Electronic Supplementary Material (ESI) for RSC Advances.

In the abbreviation for the names of divalent species under study the number **1**, **2**, **3**, **4**, and **5** stand for carbenes, silylenes, germylenes, stannylenes, and plumbylenes respectively. The subscripts s, t, and X refer to singlet, triplet, and halogen atoms (X=F, Cl, Br, I).

Table 1 Calculated total bonding energies (E) and the ΔE_{st} for the two series of BHEs ($\mathbf{1}_{s\text{-}X}$ *vs.* $\mathbf{1}_{t\text{-}X}$, $\mathbf{2}_{s\text{-}X}$ *vs.* $\mathbf{2}_{t\text{-}X}$, $\mathbf{3}_{s\text{-}X}$ *vs.* $\mathbf{3}_{t\text{-}X}$, $\mathbf{4}_{s\text{-}X}$ *vs.* $\mathbf{4}_{t\text{-}X}$ and $\mathbf{5}_{s\text{-}X}$ *vs.* $\mathbf{5}_{t\text{-}X}$ with X =F, Cl, Br and I) at UB3LYP/TZ2P.

Compound (*Singlets*)	E (kcal/mol)	Compound (*Triplets*)	E (kcal/mol)	ΔE_{st}
$\mathbf{1}_{s\text{-}F}$	-1235.67	$\mathbf{1}_{t\text{-}F}$	-1235.16	0.51
$\mathbf{1}_{s\text{-}Cl}$	-1140.16	$\mathbf{1}_{t\text{-}Cl}$	-1135.87	4.29
$\mathbf{1}_{s\text{-}Br}$	-1108.12	$\mathbf{1}_{t\text{-}Br}$	-1103.27	4.85
$\mathbf{1}_{s\text{-}I}$	-1082.42	$\mathbf{1}_{t\text{-}I}$	-1076.84	5.58
$\mathbf{2}_{s\text{-}F}$	-1177.12	$\mathbf{2}_{t\text{-}F}$	-1154.34	22.78
$\mathbf{2}_{s\text{-}Cl}$	-1084.06	$\mathbf{2}_{t\text{-}Cl}$	-1056.88	27.18
$\mathbf{2}_{s\text{-}Br}$	-1052.31	$\mathbf{2}_{t\text{-}Br}$	-1024.51	27.80
$\mathbf{2}_{s\text{-}I}$	-1028.21	$\mathbf{2}_{t\text{-}I}$	-999.07	29.14
$\mathbf{3}_{s\text{-}F}$	-1164.15	$\mathbf{3}_{t\text{-}F}$	-1140.29	23.86
$\mathbf{3}_{s\text{-}Cl}$	-1070.56	$\mathbf{3}_{t\text{-}Cl}$	-1042.44	28.12
$\mathbf{3}_{s\text{-}Br}$	-1038.73	$\mathbf{3}_{t\text{-}Br}$	-1010.03	28.70
$\mathbf{3}_{s\text{-}I}$	-1014.81	$\mathbf{3}_{t\text{-}I}$	-984.75	30.06
$\mathbf{4}_{s\text{-}F}$	-1144.49	$\mathbf{4}_{t\text{-}F}$	-1122.5	21.99
$\mathbf{4}_{s\text{-}Cl}$	-1051.19	$\mathbf{4}_{t\text{-}Cl}$	-1024.4	26.79
$\mathbf{4}_{s\text{-}Br}$	-1019.57	$\mathbf{4}_{t\text{-}Br}$	-992.10	27.47
$\mathbf{4}_{s\text{-}I}$	-996.04	$\mathbf{4}_{t\text{-}I}$	-967.19	28.85
$\mathbf{5}_{s\text{-}F}$	-1169.09	$\mathbf{5}_{t\text{-}F}$	-1141.69	27.40
$\mathbf{5}_{s\text{-}Cl}$	-1075.24	$\mathbf{5}_{t\text{-}Cl}$	-1040.45	34.79
$\mathbf{5}_{s\text{-}Br}$	-1034.96	$\mathbf{5}_{t\text{-}Br}$	-1001.00	33.96
$\mathbf{5}_{s\text{-}I}$	-1018.44	$\mathbf{5}_{t\text{-}I}$	-978.46	39.98

Table 2 Calculated bonding energies (E) and the ΔE_{st} for the two series of BHEs ($\mathbf{1}_{s\text{-}X}$ *vs.* $\mathbf{1}_{t\text{-}X}$, $\mathbf{2}_{s\text{-}X}$ *vs.* $\mathbf{2}_{t\text{-}X}$, $\mathbf{3}_{s\text{-}X}$ *vs.* $\mathbf{3}_{t\text{-}X}$, $\mathbf{4}_{s\text{-}X}$ *vs.* $\mathbf{4}_{t\text{-}X}$ and $\mathbf{5}_{s\text{-}X}$ *vs.* $\mathbf{5}_{t\text{-}X}$ with X =F, Cl, Br and I) at MP2/6-311++g**.

Compound (*Singlets*)	E (hartree)	Compound (*Triplets*)	E (hartree)	ΔE_{st} (kcal/mol)
$\mathbf{1}_{s\text{-}F}$	-363.52	$\mathbf{1}_{t\text{-}F}$	-363.52	2.89
$\mathbf{1}_{s\text{-}Cl}$	-193.86	$\mathbf{1}_{t\text{-}Cl}$	-193.85	7.29
$\mathbf{1}_{s\text{-}Br}$	-190.28	$\mathbf{1}_{t\text{-}Br}$	-190.27	8.95
$\mathbf{1}_{s\text{-}I}$	-186.72	$\mathbf{1}_{t\text{-}I}$	-186.70	11.55
$\mathbf{2}_{s\text{-}F}$	-329.43	$\mathbf{2}_{t\text{-}F}$	-329.41	16.96
$\mathbf{2}_{s\text{-}Cl}$	-159.77	$\mathbf{2}_{t\text{-}Cl}$	-159.74	21.06
$\mathbf{2}_{s\text{-}Br}$	-156.20	$\mathbf{2}_{t\text{-}Br}$	-156.16	22.80
$\mathbf{2}_{s\text{-}I}$	-152.64	$\mathbf{2}_{t\text{-}I}$	-152.60	25.38
$\mathbf{3}_{s\text{-}F}$	-329.34	$\mathbf{3}_{t\text{-}F}$	-329.30	24.52
$\mathbf{3}_{s\text{-}Cl}$	-159.68	$\mathbf{3}_{t\text{-}Cl}$	-159.63	28.54
$\mathbf{3}_{s\text{-}Br}$	-156.11	$\mathbf{3}_{t\text{-}Br}$	-156.06	30.24
$\mathbf{3}_{s\text{-}I}$	-152.55	$\mathbf{3}_{t\text{-}I}$	-152.49	32.81
$\mathbf{4}_{s\text{-}F}$	-328.95	$\mathbf{4}_{t\text{-}F}$	-328.91	29.07
$\mathbf{4}_{s\text{-}Cl}$	-159.29	$\mathbf{4}_{t\text{-}Cl}$	-159.24	33.06
$\mathbf{4}_{s\text{-}Br}$	-155.72	$\mathbf{4}_{t\text{-}Br}$	-155.64	49.80
$\mathbf{4}_{s\text{-}I}$	-152.16	$\mathbf{4}_{t\text{-}I}$	-152.08	49.06
$\mathbf{5}_{s\text{-}F}$	-329.05	$\mathbf{5}_{t\text{-}F}$	-328.98	40.70
$\mathbf{5}_{s\text{-}Cl}$	-159.39	$\mathbf{5}_{t\text{-}Cl}$	-159.32	44.53
$\mathbf{5}_{s\text{-}Br}$	-155.82	$\mathbf{5}_{t\text{-}Br}$	-155.74	51.11
$\mathbf{5}_{s\text{-}I}$	-152.26	$\mathbf{5}_{t\text{-}I}$	-152.18	51.07

Table 3 Calculated sum of electronic and thermal free energies (E), zero-point vibrational energy (ZPVE), and the ΔE_{st} (in kcal/mol) for the two series of BHEs ($\mathbf{1}_{s\text{-}X}$ *vs.* $\mathbf{1}_{t\text{-}X}$, $\mathbf{2}_{s\text{-}X}$ *vs.* $\mathbf{2}_{t\text{-}X}$, $\mathbf{3}_{s\text{-}X}$ *vs.* $\mathbf{3}_{t\text{-}X}$) with X =F, Cl and Br) at CBS-QB3.

Compound (*Singlets*)	E (Hartree)	ZPVE (kcal/mol)	Compound (*Triplets*)	E (kcal/mol)	ZPVE (kcal/mol)	ΔE_{st}
$\mathbf{1}_{s\text{-}F}$	-364.98	31.04	$\mathbf{1}_{t\text{-}F}$	-364.98	31.27	1.42
$\mathbf{1}_{s\text{-}Cl}$	-1085.67	29.16	$\mathbf{1}_{t\text{-}Cl}$	-1085.66	29.34	4.32
$\mathbf{1}_{s\text{-}Br}$	-5313.49	28.51	$\mathbf{1}_{t\text{-}Br}$	-5313.48	28.66	4.93
$\mathbf{1}_{s\text{-}I}$	---	---	$\mathbf{1}_{t\text{-}I}$	---	---	---
$\mathbf{2}_{s\text{-}F}$	-616.43	28.85	$\mathbf{2}_{t\text{-}F}$	-616.40	29.08	18.81
$\mathbf{2}_{s\text{-}Cl}$	-1337.12	27.16	$\mathbf{2}_{t\text{-}Cl}$	-1337.09	27.31	21.61
$\mathbf{2}_{s\text{-}Br}$	-5564.95	26.51	$\mathbf{2}_{t\text{-}Br}$	-5564.91	26.63	22.21
$\mathbf{2}_{s\text{-}I}$	---	---	$\mathbf{2}_{t\text{-}I}$	---	---	---
$\mathbf{3}_{s\text{-}F}$	-2403.95	28.44	$\mathbf{3}_{t\text{-}F}$	-2403.92	28.63	21.68
$\mathbf{3}_{s\text{-}Cl}$	-3124.64	26.74	$\mathbf{3}_{t\text{-}Cl}$	-3124.60	26.84	24.73
$\mathbf{3}_{s\text{-}Br}$	-7352.47	26.09	$\mathbf{3}_{t\text{-}Br}$	-7352.43	26.15	25.38
$\mathbf{3}_{s\text{-}I}$	---	---	$\mathbf{3}_{t\text{-}I}$	---	---	---

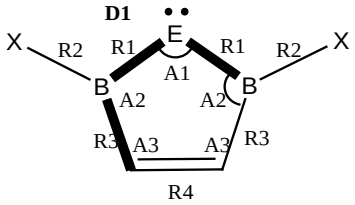
Table 4 Calculated sum of electronic and thermal free energies (E), zero-point vibrational energy (ZPVE), and the ΔE_{st} (in kcal/mol) for the two series of BHEs ($\mathbf{1}_{s\text{-}X}$ *vs.* $\mathbf{1}_{t\text{-}X}$, $\mathbf{2}_{s\text{-}X}$ *vs.* $\mathbf{2}_{t\text{-}X}$, $\mathbf{3}_{s\text{-}X}$ *vs.* $\mathbf{3}_{t\text{-}X}$) with X =F, Cl and Br) at G4MP2.

Compound (*Singlets*)	E (Hartree)	ZPVE (kcal/mol)	Compound (*Triplets*)	E (kcal/mol)	ZPVE (kcal/mol)	ΔE_{st}
$\mathbf{1}_{s\text{-}F}$	-364.90	31.22	$\mathbf{1}_{t\text{-}F}$	-364.90	31.44	2.52
$\mathbf{1}_{s\text{-}Cl}$	-1085.58	29.24	$\mathbf{1}_{t\text{-}Cl}$	-1085.58	29.41	5.02
$\mathbf{1}_{s\text{-}Br}$	-5312.92	28.63	$\mathbf{1}_{t\text{-}Br}$	-5312.91	28.76	5.71
$\mathbf{1}_{s\text{-}I}$	---	---	$\mathbf{1}_{t\text{-}I}$	---	---	---
$\mathbf{2}_{s\text{-}F}$	-616.34	29.14	$\mathbf{2}_{t\text{-}F}$	-616.31	29.32	19.99
$\mathbf{2}_{s\text{-}Cl}$	-1337.03	27.28	$\mathbf{2}_{t\text{-}Cl}$	-1336.99	27.38	22.49
$\mathbf{2}_{s\text{-}Br}$	-5564.37	26.65	$\mathbf{2}_{t\text{-}Br}$	-5564.33	26.73	23.25
$\mathbf{2}_{s\text{-}I}$	---	---	$\mathbf{2}_{t\text{-}I}$	---	---	---
$\mathbf{3}_{s\text{-}F}$	-2403.64	28.73	$\mathbf{3}_{t\text{-}F}$	-2403.60	28.90	22.12
$\mathbf{3}_{s\text{-}Cl}$	-3124.32	26.85	$\mathbf{3}_{t\text{-}Cl}$	-3124.28	26.94	25.09
$\mathbf{3}_{s\text{-}Br}$	-7351.66	26.23	$\mathbf{3}_{t\text{-}Br}$	-7351.62	26.26	25.93
$\mathbf{3}_{s\text{-}I}$	---	---	$\mathbf{3}_{t\text{-}I}$	---	---	---

Table 5 Comparison between the stability of our divalent species (*B*HËs**:** $\mathbf{1}_X$**-** $\mathbf{3}_X$) with their corresponding Arduengo's (*N*HËs) by considering their energy differences, $\delta(\Delta E_{st})$= (ΔE_{st}^{NHEs} - ΔE_{st}^{BHEs}), (in kcal/mol) at G4MP2.

X	$\mathbf{1}_X$	$\mathbf{2}_X$	$\mathbf{3}_X$
F	---	14.04	8.72
Cl	23.34	1.19	-4.56
Br	16.25	-4.65	-9.86
I	---	---	---

Table 6 Calculated bond length (R1–R4) in Å, bond angles (A1–A3) and dihedral angles (D1) in Degree (°), for the two series of BHEs ($\mathbf{1}_{s\text{-}X}$ *vs.* $\mathbf{1}_{t\text{-}X}$, $\mathbf{2}_{s\text{-}X}$ *vs.* $\mathbf{2}_{t\text{-}X}$, $\mathbf{3}_{s\text{-}X}$ *vs.* $\mathbf{3}_{t\text{-}X}$, $\mathbf{4}_{s\text{-}X}$ *vs.* $\mathbf{4}_{t\text{-}X}$ and $\mathbf{5}_{s\text{-}X}$ *vs.* $\mathbf{5}_{t\text{-}X}$ with X =F, Cl, Br and I) at UB3LYP/TZ2P.



Compound	R1	R2	R3	R4	B—B	A1	A2	A3	*D1
$\mathbf{1}_{s\text{-}F}$	1.512	1.331	1.578	1.391	2.363	102.8	94.1	107.9	58.3
$\mathbf{1}_{s\text{-}Cl}$	1.503	1.757	1.577	1.390	2.343	102.4	93.1	108.0	61.0
$\mathbf{1}_{s\text{-}Br}$	1.500	1.929	1.575	1.391	2.348	102.5	93.5	107.5	60.2
$\mathbf{1}_{s\text{-}I}$	1.495	2.144	1.571	1.390	2.286	99.7	94.5	106.6	61.4
$\mathbf{1}_{t\text{-}F}$	1.547	1.336	1.587	1.378	2.510	108.4	104.9	110.9	0.0
$\mathbf{1}_{t\text{-}Cl}$	1.542	1.761	1.585	1.380	2.521	109.7	104.1	111.1	0.0
$\mathbf{1}_{t\text{-}Br}$	1.538	1.935	1.582	1.382	2.513	109.5	104.3	110.9	0.0
$\mathbf{1}_{t\text{-}I}$	1.532	2.150	1.579	1.383	2.500	109.4	104.6	110.7	0.0
$\mathbf{2}_{s\text{-}F}$	2.051	1.342	1.545	1.399	2.449	73.3	95.4	109.9	66.8
$\mathbf{2}_{s\text{-}Cl}$	2.041	1.766	1.533	1.406	2.395	71.9	92.7	108.8	72.1
$\mathbf{2}_{s\text{-}Br}$	2.037	1.940	1.530	1.407	2.387	71.1	93.5	108.7	71.1
$\mathbf{2}_{s\text{-}I}$	2.027	2.158	1.526	1.409	2.313	69.6	94.7	107.2	71.3
$\mathbf{2}_{t\text{-}F}$	2.037	1.338	1.584	1.371	2.868	89.5	107.1	118.2	0.0
$\mathbf{2}_{t\text{-}Cl}$	2.029	1.764	1.582	1.373	2.899	91.2	105.6	118.8	0.0
$\mathbf{2}_{t\text{-}Br}$	1.996	1.924	1.569	1.356	2.876	92.2	104.9	119.0	0.0
$\mathbf{2}_{t\text{-}I}$	2.015	2.158	1.576	1.377	2.882	91.3	105.8	118.5	0.0
$\mathbf{3}_{s\text{-}F}$	2.135	1.340	1.541	1.400	2.489	71.3	95.4	110.7	66.8
$\mathbf{3}_{s\text{-}Cl}$	2.128	1.765	1.529	1.407	2.451	70.3	92.7	110.0	71.5
$\mathbf{3}_{s\text{-}Br}$	2.122	1.959	1.526	1.406	2.451	70.5	93.0	110.0	71.1
$\mathbf{3}_{s\text{-}I}$	2.112	2.157	1.523	1.410	2.363	68.0	94.4	108.2	71.2
$\mathbf{3}_{t\text{-}F}$	2.093	1.335	1.584	1.37	2. 918	88.4	106.6	119.2	0.0
$\mathbf{3}_{t\text{-}Cl}$	2.088	1.761	1.581	1.373	2.952	90.0	105.0	120.0	0.0
$\mathbf{3}_{t\text{-}Br}$	2.085	1.933	1.578	1.375	2.948	90.0	105.1	119.9	0.0
$\mathbf{3}_{t\text{-}I}$	2.075	2.152	1.574	1.376	2.934	90.0	105.4	119.7	0.0
$\mathbf{4}_{s\text{-}F}$	2.356	1.341	1.543	1.395	2.624	67.7	98.5	113.5	61.0
$\mathbf{4}_{s\text{-}Cl}$	2.345	1.765	1.527	1.406	2.565	66.3	94.7	112.3	68.0
$\mathbf{4}_{s\text{-}Br}$	2.343	1.960	1.524	1.409	2.581	66.8	94.7	112.6	67.8
$\mathbf{4}_{s\text{-}I}$	2.332	2.205	1.518	1.412	2.452	63.3	96.3	110.0	68.9
$\mathbf{4}_{t\text{-}F}$	2.313	1.335	1.585	1.370	3.041	82.2	107.1	121.5	0.0
$\mathbf{4}_{t\text{-}Cl}$	2.308	1.760	1.580	1.373	3.077	83.6	105.6	122.5	0.0
$\mathbf{4}_{t\text{-}Br}$	2.306	1.957	1.578	1.376	3.079	83.7	105.5	122.6	0.0
$\mathbf{4}_{t\text{-}I}$	2.294	2.198	1.573	1.378	3.049	83.3	106.3	121.9	0.0
$\mathbf{5}_{s\text{-}F}$	2.491	1.342	1.542	1.393	2.643	64.1	100.1	113.9	59.8
$\mathbf{5}_{s\text{-}Cl}$	2.477	1.769	1.527	1.402	2.586	62.9	97.6	113.3	66.2

5$_{s\text{-}Br}$	2.473	1.945	1.525	1.404	2.585	63.0	97.6	112.8	64.9
5$_{s\text{-}I}$	2.461	2.211	1.518	1.408	2.482	60.6	98.7	110.7	65.8
5$_{t\text{-}F}$	2.394	1.335	1.583	1.370	3.101	80.7	106.5	123.1	0.0
5$_{t\text{-}Cl}$	2.456	1.774	1.494	1.453	3.283	83.9	100.3	127.8	0.0
5$_{t\text{-}Br}$	2.449	1.948	1.493	1.454	3.279	84.1	100.3	127.7	0.0
5$_{t\text{-}I}$	2.443	2.167	1.492	1.454	3.260	83.7	100.9	127.3	0.0

Table 7 "Wiberg bond indices" (WBI) for the singlet BHEs ($\mathbf{1}_{s\text{-}X}$, $\mathbf{2}_{s\text{-}X}$, $\mathbf{3}_{s\text{-}X}$, $\mathbf{4}_{s\text{-}X}$ and $\mathbf{5}_{s\text{-}X}$ with X = H, F, Cl, Br and I) at B3LYP/TZ2P.

	Ë—C_{DB}	Ë—‖[a]	B—B	C=C	Ë-B	B-C_{DB}	X-B
$\mathbf{1}_F$	0.249	0.498	0.105	1.674	1.191	0.911	0.871
$\mathbf{1}_{Cl}$	0.248	0.496	0.114	1.672	1.225	0.933	1.147
$\mathbf{1}_{Br}$	0.247	0.494	0.113	1.671	1.237	0.935	1.146
$\mathbf{1}_I$	0.236	0.472	0.123	1.670	1.241	0.940	1.170
$\mathbf{2}_F$	0.197	0.394	0.235	1.605	0.963	1.024	0.845
$\mathbf{2}_{Cl}$	0.200	0.400	0.278	1.558	0.933	1.068	1.151
$\mathbf{2}_{Br}$	0.195	0.390	0.285	1.550	0.940	1.070	1.157
$\mathbf{2}_I$	0.188	0.376	0.322	1.536	0.933	1.074	1.196
$\mathbf{3}_F$	0.154	0.308	0.225	1.643	0.931	1.026	0.835
$\mathbf{3}_{Cl}$	0.149	0.298	0.269	1.597	0.901	1.072	1.144
$\mathbf{3}_{Br}$	0.147	0.294	0.279	1.583	0.903	1.073	1.151
$\mathbf{3}_I$	0.142	0.284	0.323	1.564	0.892	1.078	1.190
$\mathbf{4}_F$	0.123	0.246	0.214	1.669	0.890	1.028	0.822
$\mathbf{4}_{Cl}$	0.127	0.254	0.269	1.600	0.840	1.084	1.139
$\mathbf{4}_{Br}$	0.125	0.250	0.279	1.584	0.836	1.085	1.148
$\mathbf{4}_I$	0.125	0.250	0.343	1.553	0.811	1.095	1.192
$\mathbf{5}_F$	---	---	---	---	---	---	---
$\mathbf{5}_{Cl}$	0.091	0.182	0.281	1.644	0.812	1.074	1.126
$\mathbf{5}_{Br}$	0.089	0.178	0.294	1.627	0.802	1.073	1.134
$\mathbf{5}_I$	0.090	0.180	0.362	1.590	0.774	1.083	1.177

[a] ‖ is a symbol for C=C bond. The values of the **Ë—‖** column are the products of the first column multiplied by 2 ($WBI_{(Ë–‖)} = WBI_{(Ë–C^{DB})} \times 2$)

Table 8 Calculated donor-acceptor energies for the most important interactions (the conventional statement for each donor and acceptor orbital is written in brackets) at UB3LYP/6-311++g**.

	LP(X)→LP*(B) **[n→$p_{(B)}$]**	**BD(C=C)→LP*(B)** **[π→$p_{(B)}$]**	**BD(C=C)→LP*(Ë)** **[π→$p_{(Ë)}$]**	**BD(B-C_{DB}[1])→LP*(Ë)** **[σ→$p_{(Ë)}$]**	**BD(B-E)→LP*(B_{opp}[2])** **[σ→$p_{(B)}$]**
1_F	36.68	7.65	23.00	18.27	94.41
1_{Cl}	34.10	8.60	23.08	17.64	100.25
1_{Br}	29.63	8.94	21.87	17.1	101.81
2_F	40.21	12.58	13.62	4.68	15.63
2_{Cl}	39.16	14.47	15.27	4.36	17.58
2_{Br}	34.73	15.07	14.11	3.99	18.27
3_F	40.21	13.49	10.90	3.41	13.95
3_{Cl}	39.27	15.41	11.74	3.02	15.70
3_{Br}	35.18	15.94	11.65	2.78	16.26

[1] C_{DB}=$C_{Double\ Bond}$
[2] B_{opp}=$B_{opposite}$

Table 9 Calculated contribution percentage for the estimation of σ and *p* atomic orbitals in the HOMO (and HOMO-1 anywhere needed) and LUMO of singlet BHEs ($\mathbf{1}_{s\text{-}X}$, $\mathbf{2}_{s\text{-}X}$, $\mathbf{3}_{s\text{-}X}$, $\mathbf{4}_{s\text{-}X}$ and $\mathbf{5}_{s\text{-}X}$ with X = H, F, Cl, Br and I) respectively, at UB3LYP/TZ2P.

DS	E_{HOMO-1} kcal/mol	%SFO contribution in HOMO-1 of Ë	E_{HOMO} kcal/mol	%SFO contribution in HOMO of Ë	E_{LUMO} kcal/mol	%SFO contribution in LUMO of Ë
$\mathbf{1}_{H}$	---	---	-166.976	44.75%p_x + 13.70%s	-60.905	72.18%p_z
$\mathbf{2}_{H}$	---	---	-155.832	38.86%p_x + 20.72%s	-49.282	83.67%p_z
$\mathbf{3}_{H}$	---	---	-153.473	41.44%p_x + 13.99%s	-51.614	89.96%p_z
$\mathbf{4}_{H}$	---	---	-143.942	20.37%p_x + 17.31%s + 14.87%p_z	-56.673	54.78%p_x + 38.13%p_z
$\mathbf{5}_{H}$	-138.131	30.85%p_x + 15.43%s	-137.695	33.01%p_y	-66.429	77.12%p_x + 15.66%p_z
$\mathbf{1}_{F}$	---	---	-171.090	51.59%p_x + 13.26%s	-79.439	72.18%p_z
$\mathbf{1}_{Cl}$	---	---	-171.279	17.89%p_x + 12.63%s	-75.407	71.42%p_z
$\mathbf{1}_{Br}$	---	---	-171.012	44.28%p_x + 11.35%s	-77.060	70.11%p_z
$\mathbf{1}_{I}$	---	---	-169.616	28.53%p_x + 6.34%s	-79.176	69.13%p_z
$\mathbf{2}_{F}$	---	---	-158.028	40.98%p_x + 19.70%s	-63.752	80.94%p_z
$\mathbf{2}_{Cl}$	---	---	-158.285	35.78%p_x + 17.67%s	-58.433	81.74%p_z
$\mathbf{2}_{Br}$	-158.877	32.95%p_x + 15.44%s	-158.414	22.21%p_y	-60.878	79.32%p_z
$\mathbf{2}_{I}$	-158.441	21.74%p_x + 9.55%s	-154.281	15.52%p_y	-63.548	76.34%p_z
$\mathbf{3}_{F}$	---	---	-157.152	42.34%p_x + 13.95%s	-64.854	80.85%p_z
$\mathbf{3}_{Cl}$	-156.228	36.83%p_x + 12.06%s	-154.827	31.07%p_y	-60.316	81.09%p_z
$\mathbf{3}_{Br}$	-157.163	33.28%p_x + 10.43%s	-155.277	26.66%p_y	-62.156	80.16%p_z
$\mathbf{3}_{I}$	-156.530	22.74%p_x + 6.98%s	-151.675	19.95%p_y	-64.789	78.60%p_z
$\mathbf{4}_{F}$	---	---	-146.184	32.66%p_x + 19.33%s	-69.991	69.63%p_z + 18.71%p_x
$\mathbf{4}_{Cl}$	-146.685	31.76%p_x + 16.51%s	-146.265	28.10%p_y	-65.513	79.35%p_z + 10.78%p_x
$\mathbf{4}_{Br}$	-147.888	24.06%p_x + 15.02%s	-147.465	24.90%p_y	-67.247	58.88%p_z + 30.50%p_x
$\mathbf{4}_{I}$	-150.457	16.91%p_x + 10.74%s	-145.889	19.47%p_y	-70.584	59.63%p_z + 30.80%p_x
$\mathbf{5}_{F}$	-144.031	32.94%p_x + 17.40%s	-142.490	36.06%p_y	-71.894	71.71%p_z + 18.98%p_x
$\mathbf{5}_{Cl}$	-144.185	29.32%p_x + 14.58%s	-141.474	29.84%p_y	-69.481	70.65%p_z + 21.06%p_x
$\mathbf{5}_{Br}$	-145.261	27.82%p_x + 13.35%s	-142.472	27.39%p_y	-71.103	70.75%p_z + 20.39%p_x
$\mathbf{5}_{I}$	-148.106	19.74%p_x + 9.97%s	-142.520	21.73%p_y	-74.605	68.62%p_z + 22.90%p_x

Table 10 Contribution (%) of s and p atomic orbital in the hybrid orbital of divalent atom (E) in its Ë-B bonding and in lone pair (LP) orbitals.

	Ë Hybrid orbital in $\sigma_{B\text{-}Ë}$ bonds	**Average hybrid for Ë in $\sigma_{B\text{-}Ë}$ bonds**	**Ë Hybrid in LP orbitals**	**Average hybrid for Ë in LP orbitals**
$\mathbf{1_F}$	$sp^{0.94}$		---	
$\mathbf{1_{Cl}}$	sp	$sp^{0.99}$	---	
$\mathbf{1_{Br}}$	sp		---	
$\mathbf{1_I}$	sp		---	
$\mathbf{2_F}$	$sp^{8.42}$		$sp^{0.27}$	
$\mathbf{2_{Cl}}$	$sp^{7.3}$	$sp^{7.27}$	$sp^{0.32}$	$sp^{0.32}$
$\mathbf{2_{Br}}$	$sp^{6.88}$		$sp^{0.34}$	
$\mathbf{2_I}$	$sp^{6.47}$		$sp^{0.36}$	
$\mathbf{3_F}$	$sp^{12.12}$		$sp^{0.18}$	
$\mathbf{3_{Cl}}$	$sp^{10.5}$	$sp^{10.42}$	$sp^{0.21}$	$sp^{0.21}$
$\mathbf{3_{Br}}$	$sp^{9.8}$		$sp^{0.22}$	
$\mathbf{3_I}$	$sp^{9.25}$		$sp^{0.23}$	
$\mathbf{4_F}$	$sp^{12.69}$		$sp^{0.17}$	
$\mathbf{4_{Cl}}$	$sp^{11.06}$	$sp^{10.99}$	$sp^{0.19}$	$sp^{0.19}$
$\mathbf{4_{Br}}$	$sp^{10.43}$		$sp^{0.20}$	
$\mathbf{4_I}$	$sp^{9.79}$		$sp^{0.21}$	
$\mathbf{5_F}$	---		---	
$\mathbf{5_{Cl}}$	$sp^{12.94}$	$sp^{12.16}$	$sp^{0.16}$	$sp^{0.16}$
$\mathbf{5_{Br}}$	$sp^{12.16}$		$sp^{0.17}$	
$\mathbf{5_I}$	$sp^{11.30}$		$sp^{0.18}$	

Table 11 Calculated global electrophilicity (ω) and Nucleophilicity indices (N)[a] for the singlet state of all BHEs under study compared to their analogues *N*HËs.

Compound	Global Electrophilicity ω (eV)		Nucleophilicity index (*N*) HOMO(TCNE)=-9.42 eV	
	BHEs	NHEs	BHEs	NHEs
$\mathbf{1}_{s\text{-}F}$	3.09	1.35	2.16	1.82
$\mathbf{1}_{s\text{-}Cl}$	3.03	2.27	2.11	2.44
$\mathbf{1}_{s\text{-}Br}$	3.11	3.06	2.11	2.64
$\mathbf{1}_{s\text{-}I}$	3.14	3.52	2.24	3.04
$\mathbf{2}_{s\text{-}F}$	2.52	1.70	2.67	3.17
$\mathbf{2}_{s\text{-}Cl}$	2.44	2.00	2.60	3.32
$\mathbf{2}_{s\text{-}Br}$	2.53	2.77	2.59	3.41
$\mathbf{2}_{s\text{-}I}$	2.86	3.30	2.69	3.58
$\mathbf{3}_{s\text{-}F}$	2.66	1.88	2.74	3.53
$\mathbf{3}_{s\text{-}Cl}$	2.63	1.90	2.71	3.64
$\mathbf{3}_{s\text{-}Br}$	2.60	2.51	2.79	3.81
$\mathbf{3}_{s\text{-}I}$	2.73	3.13	2.90	3.94
$\mathbf{4}_{s\text{-}F}$	2.85	2.09	3.13	3.99
$\mathbf{4}_{s\text{-}Cl}$	2.89	2.11	3.01	4.03
$\mathbf{4}_{s\text{-}Br}$	2.84	2.40	3.09	4.10
$\mathbf{4}_{s\text{-}I}$	2.80	3.05	3.22	4.29
$\mathbf{5}_{s\text{-}F}$	2.65	2.06	3.44	4.31
$\mathbf{5}_{s\text{-}Cl}$	2.74	2.10	3.29	4.32
$\mathbf{5}_{s\text{-}Br}$	2.71	2.28	3.34	4.38
$\mathbf{5}_{s\text{-}I}$	1.09	2.95	1.20	4.55

[a] The global Electrophilicity ($\omega=\mu^2/2\eta$; $\mu\approx(E_{HOMO}+E_{LUMO})/2$ & $\eta=E_{LUMO}-E_{HOMO}$) and Nucleophilicity index ($N=E_{HOMO(Nu)}-E_{HOMO(TCNE)}$; Tetracyanoethylene (TCNE) is chosen as the reference) [1] for all of the halogenated species are probed. μ is the chemical potential and η is the chemical hardness.

Table 12 Selected bond lengths in Å, bond angles and dihedral angles (**D1**) in Degree (°), wiberg bond indices (WBI), donor-acceptor energies, and formation energies in kcal/mol for the adducts (complexes) of $\mathbf{1}_X$-, $\mathbf{2}_X$- and $\mathbf{3}_X$-**MCl** (with X =F, Cl; M=Cu, Ag, Au) at UB3LYP/TZ2P.

			WBI						Donor-acceptor energies	
	M-Ë	B-Ë	M-Ë	B-Ë	Ë—I	D1	∠Ë-M-Cl	$\Delta E_{Complex}$	π(C=C)→*p*(Ë)	LP(M)→LP*(Ë)
$\mathbf{1}_F$		1.53		1.107	0.498	51.7			18.09	
$\mathbf{1}_F$-CuCl	1.85	1.57	0.406	0.973	0.106	46.5	177.42	-49.89	7.18	20.33
$\mathbf{1}_F$-AgCl	2.17	1.55	0.283	0.999	0.106	51.1	179.21	-32.50	5.64	9.89
$\mathbf{1}_F$-AuCl	1.94	1.58	0.745	0.930	0.093	40.5	171.29	-66.01	18.98	53.62
$\mathbf{2}_F$		2.04		0.959	0.394	55.7			8.60	
$\mathbf{2}_F$-CuCl	2.27	2.03	0.552	0.959	0.106	44.7	178.58	-35.45	7.07	7.09
$\mathbf{2}_F$-AgCl	2.51	2.03	0.474	0.962	0.093	46.7	177.30	-26.29	29.14	5.82
$\mathbf{2}_F$-AuCl	2.32	2.03	0.814	0.946	0.108	39.9	179.69	-55.41	8.54	18.35
$\mathbf{3}_F$		2.14		0.942	0.308	56.3			6.63	
$\mathbf{3}_F$-CuCl	2.34	2.11	0.520	0.943	0.093	44.0	178.69	-31.37	30.07	5.78
$\mathbf{3}_F$-AgCl	2.57	2.12	0.447	0.945	0.108	45.8	177.74	-23.40	10.28	4.96
$\mathbf{3}_F$-AuCl	2.39	2.11	0.756	0.929	0.125	39.1	179.37	-49.38	8.28	14.57
$\mathbf{1}_{Cl}$		1.52		1.141	0.496	52.9			12.56	
$\mathbf{1}_{Cl}$-CuCl	1.86	1.56	0.366	1.001	0.108	49.0	177.83	-49.01	5.90	18.56
$\mathbf{1}_{Cl}$-AgCl	2.18	1.55	0.256	1.028	0.125	52.8	179.16	-32.06	4.51	9.3
$\mathbf{1}_{Cl}$-AuCl	1.95	1.57	0.696	0.957	0.108	43.9	172.58	-64.43	13.56	49.45
$\mathbf{2}_{Cl}$		2.04		0.913	0.400	58.4			7.11	
$\mathbf{2}_{Cl}$-CuCl	2.27	2.02	0.536	0.936	0.125	48.5	178.67	-34.63	5.85	6.84
$\mathbf{2}_{Cl}$-AgCl	2.51	2.02	0.459	0.938	0.108	50.3	177.48	-25.66	29.77	5.67
$\mathbf{2}_{Cl}$-AuCl	2.33	2.02	0.797	0.924	0.157	44.1	179.84	-54.27	12.21	17.58
$\mathbf{3}_{Cl}$		2.13		0.893	0.298	59.4			11.43	
$\mathbf{3}_{Cl}$-CuCl	2.34	2.10	0.508	0.914	0.108	48.4	178.75	-30.43	30.27	5.53
$\mathbf{3}_{Cl}$-AgCl	2.58	2.11	0.435	0.915	0.157	50.0	177.76	-22.40	13.51	4.81
$\mathbf{3}_{Cl}$-AuCl	2.40	2.10	0.745	0.903	0.147	43.9	179.46	-48.19	13.66	14

Fig. 1 Energies of bis(boryl)-based divalents as a function of their dihedral angle D1(∠C-B-E-B) for puckered singlets (**3**$_{s\text{-}X}$, with the minimum at ~60º), at UB3LYP/TZ2P.

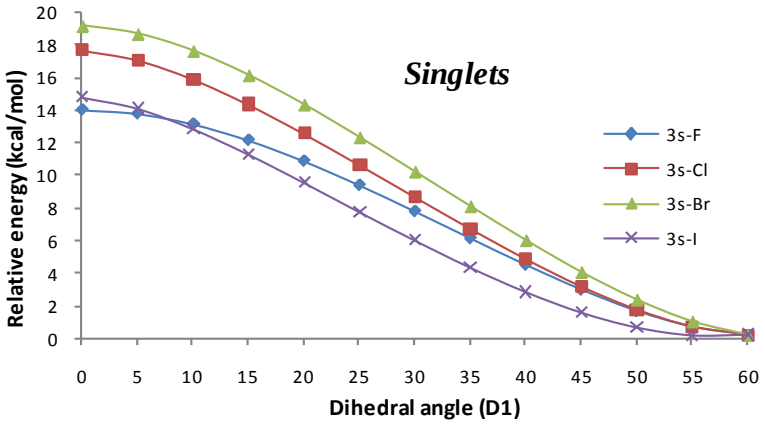


Fig. 2 $\Delta E_{(t\text{-}s)}$ *vs.* atomic volume for halogenated BHEs at B3LYP/6-311++g**.

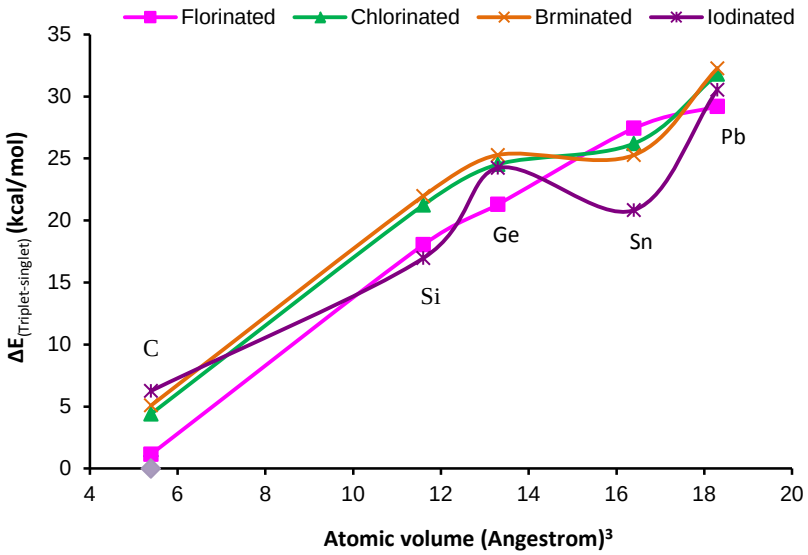


Fig. 3 Linear relationships between singlet LUMO–HOMO energy gaps $\Delta E_{(LUMO\text{-}HOMO)}$, and their corresponding singlet–triplet energy separations (ΔE_{st}), for the two series of halogenated five-membered-rings: $\mathbf{3}_{s\text{-}X}$ and $\mathbf{5}_{s\text{-}X}$; with correlation factors: 0.918 and 0.924, respectively

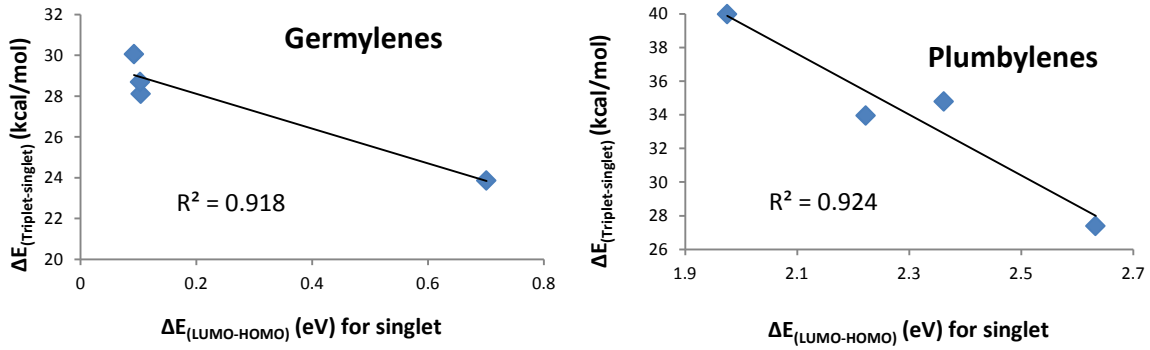


Fig. 4 Linear relationships between the B-E-B angles and their corresponding halogen atom radius, for the five-membered-rings: $\mathbf{2}_{s\text{-}X}$ (a), $\mathbf{3}_{s\text{-}X}$ (b), $\mathbf{4}_{s\text{-}X}$ (c), $\mathbf{5}_{s\text{-}X}$ (d); with correlation factors: 0.844, 0.703, 0.970 and 0.990, respectively

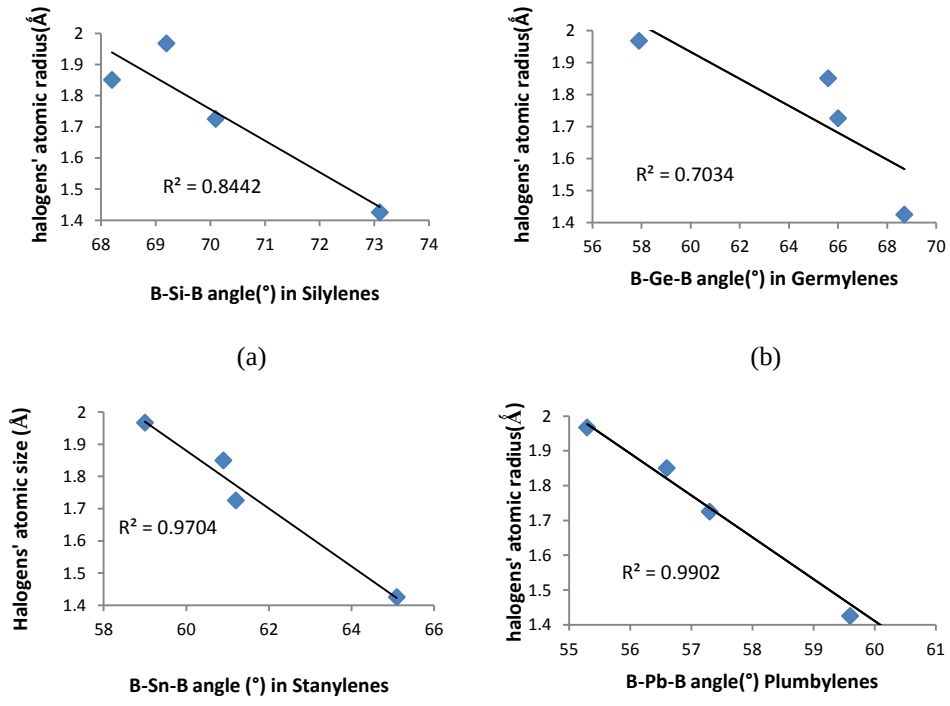
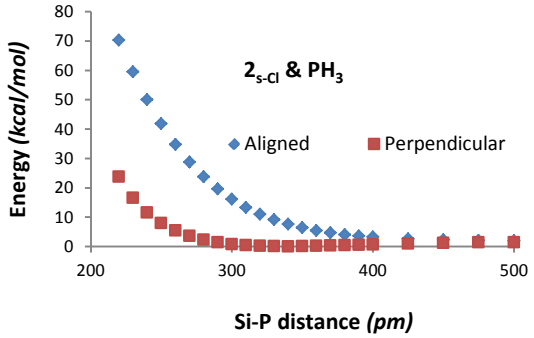
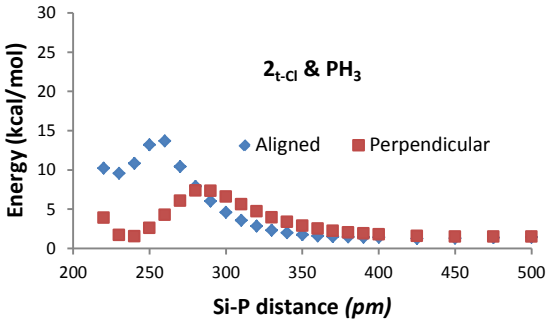


Fig. 5 Graphs showing relative energies for the interaction of Lewis base (PH_3) to (a) $\mathbf{2}_{s\text{-}Cl}$ and (b) $\mathbf{2}_{t\text{-}Cl}$.

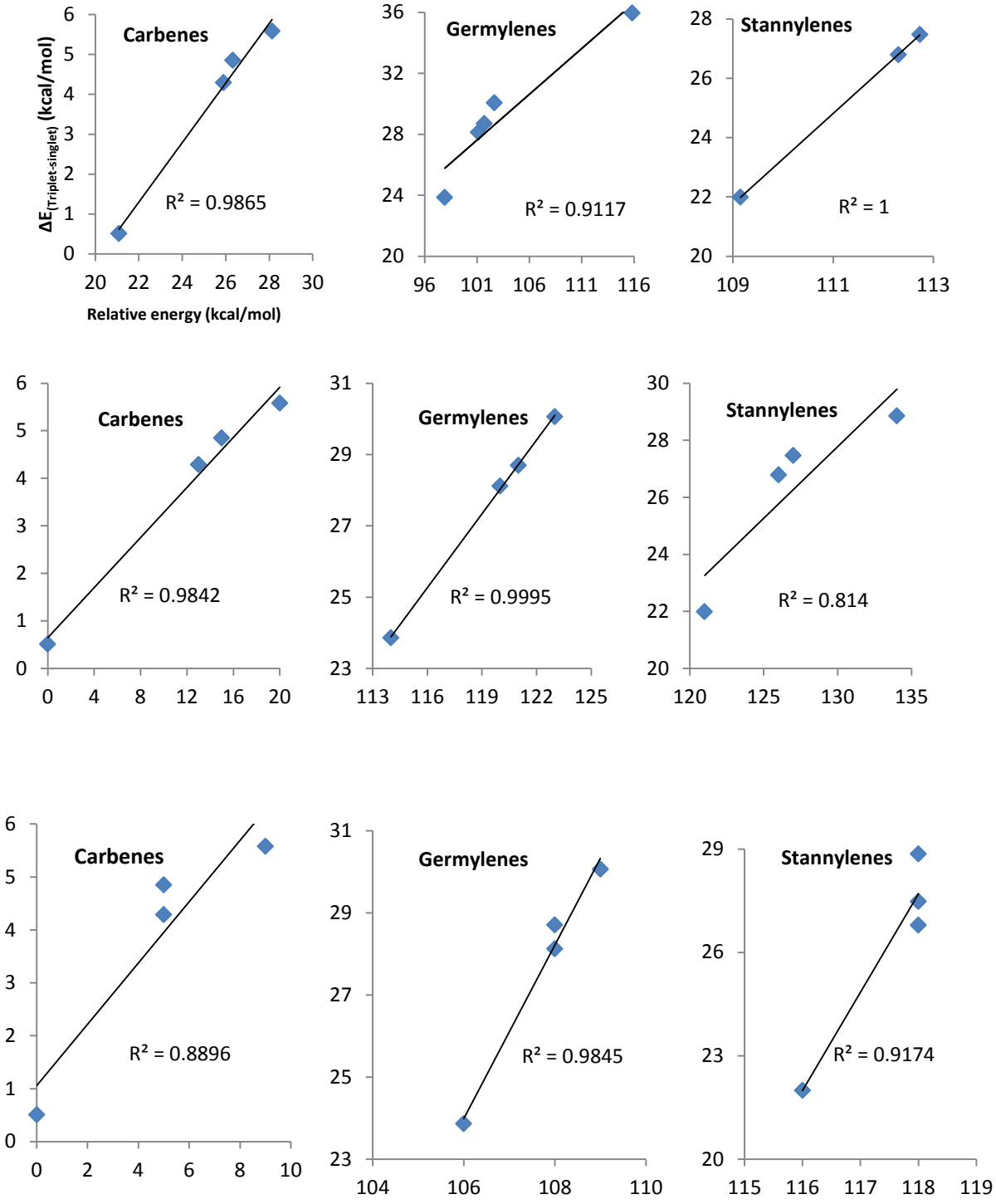


(a)



(b)

Fig. 6 Correlation diagrams showing high correlation between the relative energies of the reactions (Scheme 4, Table 8S) and ΔE_{st}



[1] Kassaee MZ, Momeni MR, Shakib FA, Najafi Z, Zandi H (2011) J Phys Org Chem 24:1022