Electronic Supplementary Information

Anisotropic and amphoteric characteristics of diverse carbenes

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1. Relative energies (kcal/mol) for CH_2, CF_2, and $C(NHCH)_2$©

Table S1. Relative energies (kcal/mol) of the triplet state with respect to the singlet state for different carbenes.[a]

Species	MP2			CCSD			CCSD(T)		
	aVTZ	aVQZ	CBS	aVTZ	aVQZ	CBS	aVTZ	aVQZ	CBS
CH_2	-14.54	-13.90	-13.43	-10.67	-10.41	-10.23	-9.70	-9.43	-9.23(-8.84)
CF_2	54.08	54.77	55.28	54.16	54.43	54.63	56.36	56.66	56.88(56.77)
$C(NHCH)_2$©	90.34	91.33	92.05	83.32	84.15	84.76	85.73	86.43	86.94(87.56)

[a]All structures were optimized at the given level of theory except that the CCSD(T)/aVQZ structures used the optimized CCSD(T)/aVTZ geometries. The CCSD(T)/CBS values in parentheses denote the zero-point-energy (ZPE) corrected relative energies where the ZPE were corrected using CCSD/aVTZ frequencies for CH_2/CF_2 and MP2/aVTZ frequencies for $C(NHCH)_2$©.

2. Electrostatic potential maps and multipole charge models for CH_2, CF_2, and $C(NHCH)_2$©

In the case of singlet species, the 1+6 point charges correspond to two point charges per cartesian axis and a point charge on :C to keep the total charge zero (Here, the charge on :C is positive, while all the outershell point charges are negative). The triplet case is simpler with a model where two main point charges corresponding to two p orbitals are placed on the (±x)z plane, one point charge is along the -z direction, and two point charges are along ±y direction. Namely, the singlet state uses a model with charges located on :C at the origin of coordinates, two equivalent q_x charges along the ±x direction, two equivalent q_y charges along the ±y direction, and two q_{z1} and q_{z2} charges along the ±z direction. For the triplet state, we have considered q_C on :C at the origin of coordinates, two equivalent q_y charges along the ±y direction, and two equivalent q_{xz} charges along the ±x direction for the +z direction, and one q_z charge along the -z direction. A simplified 4+1 point model with charges at the carbon center, two equivalent q_{xz} charges along the ±x direction for the +z direction, and two equivalent q_{yz} charges along the ±y direction for the -z direction, while the chemical interpretation is less intuitive.

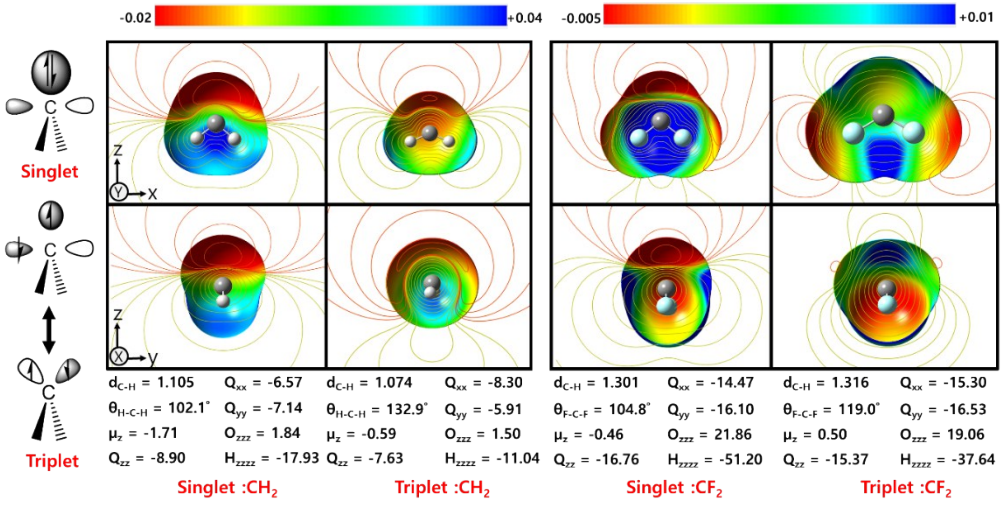


Figure S1. Electrostatic potential (EP) maps at the MP2/aVTZ of singlet/triplet states of CH_2 and CF_2, with multipole moments at CCSD/aVTZ at the optimized CCSD(T)/aV5Z geometries (d: distance and θ: angle). Distances are in Å; 2^n-multipole moments [Dipole (μ), quadrupole (Q), octupole (O), and hexapole (H) moments] in Debye·$Å^{n-1}$.

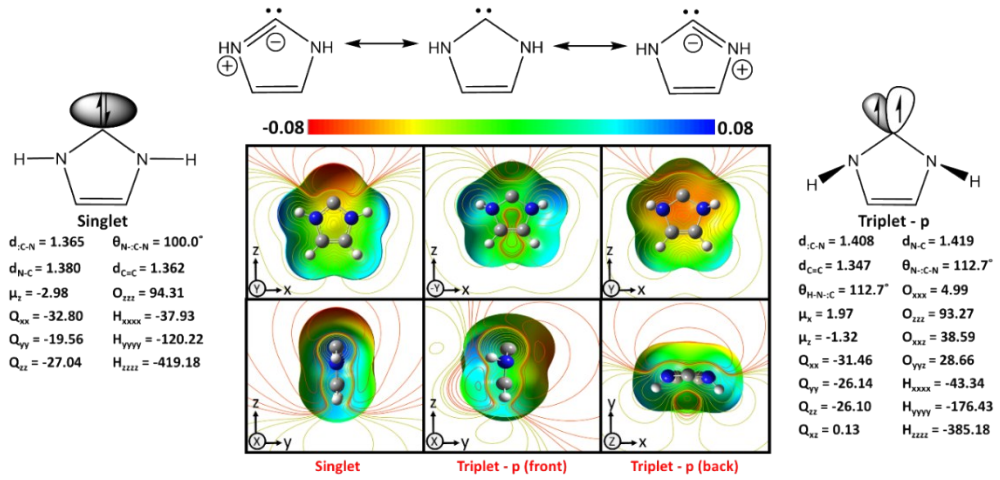


Figure S2: EP maps at the MP2/aVTZ level and multipole moments at the CCSD/aVTZ level on the optimized CCSD(T)/aVTZ geometries of singlet and triplet imidazol-2-ylidene ($C(NHCH)_2^{©}$). Distances are in Å; 2^n-multipole moments in Debye·$Å^{n-1}$.

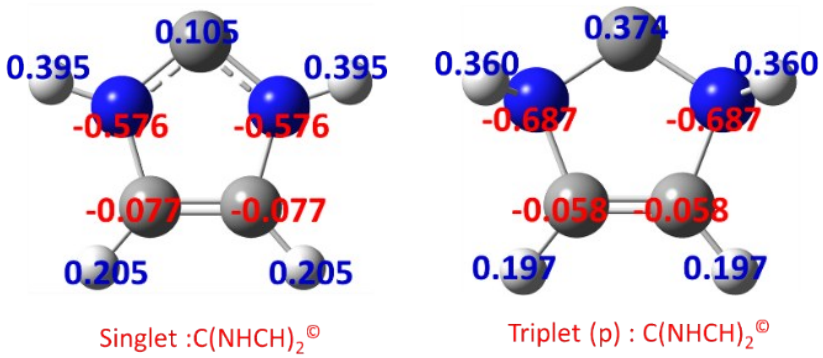


Figure S3. NBO charges of carbenes (in au) at the CCSD/aVTZ//CCSD(T)/aV5Z(aVTZ) level of theory for $C(NHCH)_2^{©}$.

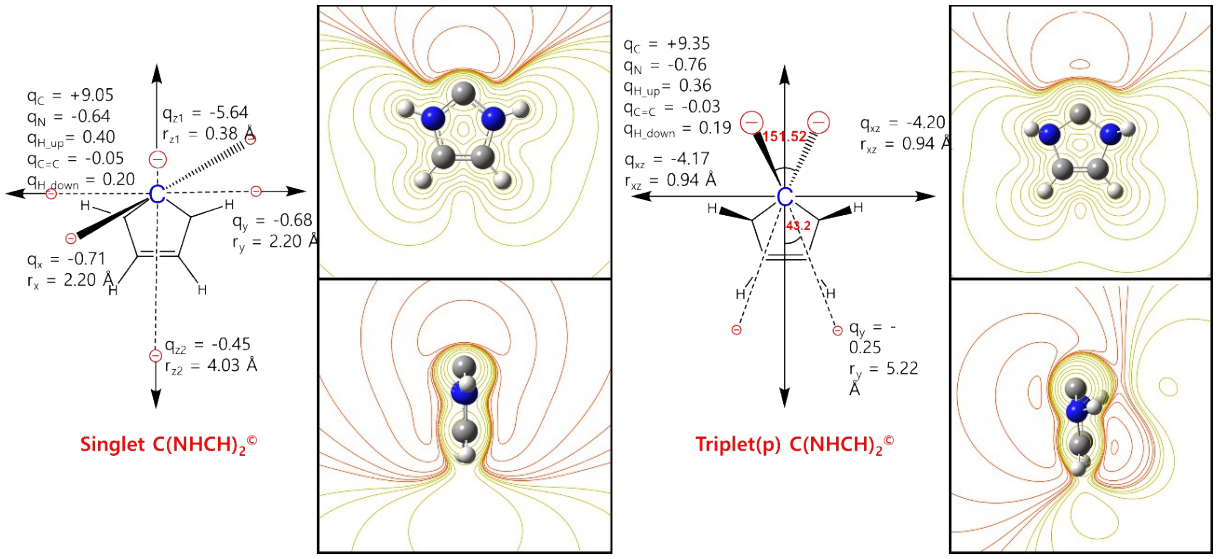


Figure S4. Multipole models for interaction potentials for imidazole-2-ylidene (C(NHCH)$_2$©) which reproduce the EP maps of singlet and triplet-p C(NHCH)$_2$© at the CCSD/aVTZ//CCSD(T)/aVTZ level.

The multipole model for C(NHCH)$_2$© (Figure S4) is much more complicated due to the addition of other atoms in the ring. The singlet case using 1+6 point model still gives an accurate result that schematically simplifies the EP map. However, it was not easy to fit the triplet case by using the 1+5 point model due to the nonplanarity of the molecule arising from the protruding hydrogen atoms. In the triplet-p case, a simplified 1+4 point model was used where two inequivalent charges (q_{xz1}, q_{xz2}) are used as well as two equivalent q_{yz} charges, while the multipole moments were fit up to hexadecapole moments.

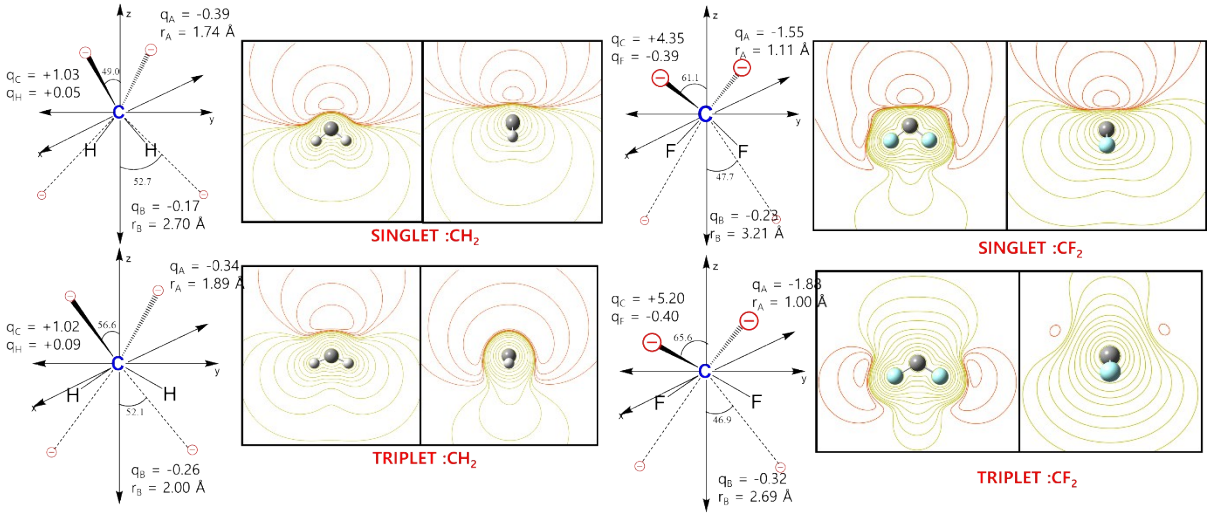


Figure S5. A 4-point model for interaction potentials for CH_2 and CF_2 which reproduces their EP maps (right) of singlet and triplet states at the CCSD(T)/aV5Z level.

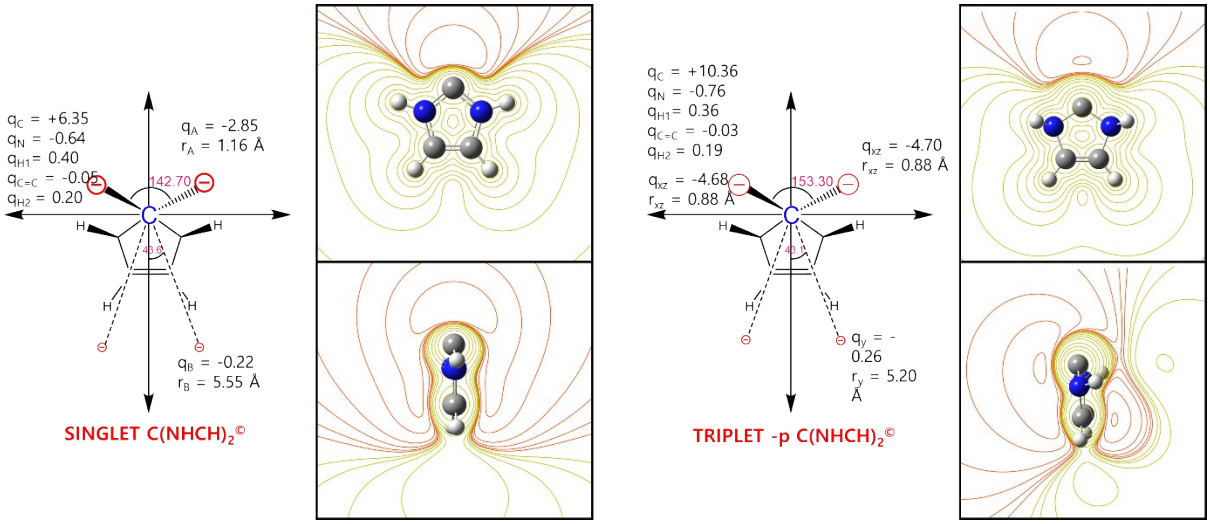


Figure S6. A 4-point model for the interaction potentials reproducing the EP maps (right) of singlet and triplet $C(NHCH)_2$© at the CCSD(T)/aVTZ level.

3. Interactions of carbenes with a Na^+/Cl^- ion or a water molecule

Table S2. Relative energies ($E^{T\text{-}S}$ in kcal/mol) of the triplet state with respect to the singlet state for CH_2, CF_2, and $C(NHCH)_2$© and their complexes with $Na^+/Cl^-/H_2O$ at the CCSD(T)/CBS on the MP2/aVTZ optimized geometry.

Species	un-complexed	Na^+	Cl^-	H_2O
CH_2	-9.25	6.18	22.08	3.01
CF_2	56.88	64.95	47.50	58.39
$C(NHCH)_2$©	86.94	98.33	84.29	91.25

Table S3. Important interaction energies (kcal/mol) and sites of carbenes with $Na^+/Cl^-/H_2O$. (Distances are in Å.)[a]

Species	Na^+	Cl^-	H of H_2O	O of H_2O
CH_2 singlet	-24.36 |C tip (2.55: C…Na)	**-38.58** |face-on (1.90: C…Cl)	-5.35 |C tip (2.097: C…H)	**-13.94** |C antiparallel face-on (1.74: C…O)
CH_2 triplet	**-8.99** |C tip (2.71: C…Na)	-6.92 |H end (2.40: H…Cl)	-1.67 |C tip (2.40: C…H)	**-1.75** |H end (O tip) (2.37: H…O)
CF_2 singlet	**-13.84** |C tip (2.62: C…Na)	-11.65 |C face-on (2.06: C…Cl)	**-2.96** |C tip (2.23: C…H)	**-2.39** |C antiparallel face-on (2.79: C…O)
CF_2 triplet	-5.73 |F end (2.38: F…Na)	**-21.12** |C tip (2.33: C…Cl)	-	**-1.71** |$O^{\delta-}$…$C^{\delta+}$, $F^{\delta-}$…$H^{\delta+}$ (2.93: C…O) -1.33 |C parallel facial on (3.21: C…O)
$C(NHCH)_2$© singlet	**-38.87** |C tip (2.45: C…Na)	-11.68 |HC=CH tip (2.71: CH…Cl)	**-9.67** |C tip (H) NH end (O lone pair) (2.00: C…H; 2.26: NH…O)	-
$C(NHCH)_2$© Triplet-p	**-27.44** |ring Ct up (2.67: C…Na) **-26.69** |C face up (2.50: C…Na)	-17.11 |NH end (2.04: NH…Cl) -14.48 |ring Ct up (3.27: C…Cl)	**-5.39** |N lone pair (2.01: N…H)	-

[a]Important interaction energies are denoted in bold.

The important interaction energies and binding sites of various carbenes with $Na^+/Cl^-/H_2O$ are summarized in Table S3. The representative interaction sites of :C are the :C tip which favors a cation or a positively charged site (such as H of H_2O) and the :C face-on site which favors an anion or a negatively charged site (such as O of H_2O). Singlet CH_2 interacts with Cl^- (-38.58 kcal/mol at the :C face-on configuration), Na^+ (-24.36 kcal, though still strong on :C tip), and O of H_2O (-13.94 kcal/mol at :C face-on antiparallel configuration). Triplet CH_2 interacts with Cl^- (-6.92 kcal/mol on CH end), Na^+ (-8.99 kcal/mol on :C tip), and H of H_2O (-1.67 kcal/mol on :C tip). Singlet CF_2 interacts with Na^+ (-13.84 kcal/mol on :C tip), Cl^- (-11.65 kcal, though still strong on :C face on configuration), and H of H_2O (-2.96 kcal/mol on :C tip). Triplet CF_2 interacts with Cl^- (-21.12 kcal/mol on C tip), Na^+ (-5.73 kcal/mol on F end), and O of H_2O (-1.71 kcal/mol with

the $O^{\delta-}\ldots C^{\delta+}$ and $F^{\delta-}\ldots H^{\delta+}$ electrostatic interactions between $O^{\delta-}H^{\delta+}$ and $C^{\delta+}F^{\delta-}$ dipoles). Singlet $C(NHCH)_2^{©}$ interacts strongly with Na^+ (-38.87 kcal/mol) at :C tip, moderately with Cl^- (-11.68 kcal/mol around two CH ends), and with H of H_2O (-9.67 kcal/mol) at :C tip (assisted by the –NH···O interaction). Triplet-p $C(NHCH)_2^{©}$ tends to interact with Na^+ (-27.44 kcal/mol on the ring-center, -26.69 kcal/mol in the :C face-up configuration), with Cl^- (-17.11 kcal/mol at the NH end, -14.48 kcal/mol at ring-center-up), and with H of H_2O (-5.39 kcal/mol at the N lone pair end). As such, the interaction sites of :C vary depending on interacting species as well as the types of carbenes and their singlet/triplet spin states.

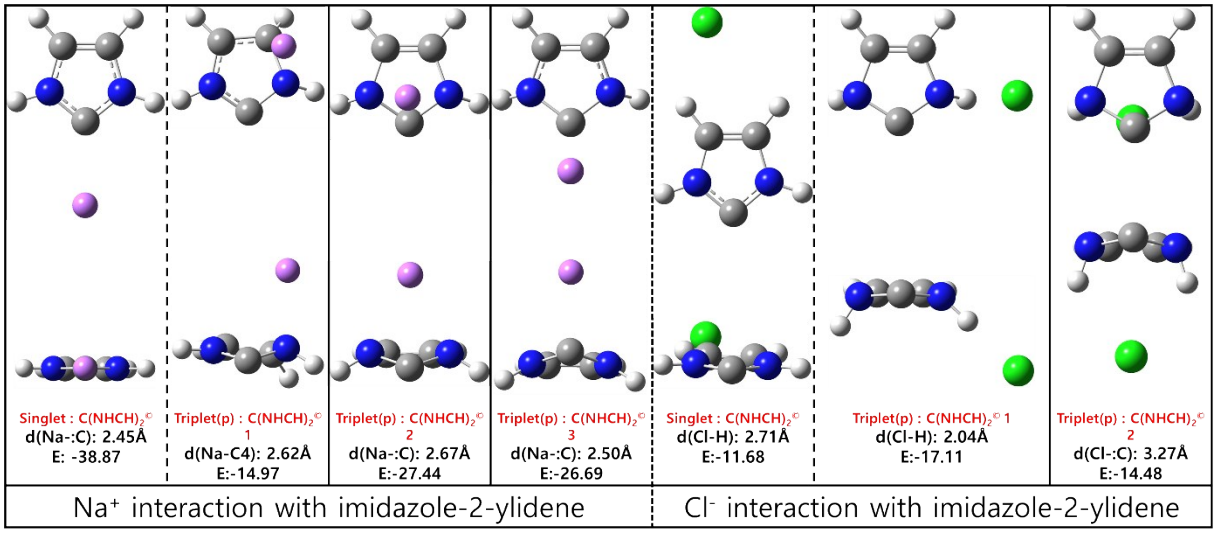


Figure S7. Interactions of singlet and triplet-p(parallel) $C(NHCH)_2^{©}$ with a Na^+/Cl^- ion and H_2O. E (kcal/mol) is the interaction energy at the CCSD(T)/CBS level on the MP2/aVTZ geometry. d is interatomic distance.

4. Electrostatic Potential (EP) for diverse Carbenes

The EP maps of singlet/triplet states for diverse carbenes (excluding already discussed representative carbenes CH_2, CF_2, $C(NHCH)_2^{©}$) are shown in Figures S8-11. Singlet highest occupied molecular orbitals (HOMOs) and triplet singly occupied molecular orbitals (SOMOs) are shown in Figures S12-15.

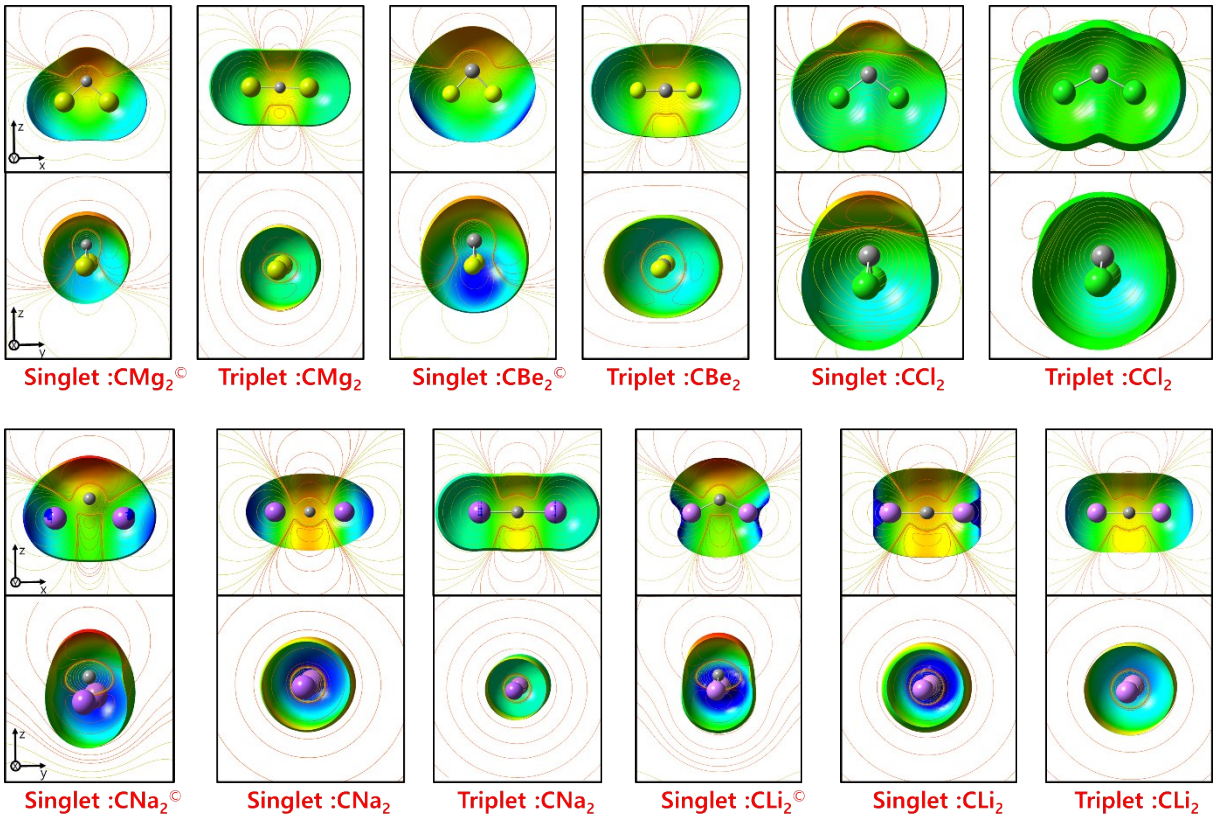


Figure S8. EP maps at the MP2/aVTZ level of singlet/triplet states of CMg_2, CBe_2, CCl_2 CNa_2, and CLi_2.

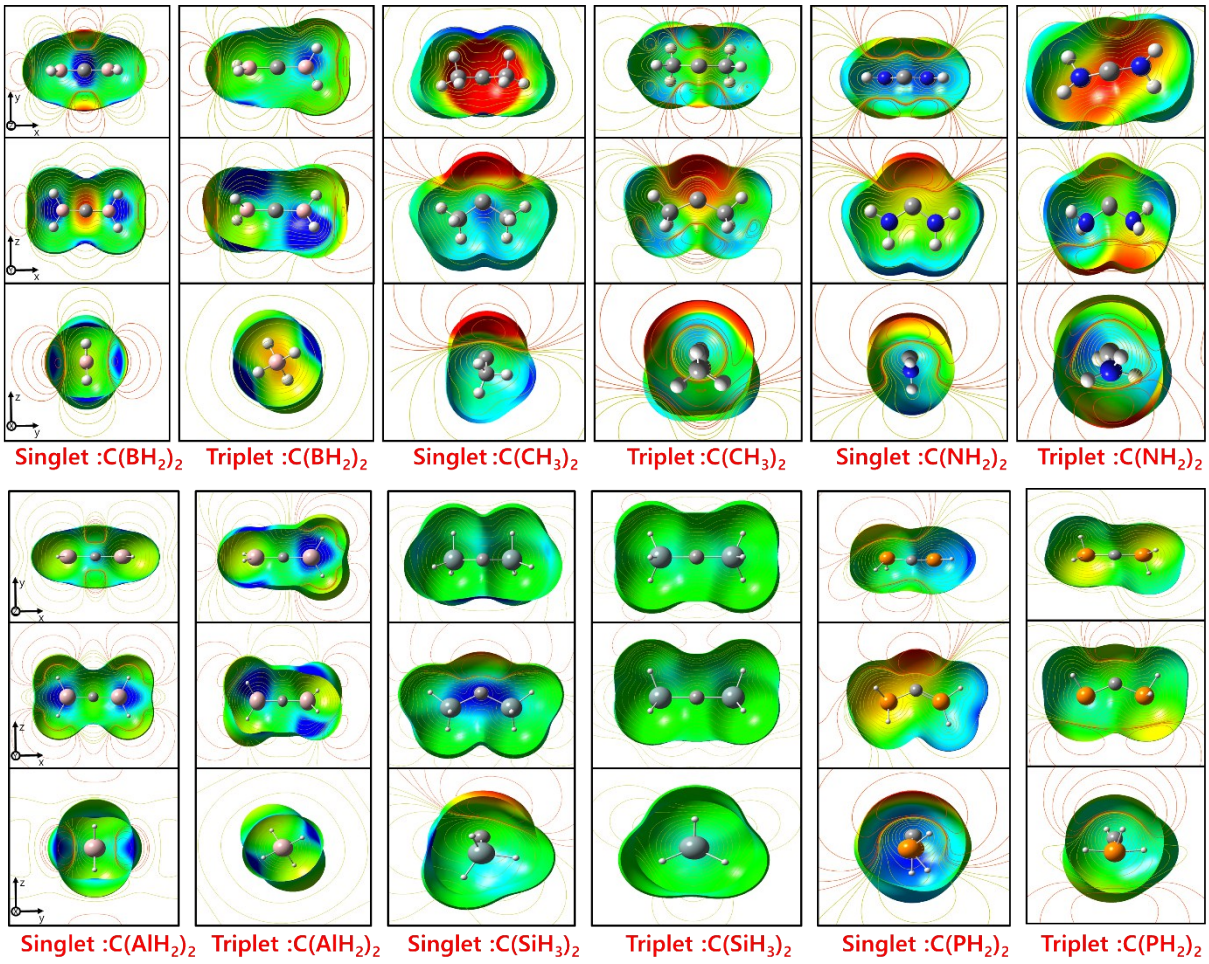


Figure S9. EP maps at the MP2/aVTZ level of singlet/triplet states of $C(BH_2)_2$, $C(CH_3)_2$, $C(NH_2)_2$, $C(AlH_2)_2$, $C(SiH_3)_2$, and $C(PH_2)_2$.

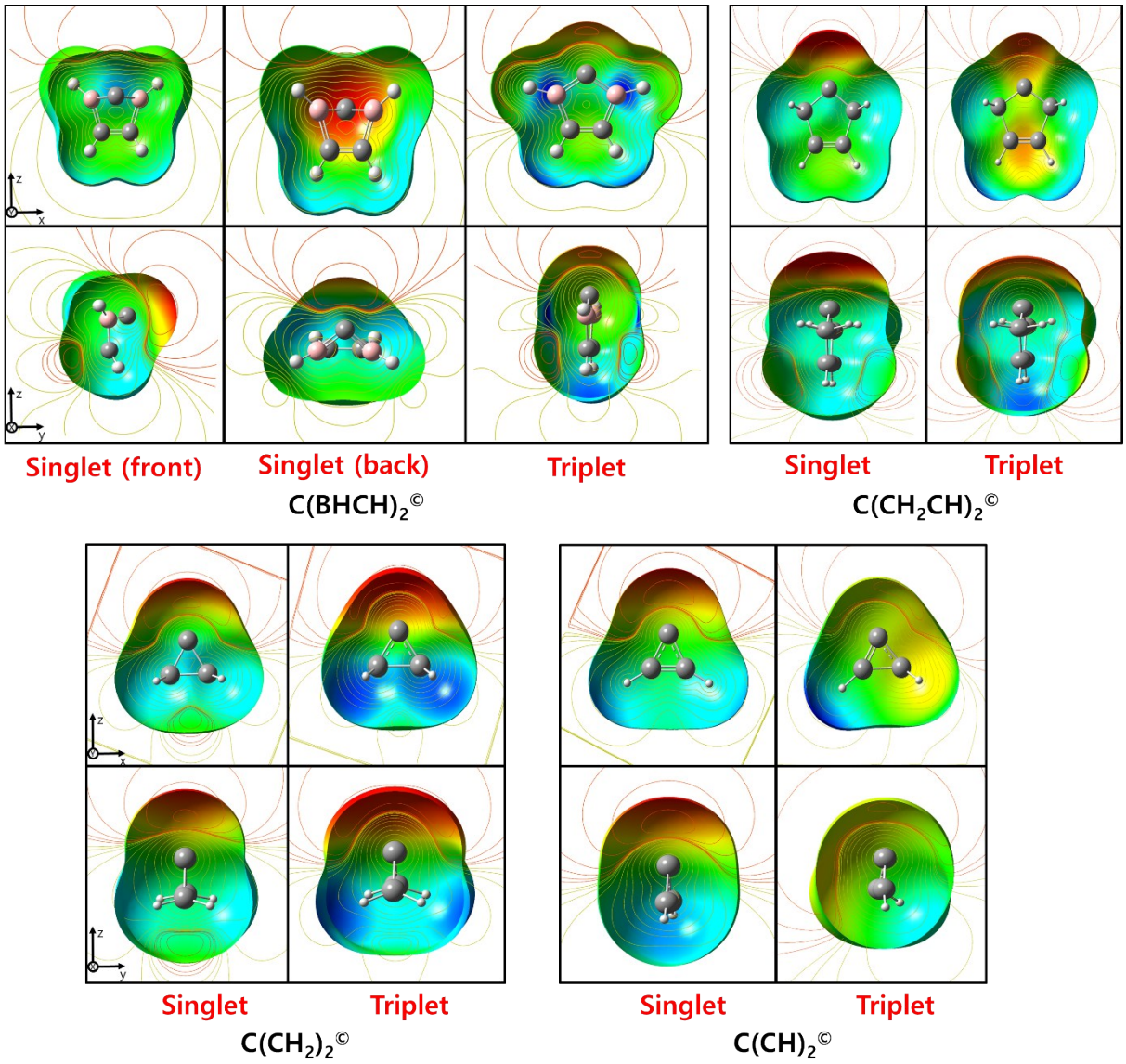
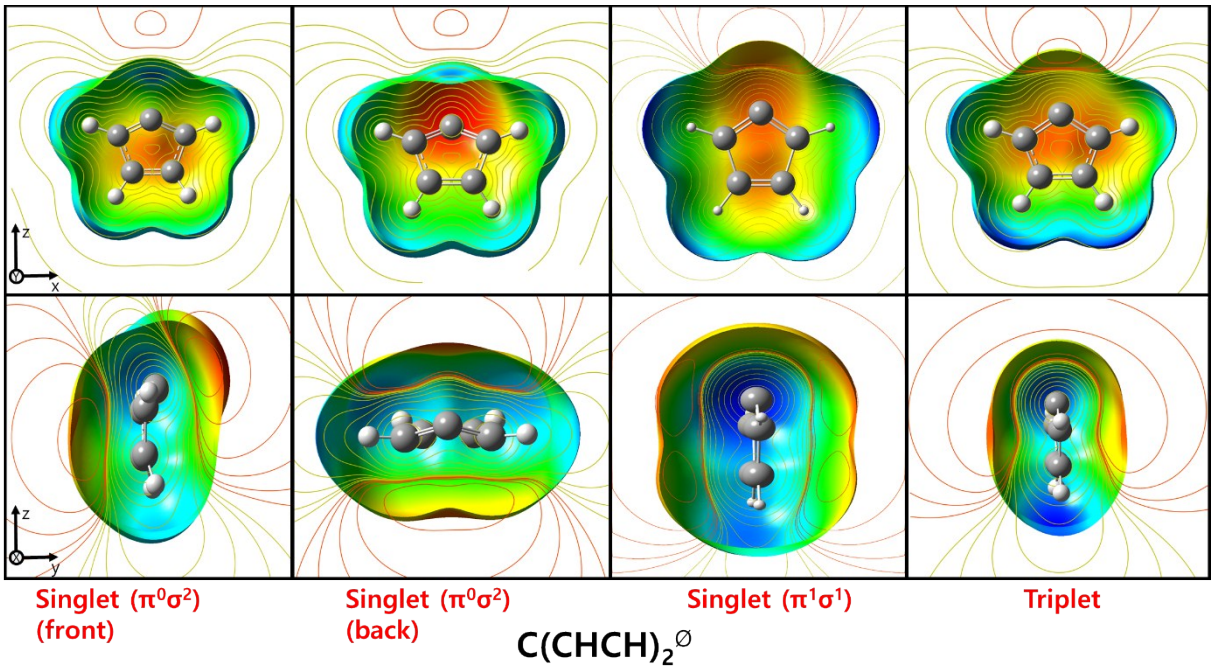


Figure S10. EP maps at the MP2/aVTZ level of singlet/triplet states of $C(BHCH)_2^{©}$, $C(CH_2CH)_2^{©}$, $(CH_2)_2^{©}$, and $(CH)_2^{©}$.



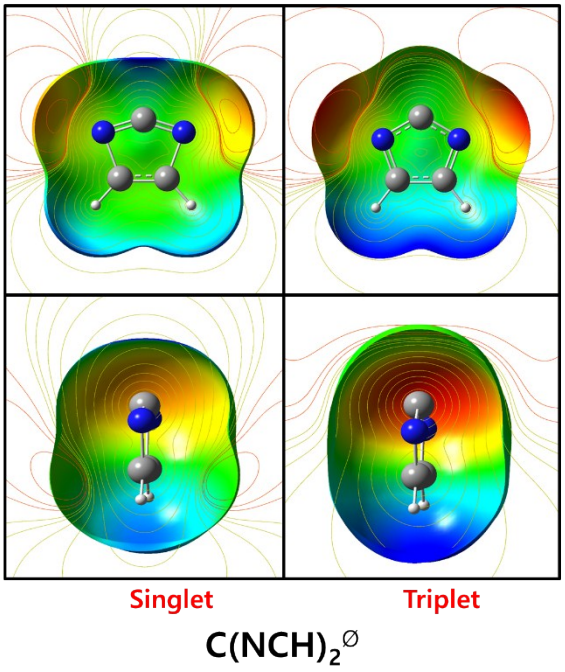


Figure S11. EP maps at the MP2/aVTZ level of singlet/triplet states of $C(CHCH)_2^{\varnothing}$ and $C(NCH)_2^{\varnothing}$

5. Frontier molecular orbitals for diverse Carbenes

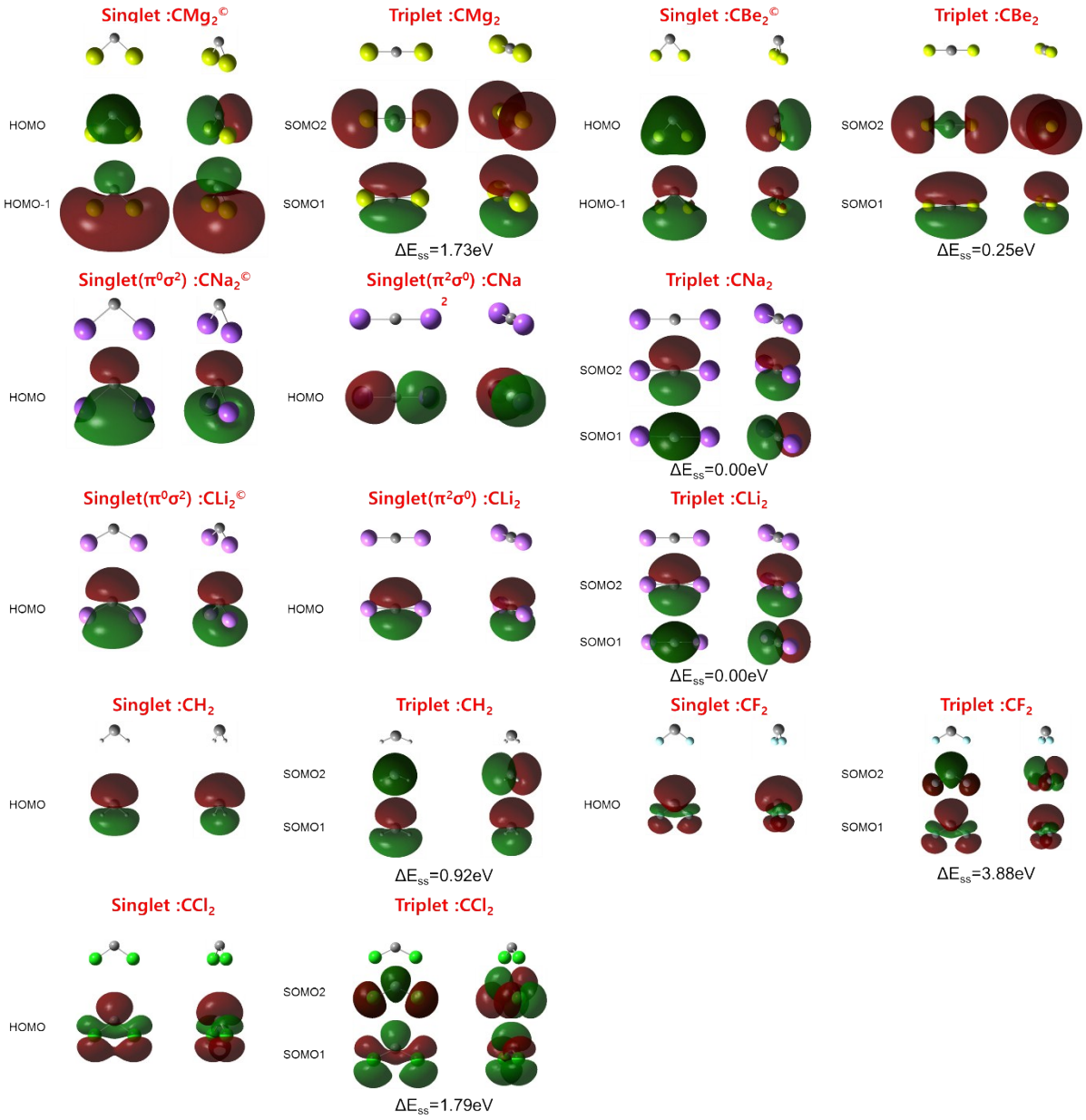


Figure S12. Frontier molecular orbitals of CMg_2, CBe_2, CNa_2, CLi_2, CH_2, CF_2 and CCl_2 at the B3LYP/aVTZ level of theory.

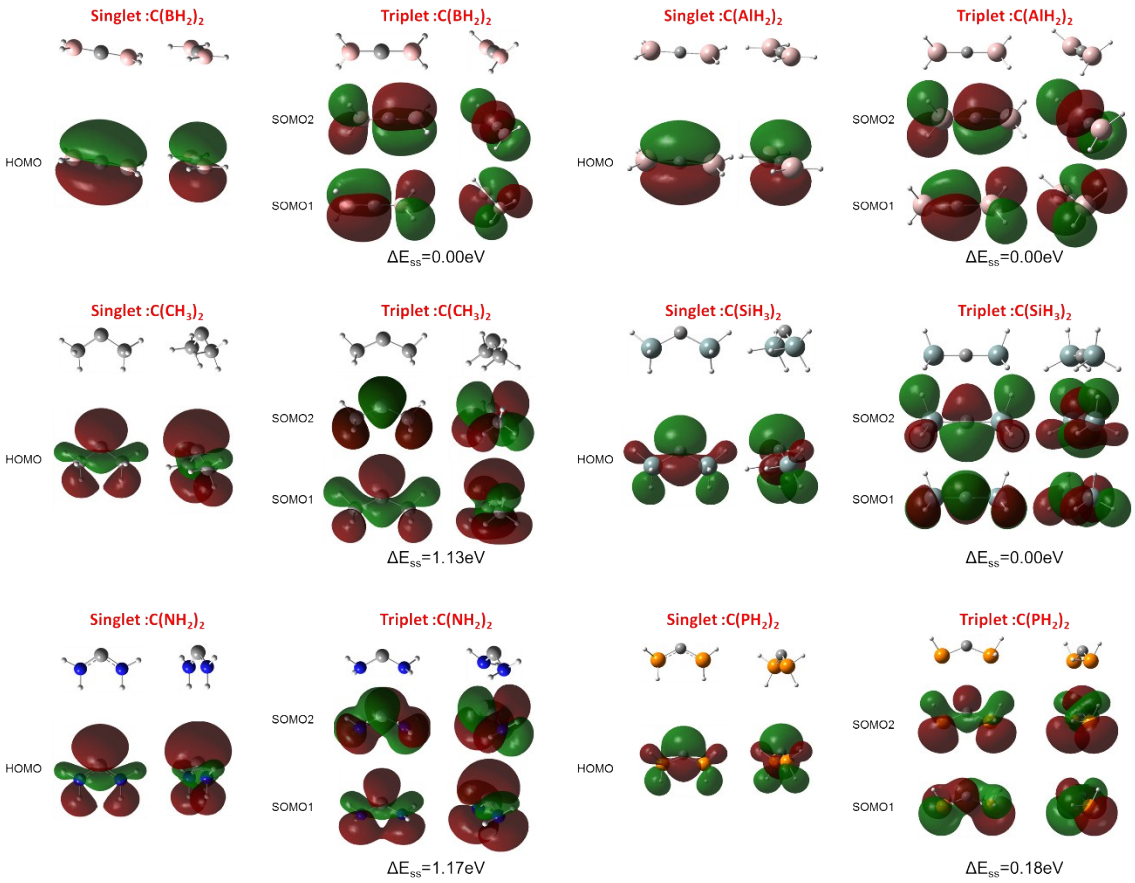


Figure S13. Frontier molecular orbitals of $C(BH_2)_2$, $C(CH_3)_2$, $C(NH_2)_2$, $C(AlH_2)_2$, $C(SiH_3)_2$, and $:C(PH_2)_2$ at the B3LYP/aVTZ level of theory.

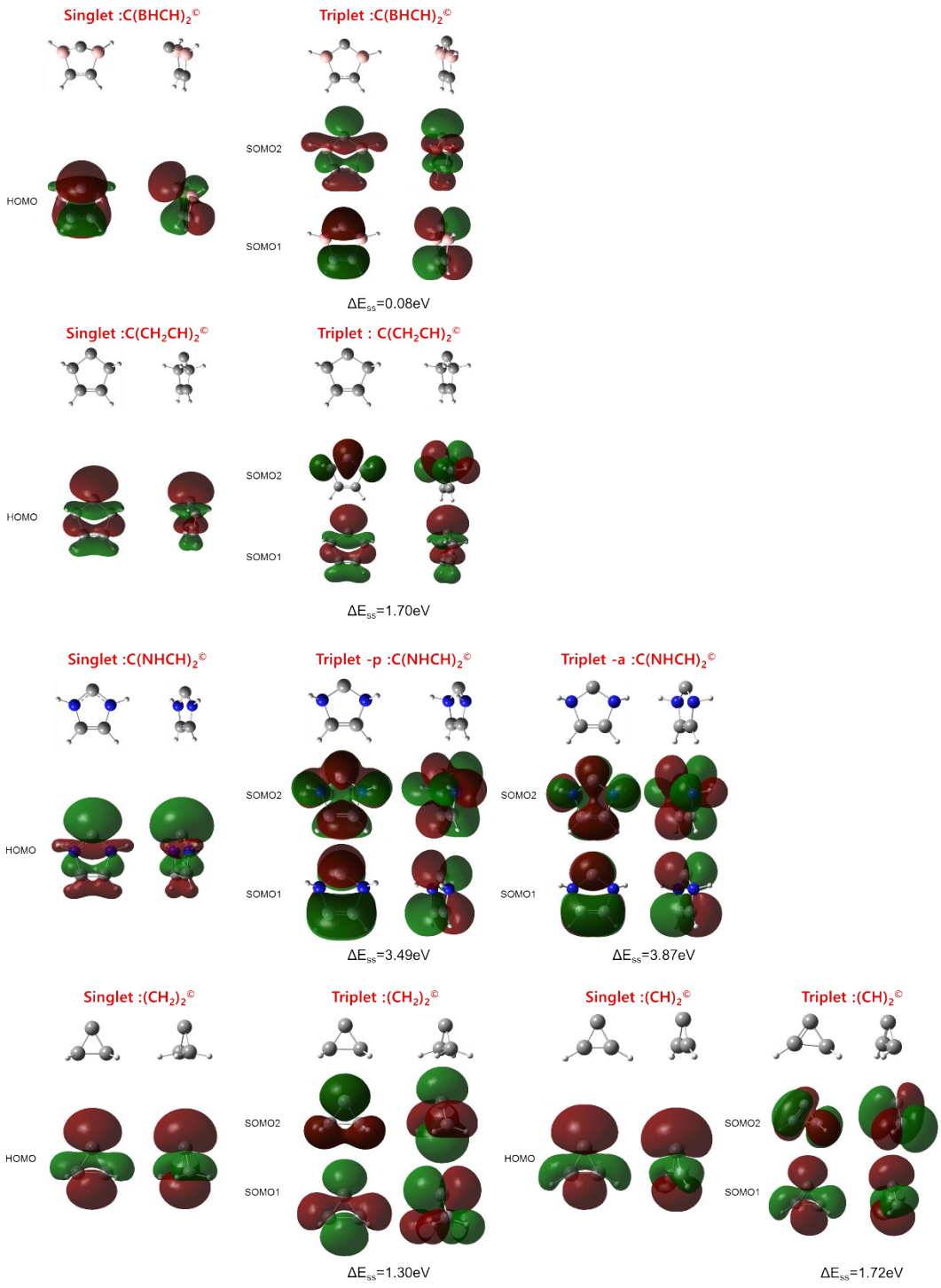


Figure S14. Frontier molecular orbitals of $C(BHCH)_2^{©}$, $C(CH_2CH)_2^{©}$, $C(NHCH)_2^{©}$, $(CH_2)_2^{©}$ and $:(CH)_2^{©}$ at the B3LYP/aVTZ level of theory.

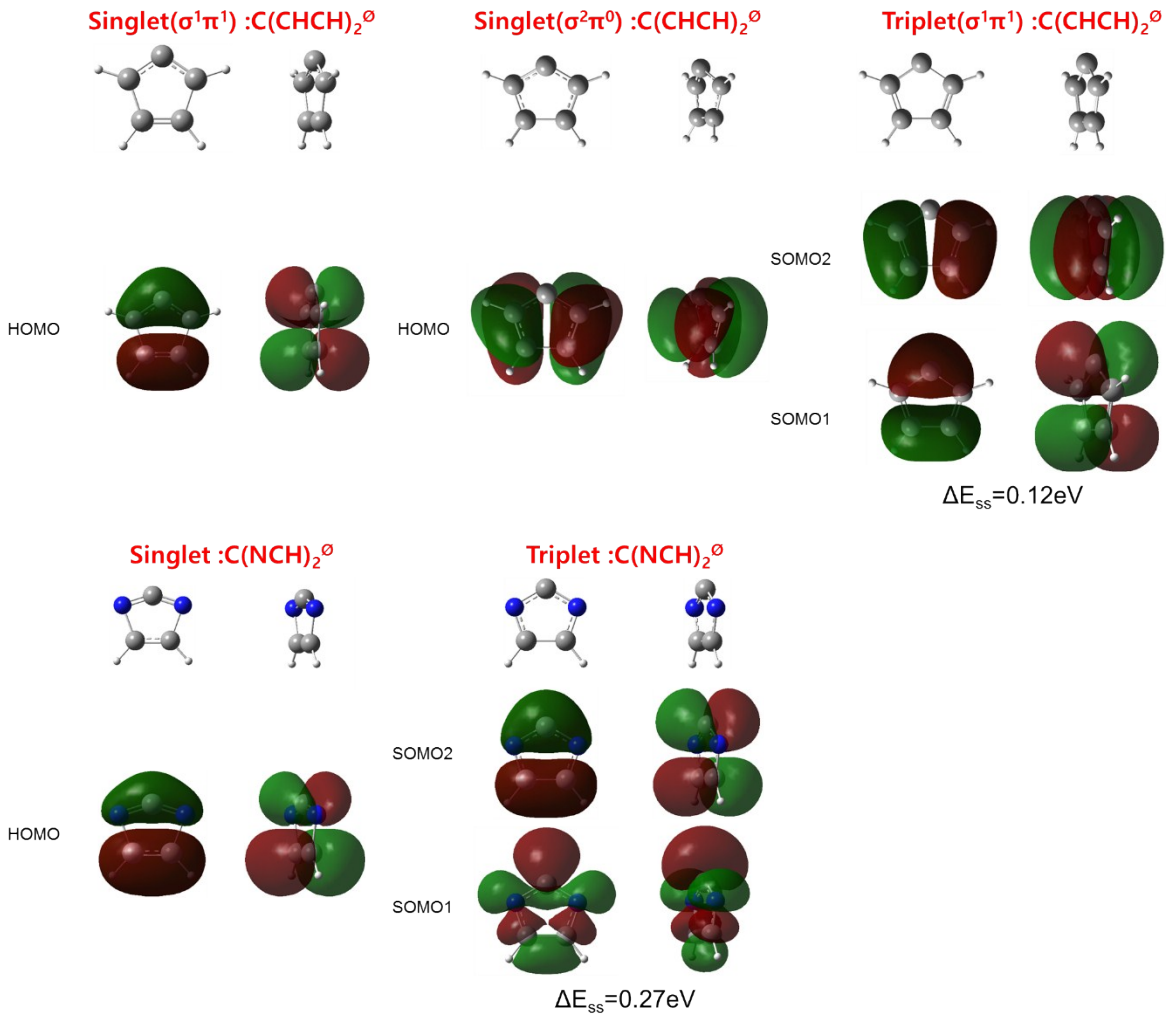


Figure S15. Frontier molecular orbitals of $C(CHCH)_2^{Ø}$, and $C(NCH)_2^{Ø}$ at the B3LYP/aVTZ level of theory.

6. Singlet-Triplet Energy Gap for diverse Carbenes

Table S4. HOMO-LUMO/SOMO1-SOMO2 energy gap/difference (E^{L-H}/E^{S1-2}) in the singlet/triplet state at the B3LYP/aVTZ, and the relative energy of the triplet with respect to the singlet (ΔE^{T-S}) in diverse carbenes.

carbenes	Singlet	Triplet	
	E^{L-H} (eV)	E^{S1-2} (eV)	E^{T-S} (kcal/mol)
CH_2	3.27	0.92	**-9.23**
CLi_2	2.34	0.00	**-2.37**
+17.77[©b]	1.30		
CNa_2	1.86	0.00	**-8.50**
+11.32[©b]	1.65		
CBe_2[©]	1.93	0.25	21.05
CMg_2[©]	1.55	1.73	14.88
CF_2	5.96	3.88	56.88
CCl_2	3.78	1.79	20.14
$C(BH_2)_2$	4.69	0.00	27.24
$C(CH_3)_2$	3.50	1.13	**1.51**
$C(NH_2)_2$	5.21	1.17	56.23
$C(AlH_2)_2$	2.32	0.00	**-8.19**
$C(SiH_3)_2$	2.23	0.00	**-22.24**
$C(PH_2)_2$	3.63	0.18	13.12
$C(CH_2)_2$[©]	3.71	1.30	15.34
$C(CH)_2$[©]	5.29	1.72	54.13
$C(BHCH)_2$[©]	4.86	0.08	18.59
$C(CH_2CH)_2$[©]	3.67	1.70	7.66
$C(NHCH)_2$[©]	5.64	3.49	86.94
		3.87	86.84
$C(CHCH)_2$[Ø]	2.49	0.12	**-5.87**[d]
+2.15[Øb]	3.12		
$C(NCH)_2$[Ø]	3.78	0.27	**0.46**

7. Geometries of diverse carbenes

CH_2*

Singlet (U)CCSD(T)/aV5Z = −39.07547337 hartree				**Triplet** (U)CCSD(T)/aV5Z = −39.09030046 hartree			
C	0.000000	0.000000	0.173574	C	0.000000	0.000000	0.107237
H	0.000000	0.858992	-0.520723	H	0.000000	0.984730	-0.321711
H	0.000000	-0.858992	-0.520723	H	0.000000	-0.984730	-0.321711

*CCSD(T)/aV5Z geometry.

CF_2*

Singlet (U)CCSD(T)/aV5Z = −237.52114803 hartree				**Triplet** (U)CCSD(T)/aV5Z = −237.43061058 hartree			
C	0.529384	0.000000	0.066173	C	0.000000	0.000000	0.500951
F	-0.264692	1.031109	0.066173	F	0.000000	1.134367	-0.166984
F	-0.264692	-1.031109	0.066173	F	0.000000	-1.134367	-0.166984

*CCSD(T)/aV5Z geometry.

CLi_2

Closed Singlet (U)CCSD(T)/aVTZ = −52.76207075 hartree				**Triplet** (U)CCSD(T)/aVTZ = −52.79479034 hartree			
C	0.000000	0.000000	0.598063	C	0.000000	0.000000	0.006184
Li	0.000000	1.667700	-0.510309	Li	0.000000	1.968093	-0.002886
Li	0.000000	-1.667700	-0.510309	Li	0.000000	-1.968093	-0.002886
Open Singlet (U)CCSD(T)/aVTZ = −52.7835295 hartree							
C	0.000000	0.000000	0.000000				
Li	0.000000	0.000000	1.964577				
Li	0.000000	0.000000	-1.964577				

CNa_2

Closed Singlet (U)CCSD(T)/aVTZ = −361.56930762 hartree				**Triplet** (U)CCSD(T)/aVTZ = −361.601091 hartree			
C	0.000000	0.000000	1.248443	C	0.000000	0.000000	0.000000
Na	0.000000	1.848988	-0.348090	Na	0.000000	0.000000	2.340000
Na	0.000000	-1.848988	-0.348090	Na	0.000000	0.000000	-2.340000
Open Singlet (U)CCSD(T)/aVTZ = −361.5881342 hartree							
C	0.000000	-0.000467	0.000000				
Na	2.338375	0.000127	0.000000				
Na	-2.338375	0.000127	0.000000				

CMg_2

Singlet (U)CCSD(T)/aVTZ = −437.16820622 hartree				**Triplet** (U)CCSD(T)/aVTZ = −437.14419067 hartree			
C	0.000000	0.000000	1.109266	C	0.000000	0.000000	0.000000
Mg	0.000000	1.489720	-0.278501	Mg	0.000000	0.000000	2.003809
Mg	0.000000	-1.489720	-0.278501	Mg	0.000000	0.000000	-2.003809

CCl_2

Singlet (U)CCSD(T)/aVTZ = −957.40113630 hartree				**Triplet** (U)CCSD(T)/aVTZ = −957.36862128 hartree			
C	0.000000	0.000000	0.851280	C	0.000000	0.000000	0.633942
Cl	0.000000	-1.407873	-0.152065	Cl	0.000000	-1.509575	-0.112795
Cl	0.000000	1.407873	-0.152065	Cl	0.000000	1.509575	-0.112795

$C(BH_2)_2$

Singlet (U)CCSD(T)/aVTZ = −89.90271524 hartree				**Triplet** (U)CCSD(T)/aVTZ = −89.86106166 hartree			
C	0.000000	0.000000	-0.000002	C	0.000000	0.000000	0.000000
B	1.435015	0.000089	0.000023	B	1.495892	0.000000	0.000000
B	-1.435015	-0.000089	-0.000021	B	-1.495893	0.000000	0.000000
H	-2.009290	1.047851	0.000448	H	-2.090980	-0.977989	0.344738
H	-2.008221	-1.048673	-0.000504	H	-2.090979	0.977990	-0.344738
H	2.009292	-1.047850	0.000510	H	2.090979	-0.344738	-0.977989
H	2.008219	1.048674	-0.000443	H	2.090979	0.344739	0.977990

$C(CH_3)_2$

Singlet (U)CCSD(T)/aVTZ = −117.57968186 hartree				**Triplet** (U)CCSD(T)/aVTZ = −117.57836204 hartree			
C	-0.036658	-0.677958	0.000000	C	0.000067	-0.497161	0.000000
C	-0.018391	0.155538	1.227410	C	0.000005	0.112371	1.346402
C	-0.018391	0.155538	-1.227410	C	0.000005	0.112371	-1.346402
H	1.068787	0.239648	-1.413133	H	0.886799	0.744111	-1.502330
H	-0.419193	-0.364009	-2.098964	H	0.000239	-0.653983	-2.125288
H	-0.422612	1.174548	-1.143030	H	-0.887061	0.743697	-1.502457
H	-0.419193	-0.364009	2.098964	H	0.000239	-0.653983	2.125288
H	1.068787	0.239648	1.413133	H	0.886799	0.744111	1.502330
H	-0.422612	1.174548	1.143030	H	-0.887061	0.743697	1.502457

$C(NH_2)_2$

Singlet (U)CCSD(T)/aVTZ = −149.74083426 hartree				**Triplet** (U)CCSD(T)/aVTZ = −149.65343492 hartree			
C	0.000000	0.000000	0.612142	C	0.000000	0.000000	0.480585
N	-0.000040	1.114980	-0.140100	N	-0.004730	1.223448	-0.188832
N	0.000040	-1.114980	-0.140100	N	0.004730	-1.223448	-0.188832
H	-0.000133	-2.006457	0.318482	H	0.493886	-1.947760	0.318541
H	-0.000137	-1.125040	-1.157144	H	-0.914447	-1.556658	-0.472591
H	0.000133	2.006457	0.318482	H	-0.493886	1.947760	0.318541
H	0.000137	1.125040	-1.157144	H	0.914447	1.556658	-0.472591

$C(AlH_2)_2$

Singlet (U)CCSD(T)/aVTZ = −524.28068086 hartree				**Triplet** (U)CCSD(T)/aVTZ = −524.29765857 hartree			
C	0.000000	0.000000	0.000000	C	0.000000	0.000000	0.000000
Al	0.000000	0.000000	1.910873	Al	0.000000	0.000000	1.938234
Al	0.000000	0.000000	-1.910873	Al	0.000000	0.000000	-1.938234
H	0.000000	-1.413961	-2.626433	H	-1.381158	0.000000	-2.718672
H	0.000000	1.413961	-2.626433	H	1.381158	0.000000	-2.718672
H	0.000000	1.413961	2.626433	H	0.000000	1.381158	2.718672
H	0.000000	-1.413961	2.626433	H	0.000000	-1.381158	2.718672

$C(SiH_3)_2$

Singlet (U)CCSD(T)/aVTZ = −619.59026584 hartree				**Triplet** (U)CCSD(T)/aVTZ = −619.62629417 hartree			
C	0.028564	-0.790188	0.000000	C	0.000000	-0.000058	0.000000
Si	-0.008358	0.088414	1.640870	Si	0.000000	-0.000061	1.838355
Si	-0.008358	0.088414	-1.640870	Si	0.000000	-0.000061	-1.838355
H	1.456290	0.379501	-1.723351	H	-1.209183	-0.698012	-2.347293
H	-0.412957	-0.814171	-2.745769	H	0.000000	1.396113	-2.347285
H	-0.776737	1.359960	-1.759547	H	1.209183	-0.698012	-2.347293
H	-0.412957	-0.814171	2.745769	H	0.000000	1.396113	2.347285
H	1.456290	0.379501	1.723351	H	-1.209183	-0.698012	2.347293
H	-0.776737	1.359960	1.759547	H	1.209183	-0.698012	2.347293

$C(PH_2)_2$

Singlet (U)CCSD(T)/aVTZ = −722.13745614 hartree				**Triplet** (U)CCSD(T)/aVTZ = −722.11951765 hartree			
C	-0.086985	-0.726970	0.126136	C	0.000000	0.000000	0.522707
P	-1.589062	0.029496	0.418434	P	-0.001454	1.635349	-0.164654
P	1.405738	0.080272	-0.056228	P	0.001454	-1.635349	-0.164654
H	1.512198	1.321283	0.626508	H	0.341168	-2.363877	1.004338
H	2.384957	-0.683330	0.604324	H	-1.387445	-1.947391	-0.108227
H	-2.558954	-0.645032	-0.344723	H	-0.341168	2.363877	1.004338
H	-1.709708	1.352428	-0.084279	H	1.387445	1.947391	-0.108227

$C(CH_2)_2$©

Singlet (U)CCSD(T)/aVTZ = −116.33501857 hartree				**Triplet** (U)CCSD(T)/aVTZ = −116.31119988 hartree			
C	-0.003796	0.808526	0.000000	C	0.000608	0.850125	0.000000
C	0.577695	-0.565683	0.000000	C	0.499789	-0.687692	0.000000
C	-0.918296	-0.388573	0.000000	C	-0.893267	-0.289957	0.000000
H	-0.007737	1.397607	0.911253	H	0.190706	1.403357	0.916731
H	-0.007737	1.397607	-0.911253	H	0.190706	1.403357	-0.916731
H	0.997777	-0.978675	0.911253	H	0.978571	-1.023803	0.916731
H	0.997777	-0.978675	-0.911253	H	0.978571	-1.023803	-0.916731

$C(CH)_2$ Ø

Singlet (U)CCSD(T)/aVTZ = −115.05764141 hartree				**Triplet** (U)CCSD(T)/aVTZ = −115.14244039 hartree			
C	-0.726948	-0.301258	0.006670	C	-0.000627	0.739805	0.000000
C	0.825338	-0.251258	-0.146058	C	0.582514	-0.456058	0.000000
C	-0.097473	0.845000	0.040833	C	-0.844665	-0.411885	0.000000
H	-1.535890	-1.006234	0.039591	H	0.077223	1.815093	0.000000
H	1.544341	-0.705465	0.533049	H	1.477684	-1.056870	0.000000

$C(BHCH)_2$©

Singlet (U)CCSD(T)/aVTZ = −165.94722486 hartree				**Triplet** (U)CCSD(T)/aVTZ = −165.91918133 hartree			
C	0.000001	-1.049166	0.668412	C	0.000000	0.000000	1.395195
C	-0.691485	0.867304	-0.037929	C	0.000000	0.687398	-0.955031
C	0.691481	0.867306	-0.037929	C	0.000000	-0.687398	-0.955031
B	1.158114	-0.627524	-0.182306	B	0.000000	1.273291	0.520213
B	-1.158113	-0.627527	-0.182307	B	0.000000	-1.273291	0.520213
H	2.053049	-1.192637	-0.712706	H	0.000000	-2.423005	0.828384
H	-2.053045	-1.192643	-0.712708	H	0.000000	2.423005	0.828384
H	-1.276836	1.722649	0.295895	H	0.000000	1.256353	-1.882772
H	1.276829	1.722653	0.295895	H	0.000000	-1.256353	-1.882772

$C(CH_2CH)_2$©

Singlet (U)CCSD(T)/aVTZ = −193.63493424 hartree				**Triplet** (U)CCSD(T)/aVTZ = −193.62371091 hartree			
C	-0.000043	-1.351632	-0.000444	C	0.000000	0.000000	-1.264616
C	-0.670688	1.003839	-0.000061	C	0.000000	0.671732	0.946558
C	0.670752	1.003797	-0.000072	C	0.000000	-0.671732	0.946558
C	-1.181402	-0.422296	0.000191	C	0.000000	1.262204	-0.456657
C	1.181376	-0.422370	0.000038	C	0.000000	-1.262204	-0.456657
H	-1.808097	-0.683335	0.866296	H	-0.881599	1.890980	-0.636258
H	1.808578	-0.683497	0.865721	H	-0.881599	-1.890980	-0.636258
H	1.809783	-0.683380	-0.864761	H	0.881599	-1.890980	-0.636258
H	-1.810349	-0.683314	-0.864186	H	0.881599	1.890980	-0.636258
H	-1.303375	1.883138	-0.000052	H	0.000000	1.289618	1.837047
H	1.303495	1.883056	-0.000085	H	0.000000	-1.289618	1.837047

$C(NHCH)_2$©

Singlet (U)CCSD(T)/aVTZ = −225.80871641 hartree				**Triplet - p** (U)CCSD(T)/aVTZ = −225.67210234 hartree			
C	-0.000029	-1.275831	-0.000151	C	-0.000261	-1.195895	-0.127952
C	-0.681203	0.932381	-0.000057	C	-0.673446	0.907041	-0.003526
C	0.681246	0.932353	-0.000122	C	0.673897	0.906781	-0.003661
N	-1.046767	-0.398386	-0.000044	N	-1.172597	-0.421146	-0.033639
N	1.046749	-0.398429	-0.000035	N	1.172368	-0.421594	-0.033551
H	1.997760	-0.723729	0.001064	H	1.847144	-0.652902	0.690864
H	-1.997792	-0.723645	0.000880	H	-1.847517	-0.652241	0.690724
H	-1.383350	1.745857	0.000356	H	-1.343649	1.748664	-0.050072
H	1.383429	1.745798	0.000235	H	1.344487	1.748092	-0.050357

	Triplet - a (U)CCSD(T)/aVTZ = −225.67225378 hartree			
	C	0.000000	0.000000	1.210686
	C	-0.002215	0.672326	-0.913301
	C	0.002215	-0.672326	-0.913301
	N	0.060882	1.179494	0.423669
	N	-0.060882	-1.179494	0.423669
	H	0.650815	-1.871720	0.635873
	H	-0.650815	1.871720	0.635873
	H	-0.029699	1.349057	-1.752117
	H	0.029699	-1.349057	-1.752117

$C(CHCH)_2$ [Ø]

Closed Singlet (U)CCSD(T)/aVTZ = −192.40590194 hartree				**Triplet** (U)CCSD(T)/aVTZ = −192.41905133 hartree			
C	-0.241346	-1.130519	0.000000	C	0.000000	0.000000	1.222852
C	0.005145	0.847290	-0.741805	C	0.000000	0.742221	-0.874577
C	0.005145	0.847290	0.741805	C	0.000000	-0.742221	-0.874577
C	0.112963	-0.452471	-1.200003	N	0.000000	1.190639	0.426030
C	0.112963	-0.452471	1.200003	N	0.000000	-1.190639	0.426030
H	0.080645	-0.818450	-2.212218	H	0.000000	2.209286	0.778142
H	0.080645	-0.818450	2.212218	H	0.000000	-2.209286	0.778142
H	-0.289204	1.705064	-1.334524	H	0.000000	1.356875	-1.764626
H	-0.289204	1.705064	1.334524	H	0.000000	-1.356875	-1.764626
Open Singlet[*] (U)CCSD/aVTZ = −192.3687017 hartree				(U)CCSD/aVTZ = −192.3779954 hartree			
C	0.000000	0.000000	1.257140	C	0.000000	1.186903	0.423472
C	0.000000	1.141616	0.472496	C	0.000000	0.741000	-0.869826
C	0.000000	-1.141616	0.472496	C	0.000000	-0.741000	-0.869826
C	0.000000	0.677049	-0.934983	C	0.000000	-1.186903	0.423472
C	0.000000	-0.677049	-0.934983	C	0.000000	0.000000	1.220915
H	0.000000	2.169441	0.797154	H	0.000000	2.203786	0.774043
H	0.000000	-2.169441	0.797154	H	0.000000	1.353228	-1.758662
H	0.000000	1.328909	-1.793655	H	0.000000	-1.353228	-1.758662
H	0.000000	-1.328909	-1.793655	H	0.000000	-2.203786	0.774043

[*]CCSD/aVTZ geometry.

$C(NCH)_2$ ø

Singlet (U)CCSD(T)/aVTZ = −224.49708443 hartree				**Triplet** (U)CCSD(T)/aVTZ = −224.49811150 hartree			
C	0.000000	0.693225	-0.833679	C	0.000000	0.737592	-0.811496
C	0.000000	-0.693225	-0.833679	C	0.000000	-0.737592	-0.811496
C	0.000000	0.000000	0.924048	C	0.000000	0.000000	1.129466
N	0.000000	-1.195540	0.547269	N	0.000000	-1.174070	0.444813
N	0.000000	1.195540	0.547269	N	0.000000	1.174070	0.444813
H	0.000000	1.416474	-1.633074	H	0.000000	1.406424	-1.661678
H	0.000000	-1.416474	-1.633074	H	0.000000	-1.406424	-1.661678