Supplementary Information for:

Sigma-Hole Carbon-Bonding Interactions in Carbon-Carbon Double Bonds: An Unnoticed Contact

David Quiñonero*
Departament de Química, Universitat de les Illes Balears, Crta. de Valldemossa km 7.5, 07122 Palma de Mallorca, Spain.

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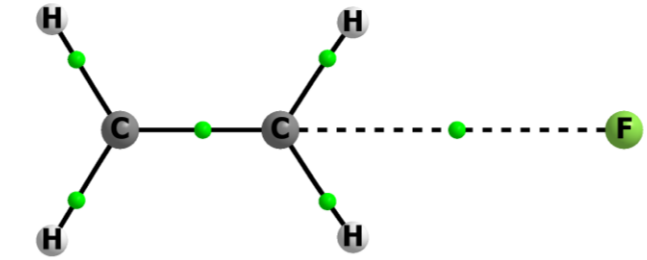
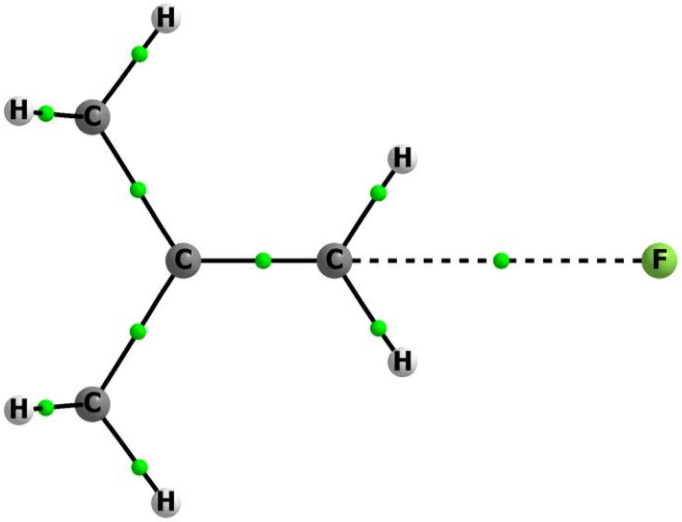
Figure S14. Geometry of a fragment of the X-ray structure with reference code LIQGOH retrieved from the CSD and its molecular graph, calculated at BP86/def2-TZVP computational level. Bond and ring critical points are denoted with green and red spheres, respectively.

Table S1. Molecular graph and geometry of the complexes calculated at RI-MP2/aug-cc-pVTZ computational level.



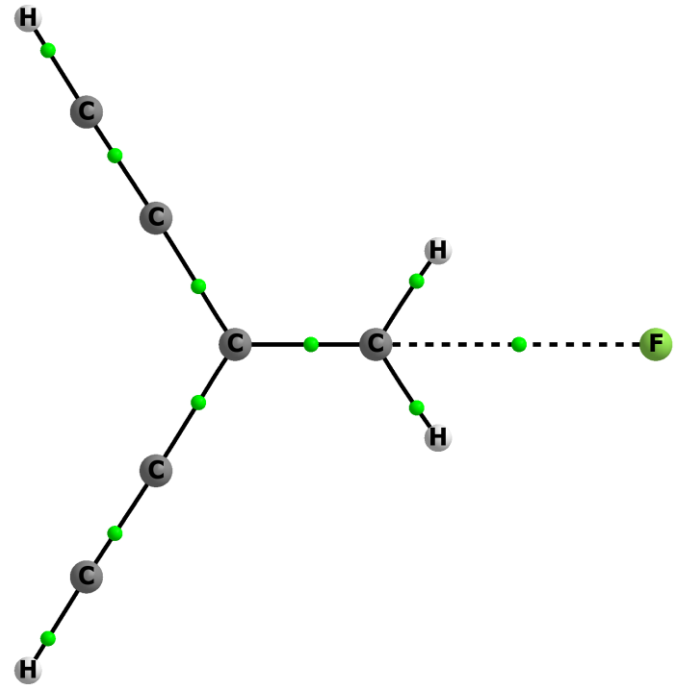
f-h

C	0.0000000	0.0000000	-1.1843520
C	0.0000000	0.0000000	0.1525435
H	-0.9226145	0.0000000	-1.7527490
H	0.9226145	0.0000000	-1.7527490
H	0.8950464	0.0000000	0.7585218
H	-0.8950464	0.0000000	0.7585218
F	0.0000000	0.0000000	3.0202629



f-me

C	0.0000000	0.0000000	-0.1307243
C	0.0000000	0.0000000	1.2078113
H	0.0000000	-0.8984379	1.8105355
H	0.0000000	0.8984379	1.8105355
C	0.0000000	1.2692206	-0.9352881
H	0.0000000	2.1417483	-0.2834170
H	0.8782963	1.3232538	-1.5865695
H	-0.8782963	1.3232538	-1.5865695
C	0.0000000	-1.2692206	-0.9352881
H	-0.8782963	-1.3232538	-1.5865695
H	0.8782963	-1.3232538	-1.5865695
H	0.0000000	-2.1417483	-0.2834170
F	0.0000000	0.0000000	4.0855300



f-cch

C	0.0000000	0.0000000	-0.0844200
C	0.0000000	0.0000000	1.2652784
H	0.8997601	0.0000000	1.8639785
H	-0.8997601	0.0000000	1.8639785
C	-1.2150344	0.0000000	-0.8455401
C	-2.2353750	0.0000000	-1.5131886
H	-3.1362948	0.0000000	-2.0734976
C	1.2150344	0.0000000	-0.8455401
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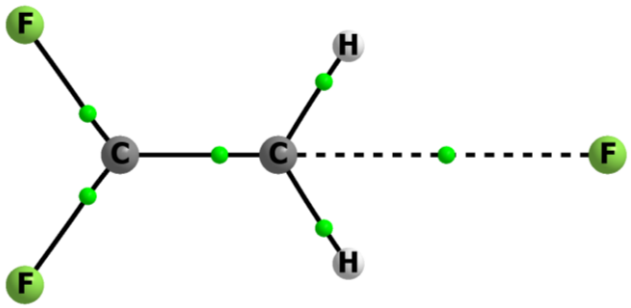
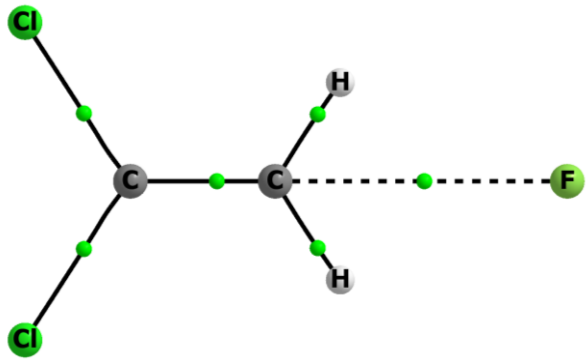
H	3.1362948	0.0000000	-2.0734976
F	0.0000000	0.0000000	3.9556370



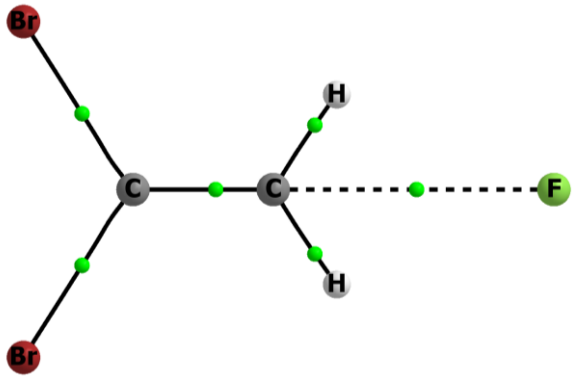
f-f

C	0.0000000	0.0000000	-1.0831872
C	0.0000000	0.0000000	0.2321315
H	0.9048100	0.0000000	0.8156050
H	-0.9048100	0.0000000	0.8156050
F	-1.0809494	0.0000000	-1.8751536
F	1.0809494	0.0000000	-1.8751536
F	0.0000000	0.0000000	2.9701529



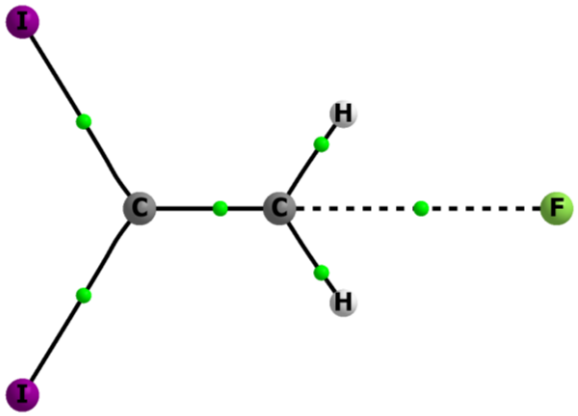
f-cl

C	0.0000000	0.0000000	-1.0340523
C	0.0000000	0.0000000	0.2916379
H	-0.9011282	0.0000000	0.8869730
H	0.9011282	0.0000000	0.8869730
Cl	1.4488144	0.0000000	-1.9987621
Cl	-1.4488144	0.0000000	-1.9987621
F	0.0000000	0.0000000	2.9659925



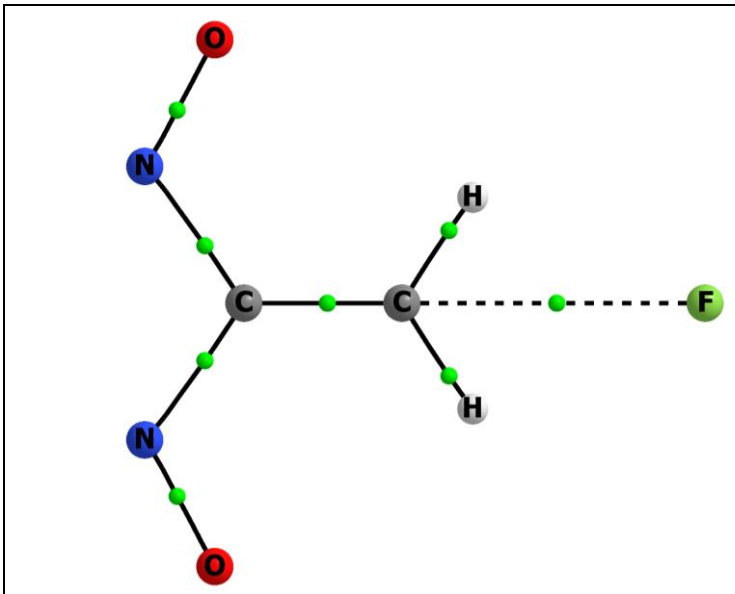
f-br

C	0.0000000	0.0000000	-1.0132537
C	0.0000000	0.0000000	0.3137804
H	-0.8992813	0.0000000	0.9145190
H	0.8992813	0.0000000	0.9145190
F	0.0000000	0.0000000	2.9685803
Br	-1.5905983	0.0000000	-2.0490725
Br	1.5905983	0.0000000	-2.0490725



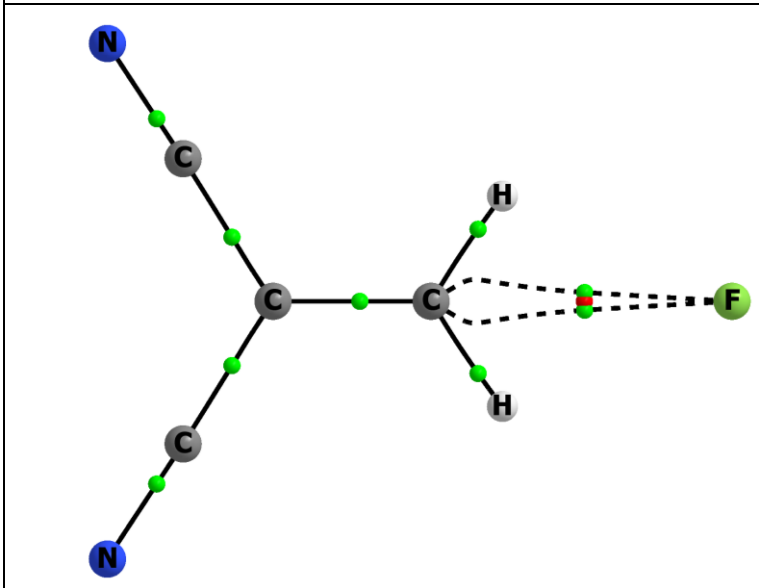
f-i

C	0.0000000	0.0000000	-0.9916257
C	0.0000000	0.0000000	0.3381595
H	-0.8965027	0.0000000	0.9458067
H	0.8965027	0.0000000	0.9458067
F	0.0000000	0.0000000	2.9729571
I	1.7697712	0.0000000	-2.1055521
I	-1.7697712	0.0000000	-2.1055521



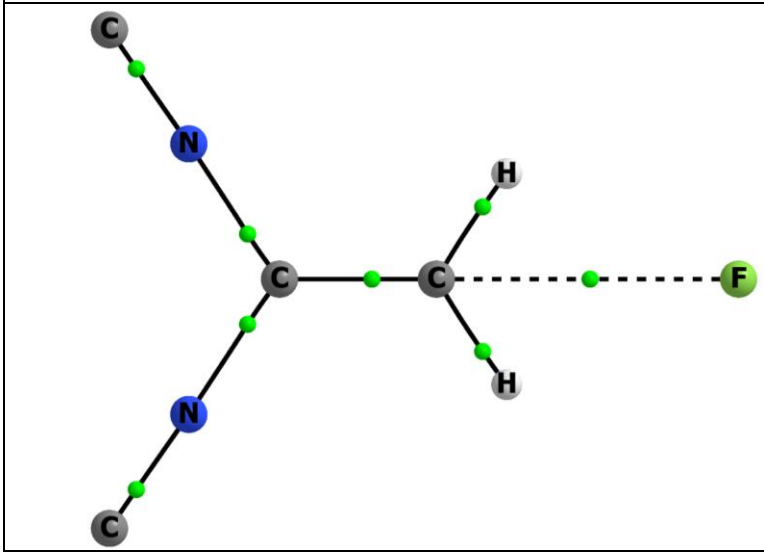
f-no

C	0.0000000	0.0000000	-0.7767786
C	0.0000000	0.0000000	0.5696607
H	0.8973411	0.0000000	1.1727940
H	-0.8973411	0.0000000	1.1727940
N	-1.1596727	0.0000000	-1.6214170
O	-2.2340038	0.0000000	-1.0240617
N	1.1596727	0.0000000	-1.6214170
O	2.2340038	0.0000000	-1.0240617
F	0.0000000	0.0000000	3.1524874



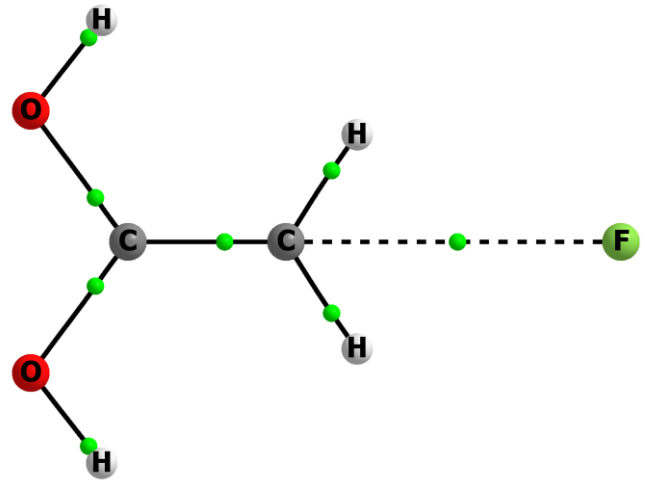
f-cn

C	0.0000000	0.0000000	-0.5340979
C	0.0000000	0.0000000	0.8114690
H	-0.8951421	0.0000000	1.4182068
H	0.8951421	0.0000000	1.4182068
C	1.2138366	0.0000000	-1.2995918
N	2.1941070	0.0000000	-1.9440672
C	-1.2138366	0.0000000	-1.2995918
N	-2.1941070	0.0000000	-1.9440672
F	0.0000000	0.0000000	3.3735333



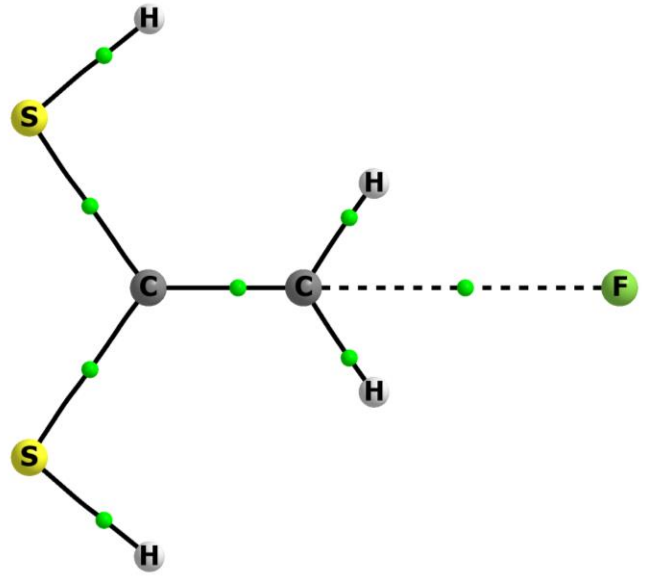
f-nc

C	0.0000000	0.0000000	-0.5189015
C	0.0000000	0.0000000	0.8156865
H	-0.8992274	0.0000000	1.4141226
H	0.8992274	0.0000000	1.4141226
F	0.0000000	0.0000000	3.3867103
C	-2.1248198	0.0000000	-1.9653803
C	2.1248198	0.0000000	-1.9653803
N	-1.1531105	0.0000000	-1.2904900
N	1.1531105	0.0000000	-1.2904900



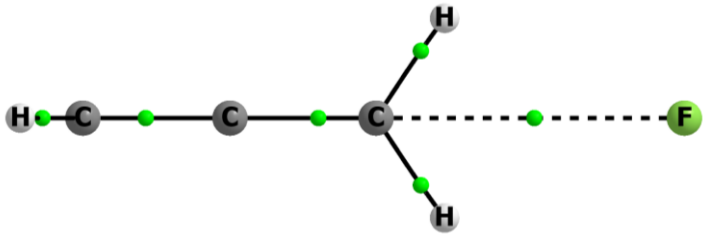
f-oh

C	0.0000000	0.0000000	-0.8073633
C	0.0000000	0.0000000	0.5237620
H	0.8982230	0.0000000	1.1226416
H	-0.8982230	0.0000000	1.1226416
F	0.0000000	0.0000000	3.3444060
O	-1.0992867	0.0000000	-1.6246769
H	-1.8567869	0.0000000	-1.0283672
O	1.0992867	0.0000000	-1.6246769
H	1.8567869	0.0000000	-1.0283672



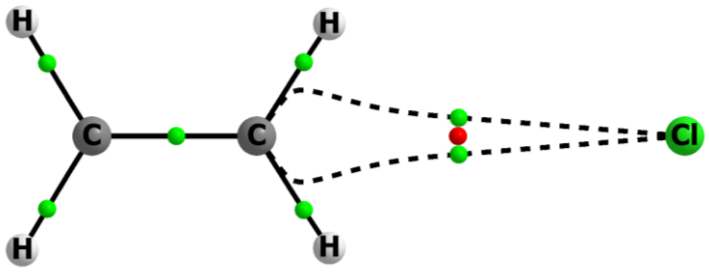
f-sh

C	0.0000000	0.0000000	-0.8044259
C	0.0000000	0.0000000	0.5304346
H	0.8959162	0.0000000	1.1373677
H	-0.8959162	0.0000000	1.1373677
F	0.0000000	0.0000000	3.2504932
S	-1.4576417	0.0000000	-1.8292454
H	-2.3086704	0.0000000	-0.7963732
S	1.4576417	0.0000000	-1.8292454
H	2.3086704	0.0000000	-0.7963732



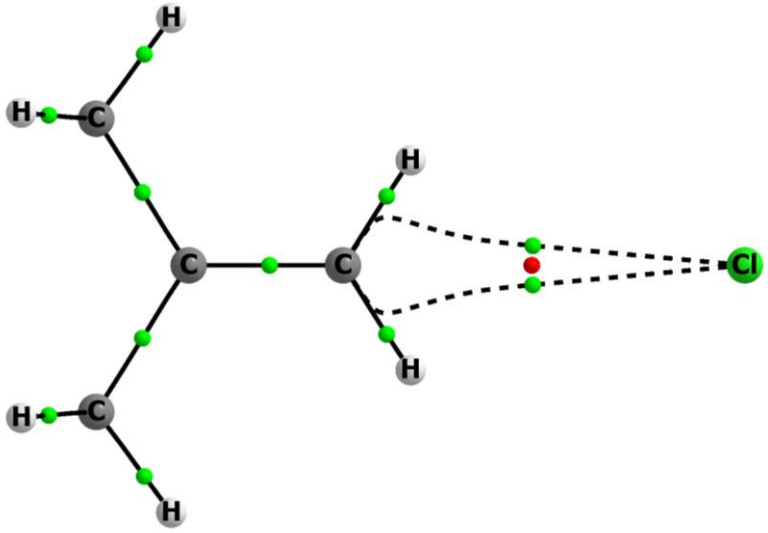
f-ch2

C	0.0000000	0.0000000	-0.5177710
C	0.0000000	0.0000000	0.7886802
H	0.0000000	0.8928520	1.4024205
H	0.0000000	-0.8928520	1.4024205
C	0.0000000	0.0000000	-1.8344513
H	0.9270239	0.0000000	-2.3945148
H	-0.9270239	0.0000000	-2.3945148
F	0.0000000	0.0000000	3.5477308



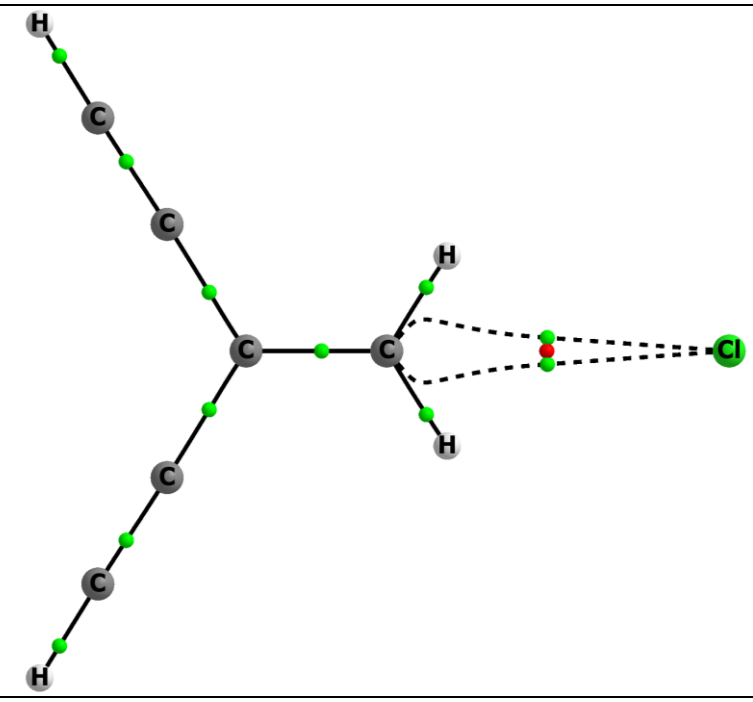
cl-h

C	0.0000000	0.0000000	-1.2659593
C	0.0000000	0.0000000	0.0697381
H	-0.9230953	0.0000000	-1.8319421
H	0.9230953	0.0000000	-1.8319421
H	0.9060951	0.0000000	0.6589508
H	-0.9060951	0.0000000	0.6589508
Cl	0.0000000	0.0000000	3.5422038



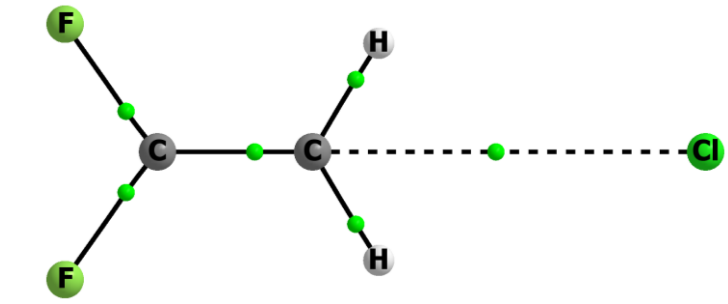
cl-me

C	0.0000000	0.0000000	-0.1764636
C	0.0000000	0.0000000	1.1615723
H	0.0000000	-0.9091342	1.7478532
H	0.0000000	0.9091342	1.7478532
C	0.0000000	1.2698471	-0.9783503
H	0.0000000	2.1430686	-0.3277530
H	0.8782395	1.3217994	-1.6287526
H	-0.8782395	1.3217994	-1.6287526
C	0.0000000	-1.2698471	-0.9783503
H	-0.8782395	-1.3217994	-1.6287526
H	0.8782395	-1.3217994	-1.6287526
H	0.0000000	-2.1430686	-0.3277530
Cl	0.0000000	0.0000000	4.6464017



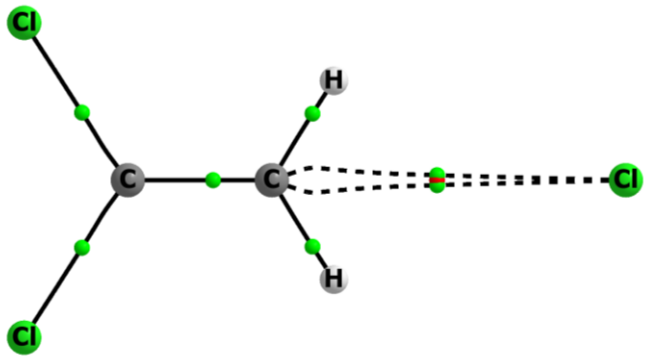
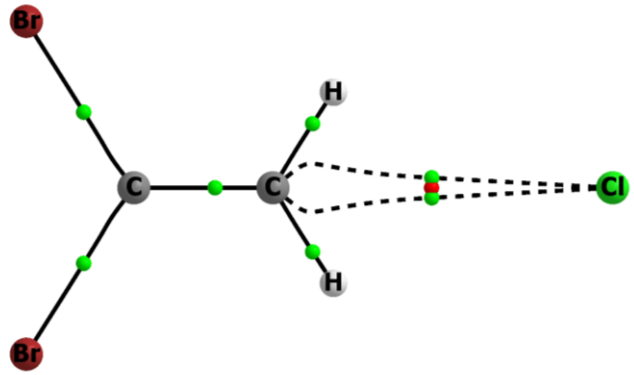
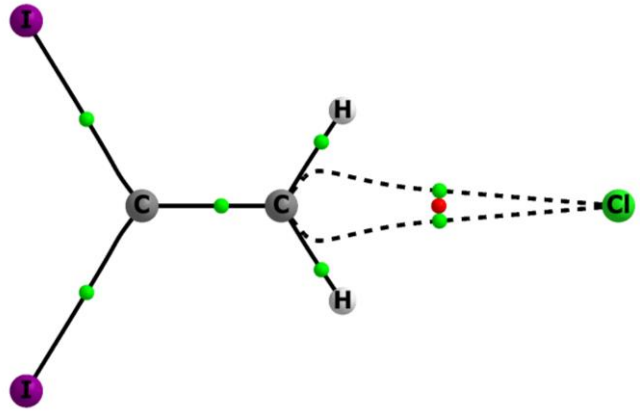
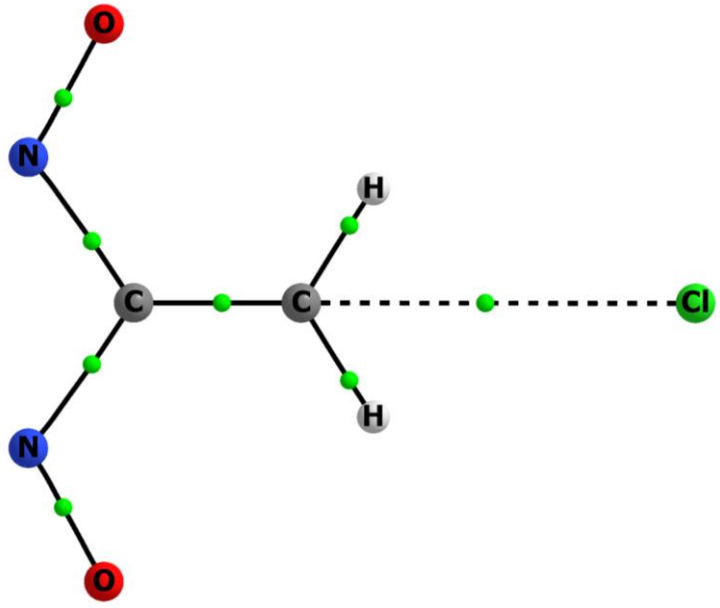
cl-cch

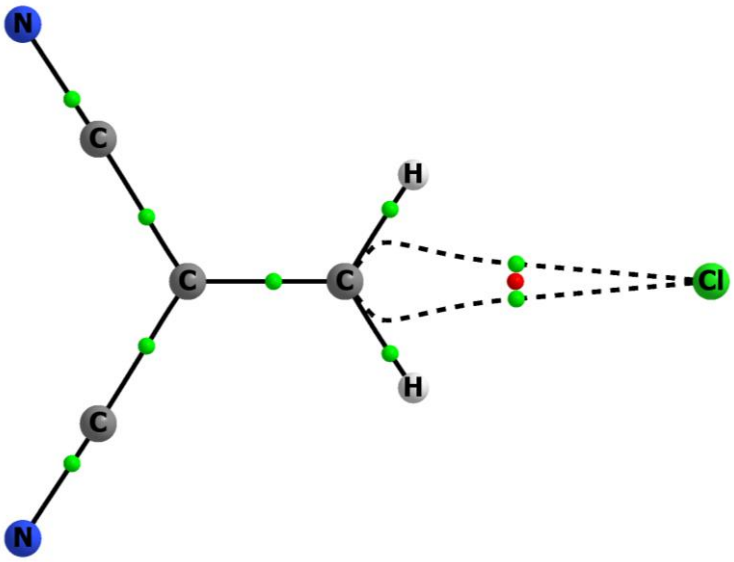
C	0.0000000	0.0000000	-0.1379793
C	0.0000000	0.0000000	1.2110394
H	0.9124140	0.0000000	1.7898841
H	-0.9124140	0.0000000	1.7898841
C	-1.2160524	0.0000000	-0.8960862
C	-2.2383058	0.0000000	-1.5597283
H	-3.1407592	0.0000000	-2.1179285
C	1.2160524	0.0000000	-0.8960862
C	2.2383058	0.0000000	-1.5597283
H	3.1407592	0.0000000	-2.1179285
Cl	0.0000000	0.0000000	4.4946578



cl-f

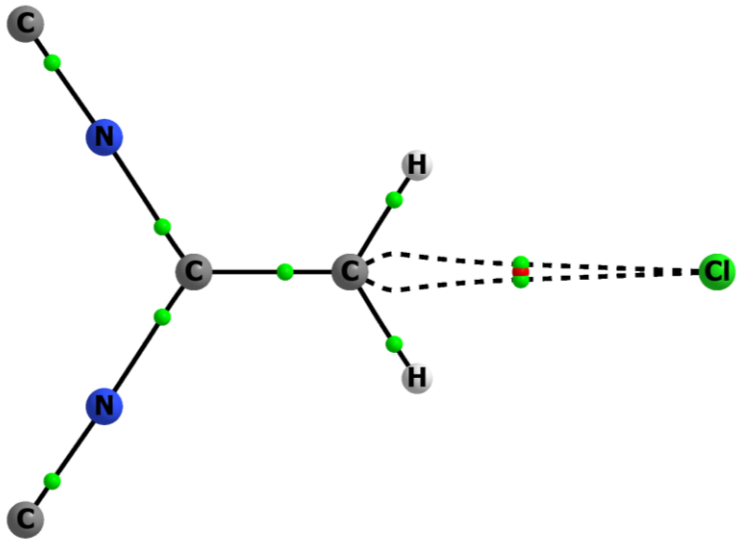
C	0.0000000	0.0000000	-1.1652080
C	0.0000000	0.0000000	0.1514962
H	0.9180329	0.0000000	0.7129058
H	-0.9180329	0.0000000	0.7129058
F	-1.0803391	0.0000000	-1.9490642
F	1.0803391	0.0000000	-1.9490642
Cl	0.0000000	0.0000000	3.4860287

	**cl-cl** C 0.0000000 0.0000000 -1.1153059 C 0.0000000 0.0000000 0.2118000 H -0.9147475 0.0000000 0.7848389 H 0.9147475 0.0000000 0.7848389 Cl 1.4486779 0.0000000 -2.0711047 Cl -1.4486779 0.0000000 -2.0711047 Cl 0.0000000 0.0000000 3.4760374
	**cl-br** C 0.0000000 0.0000000 -1.0944124 C 0.0000000 0.0000000 0.2341601 H -0.9132729 0.0000000 0.8120352 H 0.9132729 0.0000000 0.8120352 Cl 0.0000000 0.0000000 3.4782944 Br -1.5909238 0.0000000 -2.1210563 Br 1.5909238 0.0000000 -2.1210563
	**cl-i** C 0.0000000 0.0000000 -1.0721464 C 0.0000000 0.0000000 0.2591999 H -0.9106891 0.0000000 0.8437692 H 0.9106891 0.0000000 0.8437692 Cl 0.0000000 0.0000000 3.4805971 I 1.7705835 0.0000000 -2.1775945 I -1.7705835 0.0000000 -2.1775945
	**cl-no** C 0.0000000 0.0000000 -0.8363274 C 0.0000000 0.0000000 0.5070329 H 0.9131698 0.0000000 1.0854990 H -0.9131698 0.0000000 1.0854990 N -1.1648868 0.0000000 -1.6800310 O -2.2329335 0.0000000 -1.0743430 N 1.1648868 0.0000000 -1.6800310 O 2.2329335 0.0000000 -1.0743430 Cl 0.0000000 0.0000000 3.6670445



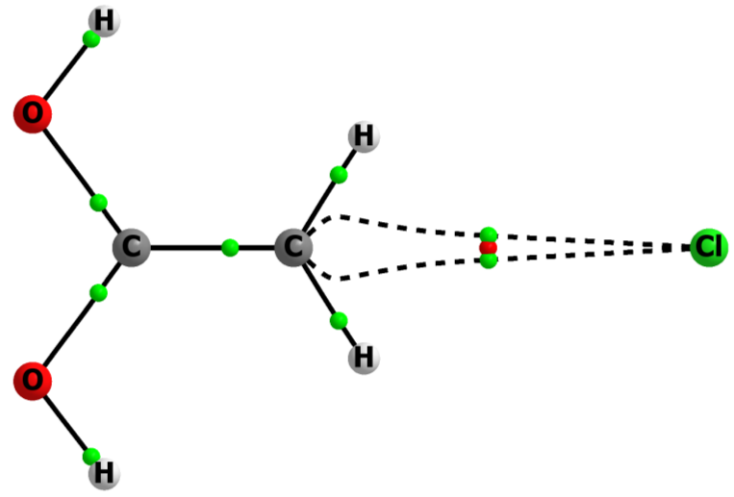
cl-cn

C	0.0000000	0.0000000	-0.5921931
C	0.0000000	0.0000000	0.7521199
H	-0.9092229	0.0000000	1.3365494
H	0.9092229	0.0000000	1.3365494
C	1.2145447	0.0000000	-1.3563965
N	2.1944525	0.0000000	-2.0009981
C	-1.2145447	0.0000000	-1.3563965
N	-2.1944525	0.0000000	-2.0009981
Cl	0.0000000	0.0000000	3.8817636



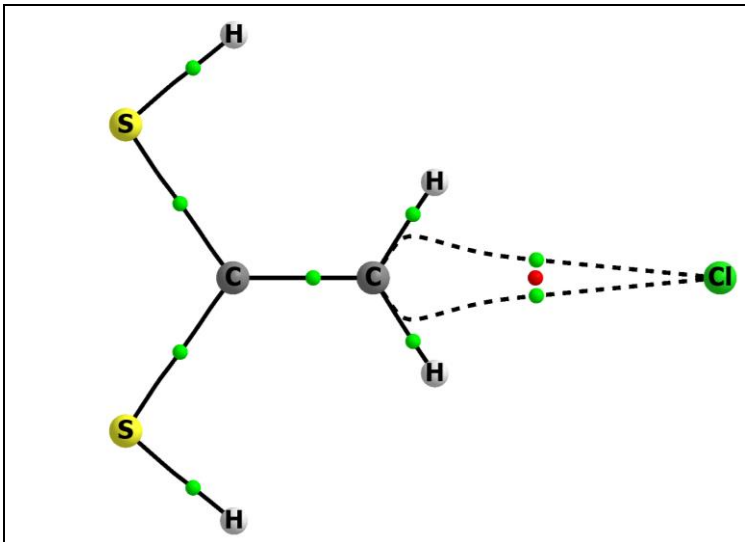
cl-nc

C	0.0000000	0.0000000	-0.5793425
C	0.0000000	0.0000000	0.7553051
H	-0.9136324	0.0000000	1.3301304
H	0.9136324	0.0000000	1.3301304
Cl	0.0000000	0.0000000	3.8970487
C	-2.1259979	0.0000000	-2.0205511
C	2.1259979	0.0000000	-2.0205511
N	-1.1536366	0.0000000	-1.3460849
N	1.1536366	0.0000000	-1.3460849



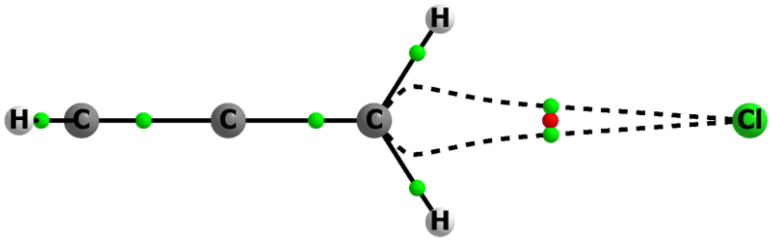
cl-oh

C	0.0000000	0.0000000	-0.8706358
C	0.0000000	0.0000000	0.4623752
H	0.9100867	0.0000000	1.0414894
H	-0.9100867	0.0000000	1.0414894
Cl	0.0000000	0.0000000	3.8797793
O	-1.0965467	0.0000000	-1.6832527
H	-1.8596277	0.0000000	-1.0939961
O	1.0965467	0.0000000	-1.6832527
H	1.8596277	0.0000000	-1.0939961



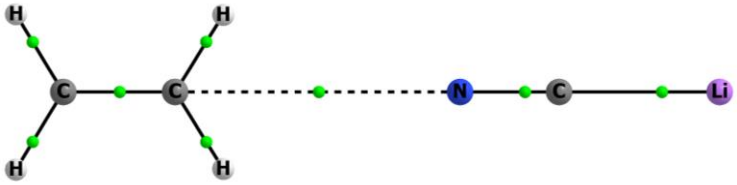
cl-sh

C	0.0000000	0.0000000	-0.8664311
C	0.0000000	0.0000000	0.4696460
H	0.9084337	0.0000000	1.0563080
H	-0.9084337	0.0000000	1.0563080
Cl	0.0000000	0.0000000	3.7741004
S	-1.4557505	0.0000000	-1.8877624
H	-2.3098005	0.0000000	-0.8572034
S	1.4557505	0.0000000	-1.8877624
H	2.3098005	0.0000000	-0.8572034



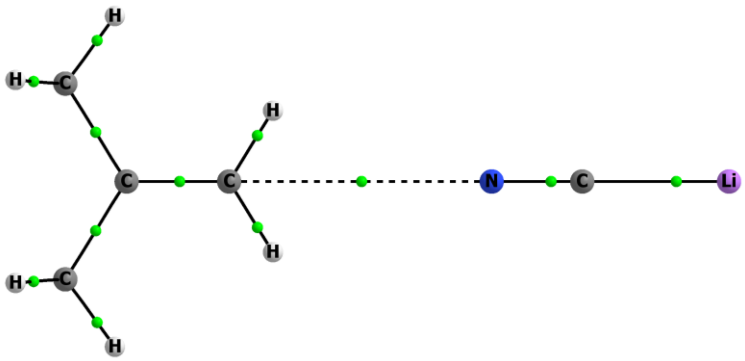
cl-ch2

C	0.0000000	0.0000000	-0.5890582
C	0.0000000	0.0000000	0.7182493
H	0.0000000	0.9079733	1.3076628
H	0.0000000	-0.9079733	1.3076628
C	0.0000000	0.0000000	-1.9035313
H	0.9276959	0.0000000	-2.4615337
H	-0.9276959	0.0000000	-2.4615337
Cl	0.0000000	0.0000000	4.0820820



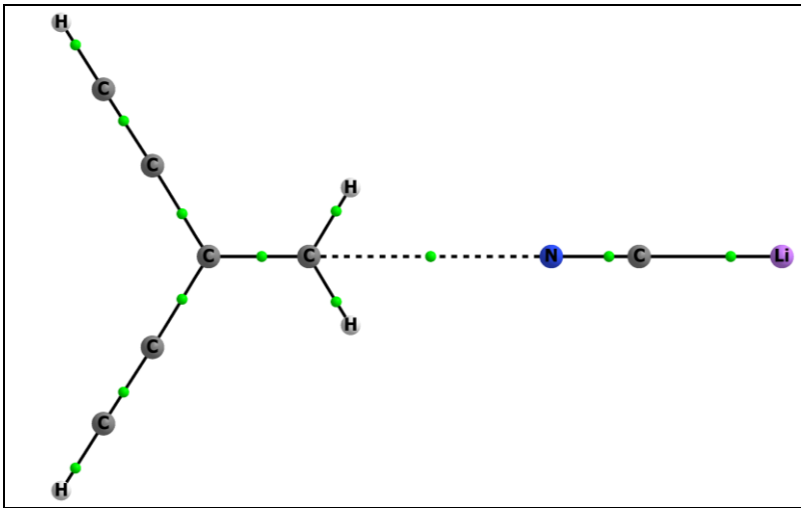
li-h

C	0.0000000	0.0000000	-2.4999171
C	0.0000000	0.0000000	-1.1658629
H	0.9147718	0.0000000	-0.5911397
H	-0.9147718	0.0000000	-0.5911397
N	0.0000000	0.0000000	2.2327852
C	0.0000000	0.0000000	3.4138221
Li	0.0000000	0.0000000	5.3288286
H	0.9230324	0.0000000	-3.0636882
H	-0.9230324	0.0000000	-3.0636882



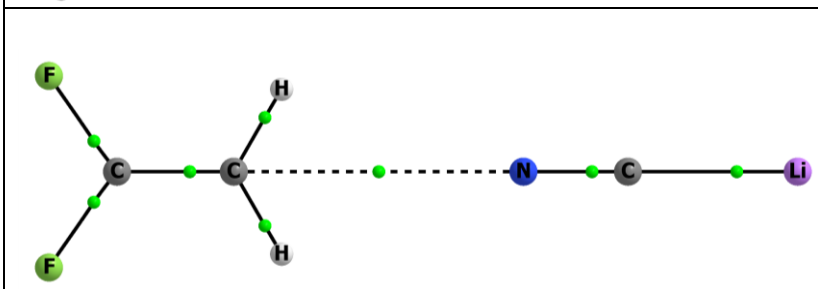
li-me

C	0.0000000	0.0000000	-1.0677428
C	0.0000000	0.0000000	0.2700022
H	0.0000000	0.9179306	0.8415720
H	0.0000000	-0.9179306	0.8415720
N	0.0000000	0.0000000	3.6933695
C	0.0000000	0.0000000	4.8744984
Li	0.0000000	0.0000000	6.7892079
C	0.0000000	1.2698003	-1.8670831
H	0.8773805	1.3173277	-2.5167057
H	-0.8773805	1.3173277	-2.5167057
H	0.0000000	2.1458935	-1.2207451
C	0.0000000	-1.2698003	-1.8670831
H	-0.8773805	-1.3173277	-2.5167057
H	0.8773805	-1.3173277	-2.5167057
H	0.0000000	-2.1458935	-1.2207451



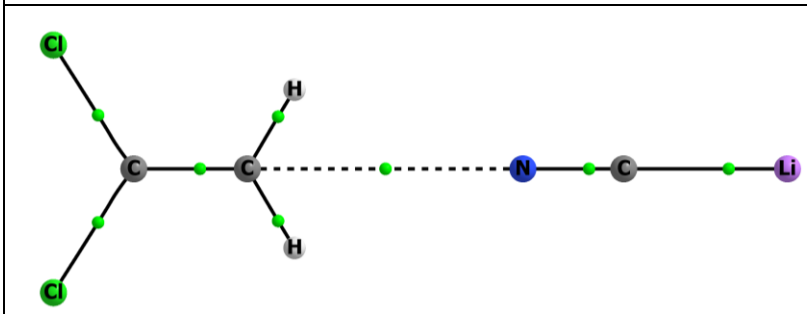
li-cch

C	0.0000000	0.0000000	-1.1515219
C	0.0000000	0.0000000	0.1969309
H	0.9229349	0.0000000	0.7567003
H	-0.9229349	0.0000000	0.7567003
N	0.0000000	0.0000000	3.4528912
C	0.0000000	0.0000000	4.6337363
Li	0.0000000	0.0000000	6.5510792
C	1.2175667	0.0000000	-1.9047548
C	2.2421851	0.0000000	-2.5631207
H	3.1398852	0.0000000	-3.1303826
C	-1.2175667	0.0000000	-1.9047548
C	-2.2421851	0.0000000	-2.5631207
H	-3.1398852	0.0000000	-3.1303826



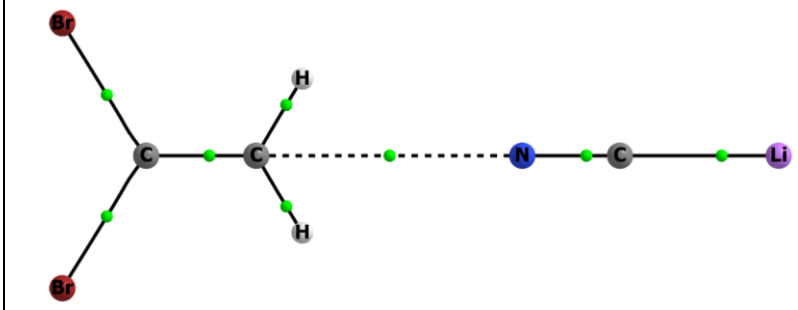
li-f

C	0.0000000	0.0000000	-2.3951161
C	0.0000000	0.0000000	-1.0755753
H	0.9285398	0.0000000	-0.5347712
H	-0.9285398	0.0000000	-0.5347712
F	-1.0793253	0.0000000	-3.1641139
F	1.0793253	0.0000000	-3.1641139
N	0.0000000	0.0000000	2.1962694
C	0.0000000	0.0000000	3.3771164
Li	0.0000000	0.0000000	5.2950758



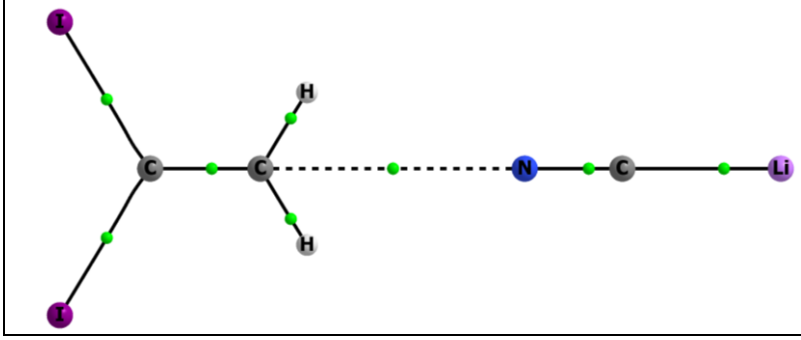
li-cl

C	0.0000000	0.0000000	-2.3513124
C	0.0000000	0.0000000	-1.0216920
H	0.9255802	0.0000000	-0.4695180
H	-0.9255802	0.0000000	-0.4695180
N	0.0000000	0.0000000	2.2057520
C	0.0000000	0.0000000	3.3865578
Li	0.0000000	0.0000000	5.3045587
Cl	-1.4482838	0.0000000	-3.2924141
Cl	1.4482838	0.0000000	-3.2924141



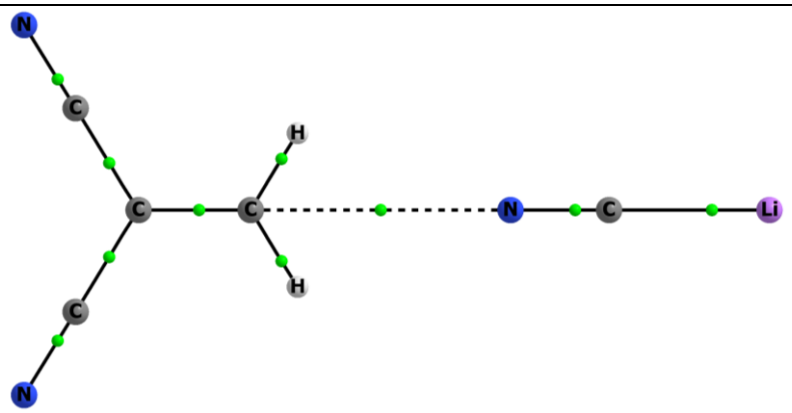
li-br

C	0.0000000	0.0000000	-2.3335245
C	0.0000000	0.0000000	-1.0024559
H	0.9243084	0.0000000	-0.4458094
H	-0.9243084	0.0000000	-0.4458094
N	0.0000000	0.0000000	2.2132982
C	0.0000000	0.0000000	3.3940923
Li	0.0000000	0.0000000	5.3120987
Br	1.5912081	0.0000000	-3.3459450
Br	-1.5912081	0.0000000	-3.3459450



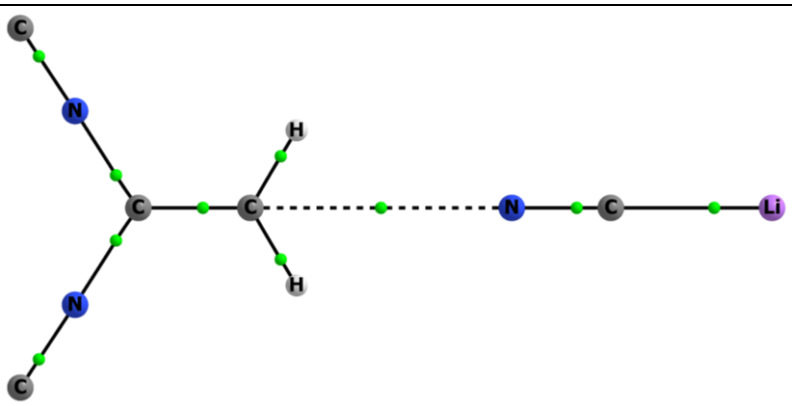
li-i

C	0.0000000	0.0000000	-2.3127516
C	0.0000000	0.0000000	-0.9790459
H	0.9218252	0.0000000	-0.4157077
H	-0.9218252	0.0000000	-0.4157077
N	0.0000000	0.0000000	2.2184842
C	0.0000000	0.0000000	3.3992791
Li	0.0000000	0.0000000	5.3172820
I	-1.7717332	0.0000000	-3.4059162
I	1.7717332	0.0000000	-3.4059162



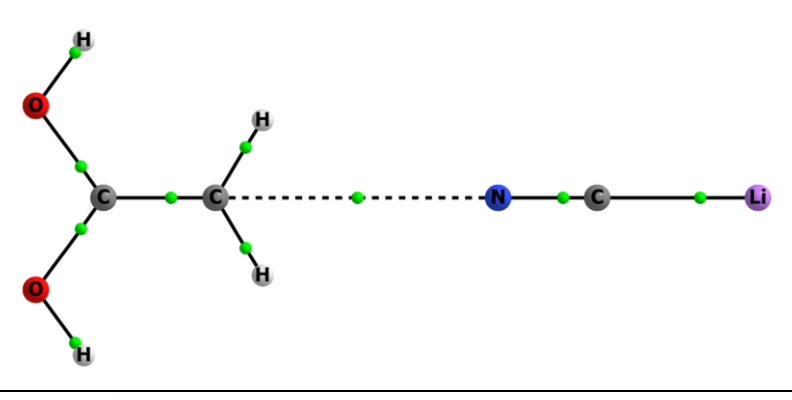
li-cn

C	0.0000000	0.0000000	-1.6861298
C	0.0000000	0.0000000	-0.3432970
H	0.9212280	0.0000000	0.2183980
H	-0.9212280	0.0000000	0.2183980
N	0.0000000	0.0000000	2.7683041
C	0.0000000	0.0000000	3.9486541
Li	0.0000000	0.0000000	5.8691310
C	1.2203399	0.0000000	-2.4400046
N	2.2177075	0.0000000	-3.0567247
C	-1.2203399	0.0000000	-2.4400046
N	-2.2177075	0.0000000	-3.0567247



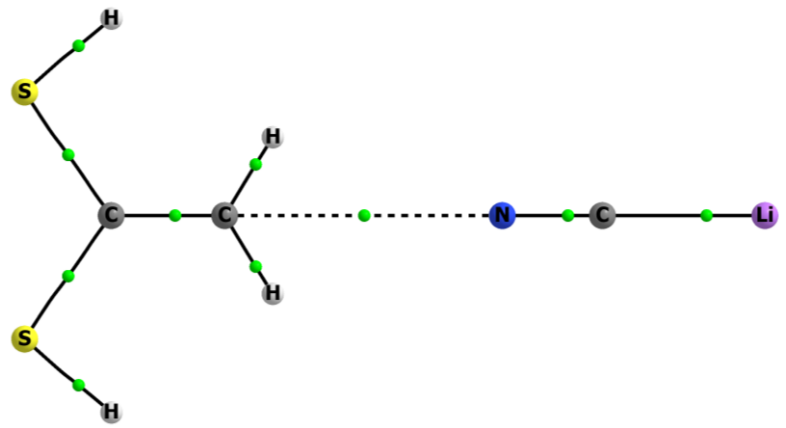
li-nc

C	0.0000000	0.0000000	-1.6746499
C	0.0000000	0.0000000	-0.3398141
H	0.9255447	0.0000000	0.2114951
H	-0.9255447	0.0000000	0.2114951
N	0.0000000	0.0000000	2.7768225
C	0.0000000	0.0000000	3.9573916
Li	0.0000000	0.0000000	5.8790795
N	1.1563633	0.0000000	-2.4294882
C	2.1451747	0.0000000	-3.0814216
N	-1.1563633	0.0000000	-2.4294882
C	-2.1451747	0.0000000	-3.0814216



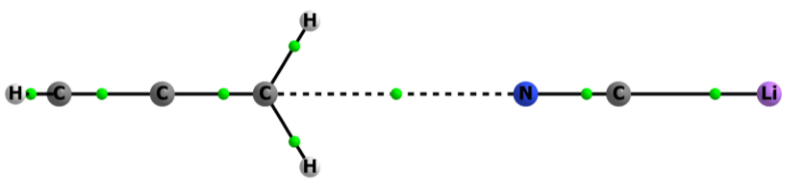
li-oh

C	0.0000000	0.0000000	-1.9498970
C	0.0000000	0.0000000	-0.6123924
H	0.9197346	0.0000000	-0.0514717
H	-0.9197346	0.0000000	-0.0514717
N	0.0000000	0.0000000	2.7548844
C	0.0000000	0.0000000	3.9359617
Li	0.0000000	0.0000000	5.8513627
O	-1.0899469	0.0000000	-2.7554416
H	-1.8654014	0.0000000	-2.1830464
O	1.0899469	0.0000000	-2.7554416
H	1.8654014	0.0000000	-2.1830464



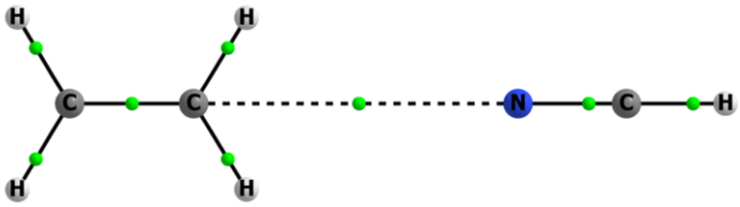
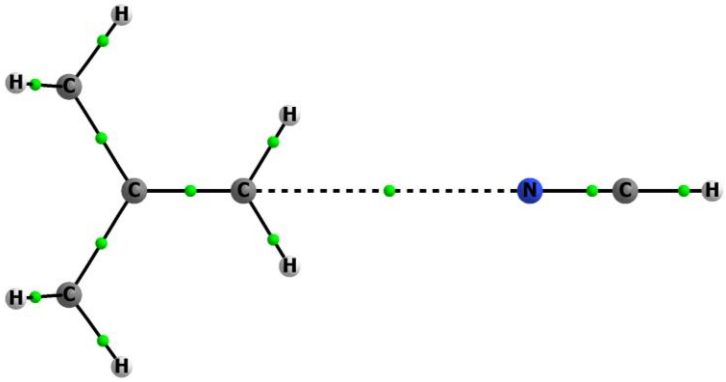
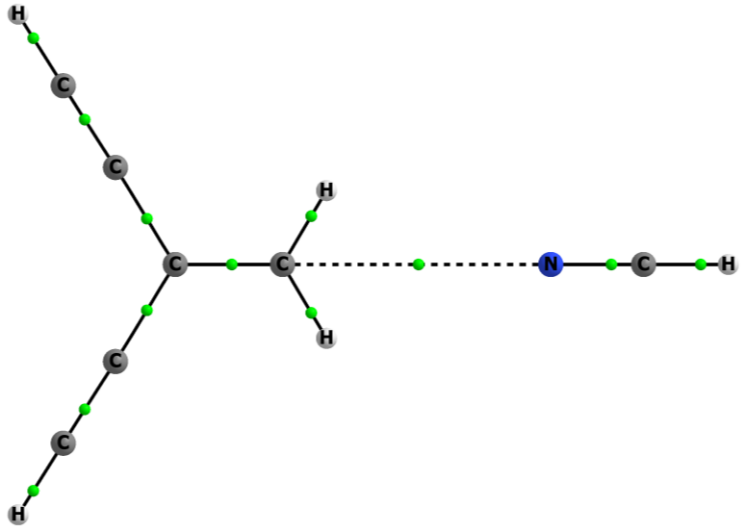
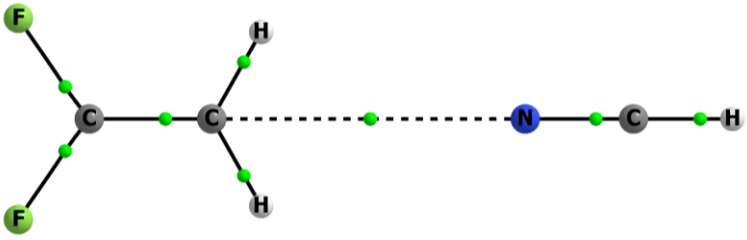
li-sh

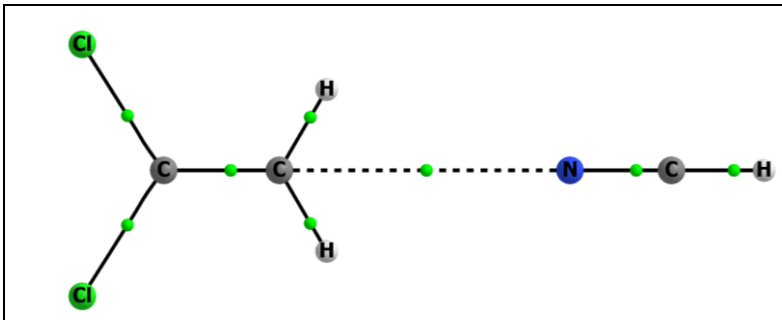
C	0.0000000	0.0000000	-1.9305071
C	0.0000000	0.0000000	-0.5918421
H	0.9187271	0.0000000	-0.0241279
H	-0.9187271	0.0000000	-0.0241279
N	0.0000000	0.0000000	2.6825628
C	0.0000000	0.0000000	3.8635356
Li	0.0000000	0.0000000	5.7796477
S	-1.4495597	0.0000000	-2.9505731
H	-2.3117282	0.0000000	-1.9269975
S	1.4495597	0.0000000	-2.9505731
H	2.3117282	0.0000000	-1.9269975



li-ch2

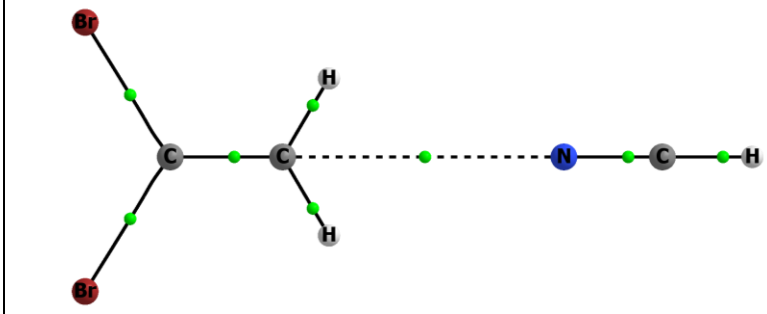
C	0.0000000	0.0000000	-0.5074222
H	0.0000000	0.9191094	0.0615395
H	0.0000000	-0.9191094	0.0615395
N	0.0000000	0.0000000	2.8045995
C	0.0000000	0.0000000	3.9855610
C	0.0000000	0.0000000	-1.8160032
C	0.0000000	0.0000000	-3.1269962
H	0.9284512	0.0000000	-3.6821858

	H -0.9284512 0.0000000 -3.6821858 Li 0.0000000 0.0000000 5.9015537
	**n-h** C 0.0000000 0.0000000 -2.4319711 C 0.0000000 0.0000000 -1.0983474 H 0.9187738 0.0000000 -0.5295637 H -0.9187738 0.0000000 -0.5295637 N 0.0000000 0.0000000 2.3932365 C 0.0000000 0.0000000 3.5603620 H 0.0000000 0.0000000 4.6256871 H 0.9231761 0.0000000 -2.9949199 H -0.9231761 0.0000000 -2.9949199
	**n-me** C 0.0000000 0.0000000 -1.0260049 C 0.0000000 0.0000000 0.3117592 H 0.0000000 0.9217278 0.8776763 H 0.0000000 -0.9217278 0.8776763 N 0.0000000 0.0000000 3.8200672 C 0.0000000 0.0000000 4.9873231 H 0.0000000 0.0000000 6.0526798 C 0.0000000 -1.2699171 -1.8242311 H 0.0000000 -2.1468903 -1.1792181 H -0.8772594 -1.3160254 -2.4735697 H 0.8772594 -1.3160254 -2.4735697 C 0.0000000 1.2699171 -1.8242311 H 0.8772594 1.3160254 -2.4735697 H -0.8772594 1.3160254 -2.4735697 H 0.0000000 2.1468903 -1.1792181
	**n-cch** C 0.0000000 0.0000000 -1.1110529 C 0.0000000 0.0000000 0.2376077 H 0.9275108 0.0000000 0.7902849 H -0.9275108 0.0000000 0.7902849 N 0.0000000 0.0000000 3.6083798 C 0.0000000 0.0000000 4.7753581 H 0.0000000 0.0000000 5.8408476 C -1.2180953 0.0000000 -1.8622727 C -2.2440841 0.0000000 -2.5181250 H -3.1420247 0.0000000 -3.0854573 C 1.2180953 0.0000000 -1.8622727 C 2.2440841 0.0000000 -2.5181250 H 3.1420247 0.0000000 -3.0854573
	**n-f** C 0.0000000 0.0000000 -2.3333823 C 0.0000000 0.0000000 -1.0128049 H 0.9331540 0.0000000 -0.4798527 H -0.9331540 0.0000000 -0.4798527 F -1.0789619 0.0000000 -3.0976676 F 1.0789619 0.0000000 -3.0976676 N 0.0000000 0.0000000 2.3673073 C 0.0000000 0.0000000 3.5342383 H 0.0000000 0.0000000 4.5996824



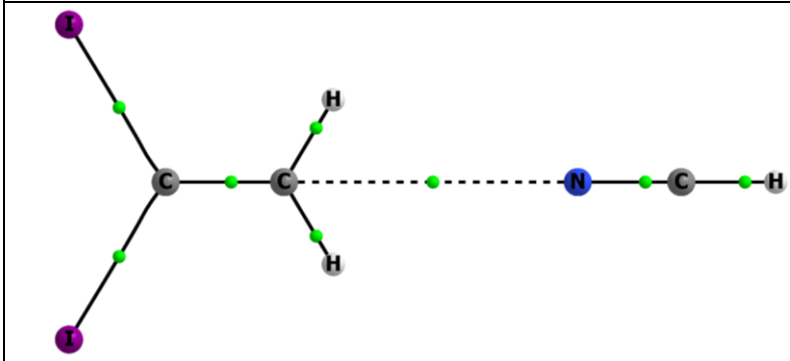
n-cl

C	0.0000000	0.0000000	-2.2916822
C	0.0000000	0.0000000	-0.9610586
H	0.9302665	0.0000000	-0.4165306
H	-0.9302665	0.0000000	-0.4165306
N	0.0000000	0.0000000	2.3809224
C	0.0000000	0.0000000	3.5478263
H	0.0000000	0.0000000	4.6133229
Cl	-1.4481384	0.0000000	-3.2281348
Cl	1.4481384	0.0000000	-3.2281348



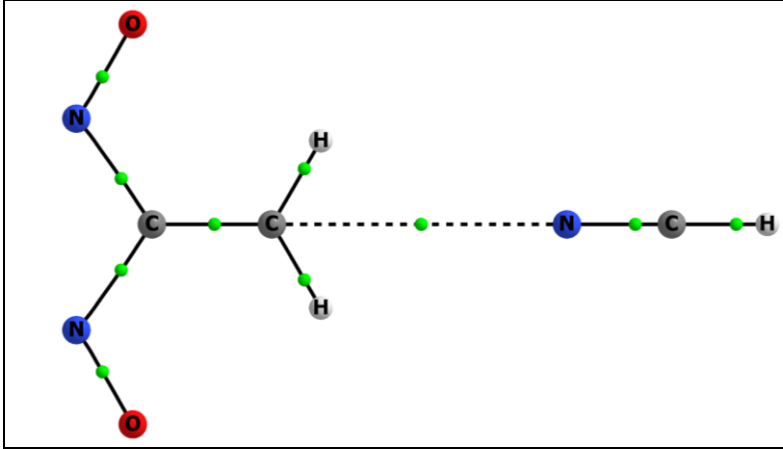
n-br

C	0.0000000	0.0000000	-2.2748730
C	0.0000000	0.0000000	-0.9427836
H	0.9290552	0.0000000	-0.3937789
H	-0.9290552	0.0000000	-0.3937789
N	0.0000000	0.0000000	2.3904529
C	0.0000000	0.0000000	3.5573549
H	0.0000000	0.0000000	4.6228626
Br	1.5913569	0.0000000	-3.2827280
Br	-1.5913569	0.0000000	-3.2827280



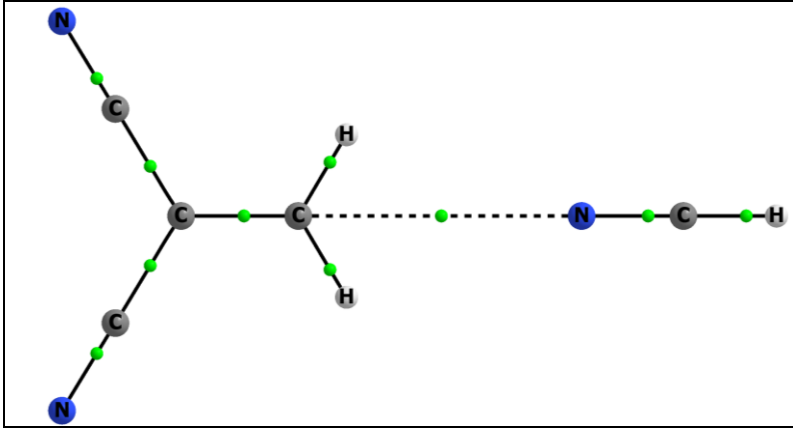
n-i

C	0.0000000	0.0000000	-2.2530367
C	0.0000000	0.0000000	-0.9183523
H	0.9266168	0.0000000	-0.3625846
H	-0.9266168	0.0000000	-0.3625846
N	0.0000000	0.0000000	2.3939335
C	0.0000000	0.0000000	3.5608491
H	0.0000000	0.0000000	4.6263696
I	-1.7722014	0.0000000	-3.3422970
I	1.7722014	0.0000000	-3.3422970



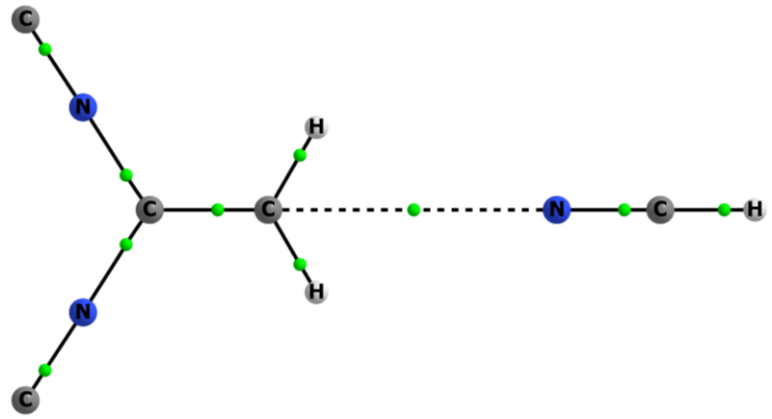
n-no

C	0.0000000	0.0000000	-1.8419510
C	0.0000000	0.0000000	-0.5049868
H	0.9324733	0.0000000	0.0392539
H	-0.9324733	0.0000000	0.0392539
N	-1.1795615	0.0000000	-2.6826059
O	-2.2310666	0.0000000	-2.0546550
N	1.1795615	0.0000000	-2.6826059
O	2.2310666	0.0000000	-2.0546550
N	0.0000000	0.0000000	2.7813553
C	0.0000000	0.0000000	3.9479484
H	0.0000000	0.0000000	5.0136482



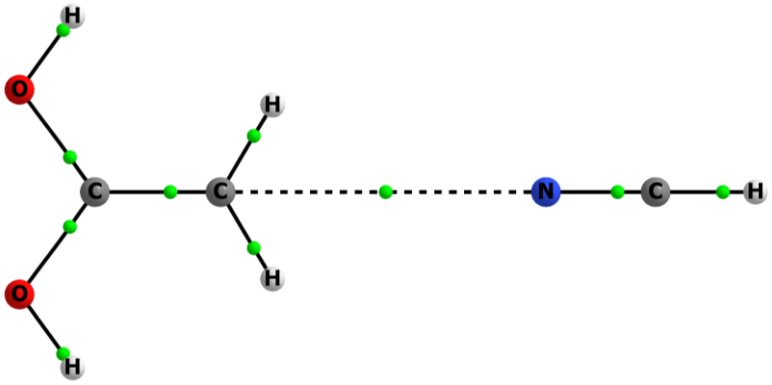
n-cn

C	0.0000000	0.0000000	-1.6425660
C	0.0000000	0.0000000	-0.2996699
H	0.9266239	0.0000000	0.2535594
H	-0.9266239	0.0000000	0.2535594
N	0.0000000	0.0000000	2.9464650
C	0.0000000	0.0000000	4.1129189
H	0.0000000	0.0000000	5.1787400
C	1.2212436	0.0000000	-2.3944145
N	2.2211500	0.0000000	-3.0070890
C	-1.2212436	0.0000000	-2.3944145
N	-2.2211500	0.0000000	-3.0070890



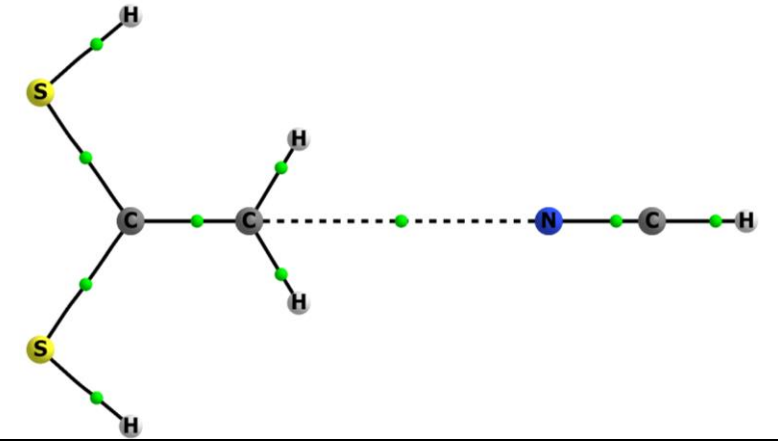
n-nc

C	0.0000000	0.0000000	-1.6311603
C	0.0000000	0.0000000	-0.2959775
H	0.9309656	0.0000000	0.2464332
H	-0.9309656	0.0000000	0.2464332
N	0.0000000	0.0000000	2.9543625
C	0.0000000	0.0000000	4.1209954
H	0.0000000	0.0000000	5.1868330
N	1.1567992	0.0000000	-2.3827383
C	2.1483282	0.0000000	-3.0312215
N	-1.1567992	0.0000000	-2.3827383
C	-2.1483282	0.0000000	-3.0312215



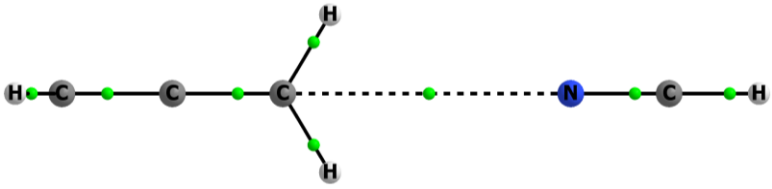
n-oh

C	0.0000000	0.0000000	-1.8963949
C	0.0000000	0.0000000	-0.5572947
H	0.9237767	0.0000000	-0.0031389
H	-0.9237767	0.0000000	-0.0031389
N	0.0000000	0.0000000	2.9079812
C	0.0000000	0.0000000	4.0751542
H	0.0000000	0.0000000	5.1405565
O	-1.0879990	0.0000000	-2.6994976
H	-1.8673310	0.0000000	-2.1323647
O	1.0879990	0.0000000	-2.6994976
H	1.8673310	0.0000000	-2.1323647



n-sh

C	0.0000000	0.0000000	1.8797807
C	0.0000000	0.0000000	0.5400974
H	-0.9230899	0.0000000	-0.0207144
H	0.9230899	0.0000000	-0.0207144
N	0.0000000	0.0000000	-2.8443940
C	0.0000000	0.0000000	-4.0114799
H	0.0000000	0.0000000	-5.0769967
S	1.4476575	0.0000000	2.8991752
H	2.3127649	0.0000000	1.8780354
S	-1.4476575	0.0000000	2.8991752
H	-2.3127649	0.0000000	1.8780354



n-ch2

C	0.0000000	0.0000000	-0.4491076
H	0.0000000	0.9238196	0.1124371
H	0.0000000	-0.9238196	0.1124371
N	0.0000000	0.0000000	2.9650069
C	0.0000000	0.0000000	4.1320764
H	0.0000000	0.0000000	5.1975275
C	0.0000000	0.0000000	-1.7580060
C	0.0000000	0.0000000	-3.0679584
H	0.9288254	0.0000000	-3.6222066
H	-0.9288254	0.0000000	-3.6222066

Table S2. C=C and C–X distances variations upon complexation (Δd_{CC} and Δd_{CX}, respectively). Distances in Å.

X	Y	Δd_{CC}	Δd_{CX}	X	Y	Δd_{CC}	Δd_{CX}
H	F^-	0.004	0.003	H	LiCN	0.001	0.001
	Cl^-	0.003	0.002		HCN	0.001	0.000
Me	F^-	0.001	0.003	Me	LiCN	0.000	0.000
	Cl^-	0.000	0.002		HCN	0.000	0.000
C≡CH	F^-	0.001	0.001	C≡CH	LiCN	-0.001	0.001
	Cl^-	0.000	0.000		HCN	0.000	0.000
F	F^-	-0.006	0.020	F	LiCN	-0.001	0.005
	Cl^-	-0.004	0.015		HCN	0.000	0.002
Cl	F^-	-0.005	0.019	Cl	LiCN	-0.001	0.005
	Cl^-	-0.004	0.014		HCN	0.000	0.003
Br	F^-	-0.006	0.016	Br	LiCN	-0.002	0.004
	Cl^-	-0.004	0.011		HCN	-0.001	0.002
I	F^-	-0.006	0.012	I	LiCN	-0.002	0.003
	Cl^-	-0.005	0.008		HCN	-0.001	0.001
NO	F^-	0.010	-0.016	NO	LiCN	-	-
	Cl^-	0.007	-0.013		HCN	0.001	-0.003
CN	F^-	0.003	0.001	CN	LiCN	0.000	0.000
	Cl^-	0.001	0.001		HCN	0.000	0.000
NC	F^-	0.000	0.009	NC	LiCN	0.000	0.003
	Cl^-	0.000	0.007		HCN	0.000	0.002
OH	F^-	-0.009	0.020	OH	LiCN	-0.002	0.005
	Cl^-	-0.007	0.015		HCN	-0.001	0.002
SH	F^-	-0.005	0.013	SH	LiCN	-0.001	0.004
	Cl^-	-0.004	0.009		HCN	0.000	0.002
$=CH_2$	F^-	-0.003	0.008	$=CH_2$	LiCN	0.000	0.002
	Cl^-	-0.002	0.005		HCN	0.000	0.001

Table S3. Binding energy along the out-of-plane relaxed scan of α. E_b in kcal·mol^{-1} and α in degrees.

α	E_b	d
180	-12.86	2.738
175	-12.83	2.737
170	-12.75	2.734
165	-12.61	2.729
160	-12.43	2.723
155	-12.19	2.715
150	-11.91	2.705
145	-11.57	2.695
140	-11.18	2.683
135	-10.75	2.672
130	-10.27	2.662
125	-9.74	2.654
120	-9.16	2.651
115	-8.55	2.740
110	-7.90	2.666
105	-7.25	2.687
100	-6.62	2.717
95	-6.06	2.755
90	-5.60	2.796

Table S4. Binding energy along the in-plane relaxed scan of β. E_b in kcal·mol^{-1} and β in degrees.

β	E_b	$d_{H\cdots F-}$
180	-12.86	2.337
175	-13.01	2.186
170	-13.48	2.032
165	-14.22	1.886
160	-15.13	1.764
155	-15.54	1.676
150	-16.93	1.618
145	-17.65	1.580
140	-18.20	1.556
135	-18.56	1.540
130	-18.73	1.532
125	-18.70	1.529
120	-18.48	1.531

Table S5. Binding energies of a set of representative carbon bond and hydrogen bond complexes ($E_{b\text{-}CB}$ and $E_{b\text{-}HB}$, respectively).

X	Y	$E_{b\text{-}CB}$	$E_{b\text{-}HB}$
H	LiCN	-1.63	-2.22
	HCN	-0.63	-0.86
F	F^-	-12.86	-18.74
	Cl^-	-8.51	-9.66
	LiCN	-3.23	-
	HCN	-1.36	-2.20
CN	F^-	-27.82	-34.66
	Cl^-	-19.81	-20.43

Table S6. Total electron density energy (H_{BCP}), in au, for the intermolecular bond critical points in all complexes.

X	Y	$H_{BCP}x10^3$	X	Y	$H_{BCP}x10^3$
H	F^-	1.64	H	LiCN	1.27
	Cl^-	1.28[a]		HCN	1.09
Me	F^-	1.63	Me	LiCN	1.21
	Cl^-	1.25[a]		HCN	1.05
C≡CH	F^-	2.09	C≡CH	LiCN	1.57
	Cl^-	1.48[a]		HCN	1.33
F	F^-	1.95	F	LiCN	1.52
	Cl^-	1.47		HCN	1.30
Cl	F^-	2.12	Cl	LiCN	1.64
	Cl^-	1.52[a]		HCN	1.40
Br	F^-	2.18	Br	LiCN	1.67
	Cl^-	1.52[a]		HCN	1.42
I	F^-	2.24	I	LiCN	1.71
	Cl^-	1.52[a]		HCN	1.47
NO	F^-	2.41	NO	LiCN	-
	Cl^-	1.53		HCN	1.53
CN	F^-	2.51[a]	CN	LiCN	1.91
	Cl^-	1.52[a]		HCN	1.63
NC	F^-	2.42	NC	LiCN	1.89
	Cl^-	1.53[a]		HCN	1.61
OH	F^-	1.75	OH	LiCN	1.31
	Cl^-	1.36[a]		HCN	1.12
SH	F^-	2.01	SH	LiCN	1.53
	Cl^-	1.46[a]		HCN	1.30
$=CH_2$	F^-	1.97	$=CH_2$	LiCN	1.46
	Cl^-	1.43[a]		HCN	1.25

Table S7. Second-order perturbation stabilization energies for the donor-acceptor Lp(Y)→σ*(C1–C2), Lp(Y)→π*(C1=C2), and Lp(Y)→σ*(C2–H) (σ*, π*, and σ*(H), respectively, in kcal·mol^{-1}) and electron charge transfer from the Lewis base to the Lewis acid (Δq in au) calculated from the NBO atomic charges in **li-x** and **n-x** complexes.

X	Y	σ*	π*	σ*(H)	Δq
H	LiCN	0.34	-	-	-0.0008
	HCN	0.22	-	-	-0.0006
Me	LiCN	0.20	-	-	-0.0003
	HCN	0.12	-	-	-0.0002
C≡CH	LiCN	0.41	-	-	-0.0011
	HCN	0.22	-	-	-0.0008
F	LiCN	0.33	-	-	-0.0004
	HCN	0.16	-	-	-0.0003
Cl	LiCN	0.28	-	-	-0.0007
	HCN	0.14	-	-	-0.0006
Br	LiCN	0.28	-	-	-0.0008
	HCN	0.15	-	-	-0.0006
I	LiCN	0.34	-	-	-0.0011
	HCN	0.19	-	-	-0.0007
NO	LiCN	-	-	-	-
	HCN	0.25	-	-	-0.0007
CN	LiCN	0.66	-	-	-0.0020
	HCN	0.35	-	-	-0.0013
NC	LiCN	0.62	-	-	-0.0016
	HCN	0.32	-	-	-0.0011
OH	LiCN	0.25	-	-	-0.0003
	HCN	0.13	-	-	-0.0002
SH	LiCN	0.24	-	-	-0.0004
	HCN	0.13	-	-	-0.0004
$=CH_2$	LiCN	0.38	-	-	-0.0008
	HCN	0.22	-	-	-0.0005

Table S8. DF-DFT-SAPT total energy (E_{SAPT}) and its exchange, electrostatic, induction, and dispersion energy contributions (E_{exch}, E_{el}, E_i, and E_d, respectively) of all complexes. Energies in kcal·mol^{-1}.

X	Y	E_{ex}	E_{el}	E_i	E_d	E_{SAPT}	X	Y	E_{ex}	E_{el}	E_i	E_d	E_{SAPT}
H	F^-	9.8	-6.7	-5.9	-2.7	-5.6	H	LiCN	1.7	-1.1	-0.6	-1.2	-1.2
	Cl^-	5.6	-3.8	-3.1	-2.3	-3.6		HCN	1.0	-0.6	-0.2	-0.9	-0.6
Me	F^-	9.5	-3.5	-6.8	-2.8	-3.7	Me	LiCN	1.6	-0.2	-0.6	-1.2	-0.5
	Cl^-	5.4	-1.4	-3.6	-2.4	-2.1		HCN	1.0	-0.1	-0.2	-0.9	-0.3
C≡CH	F^-	15.6	-13.8	-9.9	-3.7	-11.9	C≡CH	LiCN	2.6	-2.7	-0.9	-1.6	-2.6
	Cl^-	8.9	-8.4	-5.4	-3.2	-8.1		HCN	1.4	-1.3	-0.3	-1.1	-1.3
F	F^-	13.3	-14.6	-6.8	-3.3	-11.4	F	LiCN	2.4	-2.9	-0.7	-1.4	-2.6
	Cl^-	7.6	-9.2	-3.5	-2.7	-7.8		HCN	1.3	-1.3	-0.2	-1.0	-1.2
Cl	F^-	16.2	-16.8	-9.2	-3.8	-13.6	Cl	LiCN	2.8	-3.4	-0.9	-1.6	-3.1
	Cl^-	9.3	-10.6	-4.9	-3.2	-9.4		HCN	1.5	-1.6	-0.3	-1.2	-1.5
Br	F^-	17.2	-17.4	-10.1	-4.0	-14.3	Br	LiCN	2.9	-3.5	-1.0	-1.7	-3.2
	Cl^-	9.8	-10.9	-5.5	-3.4	-9.9		HCN	1.6	-1.6	-0.3	-1.2	-1.5
I	F^-	18.4	-17.4	-11.4	-4.2	-14.6	I	LiCN	3.1	-3.5	-1.1	-1.8	-3.2
	Cl^-	10.5	-10.8	-6.2	-3.6	-10.0		HCN	1.7	-1.6	-0.3	-1.3	-1.5
NO	F^-	21.2	-29.3	-10.6	-4.4	-23.1	NO	LiCN	-	-	-	-	-
	Cl^-	12.4	-19.5	-5.8	-3.7	-16.6		HCN	1.9	-2.9	-0.4	-1.2	-2.6
CN	F^-	22.5	-32.6	-11.4	-4.6	-26.2	CN	LiCN	4.0	-7.6	-1.3	-1.9	-6.7
	Cl^-	13.5	-22.6	-6.5	-3.9	-19.5		HCN	2.1	-3.4	-0.4	-1.3	-3.1
NC	F^-	21.6	-28.0	-11.1	-4.5	-21.9	NC	LiCN	3.9	-6.3	-1.2	-1.9	-5.4
	Cl^-	12.9	-19.1	-6.1	-3.8	-16.1		HCN	2.0	-2.8	-0.4	-1.3	-2.5
OH	F^-	10.9	-8.9	-6.7	-3.0	-7.6	OH	LiCN	1.8	-1.2	-0.6	-1.3	-1.3
	Cl^-	6.3	-5.5	-3.5	-3.6	-5.4		HCN	1.0	-0.5	-0.2	-1.0	-0.6
SH	F^-	14.6	-12.5	-9.4	-3.7	-11.0	SH	LiCN	2.5	-2.3	-0.9	-1.6	-2.3
	Cl^-	8.5	-8.0	-5.1	-3.2	-7.8		HCN	1.4	-1.0	-0.2	-1.1	-1.0
$=CH_2$	F^-	13.1	-10.2	-8.1	-3.3	-8.5	$=CH_2$	LiCN	2.2	-1.8	-0.7	-1.4	-1.8
	Cl^-	7.3	-5.8	-4.2	-2.8	-5.5		HCN	1.2	-0.9	-0.2	-1.0	-0.9

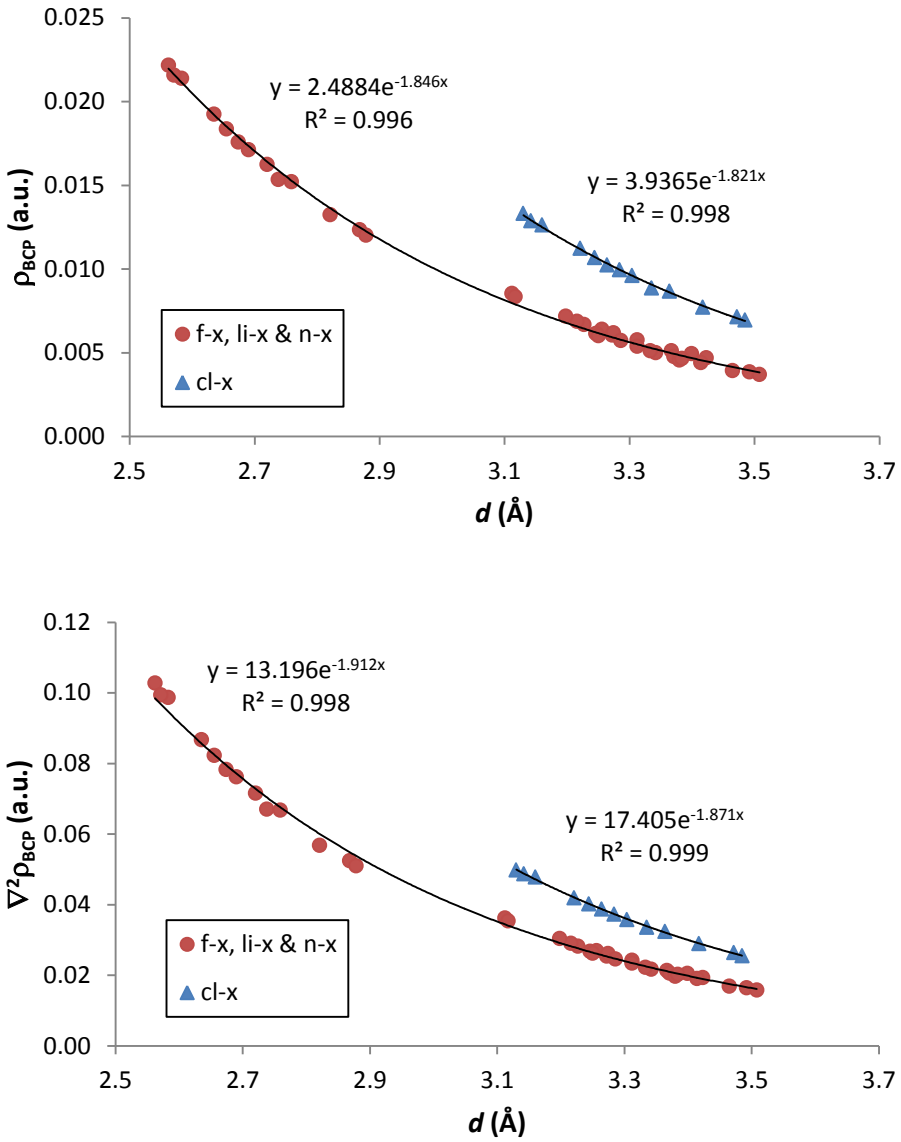


Figure S1. Exponential relationship between C···Y equilibrium distance and the electron density (top) and laplacian (bottom) at the BCP (ρ and $\nabla^2\rho$, respectively, in a.u.) for the complexes.

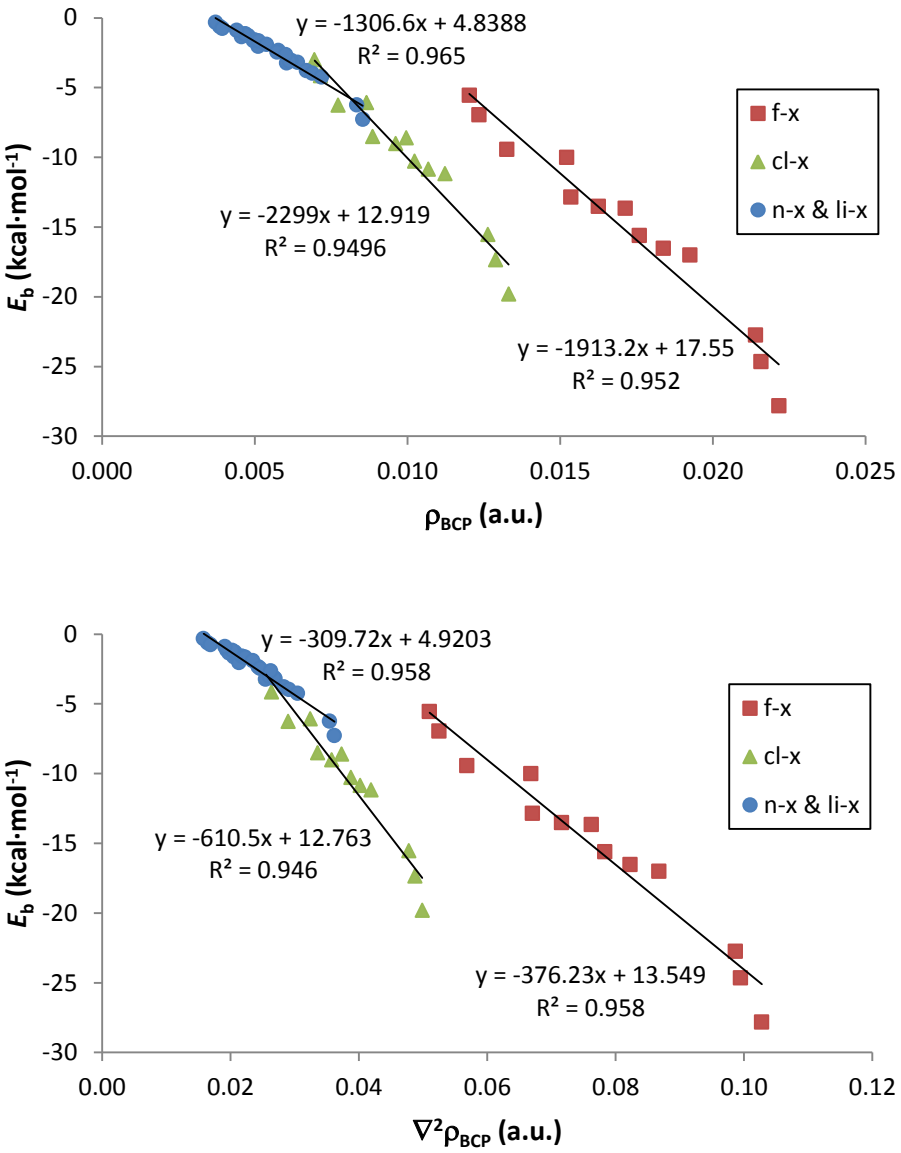


Figure S2. Electron density (ρ, top) and Laplacian ($\nabla^2\rho$, bottom) at the intermolecular BCP versus the binding energy.

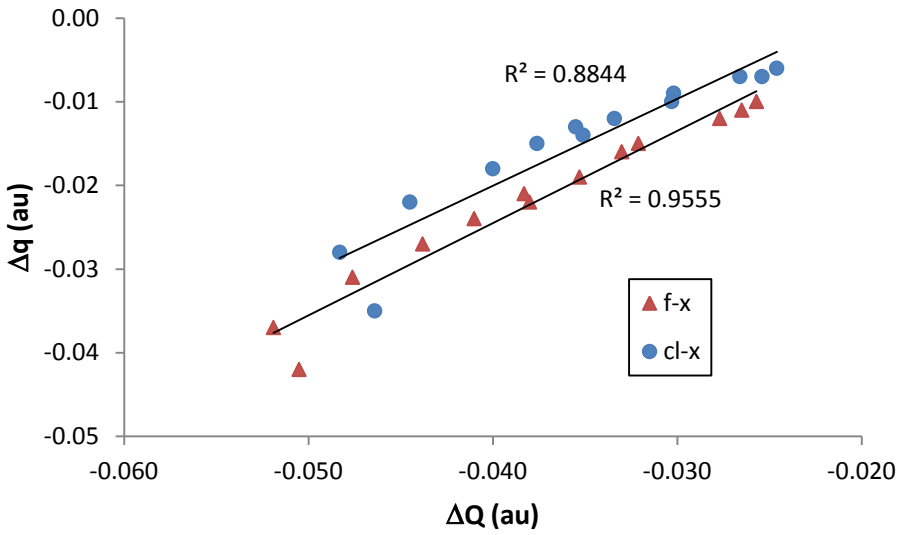


Figure S3. AIM Electronic charge shift (ΔQ) from the Lewis base to the Lewis acid versus NBO electronic charge shift (Δq) from the Lewis base to the Lewis in **f-x** and **cl-x** complexes.

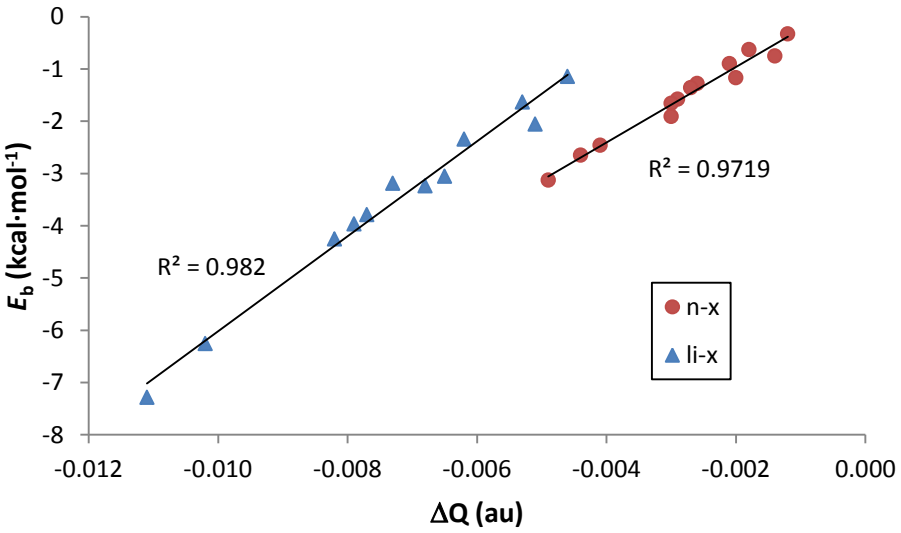


Figure S4. AIM Electronic charge shift (ΔQ) from the Lewis base to the Lewis acid versus the binding energy (E_b) in **li-x** and **n-x** complexes.

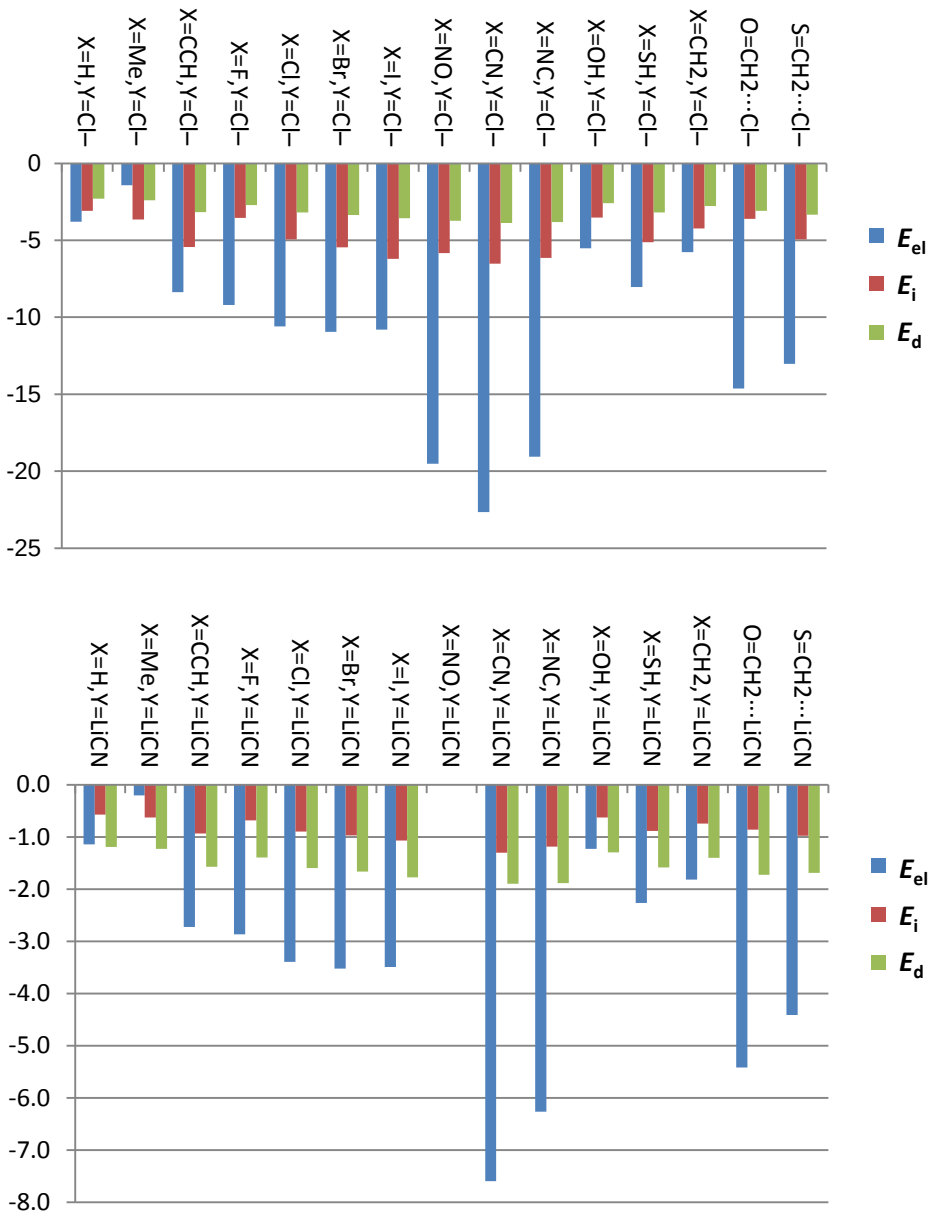


Figure S5. SAPT electrostatic, induction, and dispersion energy contributions (E_{el}, E_i, and E_d, respectively) of **cl-x** (top) and **li-x** (bottom) complexes. Energies in kcal·mol^{-1}.

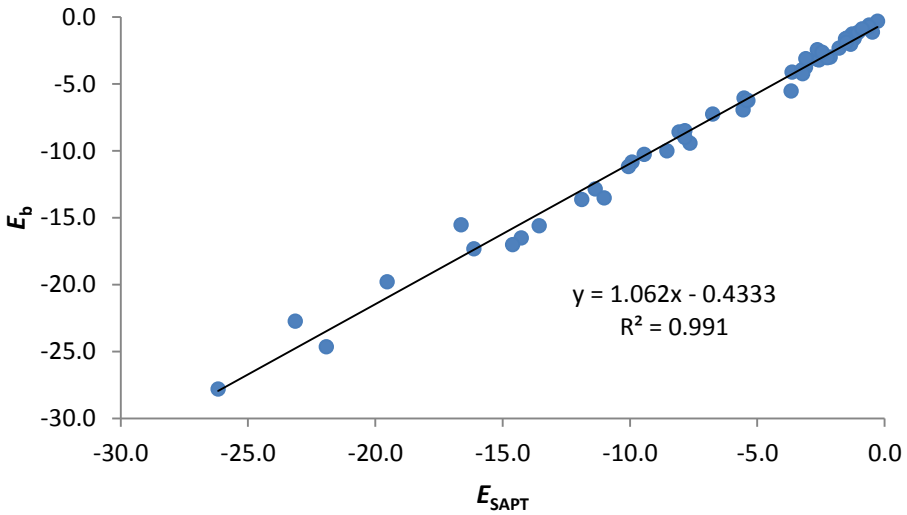


Figure S6. Representation of the SAPT total energy (E_{SAPT}) versus the binding energy (E_b) for all complexes. Energies in kcal·mol^{-1}.

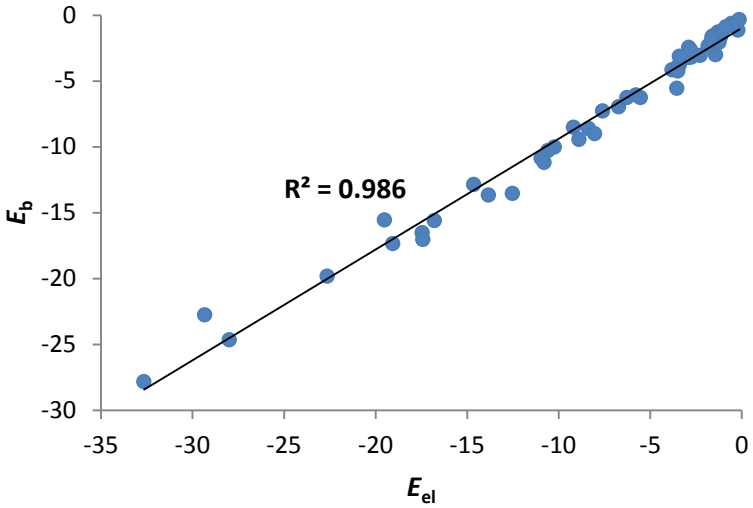


Figure S7. Representation of the SAPT electrostatic contribution (E_{el}) versus the binding energy (E_b) for all complexes. Energies in kcal·mol^{-1}.

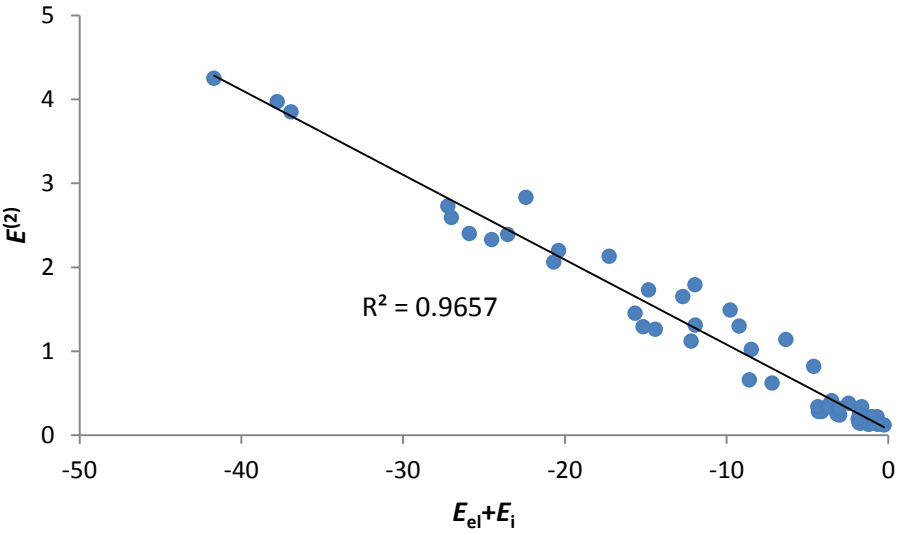


Figure S8. Representation of the sum of E_{el} and E_i (E_{el}+E_i) versus the second-order perturbation stabilization energies for the donor-acceptor Lp(Y)→σ*(C1–C2) and Lp(Y)→π*(C1=C2) ($E^{(2)}$) for all complexes. Energies in kcal·mol^{-1}.

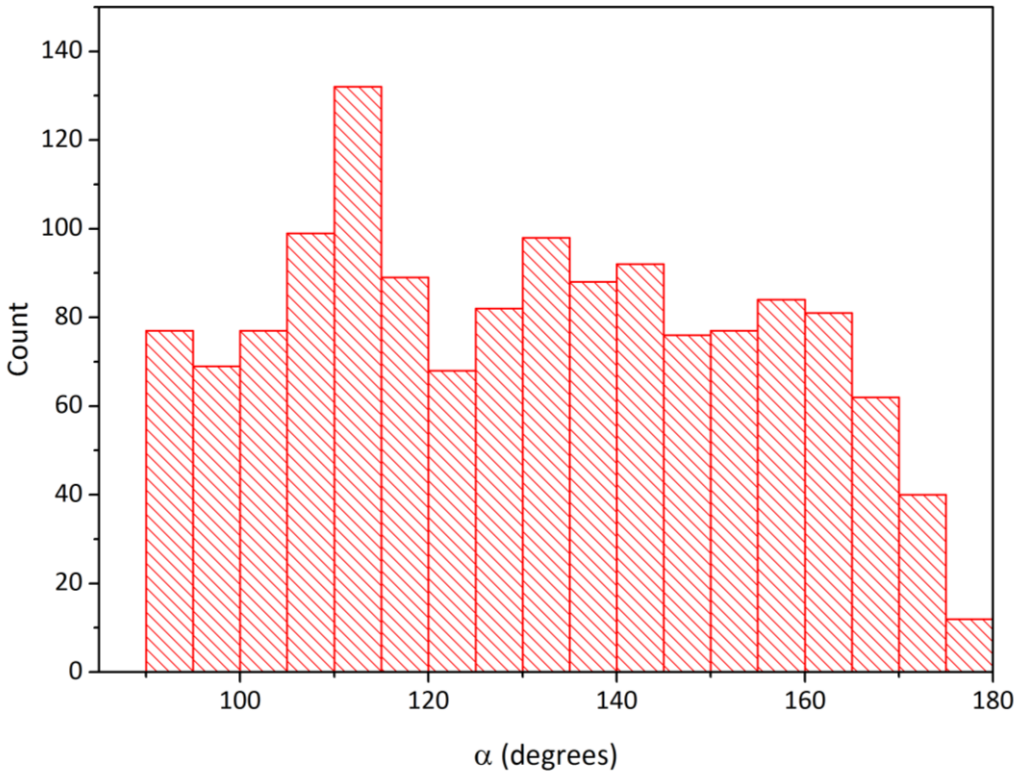


Figure S9. Histogram of the β angle distribution in neutral carbon-bonding complexes retrieved from the CSD search.

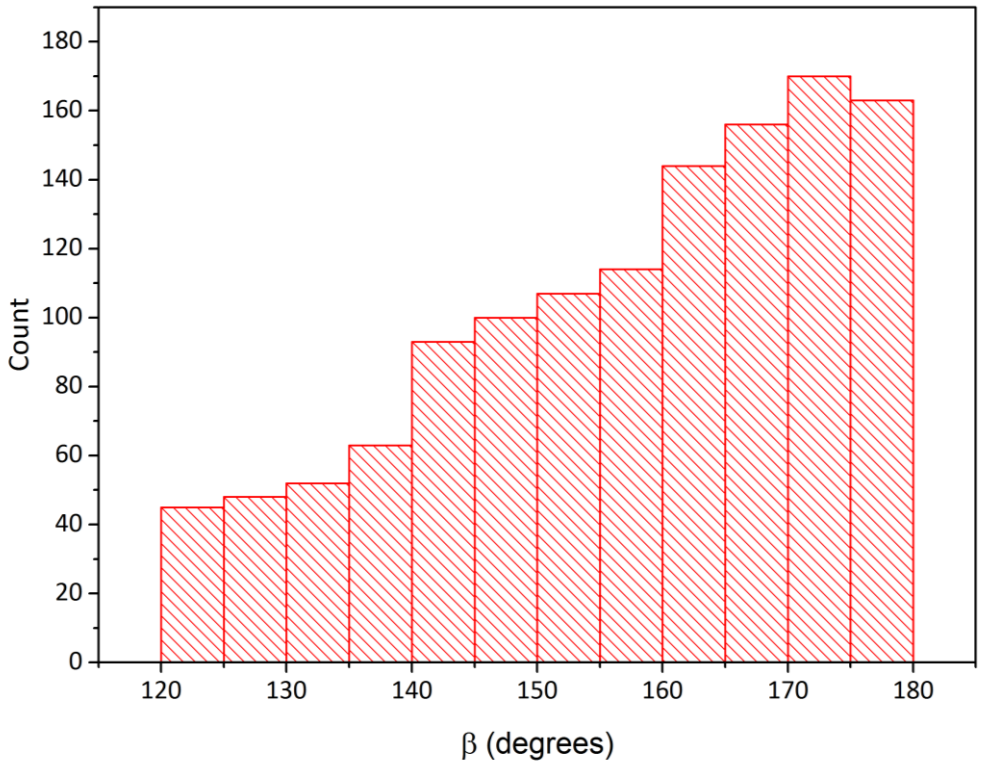


Figure S10. Histogram of the β angle distribution in neutral carbon-bonding complexes retrieved from the CSD search.

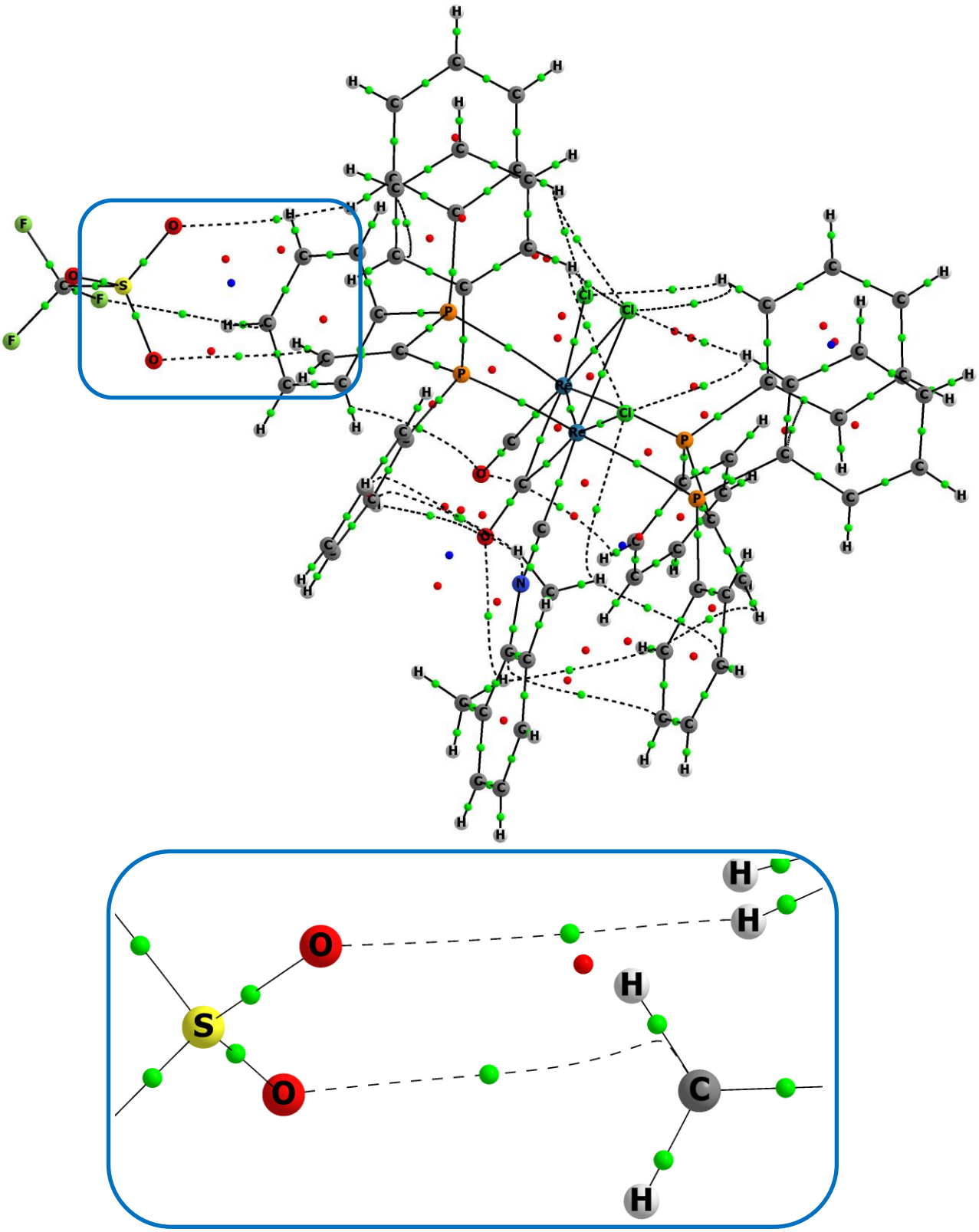


Figure S11. Geometry of a fragment of the X-ray structure with reference code EBOJOU retrieved from the CSD and its molecular graph, calculated at BP86/def2-TZVP computational level. Bond, ring and cage critical points are denoted with green, red and blue spheres, respectively.

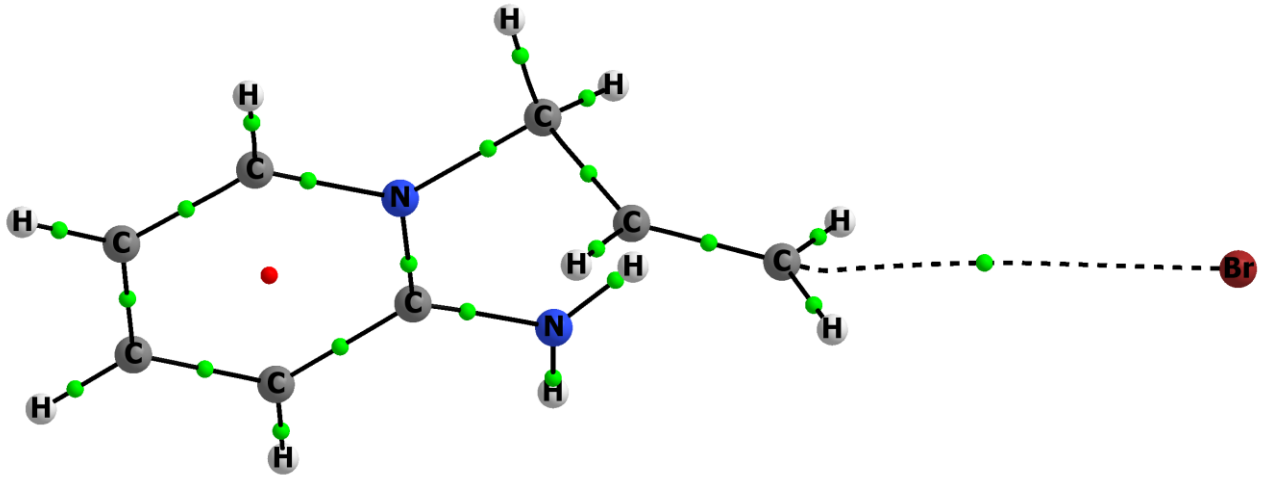


Figure S12. Geometry of a fragment of the X-ray structure with reference code IGAMAG retrieved from the CSD and its molecular graph, calculated at BP86/def2-TZVP computational level. Bond and ring critical points are denoted with green and red spheres, respectively.

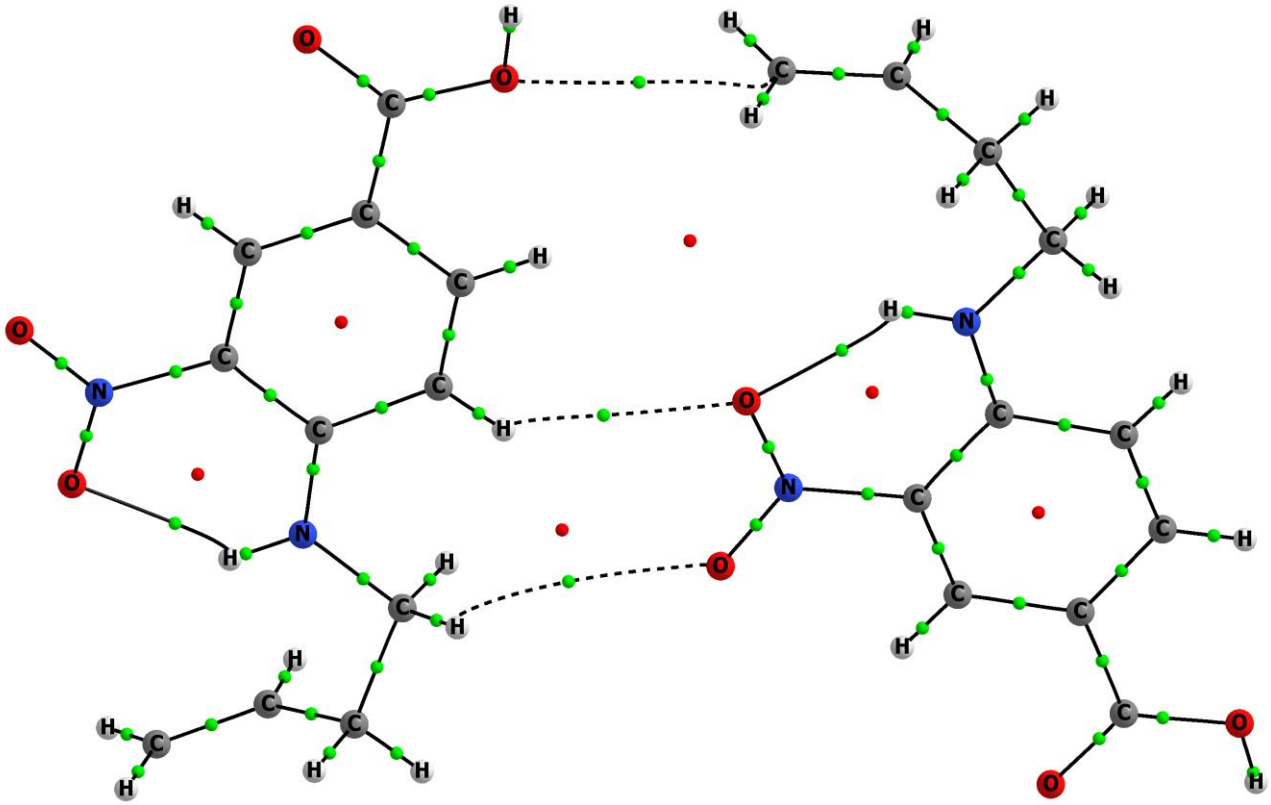


Figure S13. Geometry of a fragment of the X-ray structure with reference code POWLOD retrieved from the CSD and its molecular graph, calculated at BP86/def2-TZVP computational level. Bond and ring critical points are denoted with green and red spheres, respectively.

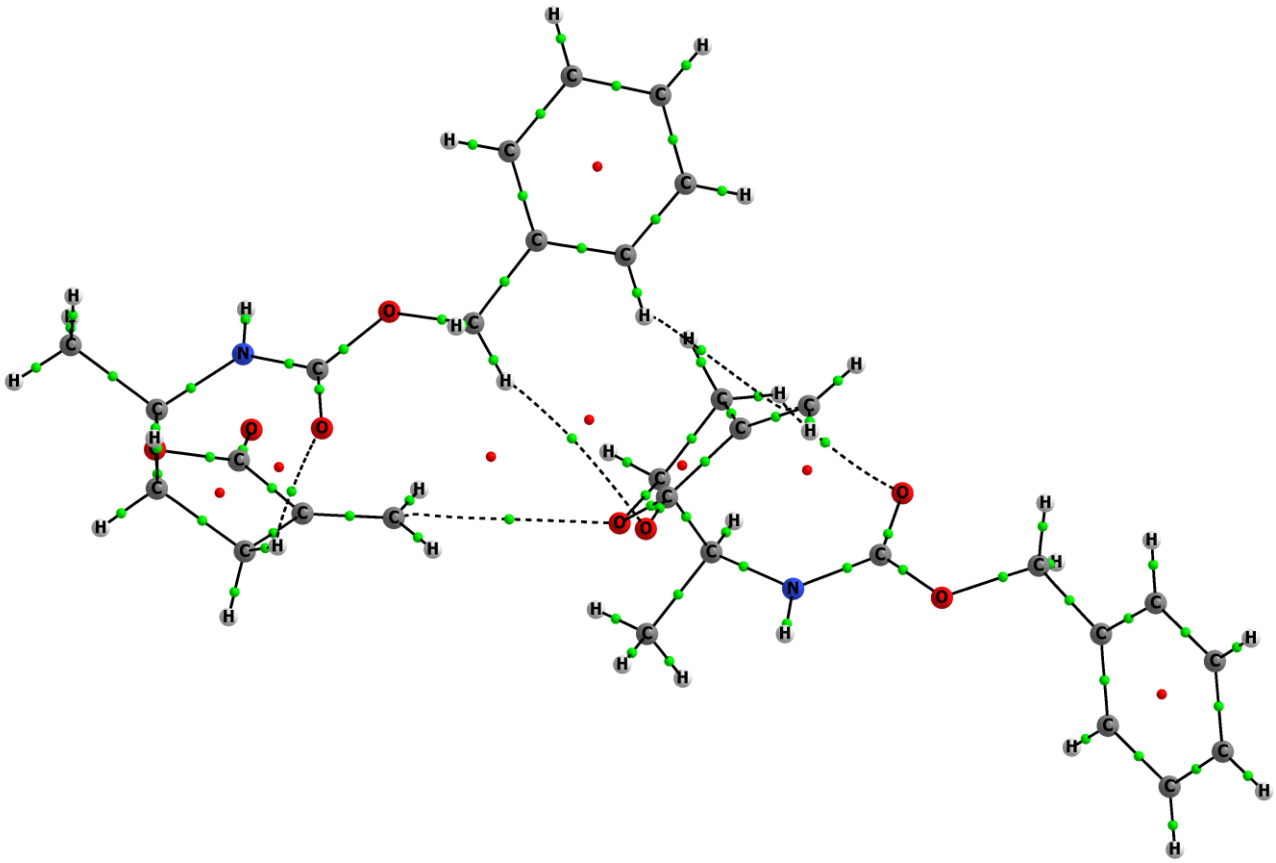


Figure S14. Geometry of a fragment of the X-ray structure with reference code LIQGOH retrieved from the CSD and its molecular graph, calculated at BP86/def2-TZVP computational level. Bond and ring critical points are denoted with green and red spheres, respectively.