Supporting Information

Origin of ^{13}C NMR chemical shifts elucidated based on molecular orbital theory: paramagnetic contributions from orbital-to-orbital transitions for the pre-α, α, β, α-X, β-X and *ipso*-X effects, along with effects from characteristic bonds and groups†

Waro Nakanishi,* Satoko Hayashi* and Keigo Matsuzaki

Faculty of Systems Engineering, Wakayama University,
930 Sakaedani, Wakayama 640-8510, Japan.
E-mail: nakanisi@wakayama-u.ac.jp and hayashi3@wakayama-u.ac.jp

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Table S1. The σ^t(C: S), and $-\Delta\sigma^t$(C: S) and $\delta(C)_{obsd}$ for various 40 species (54 plots), calculated with the GIAO-DFT method under B3LYP/BSS-A.

Species	(symmetry)		σ^t(C)	$-\Delta\sigma^t(C)_{TMS}$	$\delta(C)_{obsd}$
TMS	$SiMe_4$ (T_d)		182.99	0.00	0.0
methane	CH_4 (T_d)		189.32	-6.33	-4.6
ethane	(CH_3CH_3: D_{3d})		173.39	9.60	7.3
propane	$CH_3CH_2CH_3$ (C_{2v})		160.10	22.89	16.4
n-pentane	*n*-C_5H_{12} (C_{2v})		140.94	42.05	34.8
n-heptane	*n*-C_7H_{16} (C_{2v})		144.07	38.92	29.5
n-nonane	(C_{2v})		144.20	38.79	29.8
methylamine	(CH_3NH_2: C_s)		150.01	32.98	28.4
methanol	(CH_3OH: C_s)		127.49	55.50	50.2
fluoromethane	(CH_3F: C_{3v})		106.99	76.00	71.6
dimethylamine	Me_2NH (C_s)		141.04	41.95	38.2
trimethylamine	Me_3N (C_{3v})		133.29	49.70	47.6
acetonitrile	MeCN (C_{3v})		181.70	1.29	1.7
methyl isocyanide	MeNC (C_{3v})		156.37	26.62	26.8
nitromethane	$MeNO_2$ (C_s)		117.50	65.49	62.5
acetaldehyde	CH_3CHO (C_s)		148.14	34.85	31.3
acetone	CH_3COCH_3 (C_{2v})		151.13	31.86	30.9
acetic acid	CH_3COOH (C_s)		162.24	20.75	20.8
methyl acetate	CH_3COOCH_3 (C_s)		160.82	22.17	20.6
methanethiol	CH_3SH (Cs)		170.23	12.76	6.5
dimethyl sulfide	CH_3SCH_3 (C_{2v})		159.29	23.70	19.3
DMSO	$CH_3S(O)CH_3$ (C_s)		136.64	46.35	41.0
methane sulfonic acid	CH_3SO_3H (C_1)		139.67	43.32	39.6
chloromethane	CH_3Cl (C_{3v})		150.42	32.57	25.6
dimethyl ether	CH_3OCH_3 (C_{2v})		119.08	63.91	60.9
methyl ethyl ether	MeOEt (C_s)		120.39	62.60	57.6
methyl iso-propyl ether	MeOPr-*i* (C_1)		123.55	59.44	54.9
methyl tert-butyl ether	MeOBu-*t* (C_s)		130.74	52.25	49.4
ethylene	$CH_2=CH_2$ (D_{2h})		52.08	130.91	123.3
trans-butadiene	*t*-$CH_2=CHCH=CH_2$ (C_{2h})	C1	58.69	124.30	117.5
		C2	34.39	148.60	137.8
cis-butadiene	*c*-$CH_2=CHCH=CH_2$ (C_2)	C1	58.85	124.14	117.5
		C2	34.12	148.87	137.8
propylene	$CH_2=CHCH_3$ (C_s)	C1	37.20	145.79	140.2
		C2	61.63	121.36	115.7
			159.86	23.13	24.2
vinyl alcohol	$CH_2=CHOH$ (C_s)	C1	26.57	156.42	149.0
		C2	89.96	93.03	88.0
methyl vinyl ether	$CH_2=CHOMe$ (C_s)	C1	19.36	163.63	152.9
		C2	97.51	85.48	85.5
acrolein	$CH_2=CHCHO$ (C_s)	C4	33.08	149.91	138.5
		C1	37.88	145.11	138.0
methyl vinyl ketone	$CH_2=CHCOCH_3$ (C_s)	C4	33.38	149.61	137.5
		C1	48.01	134.98	129.0
cis-acrylic acid	*c*-$CH_2=CHCOOH$ (C_s)	C4	47.71	135.28	128.1
		C1	40.18	142.81	133.2
trans-acrylic acid	*t*-$CH_2=CHCOOH$ (C_s)	C2	44.90	138.09	128.1
		C1	43.00	139.99	133.2
nitroethylene	$CH_2=CHNO_2$ (C_s)	C4	26.55	156.44	144.7
		C1	53.02	129.97	121.5
isocyanoethylene	$CH_2=CHNC$ (C_s)	C1	55.11	127.88	121.0
		C4	56.04	126.95	119.3
N,*N*-dimethylethenamine	(C_1)	C13	166.61	16.38	12.8
		C10	124.24	58.75	53.6
		C1	138.89	44.10	44.6

Table S2. The σ^t(C: S), and $-\Delta\sigma^t$(C: S) and $\delta(C)_{obsd}$ for various 40 species (54 plots), calculated with the GIAO-DFT method under CAM-B3LYP/BSS-A.

Species	(symmetry)		σ^t(C)	$-\Delta\sigma^t(C)_{TMS}$	$\delta(C)_{obsd}$
TMS	$SiMe_4$ (T_d)		186.63	0.00	0.0
methane	CH_4 (T_d)		192.76	-6.13	-4.6
ethane	(CH_3CH_3: D_{3d})		177.83	8.80	7.3
propane	$CH_3CH_2CH_3$ (C_{2v})		165.50	21.13	16.4
n-pentane	*n*-C_5H_{12} (C_{2v})		145.62	41.01	34.8
n-heptane	*n*-C_7H_{16} (C_{2v})		148.90	37.73	29.5
n-nonane	(C_{2v})		149.00	37.63	29.8
methylamine	(CH_3NH_2: C_s)		154.83	31.80	28.4
methanol	(CH_3OH: C_s)		131.95	54.67	50.2
fluoromethane	(CH_3F: C_{3v})		110.87	75.76	71.6
dimethylamine	Me_2NH (C_s)		145.61	41.02	38.2
trimethylamine	Me_3N (C_{3v})		137.49	49.14	47.6
acetonitrile	MeCN (C_{3v})		186.01	0.62	1.7
methyl isocyanide	MeNC (C_{3v})		160.55	26.08	26.8
nitromethane	$MeNO_2$ (C_s)		121.34	65.29	62.5
acetaldehyde	CH_3CHO (C_s)		151.71	34.91	31.3
acetone	CH_3COCH_3 (C_{2v})		154.35	32.28	30.9
acetic acid	CH_3COOH (C_s)		165.68	20.95	20.8
methyl acetate	CH_3COOCH_3 (C_s)		164.24	22.39	20.6
methanethiol	CH_3SH (Cs)		176.13	10.50	6.5
dimethyl sulfide	CH_3SCH_3 (C_{2v})		164.74	21.89	19.3
DMSO	$CH_3S(O)CH_3$ (C_s)		146.86	39.77	41.0
methane sulfonic acid	CH_3SO_3H (C_1)		147.15	39.48	39.6
chloromethane	CH_3Cl (C_{3v})		156.74	29.89	25.6
dimethyl ether	CH_3OCH_3 (C_{2v})		123.44	63.19	60.9
methyl ethyl ether	MeOEt (C_s)		124.81	61.82	57.6
methyl iso-propyl ether	MeOPr-*i* (C_1)		138.12	48.51	54.9
methyl tert-butyl ether	MeOBu-*t* (C_s)		135.32	51.31	49.4
ethylene	$CH_2=CH_2$ (D_{2h})		53.26	133.36	123.3
trans-butadiene	*t*-$CH_2=CHCH=CH_2$ (C_{2h})	C1	60.30	126.32	117.5
		C2	35.87	150.76	137.8
cis-butadiene	*c*-$CH_2=CHCH=CH_2$ (C_2)	C1	63.19	123.43	117.5
		C2	37.91	148.72	137.8
propylene	$CH_2=CHCH_3$ (C_s)	C1	38.98	147.64	140.2
		C2	63.02	123.61	115.7
			164.24	22.39	24.2
vinyl alcohol	$CH_2=CHOH$ (C_s)	C1	28.47	158.16	149.0
		C2	91.34	95.28	88.0
methyl vinyl ether	$CH_2=CHOMe$ (C_s)	C1	20.90	165.73	152.9
		C2	99.08	87.54	85.5
acrolein	$CH_2=CHCHO$ (C_s)	C4	34.68	151.94	138.5
		C1	39.88	146.75	138.0
methyl vinyl ketone	$CH_2=CHCOCH_3$ (C_s)	C4	34.90	151.73	137.5
		C1	49.45	137.18	129.0
cis-acrylic acid	*c*-$CH_2=CHCOOH$ (C_s)	C4	49.77	136.86	128.1
		C1	41.19	145.43	133.2
trans-acrylic acid	*t*-$CH_2=CHCOOH$ (C_s)	C2	46.89	139.74	128.1
		C1	44.06	142.57	133.2
nitroethylene	$CH_2=CHNO_2$ (C_s)	C4	29.43	157.20	144.7
		C1	53.94	132.69	121.5
isocyanoethylene	$CH_2=CHNC$ (C_s)	C1	57.65	128.98	121.0
		C4	56.11	130.52	119.3
N,*N*-dimethylethenamine	(C_1)	C13	170.66	15.96	12.8
		C10	129.33	57.30	53.6
		C1	136.45	50.18	44.6

Table S3. The σ^t(C: S), and $-\Delta\sigma^t$(C: S) and $\delta(C)_{obsd}$ for various 40 species (54 plots), calculated with the GIAO-DFT method under PBE/BSS-A.

Species	(symmetry)		σ^t(C)	$-\Delta\sigma^t(C)_{TMS}$	$\delta(C)_{obsd}$
TMS	$SiMe_4$ (T_d)		181.82	0.00	0.0
methane	CH_4 (T_d)		189.44	-7.62	-4.6
ethane	(CH_3CH_3: D_{3d})		172.53	9.29	7.3
propane	$CH_3CH_2CH_3$ (C_{2v})		158.68	23.14	16.4
n-pentane	*n*-C_5H_{12} (C_{2v})		138.77	43.05	34.8
n-heptane	*n*-C_7H_{16} (C_{2v})		142.18	39.64	29.5
n-nonane	(C_{2v})		142.31	39.51	29.8
methylamine	(CH_3NH_2: C_s)		148.22	33.60	28.4
methanol	(CH_3OH: C_s)		125.11	56.71	50.2
fluoromethane	(CH_3F: C_{3v})		104.13	77.69	71.6
dimethylamine	Me_2NH (C_s)		138.76	43.06	38.2
trimethylamine	Me_3N (C_{3v})		130.83	50.99	47.6
acetonitrile	MeCN (C_{3v})		180.44	1.38	1.7
methyl isocyanide	MeNC (C_{3v})		155.55	26.27	26.8
nitromethane	$MeNO_2$ (C_s)		116.56	65.26	62.5
acetaldehyde	CH_3CHO (C_s)		146.41	35.42	31.3
acetone	CH_3COCH_3 (C_{2v})		149.84	31.99	30.9
acetic acid	CH_3COOH (C_s)		161.93	19.89	20.8
methyl acetate	CH_3COOCH_3 (C_s)		160.59	21.23	20.6
methanethiol	CH_3SH (Cs)		169.38	12.45	6.5
dimethyl sulfide	CH_3SCH_3 (C_{2v})		157.68	24.14	19.3
DMSO	$CH_3S(O)CH_3$ (C_s)		137.46	44.36	41.0
methane sulfonic acid	CH_3SO_3H (C_1)		140.54	41.28	39.6
chloromethane	CH_3Cl (C_{3v})		150.09	31.73	25.6
dimethyl ether	CH_3OCH_3 (C_{2v})		115.95	65.88	60.9
methyl ethyl ether	MeOEt (C_s)		117.41	64.42	57.6
methyl iso-propyl ether	MeOPr-*i* (C_1)		131.84	49.99	54.9
methyl tert-butyl ether	MeOBu-*t* (C_s)		128.48	53.34	49.4
ethylene	$CH_2=CH_2$ (D_{2h})		51.43	130.39	123.3
trans-butadiene	*t*-$CH_2=CHCH=CH_2$ (C_{2h})	C1	57.93	123.89	117.5
		C2	34.20	147.62	137.8
cis-butadiene	*c*-$CH_2=CHCH=CH_2$ (C_2)	C1	61.90	119.92	117.5
		C2	36.78	145.04	137.8
propylene	$CH_2=CHCH_3$ (C_s)	C1	37.45	144.38	140.2
		C2	60.96	120.86	115.7
			158.11	23.72	24.2
vinyl alcohol	$CH_2=CHOH$ (C_s)	C1	27.11	154.71	149.0
		C2	90.87	90.95	88.0
methyl vinyl ether	$CH_2=CHOMe$ (C_s)	C1	20.37	161.45	152.9
		C2	97.94	83.88	85.5
acrolein	$CH_2=CHCHO$ (C_s)	C4	33.28	148.54	138.5
		C1	35.72	146.10	138.0
methyl vinyl ketone	$CH_2=CHCOCH_3$ (C_s)	C4	33.88	147.94	137.5
		C1	47.31	134.51	129.0
cis-acrylic acid	*c*-$CH_2=CHCOOH$ (C_s)	C4	47.08	134.75	128.1
		C1	40.20	141.62	133.2
trans-acrylic acid	*t*-$CH_2=CHCOOH$ (C_s)	C2	44.42	137.41	128.1
		C1	43.15	138.68	133.2
nitroethylene	$CH_2=CHNO_2$ (C_s)	C4	25.98	155.84	144.7
		C1	53.63	128.19	121.5
isocyanoethylene	$CH_2=CHNC$ (C_s)	C1	55.06	126.76	121.0
		C4	56.19	125.63	119.3
N,*N*-dimethylethenamine	(C_1)	C13	165.89	15.93	12.8
		C10	121.55	60.27	53.6
		C1	129.74	52.08	44.6

Table S4. The σ^t(C: S), and $-\Delta\sigma^t$(C: S) and $\delta(C)_{obsd}$ for various 40 species (54 plots), calculated with the GIAO-DFT method under PBE0/BSS-A.

Species	(symmetry)		σ^t(C)	$-\Delta\sigma^t(C)_{TMS}$	$\delta(C)_{obsd}$
TMS	$SiMe_4$ (T_d)		187.78	0.00	0.0
methane	CH_4 (T_d)		193.26	-5.48	-4.6
ethane	(CH_3CH_3: D_{3d})		178.68	9.10	7.3
propane	$CH_3CH_2CH_3$ (C_{2v})		166.69	21.10	16.4
n-pentane	*n*-C_5H_{12} (C_{2v})		147.39	40.39	34.8
n-heptane	*n*-C_7H_{16} (C_{2v})		150.50	37.29	29.5
n-nonane	(C_{2v})		150.62	37.16	29.8
methylamine	(CH_3NH_2: C_s)		155.86	31.92	28.4
methanol	(CH_3OH: C_s)		133.95	53.83	50.2
fluoromethane	(CH_3F: C_{3v})		114.00	73.78	71.6
dimethylamine	Me_2NH (C_s)		146.71	41.07	38.2
trimethylamine	Me_3N (C_{3v})		138.75	49.03	47.6
acetonitrile	MeCN (C_{3v})		186.23	1.55	1.7
methyl isocyanide	MeNC (C_{3v})		161.84	25.94	26.8
nitromethane	$MeNO_2$ (C_s)		124.54	63.24	62.5
acetaldehyde	CH_3CHO (C_s)		153.37	34.41	31.3
acetone	CH_3COCH_3 (C_{2v})		156.00	31.78	30.9
acetic acid	CH_3COOH (C_s)		167.36	20.43	20.8
methyl acetate	CH_3COOCH_3 (C_s)		166.08	21.70	20.6
methanethiol	CH_3SH (Cs)		176.75	11.03	6.5
dimethyl sulfide	CH_3SCH_3 (C_{2v})		165.67	22.12	19.3
DMSO	$CH_3S(O)CH_3$ (C_s)		148.14	39.64	41.0
methane sulfonic acid	CH_3SO_3H (C_1)		149.93	37.85	39.6
chloromethane	CH_3Cl (C_{3v})		158.04	29.74	25.6
dimethyl ether	CH_3OCH_3 (C_{2v})		125.22	62.57	60.9
methyl ethyl ether	MeOEt (C_s)		126.49	61.29	57.6
methyl iso-propyl ether	MeOPr-*i* (C_1)		139.95	47.83	54.9
methyl tert-butyl ether	MeOBu-*t* (C_s)		137.04	50.74	49.4
ethylene	$CH_2=CH_2$ (D_{2h})		56.14	131.64	123.3
trans-butadiene	*t*-$CH_2=CHCH=CH_2$ (C_{2h})	C1	62.52	125.26	117.5
		C2	39.78	148.01	137.8
cis-butadiene	*c*-$CH_2=CHCH=CH_2$ (C_2)	C1	65.66	122.12	117.5
		C2	41.93	145.85	137.8
propylene	$CH_2=CHCH_3$ (C_s)	C1	42.82	144.96	140.2
		C2	65.35	122.43	115.7
			164.87	22.91	24.2
vinyl alcohol	$CH_2=CHOH$ (C_s)	C1	32.92	154.86	149.0
		C2	94.61	93.17	88.0
methyl vinyl ether	$CH_2=CHOMe$ (C_s)	C1	25.93	161.86	152.9
		C2	101.73	86.05	85.5
acrolein	$CH_2=CHCHO$ (C_s)	C4	38.89	148.89	138.5
		C1	41.29	146.50	138.0
methyl vinyl ketone	$CH_2=CHCOCH_3$ (C_s)	C4	39.09	148.70	137.5
		C1	51.57	136.21	129.0
cis-acrylic acid	*c*-$CH_2=CHCOOH$ (C_s)	C4	52.93	134.85	128.1
		C1	43.74	144.04	133.2
trans-acrylic acid	*t*-$CH_2=CHCOOH$ (C_s)	C2	50.15	137.63	128.1
		C1	46.93	140.85	133.2
nitroethylene	$CH_2=CHNO_2$ (C_s)	C4	33.29	154.49	144.7
		C1	56.65	131.13	121.5
isocyanoethylene	$CH_2=CHNC$ (C_s)	C1	59.99	127.79	121.0
		C4	60.24	127.54	119.3
N,*N*-dimethylethenamine	(C_1)	C13	172.06	15.72	12.8
		C10	130.96	56.82	53.6
		C1	137.67	50.11	44.6

Table S5. The σ^t(C: S), and $-\Delta\sigma^t$(C: S) and $\delta(C)_{obsd}$ for various 40 species (54 plots), calculated with the GIAO-DFT method under LC-ωPBE/BSS-A.

Species	(symmetry)		σ^t(C)	$-\Delta\sigma^t(C)_{TMS}$	$\delta(C)_{obsd}$
TMS	$SiMe_4$ (T_d)		192.27	0.00	0.0
methane	CH_4 (T_d)		196.42	-4.15	-4.6
ethane	(CH_3CH_3: D_{3d})		184.00	8.27	7.3
propane	$CH_3CH_2CH_3$ (C_{2v})		173.58	18.69	16.4
n-pentane	*n*-C_5H_{12} (C_{2v})		154.78	37.49	34.8
n-heptane	*n*-C_7H_{16} (C_{2v})		157.44	34.83	29.5
n-nonane	(C_{2v})		157.55	34.72	29.8
methylamine	(CH_3NH_2: C_s)		161.80	30.47	28.4
methanol	(CH_3OH: C_s)		138.67	53.60	50.2
fluoromethane	(CH_3F: C_{3v})		116.47	75.80	71.6
dimethylamine	Me_2NH (C_s)		152.83	39.44	38.2
trimethylamine	Me_3N (C_{3v})		144.55	47.72	47.6
acetonitrile	MeCN (C_{3v})		190.21	2.06	1.7
methyl isocyanide	MeNC (C_{3v})		165.45	26.82	26.8
nitromethane	$MeNO_2$ (C_s)		127.05	65.22	62.5
acetaldehyde	CH_3CHO (C_s)		157.38	34.89	31.3
acetone	CH_3COCH_3 (C_{2v})		159.23	33.04	30.9
acetic acid	CH_3COOH (C_s)		170.26	22.01	20.8
methyl acetate	CH_3COOCH_3 (C_s)		169.04	23.23	20.6
methanethiol	CH_3SH (Cs)		183.81	8.46	6.5
dimethyl sulfide	CH_3SCH_3 (C_{2v})		173.07	19.20	19.3
DMSO	$CH_3S(O)CH_3$ (C_s)		156.61	35.66	41.0
methane sulfonic acid	CH_3SO_3H (C_1)		153.66	38.61	39.6
chloromethane	CH_3Cl (C_{3v})		165.44	26.83	25.6
dimethyl ether	CH_3OCH_3 (C_{2v})		130.13	62.14	60.9
methyl ethyl ether	MeOEt (C_s)		131.30	60.97	57.6
methyl iso-propyl ether	MeOPr-*i* (C_1)		143.79	48.48	54.9
methyl tert-butyl ether	MeOBu-*t* (C_s)		141.41	50.86	49.4
ethylene	$CH_2=CH_2$ (D_{2h})		56.03	136.24	123.3
trans-butadiene	*t*-$CH_2=CHCH=CH_2$ (C_{2h})	C1	62.54	129.73	117.5
		C2	40.82	151.45	137.8
cis-butadiene	*c*-$CH_2=CHCH=CH_2$ (C_2)	C1	64.73	127.54	117.5
		C2	42.02	150.25	137.8
propylene	$CH_2=CHCH_3$ (C_s)	C1	43.65	148.62	140.2
		C2	65.14	127.13	115.7
			170.45	21.82	24.2
vinyl alcohol	$CH_2=CHOH$ (C_s)	C1	33.03	159.24	149.0
		C2	94.03	98.24	88.0
methyl vinyl ether	$CH_2=CHOMe$ (C_s)	C1	25.45	166.82	152.9
		C2	101.65	90.62	85.5
acrolein	$CH_2=CHCHO$ (C_s)	C4	39.45	152.82	138.5
		C1	43.01	149.26	138.0
methyl vinyl ketone	$CH_2=CHCOCH_3$ (C_s)	C4	39.28	152.99	137.5
		C1	52.20	140.07	129.0
cis-acrylic acid	*c*-$CH_2=CHCOOH$ (C_s)	C4	53.42	138.85	128.1
		C1	43.80	148.47	133.2
trans-acrylic acid	*t*-$CH_2=CHCOOH$ (C_s)	C2	50.78	141.49	128.1
		C1	46.95	145.32	133.2
nitroethylene	$CH_2=CHNO_2$ (C_s)	C4	34.08	158.19	144.7
		C1	56.75	135.52	121.5
isocyanoethylene	$CH_2=CHNC$ (C_s)	C1	60.27	132.00	121.0
		C4	58.97	133.30	119.3
N,*N*-dimethylethenamine	(C_1)	C13	176.94	15.33	12.8
		C10	137.82	54.45	53.6
		C1	143.56	48.71	44.6

Table S6. The σ^t(C: S), and $-\Delta\sigma^t$(C: S) and $\delta(C)_{obsd}$ for various 40 species (54 plots), calculated with the GIAO-DFT method under ωB97X-D/BSS-A.

Species	(symmetry)		σ^t(C)	$-\Delta\sigma^t(C)_{TMS}$	$\delta(C)_{obsd}$
TMS	$SiMe_4$ (T_d)		188.17	0.00	0.0
methane	CH_4 (T_d)		192.93	-4.76	-4.6
ethane	(CH_3CH_3: D_{3d})		178.91	9.26	7.3
propane	$CH_3CH_2CH_3$ (C_{2v})		167.63	20.54	16.4
n-pentane	*n*-C_5H_{12} (C_{2v})		148.34	39.83	34.8
n-heptane	*n*-C_7H_{16} (C_{2v})		151.40	36.77	29.5
n-nonane	(C_{2v})		151.39	36.78	29.8
methylamine	(CH_3NH_2: C_s)		156.46	31.71	28.4
methanol	(CH_3OH: C_s)		134.57	53.60	50.2
fluoromethane	(CH_3F: C_{3v})		114.22	73.95	71.6
dimethylamine	Me_2NH (C_s)		147.30	40.87	38.2
trimethylamine	Me_3N (C_{3v})		139.09	49.08	47.6
acetonitrile	MeCN (C_{3v})		186.29	1.88	1.7
methyl isocyanide	MeNC (C_{3v})		161.30	26.87	26.8
nitromethane	$MeNO_2$ (C_s)		123.55	64.63	62.5
acetaldehyde	CH_3CHO (C_s)		153.58	34.59	31.3
acetone	CH_3COCH_3 (C_{2v})		155.48	32.69	30.9
acetic acid	CH_3COOH (C_s)		166.70	21.47	20.8
methyl acetate	CH_3COOCH_3 (C_s)		165.37	22.80	20.6
methanethiol	CH_3SH (Cs)		177.23	10.94	6.5
dimethyl sulfide	CH_3SCH_3 (C_{2v})		166.46	21.71	19.3
DMSO	$CH_3S(O)CH_3$ (C_s)		148.52	39.66	41.0
methane sulfonic acid	CH_3SO_3H (C_1)		149.11	39.07	39.6
chloromethane	CH_3Cl (C_{3v})		157.78	30.39	25.6
dimethyl ether	CH_3OCH_3 (C_{2v})		125.94	62.23	60.9
methyl ethyl ether	MeOEt (C_s)		127.11	61.07	57.6
methyl iso-propyl ether	MeOPr-*i* (C_1)		139.86	48.32	54.9
methyl tert-butyl ether	MeOBu-*t* (C_s)		137.26	50.91	49.4
ethylene	$CH_2=CH_2$ (D_{2h})		56.10	132.07	123.3
trans-butadiene	*t*-$CH_2=CHCH=CH_2$ (C_{2h})	C1	65.34	122.83	117.5
		C2	39.94	148.24	137.8
cis-butadiene	*c*-$CH_2=CHCH=CH_2$ (C_2)	C1	65.66	122.52	117.5
		C2	41.69	146.48	137.8
propylene	$CH_2=CHCH_3$ (C_s)	C1	42.68	145.49	140.2
		C2	65.34	122.83	115.7
			165.74	22.43	24.2
vinyl alcohol	$CH_2=CHOH$ (C_s)	C1	32.61	155.56	149.0
		C2	94.07	94.10	88.0
methyl vinyl ether	$CH_2=CHOMe$ (C_s)	C1	25.18	162.99	152.9
		C2	101.47	86.70	85.5
acrolein	$CH_2=CHCHO$ (C_s)	C4	38.43	149.75	138.5
		C1	43.00	145.17	138.0
methyl vinyl ketone	$CH_2=CHCOCH_3$ (C_s)	C4	38.48	149.70	137.5
		C1	52.18	135.99	129.0
cis-acrylic acid	*c*-$CH_2=CHCOOH$ (C_s)	C4	52.52	135.65	128.1
		C1	44.41	143.76	133.2
trans-acrylic acid	*t*-$CH_2=CHCOOH$ (C_s)	C2	49.81	138.37	128.1
		C1	47.64	140.53	133.2
nitroethylene	$CH_2=CHNO_2$ (C_s)	C4	32.39	155.78	144.7
		C1	57.32	130.85	121.5
isocyanoethylene	$CH_2=CHNC$ (C_s)	C1	60.56	127.61	121.0
		C4	59.03	129.14	119.3
N,*N*-dimethylethenamine	(C_1)	C13	171.98	16.20	12.8
		C10	131.19	56.98	53.6
		C1	138.12	50.06	44.6

Table S7. The σ^t(C: S), and $-\Delta\sigma^t$(C: S) and $\delta(C)_{obsd}$ for various 40 species (54 plots), calculated with the GIAO-DFT method under MP2/BSS-A.

Species	(symmetry)		σ^t(C)	$-\Delta\sigma^t(C)_{TMS}$	$\delta(C)_{obsd}$
TMS	$SiMe_4$ (T_d)		197.32	0.00	0.0
methane	CH_4 (T_d)		201.35	-4.02	-4.6
ethane	(CH_3CH_3: D_{3d})		188.18	9.14	7.3
propane	$CH_3CH_2CH_3$ (C_{2v})		176.73	20.59	16.4
n-pentane	*n*-C_5H_{12} (C_{2v})		156.45	40.87	34.8
n-heptane	*n*-C_7H_{16} (C_{2v})		159.47	37.86	29.5
n-nonane	(C_{2v})		159.43	37.89	29.8
methylamine	(CH_3NH_2: C_s)		164.24	33.08	28.4
methanol	(CH_3OH: C_s)		142.66	54.66	50.2
fluoromethane	(CH_3F: C_{3v})		122.79	74.54	71.6
dimethylamine	Me_2NH (C_s)		155.11	42.21	38.2
trimethylamine	Me_3N (C_{3v})		145.86	51.46	47.6
acetonitrile	MeCN (C_{3v})		193.63	3.69	1.7
methyl isocyanide	MeNC (C_{3v})		168.67	28.66	26.8
nitromethane	$MeNO_2$ (C_s)		135.04	62.29	62.5
acetaldehyde	CH_3CHO (C_s)		163.05	34.27	31.3
acetone	CH_3COCH_3 (C_{2v})		165.09	32.23	30.9
acetic acid	CH_3COOH (C_s)		176.02	21.30	20.8
methyl acetate	CH_3COOCH_3 (C_s)		174.73	22.60	20.6
methanethiol	CH_3SH (Cs)		187.17	10.15	6.5
dimethyl sulfide	CH_3SCH_3 (C_{2v})		175.30	22.02	19.3
DMSO	$CH_3S(O)CH_3$ (C_s)		157.69	39.63	41.0
methane sulfonic acid	CH_3SO_3H (C_1)		159.57	37.75	39.6
chloromethane	CH_3Cl (C_{3v})		168.74	28.59	25.6
dimethyl ether	CH_3OCH_3 (C_{2v})		137.16	60.16	60.9
methyl ethyl ether	MeOEt (C_s)		138.17	59.16	57.6
methyl iso-propyl ether	MeOPr-*i* (C_1)		147.67	49.65	54.9
methyl tert-butyl ether	MeOBu-*t* (C_s)		147.28	50.04	49.4
ethylene	$CH_2=CH_2$ (D_{2h})		62.47	134.86	123.3
trans-butadiene	*t*-$CH_2=CHCH=CH_2$ (C_{2h})	C1	69.27	128.05	117.5
		C2	46.82	150.50	137.8
cis-butadiene	*c*-$CH_2=CHCH=CH_2$ (C_2)	C1	70.17	127.16	117.5
		C2	48.53	148.79	137.8
propylene	$CH_2=CHCH_3$ (C_s)	C1	59.33	137.99	140.2
		C2	79.57	117.75	115.7
			174.74	22.59	24.2
vinyl alcohol	$CH_2=CHOH$ (C_s)	C1	45.61	151.71	149.0
		C2	107.50	89.82	88.0
methyl vinyl ether	$CH_2=CHOMe$ (C_s)	C1	37.79	159.53	152.9
		C2	114.20	83.12	85.5
acrolein	$CH_2=CHCHO$ (C_s)	C4	51.86	145.47	138.5
		C1	61.36	135.96	138.0
methyl vinyl ketone	$CH_2=CHCOCH_3$ (C_s)	C4	52.41	144.91	137.5
		C1	68.90	128.42	129.0
cis-acrylic acid	*c*-$CH_2=CHCOOH$ (C_s)	C4	66.26	131.07	128.1
		C1	63.68	133.64	133.2
trans-acrylic acid	*t*-$CH_2=CHCOOH$ (C_s)	C2	63.90	133.42	128.1
		C1	65.20	132.12	133.2
nitroethylene	$CH_2=CHNO_2$ (C_s)	C4	46.86	150.47	144.7
		C1	76.72	120.60	121.5
isocyanoethylene	$CH_2=CHNC$ (C_s)	C1	75.91	121.41	121.0
		C4	72.41	124.92	119.3
N,*N*-dimethylethenamine	(C_1)	C13	181.08	16.25	12.8
		C10	137.82	59.51	53.6
		C1	144.94	52.39	44.6

Table S8. The σ^t(C: S), and $-\Delta\sigma^t$(C: S) and $\delta(C)_{obsd}$ for various 40 species (54 plots), calculated with the GIAO-DFT method of B3LYP/BSS-A under the solvent effect of $CHCl_3$.

Species	(symmetry)		σ^t(C)	$-\Delta\sigma^t(C)_{TMS}$	$\delta(C)_{obsd}$
TMS	$SiMe_4$ (T_d)		183.45	0.00	0.0
methane	CH_4 (T_d)		189.75	-6.29	-4.6
ethane	(CH_3CH_3: D_{3d})		173.69	9.76	7.3
propane	$CH_3CH_2CH_3$ (C_{2v})		160.29	23.16	16.4
n-pentane	*n*-C_5H_{12} (C_{2v})		141.16	42.30	34.8
n-heptane	*n*-C_7H_{16} (C_{2v})		144.29	39.17	29.5
n-nonane	(C_{2v})		144.39	39.06	29.8
methylamine	(CH_3NH_2: C_s)		150.18	33.27	28.4
methanol	(CH_3OH: C_s)		127.30	56.15	50.2
fluoromethane	(CH_3F: C_{3v})		105.90	77.56	71.6
dimethylamine	Me_2NH (C_s)		141.30	42.16	38.2
trimethylamine	Me_3N (C_{3v})		133.54	49.91	47.6
acetonitrile	MeCN (C_{3v})		181.97	1.49	1.7
methyl isocyanide	MeNC (C_{3v})		155.96	27.50	26.8
nitromethane	$MeNO_2$ (C_s)		115.52	67.93	62.5
acetaldehyde	CH_3CHO (C_s)		147.47	35.98	31.3
acetone	CH_3COCH_3 (C_{2v})		150.11	33.34	30.9
acetic acid	CH_3COOH (C_s)		161.68	21.78	20.8
methyl acetate	CH_3COOCH_3 (C_s)		160.34	23.12	20.6
methanethiol	CH_3SH (Cs)		170.38	13.08	6.5
dimethyl sulfide	CH_3SCH_3 (C_{2v})		159.72	23.73	19.3
DMSO	$CH_3S(O)CH_3$ (C_s)		138.63	44.82	41.0
methane sulfonic acid	CH_3SO_3H (C_1)		141.59	41.86	39.6
chloromethane	CH_3Cl (C_{3v})		149.76	33.69	25.6
dimethyl ether	CH_3OCH_3 (C_{2v})		119.14	64.31	60.9
methyl ethyl ether	MeOEt (C_s)		120.49	62.97	57.6
methyl iso-propyl ether	MeOPr-*i* (C_1)		133.47	49.98	54.9
methyl tert-butyl ether	MeOBu-*t* (C_s)		130.67	52.79	49.4
ethylene	$CH_2=CH_2$ (D_{2h})		51.68	131.77	123.3
trans-butadiene	*t*-$CH_2=CHCH=CH_2$ (C_{2h})	C1	58.32	125.14	117.5
		C2	34.14	149.31	137.8
cis-butadiene	*c*-$CH_2=CHCH=CH_2$ (C_2)	C1	62.01	121.45	117.5
		C2	36.33	147.12	137.8
propylene	$CH_2=CHCH_3$ (C_s)	C1	35.74	147.72	140.2
		C2	62.44	121.01	115.7
			160.08	23.37	24.2
vinyl alcohol	$CH_2=CHOH$ (C_s)	C1	24.72	158.74	149.0
		C2	91.82	91.63	88.0
methyl vinyl ether	$CH_2=CHOMe$ (C_s)	C1	19.10	164.35	152.9
		C2	97.53	85.92	85.5
acrolein	$CH_2=CHCHO$ (C_s)	C4	34.05	149.41	138.5
		C1	33.04	150.42	138.0
methyl vinyl ketone	$CH_2=CHCOCH_3$ (C_s)	C4	34.44	149.02	137.5
		C1	43.47	139.99	129.0
cis-acrylic acid	*c*-$CH_2=CHCOOH$ (C_s)	C4	48.02	135.43	128.1
		C1	38.25	145.20	133.2
trans-acrylic acid	*t*-$CH_2=CHCOOH$ (C_s)	C2	45.88	137.57	128.1
		C1	39.93	143.52	133.2
nitroethylene	$CH_2=CHNO_2$ (C_s)	C4	26.54	156.92	144.7
		C1	48.91	134.55	121.5
isocyanoethylene	$CH_2=CHNC$ (C_s)	C1	52.33	131.13	121.0
		C4	55.91	127.55	119.3
N,*N*-dimethylethenamine	(C_1)	C13	166.68	16.77	12.8
		C10	124.47	58.99	53.6
		C1	132.41	51.05	44.6

Table S9. The σ^t(C: S), and $-\Delta\sigma^t$(C: S) and $\delta(C)_{obsd}$ for various 40 species (54 plots), calculated with the GIAO-DFT method under B3LYP/def2TZVP.

Species	(symmetry)		σ^t(C)	$-\Delta\sigma^t(C)_{TMS}$	$\delta(C)_{obsd}$
TMS	$SiMe_4$ (T_d)		183.49	0.00	0.0
methane	CH_4 (T_d)		190.37	-6.88	-4.6
ethane	(CH_3CH_3: D_{3d})		173.87	9.61	7.3
propane	$CH_3CH_2CH_3$ (C_{2v})		160.72	22.77	16.4
n-pentane	*n*-C_5H_{12} (C_{2v})		141.79	41.70	34.8
n-heptane	*n*-C_7H_{16} (C_{2v})		145.06	38.43	29.5
n-nonane	(C_{2v})		145.13	38.36	29.8
methylamine	(CH_3NH_2: C_s)		150.79	32.70	28.4
methanol	(CH_3OH: C_s)		128.75	54.74	50.2
fluoromethane	(CH_3F: C_{3v})		108.75	74.74	71.6
dimethylamine	Me_2NH (C_s)		142.13	41.36	38.2
trimethylamine	Me_3N (C_{3v})		134.60	48.89	47.6
acetonitrile	MeCN (C_{3v})		182.83	0.66	1.7
methyl isocyanide	MeNC (C_{3v})		158.13	25.36	26.8
nitromethane	$MeNO_2$ (C_s)		119.19	64.29	62.5
acetaldehyde	CH_3CHO (C_s)		149.61	33.87	31.3
acetone	CH_3COCH_3 (C_{2v})		152.45	31.04	30.9
acetic acid	CH_3COOH (C_s)		163.38	20.11	20.8
methyl acetate	CH_3COOCH_3 (C_s)		161.72	21.76	20.6
methanethiol	CH_3SH (C_s)		170.71	12.78	6.5
dimethyl sulfide	CH_3SCH_3 (C_{2v})		160.07	23.42	19.3
DMSO	$CH_3S(O)CH_3$ (C_s)		140.89	42.59	41.0
methane sulfonic acid	CH_3SO_3H (C_1)		142.75	40.74	39.6
chloromethane	CH_3Cl (C_{3v})		151.19	32.30	25.6
dimethyl ether	CH_3OCH_3 (C_{2v})		120.43	63.06	60.9
methyl ethyl ether	MeOEt (C_s)		121.74	61.75	57.6
methyl iso-propyl ether	MeOPr-*i* (C_1)		135.03	48.46	54.9
methyl tert-butyl ether	MeOBu-*t* (C_s)		132.32	51.16	49.4
ethylene	$CH_2=CH_2$ (D_{2h})		54.31	129.17	123.3
trans-butadiene	*t*-$CH_2=CHCH=CH_2$ (C_{2h})	C1	61.16	122.32	117.5
		C2	36.46	147.03	137.8
cis-butadiene	*c*-$CH_2=CHCH=CH_2$ (C_2)	C1	64.40	119.08	117.5
		C2	38.83	144.66	137.8
propylene	$CH_2=CHCH_3$ (C_s)	C1	39.27	144.22	140.2
		C2	63.78	119.70	115.7
		C3	160.66	22.83	24.2
vinyl alcohol	$CH_2=CHOH$ (C_s)	C1	28.52	154.97	149.0
		C2	92.54	90.94	88.0
methyl vinyl ether	$CH_2=CHOMe$ (C_s)	C1	21.69	161.79	152.9
		C2	99.37	84.11	85.5
acrolein	$CH_2=CHCHO$ (C_s)	C4	35.80	147.69	138.5
		C1	40.42	143.07	138.0
methyl vinyl ketone	$CH_2=CHCOCH_3$ (C_s)	C4	36.01	147.47	137.5
		C1	50.36	133.13	129.0
cis-acrylic acid	*c*-$CH_2=CHCOOH$ (C_s)	C4	49.85	133.64	128.1
		C1	42.85	140.64	133.2
trans-acrylic acid	*t*-$CH_2=CHCOOH$ (C_s)	C2	47.28	136.21	128.1
		C1	45.34	138.14	133.2
nitroethylene	$CH_2=CHNO_2$ (C_s)	C4	28.53	154.95	144.7
		C1	55.55	127.94	121.5
isocyanoethylene	$CH_2=CHNC$ (C_s)	C1	58.32	125.17	121.0
		C4	57.49	126.00	119.3
N,*N*-dimethylethenamine	(C_1)	C13	167.52	15.97	12.8
		C10	125.06	58.43	53.6
		C1	133.25	50.24	44.6

Table S10. The $-\Delta\sigma^t(C_i: i = 1–5)_{calcd:TMS}$ and $\delta(C_i: i = 1–5)_{obsd:TMS}$ for some conformers in *n*-Pentane, calculated with the GIAO-DFT method under B3LYP/BSS-A.[a]

Species[b]	ΔE^a/kJmol^{-1}	$-\Delta\sigma^t(C1)_{TMS}$	$-\Delta\sigma^t(C2)_{TMS}$	$-\Delta\sigma^t(C3)_{TMS}$	$-\Delta\sigma^t(C4)_{TMS}$	$-\Delta\sigma^t(C5)_{TMS}$
tt	0.00	17.44	30.67	42.05	30.67	17.44
tg	3.69	15.05	28.70	39.53	26.74	17.53
gt	7.21	13.87	23.72	38.12	23.72	13.87
gg_A	6.75	13.53	22.17	34.86	22.17	13.53
gg_B	14.25	17.04	31.57	36.40	29.53	19.91
$\delta(C_i)_{obsd}$	--	14.20	22.80	34.80	22.80	14.20

[a] $-\Delta\sigma^t(C)_{calcd:TMS} = -[\sigma^t(C: n\text{-pentane})_{calcd} - [\sigma^t(C: TMS)_{calcd}]$.
[b]

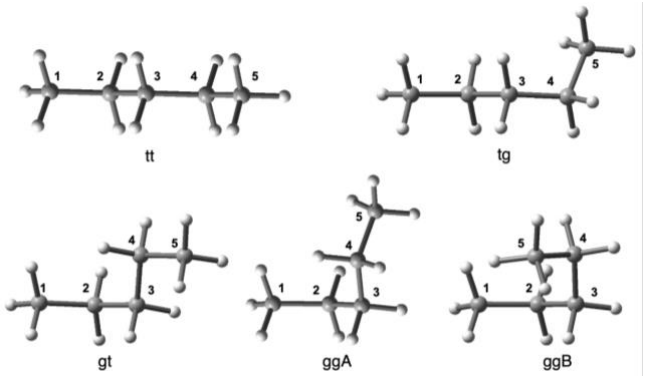

Table S11. The σ^m(C: S), $\Delta\sigma^m$(C: S) and $\Delta\sigma^m$(C: S)$_e$ (m = d, p and t) for various species of **1**–**56** and **S1**–**S20**, along with the pre-α, α, β, γ, δ, α-X, β-X and *ipso*-X (*i*-X) effects and the effects from the characteristic bonds and groups,[a,b] together with the Q(C) values.

Nos.	Species	sym	Q(C)	σ^d(C)	σ^p(C)[c]	σ^t(C)	$\Delta\sigma^t$(C)	$\Delta\sigma^d$(C)$_e$[d]	$\Delta\sigma^p$(C)$_e$[d]	$\Delta\sigma^t$(C)$_e$[d]	effect
1	C^{4-}	O_h	-4.000	274.39	0.00	274.39	0.00	0.00	0.00	0.00	---
2	HC^{3-}	$C_{\infty v}$	-1.815	264.04	1807.41	2071.45	1797.06	-10.35	1807.41	1797.06	pre-α
3	H_2C^{2-}	C_{2v}	-2.156	261.96	137.46	399.42	125.03	-6.22	68.73	62.51	pre-α
4	H_3C^-	C_{3v}	-1.400	249.53	-2.26	247.26	-27.13	-8.29	-0.75	-9.04	pre-α
5	CH_4	T_d	-0.805	238.98	-49.66	189.32	-85.08	-8.85	-12.42	-21.27	pre-α
6	MeH_2C^-	C_s	-1.000	250.87	-98.55	152.32	-122.08	1.34	-96.29	-94.95	α
7	EtH_2C^-	C_s	-0.915	248.89	-82.29	166.59	-107.80	-1.98	16.26	14.28	β
8	*i*-PrH_2C^-	C_1	-0.923	236.54	-94.11	142.43	-131.96	-7.16	2.22	-4.94	β
9	*t*-BuH_2C^-	C_s	-0.985	236.18	-62.01	174.16	-100.23	-4.90	12.18	7.28	β
10	*n*-PrH_2C^-	C_s	-0.990	260.85	-87.90	172.96	-101.44	11.97	-5.61	-5.61	γ
11	*n*-BuH_2C^-	C_s	-0.938	262.85	-88.82	174.03	-100.37	1.99	-0.92	1.07	δ
12	$MeCH_3$	D_{3d}	-0.571	238.60	-65.21	173.39	-101.00	-0.38	-15.55	-15.92	α
13a	$EtCH_3$	C_{2v}	-0.568	232.81	-68.71	164.10	-110.30	-5.79	-3.51	-9.29	β
13b	Me_2CH_2	C_{2v}	-0.382	251.23	-91.12	160.10	-114.29	6.12	-20.73	-14.61	α
14a	*i*-$PrCH_3$	C_{3v}	-0.565	230.20	-73.87	156.33	-118.06	-4.20	-4.33	-8.53	β
14b	Me_3CH	C_{3v}	-0.232	267.54	-114.35	153.19	-121.21	9.52	-21.56	-12.04	α
15	*t*-$BuCH_3$	T_d	-0.563	229.82	-78.63	151.19	-123.20	-2.93	-4.47	-7.40	β
16a	*n*-$PrCH_3$	C_{2h}	-0.565	236.01	-70.67	165.34	-109.05	3.20	-1.96	1.24	γ
16b	$EtMeCH_2$	C_{2h}	-0.377	244.34	-93.60	150.74	-123.66	-6.89	-2.48	-9.37	β
17a	*n*-$BuCH_3$	C_{2v}	-0.375	233.25	-67.69	165.55	-108.84	-2.77	2.98	0.21	δ
17b	*n*-$PrMeCH_2$	C_{2v}	-0.564	252.13	-99.81	152.32	-122.08	7.79	-6.21	1.58	γ
18a	*i*-$PrMeCH_2$	C_1	-0.372	247.55	-102.18	145.37	-129.02	-1.84	-5.53	-7.37	β
18b	$EtMe_2CH$	C_1	-0.225	265.39	-118.76	146.63	-127.77	-2.15	-4.41	-6.56	β
19	*t*-$BuMeCH_2$	C_s	-0.371	251.79	-112.21	139.58	-134.81	0.19	-7.03	-6.84	β
20	*n*-$BuMeCH_2$	C_{2h}	-0.374	243.63	-101.29	142.33	-132.06	-8.50	-1.48	-9.98	δ
21	*i*-$PrMe_2CH$	C_{2h}	-0.219	259.35	-118.14	141.21	-133.18	-4.10	-1.89	-5.99	β
22	*t*-$BuMe_2CH$	C_s	-0.215	265.19	-127.39	137.80	-136.60	-0.78	-4.35	-5.13	β
23	*n*-$PrMe_2CH$	C_1	-0.224	274.83	-128.33	146.50	-127.90	9.44	-9.57	-0.13	γ
24	*n*-$BuMe_2CH$	C_1	-0.223	276.20	-128.65	147.55	-126.84	1.37	-0.31	1.06	δ
25	H_3C^+	C_{3v}	0.362	240.45	-467.68	-227.23	-501.62	1.48	-418.02	-416.55	*e*
26	MeH_2C^+	C_s	-0.215	242.18	-219.86	22.32	-252.08	1.73	247.82	249.55	α
27	EtH_2C^+	C_s	-0.256	242.53	-140.46	102.07	-172.33	0.35	79.40	79.75	β
28	*i*-PrH_2C^+	C_1	-0.472	256.69	-139.73	116.96	-157.44	7.26	40.07	47.32	β
29	*t*-BuH_2C^+	C_1	-0.489	270.61	-149.75	120.85	-153.54	9.48	23.37	32.84	β
30	Me_2HC^+	C_2	0.396	247.98	-400.37	-152.39	-426.79	3.76	33.66	37.42	α
31	$EtMeHC^+$	C_1	0.366	256.56	-396.76	-140.20	-414.59	8.58	3.61	12.19	β
32	*i*-$PrMeHC^+$	C_1	0.174	268.19	-284.57	-16.39	-290.78	10.10	57.90	68.00	β
33	*t*-$BuMeHC^+$	C_1	-0.327	293.49	-182.60	110.89	-163.50	15.17	72.59	87.76	β
34	Me_3C^+	C_1	0.536	242.28	-411.12	-168.84	-443.23	0.61	18.86	19.46	α
35	$EtMe_2C^+$	C_1	0.540	242.21	-414.36	-172.15	-446.55	-0.07	-3.24	-3.31	β
36	*i*-$PrMe_2C^+$	C_1	0.544	242.44	-404.51	-162.07	-436.46	0.08	3.30	3.39	β
37	*t*-$BuMe_2C^+$	C_1	0.537	242.76	-402.64	-159.88	-434.27	0.16	2.83	2.99	β

[a]Calculated with the GIAO-DFT method under B3LYP/BSS-A. [b]$\Delta\sigma^m$(C: S) = σ^m(C: S) – σ^m(C: C^{4-}) (m = d, p and t). [c]$\Delta\sigma^p$(C) = σ^p(C), since σ^p(C: C^{4-}) = 0 ppm. [d]$\Delta\sigma^m$(C: S) = (1/n)($\Delta\sigma^m$(C: S) – $\Delta\sigma^m$(C: S_e)), see text for n, S and S_e (m = d, p and t). [e]The effect beeing not defined.

(Table S11 continues)

Nos.	Species	sym	Q(C)	σ^d(C)	σ^p(C)[c]	σ^t(C)	$\Delta\sigma^t$(C)	$\Delta\sigma^d(C)_e$[d]	$\Delta\sigma^p(C)_e$[d]	$\Delta\sigma^t(C)_e$[d]	effect
38	CH_3OH	C_s	-0.191	232.16	-104.67	127.49	-146.90	-6.82	-55.01	-61.82	α-X
39	CH_3SH	C_s	-0.692	243.86	-73.63	170.23	-104.16	4.88	-23.97	-19.09	α-X
40	CH_3SeH	C_s	-0.737	240.42	-66.34	174.08	-100.31	1.45	-16.68	-15.23	α-X
41	H_3CSSCH_3	C_2	-0.709	241.38	-85.75	155.63	-118.77	2.40	-36.09	-33.69	α-X
42	CH_3F	C_{3v}	-0.066	232.99	-126.01	106.99	-167.41	-5.98	-76.35	-82.33	α-X
43	CH_3Cl	C_{3v}	-0.529	243.61	-93.19	150.42	-123.98	4.63	-43.53	-38.90	α-X
44	CH_3Br	C_{3v}	-0.601	241.70	-83.06	158.65	-115.75	2.73	-33.40	-30.67	α-X
45	CH_3I	C_{3v}	-0.719	236.32	-56.17	180.15	-94.24	-2.66	-6.51	-9.17	α-X
46	CH_3CO_2Me	C_s	-0.666	248.04	-87.22	160.82	-113.58	9.06	-37.56	-28.50	α-X
47	CH_3CN	C_{3v}	-0.677	220.25	-38.56	181.70	-92.70	-18.72	11.10	-7.62	α-X
48	CH_3NH_2	C_1	-0.360	229.80	-79.79	150.01	-124.39	-9.18	-30.13	-39.31	α-X
49	CH_3NO_2	C_s	-0.410	231.58	-114.08	117.50	-156.90	-7.40	-64.42	-71.82	α-X
50a	$CH_3\mathbf{C}H_2OH$	C_s	-0.016	225.96	-108.36	117.60	-156.80	-12.64	-43.15	-55.79	α-X
50b	$\mathbf{C}H_3CH_2OH$		-0.587	245.33	-81.19	164.14	-110.26	6.73	-15.98	-9.25	β-X
S1a	$CH_3\mathbf{C}H_2SH$	C_s	-0.484	250.44	-95.01	155.44	-118.96	11.84	-29.80	-17.96	α-X
S1b	$\mathbf{C}H_3CH_2SH$		-0.583	236.08	-69.55	166.53	-107.86	-2.51	-4.34	-6.86	β-X
S2a	$CH_3\mathbf{C}H_2SeH$	C_s	-0.521	243.61	-86.59	157.02	-117.37	5.01	-21.38	-16.37	α-X
S2b	$\mathbf{C}H_3CH_2SeH$		-0.589	239.54	-72.79	166.75	-107.64	0.94	-7.58	-6.64	β-X
S3a	$CH_3\mathbf{C}H_2F$	C_s	0.103	242.30	-77.83	164.47	-109.92	3.71	-12.63	-8.92	α-X
S3b	$\mathbf{C}H_3CH_2F$		-0.610	228.26	-132.05	96.21	-178.19	-10.34	-66.85	-77.18	β-X
S4a	$CH_3\mathbf{C}H_2Cl$	C_s	-0.332	254.00	-121.40	132.61	-141.79	15.41	-56.19	-40.79	α-X
S4b	$\mathbf{C}H_3CH_2Cl$		-0.588	231.68	-70.51	161.17	-113.23	-6.92	-5.30	-12.22	β-X
S5a	$CH_3\mathbf{C}H_2Br$	C_s	-0.392	247.97	-110.45	137.53	-136.87	9.38	-45.24	-35.87	α-X
S5b	$\mathbf{C}H_3CH_2Br$		-0.592	235.52	-74.81	160.71	-113.68	-3.08	-9.60	-12.68	β-X
S6a	$CH_3\mathbf{C}H_2I$	C_s	-0.491	244.82	-89.98	154.84	-119.56	6.22	-24.77	-18.55	α-X
S6b	$\mathbf{C}H_3CH_2I$		-0.594	232.06	-72.45	159.60	-114.79	-6.54	-7.25	-13.79	β-X
S7a	$CH_3\mathbf{C}H_2CO_2Me$	C_s	-0.475	278.88	-127.14	151.73	-122.66	40.28	-61.94	-21.66	α-X
S7b	$\mathbf{C}H_3CH_2CO_2Me$		-0.569	223.20	-51.08	172.13	-102.27	-15.39	14.13	-1.26	β-X
S8a	$CH_3\mathbf{C}H_2CN$	C_s	-0.484	235.78	-66.79	168.99	-105.40	-2.82	-1.58	-4.40	α-X
S8b	$\mathbf{C}H_3CH_2CN$		-0.554	221.77	-52.62	169.15	-105.25	-16.83	12.59	-4.24	β-X
S9a	$CH_3\mathbf{C}H_2NH_2$	C_s	-0.182	237.44	-99.33	138.11	-136.28	-1.16	-34.12	-35.28	α-X
S9b	$\mathbf{C}H_3CH_2NH_2$		-0.586	236.72	-79.48	157.24	-117.15	-1.87	-14.27	-16.15	β-X
S10a	$CH_3\mathbf{C}H_2NO_2$	C_s	-0.222	239.28	-131.11	108.17	-166.22	0.68	-65.90	-65.22	α-X
S10b	$\mathbf{C}H_3CH_2NO_2$		-0.597	238.65	-68.48	170.18	-104.22	0.06	-3.27	-3.22	β-X
51	$H_2\mathbf{C}{=}CH_2$	D_{2h}	-0.365	246.91	-194.83	52.08	-222.31	8.31	-129.62	-121.31	C_2H_4
52	$H\mathbf{C}{\equiv}CH$	$D_{\infty h}$	-0.225	255.62	-145.56	110.06	-164.34	17.03	-80.36	-63.33	C_2H_2

[a]Calculated with the GIAO-DFT method under B3LYP/BSS-A. [b]$\Delta\sigma^m$(C: S) = σ^m(C: S) – σ^m(C: C^{4-}) (m = d, p and t). [c]$\Delta\sigma^p$(C) = σ^p(C), since σ^p(C: C^{4-}) = 0 ppm. [d]$\Delta\sigma^m$(C: S) = (1/n)($\Delta\sigma^m$(C: S) – $\Delta\sigma^m$(C: S_e)), see text for n, S and S_e (m = d, p and t).

(Table S11 continues)

Nos.	Species	sym	Q(C)	σ^d(C)	σ^p(C)[c]	σ^t(C)	$\Delta\sigma^t$(C)	$\Delta\sigma^d(C)_e$[d]	$\Delta\sigma^p(C)_e$[d]	$\Delta\sigma^t(C)_e$[d]	effect
53	**C**$_6$H$_6$	D_{6h}	-0.106	239.66	-192.70	46.96	-227.43	1.06	-127.49	-126.43	C_6H_6
			-0.240	240.22	-193.26	46.96	-227.44	1.62	-128.06	-126.43	C_6H_6
54	C_6H_5OH (ipso)	C_s	0.449	258.53	-243.01	15.52	-258.88	18.86	-50.31	-31.45	*i*-X
S11	C_6H_5SH (ipso)	C_s	-0.155	157.15	-122.23	34.92	-239.47	-82.51	70.47	-12.04	*i*-X
S12	C_6H_5SeH (ipso)	C_1	-0.185	251.05	-219.65	31.40	-243.00	11.38	-26.95	-15.57	*i*-X
S13	C_6H_5F (ipso)	C_{2v}	0.542	274.86	-267.63	7.22	-267.17	35.19	-74.93	-39.74	*i*-X
S14	C_6H_5Cl (ipso)	C_{2v}	-0.038	213.33	-181.55	31.78	-242.62	-26.34	11.15	-15.19	*i*-X
S15	C_6H_5Br (ipso)	C_{2v}	-0.082	239.21	-206.95	32.25	-242.14	-0.46	-14.25	-14.71	*i*-X
S16	C_6H_5I (ipso)	C_{2v}	-0.181	211.11	-169.14	41.97	-232.42	-28.55	23.56	-4.99	*i*-X
S17	$C_6H_5CO_2Me$ (ipso)	C_s	-0.043	200.85	-156.64	44.21	-230.18	-38.81	36.06	-2.75	*i*-X
S18	C_6H_5CN (ipso)	C_{2v}	-0.165	188.29	-127.29	61.00	-213.40	-51.37	65.41	14.04	*i*-X
S19	$C_6H_5NH_2$ (ipso)	C_s	0.330	257.25	-231.43	25.81	-248.58	17.59	-38.73	-21.15	*i*-X
S20	$C_6H_5NO_2$ (ipso)	C_{2v}	0.187	270.95	-246.35	24.59	-249.80	31.29	-53.65	-22.37	*i*-X
55	H_2**C**=O	C_{2v}	0.307	245.20	-263.64	-18.44	-292.83	13.05	-158.97	-145.93	C=O
56	H(HO)**C**=O	C_s	0.675	245.49	-228.53	16.97	-257.43	13.34	-123.86	-110.53	OC=O

[a]Calculated with the GIAO-DFT method under B3LYP/BSS-A. [b]$\Delta\sigma^m$(C: S) = σ^m(C: S) – σ^m(C: C^{4-}) (*m* = d, p and t). [c]$\Delta\sigma^p$(C) = σ^p(C), since σ^p(C: C^{4-}) = 0 ppm. [d]$\Delta\sigma^m$(C: S) = (1/*n*)($\Delta\sigma^m$(C: S) – $\Delta\sigma^m$(C: S_e)), see text for *n*, S and S_e (*m* = d, p and t).

Table S12. The σ^m(C: S) (m = d, p and t), $\sigma^p_{i\to j}$, $\sigma^p_{i\to j}$, $\Delta\sigma^t$(C: S) and $\delta(C)_{obsd}$ for various species of **1**–**56** and **S21**–**S70**.[a]

Nos	Species	σ^d	σ^p	$\sigma^p_{i\to j}$[b]	$\sigma^p_{i\to a}$[c]	σ^t	$\Delta\sigma^t(C^{4-})$[d]	$\Delta\sigma^t$(TMS)[d]	$\delta(C)_{obsd}$[e]
1	$\mathbf{C}^{4-}$	274.39	0.00	---	---	274.39	0.00	---	---
S21	$(\mathbf{C}H_3)_4Si$ (T_d)	248.95	65.96	---	---	182.99	-91.40	0.00	0.0
5	$\mathbf{C}H_4$ (T_d)	238.98	49.66	125.55	175.21	189.32	-85.07	-6.33	-4.6
12	$\mathbf{C}H_3CH_3$ (D_{3d})	238.60	65.21	121.88	187.09	173.39	-101.00	9.60	6.9
13	$\mathbf{C}H_3CH_2CH_3$ (C_{2v})	251.23	91.12	83.64	174.77	160.10	-114.29	22.89	16.4
17	*n*-C_5H_{12} (C_{2v})	236.68	95.74	124.40	220.14	140.94	-133.45	42.05	34.2
S22	*n*-C_7H_{16} (C_{2v})	251.38	107.31	88.74	196.05	144.07	-130.32	38.92	29.3
S23	*n*-nonane (C_{2v})	246.58	102.38	116.20	218.58	144.20	-130.19	38.79	29.8
S24	*n*-undecane (C_{2v})	257.19	112.95	---	---	144.24	-130.15	38.75	29.9
S25	*n*-tridecane (C_{2v})	249.18	104.87	---	---	144.31	-130.08	38.68	29.9
S26	*n*-pentadecane (C_{2v})	246.14	101.81	---	---	144.34	-130.05	38.65	29.9
48	$\mathbf{C}H_3NH_2$ (C_s)	229.80	79.79	127.33	207.12	150.01	-124.38	32.98	28.4
38	$\mathbf{C}H_3OH$ (C_s)	232.16	104.67	109.59	214.26	127.49	-146.90	55.50	50.2
39	$\mathbf{C}H_3SH$ (C_s)	243.86	73.63	108.92	182.55	170.23	-104.16	12.76	6.5
S27	$\mathbf{C}H_3SCH_3$ (C_{2v})	243.04	83.75	109.94	193.69	159.29	-115.10	23.70	18.1
S28	$\mathbf{C}H_3S(O)CH_3$ (C_s)	247.68	111.05	83.30	194.34	136.64	-137.75	46.35	41.0
S29	$\mathbf{C}H_3SO_2CH_3$ (C_{2v})	245.01	107.45	95.39	202.85	137.56	-136.83	45.43	42.6
S30	$\mathbf{C}H_3SO_3H$ (C_1)	246.80	107.13	85.97	193.10	139.67	-134.72	43.32	39.1
42	$\mathbf{C}H_3F$ (C_{3v})	232.99	126.01	97.78	223.78	106.99	-167.40	76.00	71.6
S31	$\mathbf{C}H_2F_2$ (C_{2v})	232.49	167.45	72.95	240.41	65.33	-209.06	117.66	109.0
S32	$\mathbf{C}HF_3$ (C_{3v})	233.47	179.28	60.17	239.45	54.19	-220.20	128.80	116.0
S33	$\mathbf{C}F_4$ (T_d)	235.84	187.95	48.31	236.26	47.89	-226.50	135.10	122.3
S34	$(\mathbf{C}H_3)_2NH$ (C_s)	233.02	91.99	120.41	212.40	141.04	-133.35	41.95	38.2
S35	$(\mathbf{C}H_3)_3N$ (C_{3v})	235.94	102.65	114.79	217.44	133.29	-141.10	49.70	47.6
43	$\mathbf{C}H_3Cl$ (C_{3v})	243.61	93.19	98.87	192.06	150.42	-123.97	32.57	25.6
S36	$\mathbf{C}H_2Cl_2$ (C_{2v})	253.17	142.22	67.87	210.09	110.95	-163.44	72.04	53.5
S37	$\mathbf{C}HCl_3$ (C_{3v})	267.64	194.69	26.77	221.46	72.95	-201.44	110.04	77.2
S38	$\mathbf{C}Cl_4$ (T_d)	283.05	248.49	14.05	234.44	34.56	-239.83	148.43	96.1
S39	$\mathbf{C}H_3Br$ (C_{3v})	241.70	-83.06	---	---	158.65	-115.74	24.34	9.6
S40	$\mathbf{C}H_2Br_2$ (C_{2v})	253.38	-136.40	---	---	116.98	-157.41	66.01	21.6
S41	$\mathbf{C}HBr_3$ (C_{3v})	266.11	-194.70	---	---	71.41	-202.98	111.58	11.0
S42	$\mathbf{C}Br_4$ (T_d)	277.75	-254.74	---	---	23.01	-251.38	159.98	-29.7
46	$\mathbf{C}H_3COOCH_3$ (C_s)	248.04	87.22	74.13	161.35	160.82	-113.57	22.17	20.6
S43	$\mathbf{C}H_3OCH_3$ (C_{2v})	234.85	115.77	105.27	221.04	119.08	-155.31	63.91	61.2
S44	$\mathbf{C}H_3OEt$ (C_s)	235.22	114.82	105.92	220.74	120.39	-154.00	62.60	64.3
S45	$\mathbf{C}H_3OPr$-*i* (C_1)	236.44	112.90	108.23	221.13	123.55	-150.84	59.44	56.4
S46	$\mathbf{C}H_3OBu$-*t* (C_s)	236.89	106.15	112.12	218.27	130.74	-143.65	52.25	50.1
47	$\mathbf{C}H_3CN$ (C_{3v})	220.25	38.56	166.16	204.72	181.70	-92.69	1.29	1.9
S47	$\mathbf{C}H_3NC$ (C_{3v})	233.20	76.83	120.88	171.36	156.37	-118.02	26.62	25.9
49	$\mathbf{C}H_3NO_2$ (C_s)	231.58	114.08	107.14	221.22	117.50	-156.89	65.49	62.5
S48	$\mathbf{C}H_3CHO$ (C_s)	248.87	100.73	83.69	184.42	148.14	-126.25	34.85	30.9
S49	$\mathbf{C}H_3COCH_3$ (C_{2v})	242.82	91.69	90.74	182.43	151.13	-123.26	31.86	30.9
S50	$\mathbf{C}H_3COOH$ (C_s)	248.81	86.56	79.87	166.43	162.24	-112.15	20.75	20.8

[a]Calculated with the GIAO-DFT method under B3LYP/BSS-A. [b]Main contributions from the occupied-to-occupied orbital transitions on σ^p(C). [c]Main contributions from the occupied-to-unoccupied orbital transitions on σ^p(C). [d]$\Delta\sigma^p$(C: S) = σ^p(C: S) – σ^p(C: C^{4-} or TMS). [e]Ovserved values.

(Table S12 continues)

Nos	Species	σ^d	σ^p	$\sigma^p_{i\rightarrow j}$ [b]	$\sigma^p_{i\rightarrow a}$ [c]	σ^t	$\Delta\sigma^t(C^{4-})$ [d]	$\Delta\sigma^t(TMS)$ [d]	$\delta(C)_{obsd}$ [e]
51	CH_2=CH_2 (D_{2h})	246.91	194.83	69.30	264.12	52.08	-222.31	130.91	123.3
S51	*c*-CH_2=CHCH=CH_2 (C_{2v})	249.95	201.24	80.13	281.37	48.70	-225.69	134.29	124.0
S52		*t*-CH_2=CHCH=CH_2 (C_{2h})	243.18	196.30	91.77	288.07	46.88	-227.51	
	136.11	125.0							
S53a	CH_2=$CHCH_3$ (C_s)	257.27	220.07	42.14	262.22	37.20	-237.19	145.79	133.9
S53b		233.71	172.08	110.86	282.94	61.63	-212.76	121.36	115.7
S54a		CH_2=$C(CH_3)_2$ (C_{2v})	257.96	231.96	54.59	286.55	26.00	-248.39	
	156.99	142.2							
S54b			230.39	163.89	138.33	302.22	66.50	-207.89	116.49
	109.8								
S55a	CH_2=$CHCH_2CH_3$ (C_1)	253.85	224.16	43.93	268.09	29.69	-244.70	153.30	140.2
S55b		226.97	163.70	137.06	300.76	63.27	-211.12	119.72	113.5
S56a	CH_2=$CHCH(CH_3)_2$ (C_1)	242.06	216.86	79.11	295.96	25.20	-249.19	157.79	146.0
S56b		226.45	159.59	138.69	298.28	66.86	-207.53	116.13	111.3
S57a	CH_2=$CHC(CH_3)_3$ (C_s)	252.36	232.00	41.11	273.11	20.35	-254.04	162.64	149.8
S57b		226.41	158.03	150.01	308.04	68.38	-206.01	114.61	109.0
S58a	CH_2=CHOH (C_s)	244.16	-217.60	58.85	-276.45	26.57	-247.82	156.42	149.0
S58b		242.42	-152.46	88.19	-240.65	89.96	-184.43	93.03	88.0
S59a	CH_2=CH(OMe) (C_s)	256.45	-237.09	24.22	-261.31	19.36	-255.03	163.63	152.9
S59b		240.60	-143.09	103.16	-246.25	97.51	-176.88	85.48	85.5
S60a	CH_2=$CH(OCOCH_3)$ (C_s)	276.98	-245.31	---	---	31.67	-242.72	151.32	141.4
S60b		218.39	-134.85	---	---	83.53	-190.86	99.46	97.5
S61a	CH_2=CHF (C_s)	256.61	-240.72	11.05	-251.77	15.89	-258.50	167.10	147.7
S61b		240.84	-157.23	96.96	-254.19	83.61	-190.78	99.38	88.5
S62a	CH_2=CHCl (C_s)	256.35	-216.56	45.45	-262.01	39.78	-234.61	143.21	126.1
S62b		242.92	-182.88	83.68	-266.56	60.04	-214.35	122.95	117.4
S63a	CH_2=CHCHO (C_s)	268.90	-235.82	9.94	-245.77	33.08	-241.31	149.91	138.5
S63b		232.74	-194.86	111.09	-305.96	37.88	-236.51	145.11	138.0
S64a	CH_2=$CHCOCH_3$ (C_s)	260.78	-227.40	36.89	-264.30	33.38	-241.01	149.61	137.5
S64b		220.24	-172.23	147.25	-319.48	48.01	-226.38	134.98	129.0
S65a	*c*-CH_2=CHCOOH (C_s)	278.10	230.40	29.46	200.93	47.71	-226.68	135.28	128.1
S65b		226.69	186.51	132.80	319.31	40.18	-234.21	142.81	133.2
S66a	*t*-CH_2=CHCOOH (C_s)	263.04	218.14	29.41	247.55	44.90	-229.49	138.09	128.1
S66b		234.03	191.03	101.51	292.53	43.00	-231.39	139.99	133.2
S67a	CH_2=$CHNO_2$ (C_s)	268.67	-242.12	-5.40	-236.73	26.55	-247.84	156.44	144.7
S67b		223.46	-170.43	121.43	-291.87	53.02	-221.37	129.97	121.5
S68a	CH_2=CHCN (C_s)	208.39	-142.42	176.84	-319.26	65.97	-208.42	117.02	107.8
S68b		251.42	-212.96	36.03	-248.99	38.46	-235.93	144.53	137.5
S69a	CH_2=CHNC (C_s)	262.73	-207.62	7.57	-215.19	55.11	-219.28	127.88	121.0
S69b		230.65	-174.61	118.10	-292.71	56.04	-218.35	126.95	119.3
S70a	N,N-Me_2EtN (C_1)	259.79	-229.47	31.16	-260.63	30.32	-244.07	152.67	144.5
S70b		230.90	-131.74	136.19	-267.93	99.16	-175.23	83.83	81.8

[a]Calculated with the GIAO-DFT method under B3LYP/BSS-A. [b]Main contributions from the occupied-to-occupied orbital transitions on σ^p(C). [c]Main contributions from the occupied-to-unoccupied orbital transitions on σ^p(C). [d]$\Delta\sigma^p$(C: S) = σ^p(C: S) – σ^p(C: C^{4-} or TMS). [e]Ovserved values.

Table S13. The σ^{d}(C), σ^{p}(C) and σ^{t}(C) values of **C**H_3NH_2 and **C**H_3NO_2, given separately by each ψ_i.[a]

MO (i in ψ_i)	σ^{d}_i(C)	σ^{p}_i(C)	σ^{t}_i(C)
CH_3NH_2 (C_s)			
1 (A′); 2 (A′)	200.32	0.03	200.35
3 (A′)	6.57	–6.29	0.28
4 (A′)	22.01	4.47	26.48
5 (A″)	2.62	–18.33	–15.70
6 (A′)	2.50	–46.12	–43.62
7 (A′)	2.37	–60.62	–58.25
8 (A″)	–3.37	–61.13	–64.49
9 (A′)	–3.23	–19.13	–22.37
ψ_{occ} to ψ_{occ}		127.33	
total	229.80	–79.79	150.01
CH_3NO_2 (C_s)			
1 (A′)–4 (A′)	200.29	0.03	200.32
5 (A′); 6 (A″)	0.28	–2.00	–1.72
7 (A′); 8 (A′)	27.23	–2.54	24.69
9 (A′)	2.44	–13.41	–10.97
10 (A′)	1.87	–3.54	–1.67
11 (A″)	0.89	–11.81	–10.92
12 (A″)	–3.23	–81.05	–84.28
13 (A′)	–3.43	–77.33	–80.76
14 (A″)	–0.02	–0.25	–0.28
15 (A′)	7.39	–12.65	–5.26
16 (A″)	–2.13	–16.67	–18.80
ψ_{occ} to ψ_{occ}		107.14	
total	231.58	–114.08	117.50

[a]Calculated with the GIAO method under B3LYP/BSS-A.

Table S14. Main contributions from the $\psi_i \rightarrow \psi_a$ transitions on $\sigma^p_{i\rightarrow a:kk}$(C: k = x, y and/or z) in $^{C}H_3NH_2$ and $^{C}H_3NO_2$.[a,b]

$i \rightarrow a$[c]	$\sigma^p_{i\rightarrow a:xx}$(C)	$\sigma^p_{i\rightarrow a:yy}$(C)	$\sigma^p_{i\rightarrow a:zz}$(C)	$\sigma^p_{i\rightarrow a}$(C)
$^{C}H_3NH_2$ (C_s)				
7→26	0.00	0.00	–19.88	–6.63
7→41	0.00	0.00	–18.80	–6.27
8→23	–0.89	–31.43	0.00	–10.77
8→26	–22.94	–0.26	0.00	–7.73
8→40	–16.55	–1.82	0.00	–6.12
$^{C}H_3NO_2$ (C_s)				
12→22	–19.21	–0.65	0.00	–6.62
12→28	–28.68	–0.06	0.00	–9.58
12→29	–2.96	–29.16	0.00	–10.71
12→50	–8.52	–11.63	0.00	–6.72
13→24	0.00	0.00	–18.14	–6.05
13→28	0.00	0.00	–31.64	–10.55
13→30	0.61	–20.27	0.00	–6.55

[a]Calculated with the GIAO method under B3LYP/BSS-A. [b]Magnitudes of $\sigma^p_{i\rightarrow a}$(C) larger than 6 ppm are shown. [c]In $\psi_i \rightarrow \psi_a$.

Table S15. The σ^d(C), σ^p(C) and σ (C) values of $^{C}_6H_5OH$ (C_s), given separately by each ψ_i.[a]

MO (i in ψ_i)	σ^d_i(C)	σ^p_i(C)	σ^t_i(C)
1 (A')	0.00	0.00	0.01
2 (A')	200.29	0.00	200.29
3 (A')–7 (A')	0.18	0.19	0.38
8 (A')–12 (A')	34.07	–24.22	9.84
13 (A')	1.85	–9.58	–7.73
14 (A')	3.85	–25.61	–21.76
15 (A')	1.88	–8.29	–6.41
16 (A')	4.58	–34.11	–29.53
17 (A')	–7.87	–54.23	–62.10
18 (A')	8.21	–8.07	0.14
19 (A')	13.08	–21.65	–8.57
20 (A")	–5.28	–19.77	–25.05
21 (A')	1.51	–3.40	–1.89
22 (A')	–4.26	–52.51	–56.77
23 (A")	1.72	–0.79	0.92
24 (A")	1.90	–1.80	0.10
25 (A")	5.27	–14.78	–9.51
ψ_{occ} to ψ_{occ}		33.17	
total	260.97	–245.45	15.52

[a]Calculated with the GIAO method under B3LYP/BSS-A.

Table S16. Main contributions from the $\psi_i \rightarrow \psi_a$ transitions on the σ^p(C) of C_6H_5OH (C_s).[a,b]

$i \rightarrow a$[b]	$\sigma^p_{i \rightarrow a:xx}$(C)	$\sigma^p_{i \rightarrow a:yy}$(C)	$\sigma^p_{i \rightarrow a:zz}$(C)	$\sigma^p_{i \rightarrow a}$(C)
12→87	2.65	15.40	0.00	6.01
14→28	–26.78	–0.11	0.00	–8.96
16→28	–19.19	–53.50	0.00	–24.23
17→28	–25.53	–12.31	0.00	–12.62
17→87	–24.92	–2.75	0.00	–9.22
18→28	–0.68	–43.06	0.00	–14.58
18→87	–0.18	20.94	0.00	6.92
20→28	–14.26	–18.78	0.00	–11.01
21→28	17.26	3.31	0.00	6.86
22→28	0.60	–17.40	0.00	–5.60
22→38	0.24	–16.23	0.00	–5.33
22→44	–1.68	–28.12	0.00	–9.93
22→54	–0.98	–24.48	0.00	–8.49

[a]Calculated with the GIAO method under B3LYP/BSS-A. [b]The magnitudes of $\sigma^p_{i \rightarrow a}$(C) larger than 5 ppm are shown. [c]In $\psi_i \rightarrow \psi_a$.

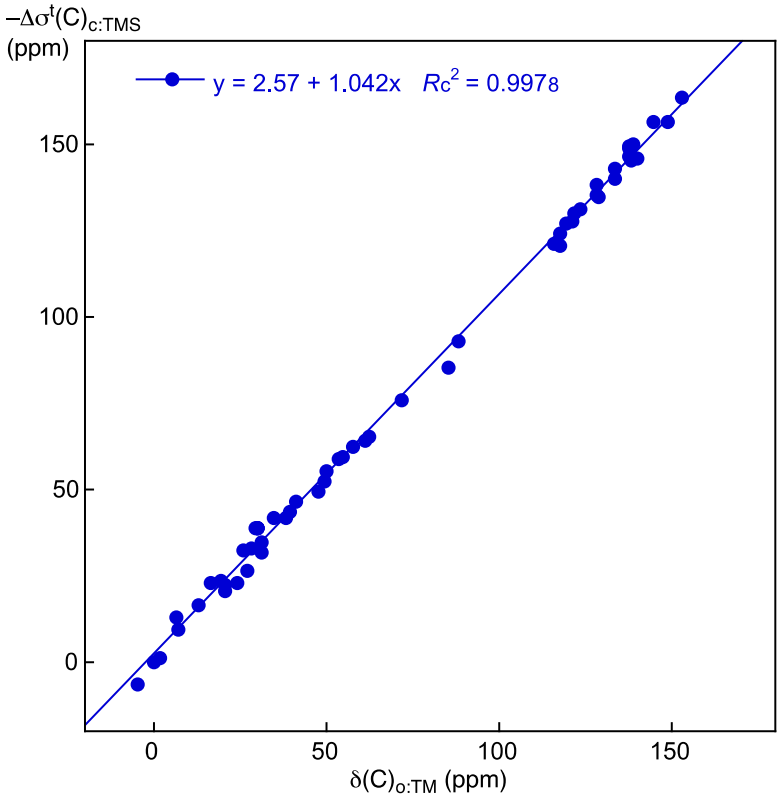

Fig. S1 Plot of δ(C: S)$_{obsd:TMS}$ versus −Δσ^t(C: S)$_{calcd:TMS}$ for 40 species (54 plots) of the Table S1, calculated with the GIAO-DFT method under B3LYP/BSS-A.

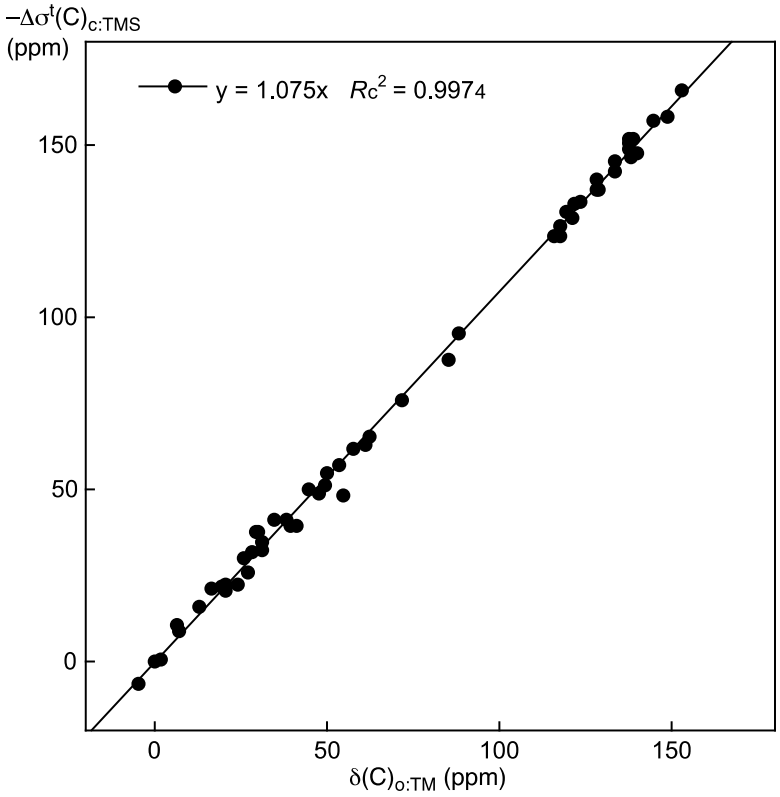

Fig. S2 Plot of δ(C: S)$_{obsd:TMS}$ versus −Δσ^t(C: S)$_{calcd:TMS}$ for 40 species (54 plots) of the Table S2, calculated with the GIAO-DFT method under CAM-B3LYP/BSS-A.

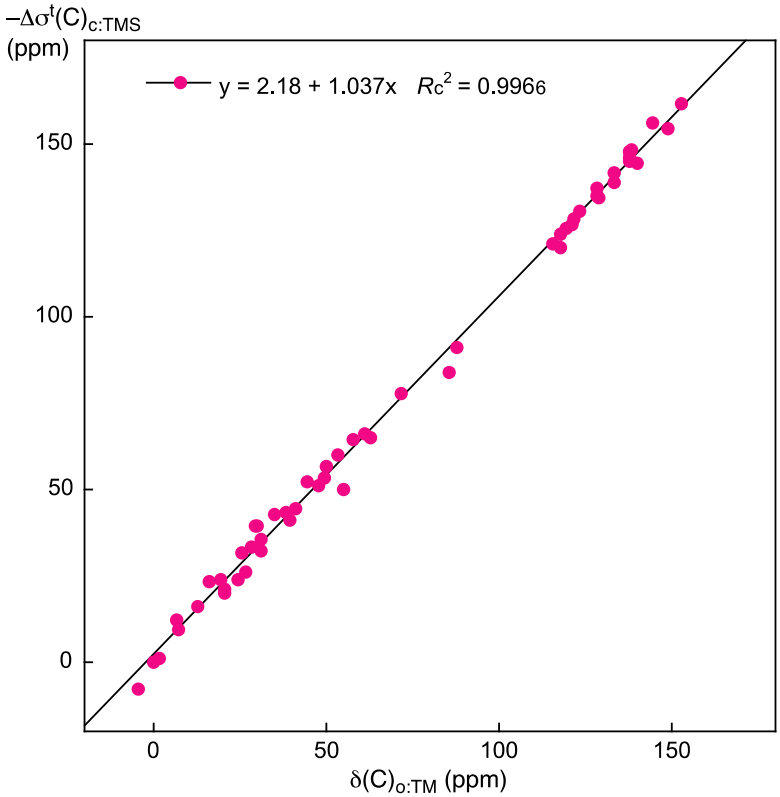

Fig. S3 Plot of $\delta(C: S)_{obsd:TMS}$ versus $-\Delta\sigma^t(C: S)_{calcd:TMS}$ for 40 species (54 plots) of the Table S3, calculated with the GIAO-DFT method under PBE/BSS-A.

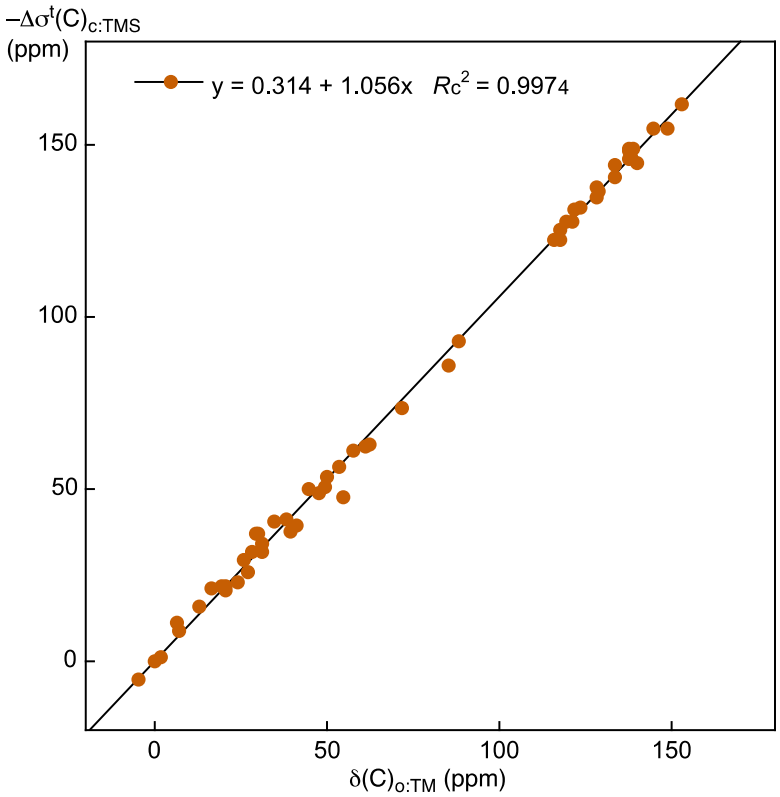

Fig. S4 Plot of $\delta(C: S)_{obsd:TMS}$ versus $-\Delta\sigma^t(C: S)_{calcd:TMS}$ for 40 species (54 plots) of the Table S4, calculated with the GIAO-DFT method under PBE0/BSS-A

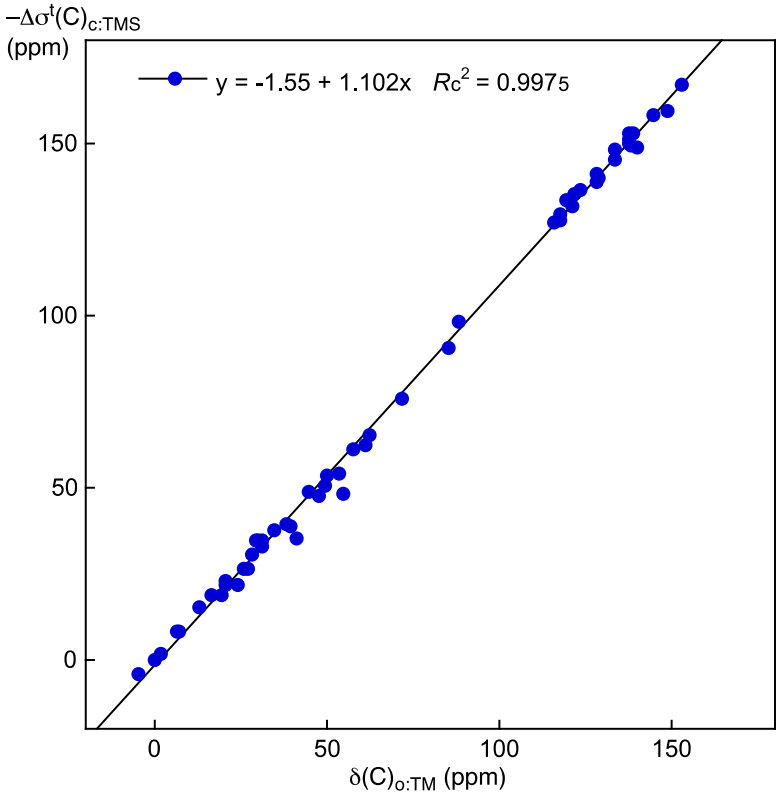

Fig. S5 Plot of $\delta(C: S)_{obsd:TMS}$ versus $-\Delta\sigma^t(C: S)_{calcd:TMS}$ for 40 species (54 plots) of the Table S5, calculated with the GIAO-DFT method under LC-ωPBE/BSS-A.

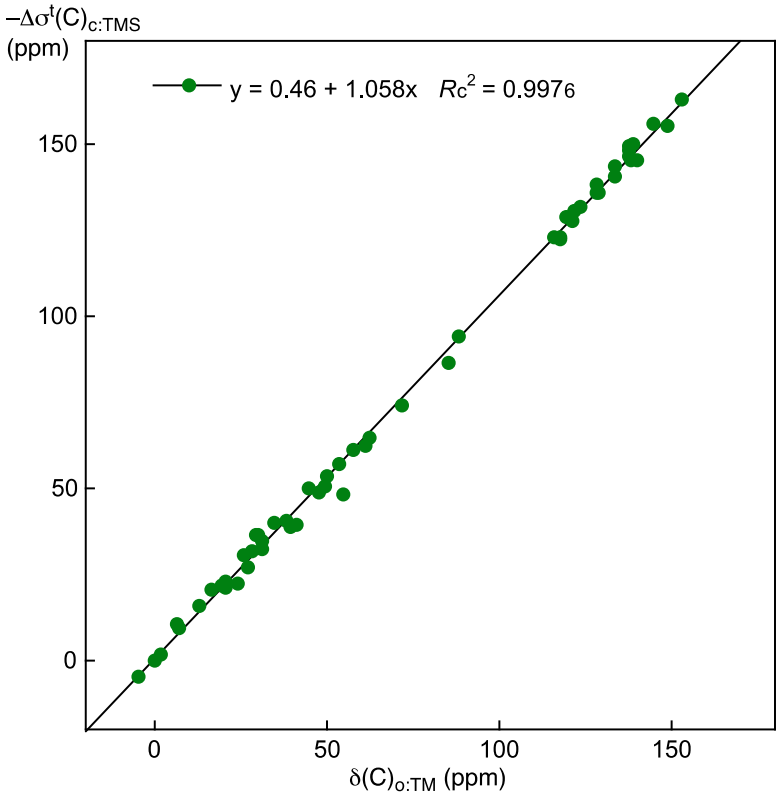

Fig. S6 Plot of $\delta(C: S)_{obsd:TMS}$ versus $-\Delta\sigma^t(C: S)_{calcd:TMS}$ for 40 species (54 plots) of the Table S6, calculated with the GIAO-DFT method under ωB97X-D/BSS-A.

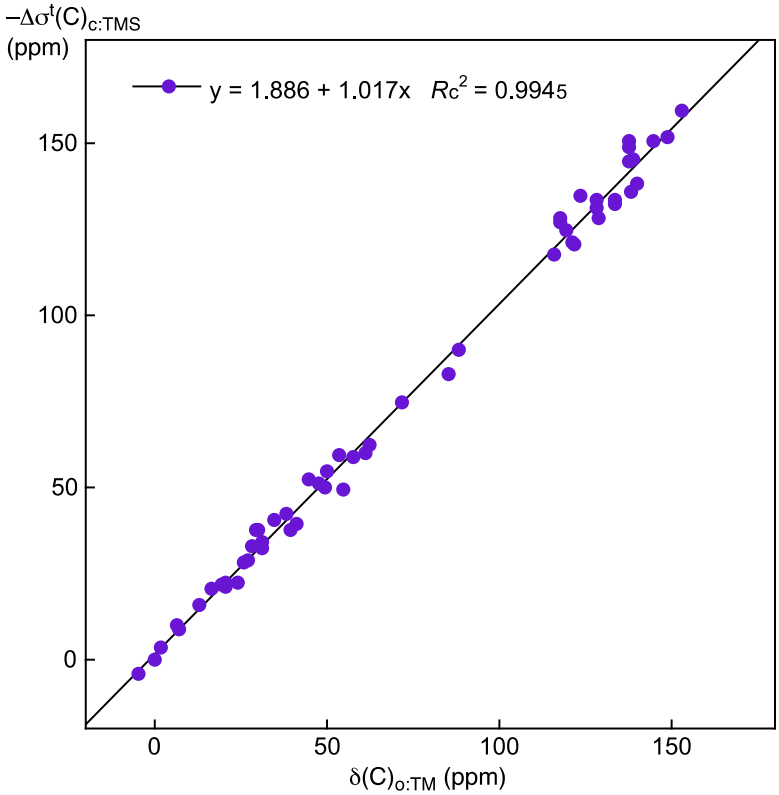

Fig. S7 Plot of δ(C: S)$_{obsd:TMS}$ versus −Δσ^t(C: S)$_{calcd:TMS}$ for 40 species (54 plots) of the Table S7, calculated with the GIAO-DFT method under MP2/BSS-A.

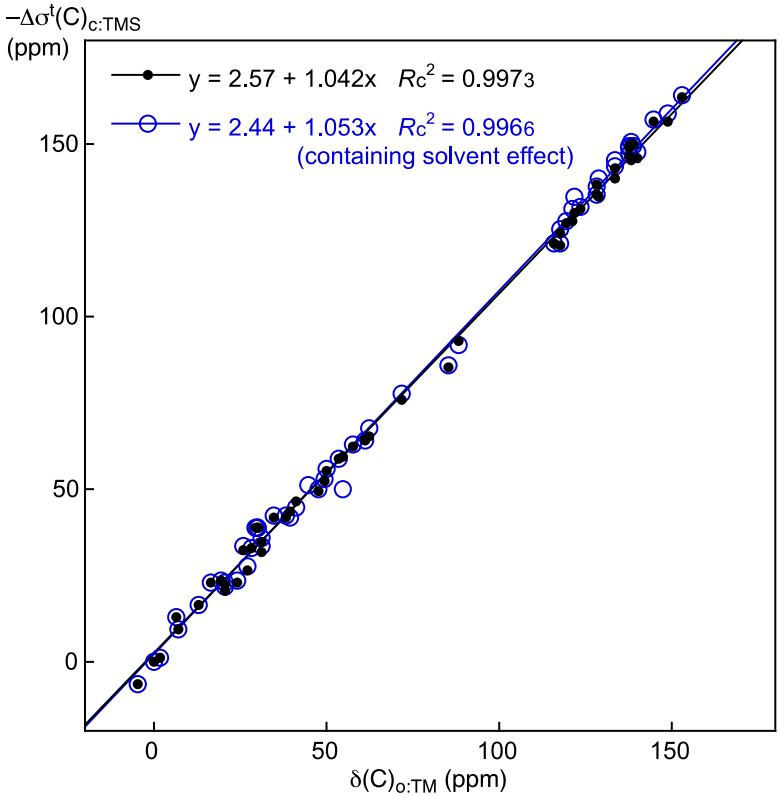

Fig. S8 Plots of δ(C: S)$_{obsd:TMS}$ versus −Δσ^t(C: S)$_{calcd:TMS}$ for 40 species (54 plots) of the Table S8, calculated with the GIAO-DFT method of B3LYP/BSS-A containing the solvent effect of $CHCl_3$.

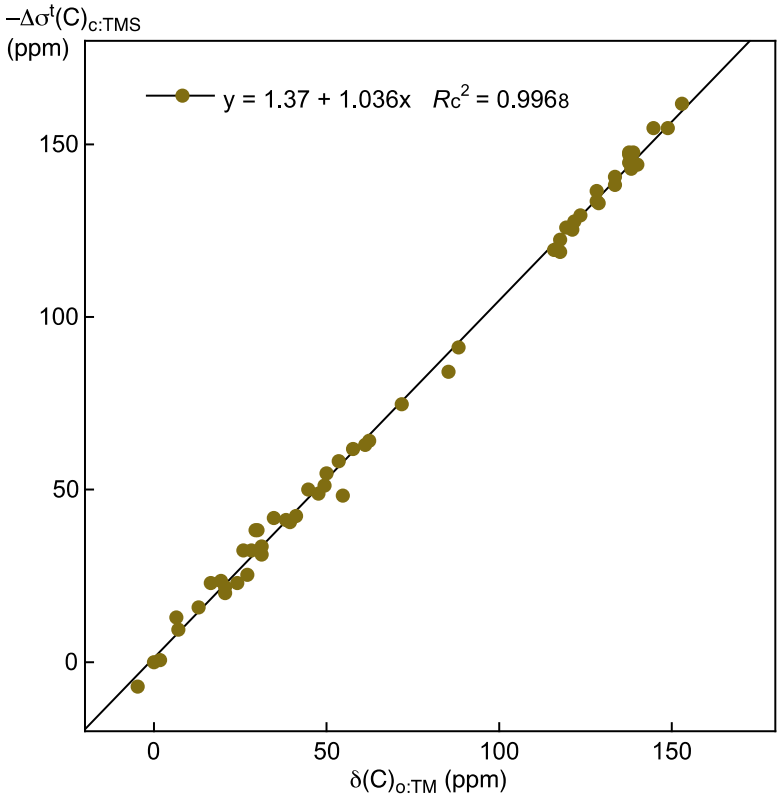

Fig. S9 Plot of δ(C: S)$_{obsd:TMS}$ versus −Δσ^t(C: S)$_{calcd:TMS}$ for 40 species (54 plots) of the Table S9, calculated with the GIAO-DFT method under B3LYP/def2TZVP.

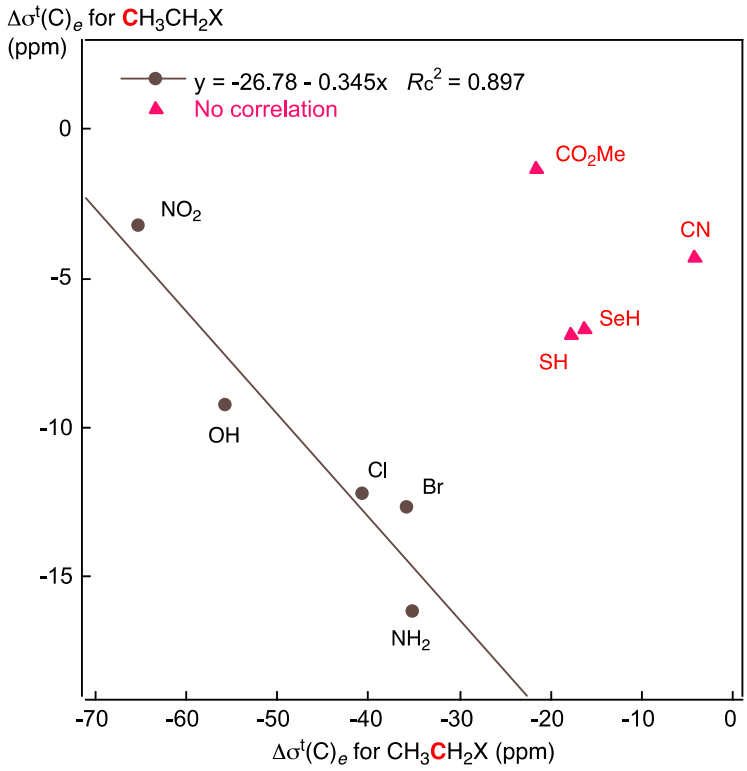

Fig. S10 Plot of Δσ^t(C)$_e$ for **C**H$_3$CH$_2$X versus those of CH$_3$**C**H$_2$X, where X are shown in the figure. (Data for X = F are omitted.).

Origin of the α-X effect

The α-X effect is examined for **C**H_3–X from **C**H_4 and CH_3**C**H_2–X from CH_3**C**H_3 (X = OH, SH, SeH, $SSCH_3$, F, Cl, Br, I, CO_2Me, CN, NH_2 and/or NO_2) (see Scheme 3, Table 2 and Table S1 of the ESI†). The ($\Delta\sigma^d(C)_e$, $\Delta\sigma^p(C)_e$, $\Delta\sigma^t(C)_e$) values of (–18.7 ~ 40.3, –76.4 ~ –11.1, –82.3 ~ –4.4 ppm) are calculated for the species.

Table S13 lists the $\sigma^d(C)$, $\sigma^p(C)$ and $\sigma^t(C)$ values for **C**H_3NH_2 and **C**H_3NO_2 separately for each MO. In the case of **C**H_3NH_2, which has a very strong electron donating X of NH_2, the outer Mos of the HOMO–1 (ψ_8) ~ HOMO–3 (ψ_6) contribute greatly to $\sigma^p(C)$. In the case of **C**H_3NO_2, with the very strong electron accepting group X of NO_2, the somewhat more inner HOMO–3 (ψ_{13}) and HOMO–4 (ψ_{12}) also strongly affect $\sigma^p(C)$. Table S14 lists the $\psi_i \rightarrow \psi_a$ transitions contributing to $\sigma^p_{i\rightarrow a:kk}(C)$: $k = x$, y and/or z), which are greater than approximately 20 ppm in magnitude. The contributions to **C**H_3NH_2 are large for the $\psi_i \rightarrow \psi_a$ transitions of $\psi_7 \rightarrow \psi_{26}$ ($\sigma^p_{7\rightarrow 26:zz}(C)$ = –19.9 ppm), $\psi_7 \rightarrow \psi_{41}$ ($\sigma^p_{7\rightarrow 41:zz}(C)$ = –18.8 ppm), $\psi_8 \rightarrow \psi_{23}$ ($\sigma^p_{8\rightarrow 23:yy}(C)$ = –31.4 ppm) and $\psi_8 \rightarrow \psi_{26}$ ($\sigma^p_{8\rightarrow 26:xx}(C)$ = –22.9 ppm). The contributions from the $\psi_i \rightarrow \psi_a$ transitions in **C**H_3NO_2 are large for $\psi_{12} \rightarrow \psi_{28}$ ($\sigma^p_{12\rightarrow 28:xx}(C)$ = –28.7 ppm) and $\psi_{12} \rightarrow \psi_{29}$ ($\sigma^p_{12\rightarrow 29:yy}(C)$ = –29.2 ppm) and $\psi_{13} \rightarrow \psi_{28}$ ($\sigma^p_{13\rightarrow 28:zz}(C)$ = –31.6 ppm).

Figs. S11a and S11b show the $\psi_i \rightarrow \psi_a$ transitions of $\psi_7 \rightarrow \psi_{26}$, $\psi_7 \rightarrow \psi_{41}$, $\psi_8 \rightarrow \psi_{23}$ and $\psi_8 \rightarrow \psi_{26}$ for **C**H_3NH_2 and those of $\psi_{12} \rightarrow \psi_{28}$, $\psi_{12} \rightarrow \psi_{29}$, $\psi_{13} \rightarrow \psi_{28}$ and $\psi_{13} \rightarrow \psi_{30}$ for **C**H_3NO_2, respectively. The α-X effect is well visualized both for X of a very good donor and a very good acceptor, employing $\psi_i \rightarrow \psi_a$ transitions.

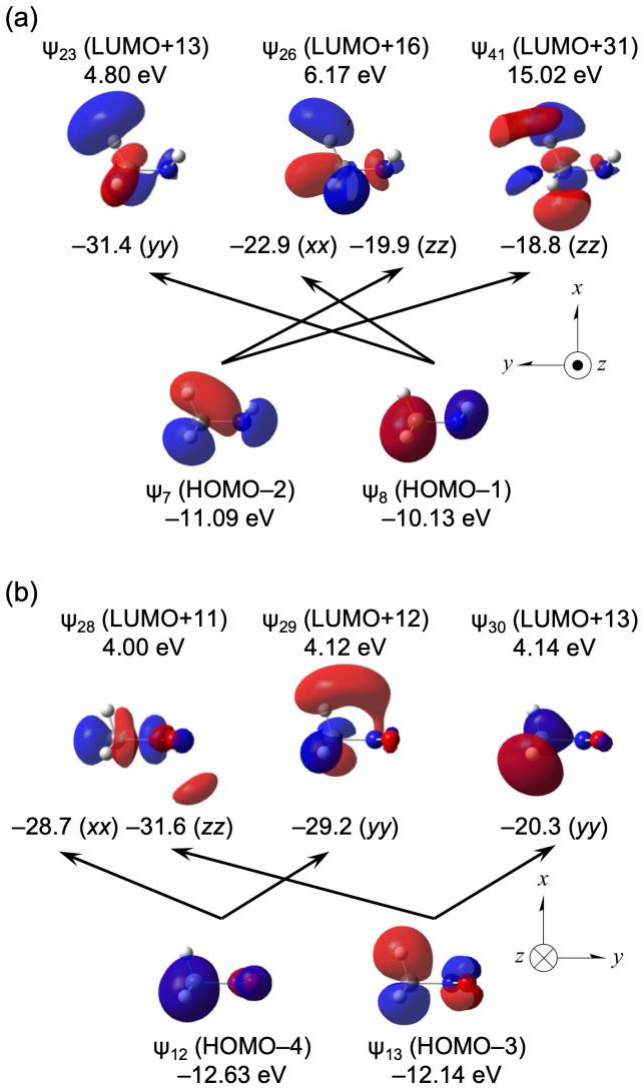

Fig. S11 Contributions from each $\psi_i \rightarrow \psi_a$ transition to the components of σ^p(C) in **C**H_3NH_2 (C_s) (a) and **C**H_3NO_2 (C_s) (b), together with the axes with an isovalue of 0.04 au.

Table S15 lists the σ^{d}(C), σ^{p}(C) and σ^{t}(C) values of C_6H_5OH, separately for each MO. The outer MOs of HOMO–3 (ψ_{22}), HOMO–8 (ψ_{17}) and HOMO–9 (ψ_{16}) contribute greatly to σ^{p}(C). Table S16 lists the $\psi_i \rightarrow \psi_a$ transitions contributing to $\sigma^{p}_{i\rightarrow a:kk}$(C: $k = x$, y and/or z), which are greater than 18 ppm. The $\psi_i \rightarrow \psi_a$ transitions of $\psi_{16} \rightarrow \psi_{28}$ ($\sigma^{p}_{16\rightarrow 28:yy}$(C) = –53.5 ppm), $\psi_{17} \rightarrow \psi_{28}$ ($\sigma^{p}_{17\rightarrow 28:xx}$(C) = –25.5 ppm), $\psi_{17} \rightarrow \psi_{87}$ ($\sigma^{p}_{17\rightarrow 87:xx}$(C) = –24.9 ppm) and $\psi_{22} \rightarrow \psi_{44}$ ($\sigma^{p}_{22\rightarrow 44:yy}$(C) = –28.1 ppm) contribute a lot to $\sigma^{p}_{i\rightarrow a:kk}$(C: $k = x$, y and/or z).

Fig. S12 shows the $\psi_i \rightarrow \psi_a$ transitions of $\psi_{16} \rightarrow \psi_{28}$, $\psi_{17} \rightarrow \psi_{28}$, $\psi_{17} \rightarrow \psi_{87}$ and $\psi_{22} \rightarrow \psi_{44}$, where the transitions of large contributions are omitted if the contributions from ψ_i are small in C_6H_5OH. The *i*-X effect is well visualized through the occupied-to-unoccupied orbital transitions.

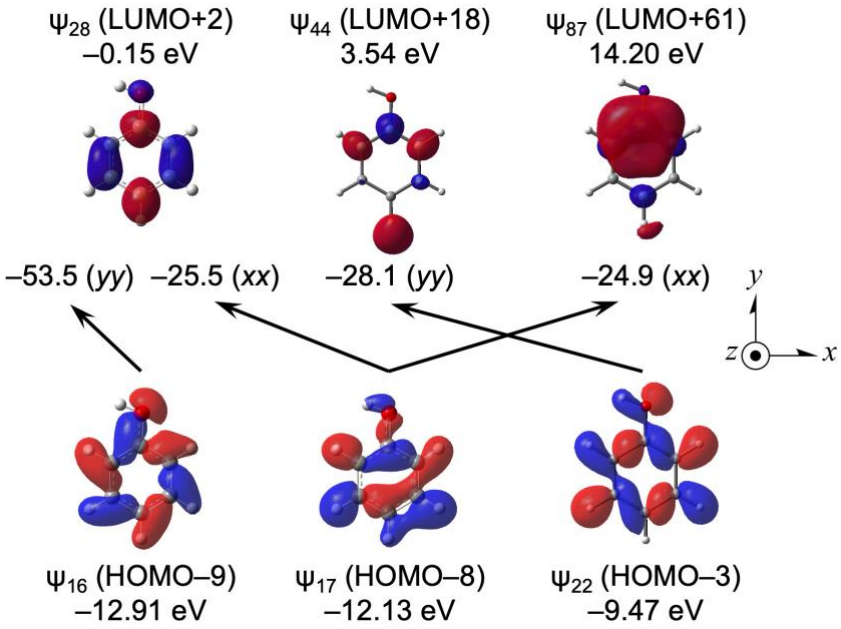

Fig. S12 Contributions from each $\psi_i \rightarrow \psi_a$ transition to the components of σ^{p}(C) in C_6H_5OH (C_s), together with their axes, with an isovalue of 0.04 au.

Optimized structures given by Cartesian coordinates

Optimized structures given by Cartesian coordinates for examined molecules, together with the total energies with the B3LYP/BSS-A method of the Gaussian 09 program.

Compound **1**: C^{4-}
Symmetry O_h
energy E = -36.7801429 a.u.
Standard orientation

6	0	0.000000	0.000000	0.000000

Compound **2**: HC^{3-}
Symmetry $C_{\infty v}$
energy E = -38.0130639 a.u.
Standard orientation

6	0	0.000000	0.000000	0.156326
1	0	0.000000	0.000000	-0.937956

Compound **3**: H_2C^{2-}
Symmetry C_{2v}
energy E = -38.9775351 a.u.
Standard orientation

6	0	0.000000	0.000000	0.167545
1	0	0.000000	0.896970	-0.502636
1	0	0.000000	-0.896970	-0.502636

Compound **4**: H_3C^-
Symmetry C_{3v}
energy E = -39.8601650 a.u.
Standard orientation

6	0	0.000000	0.000000	0.125904
1	0	0.000000	1.034205	-0.251808
1	0	-0.895648	-0.517103	-0.251808
1	0	0.895648	-0.517103	-0.251808

Compound **5**: H_4C
Symmetry T_d
energy E = -40.5373993 a.u.
Standard orientation

6	0	0.000000	0.000000	0.000000
1	0	0.628183	0.628183	0.628183
1	0	-0.628183	-0.628183	0.628183
1	0	-0.628183	0.628183	-0.628183
1	0	0.628183	-0.628183	-0.628183

Compound **6**: $CH_3C^-H_2$
Symmetry C_s
energy E = -79.1810665 a.u.
Standard orientation

6	0	-0.057382	0.839127	0.000000
1	0	0.464931	1.234220	0.884887
1	0	0.464931	1.234220	-0.884887
6	0	-0.057382	-0.686321	0.000000
1	0	-0.589406	-1.084501	0.872860

1	0	0.937537	-1.216275	0.000000
1	0	-0.589406	-1.084501	-0.872860

Compound **7**: $CH_3CH_2C^-H_2$
Symmetry C_s
energy E = -118.5172821 a.u.
Standard orientation

6	0	1.399387	0.032490	0.000000
1	0	1.684595	-0.508657	0.907410
1	0	1.684595	-0.508657	-0.907410
6	0	0.000000	0.561733	0.000000
1	0	-0.161604	1.210278	0.876171
1	0	-0.161604	1.210278	-0.876171
6	0	-1.174732	-0.464023	0.000000
1	0	-1.115800	-1.109846	0.880568
1	0	-1.115800	-1.109846	-0.880568
1	0	-2.162309	0.035245	0.000000

Compound **8**: $(CH_3)_2CHC^-H_2$
Symmetry C_1
energy E = -157.8480286 a.u.
Standard orientation

6	0	-0.645654	0.747959	-0.239830
1	0	-0.543113	0.882597	-1.312328
1	0	-1.172969	1.563073	0.248472
6	0	0.529049	0.318316	0.433129
1	0	0.545859	0.424163	1.516965
6	0	-1.512463	-0.595847	0.027373
1	0	-1.086021	-1.455442	-0.479282
1	0	-1.650074	-0.797593	1.085885
1	0	-2.475959	-0.347752	-0.416030
6	0	1.677203	-0.308679	-0.179158
1	0	2.478375	0.448376	-0.054683
1	0	1.569485	-0.527819	-1.237330
1	0	2.045611	-1.160098	0.399250

Compound **9**: $(CH_3)_3CC^-H_2$
Symmetry C_s
energy E = -197.1755240 a.u.
Standard orientation

6	0	-0.852911	-0.111921	0.732602
1	0	-1.064772	0.713692	1.411046
1	0	-1.011118	-1.071652	1.220104
6	0	0.473257	0.000616	0.149778
6	0	-1.855058	0.001601	-0.485944
1	0	-1.763419	0.959101	-0.991756
1	0	-2.853054	-0.079492	-0.061180
1	0	-1.708433	-0.806016	-1.198506
6	0	1.060857	1.314857	-0.102031
1	0	1.915970	1.401209	0.588948
1	0	1.511995	1.369067	-1.095735
1	0	0.386106	2.145125	0.081484
6	0	1.224772	-1.207742	-0.185782
1	0	1.683855	-1.527043	0.766457
1	0	2.025053	-1.053805	-0.904031
1	0	0.572319	-2.034653	-0.468575

Compound **10**: $CH_3(CH_2)_2C^-H_2$
Symmetry C_s
energy E = -157.8425845 a.u.
Standard orientation

6	0	1.507664	-1.435026	0.000000
1	0	2.089417	-1.208068	0.902410
1	0	2.089417	-1.208068	-0.902410
6	0	0.138578	-0.809536	0.000000
1	0	-0.433547	-1.160051	-0.875891
1	0	-0.433547	-1.160051	0.875891
6	0	0.000000	0.744578	0.000000
1	0	0.528914	1.137382	-0.874414
1	0	0.528914	1.137382	0.874414
6	0	-1.455368	1.234687	0.000000
1	0	-1.989385	0.863676	0.880373
1	0	-1.989385	0.863676	-0.880373
1	0	-1.536040	2.325907	0.000000

Compound **11**: $CH_3(CH_2)_3C^-H_2$
Symmetry C_s
energy E = -197.1707841 a.u.
Standard orientation

6	0	2.632325	0.653726	0.000000
1	0	2.726921	1.264881	0.904306
1	0	2.726921	1.264881	-0.904306
6	0	1.440253	-0.258483	0.000000
1	0	1.478752	-0.925982	-0.876478
1	0	1.478752	-0.925982	0.876478
6	0	0.000000	0.357618	0.000000
1	0	-0.093093	1.009067	-0.875585
1	0	-0.093093	1.009067	0.875585
6	0	-1.120783	-0.683156	0.000000
1	0	-1.003232	-1.334714	0.873656
1	0	-1.003232	-1.334714	-0.873656
6	0	-2.536313	-0.101305	0.000000
1	0	-2.704396	0.524893	-0.879251
1	0	-2.704396	0.524893	0.879251
1	0	-3.302793	-0.886687	0.000000

Compound **12**: CH_3CH_3
Symmetry D_{3d}
energy E = -79.8627762 a.u.
Standard orientation

6	0	0.000000	0.000000	0.763656
1	0	0.000000	1.016030	1.160566
1	0	0.879908	-0.508015	1.160566
1	0	-0.879908	-0.508015	1.160566
6	0	0.000000	0.000000	-0.763656
1	0	0.879908	0.508015	-1.160566
1	0	0.000000	-1.016030	-1.160566
1	0	-0.879908	0.508015	-1.160566

Compound **13**: $CH_3CH_2CH_3$
Symmetry C_{2v}
energy E = -119.1901946 a.u.
Standard orientation

6	0	0.000000	0.000000	0.584828
1	0	-0.873548	0.000000	1.241908
1	0	0.873548	0.000000	1.241908
6	0	0.000000	1.273856	-0.259186
1	0	-0.880647	1.318111	-0.903259
1	0	0.880647	1.318111	-0.903259
1	0	0.000000	2.168223	0.365244
6	0	0.000000	-1.273856	-0.259186
1	0	-0.880647	-1.318111	-0.903259
1	0	0.880647	-1.318111	-0.903259
1	0	0.000000	-2.168223	0.365244

Compound **14**: $(CH_3)_3CH$
Symmetry C_{3v}
energy E = -158.5183940 a.u.
Standard orientation

6	0	0.000000	0.000000	0.371430
1	0	0.000000	0.000000	1.466621
6	0	0.000000	1.458049	-0.095548
1	0	0.000000	1.515410	-1.186954
1	0	-0.882013	1.990442	0.264256
1	0	0.882013	1.990442	0.264256
6	0	-1.262708	-0.729025	-0.095548
1	0	-1.312384	-0.757705	-1.186954
1	0	-2.164780	-0.231375	0.264256
1	0	-1.282767	-1.759067	0.264256
6	0	1.262708	-0.729025	-0.095548
1	0	1.282767	-1.759067	0.264256
1	0	2.164780	-0.231375	0.264256
1	0	1.312384	-0.757705	-1.186954

Compound **15**: $(CH_3)_4C$
Symmetry T_d
energy E = -197.8461248 a.u.
Standard orientation

6	0	0.000000	0.000000	0.000000
6	0	0.886869	0.886869	0.886869
1	0	0.282226	1.529632	1.529632
1	0	1.529632	1.529632	0.282226
1	0	1.529632	0.282226	1.529632
6	0	-0.886869	-0.886869	0.886869
1	0	-0.282226	-1.529632	1.529632
1	0	-1.529632	-1.529632	0.282226
1	0	-1.529632	-0.282226	1.529632
6	0	-0.886869	0.886869	-0.886869
1	0	-0.282226	1.529632	-1.529632
1	0	-1.529632	1.529632	-0.282226
1	0	-1.529632	0.282226	-1.529632
6	0	0.886869	-0.886869	-0.886869
1	0	0.282226	-1.529632	-1.529632
1	0	1.529632	-1.529632	-0.282226
1	0	1.529632	-0.282226	-1.529632

Compound **16**: $CH_3CH_2CH_2CH_3$
Symmetry C_{2h}
energy E = -158.5174535 a.u.
Standard orientation

6	0	-0.420075	0.639038	0.000000
1	0	-1.078107	0.634985	0.874164
1	0	-1.078107	0.634985	-0.874164
6	0	0.420075	1.915190	0.000000
1	0	1.063658	1.962778	0.880689
1	0	1.063658	1.962778	-0.880689
1	0	-0.207795	2.807054	0.000000
6	0	0.420075	-0.639038	0.000000
1	0	1.078107	-0.634985	0.874164
1	0	1.078107	-0.634985	-0.874164
6	0	-0.420075	-1.915190	0.000000
1	0	-1.063658	-1.962778	0.880689
1	0	-1.063658	-1.962778	-0.880689
1	0	0.207795	-2.807054	0.000000

Compound **17**: $CH_3(CH_2)_3CH_3$
Symmetry C_{2v}
energy E = -197.8446211 a.u.
Standard orientation

6	0	0.000000	0.000000	0.314051
1	0	0.874767	0.000000	0.973066
1	0	-0.874767	0.000000	0.973066
6	0	0.000000	1.280664	-0.521747
1	0	0.874141	1.280205	-1.179593
1	0	-0.874141	1.280205	-1.179593
6	0	0.000000	2.553732	0.323488
1	0	0.880636	2.598890	0.967283
1	0	-0.880636	2.598890	0.967283
1	0	0.000000	3.447961	-0.301044
6	0	0.000000	-1.280664	-0.521747
1	0	0.874141	-1.280205	-1.179593
1	0	-0.874141	-1.280205	-1.179593
6	0	0.000000	-2.553732	0.323488
1	0	0.880636	-2.598890	0.967283
1	0	-0.880636	-2.598890	0.967283
1	0	0.000000	-3.447961	-0.301044

Compound **18**: $(CH_3)_2CHCH_2CH_3$
Symmetry C_1
energy E = -197.8440349 a.u.
Standard orientation

6	0	0.480203	-0.002963	-0.327738
6	0	0.664189	1.450098	0.121208
1	0	1.555482	1.887583	-0.331413
1	0	-0.184071	2.076500	-0.154180
1	0	0.782805	1.506691	1.206422
6	0	1.734302	-0.823998	-0.013200
1	0	1.915030	-0.859177	1.064125
1	0	1.636356	-1.851736	-0.366771
1	0	2.619518	-0.391558	-0.482369
1	0	0.343244	-0.004042	-1.415429
6	0	-0.763812	-0.657067	0.294454
1	0	-0.667202	-0.630343	1.385068
1	0	-0.771412	-1.715134	0.017916
6	0	-2.097067	-0.031970	-0.116498
1	0	-2.186523	1.001019	0.220300
1	0	-2.215593	-0.038161	-1.202172
1	0	-2.934516	-0.586236	0.309143

Compound **19**: $(CH_3)_3CCH_2CH_3$
Symmetry C_s
energy E = -237.1699657 a.u.
Standard orientation

6	0	1.169577	0.270459	0.000000
1	0	1.487243	0.847637	0.873662
1	0	1.487243	0.847637	-0.873662
6	0	1.908541	-1.068650	0.000000
1	0	1.672908	-1.666295	-0.880970
1	0	1.672908	-1.666295	0.880970
1	0	2.986876	-0.904205	0.000000
6	0	-0.377216	0.217889	0.000000
6	0	-0.899202	-0.498742	-1.255581
1	0	-0.597420	-1.546139	-1.280662
1	0	-1.989991	-0.471618	-1.288530
1	0	-0.527260	-0.020297	-2.163996
6	0	-0.899202	-0.498742	1.255581
1	0	-1.989991	-0.471618	1.288530
1	0	-0.597420	-1.546139	1.280662
1	0	-0.527260	-0.020297	2.163996
6	0	-0.899202	1.663902	0.000000
1	0	-0.553525	2.206864	0.881942
1	0	-0.553525	2.206864	-0.881942
1	0	-1.990568	1.687195	0.000000

Compound **20**: $CH_3(CH_2)_4CH_3$
Symmetry C_{2h}
energy E = -237.1717998 a.u.
Standard orientation

6	0	0.005749	0.764488	0.000000
1	0	-0.542528	1.129769	0.874767
1	0	-0.542528	1.129769	-0.874767
6	0	1.410752	1.368804	0.000000
1	0	1.958605	1.004624	0.874085
1	0	1.958605	1.004624	-0.874085
6	0	1.410752	2.896907	0.000000
1	0	0.899126	3.290481	0.880585
1	0	0.899126	3.290481	-0.880585
1	0	2.425514	3.296781	0.000000
6	0	-0.005749	-0.764488	0.000000
1	0	0.542528	-1.129769	0.874767
1	0	0.542528	-1.129769	-0.874767
6	0	-1.410752	-1.368804	0.000000
1	0	-1.958605	-1.004624	0.874085
1	0	-1.958605	-1.004624	-0.874085
6	0	-1.410752	-2.896907	0.000000
1	0	-0.899126	-3.290481	0.880585
1	0	-0.899126	-3.290481	-0.880585
1	0	-2.425514	-3.296781	0.000000

Compound **21**: $(CH_3)_2CHCH(CH_3)_2$
Symmetry C_{2h}
energy E = -237.1687932 a.u.
Standard orientation

6	0	0.231406	0.739007	0.000000
1	0	1.328494	0.732030	0.000000

6	0	-0.231406	1.496844	1.250973
1	0	-1.321298	1.480548	1.334257
1	0	0.180049	1.078541	2.167942
1	0	0.077704	2.541917	1.201349
6	0	-0.231406	1.496844	-1.250973
1	0	0.077704	2.541917	-1.201349
1	0	0.180049	1.078541	-2.167942
1	0	-1.321298	1.480548	-1.334257
6	0	-0.231406	-0.739007	0.000000
1	0	-1.328494	-0.732030	0.000000
6	0	0.231406	-1.496844	-1.250973
1	0	1.321298	-1.480548	-1.334257
1	0	-0.180049	-1.078541	-2.167942
1	0	-0.077704	-2.541917	-1.201349
6	0	0.231406	-1.496844	1.250973
1	0	-0.077704	-2.541917	1.201349
1	0	-0.180049	-1.078541	2.167942
1	0	1.321298	-1.480548	1.334257

Compound **22**: $(CH_3)_3CCH(CH_3)_2$
Symmetry C_s
energy E = -276.4927327 a.u.
Standard orientation

6	0	0.594102	0.761242	0.000000
1	0	1.667444	0.538519	0.000000
6	0	0.312734	1.606711	1.250275
1	0	-0.739922	1.886456	1.318385
1	0	0.584575	1.094524	2.171695
1	0	0.889440	2.532104	1.211275
6	0	0.312734	1.606711	-1.250275
1	0	0.889440	2.532104	-1.211275
1	0	0.584575	1.094524	-2.171695
1	0	-0.739922	1.886456	-1.318385
6	0	-0.117075	-0.634080	0.000000
6	0	0.312734	-1.435826	-1.242271
1	0	1.400475	-1.510201	-1.306258
1	0	-0.048594	-0.987031	-2.166715
1	0	-0.086337	-2.450492	-1.195233
6	0	0.312734	-1.435826	1.242271
1	0	-0.086337	-2.450492	1.195233
1	0	-0.048594	-0.987031	2.166715
1	0	1.400475	-1.510201	1.306258
6	0	-1.649604	-0.505311	0.000000
1	0	-2.013421	0.022046	-0.882169
1	0	-2.110042	-1.495062	0.000000
1	0	-2.013421	0.022046	0.882169

Compound **23**: $(CH_3)_2CHCH_2CH_2CH_3$
Symmetry C_1
energy E = -237.1687932 a.u.
Standard orientation

6	0	1.071996	-0.012812	-0.332282
1	0	1.023359	0.045039	-1.425819
6	0	2.151316	-1.036715	0.032678
1	0	1.916952	-2.022764	-0.371833
1	0	2.241858	-1.135939	1.117216
1	0	3.127305	-0.739243	-0.354260
6	0	1.450613	1.375198	0.195296

1	0	0.741430	2.141584	-0.116614
1	0	2.436020	1.673667	-0.166125
1	0	1.485015	1.376656	1.287887
6	0	-0.304462	-0.478471	0.168271
1	0	-0.457042	-1.513826	-0.153000
1	0	-0.293506	-0.501268	1.264165
6	0	-1.495295	0.356029	-0.307823
1	0	-1.399469	1.383061	0.051014
1	0	-1.479952	0.411427	-1.400626
6	0	-2.838553	-0.210332	0.152209
1	0	-2.989039	-1.224207	-0.224005
1	0	-2.895944	-0.252293	1.241708
1	0	-3.670670	0.400720	-0.199796

Compound **24**: $(CH_3)_2CH(CH_2)_3CH_3$
Symmetry C_1
energy E = -276.4927327 a.u.
Standard orientation

6	0	-1.641597	0.030984	-0.342312
1	0	-1.545445	0.112775	-1.431169
6	0	-2.816460	-0.906571	-0.047225
1	0	-3.749044	-0.514340	-0.456163
1	0	-2.652738	-1.896605	-0.475998
1	0	-2.953762	-1.030073	1.029942
6	0	-1.922364	1.432157	0.210570
1	0	-2.860372	1.826165	-0.184061
1	0	-1.135036	2.140140	-0.046824
1	0	-2.006679	1.407685	1.300192
6	0	-0.329577	-0.562475	0.195347
1	0	-0.388847	-0.616496	1.288500
1	0	-0.249761	-1.596927	-0.153807
6	0	0.943737	0.184851	-0.206394
1	0	0.974847	0.284056	-1.296808
1	0	0.923692	1.202771	0.191547
6	0	2.223983	-0.504688	0.269671
1	0	2.256815	-1.520758	-0.134356
1	0	2.190608	-0.612612	1.357838
6	0	3.496105	0.242554	-0.128244
1	0	3.509267	1.249967	0.292428
1	0	3.573815	0.338122	-1.213127
1	0	4.389674	-0.274748	0.223384

Compound **25**: H_3C^+
Symmetry C_{3v}
energy E = -39.4942274 a.u.
Standard orientation

6	0	0.000000	0.000000	0.000002
1	0	0.000000	1.090611	-0.000004
1	0	0.944497	-0.545306	-0.000004
1	0	-0.944497	-0.545306	-0.000004

Compound **26**: $CH_3C^+H_2$
Symmetry C_s
energy E = -78.8905678 a.u.
Standard orientation

6	0	-0.064110	0.688210	0.000000
1	0	-0.072782	1.243215	0.932457

1	0	-0.072782	1.243215	-0.932457
6	0	-0.064110	-0.688210	0.000000
1	0	-0.072783	-1.243214	0.932457
1	0	1.060452	-0.000001	0.000000
1	0	-0.072783	-1.243214	-0.932457

Compound **27**: $CH_3CH_2C^+H_2$
Symmetry C_s
energy E = -118.2376403 a.u.
Standard orientation

6	0	0.000000	0.897191	0.000000
1	0	0.249432	1.406255	0.919802
1	0	0.249432	1.406255	-0.919802
6	0	0.811234	-0.628973	0.000000
1	0	1.375984	-0.577683	0.922625
1	0	1.375984	-0.577683	-0.922625
1	0	0.305039	-1.605513	0.000000
6	0	-0.944838	-0.117440	0.000000
1	0	-1.377123	-0.478150	0.924466
1	0	-1.377123	-0.478150	-0.924466

Compound **28**: $(CH_3)_2CHC^+H_2$
Symmetry C_1
energy E = -157.5874653 a.u.
Standard orientation

6	0	-0.645654	0.747959	-0.239830
1	0	-0.543113	0.882597	-1.312328
1	0	-1.172969	1.563073	0.248472
6	0	0.529049	0.318316	0.433129
1	0	0.545859	0.424163	1.516965
6	0	-1.512463	-0.595847	0.027373
1	0	-1.086021	-1.455442	-0.479282
1	0	-1.650074	-0.797593	1.085885
1	0	-2.475959	-0.347752	-0.416030
6	0	1.677203	-0.308679	-0.179158
1	0	2.478375	0.448376	-0.054683
1	0	1.569485	-0.527819	-1.237330
1	0	2.045611	-1.160098	0.399250

Compound **29**: $(CH_3)_3CC^+H_2$
Symmetry C_1
energy E = -196.9399794 a.u.
Standard orientation

6	0	-0.852911	-0.111921	0.732602
1	0	-1.064772	0.713692	1.411046
1	0	-1.011118	-1.071652	1.220104
6	0	0.473257	0.000616	0.149778
6	0	-1.855058	0.001601	-0.485944
1	0	-1.763419	0.959101	-0.991756
1	0	-2.853054	-0.079492	-0.061180
1	0	-1.708433	-0.806016	-1.198506
6	0	1.060857	1.314857	-0.102031
1	0	1.915970	1.401209	0.588948
1	0	1.511995	1.369067	-1.095735
1	0	0.386106	2.145125	0.081484
6	0	1.224772	-1.207742	-0.185782
1	0	1.683855	-1.527043	0.766457

1	0	2.025053	-1.053805	-0.904031
1	0	0.572319	-2.034653	-0.468575

Compound **30**: $(CH_3)_2C^+H$
Symmetry C_2
energy E = -118.2539123 a.u.
Standard orientation

6	0	0.000000	0.000000	0.451823
1	0	0.000000	0.000000	1.541900
6	0	0.000000	1.277873	-0.197414
1	0	-1.035947	1.642690	-0.003286
1	0	0.162796	1.257899	-1.270705
1	0	0.608421	2.017445	0.332058
6	0	0.000000	-1.277873	-0.197414
1	0	1.035947	-1.642690	-0.003286
1	0	-0.162796	-1.257899	-1.270705
1	0	-0.608421	-2.017445	0.332058

Compound **31**: $CH_3CH_2C^+HCH_3$
Symmetry C_1
energy E = -157.5867293 a.u.
Standard orientation

6	0	-0.597922	-0.372526	-0.133580
1	0	-0.452372	-1.423226	-0.387732
6	0	-1.951305	0.059178	0.112242
1	0	-2.195921	-0.419541	1.084209
1	0	-2.081169	1.132649	0.213873
1	0	-2.665675	-0.399848	-0.576627
6	0	0.562372	0.457246	-0.128531
1	0	0.390846	1.439521	0.313252
1	0	0.474887	0.645017	-1.245309
6	0	1.935740	-0.156335	0.141574
1	0	2.060946	-0.309202	1.212375
1	0	2.060124	-1.111267	-0.366544
1	0	2.715027	0.520514	-0.197729

Compound **32**: $(CH_3)_2CHC^+HCH_3$
Symmetry C_1
energy E = -196.9216377 a.u.
Standard orientation

6	0	0.608998	-0.367371	0.379704
1	0	0.451038	-0.550398	1.439334
6	0	1.996597	-0.421462	-0.109030
1	0	2.102442	-0.123105	-1.148987
1	0	2.683789	0.130694	0.531605
1	0	2.289851	-1.477102	-0.023469
6	0	-0.534708	-0.173260	-0.406213
1	0	-0.379205	-0.192354	-1.480168
6	0	-1.901239	-0.613488	0.058084
1	0	-2.039252	-1.664135	-0.197920
1	0	-2.021367	-0.505174	1.135500
1	0	-2.681459	-0.044874	-0.444019
6	0	-0.161927	1.428089	0.044879
1	0	0.404463	1.880312	-0.757887
1	0	-1.176980	1.806167	0.136388
1	0	0.320358	1.624923	1.005078

Compound **33**: $(CH_3)_3CC^+HCH_3$
Symmetry C_1
energy E = -236.2700082 a.u.
Standard orientation

6	0	-0.669180	-0.282559	-0.417256
1	0	-0.654808	-0.907723	-1.312420
6	0	-1.720797	0.818813	-0.526293
1	0	-1.863293	1.353468	0.411568
1	0	-1.461425	1.538852	-1.301684
1	0	-2.675261	0.370507	-0.795032
6	0	0.694916	0.107610	-0.089571
6	0	1.815543	-0.739763	-0.502786
1	0	1.517705	-1.680433	-0.955571
1	0	2.373320	-0.155207	-1.252537
1	0	2.528582	-0.889556	0.311064
6	0	0.975540	1.338336	0.651094
1	0	0.207436	1.559180	1.392784
1	0	1.971515	1.374756	1.081798
1	0	0.887427	2.154459	-0.084993
6	0	-1.008213	-1.275640	0.780368
1	0	-0.319201	-2.113778	0.841714
1	0	-1.035362	-0.748562	1.731091
1	0	-2.003492	-1.656742	0.558882

Compound **34**: $(CH_3)_3C^+$
Symmetry C_1
energy E = -157.6094446 a.u.
Standard orientation

6	0	-0.002204	-0.000237	-0.005383
6	0	0.992254	-1.067584	-0.008699
1	0	1.492337	-1.033415	0.972915
1	0	1.797888	-0.836142	-0.713801
1	0	0.588860	-2.060822	-0.176052
6	0	0.428343	1.391674	0.014457
1	0	1.478616	1.535523	0.250514
1	0	-0.226685	2.011692	0.630529
1	0	0.253662	1.754471	-1.015183
6	0	-1.423586	-0.323618	-0.010236
1	0	-2.079107	0.532168	-0.138408
1	0	-1.644037	-1.122184	-0.723855
1	0	-1.630374	-0.782701	0.972511

Compound **35**: $CH_3CH_2C^+(CH_3)_2$
Symmetry C_1
energy E = -196.9401512 a.u.
Standard orientation

6	0	0.530990	-0.000863	-0.007060
6	0	1.808717	-0.710332	0.015809
1	0	2.330957	-0.424498	0.940742
1	0	1.724160	-1.791030	-0.041290
1	0	2.457485	-0.323039	-0.778495
6	0	0.519631	1.456411	-0.008121
1	0	1.503569	1.912840	0.008895
1	0	-0.049990	1.800969	-0.882240
1	0	-0.088232	1.806600	0.836638
6	0	-0.713103	-0.766702	-0.030859
1	0	-0.612422	-1.535055	0.752639

1	0	-0.621214	-1.392266	-0.938511
6	0	-2.052055	-0.048764	0.026399
1	0	-2.166012	0.518022	0.949987
1	0	-2.187851	0.629535	-0.815058
1	0	-2.855532	-0.780580	-0.010320

Compound **36**: $(CH_3)_2CHC^+(CH_3)_2$
Symmetry C_1
energy E = -236.2700082 a.u.
Standard orientation

6	0	0.694917	0.107613	-0.089571
6	0	0.975533	1.338335	0.651096
1	0	1.971509	1.374768	1.081797
1	0	0.887407	2.154458	-0.084991
1	0	0.207426	1.559177	1.392784
6	0	1.815548	-0.739758	-0.502785
1	0	2.528580	-0.889555	0.311068
1	0	1.517710	-1.680426	-0.955574
1	0	2.373326	-0.155203	-1.252536
6	0	-0.669179	-0.282561	-0.417257
1	0	-0.654805	-0.907727	-1.312420
6	0	-1.008210	-1.275641	0.780368
1	0	-2.003487	-1.656750	0.558882
1	0	-0.319191	-2.113774	0.841716
1	0	-1.035364	-0.748562	1.731091
6	0	-1.720796	0.818809	-0.526295
1	0	-1.863303	1.353457	0.411569
1	0	-1.461423	1.538855	-1.301680
1	0	-2.675257	0.370502	-0.795044

Compound **37**: $(CH_3)_3CC^+(CH_3)_2$
Symmetry C_1
energy E = -275.5958819 a.u.
Standard orientation

6	0	-0.848508	0.005958	-0.078007
6	0	-1.628735	-1.235100	-0.090714
1	0	-2.522622	-1.155552	0.528276
1	0	-2.005353	-1.322132	-1.124446
1	0	-1.066961	-2.135086	0.126537
6	0	-1.600460	1.267669	-0.095511
1	0	-2.659976	1.144757	0.104150
1	0	-1.163674	2.014393	0.568283
1	0	-1.473802	1.693601	-1.102254
6	0	0.616272	0.000998	-0.047509
6	0	0.812336	-0.152774	1.534165
1	0	1.893488	-0.147132	1.669257
1	0	0.388985	0.681017	2.088897
1	0	0.416932	-1.091318	1.913253
6	0	1.272617	-1.207738	-0.742641
1	0	0.944664	-2.165598	-0.347723
1	0	1.080732	-1.188330	-1.815002
1	0	2.348991	-1.147330	-0.595813
6	0	1.279745	1.308461	-0.503651
1	0	1.087290	1.495972	-1.560189
1	0	0.955126	2.176306	0.066134
1	0	2.356574	1.221587	-0.376153

Compound **38**: CH_3OH
Symmetry C_s
energy E = -115.7743176 a.u.
Standard orientation

6	0	-0.046432	0.664807	0.000000
1	0	0.438471	1.075495	0.890506
1	0	0.438471	1.075495	-0.890506
1	0	-1.087885	0.979086	0.000000
8	0	-0.046432	-0.756172	0.000000
1	0	0.860988	-1.069539	0.000000

Compound **39**: CH_3SH
Symmetry C_s
energy E = -438.7536229 a.u.
Standard orientation

6	0	0.047843	1.157308	0.000000
1	0	1.092597	1.459044	0.000000
1	0	-0.430770	1.551802	0.892164
1	0	-0.430770	1.551802	-0.892164
16	0	0.047843	-0.666819	0.000000
1	0	-1.283610	-0.837392	0.000000

Compound **40**: CH_3SeH
Symmetry C_s
energy E = -2442.0836083 a.u.
Standard orientation

6	0	0.031553	1.546876	0.000000
34	0	0.031553	-0.423773	0.000000
1	0	-1.432546	-0.563131	0.000000
1	0	-0.453229	1.923810	0.894191
1	0	-0.453229	1.923810	-0.894191
1	0	1.076890	1.842548	0.000000

Compound **41**: CH_3SSCH_3
Symmetry C_2
energy E = -876.3114452 a.u.
Standard orientation

6	0	0.966120	1.648448	0.788556
1	0	0.782868	1.232418	1.775956
1	0	0.228330	2.411204	0.554989
1	0	1.963302	2.088181	0.765415
16	0	0.966120	0.347540	-0.489231
16	0	-0.966120	-0.347540	-0.489231
6	0	-0.966120	-1.648448	0.788556
1	0	-0.782868	-1.232418	1.775956
1	0	-0.228330	-2.411204	0.554989
1	0	-1.963302	-2.088181	0.765415

Compound **42**: CH_3F
Symmetry C_{3v}
energy E = -139.8002847 a.u.
Standard orientation

6	0	0.000000	0.000000	-0.636070
9	0	0.000000	0.000000	0.752737
1	0	1.031653	0.000000	-0.986072
1	0	-0.515827	0.893438	-0.986072

1	0	-0.515827	-0.893438	-0.986072

Compound **43**: CH_3Cl
Symmetry C_{3v}
energy E = -500.1598382 a.u.
Standard orientation

6	0	0.000000	0.000000	-1.133585
17	0	0.000000	0.000000	0.660275
1	0	-1.029529	0.000000	-1.474386
1	0	0.514764	0.891598	-1.474386
1	0	0.514764	-0.891598	-1.474386

Compound **44**: CH_3Br
Symmetry C_{3v}
energy E = -2614.0807337 a.u.
Standard orientation

6	0	0.000000	0.000000	-1.535565
35	0	0.000000	0.000000	0.422953
1	0	0.000000	1.032294	-1.863318
1	0	-0.893993	-0.516147	-1.863318
1	0	0.893993	-0.516147	-1.863318

Compound **45**: CH_3I
Symmetry C_{3v}
energy E = -6960.4728009 a.u.
Standard orientation

6	0	0.000000	0.000000	-1.831482
53	0	0.000000	0.000000	0.329498
1	0	0.000000	1.032342	-2.158165
1	0	-0.894034	-0.516171	-2.158165
1	0	0.894034	-0.516171	-2.158165

Cf: The basis set of the Sapporo-TZP with diffuse functions of the 1s1p type (Sapporo-TZP + 1s1p) was employed for Iodine atom, implemented from Sapporo Basis Set Factory.[*Ref*]
[*Ref*]T. Noro, M. Sekiya and T. Koga, *Theor. Chem. Acc.*, 2012, **131**, 1124.

Compound **46**: $CH_3C(=O)OCH_3$
Symmetry C_s
energy E = -268.4952145 a.u.
Standard orientation

6	0	1.126869	1.492588	0.000000
1	0	1.754996	1.344233	0.877931
1	0	1.754996	1.344233	-0.877931
1	0	0.720578	2.498624	0.000000
6	0	0.000000	0.495099	0.000000
8	0	-1.173541	0.763356	0.000000
8	0	0.470706	-0.768723	0.000000
6	0	-0.518727	-1.808865	0.000000
1	0	-1.146688	-1.737895	-0.885991
1	0	-1.146688	-1.737895	0.885991
1	0	0.036636	-2.741299	0.000000

Compound **47**: CH_3CN
Symmetry C_{3v}
energy E = -132.8056202 a.u.

Standard orientation

6	0	0.000000	0.000000	-1.174036
1	0	0.000000	1.022326	-1.549601
1	0	-0.885360	-0.511163	-1.549601
1	0	0.885360	-0.511163	-1.549601
6	0	0.000000	0.000000	0.280619
7	0	0.000000	0.000000	1.429901

Compound **48**: CH_3NH_2
Symmetry C_s
energy E = -95.9014753 a.u.
Standard orientation

6	0	-0.049039	0.706320	0.000000
1	0	-0.587090	1.065154	0.877309
1	0	-0.587090	1.065154	-0.877309
1	0	0.944853	1.170640	0.000000
7	0	-0.049039	-0.757196	0.000000
1	0	0.433415	-1.119248	0.812978
1	0	0.433415	-1.119248	-0.812978

Compound **49**: CH_3NO_2
Symmetry C_s
energy E = -245.1096821 a.u.
Standard orientation

6	0	0.000236	-1.323947	0.000000
1	0	-0.491705	-1.663804	0.903474
1	0	1.044526	-1.626712	0.000000
1	0	-0.491705	-1.663804	-0.903474
7	0	-0.009474	0.174306	0.000000
8	0	0.000236	0.729866	1.083481
8	0	0.000236	0.729866	-1.083481

Compound **50**: CH_3CH_2OH
Symmetry C_s
energy E = -155.106985 a.u.
Standard orientation

6	0	-1.176718	-0.399986	0.000000
1	0	-1.152216	-1.037957	0.883327
1	0	-1.152216	-1.037957	-0.883327
1	0	-2.115220	0.155476	0.000000
6	0	0.000000	0.553216	0.000000
8	0	1.199561	-0.220669	0.000000
1	0	1.956530	0.370327	0.000000
1	0	-0.036528	1.198039	0.885102
1	0	-0.036528	1.198039	-0.885102

Compound **51**: $H_2C{=}CH_2$
Symmetry D_{2h}
energy E = -78.6220932 a.u.
Standard orientation

6	0	0.000000	0.000000	0.662352
6	0	0.000000	0.000000	-0.662352
1	0	0.000000	0.920632	1.231614
1	0	0.000000	-0.920632	1.231614
1	0	0.000000	0.920632	-1.231614
1	0	0.000000	-0.920632	-1.231614

Compound **52**: HC≡CH
Symmetry $D_{\infty h}$
energy E = -77.3623376 a.u.
Standard orientation

6	0	0.000000	0.000000	0.598143
6	0	0.000000	0.000000	-0.598143
1	0	0.000000	0.000000	1.659887
1	0	0.000000	0.000000	-1.659887

Compound **53**: C_6H_6
Symmetry D_{6h}
energy E = -232.3293476 a.u.
Standard orientation

6	0	0.000000	1.390962	0.000000
6	0	1.204608	0.695481	0.000000
6	0	1.204608	-0.695481	0.000000
6	0	0.000000	-1.390962	0.000000
6	0	-1.204608	-0.695481	0.000000
6	0	-1.204608	0.695481	0.000000
1	0	0.000000	2.472877	0.000000
1	0	2.141574	1.236438	0.000000
1	0	2.141574	-1.236438	0.000000
1	0	0.000000	-2.472877	0.000000
1	0	-2.141574	-1.236438	0.000000
1	0	-2.141574	1.236438	0.000000

Compound **54**: C_6H_5OH
Symmetry C_s
energy E = -307.5829283 a.u.
Standard orientation

6	0	1.215737	-1.135690	0.000000
6	0	1.212675	0.251937	0.000000
6	0	0.000000	0.936403	0.000000
6	0	-1.200396	0.230572	0.000000
6	0	-1.183473	-1.159574	0.000000
6	0	0.021631	-1.851025	0.000000
1	0	2.160836	-1.662262	0.000000
1	0	2.134207	0.816856	0.000000
1	0	-2.142818	0.765700	0.000000
1	0	-2.120198	-1.700802	0.000000
1	0	0.031424	-2.931808	0.000000
8	0	0.047984	2.302030	0.000000
1	0	-0.844358	2.660331	0.000000

Compound **55**: HC(=O)H
Symmetry C_{2v}
energy E = -114.5499452 a.u.
Standard orientation

6	0	0.000000	0.000000	-0.526024
8	0	0.000000	0.000000	0.672428
1	0	0.000000	0.938212	-1.111639
1	0	0.000000	-0.938212	-1.111639

Compound **56**: HC(=O)OH

Symmetry C_s
energy E = -189.8416527 a.u.
Standard orientation

6	0	0.000000	0.420408	0.000000
8	0	1.157012	0.116930	0.000000
1	0	-0.382893	1.447570	0.000000
8	0	-1.026765	-0.445362	0.000000
1	0	-0.659085	-1.342561	0.000000

Appendix

Procedure to draw the selected contributions from each ψ_i to σ^d and σ^p and each $\psi_i \rightarrow \psi_a$ transition, using molecular orbitals

(The procedure, analyzing the output of Gaussian program, with the utility program, is explained, exemplified by CH_4: The output format below is the same as that from the program.)

Output

SP: B3LYP/6-311++G(3df,3pd)

Number of Basis Functions	=	121
Number of Orbitals	=	121
Number of Atoms	=	5
Multiplicity	=	1
Number of Electrons	=	10

Diamagnetic MO contribution

1	200.27845	200.27845	200.27845
2	26.97198	26.97198	26.97198
3	0.81211	0.81211	10.10126
4	0.81211	10.10126	0.81211
5	10.10126	0.81211	0.81211
SUM	238.97591	238.97591	238.97591

Paramagnetic MO contribution

OCC x OCC	125.55119	125.55119	125.55119
1	0.00002	0.00002	0.00002
2	0.33164	0.33164	0.33164
3	-87.47495	-87.47495	-0.59302
4	-87.47495	-0.59302	-87.47495
5	-0.59302	-87.47495	-87.47495
SUM	-49.66007	-49.66007	-49.66007

Contributions from each $\psi_i \rightarrow \psi_a$ transition to σ_i^p

Output

SP: B3LYP/6-311++G(3df,3pd)

Number of Basis Functions	=	121
Number of Orbitals	=	121
Number of Atoms	=	5
Multiplicity	=	1
Number of Electrons	=	10

Diamagnetic MO contribution

1	200.27845	200.27845	200.27845
2	26.97198	26.97198	26.97198
3	0.81211	0.81211	10.10126
4	0.81211	10.10126	0.81211
5	10.10126	0.81211	0.81211
SUM	238.97591	238.97591	238.97591

Paramagnetic MO contribution

OCC-->OCC	125.55119	125.55119	125.55119
--			
1--> 6	0.00000	0.00000	0.00000
1--> 7	0.00000	0.00000	0.00000
1--> 8	0.00000	0.00000	0.00000
1--> 9	0.00000	0.00000	0.00000
1--> 10	0.00000	0.00000	0.00000
---		-- omitted --	---
1-->121	0.00000	0.00000	0.00000
--			
2--> 6	0.00000	0.00000	0.00000
2--> 7	0.00000	0.00000	0.00000
2--> 8	0.00000	0.00000	0.00000
2--> 9	0.00000	0.00000	0.00000
2--> 10	0.00000	0.00000	0.00000
2--> 11	0.00000	0.00000	0.00000
2--> 12	0.00000	0.00000	0.00000
2--> 13	0.00000	0.00000	0.00000
2--> 14	0.00000	0.00000	0.00000
2--> 15	0.00000	0.00000	0.00000
2--> 16	0.00000	0.00000	0.00000
2--> 17	0.00000	0.00000	0.00000
2--> 18	0.00000	0.00000	0.00000
2--> 19	0.00000	0.00000	0.00000
2--> 20	0.00000	0.00000	0.00000
2--> 21	0.00000	0.00000	0.00000
2--> 22	0.00000	0.00000	0.00000
2--> 23	0.00000	0.00000	0.00000
2--> 24	0.08601	0.00000	0.00000
2--> 25	0.00000	0.08601	0.00000
2--> 26	0.00000	0.00000	0.08601
---		-- omitted --	---
2-->121	0.00000	0.00000	0.00000
--			
3--> 6	0.00000	0.00000	0.00000
3--> 7	-10.57648	0.00000	0.00000

3--> 8	0.00000	0.00000	0.00000
3--> 9	0.00000	-10.57648	0.00000
3--> 10	-0.81361	0.00000	0.00000
3--> 11	0.00000	0.00000	0.00000
3--> 12	0.00000	-0.81361	0.00000
---		-- omitted --	---
3-->121	0.00000	0.00000	0.00000
--			
4--> 6	0.00000	0.00000	0.00000
4--> 7	0.00000	0.00000	0.00000
4--> 8	-10.57648	0.00000	0.00000
4--> 9	0.00000	0.00000	-10.57648
4--> 10	0.00000	0.00000	0.00000
4--> 11	-0.81361	0.00000	0.00000
4--> 12	0.00000	0.00000	-0.81361
4--> 13	0.00000	0.00000	0.00000
4--> 14	-33.27102	0.00000	0.00000
4--> 15	0.00000	0.00000	0.00000
4--> 16	0.00000	0.00000	-33.27102
4--> 17	0.00000	0.00000	0.00000
---		-- omitted --	---
4-->121	0.00000	0.00000	0.00000
--			
5--> 6	0.00000	0.00000	0.00000
5--> 7	0.00000	0.00000	-10.57648
5--> 8	0.00000	-10.57648	0.00000
5--> 9	0.00000	0.00000	0.00000
5--> 10	0.00000	0.00000	-0.81361
5--> 11	0.00000	-0.81361	0.00000
5--> 12	0.00000	0.00000	0.00000
5--> 13	0.00000	0.00000	0.00000
5--> 14	0.00000	-33.27102	0.00000
5--> 15	0.00000	0.00000	-33.27102
5--> 16	0.00000	0.00000	0.00000
---		-- omitted --	---
5-->119	0.00000	-0.67620	0.00000
5-->120	0.00000	0.00000	0.00000
5-->121	0.00000	0.00000	0.00000
SUM	-49.66007	-49.66007	-49.66007

Drawing steps:

1. Selecting transitions in the above output terms, of which contributions are larger than a certain value.
2. Drawing the molecular orbitals in the selected transitions using GaussView with an isovalue of 0.04 au.
3. Completing the transition maps of interest, using the molecular orbitals drawn above. (See Figs. 6–13 in the text.)

The input section of this utility program is as follows, although it is not shown in the Appendix:

Input
FChk file: CH4Td-B6G6NMR.FChk
CH4Td-B6G6NMR NMR B3LYP/6-311++G(3df,3pd) SCF=(Direct,Tight) IOp(10/21=11) IOp(10/33=1) IOp(10/75=1) 6D 10F FChk=All POP=Full GFInput