Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Inverse halogen dependence in anion ^{13}C NMR

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1 Cartesian coordinates

Optimized geometries were obtained through CCSD theory with aug-cc-pVTZ basis set for all atoms except iodine for which aug-cc-pVTZ-PP was applied. These geometries correspond to energy minima on the potential energy surface and only real frequencies were obtained from the Hessian second order matrix.

Methane (CH_4):

C	0.00000000	0.00000000	0.00000000
H	0.00000000	1.02612300	-0.36278900
H	0.88864900	-0.51306200	-0.36278900
H	-0.88864900	-0.51306200	-0.36278900
H	0.00000000	0.00000000	1.08836800

HF Energy: -40.2135973 a.u.
CCSD Energy: -40.4343745 a.u.

Trifluoromethane (CHF_3):

C	0.00000000	-0.00000000	0.00000000
F	0.00000000	1.24623200	-0.46699400
F	1.07926800	-0.62311600	-0.46699400
F	-1.07926800	-0.62311600	-0.46699400
H	0.00000000	-0.00000000	1.08659700

HF Energy: -336.9119876 a.u.
CCSD Energy: -337.8500545 a.u.

Trifluoromethyl cation (CF_3^+):

C	0.00000000	-0.00000000	0.00000000
F	0.00000000	1.22901000	0.00045000
F	1.06435400	-0.61450500	0.00045000
F	-1.06435400	-0.61450500	0.00045000

HF Energy: -335.948098 a.u.
CCSD Energy: -336.8390365 a.u.

Trifluoromethyl anion (CF_3^-):

C	0.00000000	-0.00000000	0.00000000
F	0.00000000	1.25386600	-0.66542100
F	1.08587900	-0.62693300	-0.66542100
F	-1.08587900	-0.62693300	-0.66542100

HF Energy: -336.2776675 a.u.
CCSD Energy: -337.2280157 a.u.

Trichloromethane ($CHCl_3$):

C	0.00000000	0.00000000	0.00000000
Cl	0.00000000	1.68109500	-0.54408000
Cl	1.45587100	-0.84054700	-0.54408000
Cl	-1.45587100	-0.84054700	-0.54408000
H	0.00000000	0.00000000	1.08009100

HF Energy: -1417.0024989 a.u.
CCSD Energy: -1417.8025167 a.u.

Trichloromethyl cation (CCl_3^+):

C	0.00000000	0.00000000	0.00000000
Cl	0.00000000	1.64904300	-0.00008800
Cl	1.42811300	-0.82452200	-0.00008800
Cl	-1.42811300	-0.82452200	-0.00008800

HF Energy: -1416.0837818 a.u.
CCSD Energy: -1416.8447435 a.u.

Trichloromethyl anion (CCl_3^-):

C	0.00000000	0.00000000	-0.66023000
Cl	0.00000000	1.69895700	0.14364500
Cl	1.47134000	-0.84947800	0.14364500
Cl	-1.47134000	-0.84947800	0.14364500

HF Energy: -1416.4083861 a.u.
CCSD Energy: -1417.2122562 a.u.

Tribromomethane ($CHBr_3$):

C	0.00000000	-0.00000000	0.00000000
Br	0.00000000	1.83490200	-0.56767100
Br	1.58907200	-0.91745100	-0.56767100
Br	-1.58907200	-0.91745100	-0.56767100
H	0.00000000	-0.00000000	1.07865400

HF Energy: -7755.8271134 a.u.
CCSD Energy: -7756.7324983 a.u.

Tribromomethyl cation (CBr_3^+):

C	0.00000000	0.00000000	0.00000000
Br	0.00000000	1.80755100	0.00006500

Br	1.56538500	-0.90377500	0.00006500
Br	-1.56538500	-0.90377500	0.00006500

HF Energy: -7754.912321 a.u.
CCSD Energy: -7755.7823191 a.u.

Tribromomethyl anion (CBr_3^-):

C	0.00000000	-0.00000000	0.00000000
Br	0.00000000	1.85510800	-0.85124000
Br	1.60657100	-0.92755400	-0.85124000
Br	-1.60657100	-0.92755400	-0.85124000

HF Energy: -7755.2452733 a.u.
CCSD Energy: -7756.1510289 a.u.

Triiodomethane (CHI_3):

C	0.00000000	-0.00000000	0.00000000
I	0.00000000	2.04938400	-0.58906700
I	1.77481800	-1.02469200	-0.58906700
I	-1.77481800	-1.02469200	-0.58906700
H	0.00000000	-0.00000000	1.07988200

HF Energy: -922.4210916 a.u.
CCSD Energy: -923.2730134 a.u.

Triiodomethyl cation (CI_3^+):

C	0.00000000	0.00000000	0.00000000
I	0.00000000	2.02708300	-0.00002200
I	1.75550600	-1.01354200	-0.00002200
I	-1.75550600	-1.01354200	-0.00002200

HF Energy: -921.5190798 a.u.
CCSD Energy: -922.339006 a.u.

Triiodomethyl anion (CI_3^-):

C	0.00000000	-0.00000000	0.00000000
I	0.00000000	2.06272200	-0.88670800
I	1.78637000	-1.03136100	-0.88670800
I	-1.78637000	-1.03136100	-0.88670800

HF Energy: -921.8470881 a.u.
CCSD Energy: -922.6997852 a.u.

2 Geometrical parameters

Table S1: Bond lengths (in Å) and bond angles (in °) calculated[a] for CHX_3, CX_3^+, and CX_3^- (X = F, Cl, Br, or I) molecules.

	Neutral (CHX_3)				Cation (CX_3^+)				Anion (CX_3^-)			
	F	**Cl**	**Br**	**I**	**F**	**Cl**	**Br**	**I**	**F**	**Cl**	**Br**	**I**
$\mathbf{r_{C\text{-}H}}$	1.087	1.080	1.079	1.080	-	-	-	-	-	-	-	-
$\mathbf{r_{C\text{-}X}}$	1.331	1.767	1.921	2.132	1.229	1.649	1.807	2.027	1.419	1.879	2.041	2.245
$\mathbf{\angle_{H\text{-}C\text{-}X}}$	110.5	107.9	107.2	106.0	-	-	-	-	-	-	-	-
$\mathbf{\angle_{X\text{-}C\text{-}X}}$	108.4	111.0	111.6	112.7	120.0	120.0	120.0	120.0	99.8	103.0	103.8	105.4

[a] Calculations were performed through CCSD theory with aug-cc-pVTZ basis set for all atoms except iodine for which aug-cc-pVTZ-PP was applied.

3 DFT benchmark

The calibration study was performed for CHX_3 and CX_3^+ compounds to find the level of theory able to reproduce the experimental values. The role of ten different functionals (KT2, OLYP, OPBE, PBE, PW91, B1PW91, B3LYP, OPBE0, and PBE0) and seven basis sets (TZ2P, TZ2P-J, ATZ2P, QZ3P-1D, jcpl, QZ4P, and QZ4P-J) was evaluated as well as the inclusion of implict solvent (COSMO) and terms from DFT exchange-correlation response kernel (f_{XC}). The δ^{13}C of anions were also calculated in the same levels of theory. The relativistic correction SO-ZORA was applied to all chemical shift calculations. Results are displayed in Tables S2-S11.

GGA functionals (KT2, OLYP, OPBE, PBE, and PW91) show large deviations from experimental values, and no systematic improvement is observed with the increase of the size of basis set. The inclusion of solvent is important to decrease the root mean square deviation (RMSD) for cations, however, the opposite effect is observed for neutral compounds. The effect of f_{XC} is inconsistent for OLYP, PBE, and PW91 functionals as deviations significantly decrease for bromine and iodine derivatives of CHX_3, but it increases for CX_3^+. The f_{XC} is not implement to be used with KT2 and OPBE in the ADF program.

On the other hand, results from hybrid functionals (B1PW91, B3LYP, OPBE0, and PBE0) show good agreement with the experimental values, mainly the B1PW91, OPBE0, and PBE0. For these functionals, the RMSD is smaller than 10 ppm, which is acceptable for studies of δ^{13}C for molecules containing heavy atoms. In general, results obtained with hybrid functionals improve with the increase of the size of basis set, the inclusion of small effects of solvent, and f_{XC}. The inclusion of f_{XC} improves the computation of SO contributions for both CHX_3 and CX_3^+ systems, mainly reducing the RMSD when the X is bromine or iodine. The level of theory B1PW91/QZ4P/COSMO/f_{XC} was chosen for the analysis of shielding mechanisms due to smaller RMSD across the halogen series of both neutral and cations.

Regarding the anions, all levels of theory investigated display an inverse halogen dependency across the series. The main difference between them is the intensity of increased chemical shift for CI_3^-, associated with the inclusion of f_{XC}. The f_{XC} increases the δ^{13}C of CI_3^- for both GGA and hybrid functiontals.

Table S2: Carbon shielding tensor[a] (σ^{13}C) calculated for CH_4 reference molecule using different combinations of levels of theory.

Basis set	Solvent[b]	XC[c]	Functional								
			KT2	OLYP	OPBE	PBE	PW91	B1PW91	B3LYP	OPBE0	PBE0
TZ2P	isolated	-	200.50	197.22	200.66	195.73	195.11	196.65	193.25	201.42	197.84
		f_{XC}	-	197.24	-	195.74	195.12	196.66	193.26	201.43	197.85
	COSMO	-	201.29	198.01	201.54	196.57	195.94	197.51	194.02	202.31	198.70
		f_{XC}	-	198.02	-	196.58	195.95	197.52	194.04	202.32	198.71
TZ2P-J	isolated	-	192.64	187.70	190.44	188.30	187.67	189.42	186.72	192.29	190.69
		f_{XC}	-	187.72	-	188.32	187.69	189.43	186.73	192.30	190.70
	COSMO	-	193.58	188.61	191.50	189.29	188.65	190.43	187.61	193.36	191.70
		f_{XC}	-	188.63	-	189.31	188.66	190.44	187.63	193.37	191.72
ATZ2P	isolated	-	196.21	193.17	197.13	191.89	191.42	194.53	190.78	199.77	195.80
		f_{XC}	-	192.94	-	191.80	191.28	194.54	190.79	199.78	195.81
	COSMO	-	197.06	193.97	198.08	192.79	192.30	195.51	191.65	200.79	196.78
		f_{XC}	-	193.74	-	192.70	192.17	195.52	191.66	200.80	196.79
QZ3P-1D	isolated	-	195.92	190.89	193.57	191.04	190.31	191.90	189.32	195.15	193.25
		f_{XC}	-	190.87	-	191.04	190.31	191.90	189.31	195.16	193.26
	COSMO	-	196.73	191.67	194.49	191.90	191.16	192.66	189.98	195.94	194.00
		f_{XC}	-	191.65	-	191.90	191.15	192.67	189.97	195.94	194.00
jcpl	isolated	-	200.99	197.15	200.04	195.96	195.27	196.50	193.63	200.96	197.88
		f_{XC}	-	197.17	-	195.97	195.28	196.51	193.64	200.97	197.89
	COSMO	-	201.75	197.91	200.91	196.77	196.08	197.35	194.40	201.85	198.74
		f_{XC}	-	197.92	-	196.78	196.09	197.36	194.41	201.86	198.75
QZ4P	isolated	-	195.59	190.21	193.07	190.51	189.81	191.27	188.58	194.58	192.61
		f_{XC}	-	190.19	-	190.53	189.82	191.28	188.59	194.59	192.62
	COSMO	-	196.43	191.00	194.01	191.40	190.68	192.20	189.38	195.56	193.54
		f_{XC}	-	190.98	-	191.41	190.69	192.21	189.39	195.57	193.54
QZ4P-J	isolated	-	194.51	189.60	192.37	189.79	189.13	191.00	188.10	194.54	192.28
		f_{XC}	-	189.62	-	189.82	189.15	191.01	188.11	194.55	192.29
	COSMO	-	195.34	190.38	193.31	190.67	189.99	191.92	188.89	195.51	193.20
		f_{XC}	-	190.41	-	190.69	190.01	191.94	188.91	195.52	193.21

[a] in ppm. [b] COSMO was applied with parameters for chloroform. [c] Terms from the DFT exchange-correlation response kernel (f_{XC}) were included to improve the spin-orbit (SO) contribution.

Table S3: Carbon chemical shifts[a] (δ^{13}C) and the root mean square deviation (RMSD)[b] calculated for CHX_3, CX_3^+, and CX_3^- (X = F, Cl, Br, or I) molecules. Calculations were performed combining KT2 functional with different levels of theory.

Basis set	Solvent[c]	Neutral (CHX_3)					Cation (CX_3^+)					Anion (CX_3^-)			
		F	Cl	Br	I	RMSD	F	Cl	Br	I	RMSD	F	Cl	Br	I
TZ2P	**isolated**	119.57	91.96	24.53	-155.51	11.05	150.78	214.49	179.55	47.70	29.44	176.11	194.56	214.23	236.09
	COSMO	120.63	92.99	27.30	-147.43	13.93	150.65	216.35	183.19	56.95	24.56	176.57	188.42	203.15	214.80
TZ2P-J	**isolated**	126.90	93.09	23.98	-155.56	11.42	158.07	219.58	185.83	61.67	21.75	174.63	199.91	224.08	246.95
	COSMO	128.29	94.40	26.98	-147.41	14.55	157.91	221.48	189.52	70.96	16.99	176.14	194.04	212.27	223.98
ATZ2P	**isolated**	121.88	89.60	21.45	-	9.87	154.40	209.28	172.98	-	25.17	168.91	187.62	210.78	-
	COSMO	123.09	90.60	24.29	-	11.45	154.31	211.13	176.47	-	22.94	169.12	182.90	200.18	-
QZ3P-1D	**isolated**	124.49	95.30	28.26	-	15.03	155.58	219.50	186.22	-	15.68	176.37	197.11	222.91	-
	COSMO	125.75	96.23	31.14	-	16.68	155.60	221.37	189.93	-	13.40	177.35	191.90	211.56	-
jcpl	**isolated**	120.00	92.11	25.43	-155.12	11.44	151.64	214.37	179.88	46.48	29.88	175.74	194.56	215.50	237.54
	COSMO	121.03	93.11	28.13	-147.41	14.23	151.53	216.16	183.37	55.39	25.17	176.08	188.41	204.26	216.26
QZ4P	**isolated**	125.61	95.84	25.80	-152.18	13.38	155.56	221.97	187.80	64.87	19.40	177.38	197.40	222.67	244.52
	COSMO	126.89	96.88	28.78	-144.28	16.51	155.40	223.88	191.57	73.96	14.64	178.40	192.51	211.22	222.66
QZ4P-J	**isolated**	125.27	94.67	25.32	-153.86	12.51	157.01	221.06	187.71	64.05	20.01	176.62	198.02	222.95	245.38
	COSMO	126.52	95.66	28.26	-146.16	15.47	156.87	222.91	191.39	72.76	15.46	177.54	192.97	211.61	223.70
Experimental[d,e]		122.20[f]	77.22	9.67	-162.08	-	150.70[g]	236.30[g]	207.00[g]	95.00[g]	-	175.00[f]	-	-	-

[a] in ppm. [b] Estimated by the deviation between theoretical and experimental values. [c] COSMO was applied with parameters for chloroform. [d] Experimental δ^{13}C for CH_4 is equal to -8.65 ppm.[1] [e] Error = 0.01 ppm. [f] Reference 2. [g] Reference 3.

Table S4: Carbon chemical shifts[a] (δ^{13}C) and the root mean square deviation (RMSD)[b] calculated for CHX_3, CX_3^+, and CX_3^- (X = F, Cl, Br, or I) molecules. Calculations were performed combining OLYP functional with different levels of theory.

Basis set	Solvent[c]	XC[d]	Neutral (CHX_3)					Cation (CX_3^+)					Anion (CX_3^-)			
			F	Cl	Br	I	RMSD	F	Cl	Br	I	RMSD	F	Cl	Br	I
TZ2P	isolated	-	122.34	96.56	33.61	-133.63	20.96	154.21	222.70	193.98	78.34	12.69	182.50	203.01	221.20	237.55
		f_{XC}	122.10	93.93	17.15	-166.70	9.44	153.48	216.64	157.18	-0.98	54.97	182.08	204.83	240.65	361.63
	COSMO	-	123.44	97.59	36.15	-126.47	24.42	154.18	224.61	197.68	87.41	8.56	183.02	196.18	208.94	212.95
		f_{XC}	123.18	95.02	20.08	-160.93	10.34	153.46	218.54	161.00	7.11	50.41	182.60	197.56	225.66	322.10
TZ2P-J	isolated	-	127.67	95.42	31.02	-134.08	20.01	159.00	224.31	196.36	89.02	9.51	178.31	205.31	228.30	246.15
		f_{XC}	127.46	93.00	15.98	-163.26	8.91	158.37	218.74	162.42	15.54	46.55	177.93	207.37	248.55	370.93
	COSMO	-	129.03	96.69	33.81	-126.74	23.76	158.88	226.24	200.09	98.20	7.52	179.73	198.76	215.38	219.99
		f_{XC}	128.82	94.33	19.13	-157.41	10.58	158.26	220.66	166.27	23.62	42.00	179.37	200.38	232.91	330.25
ATZ2P	isolated	-	125.72	94.07	30.59	-	15.64	158.30	217.47	187.75	-	16.15	175.77	194.68	217.61	-
		f_{XC}	125.13	91.01	11.42	-	8.20	157.01	210.92	151.64	-	35.35	176.43	197.58	237.47	-
	COSMO	-	126.90	95.12	33.32	-	17.34	158.23	219.31	191.20	-	14.08	175.86	189.48	205.97	-
		f_{XC}	126.31	92.11	14.52	-	9.35	156.93	212.75	155.16	-	33.07	175.56	190.89	221.89	-
QZ3P-1D	isolated	-	126.30	98.35	36.78	-	19.99	157.73	225.72	198.34	-	8.88	182.02	203.74	229.20	-
		f_{XC}	126.04	93.49	11.60	-	9.72	157.02	214.47	143.78	-	38.79	183.15	201.68	249.39	-
	COSMO	-	127.53	99.37	39.64	-	21.74	157.74	227.65	202.07	-	7.04	182.64	198.11	216.72	-
		f_{XC}	127.26	94.57	14.82	-	10.85	157.05	215.86	146.29	-	37.17	182.49	196.39	231.27	-
jcpl	isolated	-	122.25	96.01	33.85	-133.11	21.08	154.54	221.98	193.67	77.26	13.34	181.35	202.11	221.52	237.59
		f_{XC}	122.05	93.76	19.51	-160.49	9.66	153.96	216.72	161.25	5.05	51.42	180.99	204.18	241.86	361.14
	COSMO	-	123.31	97.02	36.35	-126.27	24.43	154.52	223.81	197.23	86.05	9.30	181.83	195.28	209.11	213.00
		f_{XC}	123.10	94.82	22.35	-155.13	11.40	153.94	218.55	164.91	12.83	47.03	181.47	196.91	226.69	322.25
QZ4P	isolated	-	126.43	98.34	33.74	-129.34	23.00	156.77	227.18	199.89	94.59	6.53	181.26	202.56	227.95	243.99
		f_{XC}	126.25	96.20	20.82	-156.62	11.52	156.20	222.14	169.87	27.39	39.31	181.17	203.38	247.34	358.17
	COSMO	-	127.66	99.44	36.65	-121.87	26.78	156.61	229.15	203.69	103.61	6.54	182.38	197.40	215.42	219.55
		f_{XC}	127.48	97.34	24.05	-151.29	13.75	156.05	224.10	173.66	34.29	35.27	182.22	198.68	232.78	323.87
QZ4P-J	isolated	-	126.18	96.73	32.71	-132.10	21.37	158.27	226.15	199.15	92.30	7.57	180.53	202.59	227.38	244.03
		f_{XC}	125.98	94.31	18.56	-163.25	9.83	157.64	220.57	166.84	19.73	43.51	180.23	203.21	247.39	360.53
	COSMO	-	127.39	97.78	35.59	-124.82	25.05	158.11	228.03	202.83	100.99	6.64	181.57	197.21	214.90	219.63
		f_{XC}	127.21	95.40	21.80	-158.17	11.38	157.51	222.45	170.55	26.20	39.69	181.27	198.41	232.61	326.25
Experimental[e,f]			122.20[g]	77.22	9.67	-162.08	-	150.70[h]	236.30[h]	207.00[h]	95.00[h]	-	175.00[g]	-	-	-

[a] in ppm. [b] Estimated by the deviation between theoretical and experimental values. [c] COSMO was applied with parameters for chloroform. [d] Terms from the DFT exchange-correlation response kernel (f_{XC}) were included to improve the spin-orbit (SO) contribution. [e] Experimental δ^{13}C for CH_4 is equal to -8.65 ppm.[1] [f] Error = 0.01 ppm. [g] Reference 2. [h] Reference 3.

Table S5: Carbon chemical shifts[a] (δ^{13}C) and the root mean square deviation (RMSD)[b] calculated for CHX_3, CX_3^+, and CX_3^- (X = F, Cl, Br, or I) molecules. Calculations were performed combining OPBE functional with different levels of theory.

Basis set	Solvent[c]	Neutral (CHX_3)					Cation (CX_3^+)					Anion (CX_3^-)			
		F	Cl	Br	I	RMSD	F	Cl	Br	I	RMSD	F	Cl	Br	I
TZ2P	**isolated**	120.17	93.66	34.09	-125.99	23.31	151.81	215.52	187.35	72.70	18.14	178.24	192.93	208.67	222.21
	COSMO	121.37	94.75	36.43	-119.52	26.62	151.94	217.48	190.94	81.34	14.14	178.53	186.77	197.48	199.64
TZ2P-J	**isolated**	126.28	92.89	31.57	-126.30	22.48	157.29	217.63	190.03	84.03	14.14	175.22	196.16	215.53	229.91
	COSMO	127.82	94.28	34.19	-119.66	26.09	157.42	219.67	193.72	92.83	11.21	176.54	190.29	203.76	205.93
ATZ2P	**isolated**	124.21	91.83	32.06	-	15.48	156.71	210.88	181.94	-	20.90	172.39	186.27	206.02	-
	COSMO	125.57	92.96	34.63	-	17.15	156.85	212.83	185.40	-	18.75	172.42	181.52	195.32	-
QZ3P-1D	**isolated**	124.68	95.87	37.96	-	19.62	155.87	219.35	192.09	-	13.37	178.61	195.56	217.40	-
	COSMO	126.07	96.98	40.63	-	21.32	156.09	221.41	195.83	-	11.19	179.23	190.28	205.84	-
jcpl	**isolated**	119.38	92.61	34.15	-125.32	23.43	151.55	214.09	186.57	71.44	19.15	176.34	191.20	207.98	221.08
	COSMO	120.56	93.71	36.47	-119.18	26.61	151.70	216.01	190.05	79.81	15.25	176.62	185.08	196.73	198.68
QZ4P	**isolated**	124.72	95.97	34.84	-120.75	25.98	154.48	220.82	193.78	89.95	10.66	177.68	193.84	215.75	227.67
	COSMO	126.13	97.16	37.58	-113.95	29.62	154.56	222.90	197.55	98.54	8.61	178.70	189.08	204.20	205.37
QZ4P-J	**isolated**	124.48	94.18	33.60	-123.65	24.20	156.14	219.43	192.91	87.78	11.88	176.97	193.68	215.06	227.59
	COSMO	125.70	95.32	36.32	-117.03	27.75	156.23	221.46	196.61	96.08	9.49	177.93	188.73	203.57	205.34
Experimental[d,e]		122.20[f]	77.22	9.67	-162.08	-	150.70[g]	236.30[g]	207.00[g]	95.00[g]	-	175.00[f]	-	-	-

[a] in ppm. [b] Estimated by the deviation between theoretical and experimental values. [c] COSMO was applied with parameters for chloroform. [d] Experimental δ^{13}C for CH_4 is equal to -8.65 ppm.[1] [e] Error = 0.01 ppm. [f] Reference 2. [g] Reference 3.

Table S6: Carbon chemical shifts[a] (δ^{13}C) and the root mean square deviation (RMSD)[b] calculated for CHX_3, CX_3^+, and CX_3^- (X = F, Cl, Br, or I) molecules. Calculations were performed combining PBE functional with different levels of theory.

Basis set	Solvent[c]	XC[d]	Neutral (CHX_3)					Cation (CX_3^+)					Anion (CX_3^-)			
			F	Cl	Br	I	RMSD	F	Cl	Br	I	RMSD	F	Cl	Br	I
TZ2P	isolated	-	126.59	97.93	31.78	-145.63	17.38	159.62	230.70	200.65	77.71	10.61	191.17	210.11	229.41	247.90
		f_{XC}	126.40	96.02	20.09	-170.98	11.82	159.12	226.70	177.37	29.36	36.57	190.84	211.28	241.98	322.04
	COSMO	-	127.74	99.00	34.41	-138.14	20.56	159.58	232.75	204.48	86.86	6.40	191.50	202.18	215.20	219.73
		f_{XC}	127.56	97.14	23.05	-163.90	12.33	159.10	228.76	181.36	38.29	31.63	191.19	203.05	225.95	286.39
TZ2P-J	isolated	-	132.57	97.60	29.56	-147.47	16.82	165.42	232.82	203.15	86.82	8.81	187.35	212.96	236.72	256.42
		f_{XC}	132.40	95.77	18.47	-170.90	12.28	164.97	228.96	180.61	39.70	31.67	187.05	214.21	249.26	329.24
	COSMO	-	134.04	98.95	32.46	-139.78	20.18	165.35	234.90	207.01	96.03	7.38	188.70	205.35	221.80	226.59
		f_{XC}	133.88	97.17	21.68	-163.72	13.05	164.91	231.05	184.63	48.59	26.85	188.42	206.29	232.53	292.19
ATZ2P	isolated	-	130.33	95.81	29.06	-	16.20	164.38	225.82	194.49	-	12.29	184.20	202.23	225.75	-
		f_{XC}	129.95	93.69	16.51	-	11.23	163.58	221.60	171.77	-	23.26	184.25	203.80	238.01	-
	COSMO	-	131.62	96.87	31.82	-	17.94	164.38	227.83	198.15	-	10.60	184.23	196.30	212.39	-
		f_{XC}	131.24	94.79	19.57	-	12.76	163.57	223.62	175.55	-	20.94	183.95	197.11	222.33	-
QZ3P-1D	isolated	-	130.67	99.95	34.83	-	20.18	163.46	233.82	205.75	-	7.54	189.73	210.09	236.30	-
		f_{XC}	130.46	97.14	19.03	-	13.57	162.96	227.90	175.52	-	20.10	189.76	209.49	247.65	-
	COSMO	-	132.01	100.94	37.67	-	21.93	163.54	235.86	209.66	-	7.57	190.53	203.70	222.17	-
		f_{XC}	131.80	98.17	22.14	-	15.13	163.05	229.71	179.27	-	17.93	190.33	203.12	230.98	-
jcpl	isolated	-	126.71	97.75	32.26	-145.74	17.46	160.20	230.29	200.53	75.93	11.53	190.44	209.67	230.26	248.82
		f_{XC}	126.55	96.05	21.76	-167.77	11.75	159.78	226.68	179.27	30.19	35.86	190.14	210.96	243.02	321.69
	COSMO	-	127.84	98.79	34.84	-138.58	20.51	160.18	232.26	204.22	84.79	7.39	190.69	201.73	215.86	220.61
		f_{XC}	127.67	97.14	24.63	-161.12	12.76	159.77	228.68	183.11	38.78	31.11	190.40	202.71	226.78	286.27
QZ4P	isolated	-	131.41	100.43	31.78	-143.77	19.02	163.27	235.83	206.52	91.53	6.53	190.71	210.42	236.14	254.57
		f_{XC}	131.28	98.77	21.67	-166.05	13.29	162.87	232.27	185.77	48.38	26.40	190.57	211.14	247.99	321.88
	COSMO	-	132.77	101.54	34.73	-136.16	22.38	163.21	237.93	210.48	100.63	7.12	191.61	204.34	221.73	226.36
		f_{XC}	132.63	99.91	24.89	-159.40	14.68	162.81	234.36	189.83	56.47	21.96	191.45	205.19	232.33	289.19
QZ4P-J	isolated	-	131.08	98.89	30.77	-146.03	17.69	164.46	234.39	205.33	89.52	7.51	189.33	209.96	235.23	254.11
		f_{XC}	130.92	97.04	20.05	-170.29	12.69	164.02	230.54	183.58	43.70	29.12	189.07	210.59	247.54	323.14
	COSMO	-	132.41	99.94	33.68	-138.62	20.90	164.41	236.42	209.20	98.26	7.13	190.15	203.75	220.98	226.19
		f_{XC}	132.25	98.13	23.26	-163.83	13.47	163.97	232.57	187.56	51.39	24.85	189.89	204.55	231.92	290.79
Experimental[e,f]			122.20[g]	77.22	9.67	-162.08	-	150.70[h]	236.30[h]	207.00[h]	95.00[h]	-	175.00[g]	-	-	-

[a] in ppm. [b] Estimated by the deviation between theoretical and experimental values. [c] COSMO was applied with parameters for chloroform. [d] Terms from the DFT exchange-correlation response kernel (f_{XC}) were included to improve the spin-orbit (SO) contribution. [e] Experimental δ^{13}C for CH_4 is equal to -8.65 ppm.[1] [f] Error = 0.01 ppm. [g] Reference 2. [h] Reference 3.

Table S7: Carbon chemical shifts[a] (δ^{13}C) and the root mean square deviation (RMSD)[b] calculated for CHX_3, CX_3^+, and CX_3^- (X = F, Cl, Br, or I) molecules. Calculations were performed combining PW91 functional with different levels of theory.

Basis set	Solvent[c]	XC[d]	Neutral (CHX_3)					Cation (CX_3^+)					Anion (CX_3^-)			
			F	Cl	Br	I	RMSD	F	Cl	Br	I	RMSD	F	Cl	Br	I
TZ2P	isolated	-	127.19	98.81	31.98	-146.89	17.46	160.22	232.49	202.00	78.50	10.03	192.13	212.38	232.46	251.71
		f_{XC}	126.98	96.64	18.74	-175.20	12.79	159.66	227.96	175.61	23.89	39.34	191.75	213.56	245.63	331.82
	COSMO	-	128.33	99.88	34.65	-139.40	20.55	160.15	234.52	205.84	87.66	6.08	192.51	204.41	218.20	223.47
		f_{XC}	128.12	97.76	21.76	-168.25	12.66	159.59	230.00	179.62	32.71	34.45	192.15	205.25	229.39	295.33
TZ2P-J	isolated	-	132.99	98.37	29.59	-149.01	16.82	165.93	234.52	204.40	87.34	8.67	188.30	215.21	239.85	260.51
		f_{XC}	132.81	96.34	17.29	-174.47	13.13	165.44	230.28	179.53	35.73	33.62	187.97	216.55	253.48	341.08
	COSMO	-	134.45	99.72	32.53	-141.31	20.06	165.83	236.59	208.26	96.56	7.63	189.70	207.56	224.87	230.61
		f_{XC}	134.26	97.73	20.55	-167.43	13.35	165.34	232.34	183.55	44.49	28.86	189.37	208.54	236.51	303.12
ATZ2P	isolated	-	131.20	96.82	29.36	-	16.86	165.29	227.91	196.14	-	11.56	185.55	204.63	229.10	-
		f_{XC}	130.75	94.40	15.12	-	11.52	164.35	223.10	170.42	-	23.80	185.57	206.17	241.74	-
	COSMO	-	132.47	97.87	32.15	-	18.59	165.24	229.90	199.78	-	10.07	185.62	198.66	215.63	-
		f_{XC}	132.02	95.51	18.24	-	12.97	164.31	225.11	174.22	-	21.49	185.26	199.38	225.78	-
QZ3P-1D	isolated	-	131.12	100.47	34.75	-	20.41	163.98	235.31	206.81	-	7.69	190.80	212.25	239.49	-
		f_{XC}	130.89	97.33	17.33	-	13.40	163.42	228.41	172.22	-	21.86	190.79	211.14	253.16	-
	COSMO	-	132.45	101.48	37.64	-	22.18	164.03	237.33	210.68	-	8.01	191.49	205.76	225.17	-
		f_{XC}	132.21	98.36	20.49	-	14.88	163.48	230.11	175.65	-	19.87	191.25	204.96	234.94	-
jcpl	isolated	-	127.29	98.59	32.32	-147.30	17.42	160.81	232.12	201.87	76.51	11.04	191.49	212.05	233.45	252.94
		f_{XC}	127.12	96.71	20.63	-171.29	12.34	160.35	228.13	178.23	26.00	37.91	191.14	213.41	247.17	332.92
	COSMO	-	128.42	99.65	34.95	-140.12	20.39	160.77	234.09	205.57	85.39	7.08	191.79	204.06	218.98	224.61
		f_{XC}	128.24	97.81	23.58	-164.76	12.86	160.32	230.11	182.09	34.49	33.21	191.46	205.08	230.70	296.63
QZ4P	isolated	-	131.88	101.07	31.69	-145.58	18.84	163.84	237.54	207.67	91.85	6.79	191.68	212.56	239.36	258.81
		f_{XC}	131.74	99.28	20.79	-168.83	13.66	163.41	233.71	185.39	45.82	27.63	191.50	213.27	252.63	333.62
	COSMO	-	133.21	102.18	34.66	-137.96	22.08	163.73	239.62	211.64	100.96	7.71	192.60	206.45	224.84	230.50
		f_{XC}	133.07	100.43	24.07	-162.37	14.70	163.31	235.80	189.44	53.78	23.27	192.43	207.39	236.74	300.64
QZ4P-J	isolated	-	131.55	99.60	30.72	-147.73	17.59	165.02	236.05	206.50	89.91	7.60	190.26	212.10	238.40	258.31
		f_{XC}	131.38	97.54	18.80	-174.19	13.48	164.52	231.80	182.52	39.49	31.19	189.93	212.64	251.89	334.15
	COSMO	-	132.87	100.65	33.66	-140.33	20.68	164.92	238.05	210.36	98.63	7.58	191.15	205.86	224.03	230.26
		f_{XC}	132.70	98.63	22.08	-167.94	13.76	164.44	233.80	186.47	47.02	27.01	190.85	206.67	235.99	301.45
Experimental[e,f]			122.20[g]	77.22	9.67	-162.08	-	150.70[h]	236.30[h]	207.00[h]	95.00[h]	-	175.00[g]	-	-	-

[a] in ppm. [b] Estimated by the deviation between theoretical and experimental values. [c] COSMO was applied with parameters for chloroform. [d] Terms from the DFT exchange-correlation response kernel (f_{XC}) were included to improve the spin-orbit (SO) contribution. [e] Experimental δ^{13}C for CH_4 is equal to -8.65 ppm.[1] [f] Error = 0.01 ppm. [g] Reference 2. [h] Reference 3.

Table S8: Carbon chemical shifts[a] (δ^{13}C) and the root mean square deviation (RMSD)[b] calculated for CHX_3, CX_3^+, and CX_3^- (X = F, Cl, Br, or I) molecules. Calculations were performed combining B1PW91 functional with different levels of theory.

Basis set	Solvent[c]	XC[d]	Neutral (CHX_3)					Cation (CX_3^+)					Anion (CX_3^-)			
			F	Cl	Br	I	RMSD	F	Cl	Br	I	RMSD	F	Cl	Br	I
TZ2P	isolated	-	118.60	87.93	22.59	-153.64	9.56	158.42	245.61	221.72	112.00	12.77	184.11	198.14	222.85	269.15
		f_{XC}	118.46	86.41	13.12	-175.87	8.67	158.01	242.12	200.59	62.10	17.40	183.90	199.47	238.72	384.85
	COSMO	-	119.79	89.09	25.28	-146.18	12.68	158.14	247.55	225.58	121.64	17.58	183.75	190.19	207.68	233.96
		f_{XC}	119.65	87.61	16.06	-168.74	7.06	157.74	244.08	204.62	71.94	12.72	183.55	191.21	220.86	327.75
TZ2P-J	isolated	-	124.69	87.56	20.28	-155.28	8.25	164.06	247.99	225.37	123.44	19.11	180.98	201.48	230.14	277.50
		f_{XC}	124.56	86.09	11.17	-176.13	8.42	163.67	244.58	204.62	74.08	13.04	180.79	202.84	245.83	391.51
	COSMO	-	126.20	89.00	23.24	-147.58	11.72	163.77	249.91	229.25	133.15	24.01	181.71	193.88	214.27	240.69
		f_{XC}	126.07	87.57	14.36	-168.83	6.89	163.39	246.52	208.69	83.92	9.89	181.53	194.93	227.31	333.18
ATZ2P	isolated	-	119.74	87.75	22.01	-	9.47	159.41	242.70	220.54	-	10.00	177.68	193.75	221.76	-
		f_{XC}	119.60	86.24	12.63	-	5.68	159.00	239.25	199.23	-	6.78	177.53	194.95	237.02	-
	COSMO	-	121.11	88.88	24.76	-	11.03	159.15	244.53	224.15	-	12.02	178.21	187.72	207.47	-
		f_{XC}	120.97	87.42	15.66	-	6.87	158.75	241.10	203.03	-	5.88	178.03	188.69	220.41	-
QZ3P-1D	isolated	-	122.21	88.48	21.45	-	9.41	161.82	248.58	225.28	-	14.24	182.80	198.42	227.21	-
		f_{XC}	122.04	86.95	12.10	-	5.79	161.38	244.97	203.87	-	8.15	182.71	199.63	242.16	-
	COSMO	-	123.46	89.50	24.18	-	11.00	161.53	250.40	229.30	-	16.47	182.88	191.36	211.89	-
		f_{XC}	123.30	88.00	15.06	-	6.99	161.11	246.81	208.05	-	8.56	182.72	192.33	224.64	-
jcpl	isolated	-	118.35	87.64	23.04	-153.16	9.77	158.74	245.00	221.66	110.41	12.17	183.22	197.59	223.62	270.16
		f_{XC}	118.23	86.28	14.42	-172.93	7.72	158.39	241.80	202.05	62.28	17.21	183.02	199.01	239.63	384.48
	COSMO	-	119.53	88.77	25.69	-145.99	12.81	158.49	246.90	225.40	119.78	16.78	182.74	189.63	208.24	235.02
		f_{XC}	119.41	87.45	17.29	-166.15	6.84	158.15	243.73	205.96	71.80	12.75	182.55	190.74	221.54	327.96
QZ4P	isolated	-	122.05	88.16	21.73	-153.85	9.12	161.59	247.86	227.36	126.79	20.48	181.62	199.58	228.30	273.57
		f_{XC}	121.92	86.74	13.07	-172.84	7.38	161.24	244.58	207.67	80.97	9.71	181.48	200.83	243.40	380.30
	COSMO	-	123.46	89.32	24.72	-146.21	12.51	161.34	249.88	231.41	136.32	25.50	181.76	192.88	213.56	239.61
		f_{XC}	123.34	87.93	16.26	-165.61	6.56	160.99	246.62	211.86	90.50	8.00	181.61	193.93	226.36	328.33
QZ4P-J	isolated	-	122.86	88.85	21.53	-153.53	9.35	162.24	248.49	227.30	125.37	20.10	184.32	199.79	228.52	273.39
		f_{XC}	122.71	87.31	12.42	-173.68	7.81	161.86	245.04	206.61	77.05	11.44	184.14	201.05	243.83	381.26
	COSMO	-	124.26	90.00	24.49	-146.05	12.69	161.96	250.46	231.28	134.69	24.96	183.78	193.23	213.71	239.83
		f_{XC}	124.12	88.49	15.61	-166.58	6.82	161.60	247.03	210.75	86.39	8.97	183.61	194.28	226.73	329.91
Experimental[e,f]			122.20[g]	77.22	9.67	-162.08	-	150.70[h]	236.30[h]	207.00[h]	95.00[h]	-	175.00[g]	-	-	-

[a] in ppm. [b] Estimated by the deviation between theoretical and experimental values. [c] COSMO was applied with parameters for chloroform. [d] Terms from the DFT exchange-correlation response kernel (f_{XC}) were included to improve the spin-orbit (SO) contribution. [e] Experimental δ^{13}C for CH_4 is equal to -8.65 ppm.[1] [f] Error = 0.01 ppm. [g] Reference 2. [h] Reference 3.

Table S9: Carbon chemical shifts[a] (δ^{13}C) and the root mean square deviation (RMSD)[b] calculated for CHX_3, CX_3^+, and CX_3^- (X = F, Cl, Br, or I) molecules. Calculations were performed combining B3LYP functional with different levels of theory.

Basis set	Solvent[c]	XC[d]	Neutral (CHX_3)					Cation (CX_3^+)					Anion (CX_3^-)			
			F	Cl	Br	I	RMSD	F	Cl	Br	I	RMSD	F	Cl	Br	I
TZ2P	isolated	-	121.89	92.36	23.93	-158.79	10.53	160.63	250.05	225.05	113.11	15.34	189.75	209.98	236.69	281.20
		f_{XC}	121.71	90.24	10.47	-188.55	14.76	160.09	245.17	174.48	41.29	32.05	189.48	212.00	261.92	483.84
	COSMO	-	122.97	93.44	26.79	-150.73	13.09	160.24	251.95	228.98	122.97	20.01	189.60	201.30	220.43	244.67
		f_{XC}	122.80	91.39	13.66	-181.38	12.14	159.72	247.10	198.88	50.97	23.47	189.34	202.84	241.07	402.34
TZ2P-J	isolated	-	127.42	91.74	21.67	-160.64	9.80	165.87	251.85	228.08	123.16	20.67	185.51	212.49	244.27	290.60
		f_{XC}	127.25	89.73	8.98	-187.79	14.52	165.38	247.17	198.93	53.79	22.90	185.27	214.67	270.02	494.52
	COSMO	-	128.79	93.10	24.79	-152.32	12.44	165.42	253.69	231.98	133.07	25.46	186.38	204.17	227.26	252.28
		f_{XC}	128.64	91.14	12.42	-180.46	12.05	164.95	249.04	203.06	63.42	18.56	186.15	205.86	248.42	411.26
ATZ2P	isolated	-	122.73	91.80	22.93	-	11.38	161.27	246.99	223.84	-	13.03	182.40	204.09	234.82	-
		f_{XC}	122.55	89.68	9.62	-	7.20	160.74	242.13	193.17	-	10.43	182.26	205.91	259.07	-
	COSMO	-	123.97	92.86	25.85	-	13.03	160.85	248.72	227.42	-	14.99	183.19	197.75	219.75	-
		f_{XC}	123.79	90.79	12.89	-	8.10	160.32	243.88	196.97	-	9.14	182.96	199.22	240.09	-
QZ3P-1D	isolated	-	125.31	92.68	22.82	-	11.85	163.84	252.70	228.01	-	17.16	187.64	208.84	240.36	-
		f_{XC}	125.09	90.51	9.41	-	7.85	163.26	247.60	197.09	-	11.31	187.67	210.70	264.00	-
	COSMO	-	126.43	93.63	25.72	-	13.48	163.44	254.42	232.00	-	19.28	187.83	201.35	224.15	-
		f_{XC}	126.21	91.51	12.60	-	8.73	162.87	249.34	201.26	-	10.82	187.66	202.82	244.12	-
jcpl	isolated	-	122.32	92.51	24.51	-158.71	10.79	161.52	250.09	225.36	111.56	15.15	189.57	210.17	238.41	283.39
		f_{XC}	122.16	90.63	12.40	-184.58	13.17	161.06	245.67	197.52	43.33	27.18	189.33	212.39	264.53	487.17
	COSMO	-	123.40	93.59	27.35	-150.92	13.29	161.17	251.95	229.17	121.17	19.56	189.31	201.47	221.87	246.72
		f_{XC}	123.25	91.76	15.52	-177.78	11.10	160.73	247.55	201.52	52.70	22.62	189.07	203.19	243.29	405.79
QZ4P	isolated	-	125.24	92.40	22.92	-159.47	10.27	163.89	251.85	230.10	126.61	22.07	186.89	210.27	241.70	286.95
		f_{XC}	125.08	90.46	10.89	-183.65	12.75	163.43	247.34	202.39	62.95	18.25	186.76	212.31	266.76	479.49
	COSMO	-	126.50	93.47	26.05	-151.20	12.93	163.46	253.78	234.15	136.38	27.01	186.96	203.06	226.03	251.25
		f_{XC}	126.34	91.57	14.28	-176.43	10.61	163.02	249.28	206.59	72.28	14.46	186.78	204.79	247.03	404.69
QZ4P-J	isolated	-	125.93	92.94	22.49	-159.48	10.39	164.10	252.35	229.86	124.96	21.55	189.51	210.30	241.74	286.35
		f_{XC}	125.74	90.82	9.77	-185.30	13.57	163.62	247.59	200.67	57.82	20.72	189.34	212.33	267.03	480.65
	COSMO	-	127.17	94.00	25.60	-151.41	12.98	163.67	254.18	233.82	134.49	26.30	188.92	203.26	225.98	251.08
		f_{XC}	127.00	91.92	13.17	-178.25	11.32	163.20	249.44	204.80	66.92	16.75	188.72	204.97	247.23	406.60
Experimental[e,f]			122.20[g]	77.22	9.67	-162.08	-	150.70[h]	236.30[h]	207.00[h]	95.00[h]	-	175.00[g]	-	-	-

[a] in ppm. [b] Estimated by the deviation between theoretical and experimental values. [c] COSMO was applied with parameters for chloroform. [d] Terms from the DFT exchange-correlation response kernel (f_{XC}) were included to improve the spin-orbit (SO) contribution. [e] Experimental δ^{13}C for CH_4 is equal to -8.65 ppm.[1] [f] Error = 0.01 ppm. [g] Reference 2. [h] Reference 3.

Table S10: Carbon chemical shifts[a] (δ^{13}C) and the root mean square deviation (RMSD)[b] calculated for CHX_3, CX_3^+, and CX_3^- (X = F, Cl, Br, or I) molecules. Calculations were performed combining OPBE0 functional with different levels of theory.

Basis set	Solvent[c]	XC[d]	Neutral (CHX_3)					Cation (CX_3^+)					Anion (CX_3^-)			
			F	Cl	Br	I	RMSD	F	Cl	Br	I	RMSD	F	Cl	Br	I
TZ2P	isolated	-	115.31	85.86	25.36	-138.16	15.33	153.66	233.25	210.27	104.86	5.61	175.43	186.44	206.53	243.08
		f_{XC}	115.18	84.52	16.99	-158.20	6.54	153.28	230.04	190.80	58.16	20.41	175.23	187.59	219.31	330.46
	COSMO	-	116.53	87.00	27.78	-131.54	18.63	153.55	235.15	213.97	114.12	10.29	175.25	179.71	193.75	213.78
		f_{XC}	116.40	85.69	19.64	-151.82	8.80	153.17	231.96	194.65	67.65	15.21	175.06	180.62	204.62	287.16
TZ2P-J	isolated	-	121.29	85.14	22.91	-138.45	14.12	158.87	235.80	214.18	118.18	12.80	172.52	189.50	212.98	249.88
		f_{XC}	121.17	83.85	14.89	-157.29	4.88	158.51	232.69	195.19	72.19	13.54	172.34	190.64	225.36	334.25
	COSMO	-	122.86	86.58	25.61	-131.63	17.81	158.76	237.72	217.97	127.58	17.67	173.40	183.12	199.63	219.20
		f_{XC}	122.74	85.32	17.80	-150.75	8.07	158.40	234.62	199.14	81.77	8.64	173.23	184.03	210.17	290.15
ATZ2P	isolated	-	116.42	85.63	25.10	-	10.68	154.44	230.16	208.80	-	4.28	169.27	181.90	205.33	-
		f_{XC}	116.29	84.31	16.77	-	6.72	154.06	227.00	193.05	-	9.87	169.14	182.89	217.31	-
	COSMO	-	117.84	86.79	27.67	-	12.04	154.35	231.99	212.27	-	4.46	169.94	176.83	193.22	-
		f_{XC}	117.71	85.51	19.58	-	7.90	153.97	228.84	192.85	-	9.43	169.77	177.66	203.62	-
QZ3P-1D	isolated	-	119.21	86.51	24.64	-	10.32	157.20	236.77	214.79	-	5.86	175.27	187.31	211.45	-
		f_{XC}	119.07	85.17	16.50	-	6.32	156.81	233.49	195.35	-	7.77	175.25	188.34	223.36	-
	COSMO	-	120.46	87.53	27.15	-	11.76	157.02	238.57	218.65	-	7.76	175.41	181.25	198.38	-
		f_{XC}	120.30	86.22	19.19	-	7.64	156.63	235.30	199.33	-	5.63	175.28	182.09	208.74	-
jcpl	isolated	-	114.68	85.17	25.74	-136.84	15.93	153.56	231.99	209.78	103.70	5.25	173.85	185.06	206.19	242.11
		f_{XC}	114.57	83.97	18.16	-154.63	7.61	153.23	229.09	191.89	58.99	19.90	173.67	186.25	218.85	326.72
	COSMO	-	115.91	86.31	28.13	-130.52	19.10	153.47	233.86	213.37	112.68	9.58	173.61	178.37	193.34	213.10
		f_{XC}	115.79	85.15	20.76	-148.60	10.11	153.15	230.97	195.63	68.16	14.87	173.43	179.33	204.13	284.45
QZ4P	isolated	-	118.17	85.67	25.21	-135.33	16.16	155.81	235.54	216.43	122.37	14.70	172.78	187.55	210.84	245.56
		f_{XC}	118.05	84.43	17.63	-152.36	7.53	155.48	232.58	198.57	79.97	9.13	172.66	188.56	222.56	322.97
	COSMO	-	119.63	86.86	27.99	-128.43	19.80	155.71	237.59	220.36	131.44	19.58	173.04	181.75	198.59	217.59
		f_{XC}	119.51	85.65	20.59	-145.75	10.77	155.39	234.64	202.61	89.06	4.45	172.90	182.63	208.75	284.12
QZ4P-J	isolated	-	119.59	86.64	25.02	-135.39	16.15	157.55	236.89	217.11	121.30	14.50	176.42	188.11	211.82	246.09
		f_{XC}	119.46	85.29	17.02	-153.54	7.06	157.19	233.74	198.25	76.43	10.84	176.26	189.13	223.79	324.82
	COSMO	-	121.04	87.82	27.79	-128.58	19.78	157.41	238.88	220.96	130.23	19.29	176.01	182.41	199.41	218.38
		f_{XC}	120.91	86.49	19.99	-147.00	10.27	157.06	235.75	202.23	85.39	6.24	175.85	183.28	209.81	286.31
Experimental[e,f]			122.20[g]	77.22	9.67	-162.08	-	150.70[h]	236.30[h]	207.00[h]	95.00[h]	-	175.00[g]	-	-	-

[a] in ppm. [b] Estimated by the deviation between theoretical and experimental values. [c] COSMO was applied with parameters for chloroform. [d] Terms from the DFT exchange-correlation response kernel (f_{XC}) were included to improve the spin-orbit (SO) contribution. [e] Experimental δ^{13}C for CH_4 is equal to -8.65 ppm.[1] [f] Error = 0.01 ppm. [g] Reference 2. [h] Reference 3.

Table S11: Carbon chemical shifts[a] (δ^{13}C) and the root mean square deviation (RMSD)[b] calculated for CHX_3, CX_3^+, and CX_3^- (X = F, Cl, Br, or I) molecules. Calculations were performed combining PBE0 functional with different levels of theory.

Basis set	Solvent[c]	XC[d]	Neutral (CHX_3)					Cation (CX_3^+)					Anion (CX_3^-)			
			F	Cl	Br	I	RMSD	F	Cl	Br	I	RMSD	F	Cl	Br	I
TZ2P	isolated	-	119.77	88.61	23.15	-153.61	9.86	159.50	245.70	221.83	111.25	12.75	185.10	199.03	223.05	269.46
		f_{XC}	119.63	87.11	13.77	-175.61	8.72	159.09	242.24	200.87	61.66	17.71	184.88	200.37	239.03	386.44
	COSMO	-	120.97	89.75	25.79	-146.21	12.94	159.26	247.65	225.69	120.89	17.48	184.86	190.91	207.57	233.46
		f_{XC}	120.83	88.28	16.65	-168.54	7.33	158.86	244.20	204.90	71.49	13.10	184.65	191.94	220.78	327.80
TZ2P-J	isolated	-	125.67	88.24	20.92	-155.06	8.79	164.97	248.11	225.36	122.54	18.96	181.60	201.93	230.03	277.46
		f_{XC}	125.54	86.79	11.92	-175.67	8.55	164.58	244.73	204.80	73.54	13.50	181.40	203.30	245.77	392.40
	COSMO	-	127.18	89.66	23.84	-147.43	12.20	164.72	250.04	229.25	132.25	23.81	182.43	194.18	213.85	239.82
		f_{XC}	127.07	88.25	15.07	-168.44	7.33	164.36	246.69	208.89	83.39	10.40	182.26	195.25	226.90	332.59
ATZ2P	isolated	-	120.80	88.41	22.61	-	9.91	160.36	242.74	220.58	-	10.32	178.36	194.03	221.57	-
		f_{XC}	120.66	86.92	13.31	-	6.05	159.96	239.32	199.44	-	7.12	178.21	195.23	236.73	-
	COSMO	-	122.17	89.52	25.33	-	11.50	160.12	244.57	224.18	-	12.28	179.03	188.00	207.10	-
		f_{XC}	122.04	88.07	16.30	-	7.34	159.73	241.16	203.23	-	6.31	178.85	188.97	219.98	-
QZ3P-1D	isolated	-	123.36	89.31	22.28	-	10.11	162.86	248.87	225.50	-	14.70	183.66	198.87	227.13	-
		f_{XC}	123.20	87.81	13.08	-	6.45	162.43	245.30	204.32	-	8.68	183.60	200.07	241.90	-
	COSMO	-	124.60	90.29	24.95	-	11.69	162.59	250.67	229.48	-	16.86	183.81	191.75	211.60	-
		f_{XC}	124.43	88.81	15.95	-	7.72	162.17	247.11	208.44	-	9.14	183.65	192.70	224.22	-
jcpl	isolated	-	119.70	88.44	23.71	-152.95	10.16	159.94	245.15	221.81	109.73	12.25	184.28	198.52	223.85	270.35
		f_{XC}	119.58	87.09	15.19	-172.48	7.79	159.60	241.99	202.39	61.99	17.48	184.08	199.94	239.92	385.59
	COSMO	-	120.90	89.57	26.33	-145.85	13.18	159.75	247.06	225.56	119.10	16.76	183.94	190.41	208.17	234.41
		f_{XC}	120.78	88.26	19.03	-165.77	7.50	159.41	243.92	206.31	71.50	13.10	183.75	191.52	221.48	327.61
QZ4P	isolated	-	123.09	88.89	22.47	-153.39	9.70	162.53	248.05	227.49	126.20	20.44	182.44	199.88	227.95	273.27
		f_{XC}	122.96	87.49	13.92	-172.12	7.50	162.17	244.81	208.00	80.82	10.08	182.31	201.12	242.99	380.20
	COSMO	-	124.50	90.03	25.38	-145.83	13.04	162.30	250.08	231.54	135.69	25.41	182.61	193.10	213.03	238.66
		f_{XC}	124.37	88.65	17.02	-164.99	7.03	161.95	246.84	212.18	90.30	8.46	182.45	194.14	225.73	327.21
QZ4P-J	isolated	-	123.95	89.54	22.14	-153.28	9.85	163.23	248.70	227.37	124.54	19.99	185.23	200.05	228.18	273.09
		f_{XC}	123.81	88.01	13.14	-173.17	7.97	162.85	245.28	206.87	76.66	11.88	185.07	201.29	243.43	381.23
	COSMO	-	125.36	90.67	25.05	-145.87	13.14	162.98	250.67	231.34	133.83	24.79	184.72	193.41	213.17	238.90
		f_{XC}	125.21	89.17	16.26	-166.16	7.28	162.61	247.26	210.99	85.96	9.48	184.54	194.45	226.11	328.87
Experimental[e,f]			122.20[g]	77.22	9.67	-162.08	-	150.70[h]	236.30[h]	207.00[h]	95.00[h]	-	175.00[g]	-	-	-

[a] in ppm. [b] Estimated by the deviation between theoretical and experimental values. [c] COSMO was applied with parameters for chloroform. [d] Terms from the DFT exchange-correlation response kernel (f_{XC}) were included to improve the spin-orbit (SO) contribution. [e] Experimental δ^{13}C for CH_4 is equal to -8.65 ppm.[1] [f] Error = 0.01 ppm. [g] Reference 2. [h] Reference 3.

4 Individual contributions of the σ^{13}C NMR

In this work, the σ^{para} refers to the paramagnetic shielding obtained from SR-ZORA calculation, whereas the σ^{SO} is given by the difference between SO-ZORA and SR-ZORA calculations. The σ^{dia} contribution is obtained from SO-ZORA calculation. Table S12 shows the isotropic value for each contribution, while it is decomposed into principal components (σ_{xx}, σ_{yy}, and σ_{zz}) in Table S13.

Table S12: Carbon shielding tensors (σ)[a-c], and their diamagnetic (σ^{dia}), paramagnetic (σ^{para}), and spin-orbit (σ^{SO}) contributions[b,c] obtained for CHX_3, CX_3^+, and CX_3^- (X = F, Cl, Br, or I) compounds.

Compound	σ^{dia}	σ^{para}	σ^{SO}	σ
CHF_3	267.88	-210.36	2.54	60.06
$CHCl_3$	257.75	-179.65	15.49	93.59
$CHBr_3$	256.62	-173.95	83.91	166.58
CHI_3	236.44	-116.94	228.87	348.37
CF_3^+	265.10	-244.73	2.76	23.13
CCl_3^+	275.61	-361.00	20.19	-65.21
CBr_3^+	270.97	-417.93	117.66	-29.30
CI_3^+	266.17	-497.59	324.79	93.37
CF_3^-	262.61	-265.26	2.69	0.03
CCl_3^-	254.72	-269.71	4.46	-10.52
CBr_3^-	248.20	-286.76	-4.41	-42.96
CI_3^-	248.93	-265.34	-127.30	-143.71

[a] $\sigma = \sigma^{dia} + \sigma^{para} + \sigma^{SO}$. [b] All values are in ppm. [c] Results were obtained using B1PW91/QZ4P level of theory, the COSMO solvent model, the spin-orbit (SO) ZORA approach to consider the relativistic effects, and terms from the DFT exchange-correlation response kernel (f_{XC}) were included to improve the SO contribution.

Table S13: Carbon shielding tensors (σ)[a-c], and their diamagnetic (σ^{dia}), paramagnetic (σ^{para}), and spin-orbit (σ^{SO}) contributions[b,c] in terms of principal components (σ_{xx}, σ_{yy}, and σ_{zz}) obtained for CHX_3, CX_3^+, and CX_3^- (X = F, Cl, Br, or I) compounds.

Compound	σ_{dia}			σ_{para}			σ_{SO}			σ		
	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}
CHF_3	275.90	275.90	251.85	-211.44	-211.43	-208.21	2.19	2.19	3.25	66.65	66.65	46.89
$CHCl_3$	256.86	256.78	259.61	-158.60	-158.41	-221.94	10.77	10.76	24.94	109.03	109.13	62.61
$CHBr_3$	258.59	258.62	252.66	-151.45	-151.45	-218.96	51.09	51.09	149.55	158.22	158.25	183.26
CHI_3	235.90	235.92	237.51	-92.40	-92.38	-166.05	96.72	96.76	493.12	240.23	240.31	564.57
CF_3^+	269.56	269.55	256.20	-259.69	-259.59	-214.93	2.17	2.17	3.93	12.04	12.12	45.21
CCl_3^+	280.49	280.49	265.84	-436.66	-436.51	-209.84	14.65	14.66	31.25	-141.51	-141.37	87.26
CBr_3^+	278.86	278.87	255.18	-526.49	-526.24	-201.05	81.81	81.85	189.31	-165.82	-165.52	243.43
CI_3^+	277.18	277.14	244.20	-670.71	-670.15	-151.92	194.80	195.06	584.50	-198.73	-197.95	676.79
CF_3^-	266.27	266.28	255.28	-300.83	-300.83	-194.13	2.26	2.26	3.54	-32.30	-32.29	64.69
CCl_3^-	255.65	255.66	252.86	-291.83	-29180	-225.48	3.95	3.95	5.49	-32.23	-32.19	32.86
CBr_3^-	250.33	250.35	243.93	-311.70	-311.66	-236.91	0.73	0.73	-14.68	-60.65	-60.58	-7.66
CI_3^-	253.61	253.64	239.54	-292.76	-292.65	-210.60	-71.00	-71.03	-239.88	-110.15	-110.04	-210.93

[a] $\sigma = \sigma^{dia} + \sigma^{para} + \sigma^{SO}$. [b] All values are in ppm. [c] Results were obtained using B1PW91/QZ4P level of theory, the COSMO solvent model, the spin-orbit (SO) ZORA approach to consider the relativistic effects, and terms from the DFT exchange-correlation response kernel (f_{XC}) were included to improve the SO contribution.

5 NLMO's contributions to the σ^{13}C NMR

NLMO's contributions to diamagnetic, paramagnetic, and spin-orbit terms of the σ^{13}C NMR are displayed in Tables S14-S17 for all studied compounds. NLMOs were designated according to atom numbering present in the Figure S1.

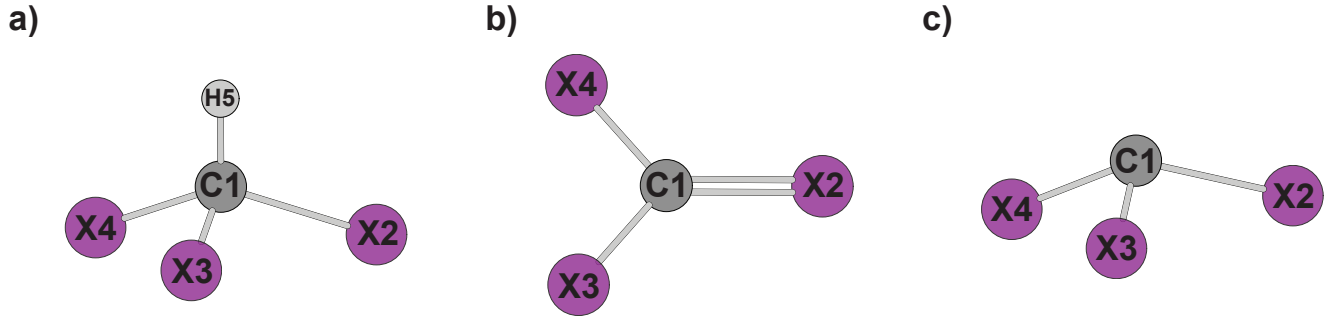

Figure S1: Structures and atom numbering of a) neutral (CHX_3), b) cation (CX_3^+), and c) anion (CX_3^-) compounds (X = F, Cl, Br, or I).

5.1 NLMO's contributions to the σ^{dia}

Table S14: NLMO's contributions[a] to the σ^{dia} of the σ^{13}C NMR obtained for CHX_3, CX_3^+, and CX_3^- (X = F, Cl, Br or I) compounds.

Parent NBO	Neutral (CHX_3)				Cation (CX_3^+)				Anion (CX_3^-)			
	F	Cl	Br	I	F	Cl	Br	I	F	Cl	Br	I
CR(C1)	200.58	200.57	200.57	200.57	200.61	200.59	200.59	200.59	200.44	200.40	200.37	200.38
ΣCR(X)[b]	0.14	0.06	-0.06	0.30	0.16	0.04	-0.04	0.56	0.10	0.06	-0.01	0.23
$\sigma_{C1\text{-}X2}$	7.83	11.10	10.20	6.58	8.93	14.68	14.32	13.52	5.38	5.85	3.36	3.58
$\sigma_{C1\text{-}X3}$	7.83	11.10	10.18	6.59	8.94	14.67	14.32	13.44	5.38	5.84	3.37	3.58
$\sigma_{C1\text{-}X4}$	7.83	11.06	10.18	6.57	8.94	14.68	14.32	13.44	5.38	5.86	3.36	3.56
$\sigma_{C1\text{-}H5}$	21.62	9.66	12.55	5.84	-	-	-	-	-	-	-	-
$\pi_{C1\text{-}X2}$	-	-	-	-	7.03	8.10	8.01	8.10	-	-	-	-
LP(C1)	-	-	-	-	-	-	-	-	29.53	22.94	25.10	26.62
$\Sigma LP_1(X)$[b]	6.68	4.27	3.67	3.07	7.06	5.21	4.05	3.78	5.43	4.33	3.51	3.37
$\Sigma LP_2(X)$[b]	7.52	4.02	4.17	3.22	12.61	7.10	5.63	3.70	4.78	4.30	4.29	3.66
$\Sigma LP_3(X)$[b]	7.86	5.92	5.18	3.68	10.84	10.53	9.77	8.89	6.20	5.15	4.85	3.77
$\sigma^*_{C1\text{-}X2}$	0.00	0.00	0.01	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.05
$\sigma^*_{C1\text{-}X3}$	0.00	0.00	0.01	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.05
$\sigma^*_{C1\text{-}X4}$	0.00	0.00	0.01	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.05
$\sigma^*_{C1\text{-}H5}$	0.00	0.00	0.00	-0.01	-	-	-	-	-	-	-	-
$\pi^*_{C1\text{-}X2}$	-	-	-	-	0.00	0.00	0.03	0.14	-	-	-	-
ΣRY(C1)[c]	0.00	0.00	-0.03	-0.19	0.00	0.00	-0.03	-0.06	0.00	0.00	-0.02	-0.01
ΣRY(X)[b,c]	0.00	0.00	0.02	0.16	0.00	0.00	0.02	0.09	0.00	0.00	0.01	0.04
ΣRY(H)[c]	0.00	0.00	-0.01	-0.05	-	-	-	-	-	-	-	-
Σ_{total}[d]	267.88	257.75	256.62	236.44	265.10	275.61	270.97	266.17	262.61	254.72	248.20	248.93

[a] in ppm. [b] Sum of halogen atom contributions. [c] Sum of Rydberg's contributions. [d] Sum of all NLMO's contributions.

5.2 NLMO's contributions to the σ^{para}

Table S15: NLMO's contributions[a] to the σ^{para} of the σ^{13}C NMR obtained for CHX_3, CX_3^+, and CX_3^- (X = F, Cl, Br, or I) compounds.

Parent NBO	Neutral (CHX_3)				Cation (CX_3^+)				Anion (CX_3^-)			
	F	Cl	Br	I	F	Cl	Br	I	F	Cl	Br	I
CR(C1)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.03	0.00	0.00
ΣCR(X)[b]	0.33	-0.15	0.34	0.21	0.39	-0.18	0.43	0.24	0.31	-0.12	0.20	0.09
$\sigma_{C1\text{-}X2}$	-38.28	-35.01	-33.88	-20.07	-61.27	-97.99	-112.83	-131.66	-41.88	-51.20	-62.76	-61.70
$\sigma_{C1\text{-}X3}$	-38.28	-35.01	-33.89	-20.05	-61.29	-97.98	-112.77	-132.50	-41.86	-51.00	-62.77	-61.70
$\sigma_{C1\text{-}X4}$	-38.28	-34.99	-33.90	-20.04	-61.29	-97.98	-112.77	-132.50	-41.87	-51.14	-62.76	-61.71
$\sigma_{C1\text{-}H5}$	-67.85	-52.41	-48.08	-34.23	-	-	-	-	-	-	-	-
$\pi_{C1\text{-}X2}$	-	-	-	-	-15.52	-21.96	-26.70	-31.58	-	-	-	-
LP(C1)	-	-	-	-	-	-	-	-	-115.34	-85.09	-61.24	-37.77
$\Sigma LP_1(X)$[b]	-13.62	-10.33	-13.03	-16.07	-27.42	-27.23	-32.09	-37.19	-13.21	-18.63	-23.63	-30.45
$\Sigma LP_2(X)$[b]	-5.07	-3.52	-2.90	-0.03	4.40	7.99	7.80	-1.56	-3.11	-2.56	-4.61	-4.31
$\Sigma LP_3(X)$[b]	-9.31	-8.23	-8.62	-6.66	-22.74	-25.67	-29.00	-30.85	-8.31	-9.94	-9.19	-7.80
$\sigma^*_{C1\text{-}X2}$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\sigma^*_{C1\text{-}X3}$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\sigma^*_{C1\text{-}X4}$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\sigma^*_{C1\text{-}H5}$	0.00	0.00	0.00	0.00	-	-	-	-	-	-	-	-
$\pi^*_{C1\text{-}X2}$	-	-	-	-	0.00	0.00	0.00	0.00	-	-	-	-
ΣRY(C1)[c]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ΣRY(X)[b,c]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ΣRY(H)[c]	0.00	0.00	0.00	0.00	-	-	-	-	-	-	-	-
Σ_{total}[d]	-210.36	-179.65	-173.95	-116.94	-244.73	-361.00	-417.93	-497.59	-265.26	-269.71	-286.76	-265.34

[a] in ppm. [b] Sum of halogen atom contributions. [c] Sum of Rydberg's contributions. [d] Sum of all NLMO's contributions.

5.3 NLMO's contributions to the σ^{SO}

Table S16: NLMO's contributions[a] to the σ^{SO} of the σ^{13}C NMR obtained for CHX_3, CX_3^+, and CX_3^- (X = F, Cl, Br, or I) compounds.

Parent NBO	Neutral (CHX_3)				Cation (CX_3^+)				Anion (CX_3^-)			
	F	Cl	Br	I	F	Cl	Br	I	F	Cl	Br	I
CR(C1)	0.64	0.60	0.37	0.26	0.46	-0.39	-4.57	-9.48	0.64	-0.41	-7.01	-34.68
ΣCR(X)[b]	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.03
$\sigma_{C1\text{-}X2}$	0.25	2.75	16.59	49.56	0.55	4.43	25.86	70.39	0.24	2.20	12.32	45.05
$\sigma_{C1\text{-}X3}$	0.25	2.75	16.51	49.56	0.55	4.43	25.87	69.66	0.24	2.19	12.34	45.18
$\sigma_{C1\text{-}X4}$	0.25	2.74	16.48	49.09	0.55	4.43	25.87	69.66	0.24	2.20	12.35	44.96
$\sigma_{C1\text{-}H5}$	0.39	-0.87	-8.17	-31.19	-	-	-	-	-	-	-	-
$\pi_{C1\text{-}X2}$	-	-	-	-	-0.05	-0.26	-1.36	-2.81	-	-	-	-
LP(C1)	-	-	-	-	-	-	-	-	0.59	-6.93	-56.64	-274.62
$\Sigma LP_1(X)$[b]	0.15	0.69	3.33	7.95	0.35	1.32	6.68	16.02	0.17	0.72	3.34	10.59
$\Sigma LP_2(X)$[b]	0.01	0.22	1.07	2.23	-0.04	-0.15	-0.62	-0.61	0.02	-0.05	0.47	-3.93
$\Sigma LP_3(X)$[b]	-0.02	0.00	0.07	0.28	-0.06	-0.29	-1.39	-2.54	-0.02	-0.01	-0.02	0.03
$\sigma^*_{C1\text{-}X2}$	0.10	3.45	18.75	45.59	0.01	3.37	22.35	64.59	0.16	2.29	7.94	13.29
$\sigma^*_{C1\text{-}X3}$	0.10	3.33	18.09	44.89	0.01	3.36	22.34	61.05	0.16	2.18	7.66	12.26
$\sigma^*_{C1\text{-}X4}$	0.10	3.21	17.45	43.07	0.01	3.36	22.34	61.05	0.16	2.24	8.23	12.77
$\sigma^*_{C1\text{-}H5}$	0.01	-0.02	0.21	0.39	-	-	-	-	-	-	-	-
$\pi^*_{C1\text{-}X2}$	-	-	-	-	-0.09	-0.52	-2.81	-7.10	-	-	-	-
ΣRY(C1)[c]	-0.05	1.69	1.97	-17.03	0.81	2.07	16.96	49.19	0.43	3.43	12.42	39.67
ΣRY(X)[b,c]	0.35	-5.06	-16.71	-11.20	-0.30	-4.96	-39.85	-114.29	-0.34	-5.60	-17.81	-37.89
ΣRY(H)[c]	-0.01	0.04	-2.09	-4.60	-	-	-	-	-	-	-	-
Σ_{total}[d]	2.54	15.49	83.91	228.87	2.76	20.19	117.66	324.79	2.69	4.46	-4.41	-127.30

[a] in ppm. [b] Sum of halogen atom contributions. [c] Sum of Rydberg's contributions. [d] Sum of all NLMO's contributions.

5.4 NLMO's contributions to the σ

Table S17: NLMO's contributions[a] to the σ of the σ^{13}C NMR obtained for CHX_3, CX_3^+, and CX_3^- (X = F, Cl, Br, or I) compounds.

Parent NBO	Neutral (CHX_3)				Cation (CX_3^+)				Anion (CX_3^-)			
	F	Cl	Br	I	F	Cl	Br	I	F	Cl	Br	I
CR(C1)	201.22	201.17	200.93	200.83	201.07	200.20	196.02	191.10	201.09	199.96	193.36	165.70
ΣCR(X)[b]	0.47	-0.10	0.27	0.54	0.54	-0.14	0.39	0.83	0.41	-0.05	0.18	0.34
$\sigma_{C1\text{-}X2}$	-30.20	-21.16	-7.10	36.07	-51.78	-78.89	-72.65	-47.75	-36.26	-43.14	-47.08	-13.06
$\sigma_{C1\text{-}X3}$	-30.20	-21.17	-7.20	36.10	-51.80	-78.87	-72.58	-49.41	-36.25	-42.97	-47.06	-12.95
$\sigma_{C1\text{-}X4}$	-30.20	-21.19	-7.25	35.62	-51.80	-78.87	-72.58	-49.41	-36.26	-43.08	-47.05	-13.19
$\sigma_{C1\text{-}H5}$	-45.84	-43.62	-43.71	-59.58	-	-	-	-	-	-	-	-
$\pi_{C1\text{-}X2}$	-	-	-	-	-8.54	-14.12	-20.04	-26.30	-	-	-	-
LP(C1)	-	-	-	-	-	-	-	-	-85.22	-69.08	-92.77	-285.78
$\Sigma LP_1(X)$[b]	-6.80	-5.38	-6.03	-5.05	-20.02	-20.70	-21.37	-17.40	-7.61	-13.58	-16.79	-16.48
$\Sigma LP_2(X)$[b]	2.47	0.72	2.34	5.42	16.97	14.93	12.81	1.52	1.69	1.68	0.15	-4.57
$\Sigma LP_3(X)$[b]	-1.48	-2.31	-3.37	-2.70	-11.97	-15.43	-20.62	-24.50	-2.13	-4.80	-4.35	-4.00
$\sigma^*_{C1\text{-}X2}$	0.10	3.45	18.76	45.63	0.01	3.37	22.35	64.59	0.16	2.29	7.95	13.34
$\sigma^*_{C1\text{-}X3}$	0.10	3.33	18.10	44.93	0.01	3.36	22.34	61.05	0.16	2.18	7.67	12.30
$\sigma^*_{C1\text{-}X4}$	0.10	3.21	17.46	43.11	0.01	3.36	22.34	61.05	0.16	2.24	8.23	12.82
$\sigma^*_{C1\text{-}H5}$	0.01	-0.02	0.21	0.38	-	-	-	-	-	-	-	-
$\pi^*_{C1\text{-}X2}$	-	-	-	-	-0.09	-0.52	-2.79	-6.96	-	-	-	-
ΣRY(C1)[c]	-0.05	1.68	1.94	-17.22	0.81	2.07	16.93	49.12	0.43	3.43	12.40	39.66
ΣRY(X)[b,c]	0.35	-5.06	-16.69	-11.04	-0.30	-4.96	-39.84	-114.20	-0.34	-5.60	-17.81	-37.84
ΣRY(H)[c]	-0.01	0.04	-2.10	-4.65	-	-	-	-	-	-	-	-
Σ_{total}[d]	60.06	93.59	166.58	348.37	23.13	-65.21	-29.30	93.37	0.03	-10.52	-42.96	-143.71

[a] in ppm. [b] Sum of halogen atom contributions. [c] Sum of Rydberg's contributions. [d] Sum of all NLMO's contributions.

6 NLMO's contributions to the σ^{13}C NMR in terms of principal axis system (PAS)

NLMO's contributions to diamagnetic, paramagnetic, and spin-orbit operators decomposed in terms of principal axis system (σ_{xx}, σ_{yy}, and σ_{zz}) of the σ^{13}C NMR are displayed in Tables S18-S29.

6.1 NLMO's contributions to the σ^{dia}

6.1.1 Neutral (CHX_3)

Table S18: NLMO's contributions[a] to the σ^{dia} in terms of principal axis system (σ_{xx}, σ_{yy}, and σ_{zz}) for CHX_3 (X = F, Cl, Br, or I) compounds.

Parent NBO	F			Cl			Br			I		
	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}
CR(C1)	200.58	200.58	200.58	200.57	200.57	200.57	200.57	200.57	200.57	200.57	200.57	200.56
ΣCR(X)[b]	0.17	0.17	0.09	0.48	0.48	-0.80	1.47	1.47	-3.12	2.97	2.97	-5.05
$\sigma_{C1\text{-}X2}$	6.67	10.93	5.89	10.98	11.15	11.17	10.19	10.19	10.21	5.01	7.66	7.09
$\sigma_{C1\text{-}X3}$	9.30	8.31	5.89	10.99	11.13	11.17	10.86	9.51	10.19	8.53	4.15	7.10
$\sigma_{C1\text{-}X4}$	10.43	7.17	5.89	11.21	10.85	11.12	9.50	10.85	10.18	5.47	7.20	7.04
$\sigma_{C1\text{-}H5}$	24.78	24.78	15.30	6.62	6.62	15.74	10.92	10.92	15.79	1.03	1.03	15.46
$\Sigma LP_1(X)$[b]	6.73	6.73	6.57	4.82	4.82	3.17	4.43	4.43	2.15	4.03	4.03	1.15
$\Sigma LP_2(X)$[b]	10.43	10.43	1.71	5.93	5.91	0.23	5.98	5.99	0.53	4.58	4.59	0.48
$\Sigma LP_3(X)$[b]	6.81	6.81	9.94	5.25	5.25	7.24	4.67	4.68	6.18	3.69	3.70	3.66
$\sigma^*_{C1\text{-}X2}$	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.04	0.06	0.02
$\sigma^*_{C1\text{-}X3}$	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.07	0.03	0.02
$\sigma^*_{C1\text{-}X4}$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.04	0.06	0.02
$\sigma^*_{C1\text{-}H5}$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.01	-0.01	-0.01
ΣRY(C1)[c]	0.00	0.00	0.00	0.00	0.00	0.00	-0.02	-0.02	-0.04	-0.13	-0.13	-0.31
ΣRY(X)[b,c]	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.02	0.03	0.10	0.11	0.26
ΣRY(H)[c]	0.00	0.00	0.00	0.00	0.00	0.00	-0.02	-0.02	0.00	-0.09	-0.09	0.01
Σ_{total}[d]	275.90	275.90	251.85	256.86	256.78	259.61	258.59	258.62	252.66	235.90	235.92	237.51

[a] in ppm. [b] Sum of halogen atom contributions. [c] Sum of Rydberg's contributions. [d] Sum of all NLMO's contributions.

6.1.2 Cation (CX_3^+)

Table S19: NLMO's contributions[a] to the σ^{dia} in terms of principal axis system (σ_{xx}, σ_{yy}, and σ_{zz}) for CX_3^+ (X = F, Cl, Br, or I) compounds.

Parent NBO	F			Cl			Br			I		
	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}
CR(C1)	200.60	200.60	200.62	200.59	200.59	200.60	200.59	200.59	200.59	200.59	200.59	200.59
ΣCR(X)[b]	0.21	0.21	0.05	0.79	0.79	-1.45	2.49	2.49	-5.10	4.56	4.56	-7.44
$\sigma_{C1\text{-}X2}$	7.63	11.94	7.24	14.83	14.12	15.07	14.05	14.51	14.39	12.49	15.05	13.01
$\sigma_{C1\text{-}X3}$	10.86	8.71	7.24	14.29	14.66	15.08	14.40	14.17	14.39	14.35	13.04	12.92
$\sigma_{C1\text{-}X4}$	10.86	8.71	7.24	14.29	14.66	15.08	14.40	14.17	14.39	14.35	13.04	12.92
$\pi_{C1\text{-}X2}$	9.90	7.65	3.52	11.02	9.35	3.74	10.74	9.54	3.74	10.69	9.88	3.72
$\Sigma LP_1(X)$[b]	6.89	6.88	7.41	5.58	5.59	4.46	4.68	4.69	2.77	4.45	4.46	2.42
$\Sigma LP_2(X)$[b]	9.86	9.87	18.08	6.26	6.25	8.80	5.27	5.26	6.37	4.06	4.05	2.97
$\Sigma LP_3(X)$[b]	12.74	14.99	4.80	12.82	14.50	4.27	12.23	13.43	3.66	11.39	12.20	3.10
$\sigma^*_{C1\text{-}X2}$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	-0.01	0.00	0.06	-0.05
$\sigma^*_{C1\text{-}X3}$	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	-0.01	0.04	0.01	-0.05
$\sigma^*_{C1\text{-}X4}$	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	-0.01	0.04	0.01	-0.05
$\pi^*_{C1\text{-}X2}$	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.03	0.01	0.17	0.18	0.08
ΣRY(C1)[c]	0.00	0.00	0.00	0.00	0.00	0.00	-0.02	-0.03	-0.05	-0.03	-0.04	-0.13
ΣRY(X)[b,c]	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.01	0.03	0.04	0.04	0.19
Σ_{total}[d]	269.55	269.56	256.20	280.49	280.49	265.84	278.86	278.87	255.18	277.18	277.14	244.20

[a] in ppm. [b] Sum of halogen atom contributions. [c] Sum of Rydberg's contributions. [d] Sum of all NLMO's contributions.

6.1.3 Anion (CX_3^-)

Table S20: NLMO's contributions[a] to the σ^{dia} in terms of principal axis system (σ_{xx}, σ_{yy}, and σ_{zz}) for CX_3^- (X = F, Cl, Br, or I) compounds.

Parent NBO	F			Cl			Br			I		
	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}
CR(C1)	200.44	200.44	200.45	200.39	200.39	200.40	200.37	200.37	200.37	200.38	200.38	200.38
ΣCR(X)[b]	0.11	0.11	0.08	0.29	0.29	-0.38	0.82	0.82	-1.68	1.81	1.81	-2.94
σ_{C1-X2}	6.27	4.71	5.17	6.57	5.76	5.22	3.58	3.91	2.59	5.31	3.22	2.22
σ_{C1-X3}	4.41	6.56	5.16	4.63	7.69	5.21	6.29	1.22	2.60	6.42	2.11	2.21
σ_{C1-X4}	5.78	5.19	5.16	7.30	5.05	5.23	1.38	6.11	2.59	1.04	7.46	2.18
LP(C1)	32.28	32.28	24.02	21.67	21.67	25.49	24.09	24.09	27.13	26.05	26.05	27.76
$\Sigma LP_1(X)$[b]	5.41	5.41	5.48	5.02	5.02	2.96	4.29	4.29	1.95	4.30	4.30	1.51
$\Sigma LP_2(X)$[b]	6.09	6.09	2.17	5.34	5.34	2.22	5.37	5.33	2.18	4.60	4.61	1.77
$\Sigma LP_3(X)$[b]	5.49	5.49	7.61	4.46	4.46	6.52	4.15	4.20	6.20	3.47	3.48	4.35
σ^*_{C1-X2}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.05	0.05	0.05
σ^*_{C1-X3}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.05	0.05	0.05
σ^*_{C1-X4}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.05	0.05	0.05
ΣRY(C1)[c]	0.00	0.00	0.00	0.00	0.00	0.00	-0.01	0.00	-0.04	0.06	0.06	-0.14
ΣRY(X)[b,c]	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.01	0.00	0.00	0.00	0.12
Σ_{total}[d]	266.27	266.28	255.28	255.65	255.66	252.86	250.33	250.35	243.93	253.61	253.64	239.54

[a] in ppm. [b] Sum of halogen atom contributions. [c] Sum of Rydberg's contributions. [d] Sum of all NLMO's contributions.

6.2 NLMO's contributions to the σ^{para}

6.2.1 Neutral (CHX_3)

Table S21: NLMO's contributions[a] to the σ^{para} in terms of principal axis system (σ_{xx}, σ_{yy}, and σ_{zz}) for CHX_3 (X = F, Cl, Br, or I) compounds.

Parent NBO	F			Cl			Br			I		
	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}
CR(C1)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ΣCR(X)[b]	0.29	0.29	0.41	-0.03	-0.05	-0.22	0.28	0.28	0.45	0.18	0.18	0.28
$\sigma_{C1\text{-}X2}$	-50.50	-10.77	-53.56	-29.07	-14.57	-61.39	-26.00	-15.93	-59.72	-8.05	-8.73	-43.44
$\sigma_{C1\text{-}X3}$	-25.99	-35.27	-53.57	-27.77	-15.85	-61.41	-8.41	-33.43	-59.82	-6.14	-10.62	-43.38
$\sigma_{C1\text{-}X4}$	-15.40	-45.86	-53.57	-8.57	-34.93	-61.47	-28.38	-13.42	-59.88	-10.87	-5.68	-43.57
$\sigma_{C1\text{-}H5}$	-101.93	-101.93	0.31	-78.71	-78.61	0.09	-72.16	-72.18	0.10	-51.52	-51.47	0.28
$\Sigma LP_1(X)$[b]	-9.91	-9.90	-21.06	-8.57	-8.58	-13.85	-10.95	-10.95	-17.18	-13.98	-13.99	-20.24
$\Sigma LP_2(X)$[b]	-6.37	-6.37	-2.47	-4.78	-4.72	-1.07	-3.86	-3.85	-0.98	0.02	-0.04	-0.06
$\Sigma LP_3(X)$[b]	-1.62	-1.62	-24.70	-1.06	-1.06	-22.56	-1.96	-1.96	-21.93	-2.03	-2.02	-15.93
$\sigma^*_{C1\text{-}X2}$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\sigma^*_{C1\text{-}X3}$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\sigma^*_{C1\text{-}X4}$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\sigma^*_{C1\text{-}H5}$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\Sigma RY(C1)$[c]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\Sigma RY(X)$[b,c]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\Sigma RY(H)$[c]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Σ_{total}[d]	-211.44	-211.43	-208.21	-158.60	-158.41	-221.94	-151.45	-151.45	-218.96	-92.40	-92.38	-166.05

[a] in ppm. [b] Sum of halogen atom contributions. [c] Sum of Rydberg's contributions. [d] Sum of all NLMO's contributions.

6.2.2 Cation (CX_3^+)

Table S22: NLMO's contributions[a] to the σ^{para} in terms of principal axis system (σ_{xx}, σ_{yy}, and σ_{zz}) for CX_3^+ (X = F, Cl, Br, or I) compounds.

Parent NBO	F			Cl			Br			I		
	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}
CR(C1)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ΣCR(X)[b]	0.42	0.42	0.32	-0.16	-0.15	-0.23	0.33	0.32	0.65	0.14	0.14	0.45
$\sigma_{C1\text{-}X2}$	-129.14	-0.08	-54.59	-237.43	-0.06	-56.49	-284.65	-0.06	-53.79	-355.89	-0.03	-39.05
$\sigma_{C1\text{-}X3}$	-32.37	-96.90	-54.60	-59.40	-178.06	-56.48	-71.17	-213.39	-53.74	-90.00	-268.17	-39.33
$\sigma_{C1\text{-}X4}$	-32.35	-96.92	-54.59	-59.39	-178.06	-56.48	-71.16	-213.40	-53.74	-90.00	-268.17	-39.33
$\pi_{C1\text{-}X2}$	-41.40	-3.88	-1.27	-69.84	4.61	-0.66	-86.55	6.74	-0.27	-108.47	13.68	0.05
$\Sigma LP_1(X)$[b]	-33.93	-33.95	-14.39	-35.49	-35.54	-10.66	-40.56	-40.62	-15.09	-47.38	-46.74	-17.46
$\Sigma LP_2(X)$[b]	22.82	22.82	-32.43	24.77	24.88	-25.70	22.88	23.03	-22.52	5.14	5.31	-15.13
$\Sigma LP_3(X)$[b]	-13.66	-51.20	-3.38	0.28	-74.14	-3.15	4.40	-88.85	-2.56	15.73	-106.16	-2.13
$\sigma^*_{C1\text{-}X2}$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\sigma^*_{C1\text{-}X3}$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\sigma^*_{C1\text{-}X4}$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\pi^*_{C1\text{-}X2}$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\Sigma RY(C1)$[c]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\Sigma RY(X)$[b,c]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Σ_{total}[d]	-259.59	-259.69	-214.93	-436.66	-436.51	-209.84	-526.49	-526.24	-201.05	-670.71	-670.15	-151.92

[a] in ppm. [b] Sum of halogen atom contributions. [c] Sum of Rydberg's contributions. [d] Sum of all NLMO's contributions.

6.2.3 Anion (CX_3^-)

Table S23: NLMO's contributions[a] to the σ^{para} in terms of principal axis system (σ_{xx}, σ_{yy}, and σ_{zz}) for CX_3^- (X = F, Cl, Br, or I) compounds.

Parent NBO	F			Cl			Br			I		
	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}
CR(C1)	0.00	0.00	0.00	-0.04	-0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ΣCR(X)[b]	0.30	0.30	0.33	-0.06	-0.06	-0.22	0.16	0.16	0.27	0.09	0.09	0.09
σ_{C1-X2}	-28.44	-45.61	-51.58	-40.79	-50.03	-62.77	-65.25	-57.66	-65.38	-83.55	-45.11	-56.45
σ_{C1-X3}	-51.47	-22.53	-51.59	-60.44	-29.58	-62.99	-36.93	-85.98	-65.39	-28.53	-100.05	-56.51
σ_{C1-X4}	-31.12	-42.90	-51.59	-34.48	-56.07	-62.87	-82.23	-40.72	-65.35	-80.88	-47.71	-56.54
LP(C1)	-173.12	-173.11	0.22	-128.49	-128.47	1.68	-92.55	-92.52	1.37	-57.37	-57.34	1.39
$\Sigma LP_1(X)$[b]	-10.78	-10.79	-18.07	-19.75	-19.75	-16.38	-25.01	-25.02	-20.87	-33.28	-33.26	-24.79
$\Sigma LP_2(X)$[b]	-3.71	-3.72	-1.90	-3.15	-3.15	-1.40	-6.29	-6.07	-1.47	-5.94	-5.93	-1.04
$\Sigma LP_3(X)$[b]	-2.49	-2.48	-19.96	-4.65	-4.64	-20.54	-3.60	-3.86	-20.09	-3.30	-3.33	-16.76
σ^*_{C1-X2}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
σ^*_{C1-X3}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
σ^*_{C1-X4}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ΣRY(C1)[c]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ΣRY(X)[b,c]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Σ_{total}[d]	-300.83	-300.83	-194.13	-291.83	-291.80	-225.48	-311.70	-311.66	-236.91	-292.76	-292.65	-210.60

[a] in ppm. [b] Sum of halogen atom contributions. [c] Sum of Rydberg's contributions. [d] Sum of all NLMO's contributions.

6.3 NLMO's contributions to the σ^{SO}

6.3.1 Neutral (CHX_3)

Table S24: NLMO's contributions[a] to the σ^{SO} in terms of principal axis system (σ_{xx}, σ_{yy}, and σ_{zz}) for CHX_3 (X = F, Cl, Br, or I) compounds.

Parent NBO	F			Cl			Br			I		
	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}
CR(C1)	0.65	0.65	0.64	0.43	0.43	0.94	-0.60	-0.60	2.29	-3.85	-3.85	8.48
ΣCR(X)[b]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.01	0.02	0.03	0.04
$\sigma_{C1\text{-}X2}$	0.29	0.01	0.45	2.79	0.80	4.66	15.37	5.28	29.12	51.31	3.03	94.34
$\sigma_{C1\text{-}X3}$	0.09	0.21	0.45	2.68	0.90	4.66	-2.08	22.68	28.92	-15.24	69.62	94.28
$\sigma_{C1\text{-}X4}$	0.07	0.23	0.45	-0.08	3.67	4.62	17.59	2.93	28.90	45.17	8.67	93.43
$\sigma_{C1\text{-}H5}$	0.48	0.48	0.20	-0.02	-0.02	-2.58	-2.66	-2.65	-19.21	-13.23	-13.29	-67.05
$\Sigma LP_1(X)$[b]	0.13	0.13	0.18	0.58	0.58	0.90	2.94	2.95	4.11	8.51	8.52	6.83
$\Sigma LP_2(X)$[b]	-0.02	-0.02	0.08	-0.03	-0.03	0.71	-0.53	-0.55	4.28	-4.82	-4.75	16.25
$\Sigma LP_3(X)$[b]	-0.01	-0.01	-0.04	0.03	0.03	-0.05	0.18	0.17	-0.14	0.41	0.33	0.09
$\sigma^*_{C1\text{-}X2}$	0.15	0.01	0.14	3.23	1.31	5.81	10.31	10.23	35.71	28.58	-3.58	111.76
$\sigma^*_{C1\text{-}X3}$	0.07	0.10	0.14	2.93	1.45	5.59	1.85	17.99	34.44	-13.88	38.50	110.04
$\sigma^*_{C1\text{-}X4}$	0.03	0.14	0.14	0.41	3.81	5.39	17.61	1.55	33.19	21.91	1.70	105.59
$\sigma^*_{C1\text{-}H5}$	0.03	0.03	-0.02	0.05	0.05	-0.16	0.41	0.41	-0.19	0.77	0.77	-0.37
ΣRY(C1)[c]	-0.1	-0.1	0.06	1.34	1.33	2.39	2.95	2.95	0.00	0.67	0.67	-52.43
ΣRY(X)[b,c]	0.33	0.34	0.39	-3.66	-3.67	-7.87	-11.31	-11.31	-27.50	-8.63	-8.63	-16.34
ΣRY(H)[c]	-0.01	-0.01	-0.02	0.10	0.10	-0.08	-0.96	-0.95	-4.37	-0.99	-0.98	-11.83
Σ_{total}[d]	2.19	2.19	3.25	10.77	10.76	24.94	51.09	51.08	149.55	96.73	96.76	493.12

[a] in ppm. [b] Sum of halogen atom contributions. [c] Sum of Rydberg's contributions. [d] Sum of all NLMO's contributions.

6.3.2 Cation (CX_3^+)

Table S25: NLMO's contributions[a] to the σ^{SO} in terms of principal axis system (σ_{xx}, σ_{yy}, and σ_{zz}) for CX_3^+ (X = F, Cl, Br, or I) compounds.

Parent NBO	F			Cl			Br			I		
	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}
CR(C1)	0.31	0.31	0.77	-1.38	-1.38	1.58	-10.32	-10.33	6.94	-26.55	-26.68	24.78
ΣCR(X)[b]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.01	0.00	0.03	0.02	0.04
$\sigma_{C1\text{-}X2}$	0.71	0.39	0.56	5.99	2.72	4.58	36.16	14.39	27.05	101.67	32.37	77.15
$\sigma_{C1\text{-}X3}$	0.47	0.63	0.56	3.54	5.17	4.58	19.83	30.75	27.03	49.11	83.87	75.99
$\sigma_{C1\text{-}X4}$	0.47	0.63	0.56	3.54	5.18	4.57	19.84	30.74	27.03	49.05	83.93	75.99
$\pi_{C1\text{-}X2}$	-0.09	-0.06	0.02	-0.47	-0.62	0.30	-2.32	-3.58	1.84	-4.99	-9.60	6.15
$\Sigma LP_1(X)$[b]	0.34	0.35	0.36	1.34	1.34	1.27	6.95	6.94	6.13	16.77	16.74	14.54
$\Sigma LP_2(X)$[b]	-0.09	-0.09	0.04	-0.37	-0.37	0.28	-1.53	-1.51	1.19	-1.50	-1.40	1.05
$\Sigma LP_3(X)$[b]	-0.09	-0.13	0.02	-0.68	-0.53	0.34	-3.74	-2.48	2.03	-9.22	-4.66	6.25
$\sigma^*_{C1\text{-}X2}$	0.00	0.01	0.02	3.14	0.51	6.45	19.02	1.93	46.09	42.54	-10.67	161.91
$\sigma^*_{C1\text{-}X3}$	0.01	0.00	0.02	1.16	2.48	6.45	6.20	14.75	46.07	1.72	28.36	153.06
$\sigma^*_{C1\text{-}X4}$	0.01	0.00	0.02	1.16	2.48	6.45	6.20	14.75	46.07	1.73	28.35	153.06
$\pi^*_{C1\text{-}X2}$	-0.13	-0.13	-0.03	-0.83	-0.83	0.09	-4.34	-4.35	0.24	-10.49	-10.52	-0.30
ΣRY(C1)[c]	0.39	0.39	1.64	1.05	1.05	4.13	8.16	8.17	34.54	16.00	16.02	115.54
ΣRY(X)[b,c]	-0.14	-0.14	-0.62	-2.54	-2.53	-9.82	-18.31	-18.31	-82.94	-31.06	-31.09	-280.72
Σ_{total}[d]	2.17	2.17	3.93	14.65	14.66	31.25	81.81	81.85	189.31	194.80	195.06	584.50

[a] in ppm. [b] Sum of halogen atom contributions. [c] Sum of Rydberg's contributions. [d] Sum of all NLMO's contributions.

6.3.3 Anion (CX_3^-)

Table S26: NLMO's contributions[a] to the σ^{SO} in terms of principal axis system (σ_{xx}, σ_{yy}, and σ_{zz}) for CX_3^- (X = F, Cl, Br, or I) compounds.

Parent NBO	F			Cl			Br			I		
	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}
CR(C1)	0.65	0.65	0.62	-0.24	-0.24	-0.74	-4.36	-4.36	-12.29	-18.33	-18.32	-67.41
ΣCR(X)[b]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.02	0.04
σ_{C1-X2}	1.73	-1.37	0.34	0.56	2.23	3.82	9.27	4.13	23.56	44.17	-6.88	97.87
σ_{C1-X3}	0.69	-0.33	0.34	2.55	0.23	3.80	0.70	12.69	23.63	-4.29	41.50	98.32
σ_{C1-X4}	-1.88	2.24	0.34	1.07	1.71	3.82	10.15	3.29	23.60	16.05	21.24	97.58
LP(C1)	0.51	0.51	0.76	-3.61	-3.61	-13.59	-27.65	-27.64	-114.64	-122.79	-122.75	-578.33
$\Sigma LP_1(X)$[b]	0.16	0.17	0.19	0.68	0.68	0.81	2.66	2.67	4.68	6.38	6.38	19.02
$\Sigma LP_2(X)$[b]	-0.03	-0.03	0.13	-0.50	-0.50	0.86	-0.68	-0.83	2.91	-4.00	-4.02	-3.77
$\Sigma LP_3(X)$[b]	-0.01	-0.01	-0.04	0.03	0.03	-0.07	0.05	0.20	-0.29	0.19	0.21	-0.30
σ^*_{C1-X2}	0.04	0.20	0.24	1.43	2.07	3.37	4.80	4.51	14.51	1.38	5.63	32.87
σ^*_{C1-X3}	0.23	0.01	0.24	2.88	0.47	3.20	1.01	8.01	13.98	-1.00	7.48	30.28
σ^*_{C1-X4}	0.09	0.15	0.24	0.83	2.60	3.29	8.16	1.45	15.08	9.73	-2.99	31.58
ΣRY(C1)[c]	0.39	0.39	0.51	2.86	2.86	4.57	7.92	7.93	21.40	15.97	15.97	87.06
ΣRY(X)[b,c]	-0.32	-0.33	-0.36	-4.57	-4.56	-7.65	-11.31	-11.32	-30.81	-14.48	-14.48	-84.69
Σ_{total}[d]	2.26	2.26	3.54	3.95	3.95	5.49	0.73	0.73	-14.68	-71.00	-71.03	-239.88

[a] in ppm. [b] Sum of halogen atom contributions. [c] Sum of Rydberg's contributions. [d] Sum of all NLMO's contributions.

6.4 NLMO's contributions to the σ

6.4.1 Neutral (CHX_3)

Table S27: NLMO's contributions[a] to the σ in terms of principal axis system (σ_{xx}, σ_{yy}, and σ_{zz}) for CHX_3 (X = F, Cl, Br, or I) compounds.

Parent NBO	F			Cl			Br			I		
	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}
CR(C1)	201.22	201.22	201.22	201.00	200.99	201.51	199.96	199.96	202.86	196.72	196.72	209.05
ΣCR(X)[b]	0.46	0.46	0.50	0.40	0.40	-1.09	1.75	1.75	-2.67	3.17	3.18	-4.74
σ_{C1-X2}	-43.54	0.17	-47.22	-15.30	-2.61	-45.56	-0.44	-0.46	-20.39	48.27	1.95	57.99
σ_{C1-X3}	-16.61	-26.75	-47.23	-14.10	-3.82	-45.59	0.36	-1.25	-20.70	-12.86	63.15	58.00
σ_{C1-X4}	-4.90	-38.47	-47.24	2.56	-20.41	-45.73	-1.29	0.36	-20.81	39.77	10.18	56.90
σ_{C1-H5}	-76.67	-76.67	15.81	-72.11	-72.01	13.25	-63.90	-63.91	-3.32	-63.71	-63.73	-51.31
$\Sigma LP_1(X)$[b]	-3.04	-3.04	-14.32	-3.17	-3.18	-9.77	-3.58	-3.58	-10.92	-1.45	-1.44	-12.27
$\Sigma LP_2(X)$[b]	4.04	4.04	-0.68	1.13	1.16	-0.13	1.60	1.60	3.84	-0.22	-0.20	16.68
$\Sigma LP_3(X)$[b]	5.18	5.18	-14.79	4.22	4.21	-15.36	2.89	2.89	-15.89	2.06	2.01	-12.17
σ^*_{C1-X2}	0.15	0.01	0.14	3.23	1.31	5.81	10.32	10.24	35.71	28.62	-3.52	111.78
σ^*_{C1-X3}	0.07	0.10	0.14	2.93	1.45	5.59	1.85	18.00	34.44	-13.82	38.53	110.06
σ^*_{C1-X4}	0.03	0.14	0.14	0.42	3.81	5.39	17.61	1.56	33.19	21.95	1.76	105.61
σ^*_{C1-H5}	0.03	0.03	-0.02	0.05	0.05	-0.16	0.41	0.41	-0.19	0.76	0.76	-0.37
ΣRY(C1)[c]	-0.10	-0.10	0.06	1.34	1.33	2.39	2.93	2.93	-0.04	0.55	0.55	-52.74
ΣRY(X)[b,c]	0.33	0.34	0.39	-3.65	-3.65	-7.87	-11.31	-11.30	-27.46	-8.53	-8.52	-16.08
ΣRY(H)[c]	-0.01	-0.01	-0.02	0.09	0.09	-0.08	-0.97	-0.97	-4.37	-1.07	-1.06	-11.83
Σ_{total}[d]	66.65	66.65	46.89	109.03	109.13	62.61	158.22	158.25	183.26	240.23	240.31	564.57

[a] in ppm. [b] Sum of halogen atom contributions. [c] Sum of Rydberg's contributions. [d] Sum of all NLMO's contributions.

6.4.2 Cation (CX_3^+)

Table S28: NLMO's contributions[a] to the σ in terms of principal axis system (σ_{xx}, σ_{yy}, and σ_{zz}) for CX_3^+ (X = F, Cl, Br, or I) compounds.

Parent NBO	F			Cl			Br			I		
	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}
CR(C1)	200.91	200.91	201.38	199.21	199.21	202.18	190.27	190.26	207.54	174.03	173.91	225.37
ΣCR(X)[b]	0.63	0.62	0.38	0.64	0.64	-1.68	2.81	2.82	-4.46	4.73	4.72	-6.95
$\sigma_{C1\text{-}X2}$	-120.80	12.25	-46.79	-216.61	16.78	-36.84	-234.44	28.84	-12.36	-241.73	47.39	51.11
$\sigma_{C1\text{-}X3}$	-21.04	-87.56	-46.80	-41.56	-158.23	-36.83	-36.95	-168.47	-12.32	-26.55	-171.26	49.58
$\sigma_{C1\text{-}X4}$	-21.02	-87.58	-46.79	-41.56	-158.23	-36.83	-36.93	-168.49	-12.32	-26.60	-171.20	49.58
$\pi_{C1\text{-}X2}$	-31.59	3.71	2.27	-59.29	13.34	3.58	-78.13	12.69	5.31	-102.77	13.96	9.93
$\Sigma LP_1(X)$[b]	-26.70	-26.72	-6.63	-28.57	-28.61	-4.93	-28.94	-29.00	-6.19	-26.15	-25.54	-0.51
$\Sigma LP_2(X)$[b]	32.60	32.61	-14.31	30.66	30.75	-16.62	26.62	26.77	-14.95	7.71	7.97	-11.10
$\Sigma LP_3(X)$[b]	-1.01	-36.33	1.44	12.42	-60.17	1.46	12.89	-77.90	3.14	17.91	-98.62	7.22
$\sigma^*_{C1\text{-}X2}$	0.00	0.01	0.02	3.14	0.51	6.45	19.02	1.94	46.08	42.54	-10.62	161.86
$\sigma^*_{C1\text{-}X3}$	0.01	0.00	0.02	1.17	2.48	6.45	6.21	14.75	46.06	1.76	28.37	153.02
$\sigma^*_{C1\text{-}X4}$	0.01	0.00	0.02	1.17	2.48	6.45	6.21	14.75	46.06	1.77	28.36	153.02
$\pi^*_{C1\text{-}X2}$	-0.13	-0.13	-0.03	-0.83	-0.83	0.10	-4.31	-4.32	0.26	-10.32	-10.35	-0.22
ΣRY(C1)[c]	0.39	0.39	1.64	1.05	1.05	4.13	8.14	8.14	34.49	15.98	15.99	115.41
ΣRY(X)[b,c]	-0.14	-0.14	-0.62	-2.54	-2.53	-9.82	-18.31	-18.29	-82.91	-31.02	-31.05	-280.54
Σ_{total}[d]	12.12	12.04	45.21	-141.51	-141.37	87.26	-165.82	-165.52	243.43	-198.73	-197.95	676.79

[a] in ppm. [b] Sum of halogen atom contributions. [c] Sum of Rydberg's contributions. [d] Sum of all NLMO's contributions.

6.4.3 Anion (CX_3^-)

Table S29: NLMO's contributions[a] to the σ in terms of principal axis system (σ_{xx}, σ_{yy}, and σ_{zz}) for CX_3^- (X = F, Cl, Br, or I) compounds.

Parent NBO	F			Cl			Br			I		
	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}
CR(C1)	201.09	201.09	201.07	200.12	200.12	199.66	196.01	196.01	188.08	182.05	182.06	132.98
ΣCR(X)[b]	0.41	0.41	0.41	0.22	0.22	-0.60	0.98	0.98	-1.41	1.92	1.91	-2.82
$\sigma_{C1\text{-}X2}$	-20.44	-42.26	-46.07	-33.66	-42.04	-53.73	-52.40	-49.61	-39.22	-34.06	-48.77	43.65
$\sigma_{C1\text{-}X3}$	-46.37	-16.29	-46.09	-53.26	-21.66	-53.98	-29.94	-72.08	-39.17	-26.40	-56.45	44.01
$\sigma_{C1\text{-}X4}$	-27.21	-35.47	-46.09	-26.11	-49.32	-53.82	-70.70	-31.31	-39.15	-63.78	-19.01	43.22
LP(C1)	-140.33	-140.32	24.99	-110.43	-110.41	13.59	-96.11	-96.07	-86.14	-154.12	-154.05	-549.18
$\Sigma LP_1(X)$[b]	-5.21	-5.21	-12.40	-14.05	-14.06	-12.62	-18.06	-18.06	-14.24	-22.61	-22.58	-4.26
$\Sigma LP_2(X)$[b]	2.35	2.34	0.40	1.69	1.68	1.68	-1.60	-1.57	3.62	-5.34	-5.34	-3.03
$\Sigma LP_3(X)$[b]	2.99	3.00	-12.39	-0.16	-0.15	-14.10	0.60	0.54	-14.19	0.36	0.35	-12.70
$\sigma^*_{C1\text{-}X2}$	0.04	0.20	0.24	1.43	2.07	3.37	4.80	4.52	14.52	1.43	5.68	32.92
$\sigma^*_{C1\text{-}X3}$	0.23	0.01	0.24	2.88	0.47	3.20	1.01	8.02	13.98	-0.94	7.53	30.33
$\sigma^*_{C1\text{-}X4}$	0.09	0.15	0.24	0.83	2.60	3.29	8.16	1.45	15.08	9.79	-2.94	31.62
ΣRY(C1)[c]	0.39	0.39	0.51	2.86	2.86	4.57	7.92	7.93	21.37	16.03	16.04	86.92
ΣRY(X)[b,c]	-0.32	-0.33	-0.36	-4.57	-4.56	-7.65	-11.30	-11.31	-30.80	-14.48	-14.48	-84.57
Σ_{total}[d]	-32.30	-32.29	64.69	-32.23	-32.19	32.86	-60.65	-60.58	-7.66	-110.15	-110.04	-210.93

[a] in ppm. [b] Sum of halogen atom contributions. [c] Sum of Rydberg's contributions. [d] Sum of all NLMO's contributions.

7 MO's contributions to the σ^{13}C NMR

MO's contributions to paramagnetic and spin-orbit terms of the σ^{13}C NMR are displayed in Tables S30-S35. Each contribution is decomposed into values from couplings between pairs of occupied MOs (occ-occ) and between occupied and vacant MOs (occ-vac).

7.1 Neutral (CHX_3)

Table S30: MO's contributions[a] to the σ^{para} in terms of principal axis system (σ_{xx}, σ_{yy}, and σ_{zz}) for CHX_3 (X = F, Cl, Br, or I) compounds.

Contribution	F			Cl			Br			I		
	occ-vac	occ-occ	total	occ-vac	occ-occ	total	occ-vac	occ-occ	total	occ-vac	occ-occ	total
σ_{xx}	-205.38	-6.06	-211.44	-222.19	63.64	-158.55	-225.75	74.30	-151.46	-252.66	160.25	-92.41
σ_{yy}	-205.37	-6.06	-211.43	-222.18	63.72	-158.46	-225.75	74.31	-151.44	-252.74	160.37	-92.37
σ_{zz}	-207.81	-0.40	-208.21	-243.88	21.95	-221.93	-263.61	44.66	-218.95	-267.59	101.53	-166.05
σ	-206.19	-4.17	-210.36	-229.42	49.77	-179.65	-238.37	64.42	-173.95	-257.66	140.72	-116.95

[a] in ppm.

Table S31: MO's contributions[a] to the σ^{SO} in terms of principal axis system (σ_{xx}, σ_{yy}, and σ_{zz}) for CHX_3 (X = F, Cl, Br, or I) compounds.

Contribution	F			Cl			Br			I		
	occ-vac	occ-occ	total	occ-vac	occ-occ	total	occ-vac	occ-occ	total	occ-vac	occ-occ	total
σ_{xx}	1.37	0.82	2.19	7.61	3.16	10.77	38.09	13.01	51.12	65.17	31.54	96.71
σ_{yy}	1.37	0.81	2.18	7.60	3.17	10.77	38.08	13.01	51.09	65.23	31.54	96.77
σ_{zz}	2.43	0.82	3.25	21.21	3.73	24.94	128.01	21.54	149.55	429.75	63.37	493.12
σ	1.72	0.82	2.54	12.14	3.35	15.49	68.06	15.85	83.92	186.72	42.15	228.87

[a] in ppm.

7.2 Cation (CX_3^+)

Table S32: MO's contributions[a] to the σ^{para} in terms of principal axis system (σ_{xx}, σ_{yy}, and σ_{zz}) for CX_3^+ (X = F, Cl, Br, or I) compounds.

Contribution	F			Cl			Br			I		
	occ-vac	occ-occ	total	occ-vac	occ-occ	total	occ-vac	occ-occ	total	occ-vac	occ-occ	total
σ_{xx}	-233.26	-26.33	-259.59	-424.81	-11.85	-436.66	-515.89	-10.60	-526.49	-671.69	0.98	-670.71
σ_{yy}	-233.32	-26.37	-259.68	-424.66	-11.85	-436.51	-515.62	-10.62	-526.24	-671.34	1.20	-670.15
σ_{zz}	-198.70	-16.23	-214.93	-221.65	11.81	-209.84	-239.50	38.45	-201.05	-227.46	75.55	-151.92
σ	-221.76	-22.98	-244.73	-357.04	-3.96	-361.00	-423.67	5.74	-417.93	-523.50	25.91	-497.59

[a] in ppm.

Table S33: MO's contributions[a] to the σ^{SO} in terms of principal axis system (σ_{xx}, σ_{yy}, and σ_{zz}) for CX_3^+ (X = F, Cl, Br, or I) compounds.

Contribution	F			Cl			Br			I		
	occ-vac	occ-occ	total	occ-vac	occ-occ	total	occ-vac	occ-occ	total	occ-vac	occ-occ	total
σ_{xx}	1.94	0.23	2.17	12.27	2.38	14.65	69.31	12.50	81.81	157.44	37.36	194.80
σ_{yy}	1.95	0.22	2.16	12.28	2.38	14.66	69.35	12.50	81.85	157.66	37.41	195.07
σ_{zz}	3.36	0.57	3.94	26.02	5.24	31.26	157.80	31.51	189.31	497.35	87.15	584.50
σ	2.42	0.34	2.76	16.86	3.33	20.19	98.82	18.84	117.66	270.82	53.98	324.79

[a] in ppm.

7.3 Anion (CX_3^-)

Table S34: MO's contributions[a] to the σ^{para} in terms of principal axis system (σ_{xx}, σ_{yy}, and σ_{zz}) for CX_3^- (X = F, Cl, Br, or I) compounds.

Contribution	F			Cl			Br			I		
	occ-vac	occ-occ	total	occ-vac	occ-occ	total	occ-vac	occ-occ	total	occ-vac	occ-occ	total
σ_{xx}	-311.51	10.67	-300.84	-375.40	83.59	-291.81	-396.43	84.74	-311.69	-390.03	97.28	-292.75
σ_{yy}	-311.51	10.68	-300.83	-375.39	83.57	-291.82	-396.43	84.76	-311.68	-390.05	97.39	-292.66
σ_{zz}	-193.37	-0.75	-194.12	-255.04	29.56	-225.48	-295.03	58.13	-236.91	-297.61	87.01	-210.60
σ	-272.13	6.87	-265.26	-335.28	65.57	-269.71	-362.63	75.87	-286.76	-359.23	93.89	-265.34

[a] in ppm.

Table S35: MO's contributions[a] to the σ^{SO} in terms of principal axis system (σ_{xx}, σ_{yy}, and σ_{zz}) for CX_3^- (X = F, Cl, Br, or I) compounds.

Contribution	F			Cl			Br			I		
	occ-vac	occ-occ	total	occ-vac	occ-occ	total	occ-vac	occ-occ	total	occ-vac	occ-occ	total
σ_{xx}	1.37	0.90	2.27	1.26	2.69	3.95	-7.58	8.31	0.73	-84.39	13.42	-70.97
σ_{yy}	1.36	0.90	2.26	1.27	2.68	3.95	-7.58	8.31	0.73	-84.51	13.45	-71.06
σ_{zz}	2.54	0.99	3.53	2.77	2.71	5.48	-25.93	11.26	-14.68	-266.79	26.92	-239.87
σ	1.76	0.93	2.69	1.77	2.69	4.46	-13.70	9.29	-4.40	-145.23	17.93	-127.30

[a] in ppm.

8 MSP contributions to the σ^{SO} of iodine compounds

Table S36: Molecular spinor pair (MSP) contributions[a] to the σ^{SO} for CHI_3, CI_3^+, and CI_3^-.

MSP	CHI_3	CI_3^+	CI_3^-	MSP	CHI_3	CI_3^+	CI_3^-
1	0.00	0.00	0.00	**43**	-0.40	-9.12	-37.12
2	0.00	0.00	0.00	**44**	0.00	0.00	0.00
3	0.00	0.00	0.00	**45**	0.00	0.00	0.00
4	0.00	0.00	0.00	**46**	0.00	0.00	0.00
5	0.00	0.00	0.00	**47**	0.00	0.01	0.00
6	0.00	0.00	0.00	**48**	0.00	0.00	0.00
7	0.00	0.00	0.00	**49**	0.00	0.00	0.00
8	0.00	0.00	0.00	**50**	-0.01	-0.01	0.00
9	0.00	0.00	0.00	**51**	-0.01	-0.01	0.00
10	0.00	0.00	0.00	**52**	-0.01	-0.01	0.00
11	0.00	0.00	0.00	**53**	0.01	0.00	0.00
12	0.00	0.00	0.00	**54**	0.01	0.01	0.00
13	0.00	0.00	0.00	**55**	0.01	0.01	0.00
14	0.00	0.00	0.00	**56**	-0.06	-0.09	-0.04
15	0.00	0.00	0.00	**57**	-0.06	-0.04	-0.03
16	0.00	0.00	0.00	**58**	0.00	-0.03	0.02
17	0.00	0.00	0.00	**59**	0.01	0.01	0.00
18	0.00	0.00	0.00	**60**	0.00	0.00	0.00
19	0.00	0.00	0.00	**61**	0.03	0.00	0.00
20	0.00	0.00	0.00	**62**	0.17	0.18	0.12
21	0.00	0.00	0.00	**63**	0.04	0.05	0.00
22	0.00	0.00	0.00	**64**	-0.01	0.05	0.00
23	0.00	0.00	0.00	**65**	0.00	-0.02	-0.01
24	0.00	0.00	0.00	**66**	-0.02	-0.01	-0.01
25	0.00	0.00	0.00	**67**	-0.03	-0.01	-0.03
26	0.00	0.00	0.00	**68**	0.00	0.01	0.01
27	0.00	0.00	0.00	**69**	0.01	0.00	0.01
28	0.00	0.00	0.00	**70**	0.01	0.00	0.01
29	0.00	0.00	0.00	**71**	34.46	50.24	23.81
30	0.00	0.00	0.00	**72**	1.06	3.18	0.98
31	0.00	0.00	0.00	**73**	-0.91	-0.90	-0.88
32	0.00	0.00	0.00	**74**	21.78	79.39	47.53
33	0.00	0.00	0.00	**75**	24.51	50.96	45.00
34	0.00	0.00	0.00	**76**	27.69	-20.64	0.34
35	0.00	0.00	0.00	**77**	-26.54	-4.60	-49.58
36	0.00	0.00	0.00	**78**	1.14	11.05	-35.85
37	0.00	0.00	0.00	**79**	-5.76	166.64	-7.71
38	0.00	0.00	0.00	**80**	79.10	-59.06	75.07
39	0.00	0.00	0.00	**81**	6.24	-25.91	-0.81
40	0.00	0.00	0.00	**82**	0.45	29.47	4.17
41	0.00	0.00	0.00	**83**	23.82	-	-210.26
42	0.00	0.00	0.00	**Total**	186.72	270.82	-145.23

[a] in ppm.

9 NBO analyses

NBO analyses were performed using B1PW91/QZ4P level of theory, the COSMO solvent model, and SO-ZORA approach.

Table S37: Energies (in au) of valence NBO's for CHX_3, CX_3^+, and CX_3^- (X = F, Cl, Br, or I) compounds.

NBO	Neutral (CHX_3)				Cation (CX_3^+)				Anion (CX_3^-)			
	F	Cl	Br	I	F	Cl	Br	I	F	Cl	Br	I
$\sigma_{C\text{-}X}$	-0.66108	-0.44456	-0.38831	-0.33524	-0.91825	-0.60345	-0.52732	-0.44645	-0.47393	-0.30506	-0.25778	-0.21157
$\sigma_{C\text{-}H}$	-0.38315	-0.38231	-0.37629	-0.36291	-	-	-	-	-	-	-	-
$\pi_{C\text{-}X}$	-	-	-	-	-0.40909	-0.30539	-0.26731	-0.22896	-	-	-	-
LP(C)	-	-	-	-	-	-	-	-	-0.08922	-0.15238	-0.18091	-0.18742
$LP_1(X)$	-0.60820	-0.48942	-0.47695	-0.39400	-0.73129	-0.57553	-0.56089	-0.47802	-0.54634	-0.41863	-0.41111	-0.33933
$LP_2(X)$	-0.16719	-0.16615	-0.15529	-0.15276	-0.31157	-0.22642	-0.19623	-0.16860	-0.07942	-0.11926	-0.11195	-0.10848
$LP_3(X)$	-0.16735	-0.15335	-0.13502	-0.12100	-0.32490	-0.23342	-0.20194	-0.17174	-0.08012	-0.09504	-0.08284	-0.07638
$\sigma^*_{C\text{-}X}$	0.37457	0.19610	0.15631	0.11623	0.40226	0.18896	0.19334	0.14725	0.38354	0.22468	0.17657	0.17515
$\sigma^*_{C\text{-}H}$	0.38540	0.45297	0.49326	0.53740	-	-	-	-	-	-	-	-
$\pi^*_{C\text{-}X}$	-	-	-	-	-0.14093	-0.14207	-0.13322	-0.12116	-	-	-	-

Table S38: Occupancy of valence NBO's for CHX_3, CX_3^+, and CX_3^- (X = F, Cl, Br, or I) compounds.

NBO	Neutral (CHX_3)				Cation (CX_3^+)				Anion (CX_3^-)			
	F	Cl	Br	I	F	Cl	Br	I	F	Cl	Br	I
$\sigma_{C\text{-}X}$	1.99561	1.99259	1.99120	1.98882	1.99718	1.99324	1.99008	1.98660	1.99332	1.99127	1.99279	1.99305
$\sigma_{C\text{-}H}$	1.99390	1.99292	1.99377	1.99442	-	-	-	-	-	-	-	-
$\pi_{C\text{-}X}$	-	-	-	-	1.99913	1.99792	1.99834	1.99736	-	-	-	-
LP(C)	-	-	-	-	-	-	-	-	1.99358	1.98137	1.98767	1.98695
$LP_1(X)$	1.99283	1.99607	1.99651	1.99633	1.98691	1.98720	1.98629	1.98341	1.99410	1.99694	1.99705	1.99690
$LP_2(X)$	1.95226	1.96052	1.96299	1.96552	1.92900	1.92823	1.93274	1.94095	1.97081	1.96931	1.96463	1.95834
$LP_3(X)$	1.94028	1.94962	1.95431	1.96215	1.79797	1.70149	1.68400	1.65292	1.95761	1.96397	1.96518	1.96798
$\sigma^*_{C\text{-}X}$	0.08545	0.07110	0.06822	0.06110	0.07311	0.07447	0.07487	0.07222	0.06872	0.06405	0.06593	0.06665
$\sigma^*_{C\text{-}H}$	0.05907	0.04121	0.03574	0.03247	-	-	-	-	-	-	-	-
$\pi^*_{C\text{-}X}$	-	-	-	-	0.39185	0.57784	0.61549	0.67939	-	-	-	-

Table S39: Atomic hybrid contributions of carbon (in %) in the main NBO's for CHX_3, CX_3^+, and CX_3^- (X = F, Cl, Br, or I) compounds.

NBO	Neutral (CHX_3)				Cation (CX_3^+)				Anion (CX_3^-)			
	F	Cl	Br	I	F	Cl	Br	I	F	Cl	Br	I
$\sigma_{C\text{-}X}$	28.47	47.60	51.23	56.65	29.33	50.76	54.85	60.42	23.90	37.18	38.87	43.06
$\sigma_{C\text{-}H}$	58.16	63.95	63.86	63.21	-	-	-	-	-	-	-	-
$\pi_{C\text{-}X}$	-	-	-	-	12.51	20.90	22.77	26.21	-	-	-	-
$\sigma^*_{C\text{-}X}$	71.53	52.40	48.77	43.35	70.67	49.24	45.15	39.58	76.10	62.82	61.13	56.94
$\sigma^*_{C\text{-}H}$	41.84	36.05	36.14	36.79	-	-	-	-	-	-	-	-
$\pi^*_{C\text{-}X}$	-	-	-	-	87.49	79.10	77.23	73.79	-	-	-	-

Table S40: The *s* character of valence NBO's for CHX_3, CX_3^+, and CX_3^- (X = F, Cl, Br, or I) compounds.

NBO	Neutral (CHX_3)				Cation (CX_3^+)				Anion (CX_3^-)			
	F	Cl	Br	I	F	Cl	Br	I	F	Cl	Br	I
$\sigma_{C\text{-}X}$ [a]	22.74	23.27	23.03	23.03	33.30	33.19	33.16	33.16	14.76	10.46	8.04	6.56
$\sigma_{C\text{-}H}$ [a]	32.23	30.12	30.81	30.82	-	-	-	-	-	-	-	-
$\pi_{C\text{-}X}$ [a]	-	-	-	-	0.00	0.00	0.00	0.00	-	-	-	-
LP(C)	-	-	-	-	-	-	-	-	60.19	69.50	76.35	80.44
LP_1(X)	73.65	82.95	84.45	81.19	72.07	84.16	88.13	89.97	75.84	80.01	81.56	78.84
LP_2(X)	0.08	3.33	5.29	10.11	0.00	0.00	0.00	0.00	0.00	6.06	7.35	10.59
LP_3(X)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\sigma^*_{C\text{-}X}$ [a]	22.74	23.27	23.03	23.03	33.30	33.19	33.16	33.16	14.76	10.46	8.04	6.56
$\sigma^*_{C\text{-}H}$ [a]	32.23	30.12	30.81	30.82	-	-	-	-	-	-	-	-
$\pi^*_{C\text{-}X}$ [a]	-	-	-	-	0.00	0.00	0.00	0.00	-	-	-	-

[a] Values refer to *s* character of carbon atom in the hybrid orbital.

10 ^{13}C NMR Spectra

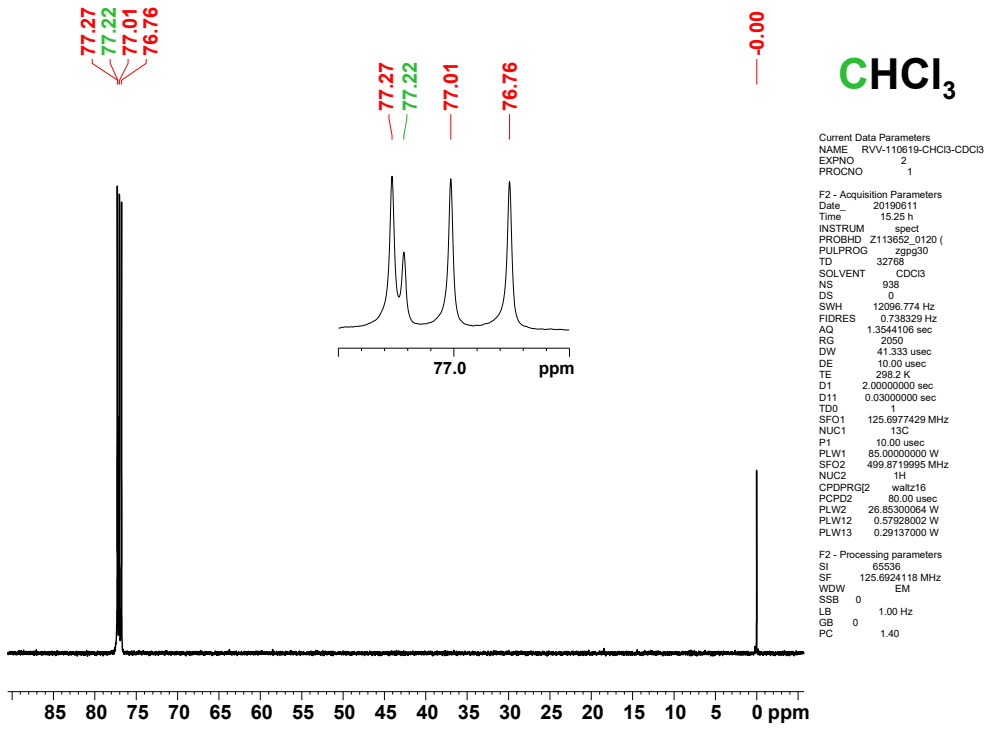

Figure S2: ^{13}C NMR spectrum of trichloromethane recorded at 125.7 MHz in $CDCl_3$.

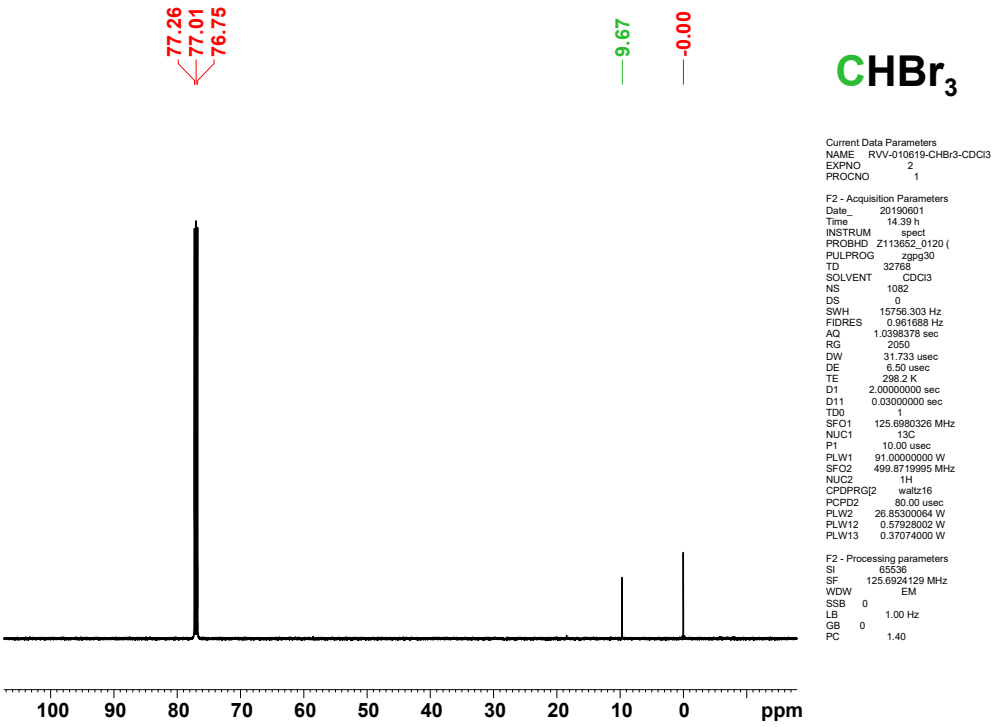

Figure S3: ^{13}C NMR spectrum of tribromomethane recorded at 125.7 MHz in $CDCl_3$.

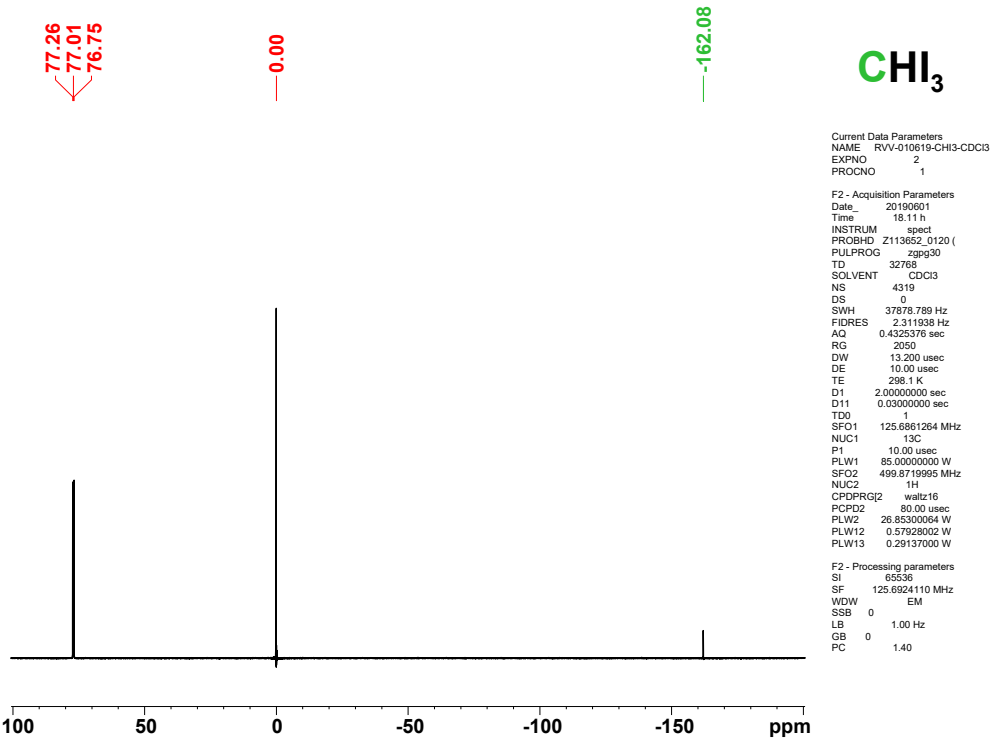

Figure S4: ^{13}C NMR spectrum of triiodomethane recorded at 125.7 MHz in $CDCl_3$.

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