.0500	1.8370	0.2750
H	0.4140	1.4250	3.0310	H	-2.2840	-0.7110	-0.4280	H	2.2870	0.5820	0.0180
H	0.1040	-2.1230	-0.9980	H	-2.0340	0.2710	-1.8860	H	-0.2350	-0.4780	-2.3160
H	-0.7580	-1.4500	-2.3980	H	-2.1570	1.0470	-0.2930	H	1.4430	0.0110	-2.0600
H	-1.4530	-1.3180	-0.7620	H	0.0940	-1.1450	-2.3160	H	0.1540	1.2330	-1.9680
H	1.9670	0.9480	-1.4790	H	-0.3140	-2.0310	-0.8320	H	0.5340	-1.7240	1.0290
H	1.3970	-0.0480	-2.8340	H	1.2610	-1.2380	-0.9750	H	1.5680	-1.7590	-0.4150
H	2.0780	-0.8140	-1.3830	N	2.7160	-0.2660	1.2570	H	-0.1730	-2.1190	-0.5560
H	-1.6050	1.0690	-0.8960	N	-0.3410	0.0500	-0.5970	N	-2.1250	0.3910	-0.5350
H	-0.9170	1.1130	-2.5390					N	0.2940	-0.0660	-0.2930
H	-0.1600	2.0340	-1.2220								
N	0.1590	-0.0310	-1.0900								
O	-1.8820	-0.0040	1.4890								

Table S5. Cartesian coordinates of the geometry optimized structures of acetone, acetonitrile and protonated acetonitrile with trimethylphosphine. Computations were done with the density functional theorem at the B3LYP-D3/def2-TZVP level of theory. For references purposes, a methane dimer was computed with ΔE = – 0.570 kcal/mol.

	$[O{=}C(CH_3)_2{\cdot\cdot}P(CH_3)_3]$ (complex)				$[N{\equiv}CCH_3{\cdots}P(CH_3)_3]$ (complex)				$[H^+{-}N{\equiv}CCH_3{\cdots}P(CH_3)_3]^+$ (Nu attack)		
	ΔE = –5.728 kcal/mol				ΔE = –4.505 kcal/mol				ΔE = –52.89 kcal/mol		
	X	**Y**	**Z**		**X**	**Y**	**Z**		**X**	**Y**	**Z**
C	-0.0790	-1.1770	2.6390	C	-0.7150	-0.1040	3.1110	C	-1.6000	0.7960	1.5620
C	-0.8240	0.0220	2.1010	C	0.6850	-0.1440	2.7180	C	-1.3020	0.0430	0.3010
C	-0.2460	1.3780	2.4320	C	0.8060	1.4120	-0.7840	C	1.6060	0.6590	0.8090
C	-0.4330	-1.4970	-1.4430	C	-1.2450	0.1540	-2.2820	C	0.5270	0.6010	-1.9370
C	1.6530	-0.0230	-2.6770	C	0.6920	-1.4050	-0.9340	C	0.7850	-1.9020	-0.4080
C	-0.4790	1.3230	-1.3990	H	-1.2420	-0.9540	2.6790	H	-2.6710	0.7840	1.7650
H	0.0730	-1.0870	3.7170	H	-1.1780	0.8060	2.7320	H	-1.2720	1.8350	1.4830
H	-0.6250	-2.0900	2.4120	H	-0.8020	-0.1340	4.1980	H	-1.0770	0.3540	2.4140
H	0.9090	-1.2160	2.1720	H	1.4890	1.3710	0.0640	H	-3.0700	-0.4800	-0.2300
H	-0.8520	2.1640	1.9870	H	0.2890	2.3730	-0.7640	H	1.5630	0.1960	1.7950
H	0.7770	1.4390	2.0520	H	1.3840	1.3430	-1.7090	H	1.3720	1.7200	0.8990
H	-0.1990	1.5150	3.5160	H	-1.9040	-0.7040	-2.4230	H	2.6160	0.5530	0.4120
H	0.1360	-2.4280	-1.4350	H	-0.5200	0.1790	-3.1000	H	-0.2540	0.1600	-2.5570
H	-0.9320	-1.3960	-2.4110	H	-1.8570	1.0570	-2.3270	H	1.5060	0.4060	-2.3750
H	-1.1890	-1.5460	-0.6580	H	1.2740	-1.2860	-1.8520	H	0.3680	1.6770	-1.8650
H	2.2790	0.8700	-2.6950	H	0.0980	-2.3170	-1.0100	H	0.7390	-2.3460	0.5870
H	0.9980	-0.0130	-3.5520	H	1.3770	-1.5110	-0.0920	H	1.7780	-2.0580	-0.8310
H	2.3080	-0.8940	-2.7390	N	1.7900	-0.1750	2.4020	H	0.0310	-2.3630	-1.0450
H	-1.2540	1.3020	-0.6330	P	-0.4210	0.0390	-0.6280	N	-2.0850	-0.5390	-0.4980
H	-0.9500	1.2530	-2.3830					P	0.4370	-0.1410	-0.3020
H	0.0530	2.2730	-1.3290								
O	-1.8190	-0.0990	1.4210								
P	0.6930	-0.0740	-1.0950								

Table S6. Numerical overview of the nature of the possibly interacting electron rich atom (ElR) found in the database with $\alpha \geq 90°$ and ***d*** ≤ 5 Å (see Figure 2).

	$N{\equiv}CCH_3{\cdots}ElR$		**$M{-}N{\equiv}CCH_3{\cdots}ElR$**	
ElR	***N***	**%**	***N***	**%**
N	26,982	26.0	10,454	15.3
O	33,886	32.7	17,435	25.5
F	25,368	24.5	27,334	40.0
P	3,767	3.63	2,860	4.19
S	3,617	3.49	2,167	3.17
Cl	7,751	7.48	6,433	9.42
As	14	0.01	58	0.08
Se	148	0.14	33	0.05
Br	1,282	1.24	683	1.00
Te	12	0.01	5	0.01
I	849	0.82	812	1.19
At	0	0.00	0	0.00
Total	103,676	100	68,274	100

Table S7. Overview of data in the IsoStar database (version 2.2.5) with indication of the type of interaction(s) that appear(s) to dominate a particular dataset (as visualized by contour surfaces): H-bonding with N (1) or with CH_3 (2), C-H⋯π-interaction with N≡C (3), π-hole interaction with N≡C (4), σ-hole interaction with CH3 (5) or random (6).

Contact Group	N_{IS} [a]	Int.[b]	Contact Group	N_{IS} [a]	Int.[b]
any C,N,O,S or H	9,930	1 & 3	any terminal O	4,996	2
any polar X-H (X= N,O or S)	4,996	1	**any C=O[c]**	**4,430**	**2**
any alkyl C-H	4,931	1	amide C=O	481	2
methylene	1,998	1 & 3	ester C=O	665	2
methyl	1,998	3	carboxylate	121	2
any aromatic C-H	4,963	1	aliphatic ether	876	2 & 5
substituted aromatic carbon	2,498	2	linking O in esters	286	2 & 4
phenyl	1,415	3	aromatic O	86	6
any NH	3,848	1	sulfoxide/sulfone O	81	2
any uncharged NH	1,647	1	**nitro[c]**	**874**	**4**
any cationic NH	345	1	any S	4,273	2 & 4
aromatic cationic N-H	95	1	any C=S	615	2
amide NH	284	1	aliphatic thioether	36	6
uncharged $C(sp^2)/C(ar)-NH_2$	163	1	aromatic S	209	6
cationic RNH_3	53	1	**any C-F[c]**	**4,053**	**4 & 5**
any OH	4,340	1	**any C-Cl[c]**	**1,321**	**4 & 5**
alcohol OH	613	1	**any C-Br[c]**	**451**	**4**
phenol OH	927	1	any C-I	115	4
water	818	1	chloride ion	407	2
aromatic or sp^2 N	2,239	2	bromide ion	178	2
Cyano[c]	**3,331**	**4**	iodide ion	358	2
pyramidal R_3N	89	2	$CONH_2$	145	1
uncharged planar R_3N	981	1			
cationic planar R_3N	269	1			

[a] Amount of data in the IsoStar database; NB: this does not necessarily correspond to the amount of data in the CSD as the IsoStar software randomly compresses datasets >5000 to a dataset with less than 5000 data points. [b] 'Int.' stands for 'Interaction type', as is explained in the table caption. [c] Illustrated in Figure S2.

Table S8. Energies of the complexes highlighted in Figure 5 computed with DFT at the B3LYP-D3/def2-TZVP level of theory.

CSD entry	Anion	$\Delta E^{1,a}$	$\Delta E^{2,b}$
KAHMEN	NO_3^-	-136.9	-28.4
EMOJOF	PF_6^-	-74.52	+22.7[c]
MURFEL	ClO_4^-	-131.8	-31.3
ACALEW	BF_4^-	-201.3	-99.0
ACEYOW	SbF_6^-	-111.2[d]	-18.0

[a] ΔE^1 was computed by single point energy computation of the geometries lifted from the CSD of the complex minus those of the complex without anion and the anion. [b] $\Delta E^2 = \Delta E^1$ minus the energy of optimized Cs salts to model the charge compensation energy. [c] The positive energy likely results from an overestimation of the charge compensation energy in $CsPF_6$, as the geometry optimized structure of EMOJOF has an energy of –79.88 kcal/mol. [d] High spin structure, which is –19 kcal/mol more stable than the low spin structure.