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Electronic Supplementary Information for manuscript:

Non-covalent sp^3 carbon bonding with $ArCF_3$ is analogous to CH-π interactions.

by

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1. Figures S1 and S2:

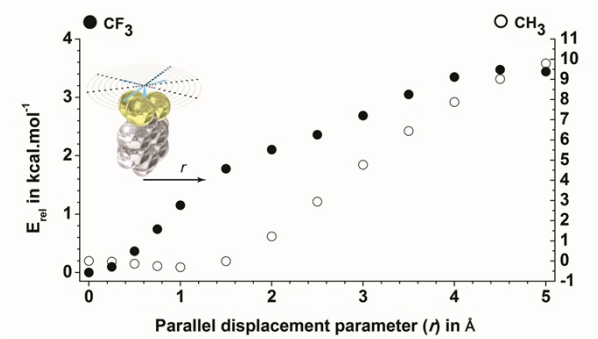

Fig. S1 E_{rel} *vs. r* plots of computed geometries for the interaction of F^- with$PhCH_3$ (open circles) $PhCF_3$ (black circles).

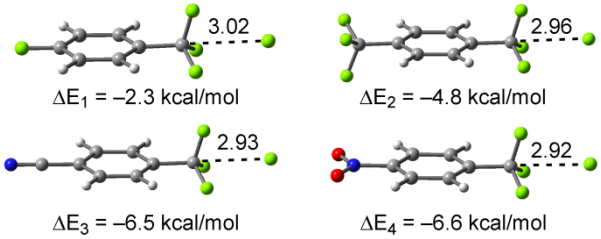

Fig. S2 RI-MP2/def2-TZVP optimized [*p*-$XC_6H_4CF_3\cdots F]^-$ complexes, interaction energies and equilibrium distances (Å).

2. Computational methods:

The energies of all complexes included in this study were computed at the RI-MP2/def2-TZVP level of theory. Since the estimated $[PhCF_3\cdots F]^-$ interaction energy is very weak (–0.6 kcal/mol) and it is in the limit of the accuracy of the theoretical method (RI-MP2/def2-TZVP), we have validate this energetic value using a higher level of theory. We have computed the interaction energy using a coupled cluster with single, double and triple excitations, CCSD(T),[1] and the same basis set. As a result, the interaction energy is –0.8 kcal/mol, in sharp agreement with the value computed at the RI-MP2/def2-TZVP level of theory. The calculations have been performed by using the program TURBOMOLE version 6.4.[2]

3. Relative interaction energies and Cartesian coordinates for $[ArCX_3\cdots F]^-$ complexes

3.1. Relative interaction energies for the $[PhCF_3\cdots F]^-$ complex

Table S1. Cartesian coordinates (Å) of the F^- and relative energies (kcal/mol) at the RI-MP2/def2-TZVP level of theory for the $[PhCF_3\cdots F]^-$ complex. The absolute energy of starting geometry is –0.6 kcal·mol^{-1}.

X	Y	Z	$\Delta E_{relative}$
-0.0524363	4.9469063	0.0000000	0.0
-0.0524363	4.9469063	0.2500000	0.10
-0.0524363	4.9469063	0.5000000	0.36
-0.0524363	4.9469063	0.7500000	0.72
-0.0524363	4.9469063	1.0000000	1.11
-0.0524363	4.9469063	1.5000000	1.65
-0.0524363	4.9469063	2.0000000	1.86
-0.0524363	4.9469063	2.5000000	1.99
-0.0524363	4.9469063	3.0000000	2.21
-0.0524363	4.9469063	3.5000000	2.51
-0.0524363	4.9469063	4.0000000	2.78
-0.0524363	4.9469063	4.5000000	2.90
-0.0524363	4.9469063	5.0000000	2.88
-0.0524363	4.9469063	-0.2500000	0.10
-0.0524363	4.9469063	-0.5000000	0.36
-0.0524363	4.9469063	-0.7500000	0.72
-0.0524363	4.9469063	-1.0000000	1.11
-0.0524363	4.9469063	-1.5000000	1.65
-0.0524363	4.9469063	-2.0000000	1.86
-0.0524363	4.9469063	-2.5000000	1.99
-0.0524363	4.9469063	-3.0000000	2.21
-0.0524363	4.9469063	-3.5000000	2.51
-0.0524363	4.9469063	-4.0000000	2.78
-0.0524363	4.9469063	-4.5000000	2.90
-0.0524363	4.9469063	-5.0000000	2.88
0.1975637	4.9469063	0.0000000	0.09
0.4475637	4.9469063	0.0000000	0.32
0.6975637	4.9469063	0.0000000	0.60
0.9475637	4.9469063	0.0000000	0.88
1.4475637	4.9469063	0.0000000	1.35
1.9475637	4.9469063	0.0000000	1.79
2.4475637	4.9469063	0.0000000	2.31
2.9475637	4.9469063	0.0000000	2.88
3.4475637	4.9469063	0.0000000	3.40
3.9475637	4.9469063	0.0000000	3.74
4.4475637	4.9469063	0.0000000	3.86
4.9475637	4.9469063	0.0000000	3.82
-0.3024363	4.9469063	0.0000000	0.11
-0.5524363	4.9469063	0.0000000	0.42
-0.8024363	4.9469063	0.0000000	0.90
-1.0524363	4.9469063	0.0000000	1.44
-1.5524363	4.9469063	0.0000000	2.32
-2.0524363	4.9469063	0.0000000	2.75
-2.5524363	4.9469063	0.0000000	3.01
-3.0524363	4.9469063	0.0000000	3.32
-3.5524363	4.9469063	0.0000000	3.67
-4.0524363	4.9469063	0.0000000	3.97
-4.5524363	4.9469063	0.0000000	4.11
-5.0524363	4.9469063	0.0000000	4.06
0.1245637	4.9469063	0.1770000	0.10
0.3015637	4.9469063	0.3540000	0.41

0.4785637	4.9469063	0.5310000	0.87
0.6555637	4.9469063	0.7080000	1.38
1.0095637	4.9469063	1.0620000	2.14
1.3635637	4.9469063	1.4160000	2.38
1.7175637	4.9469063	1.770000	2.44
2.0715637	4.9469063	2.1240000	2.62
2.4255637	4.9469063	2.4780000	2.91
2.7795637	4.9469063	2.8320000	3.22
3.1335637	4.9469063	3.1860000	3.40
3.4875637	4.9469063	3.5400000	3.41
0.1245637	4.9469063	-0.1770000	0.10
0.3015637	4.9469063	-0.3540000	0.41
0.4785637	4.9469063	-0.5310000	0.87
0.6555637	4.9469063	-0.7080000	1.38
1.0095637	4.9469063	-1.0620000	2.14
1.3635637	4.9469063	-1.4160000	2.38
1.7175637	4.9469063	-1.770000	2.44
2.0715637	4.9469063	-2.1240000	2.62
2.4255637	4.9469063	-2.4780000	2.91
2.7795637	4.9469063	-2.8320000	3.22
3.1335637	4.9469063	-3.1860000	3.40
3.4875637	4.9469063	-3.5400000	3.41
-0.2294363	4.9469063	-0.1770000	0.09
-0.4064363	4.9469063	-0.3540000	0.32
-0.5834363	4.9469063	-0.5310000	0.63
-0.7604363	4.9469063	-0.7080000	0.95
-1.1144363	4.9469063	-1.0620000	1.48
-1.4684363	4.9469063	-1.4160000	1.91
-1.8224363	4.9469063	-1.7700000	2.35
-2.1764363	4.9469063	-2.1240000	2.82
-2.5304363	4.9469063	-2.4780000	3.25
-2.8844363	4.9469063	-2.8320000	3.53
-3.2384363	4.9469063	-3.1860000	3.61
-3.5924363	4.9469063	-3.5400000	3.53
-0.2294363	4.9469063	0.1770000	0.09
-0.4064363	4.9469063	0.3540000	0.32
-0.5834363	4.9469063	0.5310000	0.63
-0.7604363	4.9469063	0.7080000	0.95
-1.1144363	4.9469063	1.0620000	1.48
-1.4684363	4.9469063	1.4160000	1.91
-1.8224363	4.9469063	1.7700000	2.35
-2.1764363	4.9469063	2.1240000	2.82
-2.5304363	4.9469063	2.4780000	3.25
-2.8844363	4.9469063	2.8320000	3.53
-3.2384363	4.9469063	3.1860000	3.61
-3.5924363	4.9469063	3.5400000	3.53

3.2 Cartesian coordinates of the optimized $[PhCF_3\cdots F]^-$ complex:

Atom	X	Y	Z
C	-0,0166784	-2,4273617	0,0000000
C	-0,0030755	-1,7271473	1,2049806
C	0,0202709	-0,3347147	1,2061440
C	0,0361491	0,3628255	0,0000000
C	0,0202709	-0,3347147	-1,2061440
C	-0,0030755	-1,7271473	-1,2049806
C	0,0092327	1,8816052	0,0000000
F	-1,2641335	2,2832211	0,0000000
F	0,6190819	2,3431976	-1,0883598
F	0,6190819	2,3431976	1,0883598
H	-0,0325971	-3,5119031	0,0000000
H	-0,0113779	-2,2664448	-2,1460631
H	-0,0113779	-2,2664448	2,1460631
H	0,0353323	0,2174627	2,1379866
H	0,0353323	0,2174627	-2,1379866
F	-0,0524363	4,9469063	0,0000000

3.3. Relative interaction energies for the $[PhCH_3\cdots F]^-$ complex

Table S2. Cartesian coordinates (Å) of the F^- and relative energies (kcal/mol) at the RI-MP2/def2-TZVP level of theory for the $[PhCH_3\cdots F]^-$ complex. The absolute energy of starting geometry is –11.0 kcal·mol^{-1}.

X	Y	Z	$\Delta E_{relative}$
-0.0036492	4.2729987	0.0000000	0
-0.0036492	4.2729987	0.2500000	-0,04
-0.0036492	4.2729987	0.5000000	-0,16
-0.0036492	4.2729987	0.7500000	-0,28
-0.0036492	4.2729987	1.0000000	-0,35
-0.0036492	4.2729987	1.5000000	-0,06
-0.0036492	4.2729987	2.0000000	0,97
-0.0036492	4.2729987	2.5000000	2,54
-0.0036492	4.2729987	3.0000000	4,27
-0.0036492	4.2729987	3.5000000	5,90
-0.0036492	4.2729987	4.0000000	7,33
-0.0036492	4.2729987	4.5000000	8,46
-0.0036492	4.2729987	5.0000000	9,26
-0.0036492	4.2729987	-0.2500000	-0,04
-0.0036492	4.2729987	-0.5000000	-0,16
-0.0036492	4.2729987	-0.7500000	-0,28
-0.0036492	4.2729987	-1.0000000	-0,35
-0.0036492	4.2729987	-1.5000000	-0,06
-0.0036492	4.2729987	-2.0000000	0,97
-0.0036492	4.2729987	-2.5000000	2,54
-0.0036492	4.2729987	-3.0000000	4,27
-0.0036492	4.2729987	-3.5000000	5,90
-0.0036492	4.2729987	-4.0000000	7,33
-0.0036492	4.2729987	-4.5000000	8,46
-0.0036492	4.2729987	-5.0000000	9,26
0.2463508	4.2729987	0.0000000	0,03
0.4963508	4.2729987	0.0000000	0,01
0.7463508	4.2729987	0.0000000	0,00
0.9963508	4.2729987	0.0000000	0,11
1.4963508	4.2729987	0.0000000	0,83
1.9963508	4.2729987	0.0000000	2,27
2.4963508	4.2729987	0.0000000	4,14
2.9963508	4.2729987	0.0000000	6,08
3.4963508	4.2729987	0.0000000	7,82
3.9963508	4.2729987	0.0000000	9,17
4.4963508	4.2729987	0.0000000	10,06
4.9963508	4.2729987	0.0000000	10,59
-0.2536492	4.2729987	0.0000000	-0,12
-0.5036492	4.2729987	0.0000000	-0,32
-0.7536492	4.2729987	0.0000000	-0,52
-1.0036492	4.2729987	0.0000000	-0,65
-1.5036492	4.2729987	0.0000000	-0,35
-2.0036492	4.2729987	0.0000000	0,88
-2.5036492	4.2729987	0.0000000	2,75
-3.0036492	4.2729987	0.0000000	4,67
-3.5036492	4.2729987	0.0000000	6,38
-4.0036492	4.2729987	0.0000000	7,89
-4.5036492	4.2729987	0.0000000	9,17
-5.0036492	4.2729987	0.0000000	10,08
0.1733508	4.2729987	0.1770000	0,00
0.3503508	4.2729987	0.3540000	-0,08
0.5273508	4.2729987	0.5310000	-0,21
0.7043508	4.2729987	0.7080000	-0,30

1.0583508	4.2729987	1.0620000	-0,05
1.4123508	4.2729987	1.4160000	1,02
1.7663508	4.2729987	1.7700000	2,71
2.1203508	4.2729987	2.1240000	4,52
2.4743508	4.2729987	2.4780000	6,16
2.8283508	4.2729987	2.8320000	7,61
3.1823508	4.2729987	3.1860000	8,84
3.5363508	4.2729987	3.5400000	9,71
-0.1806492	4.2729987	-0.1770000	-0,09
-0.3576492	4.2729987	-0.3540000	-0,23
-0.5346492	4.2729987	-0.5310000	-0,33
-0.7116492	4.2729987	-0.7080000	-0,31
-1.0656492	4.2729987	-1.0620000	0,27
-1.4196492	4.2729987	-1.4160000	1,61
-1.7736492	4.2729987	-1.7700000	3,41
-2.1276492	4.2729987	-2.1240000	5,31
-2.4816492	4.2729987	-2.4780000	7,04
-2.8356492	4.2729987	-2.8320000	8,45
-3.1896492	4.2729987	-3.1860000	9,43
-3.5436492	4.2729987	-3.5400000	10,04
0.1733508	4.2729987	-0.1770000	0,00
0.3503508	4.2729987	-0.3540000	-0,08
0.5273508	4.2729987	-0.5310000	-0,21
0.7043508	4.2729987	-0.7080000	-0,30
1.0583508	4.2729987	-1.0620000	-0,05
1.4123508	4.2729987	-1.4160000	1,02
1.7663508	4.2729987	-1.7700000	2,71
2.1203508	4.2729987	-2.1240000	4,52
2.4743508	4.2729987	-2.4780000	6,16
2.8283508	4.2729987	-2.8320000	7,61
3.1823508	4.2729987	-3.1860000	8,84
3.5363508	4.2729987	-3.5400000	9,71
-0.1733508	4.2729987	0.1770000	0,00
-0.3503508	4.2729987	0.3540000	-0,08
-0.5273508	4.2729987	0.5310000	-0,21
-0.7043508	4.2729987	0.7080000	-0,30
-1.0583508	4.2729987	1.0620000	-0,05
-1.4123508	4.2729987	1.4160000	1,02
-1.7663508	4.2729987	1.7700000	2,71
-2.1203508	4.2729987	2.1240000	4,52
-2.4743508	4.2729987	2.4780000	6,16
-2.8283508	4.2729987	2.8320000	7,61
-3.1823508	4.2729987	3.1860000	8,84
-3.5363508	4.2729987	3.5400000	9,71

3.4 Cartesian coordinates of the optimized $[PhCH_3\cdots F]^-$ complex:

Atom	X	Y	Z
C	-0.0254498	-2.8052574	0.0000000
C	-0.0112449	-2.0991751	1.2018603
C	0.0128559	-0.7055205	1.1949820
C	0.0232361	0.0252944	0.0000000
C	0.0128559	-0.7055205	-1.1949820
C	-0.0112449	-2.0991751	-1.2018603
C	0.0160815	1.5225743	0.0000000
F	-0.0036492	4.2729987	0.0000000
H	-0.0413771	-3.8901542	0.0000000
H	-0.0165051	-2.6350980	-2.1460713
H	-0.0165051	-2.6350980	2.1460713
H	0.0289564	-0.1612342	2.1347754
H	0.0289564	-0.1612342	-2.1347754
H	-0.9895727	1.9442860	0.0000000
H	0.5027905	1.9596370	-0.8690402
H	0.5027905	1.9596370	0.8690402

References:

[1] J. A. Pople, M. Head-Gordon and K. Raghavachari, *J. Chem. Phys*., 1987, **87**, 5968–5975.
[2] R. Ahlrichs, M. Bär, M. Hacer, H. Horn and C. Kömel, *Chem. Phys. Lett.*, 1989, **162**, 165–169.