Stability of Alkyl Carbocations

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Contents

Figure S8. Schematic MO diagram for a) H_3–C^+ and b) Me_3–C^+. The SOMO–SOMO interactions are shown in black and the 2c–3e$^-$ interactions are colored red. Blue represents the hyperconjugation between the Me_mH_{3-m} ··· σ_{C-H}-orbital and the C^+···. Computed at ZORA-(U)M06-2X/QZ4P.

Figure S9. Schematic MO diagram for the hyperconjugation between Me_mH_{3-m} ··· σ_{C-H} and C^+··· with m = 0–3. Computed at ZORA-(U)M06-2X/QZ4P at the equilibrium geometries.

Table S1. C–X (X = F, Cl, Br, H, CH_3) bond lengths (in Å), the heterolytic bond dissociation energies (ΔE_{BDE}^{hetero} and ΔH_{BDE}^{hetero}; in kcal mol^{-1}), and the stability analysis in terms of the partial reactions in a thermochemical cycle.[a]

Table S2. Heterolytic bond dissociation enthalpies ΔH_{BDE}^{hetero} (in kcal mol^{-1}) for C–X (X= F, Cl, Br, I, H, CH_3).

Table S3. C–X (X = F, Cl, Br, I, H, CH_3) bond lengths (in Å), the heterolytic bond dissociation energies (ΔE_{BDE}^{hetero} and ΔH_{BDE}^{hetero}; in kcal mol^{-1}), and the stability analysis in terms of the partial reactions in a thermochemical cycle.

Table S4. C–X (X = F, Cl, Br, I, H, CH_3) bond lengths (in Å), the heterolytic bond dissociation energies (ΔE_{BDE}^{hetero} and ΔH_{BDE}^{hetero}; in kcal mol^{-1}), and the stability analysis in terms of the partial reactions in a thermochemical cycle.

Table S5. C–X (X = F, Cl, Br, I, H, CH_3) bond lengths (in Å), the heterolytic bond dissociation energies (ΔE_{BDE}^{hetero} and ΔH_{BDE}^{hetero}; in kcal mol^{-1}), and the stability analysis in terms of the partial reactions in a thermochemical cycle.

Table S6. C–X (X = F, Cl, Br, I, H, CH_3) bond lengths (in Å), the heterolytic bond dissociation energies (ΔE_{BDE}^{hetero} and ΔH_{BDE}^{hetero}; in kcal mol^{-1}), and the stability analysis in terms of the partial reactions in a thermochemical cycle.

Table S7. Cartesian coordinates (in Å), energies (E, H and G, in kcal mol^{-1}), and number of imaginary vibrational frequencies (N_{imag}) of all stationary points and transition states in the gas phase, computed at ZORA-(U)M06-2X/QZ4P.

Table S8. Cartesian coordinates (in Å), energies (E, H and G, in kcal mol^{-1}), and number of imaginary vibrational frequencies (N_{imag}) of all stationary points and transition states in the gas phase, computed at COSMO(H_2O)-ZORA-(U)M06-2X/QZ4P.

Table S9. Cartesian coordinates (in Å), energies (E, H and G, in kcal mol^{-1}), and number of imaginary vibrational frequencies (N_{imag}) of all stationary points and transition states in the gas phase, computed at ZORA-(U)BLYP-D3(BJ)/QZ4P.

Table S10. Cartesian coordinates (in Å), energies (E, H and G, in kcal mol^{-1}), and number of imaginary vibrational frequencies (N_{imag}) of all stationary points and transition states in the gas phase, computed at COSMO(H_2O)-ZORA-(U)BLYP-D3(BJ)/QZ4P.

Table S11. Cartesian coordinates (in Å), energies (E, H and G, in kcal mol^{-1}), and number of imaginary vibrational frequencies (N_{imag}) of all stationary points and transition states in the gas

phase, computed at ZORA-(U)PB86-D3(BJ)/QZ4P.

Table S12. Cartesian coordinates (in Å), energies (E, H and G, in kcal mol^{-1}), and number of imaginary vibrational frequencies (N_{imag}) of all stationary points and transition states in the gas phase, computed at COSMO(H_2O)-ZORA-(U)B86-D3(BJ)/QZ4P.

Table S13. Cartesian coordinates (in Å), energies (E, H and G, in kcal mol^{-1}), and number of imaginary vibrational frequencies (N_{imag}) of all stationary points and transition states in the gas phase, computed at COSMO(DMSO)-ZORA-(U)M06-2X/QZ4P.

Table S14. Cartesian coordinates (in Å), energies (E, H and G, in kcal mol^{-1}), and number of imaginary vibrational frequencies (N_{imag}) of all stationary points and transition states in the gas phase, computed at COSMO(DCM)-ZORA-(U)M06-2X/QZ4P.

References

Computational methods

All density functional theory (DFT) calculations were performed using the Amsterdam Density Functional (ADF2018.105) software package.[1] The meta-hybrid generalized gradient approximation (GGA) functional M06-2X was used for calculating the geometries and energies.[2] Scalar relativistic effects are accounted for using the zeroth-order regular approximation (ZORA).[3] The basis set used, denoted QZ4P, is of quadruple-ζ quality for all atoms and has been improved by four sets of polarization functions.[4] The accuracies of the fit scheme (Zlm fit) and the integration grid (Becke grid) were, for all calculations, set to VERYGOOD.[5] No geometry restrictions were used unless otherwise stated. All calculated stationary points have been verified by performing a vibrational analysis at ZORA-M06-2X/QZ4P.[6] All solution phase calculations used COSMO to simulate bulk solvation (DCM, DMSO, water).[7] For these calculations, the optimized stationary points in the gas phase were fully reoptimized at COSMO-ZORA-M06-2X/QZ4P. The radical fragments were treated spin-unrestricted and the PyFrag 2019 program was used for analyzing the bond dissociation. The optimized structures were illustrated using CYLview.[8] Additionally, all systems were computed (geometry optimization and frequencies) at (COSMO-)ZORA-BLYP-D3(BJ) and (COSMO-)ZORA-BP86-D3(BJ) to study the effect of the computational method on the found trends. These data all show the same trend as our initial (COSMO-)ZORA-M06-2X/QZ4P results.

Thermochemistry

Enthalpies at 298.15 K and 1 atmosphere (ΔH_{298}) were calculated from electronic bond energies (ΔE) and vibrational frequencies using standard thermochemistry relations for an ideal gas, according to Equation (S1):[9]

$$\Delta H_{298} = \Delta E + \Delta E_{\text{trans},298} + \Delta E_{\text{rot},298} + \Delta E_{\text{vib},0} + \Delta(\Delta E_{\text{vib},0})_{298} + \Delta(pV) \quad \text{(S1)}$$

Here, $\Delta E_{\text{trans},298}$, $\Delta E_{\text{rot},298}$ and $\Delta E_{\text{vib},0}$ are the differences between the reactant and products in translational, rotational and zero-point vibrational energy, respectively. $\Delta(\Delta E_{\text{vib},0})_{298}$ is the change in the vibrational energy difference as one goes from 0 to 298.15 K. The vibrational energy corrections are identical to our frequency calculations. The molar work term $\Delta(pV)$ is $(\Delta n)RT$; $\Delta n = +1$ for one reactant dissociating into the two products. Thermal corrections for the electronic energy are neglected.

Activation strain and energy decomposition analysis

The activation strain model (ASM)[10] is a fragment-based approach in which the electronic energy, ΔE, is decomposed into two components:

$$\Delta E = \Delta E_{\text{strain}} + \Delta E_{\text{int}} \tag{S2}$$

Here, the strain energy, ΔE_{strain}, is the amount of energy required to deform the fragments from th

We further analyze ΔE_{int} in the framework of the canonical Kohn-Sham molecular orbital (MO) m

$$\Delta E_{\text{int}} = \Delta V_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{oi}} \tag{S3}$$

The term ΔV_{elstat} corresponds to the classical electrostatic interaction between the unperturbed charge distributions of the fragments in the geometry they possess in the complex. This term is usually attractive. The (steric) Pauli repulsion, ΔE_{Pauli}, between these fragments comprises the destabilizing interactions associated with the Pauli principle for fermions between occupied orbitals and is responsible for the steric repulsion. The orbital interaction, ΔE_{oi}, between these fragments in any MO model, and therefore also in Kohn-Sham theory, accounts for electron-pair bonding, charge transfer (empty/occupied orbital mixing between different fragments), and polarization (empty/occupied orbital mixing on one fragment due to the presence of another fragment).

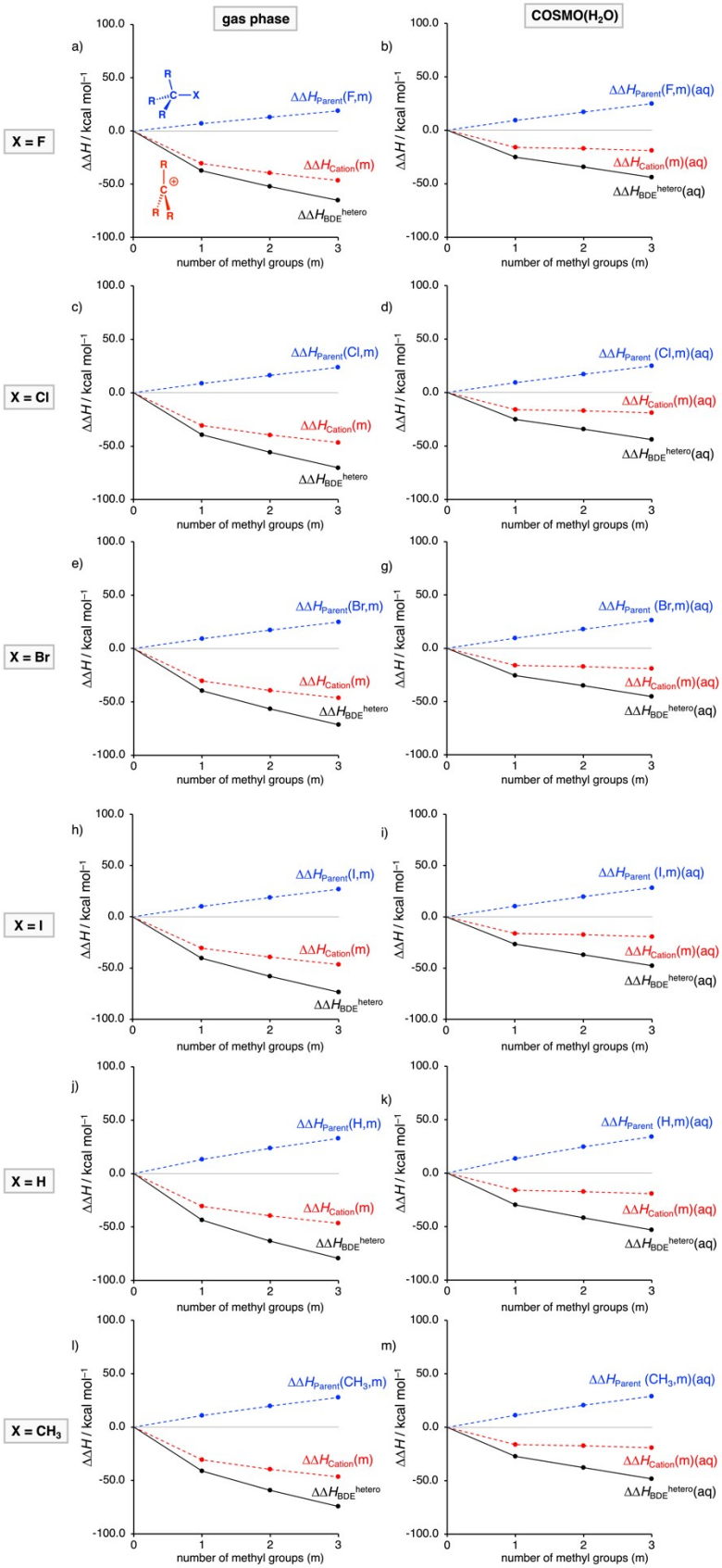


Figure S1. Effect of methyl groups on $\Delta\Delta H_{\text{Parent}}$(X,m) (blue), $\Delta\Delta H_{\text{Cation}}$(m) (red), $\Delta\Delta H_{\text{BDE}}^{\text{hetero}}$ (black; in kcal mol^{-1}) for C–X (X = F, Cl, Br, I, H, CH_3), using the isodesmic reaction shown in Eq. (1). Computed at ZORA-(U)M06-2X/QZ4P (a, c, e, h, j, l) and COSMO(H_2O)-ZORA-(U)M06-2X/QZ4P (b, d, f, g, i, k, m).

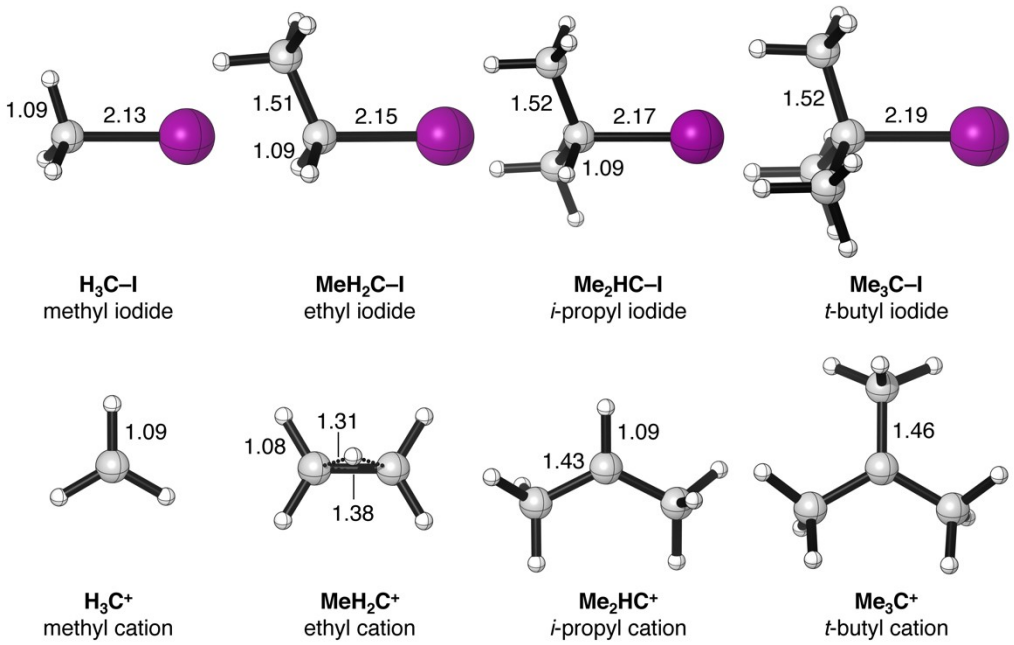


Figure S2. Structures of H_3C–I, MeH_2C–I, Me_2HC–I, Me_3C–I and their corresponding carbocation with the key distances (in Å) computed at ZORA-M06-2X/QZ4P. Atom colors: carbon (gray), hydrogen (white), iodine (purple).

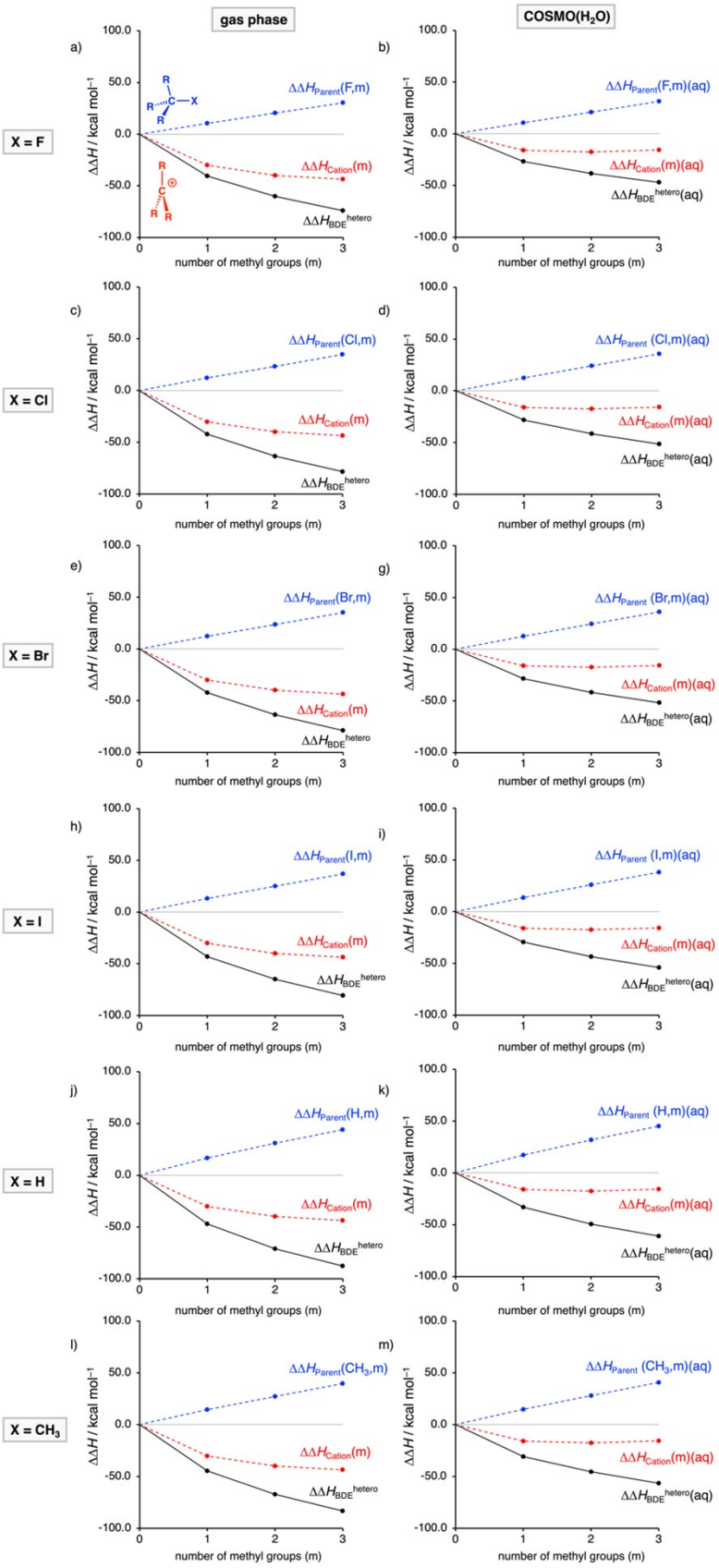


Figure S3. Effect of methyl groups on $\Delta\Delta H_{\text{Parent}}$(X,m) (blue), $\Delta\Delta H_{\text{Cation}}$(m) (red), $\Delta\Delta H_{\text{BDE}}^{\text{hetero}}$ (black; in kcal mol^{-1}) for C–X (X = F, Cl, Br, I, H, CH_3), using the isodesmic reaction shown in Eq. (1). Computed at ZORA-(U)BLYP-D3(BJ)/QZ4P (a, c, e, h, j, l) and COSMO(H_2O)-ZORA-BLYP-D3(BJ)/QZ4P (b, d, f, g, i, k, m).

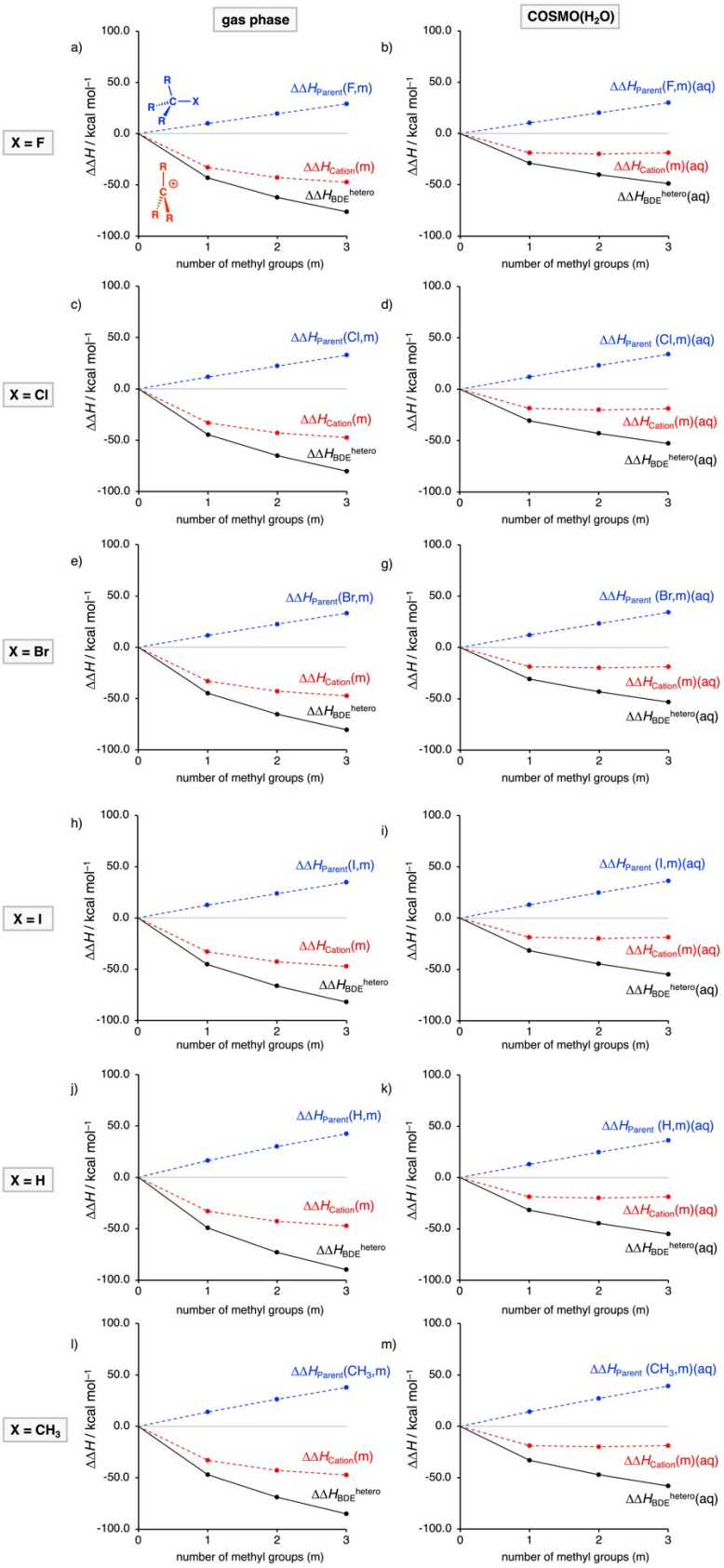


Figure S4. Effect of methyl groups on $\Delta\Delta H_{\text{Parent}}$(X,m) (blue), $\Delta\Delta H_{\text{Cation}}$(m) (red), $\Delta\Delta H_{\text{BDE}}^{\text{hetero}}$ (black; in kcal mol^{-1}) for C–X (X = F, Cl, Br, I, H, CH_3), using the isodesmic reaction shown in Eq. (1). Computed at ZORA-(U)BP86-D3(BJ)/QZ4P (a, c, e, h, j, l) and COSMO(H_2O)-ZORA-BP86-D3(BJ)/QZ4P (b, d, f, g, i, k, m).

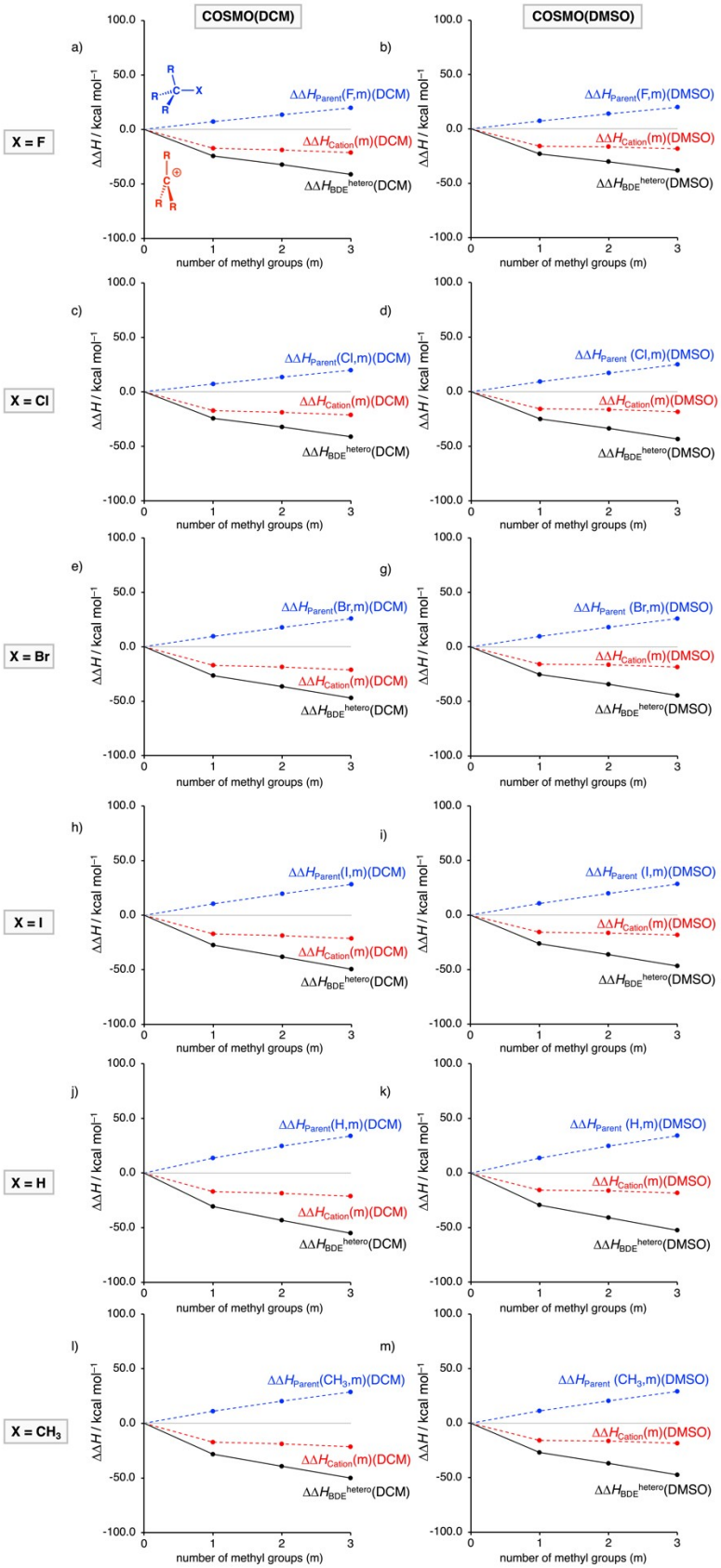


Figure S5. Effect of methyl groups on $\Delta\Delta H_{\text{Parent}}$(X,m) (blue), $\Delta\Delta H_{\text{Cation}}$(m) (red), $\Delta\Delta H_{\text{BDE}}^{\text{hetero}}$ (black; in kcal mol^{-1}) for C–X (X = F, Cl, Br, I, H, CH_3), using the isodesmic reaction shown in Eq. (1). Computed at COSMO(DCM)-ZORA-(U)M06-2X/QZ4P (a, c, e, h, j, l) and COSMO(DMSO)-ZORA-(U)M06-2X/QZ4P (b, d, f, g, i, k, m).

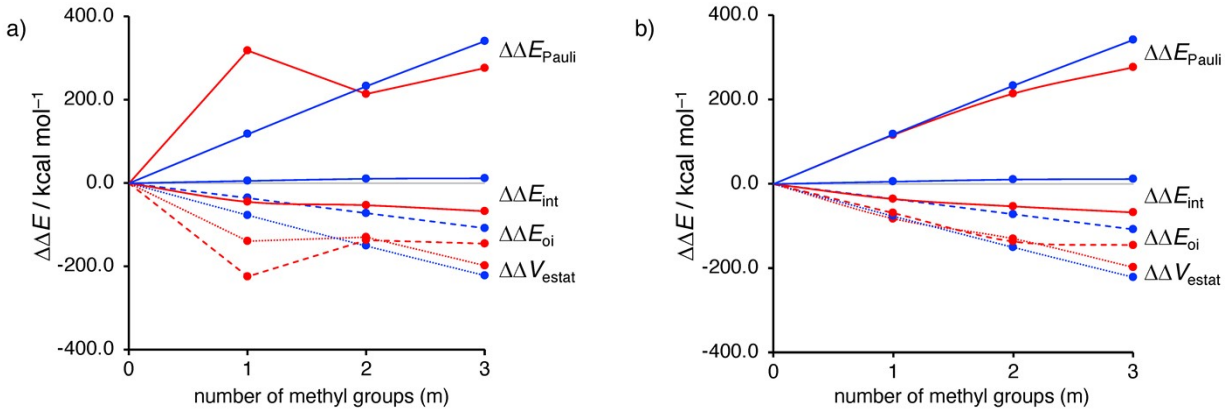


Figure S6. Effect of methyl groups on $\Delta\Delta E_{int}$, $\Delta\Delta E_{Pauli}$, $\Delta\Delta E_{oi}$, $\Delta\Delta V_{elstat}$ of the parent substrate (blue) and carbocation (red; in kcal mol^{-1}), using the (a) "non-classical" bridged and (b) classical ethyl cation (not lowest energy structure). Computed at ZORA-(U)M06-2X/QZ4P.

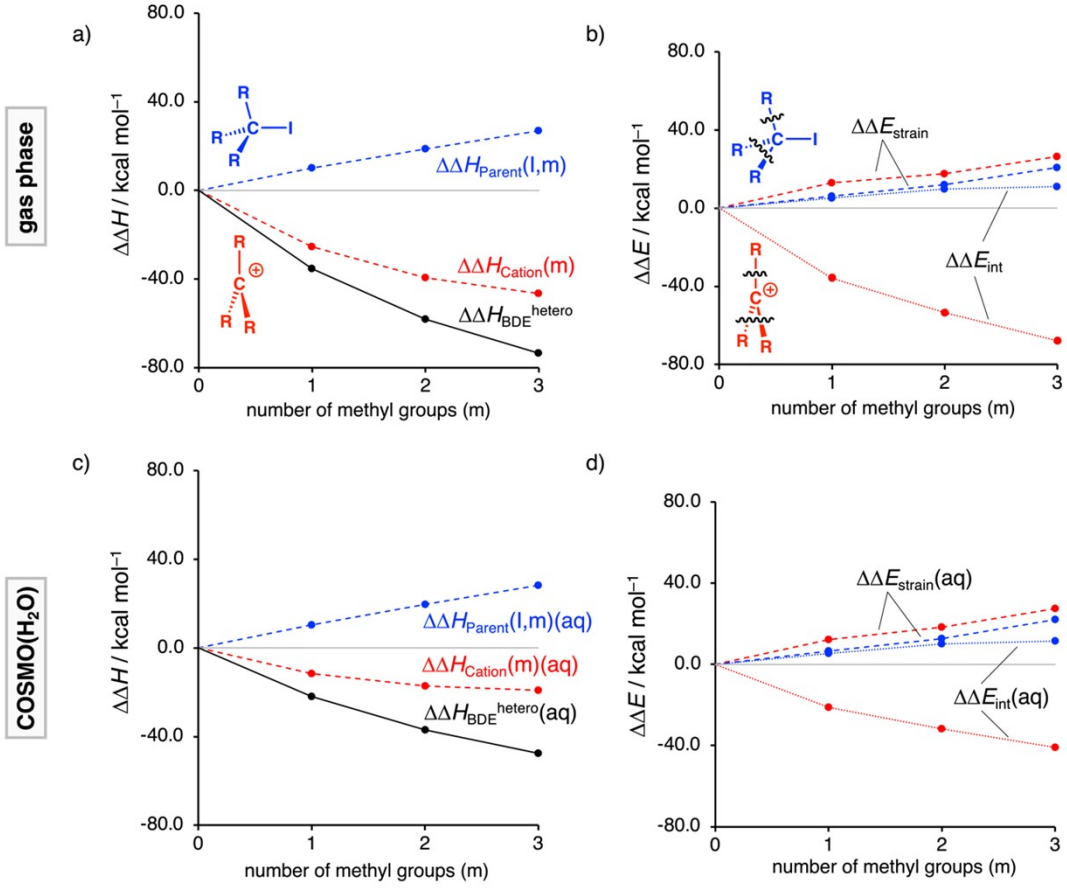


Figure S7. Effect of methyl groups $\Delta\Delta H_{Parent}$(X,m) (blue), $\Delta\Delta H_{Cation}$(m) (red), $\Delta\Delta H_{BDE}^{hetero}$ (black), and the corresponding activation strain analysis (in kcal mol^{-1}), using the classical ethyl cation (not lowest energy structure). Computed at ZORA-(U)M06-2X/QZ4P (a and b) and COSMO(H_2O)-ZORA-(U)M06-2X/QZ4P (c and d).

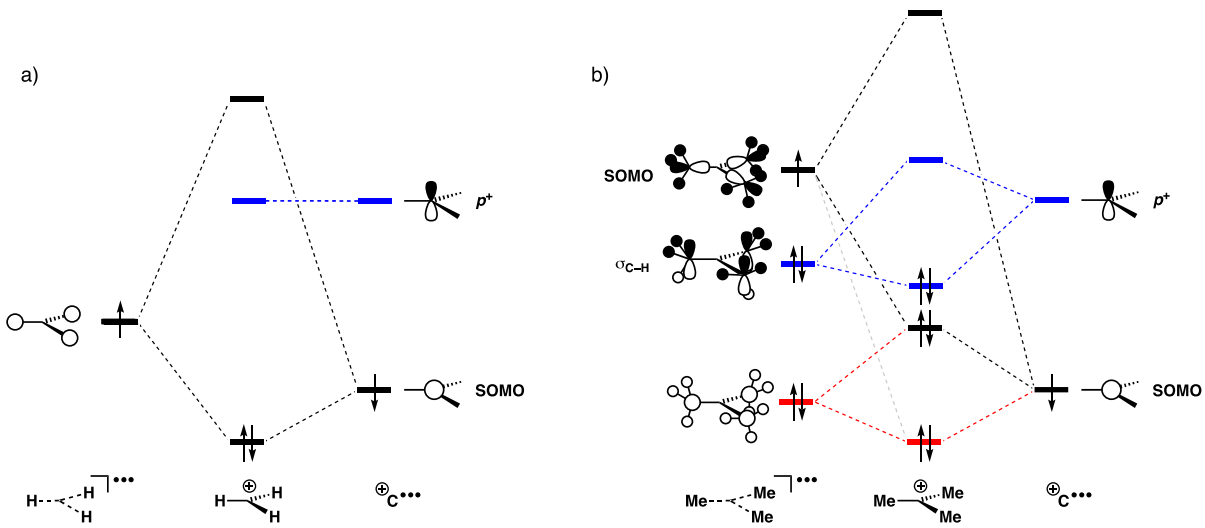
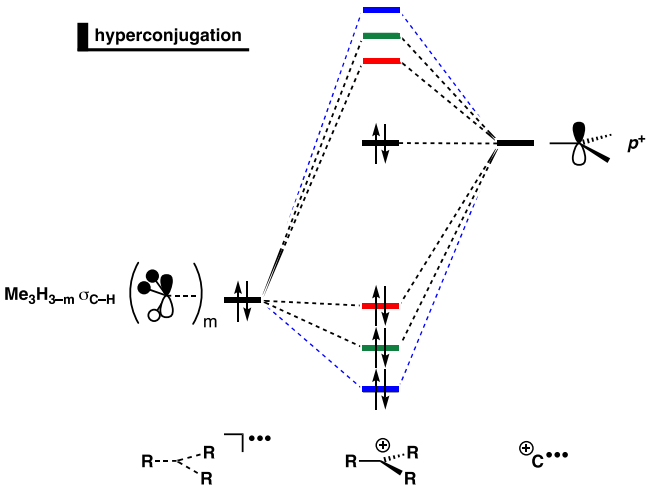


Figure S8. Schematic MO diagram for a) H_3–C^+ and b) Me_3–C^+. The SOMO–SOMO interactions are shown in black and the 2c–3e$^-$ interactions are colored red. Blue represents the hyperconjugation between the $Me_mH_{3-m}^{\bullet\bullet\bullet}$ σ_{C-H}-orbital and the $C^{+\bullet\bullet\bullet}$. Computed at ZORA-(U)M06-2X/QZ4P.



m	*S*	Δε	β pop. σ_{C-H}	β pop. p^+
0	-	-	-	0.00
1	0.24	2.2	0.84	0.14
2	0.27	2.6	0.80	0.16
3	0.33	2.4	0.78	0.22

Figure S9. Schematic MO diagram for the hyperconjugation between $Me_mH_{3-m}^{\bullet\bullet\bullet}$ σ_{C-H} and $C^{+\bullet\bullet\bullet}$ with m = 0–3. Computed at ZORA-(U)M06-2X/QZ4P at the equilibrium geometries.

Table S1. C–X (X = F, Cl, Br, H, CH_3) bond lengths (in Å), the heterolytic bond dissociation energies (ΔE_{BDE}^{hetero} and ΔH_{BDE}^{hetero}; in kcal mol^{-1}), and the stability analysis in terms of the partial reactions in a thermochemical cycle.[a]

System	r (C–X)	ΔE_{BDE}^{hetero}	ΔH_{BDE}^{hetero}	ΔH_{Parent}(X,m)	ΔH_{Cation}(m)
H_3C–F	1.380 (1.399)	267.3 (82.6)	263.0 (78.7)	–348.1 (–350.9)	–453.0 (–440.2)
MeH_2C–F	1.389 (1.409)	229.8 (59.1)	225.7 (55.4)	–341.3 (–343.6)	–483.5 (–456.3)
Me_2HC–F	1.397 (1.418)	215.0 (51.8)	210.8 (47.8)	–335.4 (337.2)	–492.4 (–457.5)
Me_3C–F	1.406 (1.427)	201.5 (43.7)	197.9 (39.6)	–329.5 (–331.0)	–499.5 (–459.4)
H_3C–Cl	1.780 (1.790)	230.1 (70.9)	226.7 (67.9)	–329.8 (–331.6)	–453.0 (–440.2)
MeH_2C–Cl	1.793 (1.807)	190.9 (45.7)	187.6 (42.7)	–321.2 (322.5)	–483.5 (–456.3)
Me_2HC–Cl	1.807 (1.824)	174.7 (36.9)	171.1 (33.5)	–313.6 (–314.5)	–492.4 (–457.5)
Me_3C–Cl	1.822 (1.842)	159.7 (27.4)	156.7 (23.8)	–306.3 (–306.7)	–499.5 (–459.4)
H_3C–Br	1.941 (1.950)	221.0 (68.1)	218.0 (65.5)	–327.8 (–329.0)	–453.0 (–440.2)
MeH_2C–Br	1.956 (1.969)	181.5 (42.6)	178.4 (39.9)	–318.8 (–319.5)	–483.5 (–456.3)
Me_2HC–Br	1.973 (1.999)	164.9 (33.4)	161.5 (30.3)	–310.7 (–311.0)	–492.4 (–457.5)
Me_3C–Br	1.993 (2.014)	149.6 (23.6)	146.7 (20.2)	–303.0 (–302.9)	–499.5 (–459.4)
H_3C–H	1.086 (1.087)	324.4 (154.9)	316.8 (147.7)	–330.3 (–329.8)	–453.0 (–440.2)
MeH_2C–H	1.089 (1.089)	281.3 (125.7)	273.2 (118.0)	–317.2 (–316.2)	–483.5 (–456.3)
Me_2HC–H	1.091 (1.091)	262.2 (114.1)	253.6 (105.8)	–306.6 (–305.1)	–492.4 (–457.5)
Me_3C–H	1.093 (1.093)	245.8 (103.1)	237.6 (94.5)	–297.6 (–295.7)	–499.5 (–459.4)
H_3C–CH_3	1.525 (1.526)	323.7 (159.8)	316.4 (153.4)	–323.4 (–323.7)	–453.0 (–440.2)
MeH_2C–CH_3	1.525 (1.525)	282.5 (132.6)	275.2 (126.2)	–312.7 (–312.6)	–483.5 (–456.3)
Me_2HC–CH_3	1.527 (1.527)	264.8 (122.4)	257.3 (115.6)	–303.7 (–303.6)	–492.4 (–457.5)
Me_3C–CH_3	1.530 (1.530)	249.2 (112.2)	242.2 (105.2)	–295.7 (–294.7)	–499.5 (–459.4)

[a] Computed at ZORA-(U)M06-2X/QZ4P and COSMO(H_2O)-ZORA-(U)M06-2X/QZ4P in parentheses, at 298.15 K and 1 atm.

Table S2. Heterolytic bond dissociation enthalpies ΔH_{BDE}^{hetero} (in kcal mol^{-1}) for C–X (X= F, Cl, Br, I, H, CH_3).

System	Experimental[a]	ZORA-M06-2X /QZ4P[b]	ZORA-BLYP-D3(BJ) /QZ4P[b]	ZORA-BP86-D3(BJ) /QZ4P[b]
H_3C–F	258.5 ± 0.6	263.0	258.7	265.1
MeH_2C–F	n.d.	225.7	218.1	222.1
Me_2HC–F	n.d.	210.8	198.4	203.0
Me_3C–F	n.d.	197.9	184.6	188.9
H_3C–Cl	227.2 ± 0.4	226.7	226.0	232.2
MeH_2C–Cl	188.3 ± 1.1	187.6	183.8	187.6
Me_2HC–Cl	169.9 ± 0.8	171.1	162.8	167.2
Me_3C–Cl	153.6 ± 1.2	156.7	147.7	152.0
H_3C–Br	219.6 ± 0.5	218.0	219.8	225.3
MeH_2C–Br	179.8 ± 1.1	178.4	177.4	180.5
Me_2HC–Br	162.6 ± 1.0	161.5	156.2	160.0
Me_3C–Br	145.1 ± 1.1	146.7	141.0	144.8
H_3C–I	213.5 ± 0.5	210.7	214.7	219.5
MeH_2C–I	172.7 ± 1.2	170.1	171.5	174.1
Me_2HC–I	154.3 ± 1.3	152.5	149.6	153.1
Me_3C–I	136.6 ± 1.3	137.2	134.0	137.5
H_3C–H	314.5 ± 0.4	316.8	311.8	316.4
MeH_2C–H	270.6 ± 1.1	273.2	264.9	267.0
Me_2HC–H	249.4 ± 0.8	253.6	240.8	243.5
Me_3C–H	231.2 ± 1.1	237.6	224.2	226.6
H_3C–CH_3	315.3 ± 0.9	316.4	311.1	317.4
MeH_2C–CH_3	274.2 ± 1.3	275.2	266.5	270.5
Me_2HC–CH_3	255.1 ± 1.2	257.3	243.8	248.5
Me_3C–CH_3	237.9 ± 1.3	242.2	227.8	232.3

[a] Reference 13. [b] This work, computed at 298.15 K and 1 atm at the equilibrium geometries.

Table S3. C–X (X = F, Cl, Br, I, H, CH_3) bond lengths (in Å), the heterolytic bond dissociation energies (ΔE_{BDE}^{hetero} and ΔH_{BDE}^{hetero}; in kcal mol^{-1}), and the stability analysis in terms of the partial reactions in a thermochemical cycle.[a]

System	r (C–X)	ΔE_{BDE}^{hetero}	ΔH_{BDE}^{hetero}	ΔH_{Parent}(X,m)	ΔH_{Cation}(m)
H_3C–F	1.413 (1.436)	262.5 (79.4)	258.7 (75.7)	–351.4 (–354.2)	–452.4 (–439.6)
MeH_2C–F	1.425 (1.452)	222.2 (53.0)	218.1 (49.0)	–341.0 (–343.5)	–482.6 (–455.7)
Me_2HC–F	1.438 (1.468)	202.3 (40.9)	198.4 (37.3)	–331.1 (–333.3)	–492.3 (–457.2)
Me_3C–F	1.451 (1.483)	187.9 (31.8)	184.6 (28.7)	–320.9 (–322.8)	–496.0 (–455.3)
H_3C–Cl	1.818 (1.832)	229.1 (72.3)	226.0 (69.4)	–332.9 (–334.4)	–452.4 (–439.6)
MeH_2C–Cl	1.836 (1.856)	187.3 (44.4)	183.8 (41.1)	–320.9 (–322.1)	–482.6 (–455.7)
Me_2HC–Cl	1.857 (1.883)	166.1 (31.0)	162.8 (27.9)	–309.6 (–310.5)	–492.3 (–457.2)
Me_3C–Cl	1.880 (1.913)	150.6 (20.8)	147.7 (18.1)	–298.2 (–298.8)	–496.0 (–455.3)
H_3C–Br	1.985 (1.996)	222.6 (72.0)	219.8 (69.5)	–330.4 (–331.0)	–452.4 (–439.6)
MeH_2C–Br	2.007 (2.025)	180.6 (44.0)	177.4 (40.9)	–318.2 (–318.5)	–482.6 (–455.7)
Me_2HC–Br	2.032 (2.057)	159.3 (30.5)	156.2 (27.6)	–306.7 (–306.7)	–492.3 (–457.2)
Me_3C–Br	2.060 (2.094)	143.6 (20.2)	141.0 (17.7)	–295.2 (–294.9)	–496.0 (–455.3)
H_3C–I	2.186 (2.190)	217.1 (75.9)	214.7 (73.7)	–323.3 (–321.9)	–321.9 (–439.6)
MeH_2C–I	2.211 (2.220)	174.5 (47.1)	171.5 (44.2)	–310.3 (–308.5)	–308.5 (–455.7)
Me_2HC–I	2.240 (2.255)	152.5 (32.9)	149.6 (30.2)	–298.2 (–296.0)	–296.0 (–457.2)
Me_3C–I	2.273 (2.295)	136.5 (22.1)	134.0 (19.7)	–286.0 (–283.7)	–283.7 (–455.3)
H_3C–H	1.094 (1.094)	319.1 (151.8)	311.8 (144.8)	–334.8 (–334.1)	–452.4 (–439.6)
MeH_2C–H	1.096 (1.097)	273.0 (119.5)	264.9 (111.6)	–318.1 (–316.9)	–482.6 (–455.7)
Me_2HC–H	1.099 (1.099)	249.0 (103.2)	240.8 (95.3)	–303.7 (–302.1)	–492.3 (–457.2)
Me_3C–H	1.101 (1.101)	232.0 (91.6)	224.2 (83.9)	–290.8 (–288.9)	–496.0 (–455.3)
H_3C–CH_3	1.538 (1.538)	318.0 (157.7)	311.1 (151.3)	–326.6 (–325.6)	–452.4 (–439.6)
MeH_2C–CH_3	1.538 (1.538)	273.9 (127.4)	266.5 (120.6)	–312.2 (–310.8)	–482.6 (–455.7)
Me_2HC–CH_3	1.540 (1.540)	251.0 (112.4)	243.8 (105.8)	–299.3 (–297.6)	–492.3 (–457.2)
Me_3C–CH_3	1.545 (1.545)	234.5 (101.1)	227.8 (94.9)	–286.9 (–284.9)	–496.0 (–455.3)

[a] Computed at ZORA-BLYP-D3(BJ)/QZ4P and COSMO(H_2O)-ZORA-BLYP-D3(BJ)/QZ4P in parentheses, at 298.15 K and 1 atm.

Table S4. C–X (X = F, Cl, Br, I, H, CH_3) bond lengths (in Å), the heterolytic bond dissociation energies (ΔE_{BDE}^{hetero} and ΔH_{BDE}^{hetero}; in kcal mol^{-1}), and the stability analysis in terms of the partial reactions in a thermochemical cycle.[a]

System	r (C–X)	ΔE_{BDE}^{hetero}	ΔH_{BDE}^{hetero}	ΔH_{Parent}(X,m)	ΔH_{Cation}(m)
H_3C–F	1.400 (1.420)	269.0 (85.5)	265.1 (81.8)	–352.9 (–355.5)	–453.5 (–440.5)
MeH_2C–F	1.412 (1.436)	226.0 (56.5)	222.1 (52.7)	–342.9 (–345.1)	–486.5 (–459.3)
Me_2HC–F	1.424 (1.450)	206.9 (45.4)	203.0 (41.7)	–333.5 (–335.4)	–496.2 (–460.5)
Me_3C–F	1.437 (1.464)	192.2 (36.0)	188.9 (32.9)	–323.9 (–325.5)	–500.7 (–459.4)
H_3C–Cl	1.797 (1.809)	235.3 (77.7)	232.2 (74.8)	–335.4 (–337.0)	–453.5 (–440.5)
MeH_2C–Cl	1.815 (1.832)	190.9 (47.3)	187.6 (44.1)	–323.8 (–325.1)	–486.5 (–459.3)
Me_2HC–Cl	1.833 (1.856)	170.6 (35.0)	167.2 (31.8)	–313.1 (–314.0)	–496.2 (–460.5)
Me_3C–Cl	1.854 (1.881)	154.9 (24.6)	152.0 (21.8)	–302.4 (–302.9)	–500.7 (–459.4)
H_3C–Br	1.961 (1.970)	228.1 (76.8)	225.3 (74.2)	–333.6 (–332.2)	–453.5 (–440.5)
MeH_2C–Br	1.981 (1.997)	183.6 (46.3)	180.5 (43.4)	–321.9 (–320.1)	–486.5 (–459.3)
Me_2HC–Br	2.004 (2.026)	163.2 (33.9)	160.0 (30.9)	–311.1 (–308.9)	–496.2 (–460.5)
Me_3C–Br	2.029 (2.057)	147.4 (23.4)	144.8 (21.0)	–300.4 (–297.9)	–500.7 (–459.4)
H_3C–I	2.159 (2.163)	222.0 (79.8)	219.5 (77.4)	–327.3 (–326.4)	–453.5 (–440.5)
MeH_2C–I	2.183 (2.191)	176.9 (48.5)	174.1 (45.8)	–314.9 (–313.6)	–486.5 (–459.3)
Me_2HC–I	2.210 (2.223)	156.0 (35.6)	153.1 (32.8)	–303.6 (–301.8)	–496.2 (–460.5)
Me_3C–I	2.239 (2.258)	140.0 (24.8)	137.5 (22.4)	–292.5 (–290.3)	–500.7 (–459.4)
H_3C–H	1.095 (1.095)	323.7 (156.6)	316.4 (149.6)	–337.1 (–336.5)	–453.5 (–440.5)
MeH_2C–H	1.098 (1.098)	275.0 (121.7)	267.0 (114.0)	–320.8 (–319.6)	–486.5 (–459.3)
Me_2HC–H	1.101 (1.101)	251.7 (106.4)	243.5 (98.4)	–306.9 (–305.3)	–496.2 (–460.5)
Me_3C–H	1.103 (1.103)	234.5 (94.5)	226.6 (86.8)	–294.6 (–292.6)	–500.7 (–459.4)
H_3C–CH_3	1.530 (1.531)	324.4 (163.3)	317.4 (156.9)	–329.3 (–328.5)	–453.5 (–440.5)
MeH_2C–CH_3	1.531 (1.531)	277.7 (130.5)	270.5 (123.8)	–315.4 (–314.2)	–486.5 (–459.3)
Me_2HC–CH_3	1.533 (1.533)	255.6 (116.5)	248.5 (109.8)	–303.0 (–301.4)	–496.2 (–460.5)
Me_3C–CH_3	1.537 (1.537)	239.0 (105.1)	232.3 (98.9)	–291.4 (–289.0)	–500.7 (–459.4)

[a] Computed at ZORA-BP86-D3(BJ)/QZ4P and COSMO(H_2O)-ZORA-BP86-D3(BJ)/QZ4P in parentheses, at 298.15 K and 1 atm.

Table S5. C–X (X = F, Cl, Br, I, H, CH_3) bond lengths (in Å), the heterolytic bond dissociation energies (ΔE_{BDE}^{hetero} and ΔH_{BDE}^{hetero}; in kcal mol^{-1}), and the stability analysis in terms of the partial reactions in a thermochemical cycle.[a]

System	r (C–X)	ΔE_{BDE}^{hetero}	ΔH_{BDE}^{hetero}	ΔH_{Parent}(X,m)	ΔH_{Cation}(m)
H_3C–F	1.398	84.6	80.7	–350.7	–439.7
MeH_2C–F	1.407	61.4	57.6	–343.4	–455.5
Me_2HC–F	1.416	54.5	50.5	–337.0	–456.1
Me_3C–F	1.426	46.3	42.3	–330.7	–458.1
H_3C–Cl	1.791	72.7	69.7	–331.6	–439.7
MeH_2C–Cl	1.806	47.8	44.7	–322.4	–455.5
Me_2HC–Cl	1.823	39.5	36.1	–314.5	–456.1
Me_3C–Cl	1.841	29.9	26.3	–306.7	–458.1
H_3C–Br	1.950	69.8	67.2	–328.8	–439.7
MeH_2C–Br	1.969	44.6	41.8	–319.3	–455.5
Me_2HC–Br	1.989	35.9	32.8	–310.9	–456.1
Me_3C–Br	2.012	26.0	22.7	–302.8	–458.1
H_3C–I	2.136	70.7	68.4	–320.6	–439.7
MeH_2C–I	2.157	44.6	42.0	–310.2	–455.5
Me_2HC–I	2.181	35.2	32.2	–301.0	–456.1
Me_3C–I	2.208	24.8	21.6	–292.3	–458.1
H_3C–H	1.087	156.9	149.8	–329.8	–439.7
MeH_2C–H	1.089	128.0	120.4	–316.2	–455.5
Me_2HC–H	1.091	117.0	108.7	–305.1	–456.1
Me_3C–H	1.093	105.9	97.3	–295.7	–458.1
H_3C–CH_3	1.526	161.9	155.4	–322.8	–439.7
MeH_2C–CH_3	1.525	135.0	128.4	–311.7	–455.5
Me_2HC–CH_3	1.527	125.2	118.2	–302.3	–456.1
Me_3C–CH_3	1.530	115.0	108.0	–293.8	–458.1

[a] Computed at COSMO(DMSO)-ZORA-M06-2X/QZ4P, at 298.15 K and 1 atm.

Table S6. C–X (X = F, Cl, Br, I, H, CH_3) bond lengths (in Å), the heterolytic bond dissociation energies (ΔE_{BDE}^{hetero} and ΔH_{BDE}^{hetero}; in kcal mol^{-1}), and the stability analysis in terms of the partial reactions in a thermochemical cycle.[a]

System	r (C–X)	ΔE_{BDE}^{hetero}	ΔH_{BDE}^{hetero}	ΔH_{Parent}(X,m)	ΔH_{Cation}(m)
H_3C–F	1.396	101.6	97.7	–350.4	–440.6
MeH_2C–F	1.405	77.2	73.4	–343.2	–457.7
Me_2HC–F	1.414	69.4	65.4	–336.8	–459.3
Me_3C–F	1.423	60.6	56.6	–330.6	–461.9
H_3C–Cl	1.789	87.5	84.5	–331.3	–440.6
MeH_2C–Cl	1.805	61.4	58.3	–322.3	–457.7
Me_2HC–Cl	1.821	52.1	48.7	–314.3	–459.3
Me_3C–Cl	1.838	42.0	38.5	–306.6	–461.9
H_3C–Br	1.948	84.1	81.4	–328.7	–440.6
MeH_2C–Br	1.967	57.6	54.8	–319.3	–457.7
Me_2HC–Br	1.987	48.0	44.8	–310.9	–459.3
Me_3C–Br	2.010	37.6	34.2	–302.8	–461.9
H_3C–I	2.136	84.2	81.8	–302.8	–440.6
MeH_2C–I	2.156	56.9	54.3	–310.4	–457.7
Me_2HC–I	2.179	46.5	43.5	–301.2	–459.3
Me_3C–I	2.206	35.6	32.4	–292.6	–461.9
H_3C–H	1.086	173.3	166.1	–329.8	–440.6
MeH_2C–H	1.089	143.2	135.5	–316.3	–457.7
Me_2HC–H	1.091	131.1	122.8	–305.2	–459.3
Me_3C–H	1.093	119.6	110.9	–295.9	–461.9
H_3C–CH_3	1.526	177.4	170.9	–322.8	–440.6
MeH_2C–CH_3	1.525	149.3	142.7	–311.8	–457.7
Me_2HC–CH_3	1.527	138.6	131.7	–302.4	–459.3
Me_3C–CH_3	1.530	127.8	120.8	–294.0	–461.9

[a] Computed at COSMO(DCM)-ZORA-M06-2X/QZ4P, at 298.15 K and 1 atm.

Table S7. Cartesian coordinates (in Å), energies (*E*, *H* and *G*, in kcal mol^{-1}), and number of imaginary vibrational frequencies (N_{imag}) of all stationary points and transition states in the gas phase, computed at ZORA-(U)M06-2X/QZ4P.

H_3C-F
E = -793.95
H = -766.66
G = -782.51
$\boldsymbol{N_{imag}}$ = 0

C	0.00000000	0.00000000	0.13476600
H	-0.51470400	0.89149400	0.48602800
H	-0.51470400	-0.89149400	0.48602800
H	1.02940800	0.00000000	0.48602800
F	0.00000000	0.00000000	-1.24532100

MeH_2C-F
E = -1305.29
H = -1259.34
G = -1278.14
$\boldsymbol{N_{imag}}$ = 0

C	0.20808800	-1.79710700	0.07562500
H	-0.05352500	-0.89557900	0.62862500
H	0.00373000	-2.66646100	0.69972900
H	2.31130900	-1.71570500	0.46707200
F	-0.63958900	-1.86827100	-1.02181000
C	1.64298300	-1.76952500	-0.39113800
H	1.87658100	-2.66916700	-0.95619700
H	1.82094100	-0.90282400	-1.02387200

Me_2HC-F
E = -1817.10
H = -1752.85
G = -1773.70
$\boldsymbol{N_{imag}}$ = 0

C	0.92369200	-1.37696200	0.00000000
H	0.11040500	-2.10473200	0.00000000
H	2.53300300	-0.75218900	-1.27202300
H	2.20015800	-2.48914700	1.32017100
F	0.31512600	-0.11948500	0.00000000
C	1.74333700	-1.50224100	1.26492400
H	2.53300300	-0.75218900	1.27202300
H	1.11623500	-1.35903100	2.14174300
C	1.74333700	-1.50224100	-1.26492400
H	2.20015800	-2.48914700	-1.32017100
H	1.11623500	-1.35903100	-2.14174300

Me_3C-F
E = -2328.89
H = -2246.47
G = -2269.12
$\boldsymbol{N_{imag}}$ = 0

C	0.16960000	-1.89638900	0.00000000
H	0.47340500	-3.57234900	1.31667400
H	0.03220100	-2.06964400	-2.13980500
H	2.29984000	-2.20708600	0.00000000
F	-0.67221500	-0.77041500	0.00000000
C	1.59557900	-1.37642100	0.00000000
H	1.77347100	-0.76815500	-0.88473300
H	1.77347100	-0.76815500	0.88473300
C	-0.15066300	-2.68174700	-1.25874200
H	0.47340500	-3.57234900	-1.31667400
H	-1.19517800	-2.98729100	-1.25507300
C	-0.15066300	-2.68174700	1.25874200
H	0.03220100	-2.06964400	2.13980500
H	-1.19517800	-2.98729100	1.25507300

$H_3C–Cl$
E = -720.74
H = -694.37
G = -711.04
N_{imag} = 0

C	0.00000000	0.00000000	0.12123600
H	-0.51399100	0.89025800	0.46253500
H	-0.51399100	-0.89025800	0.46253500
H	1.02798100	0.00000000	0.46253500
Cl	0.00000000	0.00000000	-1.65830700

$MeH_2C–Cl$
E = -1230.39
H = -1185.23
G = -1204.77
N_{imag} = 0

C	0.21744400	-1.79970300	0.07355300
H	-0.05109300	-0.91625600	0.64322000
H	-0.00758300	-2.68286100	0.66223000
H	1.85847700	-0.88741500	-0.97977300
Cl	-0.88954900	-1.84192500	-1.33569500
C	1.66221100	-1.76883700	-0.37405800
H	2.31466800	-1.74406100	0.49838700
H	1.90167500	-2.65175300	-0.96179400

$Me_2HC–Cl$
E = -1740.76
H = -1677.15
G = -1698.67
N_{imag} = 0

C	0.22988300	-1.81689800	0.08911400
H	-0.00999100	-0.90283300	0.62550800
H	0.57811500	-3.01962700	1.82660200
H	1.83736600	-0.90795500	-1.03336900
Cl	-0.88869600	-1.81095800	-1.32959100
C	1.66086900	-1.78008100	-0.40929700

H	2.34099200	-1.74530400	0.44208600
H	1.87950700	-2.67405100	-0.99118500
C	-0.06743300	-3.02983300	0.94809100
H	-1.10364000	-3.03458400	1.27594300
H	0.12425600	-3.94354000	0.38774900

$Me_3C–Cl$
E = -2251.14
H = -2169.27
G = -2192.45
N_{imag} = 0

C	0.19381600	-1.79140900	0.09490900
H	0.52350700	-0.40554400	1.69596900
H	0.58185000	-2.97489000	1.83895500
H	1.78481700	-0.93627100	-1.09104700
Cl	-0.92262300	-1.89684400	-1.34125000
C	-0.12958400	-0.49864700	0.82718400
H	0.02773100	0.36127600	0.17978400
H	-1.16305700	-0.49558600	1.16669200
C	1.61830100	-1.78932300	-0.43689500
H	2.31390900	-1.72757300	0.40113200
H	1.82378400	-2.70118900	-0.99333900
C	-0.07330900	-3.00772000	0.96737600
H	-1.10622100	-3.01857600	1.30845000
H	0.12281600	-3.92646400	0.41892400

$H_3C–Br$
E = -701.06
H = -675.04
G = -692.52
N_{imag} = 0

C	0.00000000	0.00000000	1.07820500
H	-1.03018100	0.00000000	1.40884800
H	0.51509000	-0.89216300	1.40884800
H	0.51509000	0.89216300	1.40884800
Br	0.00000000	0.00000000	-0.86230300

$MeH_2C–Br$
E = -1210.35
H = -1165.47
G = -1185.84
N_{imag} = 0

C	0.16346500	0.01436100	0.00000000
H	-0.10323600	0.58013300	-0.88498500
H	-0.10323600	0.58013300	0.88498500
H	2.25005000	0.47704900	0.00000000
Br	-1.02776300	-1.53725900	0.00000000
C	1.61465600	-0.40939800	0.00000000
H	1.84770200	-1.00020300	0.88235600
H	1.84770200	-1.00020300	-0.88235600

$Me_2HC–Br$

E = -1720.33
H = -1656.95
G = -1679.25
N_{imag} = 0

C	0.21357800	-2.05527400	-0.16537900
H	-0.11566100	-2.25565600	0.84925600
H	0.22706600	-3.01678500	-2.09067900
H	2.29558800	-2.40526600	0.16197800
Br	-0.95069300	-0.56602700	-0.73161600
C	1.65534700	-1.59209400	-0.18408400
H	1.95604800	-1.32502900	-1.19573400
H	1.80675500	-0.73192300	0.46227300
C	-0.03861800	-3.25018200	-1.06105800
H	0.58101200	-4.08377800	-0.72620900
H	-1.08020100	-3.55814000	-1.03186700

$Me_3C–Br$

E = -2230.36
H = -2148.70
G = -2172.68
N_{imag} = 0

C	0.00000500	0.00001500	1.60106800
H	-1.27667900	0.74651900	3.14305500
H	0.87405800	-1.97689800	1.69185900
H	1.28420700	0.73350500	3.14305500
Br	-0.00001100	0.00014800	-0.39158100
C	1.26010400	0.71903200	2.05138500
H	2.15131300	0.20917800	1.69283100
H	1.27523600	1.74527700	1.69172100
C	-0.00741500	-1.45086900	2.05112000
H	-0.00752400	-1.47932300	3.14278200
H	-0.89425300	-1.96783800	1.69191200
C	-1.25268400	0.73186100	2.05138500
H	-1.25731000	1.75822600	1.69177400
H	-2.14904600	0.23116600	1.69276600

$H_3C–I$

E = -683.69
H = -657.98
G = -676.02
N_{imag} = 0

C	0.00000000	0.00000000	1.07956000
H	-1.03109200	0.00000000	1.40538700
H	0.51554600	-0.89295200	1.40538700
H	0.51554600	0.89295200	1.40538700
I	0.00000000	0.00000000	-1.05243000

$MeH_2C–I$

E = -1192.11
H = -1147.47
G = -1168.4
N_{imag} = 0

C	0.21542600	-1.79374700	0.06964100
H	-0.06588500	-0.89744600	0.60923600
H	-0.01704200	-2.66518900	0.66986000
H	2.31310600	-1.72077400	0.47980900
I	-1.14841900	-1.88764900	-1.58965400
C	1.65714300	-1.76958300	-0.39056400
H	1.90407700	-2.66482800	-0.95596600
H	1.85477400	-0.90374600	-1.01776000

$Me_2HC–I$

E = -1701.40
H = -1638.20
G = -1661.06
N_{imag} = 0

C	0.21146300	-2.05073800	-0.17014000
H	-0.12358700	-2.24468700	0.84357200
H	0.22785500	-3.02535300	-2.09352800
H	2.29082400	-2.40954200	0.16221400
I	-1.07375300	-0.41357100	-0.78511000
C	1.65604800	-1.59152400	-0.18471700
H	1.96486100	-1.32505300	-1.19417100
H	1.81384100	-0.73329000	0.46277800
C	-0.03845400	-3.25063600	-1.06217000
H	0.58433700	-4.08051400	-0.72174100
H	-1.07826000	-3.56486900	-1.03455000

$Me_3C–I$

E = -2210.99
H = -2129.48
G = -2153.99
N_{imag} = 0

C	0.20012300	-2.06221100	-0.14538600
H	0.39840900	-3.18078800	1.66154300
H	0.27028300	-3.02551600	-2.08651500
H	2.28968500	-2.36477000	0.16700500
I	-1.08029000	-0.43995700	-0.88073600
C	1.63648800	-1.56725200	-0.19643000
H	1.93395600	-1.31587400	-1.21191700
H	1.77800500	-0.69320500	0.43518000
C	-0.00841700	-3.25748800	-1.06112900
H	0.62347300	-4.07687200	-0.70881900
H	-1.04322200	-3.59201900	-1.04789100
C	-0.23014000	-2.37236800	1.27919800
H	-0.10918600	-1.50765900	1.92770600
H	-1.26765600	-2.69621600	1.31913100

$H_3C–H$
E = -734.90
H = -704.28
G = -717.53
N_{imag} = 0

C	0.00000000	0.00000000	0.00000000
H	0.62702400	-0.62702400	0.62702400
H	-0.62702400	-0.62702400	-0.62702400
H	0.62702400	0.62702400	-0.62702400
H	-0.62702400	0.62702400	0.62702400

$MeH_2C–H$
E = -1240.58
H = -1190.70
G = -1206.91
N_{imag} = 0

C	0.00000000	0.00000000	0.76254800
H	0.00000000	1.01472900	1.15671600
H	0.87878100	-0.50736500	1.15671600
H	0.87878100	0.50736500	-1.15671600
H	-0.87878100	-0.50736500	1.15671600
C	0.00000000	0.00000000	-0.76254800
H	0.00000000	-1.01472900	-1.15671600
H	-0.87878100	0.50736500	-1.15671600

$Me_2HC–H$
E = -1748.18
H = -1679.54
G = -1698.64
N_{imag} = 0

C	0.00000000	0.00000000	-1.13152000
H	0.87317500	0.00000000	-0.47776900
H	-0.87948300	-1.29724000	-2.62686600
H	0.87948300	1.29724000	-2.62686600
H	-0.87317500	0.00000000	-0.47776900
C	0.00000000	1.26476000	-1.98350300
H	-0.87948300	1.29724000	-2.62686600
H	0.00000000	2.16421000	-1.37026200
C	0.00000000	-1.26476000	-1.98350300
H	0.87948300	-1.29724000	-2.62686600
H	0.00000000	-2.16421000	-1.37026200

$Me_3C–H$
E = -2257.09
H = -2170.04
G = -2190.85
N_{imag} = 0

C	0.00000000	0.00000000	1.57259300
H	-1.48788500	0.00000000	3.14099600
H	1.75581600	-1.27651100	1.69760800
H	0.74394200	1.28854600	3.14099600

H	0.00000000	0.00000000	0.47973400
C	0.72497900	1.25570100	2.04995100
H	1.75581600	1.27651100	1.69760800
H	0.22758200	2.15883700	1.69760800
C	0.72497900	-1.25570100	2.04995100
H	0.74394200	-1.28854600	3.14099600
H	0.22758200	-2.15883700	1.69760800
C	-1.44995800	0.00000000	2.04995100
H	-1.98339900	0.88232600	1.69760800
H	-1.98339900	-0.88232600	1.69760800

$H_3C–CH_3$
E = -1240.58
H = -1190.70
G = -1206.91
N_{imag} = 0

C	0.00000000	0.00000000	0.76254800
H	0.00000000	1.01472900	1.15671600
H	0.87878100	-0.50736500	1.15671600
H	0.87878100	0.50736500	-1.15671600
H	-0.87878100	-0.50736500	1.15671600
C	0.00000000	0.00000000	-0.76254800
H	0.00000000	-1.01472900	-1.15671600
H	-0.87878100	0.50736500	-1.15671600

$MeH_2C–CH_3$
E = -1748.18
H = -1679.54
G = -1698.64
N_{imag} = 0

C	0.00000000	0.00000000	-1.13152000
H	0.87317500	0.00000000	-0.47776900
H	-0.87948300	-1.29724000	-2.62686600
H	0.87948300	1.29724000	-2.62686600
H	-0.87317500	0.00000000	-0.47776900
C	0.00000000	1.26476000	-1.98350300
H	-0.87948300	1.29724000	-2.62686600
H	0.00000000	2.16421000	-1.37026200
C	0.00000000	-1.26476000	-1.98350300
H	0.87948300	-1.29724000	-2.62686600
H	0.00000000	-2.16421000	-1.37026200

$Me_2HC–CH_3$
E = -2257.09
H = -2170.04
G = -2190.85
N_{imag} = 0

C	0.00000000	0.00000000	1.57259300
H	-1.48788500	0.00000000	3.14099600
H	1.75581600	-1.27651100	1.69760800
H	0.74394200	1.28854600	3.14099600

H	0.00000000	0.00000000	0.47973400
C	0.72497900	1.25570100	2.04995100
H	1.75581600	1.27651100	1.69760800
H	0.22758200	2.15883700	1.69760800
C	0.72497900	-1.25570100	2.04995100
H	0.74394200	-1.28854600	3.14099600
H	0.22758200	-2.15883700	1.69760800
C	-1.44995800	0.00000000	2.04995100
H	-1.98339900	0.88232600	1.69760800
H	-1.98339900	-0.88232600	1.69760800

$Me_3C–CH_3$
E = -2766.82
H = -2661.47
G = -2683.08
N_{imag} = 0

C	-0.00002200	-0.00002900	1.55710000
H	-1.23237700	0.79987800	3.15734300
H	0.77661700	-2.02269900	1.71534300
H	1.30873800	0.66735300	3.15740200
H	0.05332500	1.01764700	-0.36146900
C	1.28545800	0.65455100	2.06714400
H	2.16366400	0.11090700	1.71704900
H	1.36320900	1.68399300	1.71562000
C	-0.07586900	-1.44056600	2.06713700
H	-0.07614000	-1.46721300	3.15739200
H	-0.98587800	-1.92926400	1.71724400
C	-1.20959100	0.78603800	2.06709600
H	-1.17784900	1.81835900	1.71686100
H	-2.13998800	0.33864700	1.71555900
C	0.00000700	0.00002000	0.02705800
H	0.85461600	-0.55501900	-0.36144100
H	-0.90792200	-0.46260400	-0.36154700

F^-
E = -180.01
H = -179.12
G = -186.87
N_{imag} = 0

Cl^-
E = -144.03
H = -143.14
G = -150.89
N_{imag} = 0

Br^-
E = -133.41
H = -132.52
G = -140.27

N_{imag} = 0

I^-
E = -123.70
H = -122.81
G = -130.56
N_{imag} = 0

H^-
E = -63.88
H = -62.99
G = -70.74
N_{imag} = 0

H_3C^-
E = -570.26
H = -549.80
G = -563.57
N_{imag} = 0

H_3C^+
E = -346.65
H = -324.50
G = -337.79
N_{imag} = 0

C	0.00000000	0.00000000	0.00000000
H	-0.54451800	0.94313200	0.00000000
H	-0.54451800	-0.94313200	0.00000000
H	1.08903500	0.00000000	0.00000000

MeH_2C^+
E = -895.45
H = -854.53
G = -870.77
N_{imag} = 0

C	0.00000000	-0.68821700	1.05194400
H	0.93353500	1.23988500	1.05547800
H	-0.93353500	1.23988500	1.05547800
C	0.00000000	0.68821700	1.05194400
H	0.93353500	-1.23988500	1.05547800
H	0.00000000	0.00000000	-0.06247600
H	-0.93353500	-1.23988500	1.05547800

Me_2HC^+
E = -1422.07
H = -1362.94
G = -1382.31
N_{imag} = 0

C	0.00000000	0.00000000	-0.56170900
H	-1.07218200	0.65996500	1.16133300
H	-1.84922200	-0.39823000	-0.03927400

H	1.84922200	0.39823000	-0.03927400
C	1.17845500	-0.48346600	0.09610700
H	1.07218200	-0.65996500	1.16133300
H	1.68598100	-1.27879700	-0.44882400
H	0.00000000	0.00000000	-1.65033600
C	-1.17845500	0.48346600	0.09610700
H	-1.68598100	1.27879700	-0.44882400

Me_3C^+
E = -1947.37
H = -1869.47
G = -1892.08
N_{imag} = 0

C	0.92518200	-1.42899000	0.47943700
H	0.88249700	0.67463600	0.89437300
H	0.48388200	-2.97225700	1.69009800
H	2.21387800	-1.28265900	-1.07053100
C	2.30806200	-1.43199400	0.02102600
H	2.88583400	-0.59042100	0.39361100
H	2.80632100	-2.38720300	0.16117600
C	0.21895300	-2.68977200	0.65368300
H	-0.86257500	-2.59540000	0.61812200
H	0.60336500	-3.48650900	0.02092800
C	0.22722400	-0.17294000	0.72640400
H	-0.33338900	0.00578900	-0.20812200
H	-0.53725300	-0.27518900	1.49588500

•••CF
E = -270.05
H = -266.12
G = -280.52
N_{imag} = 0

C	0.00000000	0.00000000	-4.31954000
F	0.00000000	0.00000000	-3.00185300

•••CCl
E = -215.54
H = -212.14
G = -227.33
N_{imag} = 0

C	0.00000000	0.00000000	-4.62988100
Cl	0.00000000	0.00000000	-2.97890900

•••CBr
E = -198.02
H = -194.83
G = -210.85
N_{imag} = 0

C	0.00000000	0.00000000	-4.85044900
Br	0.00000000	0.00000000	-3.03094400

•••CI
E = -187.13
H = -184.11
G = -200.71
N_{imag} = 0

C	0.00000000	0.00000000	-5.02279700
I	0.00000000	0.00000000	-2.99836100

•••CH
E = -228.15
H = -221.58
G = -233.75
N_{imag} = 0

C	0.00000000	0.00000000	-0.58326800
H	0.00000000	0.00000000	-1.67281900

•••CMe
E = -741.01
H = -714.94
G = -730.58
N_{imag} = 0

C	0.00000000	0.00000000	-4.64023100
H	0.51215300	-0.88707500	-2.77335100
C	0.00000000	0.00000000	-3.15077300
H	0.51215300	0.88707500	-2.77335100
H	-1.02430600	0.00000000	-2.77335100

•H
E = -51.69
H = -50.80
G = -58.55
N_{imag} = 0

•Me
E = -571.49
H = -550.29
G = -563.83
N_{imag} = 0

C	0.00914500	-0.00248200	-0.72627600
H	-0.01979000	-0.00785000	-1.80145000
H	-0.57896200	-0.70984900	-0.16893300
H	0.62619700	0.71026400	-0.20847100

•••C^+
E = 279.96
H = 280.85
G = 273.10
N_{imag} = 0

Table S8. Cartesian coordinates (in Å), energies (*E*, *H* and *G*, in kcal mol^{-1}), and number of imaginary vibrational frequencies (N_{imag}) of all stationary points and transition states in the gas phase, computed at COSMO(H_2O)-ZORA-(U)M06-2X/QZ4P.

H_3C-F
E = -796.92
H = -769.74
G = -785.61
$\boldsymbol{N_{imag}}$ = 0

C	0.00000000	0.00000000	0.14583500
H	-0.51548900	0.89285200	0.48486400
H	-0.51548900	-0.89285200	0.48486400
H	1.03097700	0.00000000	0.48486400
F	0.00000000	0.00000000	-1.25289700

MeH_2C-F
E = -1308.18
H = -1262.46
G = -1281.28
$\boldsymbol{N_{imag}}$ = 0

C	0.21557200	-1.79653900	0.08385500
H	-0.05313800	-0.89432700	0.62734800
H	0.00414600	-2.66786800	0.69843800
H	2.30806300	-1.71575100	0.46674800
F	-0.64750500	-1.86865300	-1.02705800
C	1.64313300	-1.76961500	-0.39366900
H	1.87806400	-2.67166400	-0.95480500
H	1.82218400	-0.90022400	-1.02282400

Me_2HC-F
E = -1819.94
H = -1756.00
G = -1776.88
$\boldsymbol{N_{imag}}$ = 0

C	0.92878600	-1.38619700	0.00000000
H	0.10962200	-2.10350500	0.00000000
H	2.53598200	-0.75250300	-1.27071100
H	2.19880500	-2.48784000	1.31774400
F	0.30801500	-0.11122500	0.00000000
C	1.74384000	-1.50032600	1.26522600
H	2.53598200	-0.75250300	1.27071100
H	1.11550700	-1.36206500	2.14223900
C	1.74384000	-1.50032600	-1.26522600
H	2.19880500	-2.48784000	-1.31774400
H	1.11550700	-1.36206500	-2.14223900

Me_3C-F
E = -2331.70
H = -2249.66
G = -2272.33
$\boldsymbol{N_{imag}}$ = 0

C	0.17560800	-1.90442600	0.00000000
H	0.47308500	-3.57056100	1.31497700
H	0.03516400	-2.06984700	-2.14056800
H	2.29739100	-2.20681200	0.00000000
F	-0.67914300	-0.76119400	0.00000000
C	1.59518400	-1.37486400	0.00000000
H	1.77414200	-0.76981800	-0.88701200
H	1.77414200	-0.76981800	0.88701200
C	-0.15175600	-2.68078300	-1.25925700
H	0.47308500	-3.57056100	-1.31497700
H	-1.19551600	-2.98968500	-1.25357700
C	-0.15175600	-2.68078300	1.25925700
H	0.03516400	-2.06984700	2.14056800
H	-1.19551600	-2.98968500	1.25357700

$H_3C–Cl$
E = -722.78
H = -696.51
G = -713.19
N_{imag} = 0

C	0.00000000	0.00000000	0.12946800
H	-0.51498900	0.89198600	0.46091000
H	-0.51498900	-0.89198600	0.46091000
H	1.02997700	0.00000000	0.46091000
Cl	0.00000000	0.00000000	-1.66166300

$MeH_2C–Cl$
E = -1232.32
H = -1187.35
G = -1206.94
N_{imag} = 0

C	0.22325600	-1.79949600	0.07970900
H	-0.05118400	-0.91458400	0.64176100
H	-0.00760300	-2.68455900	0.66083000
H	1.86072000	-0.88489900	-0.97878800
Cl	-0.89626000	-1.84213400	-1.33809600
C	1.66270500	-1.76885400	-0.37695900
H	2.31058200	-1.74417500	0.49839900
H	1.90403500	-2.65411200	-0.96078400

$Me_2HC–Cl$
E = -1742.63
H = -1679.29
G = -1700.85
N_{imag} = 0

C	0.23533600	-1.81735800	0.09560600
H	-0.01119700	-0.90236300	0.62454600
H	0.57848200	-3.01751400	1.82366500
H	1.83892000	-0.90619700	-1.03169600
Cl	-0.89552500	-1.80790500	-1.33538700
C	1.66113800	-1.78096400	-0.41144900

H	2.33741200	-1.74536000	0.44237600
H	1.88182900	-2.67689300	-0.98994100
C	-0.06842600	-3.03165600	0.94679300
H	-1.10338600	-3.03355000	1.27905800
H	0.12664500	-3.94590500	0.38808200

$Me_3C–Cl$
E = -2252.98
H = -2171.41
G = -2194.63
N_{imag} = 0

C	0.19930700	-1.79088200	0.10197800
H	0.52330400	-0.40711000	1.69406900
H	0.58107400	-2.97336800	1.83712900
H	1.78610100	-0.93402300	-1.08991900
Cl	-0.92939900	-1.89743400	-1.34993300
C	-0.13095700	-0.49754100	0.82646700
H	0.03023400	0.36268700	0.18016600
H	-1.16334900	-0.49638800	1.16975100
C	1.61849700	-1.78943300	-0.43887500
H	2.31150100	-1.72755400	0.40069300
H	1.82521300	-2.70336500	-0.99176000
C	-0.07473100	-3.00897100	0.96672800
H	-1.10682000	-3.01769000	1.31084200
H	0.12576100	-3.92768600	0.41950600

$H_3C–Br$
E = -702.91
H = -676.99
G = -694.49
N_{imag} = 0

C	0.00000000	0.00000000	1.08564200
H	-1.03221400	0.00000000	1.40702700
H	0.51610700	-0.89392400	1.40702700
H	0.51610700	0.89392400	1.40702700
Br	0.00000000	0.00000000	-0.86427500

$MeH_2C–Br$
E = -1212.12
H = -1167.44
G = -1187.85
N_{imag} = 0

C	0.16898600	0.02023600	0.00000000
H	-0.10327300	0.57849100	-0.88681500
H	-0.10327300	0.57849100	0.88681500
H	2.24570800	0.47713800	0.00000000
Br	-1.03383300	-1.53911800	0.00000000
C	1.61517100	-0.41232100	0.00000000
H	1.84992700	-0.99915200	0.88478400
H	1.84992700	-0.99915200	-0.88478400

$Me_2HC–Br$

E = -1722.05
H = -1658.95
G = -1681.30
N_{imag} = 0

C	0.21900200	-2.06187200	-0.16337500
H	-0.11663200	-2.25469200	0.84941700
H	0.23031500	-3.01812200	-2.09257000
H	2.29210900	-2.40520600	0.16195900
Br	-0.95744600	-0.55976900	-0.73049200
C	1.65582900	-1.59021900	-0.18571000
H	1.95846400	-1.32728300	-1.19806600
H	1.80770000	-0.73270100	0.46423900
C	-0.03945000	-3.24960300	-1.06337200
H	0.58064600	-4.08071500	-0.72470900
H	-1.08031800	-3.55997200	-1.03043900

$Me_3C–Br$

E = -2232.07
H = -2150.74
G = -2174.80
N_{imag} = 0

C	0.00000200	0.00001800	1.61123800
H	-1.27602900	0.74624400	3.14139700
H	0.87630400	-1.97689900	1.69333900
H	1.28345400	0.73338100	3.14139700
Br	-0.00003300	0.00013200	-0.40269400
C	1.26148100	0.71984200	2.05014100
H	2.15242500	0.20709300	1.69473800
H	1.27422300	1.74719000	1.69317900
C	-0.00741100	-1.45248400	2.04979700
H	-0.00743900	-1.47872200	3.14104300
H	-0.89652800	-1.96780700	1.69351100
C	-1.25406400	0.73267600	2.05014100
H	-1.25620000	1.76016500	1.69337300
H	-2.15018400	0.22917000	1.69453300

$H_3C–I$

E = -685.19
H = -659.58
G = -677.64
N_{imag} = 0

C	0.00000000	0.00000000	1.08411000
H	-1.03260500	0.00000000	1.40369100
H	0.51630300	-0.89426200	1.40369100
H	0.51630300	0.89426200	1.40369100
I	0.00000000	0.00000000	-1.05189100

$MeH_2C–I$
E = -1193.48
H = -1149.03
G = -1170.00
N_{imag} = 0

C	0.21888200	-1.79351100	0.07318400
H	-0.06575800	-0.89610400	0.60790800
H	-0.01687700	-2.66669400	0.66843000
H	2.30932000	-1.72077500	0.48009600
I	-1.15180900	-1.88770900	-1.58987800
C	1.65729600	-1.76964800	-0.39288800
H	1.90577200	-2.66680500	-0.95506700
H	1.85635400	-0.90171400	-1.01718500

$Me_2HC–I$
E = -1702.69
H = -1639.76
G = -1662.67
N_{imag} = 0

C	0.21488200	-2.05488000	-0.16891500
H	-0.12447200	-2.24375300	0.84342700
H	0.22988200	-3.02620800	-2.09524400
H	2.28730800	-2.41016000	0.16196300
I	-1.07813200	-0.40932300	-0.78452200
C	1.65633000	-1.59016300	-0.18602000
H	1.96679900	-1.32672200	-1.19601800
H	1.81468200	-0.73435500	0.46483000
C	-0.03901300	-3.25005600	-1.06398700
H	0.58500100	-4.07723700	-0.72047800
H	-1.07809000	-3.56692100	-1.03259800

$Me_3C–I$
E = -2212.22
H = -2131.04
G = -2155.61
N_{imag} = 0

C	0.20423600	-2.06741300	-0.14304200
H	0.39820400	-3.17973100	1.66011900
H	0.27244500	-3.02586700	-2.08717200
H	2.28798800	-2.36431800	0.16682100
I	-1.08490700	-0.43376900	-0.88342800
C	1.63693900	-1.56578600	-0.19693600
H	1.93489100	-1.31775200	-1.21326900
H	1.77849100	-0.69353600	0.43741100
C	-0.00944200	-3.25750100	-1.06241300
H	0.62304500	-4.07516100	-0.70851000
H	-1.04384200	-3.59365900	-1.04611500
C	-0.23133400	-2.37162700	1.27996100
H	-0.10715600	-1.50737500	1.92872800
H	-1.26804400	-2.69869900	1.31878500

$H_3C–H$
E = -734.80
H = -704.40
G = -717.66
N_{imag} = 0

C	0.00000000	0.00000000	0.00000000
H	0.62730800	-0.62730800	0.62730800
H	-0.62730800	-0.62730800	-0.62730800
H	0.62730800	0.62730800	-0.62730800
H	-0.62730800	0.62730800	0.62730800

$MeH_2C–H$
E = -1240.35
H = -1190.75
G = -1206.98
N_{imag} = 0

C	0.00000000	0.00000000	0.76284400
H	0.00000000	1.01544900	1.15605800
H	0.87940500	-0.50772500	1.15605800
H	0.87940500	0.50772500	-1.15605800
H	-0.87940500	-0.50772500	1.15605800
C	0.00000000	0.00000000	-0.76284400
H	0.00000000	-1.01544900	-1.15605800
H	-0.87940500	0.50772500	-1.15605800

$Me_2HC–H$
E = -1747.88
H = -1679.59
G = -1698.72
N_{imag} = 0

C	0.00000000	0.00000000	-1.13126100
H	0.87394800	0.00000000	-0.47830600
H	-0.88031700	-1.29612600	-2.62670300
H	0.88031700	1.29612600	-2.62670300
H	-0.87394800	0.00000000	-0.47830600
C	0.00000000	1.26484500	-1.98385600
H	-0.88031700	1.29612600	-2.62670300
H	0.00000000	2.16419900	-1.36982800
C	0.00000000	-1.26484500	-1.98385600
H	0.88031700	-1.29612600	-2.62670300
H	0.00000000	-2.16419900	-1.36982800

$Me_3C–H$
E = -2256.78
H = -2170.12
G = -2190.98
N_{imag} = 0

C	0.00000000	0.00000000	1.57256100
H	-1.48667000	0.00000000	3.14174000
H	1.75598500	-1.27562900	1.69707100
H	0.74333500	1.28749400	3.14174000

H	0.00000000	0.00000000	0.47974700
C	0.72507500	1.25586600	2.05028800
H	1.75598500	1.27562900	1.69707100
H	0.22673500	2.15854200	1.69707100
C	0.72507500	-1.25586600	2.05028800
H	0.74333500	-1.28749400	3.14174000
H	0.22673500	-2.15854200	1.69707100
C	-1.45015000	0.00000000	2.05028800
H	-1.98272000	0.88291300	1.69707100
H	-1.98272000	-0.88291300	1.69707100

$H_3C–CH_3$
E = -1240.35
H = -1190.75
G = -1206.98
N_{imag} = 0

C	0.00000000	0.00000000	0.76284400
H	0.00000000	1.01544900	1.15605800
H	0.87940500	-0.50772500	1.15605800
H	0.87940500	0.50772500	-1.15605800
H	-0.87940500	-0.50772500	1.15605800
C	0.00000000	0.00000000	-0.76284400
H	0.00000000	-1.01544900	-1.15605800
H	-0.87940500	0.50772500	-1.15605800

$MeH_2C–CH_3$
E = -1747.88
H = -1679.59
G = -1698.72
N_{imag} = 0

C	0.00000000	0.00000000	-1.13126100
H	0.87394800	0.00000000	-0.47830600
H	-0.88031700	-1.29612600	-2.62670300
H	0.88031700	1.29612600	-2.62670300
H	-0.87394800	0.00000000	-0.47830600
C	0.00000000	1.26484500	-1.98385600
H	-0.88031700	1.29612600	-2.62670300
H	0.00000000	2.16419900	-1.36982800
C	0.00000000	-1.26484500	-1.98385600
H	0.88031700	-1.29612600	-2.62670300
H	0.00000000	-2.16419900	-1.36982800

$Me_2HC–CH_3$
E = -2256.78
H = -2170.12
G = -2190.98
N_{imag} = 0

C	0.00000000	0.00000000	1.57256100
H	-1.48667000	0.00000000	3.14174000
H	1.75598500	-1.27562900	1.69707100
H	0.74333500	1.28749400	3.14174000

H	0.00000000	0.00000000	0.47974700
C	0.72507500	1.25586600	2.05028800
H	1.75598500	1.27562900	1.69707100
H	0.22673500	2.15854200	1.69707100
C	0.72507500	-1.25586600	2.05028800
H	0.74333500	-1.28749400	3.14174000
H	0.22673500	-2.15854200	1.69707100
C	-1.45015000	0.00000000	2.05028800
H	-1.98272000	0.88291300	1.69707100
H	-1.98272000	-0.88291300	1.69707100

$Me_3C–CH_3$
E = -2766.45
H = -2661.56
G = -2684.27
N_{imag} = 0

C	-0.00001800	-0.00002100	1.55711100
H	-1.23150800	0.79911500	3.15774200
H	0.77696400	-2.02206300	1.71421100
H	1.30761300	0.66675900	3.15786200
H	0.05339500	1.01846700	-0.36044700
C	1.28570700	0.65454300	2.06724900
H	2.16322600	0.10961300	1.71645900
H	1.36236400	1.68409500	1.71481200
C	-0.07599500	-1.44077400	2.06722700
H	-0.07566900	-1.46595800	3.15783000
H	-0.98695000	-1.92814700	1.71694800
C	-1.20972500	0.78626700	2.06714100
H	-1.17650600	1.81866500	1.71627800
H	-2.13961100	0.33788900	1.71452600
C	0.00002300	0.00002200	0.02683100
H	0.85531900	-0.55548000	-0.36037700
H	-0.90862800	-0.46299600	-0.36051200

F^-
E = -281.70
H = -280.81
G = -288.56
N_{imag} = 0

Cl^-
E = -219.28
H = -218.39
G = -226.14
N_{imag} = 0

Br^-
E = -202.18
H = -201.29
G = -209.04
N_{imag} = 0

I^-
E = -183.54
H = -182.65
G = -190.40
N_{imag} = 0

H^-
E = -147.31
H = -146.42
G = -154.17
N_{imag} = 0

H_3C^-
E = -647.91
H = -627.12
G = -640.87
N_{imag} = 0

C	-0.00001400	0.00000700	-1.03004300
H	-0.50721900	0.87847300	-0.61323300
H	-0.50720000	-0.87846700	-0.61323000
H	1.01443300	-0.00001300	-0.61322600

H_3C^+
E = -432.62
H = -410.24
G = -423.52
N_{imag} = 0

C	0.00000000	0.00000000	0.00000000
H	-0.53993400	0.93519300	0.00000000
H	-0.53993400	-0.93519300	0.00000000
H	1.07986800	0.00000000	0.00000000

MeH_2C^+
E = -967.34
H = -926.30
G = -942.54
N_{imag} = 0

C	0.00000000	-0.68516700	1.05190200
H	0.93097900	1.23100500	1.05320300
H	-0.93097900	1.23100500	1.05320300
C	0.00000000	0.68516700	1.05190200
H	0.93097900	-1.23100500	1.05320300
H	0.00000000	0.00000000	-0.05329200
H	-0.93097900	-1.23100500	1.05320300

Me_2HC^+
E = -1486.46
H = -1427.36
G = -1447.08
N_{imag} = 0

C	0.00000000	0.00000000	-0.56978800

H	-1.04215100	0.67419200	1.15335600
H	-1.82171000	-0.40852100	-0.01972800
H	1.82171000	0.40852100	-0.01972800
C	1.17097600	-0.48503600	0.09462400
H	1.04215100	-0.67419200	1.15335600
H	1.68111500	-1.27109900	-0.45361100
H	0.00000000	0.00000000	-1.65285500
C	-1.17097600	0.48503600	0.09462400
H	-1.68111500	1.27109900	-0.45361100

Me_3C^+
E = -2006.34
H = -1929.21
G = -1950.56
N_{imag} = 87.33*i* (spurious imaginary frequency associated with free methyl-group rotation)

C	0.02230200	-0.00293400	0.00000000
C	-0.01249700	1.44825500	0.00000000
H	-0.43532700	1.86380000	-0.90873100
H	-0.43532700	1.86380000	0.90873100
H	1.06175600	1.70082700	0.00000000
C	0.01384700	-0.72286500	-1.26300000
H	0.39277000	-0.12248400	-2.08430600
H	0.46878400	-1.70456400	-1.20095000
H	-1.06260700	-0.86631700	-1.45340100
C	0.01384700	-0.72286500	1.26300000
H	0.46878400	-1.70456400	1.20095000
H	0.39277000	-0.12248400	2.08430600
H	-1.06260700	-0.86631700	1.45340100

•••CF
E = -270.57
H = -266.69
G = -281.10
N_{imag} = 0

C	0.00000000	0.00000000	-4.32173000
F	0.00000000	0.00000000	-2.99966300

•••CCl
E = -216.06
H = -212.68
G = -227.87
N_{imag} = 0

C	0.00000000	0.00000000	-4.63091900
Cl	0.00000000	0.00000000	-2.97787100

•••CBr
E = -199.02
H = -195.85
G = -211.88
N_{imag} = 0

C	0.00000000	0.00000000	-4.85230700
Br	0.00000000	0.00000000	-3.02908600

•••CI

E = -189.63
H = -186.64
G = -203.26
N_{imag} = 0

C	0.00000000	0.00000000	-5.02861900
I	0.00000000	0.00000000	-2.99253900

•••CH

E = -228.95
H = -222.45
G = -234.62
N_{imag} = 0

C	0.00000000	0.00000000	-0.58163800
H	0.00000000	0.00000000	-1.67444900

•••CMe

E = -740.96
H = -714.89
G = -730.54
N_{imag} = 0

C	0.00000000	0.00000000	-4.64151300
H	0.51270100	-0.88802400	-2.77427600
C	0.00000000	0.00000000	-3.14671600
H	0.51270100	0.88802400	-2.77427600
H	-1.02540100	0.00000000	-2.77427600

•H

E = -51.62
H = -50.73
G = -58.48
N_{imag} = 0

•Me

E = -571.75
H = -550.67
G = -564.21
N_{imag} = 0

C	0.00914500	-0.00248200	-0.72628000
H	-0.01981300	-0.00785400	-1.80228800
H	-0.57941700	-0.71039600	-0.16849600
H	0.62667400	0.71081500	-0.20806500

•••C^+

E = 181.28
H = 182.17
G = 174.42
N_{imag} = 0

Table S9. Cartesian coordinates (in Å), energies (*E*, *H* and *G*, in kcal mol^{-1}), and number of imaginary vibrational frequencies (N_{imag}) of all stationary points and transition states in the gas phase, computed at ZORA-(U)BLYP-D3(BJ)/QZ4P.

H_3C-F
E = -535.89
H = -509.67
G = -525.57
N_{imag} = 0

C	0.00000000	0.00000000	0.14384900
H	-0.51934900	0.89953800	0.49078700
H	-0.51934900	-0.89953800	0.49078700
H	1.03869700	0.00000000	0.49078700
F	0.00000000	0.00000000	-1.26868100

MeH_2C-F
E = -906.47
H = -862.17
G = -881.06
N_{imag} = 0

C	0.20855200	-1.79680500	0.08333600
H	-0.06060300	-0.88824500	0.63537100
H	-0.00342700	-2.67441300	0.70586200
H	2.32338800	-1.71432400	0.47135300
F	-0.67118900	-1.86917200	-1.03540600
C	1.65014600	-1.76942800	-0.39346800
H	1.89009600	-2.67532100	-0.95984400
H	1.83355500	-0.89693300	-1.02917000

Me_2HC-F
E = -1277.31
H = -1215.21
G = -1236.21
N_{imag} = 0

C	0.92965600	-1.38488100	0.00000000
H	0.10647800	-2.11185700	0.00000000
H	2.54478200	-0.75153500	-1.29457500
H	2.20345100	-2.49652400	1.34483900
F	0.28963200	-0.09732000	0.00000000
C	1.74633200	-1.50189400	1.27986500
H	2.54478200	-0.75153500	1.29457500
H	1.10989600	-1.35621500	2.15828900
C	1.74633200	-1.50189400	-1.27986500
H	2.20345100	-2.49652400	-1.34483900
H	1.10989600	-1.35621500	-2.15828900

Me_3C-F
E = -1647.77
H = -1568.00
G = -1590.89
N_{imag} = 0

C	0.17703100	-1.90637900	0.00000000
H	0.46772900	-3.58681200	1.33972100
H	0.02742100	-2.07110900	-2.15752700
H	2.32605500	-2.19774200	0.00000000
F	-0.69167800	-0.74406500	0.00000000
C	1.60861200	-1.36908100	0.00000000
H	1.78649200	-0.75633100	-0.88953800
H	1.78649200	-0.75633100	0.88953800
C	-0.15547700	-2.68772700	-1.27167900
H	0.46772900	-3.58681200	-1.33972100
H	-1.20653500	-2.99372900	-1.26806200
C	-0.15547700	-2.68772700	1.27167900
H	0.02742100	-2.07110900	2.15752700
H	-1.20653500	-2.99372900	1.26806200

$H_3C–Cl$
E = -496.01
H = -470.54
G = -487.27
N_{imag} = 0

C	0.00000000	0.00000000	0.13107000
H	-0.51818000	0.89751300	0.46868700
H	-0.51818000	-0.89751300	0.46868700
H	1.03635900	0.00000000	0.46868700
Cl	0.00000000	0.00000000	-1.68659600

$MeH_2C–Cl$
E = -865.15
H = -821.48
G = -841.16
N_{imag} = 0

C	0.21895900	-1.79943700	0.07940700
H	-0.05697100	-0.90915500	0.64758900
H	-0.01298800	-2.68946500	0.66726900
H	1.87541900	-0.88090700	-0.98190100
Cl	-0.93177700	-1.84399300	-1.35103200
C	1.67031000	-1.76860700	-0.37583700
H	2.32506600	-1.74444900	0.50553000
H	1.91823200	-2.65680100	-0.96495300

$Me_2HC–Cl$
E = -1234.71
H = -1173.12
G = -1194.82
N_{imag} = 0

C	0.23595100	-1.82017700	0.09381600
H	-0.01262600	-0.89838600	0.62605300
H	0.57262500	-3.02919500	1.84302400
H	1.84714000	-0.89498700	-1.03966800
Cl	-0.92148300	-1.79672700	-1.35827300
C	1.67251600	-1.77597300	-0.41597900

H	2.35916300	-1.73720400	0.44003900
H	1.90393300	-2.67113700	-1.00291000
C	-0.07443200	-3.03921600	0.95590600
H	-1.11633000	-3.03785000	1.28766700
H	0.11477000	-3.96480900	0.40197500

$Me_3C–Cl$
E = -1604.02
H = -1524.67
G = -1548.13
N_{imag} = 0

C	0.20128800	-1.79078700	0.10453500
H	0.51998900	-0.38525000	1.70858200
H	0.57794400	-2.99392800	1.85427700
H	1.79835100	-0.93185300	-1.10196800
Cl	-0.95056600	-1.90032700	-1.37717000
C	-0.13391000	-0.48652800	0.83227300
H	0.02379200	0.37876900	0.18203500
H	-1.17280600	-0.48241700	1.17441600
C	1.63035000	-1.78927500	-0.44391400
H	2.33735700	-1.72686700	0.39395100
H	1.83813600	-2.70580200	-1.00352400
C	-0.07756600	-3.01948000	0.97371100
H	-1.11619000	-3.03122900	1.31655100
H	0.11956800	-3.94378400	0.42309000

$H_3C–Br$
E = -482.97
H = -457.81
G = -475.38
N_{imag} = 0

C	0.00000000	0.00000000	1.09192500
H	-1.03940800	0.00000000	1.41454800
H	0.51970400	-0.90015400	1.41454800
H	0.51970400	0.90015400	1.41454800
Br	0.00000000	0.00000000	-0.89312200

$MeH_2C–Br$
E = -851.93
H = -808.52
G = -829.04
N_{imag} = 0

C	0.16743200	0.02380400	0.00000000
H	-0.11063300	0.58455200	-0.89252400
H	-0.11063300	0.58455200	0.89252400
H	2.26358500	0.48354400	0.00000000
Br	-1.06904400	-1.55737900	0.00000000
C	1.62310400	-0.40972500	0.00000000
H	1.86276400	-1.00236700	0.88792700
H	1.86276400	-1.00236700	-0.88792700

Me_2HC-Br

E = -1221.34
H = -1159.98
G = -1182.53
N_{imag} = 0

C	0.22381800	-2.06596300	-0.16499600
H	-0.11814700	-2.25568600	0.85428000
H	0.22003400	-3.03732200	-2.10630100
H	2.31928000	-2.39610200	0.17317900
Br	-0.98427200	-0.53252500	-0.72971900
C	1.66801100	-1.58447600	-0.18095400
H	1.98037600	-1.31398500	-1.19501000
H	1.81211600	-0.71882100	0.47090800
C	-0.04549000	-3.26177100	-1.06796600
H	0.56976300	-4.10861700	-0.73238300
H	-1.09526800	-3.56488600	-1.03415700

Me_3C-Br

E = -1590.55
H = -1511.40
G = -1535.05
N_{imag} = 0

C	0.00001300	-0.00002500	1.62069200
H	-1.30317400	0.76112400	3.15269900
H	0.87824900	-1.99355500	1.69047000
H	1.31083400	0.74782900	3.15272600
Br	-0.00000600	-0.00002900	-0.43934900
C	1.27276400	0.72621900	2.05420500
H	2.16784500	0.21406400	1.69041200
H	1.28707300	1.75743300	1.69056200
C	-0.00748800	-1.46538000	2.05423900
H	-0.00760500	-1.50913300	3.15276300
H	-0.89869700	-1.98438600	1.69064300
C	-1.26527000	0.73916700	2.05417900
H	-1.26902600	1.77048600	1.69057200
H	-2.16551400	0.23618600	1.69032200

H_3C-I

E = -471.80
H = -446.92
G = -465.07
N_{imag} = 0

C	0.00000000	0.00000000	1.09425900
H	-1.03988200	0.00000000	1.41358100
H	0.51994100	-0.90056500	1.41358100
H	0.51994100	0.90056500	1.41358100
I	0.00000000	0.00000000	-1.09170800

$MeH_2C–I$
E = -840.03
H = -796.85
G = -817.96
N_{imag} = 0

C	0.22041800	-1.79336900	0.07868600
H	-0.07202200	-0.89042800	0.61410800
H	-0.02282100	-2.67287200	0.67440900
H	2.32811000	-1.71927700	0.48715700
I	-1.19889600	-1.88922800	-1.61398400
C	1.66671400	-1.76930600	-0.38989200
H	1.92081200	-2.67025600	-0.95624900
H	1.87086400	-0.89822500	-1.01963500

$Me_2HC–I$
E = -1208.88
H = -1147.71
G = -1170.84
N_{imag} = 0

C	0.22157200	-2.06072500	-0.17080800
H	-0.12769700	-2.24222600	0.84713200
H	0.21925200	-3.04673700	-2.10886800
H	2.31426000	-2.40404900	0.17054600
I	-1.11404600	-0.37131200	-0.78706500
C	1.66906500	-1.58541200	-0.18122300
H	1.98957700	-1.31264400	-1.19210800
H	1.82099100	-0.72422900	0.47467900
C	-0.04412700	-3.26292500	-1.06824300
H	0.57747300	-4.10440400	-0.72812100
H	-1.09114300	-3.57511400	-1.03348300

$Me_3C–I$
E = -1577.70
H = -1498.71
G = -1523.57
N_{imag} = 0

C	0.21211800	-2.07742300	-0.13845200
H	0.39106000	-3.18736900	1.69235100
H	0.26716700	-3.03288400	-2.10116400
H	2.32075100	-2.35559900	0.16604900
I	-1.11373900	-0.39581500	-0.90075600
C	1.65024800	-1.56206000	-0.19713700
H	1.94658600	-1.30732700	-1.21840300
H	1.79010100	-0.68207400	0.43671600
C	-0.01101500	-3.26868800	-1.07031000
H	0.61982300	-4.10290900	-0.72777200
H	-1.05234100	-3.60217000	-1.05724200
C	-0.23481500	-2.37492600	1.29301400
H	-0.11608800	-1.50350000	1.94277900
H	-1.27834400	-2.69945000	1.33126800

$H_3C–H$
E = -537.34
H = -507.64
G = -520.91
N_{imag} = 0

C	0.00000000	0.00000000	0.00000000
H	0.63141600	-0.63141600	0.63141600
H	-0.63141600	-0.63141600	-0.63141600
H	0.63141600	0.63141600	-0.63141600
H	-0.63141600	0.63141600	0.63141600

$MeH_2C–H$
E = -902.17
H = -853.86
G = -870.13
N_{imag} = 0

C	0.00000000	0.00000000	0.76897200
H	0.00000000	1.02133300	1.16763300
H	0.88450000	-0.51066600	1.16763300
H	0.88450000	0.51066600	-1.16763300
H	-0.88450000	-0.51066600	1.16763300
C	0.00000000	0.00000000	-0.76897200
H	0.00000000	-1.02133300	-1.16763300
H	-0.88450000	0.51066600	-1.16763300

$Me_2HC–H$
E = -1268.90
H = -1202.42
G = -1221.62
N_{imag} = 0

C	0.00000000	0.00000000	-1.13419100
H	0.87825600	0.00000000	-0.47411100
H	-0.88508600	-1.32313000	-2.63268200
H	0.88508600	1.32313000	-2.63268200
H	-0.87825600	0.00000000	-0.47411100
C	0.00000000	1.28105700	-1.98520100
H	-0.88508600	1.32313000	-2.63268200
H	0.00000000	2.18108600	-1.35925600
C	0.00000000	-1.28105700	-1.98520100
H	0.88508600	-1.32313000	-2.63268200
H	0.00000000	-2.18108600	-1.35925600

$Me_3C–H$
E = -1636.82
H = -1552.44
G = -1573.41
N_{imag} = 0

C	0.00000000	0.00000000	1.57982300
H	-1.51910400	0.00000000	3.14891000
H	1.76864800	-1.28938700	1.69160300
H	0.75955200	1.31558200	3.14891000

H	0.00000000	0.00000000	0.47910300
C	0.73304400	1.26966900	2.05184700
H	1.76864800	1.28938700	1.69160300
H	0.23231800	2.17638800	1.69160300
C	0.73304400	-1.26966900	2.05184700
H	0.75955200	-1.31558200	3.14891000
H	0.23231800	-2.17638800	1.69160300
C	-1.46608800	0.00000000	2.05184700
H	-2.00096600	0.88700000	1.69160300
H	-2.00096600	-0.88700000	1.69160300

$H_3C–CH_3$
E = -902.17
H = -853.86
G = -870.13
N_{imag} = 0

C	0.00000000	0.00000000	0.76897200
H	0.00000000	1.02133300	1.16763300
H	0.88450000	-0.51066600	1.16763300
H	0.88450000	0.51066600	-1.16763300
H	-0.88450000	-0.51066600	1.16763300
C	0.00000000	0.00000000	-0.76897200
H	0.00000000	-1.02133300	-1.16763300
H	-0.88450000	0.51066600	-1.16763000

$MeH_2C–CH_3$
E = -1268.90
H = -1202.42
G = -1221.62
N_{imag} = 0

C	0.00000000	0.00000000	-1.13419100
H	0.87825600	0.00000000	-0.47411100
H	-0.88508600	-1.32313000	-2.63268200
H	0.88508600	1.32313000	-2.63268200
H	-0.87825600	0.00000000	-0.47411100
C	0.00000000	1.28105700	-1.98520100
H	-0.88508600	1.32313000	-2.63268200
H	0.00000000	2.18108600	-1.35925600
C	0.00000000	-1.28105700	-1.98520100
H	0.88508600	-1.32313000	-2.63268200
H	0.00000000	-2.18108600	-1.35925600

$Me_2HC–CH_3$
E = -1636.82
H = -1552.44
G = -1573.41
N_{imag} = 0

C	0.00000000	0.00000000	1.57982300
H	-1.51910400	0.00000000	3.14891000
H	1.76864800	-1.28938700	1.69160300
H	0.75955200	1.31558200	3.14891000

H	0.00000000	0.00000000	0.47910300
C	0.73304400	1.26966900	2.05184700
H	1.76864800	1.28938700	1.69160300
H	0.23231800	2.17638800	1.69160300
C	0.73304400	-1.26966900	2.05184700
H	0.75955200	-1.31558200	3.14891000
H	0.23231800	-2.17638800	1.69160300
C	-1.46608800	0.00000000	2.05184700
H	-2.00096600	0.88700000	1.69160300
H	-2.00096600	-0.88700000	1.69160300

$Me_3C–CH_3$
E = -2005.16
H = -1903.02
G = -1924.87
N_{imag} = 0

C	0.00000800	0.00002000	1.55709500
H	-1.24618100	0.80900800	3.16861700
H	0.78137700	-2.04133900	1.72007300
H	1.32340700	0.67496600	3.16868300
H	0.05378300	1.02283800	-0.38074800
C	1.29760400	0.66134800	2.07207300
H	2.18259600	0.11661700	1.72074000
H	1.37745700	1.69723100	1.71999900
C	-0.07596300	-1.45441300	2.07202900
H	-0.07718800	-1.48359000	3.16863500
H	-0.99007100	-1.94864400	1.72059000
C	-1.22163900	0.79299100	2.07201800
H	-1.19286600	1.83164200	1.72020200
H	-2.15854500	0.34366300	1.72030400
C	0.00001000	0.00010400	0.01230500
H	0.85879100	-0.55778700	-0.38089500
H	-0.91258200	-0.46465300	-0.38082800

F^-
E = -94.33
H = -93.44
G = -101.19
N_{imag} = 0

Cl^-
E = -87.90
H = -87.01
G = -94.76
N_{imag} = 0

Br^-
E = -81.37
H = -80.48
G = -88.23
N_{imag} = 0

I^-
E = -75.62
H = -74.73
G = -82.48
N_{imag} = 0

H^-
E = -39.22
H = -38.33
G = -46.08
N_{imag} = 0

H_3C^-
E = -405.10
H = -385.27
G = -399.05
N_{imag} = 0

C	0.00000000	0.00000000	-1.02685000
H	-0.51565800	0.89314600	-0.61429400
H	-0.51565800	-0.89314600	-0.61429400
H	1.03131600	0.00000000	-0.61429400

H_3C^+
E = -179.04
H = -157.54
G = -170.85
N_{imag} = 0

C	0.00000000	0.00000000	0.00000000
H	-0.54835500	0.94977800	0.00000000
H	-0.54835500	-0.94977800	0.00000000
H	1.09670900	0.00000000	0.00000000

MeH_2C^+
E = -589.94
H = -550.67
G = -567.10
N_{imag} = 0

C	0.00000000	-0.69293500	1.05241900
H	0.93706400	1.25105000	1.06049400
H	-0.93706400	1.25105000	1.06049400
C	0.00000000	0.69293500	1.05241900
H	0.93706400	-1.25105000	1.06049400
H	0.00000000	0.00000000	-0.08348900
H	-0.93706400	-1.25105000	1.06049400

Me_2HC^+
E = -980.72
H = -923.34
G = -943.36
N_{imag} = 0

C	0.00000000	0.00000000	-0.53867000

H	-1.16135000	0.51647500	1.19633100
H	-1.97092300	-0.34163800	-0.17245100
H	1.97092300	0.34163800	-0.17245100
C	1.21044900	-0.42856000	0.11061300
H	1.16135000	-0.51647500	1.19633100
H	1.63397200	-1.32057500	-0.38487000
H	0.00000000	0.00000000	-1.63393800
C	-1.21044900	0.42856000	0.11061300
H	-1.63397200	1.32057500	-0.38487000

Me_3C^+
E = -1365.56
H = -1289.94
G = -1313.91
N_{imag} = 0

C	0.91199700	-1.43362700	0.45342200
H	0.83745100	0.72629700	0.48461000
H	0.63226900	-3.13521700	1.59776100
H	2.40091100	-1.00629900	-0.93155300
C	2.32748400	-1.45283700	0.08051600
H	2.89523500	-0.74477100	0.70517100
H	2.78432400	-2.44304800	0.07484400
C	0.19714600	-2.69110500	0.67867400
H	-0.88070500	-2.58629600	0.80885600
H	0.44883100	-3.42833200	-0.09895300
C	0.20893500	-0.15715800	0.59918200
H	-0.61443700	-0.13938500	-0.13997000
H	-0.32746100	-0.14113400	1.56353100

•••CF
E = -98.22
H = -94.50
G = -108.93
N_{imag} = 0

C	0.00000000	0.00000000	-4.33324400
F	0.00000000	0.00000000	-2.98814900

•••CCl
E = -77.20
H = -73.91
G = -89.13
N_{imag} = 0

C	0.00000000	0.00000000	-4.64047800
Cl	0.00000000	0.00000000	-2.96831200

•••CBr
E = -66.68
H = -63.60
G = -79.66
N_{imag} = 0

C	0.00000000	0.00000000	-4.86558000

Br	0.00000000	0.00000000	-3.01581300

•••CI

E = -189.63
H = -186.64
G = -203.26
N_{imag} = 0

C	0.00000000	0.00000000	-5.03400500
I	0.00000000	0.00000000	-2.98715400

•••CH

E = -115.35
H = -109.07
G = -121.25
N_{imag} = 0

C	0.00000000	0.00000000	-0.57717500
H	0.00000000	0.00000000	-1.67891200

•••CMe

E = -488.54
H = -463.51
G = -479.19
N_{imag} = 0

C	0.00000000	0.00000000	-4.65152700
H	0.51659800	-0.89477500	-2.76979900
C	0.00000000	0.00000000	-3.15013300
H	0.51659800	0.89477500	-2.76979900
H	-1.03319700	0.00000000	-2.76979900

•H

E = -22.15
H = -21.26
G = -29.01
N_{imag} = 0

•Me

E = -404.92
H = -384.20
G = -398.70
N_{imag} = 0

C	0.00914700	-0.00248000	-0.72628500
H	-0.01999700	-0.00788900	-1.80911800
H	-0.58314400	-0.71487800	-0.16495400
H	0.63058300	0.71533100	-0.20477300

•••C^+

E = 357.76
H = 358.65
G = 350.90
N_{imag} = 0

Table S10. Cartesian coordinates (in Å), energies (*E*, *H* and *G*, in kcal mol^{-1}), and number of imaginary vibrational frequencies (N_{imag}) of all stationary points and transition states in the gas phase, computed at COSMO(H_2O)-ZORA-(U)BLYP-D3(BJ)/QZ4P.

H_3C-F
E = -538.85
H = -512.70
G = -528.63
$\boldsymbol{N_{imag}}$ = 0

C	0.00000000	0.00000000	0.15741600
H	-0.52017600	0.90097200	0.48945200
H	-0.52017600	-0.90097200	0.48945200
H	1.04035300	0.00000000	0.48945200
F	0.00000000	0.00000000	-1.27824100

MeH_2C-F
E = -909.42
H = -865.29
G = -884.21
$\boldsymbol{N_{imag}}$ = 0

C	0.21859500	-1.79607800	0.09370700
H	-0.06003900	-0.88690000	0.63356200
H	-0.00282100	-2.67602600	0.70390200
H	2.32025100	-1.71427200	0.47077100
F	-0.68229000	-1.86964200	-1.04261900
C	1.65020300	-1.76952700	-0.39596500
H	1.89172000	-2.67793100	-0.95775000
H	1.83489900	-0.89426500	-1.02757400

Me_2HC-F
E = -1280.23
H = -1218.35
G = -1239.40
$\boldsymbol{N_{imag}}$ = 0

C	0.93710500	-1.39719400	0.00000000
H	0.10559200	-2.10961900	0.00000000
H	2.54791000	-0.75226500	-1.29312800
H	2.20245200	-2.49495000	1.34242500
F	0.27947700	-0.08492600	0.00000000
C	1.74693200	-1.49999100	1.27982500
H	2.54791000	-0.75226500	1.29312800
H	1.10896400	-1.36012200	2.15814200
C	1.74693200	-1.49999100	-1.27982500
H	2.20245200	-2.49495000	-1.34242500
H	1.10896400	-1.36012200	-2.15814200

Me_3C-F
E = -1650.65
H = -1571.15
G = -1594.07
$\boldsymbol{N_{imag}}$ = 0

C	0.18570100	-1.91798600	0.00000000
H	0.46703700	-3.58509100	1.33851600
H	0.03103400	-2.07128900	-2.15765300
H	2.32394500	-2.19695500	0.00000000
F	-0.70222000	-0.73005900	0.00000000
C	1.60792600	-1.36776300	0.00000000
H	1.78671000	-0.75872100	-0.89193200
H	1.78671000	-0.75872100	0.89193200
C	-0.15638000	-2.68669000	-1.27186800
H	0.46703700	-3.58509100	-1.33851600
H	-1.20643800	-2.99616800	-1.26586500
C	-0.15638000	-2.68669000	1.27186800
H	0.03103400	-2.07128900	2.15765300
H	-1.20643800	-2.99616800	1.26586500

$H_3C–Cl$
E = -497.97
H = -472.56
G = -489.32
N_{imag} = 0

C	0.00000000	0.00000000	0.14071400
H	-0.51920000	0.89928100	0.46691200
H	-0.51920000	-0.89928100	0.46691200
H	1.03840000	0.00000000	0.46691200
Cl	0.00000000	0.00000000	-1.69091500

$MeH_2C–Cl$
E = -867.06
H = -823.52
G = -843.24
N_{imag} = 0

C	0.22682400	-1.79916600	0.08709200
H	-0.05684200	-0.90741100	0.64577400
H	-0.01277900	-2.69150500	0.66509900
H	1.87781100	-0.87851800	-0.98069200
Cl	-0.94141100	-1.84400900	-1.35491200
C	1.67088800	-1.76862000	-0.37868500
H	2.32086500	-1.74425100	0.50559500
H	1.92089500	-2.65933200	-0.96319900

$Me_2HC–Cl$
E = -1236.58
H = -1175.18
G = -1196.95
N_{imag} = 0

C	0.24408800	-1.82114300	0.10326600
H	-0.01412000	-0.89803600	0.62464500
H	0.57267900	-3.02757800	1.84036100
H	1.84806200	-0.89360500	-1.03783200
Cl	-0.93201800	-1.79218600	-1.36758400
C	1.67283500	-1.77712500	-0.41794300

H	2.35607300	-1.73686000	0.43998000
H	1.90644300	-2.67448600	-1.00066700
C	-0.07511200	-3.04114200	0.95456300
H	-1.11568800	-3.03643900	1.29037800
H	0.11798600	-3.96706500	0.40248500

$Me_3C–Cl$
E = -1605.86
H = -1526.75
G = -1550.30
N_{imag} = 0

C	0.21034500	-1.78990900	0.11620800
H	0.51922700	-0.38528700	1.70709900
H	0.57672500	-2.99375100	1.85307000
H	1.79905700	-0.92939300	-1.10004000
Cl	-0.96195800	-1.90126400	-1.39187900
C	-0.13511200	-0.48547100	0.83173500
H	0.02667200	0.37943600	0.18206300
H	-1.17278900	-0.48410600	1.17743500
C	1.63064900	-1.78939800	-0.44556000
H	2.33629900	-1.72710400	0.39267100
H	1.83879700	-2.70808200	-1.00138800
C	-0.07875600	-3.02063400	0.97325600
H	-1.11644200	-3.02951600	1.31885700
H	0.12302400	-3.94427900	0.42331900

$H_3C–Br$
E = -484.71
H = -459.62
G = -477.20
N_{imag} = 0

C	0.00000000	0.00000000	1.10002500
H	-1.04130400	0.00000000	1.41274700
H	0.52065200	-0.90179600	1.41274700
H	0.52065200	0.90179600	1.41274700
Br	0.00000000	0.00000000	-0.89581900

$MeH_2C–Br$
E = -853.63
H = -810.36
G = -830.93
N_{imag} = 0

C	0.17438500	0.03047300	0.00000000
H	-0.11015700	0.58239700	-0.89438800
H	-0.11015700	0.58239700	0.89438800
H	2.25892200	0.48385700	0.00000000
Br	-1.07796600	-1.56038700	0.00000000
C	1.62360500	-0.41255900	0.00000000
H	1.86535400	-1.00078300	0.89036100
H	1.86535400	-1.00078300	-0.89036100

Me_2HC-Br

E = -1223.02
H = -1161.86
G = -1184.48
N_{imag} = 0

C	0.23121100	-2.07474000	-0.16267000
H	-0.11915400	-2.25432800	0.85397300
H	0.22412200	-3.03892400	-2.10794500
H	2.31585000	-2.39609300	0.17315800
Br	-0.99474200	-0.52257000	-0.72859900
C	1.66843100	-1.58294700	-0.18281800
H	1.98308400	-1.31717000	-1.19741600
H	1.81274400	-0.72020000	0.47279500
C	-0.04593100	-3.26106800	-1.07026500
H	0.56947400	-4.10560800	-0.73097600
H	-1.09486900	-3.56650500	-1.03235700

Me_3C-Br

E = -1592.23
H = -1513.32
G = -1537.71
N_{imag} = 0

C	0.00000600	-0.00002000	1.63578500
H	-1.30363000	0.76121900	3.15107900
H	0.88050700	-1.99269500	1.69200100
H	1.31106500	0.74810200	3.15124500
Br	0.00002200	-0.00004700	-0.45823700
C	1.27389300	0.72689200	2.05327200
H	2.16820700	0.21144200	1.69249000
H	1.28512900	1.75905300	1.69241900
C	-0.00747000	-1.46670900	2.05325400
H	-0.00712500	-1.50952300	3.15122200
H	-0.90126500	-1.98337600	1.69289400
C	-1.26643700	0.73984300	2.05313300
H	-1.26698000	1.77214300	1.69251100
H	-2.16592200	0.23367500	1.69206500

H_3C-I

E = -473.22
H = -448.42
G = -466.58
N_{imag} = 0

C	0.00000000	0.00000000	1.09857100
H	-1.04112200	0.00000000	1.41197200
H	0.52056100	-0.90163800	1.41197200
H	0.52056100	0.90163800	1.41197200
I	0.00000000	0.00000000	-1.09119500

$MeH_2C–I$
E = -841.30
H = -798.25
G = -819.39
N_{imag} = 0

C	0.22428400	-1.79302200	0.08234400
H	-0.07152200	-0.88898200	0.61240400
H	-0.02224100	-2.67407900	0.67292000
H	2.32429200	-1.71973400	0.48753000
I	-1.20311500	-1.88977300	-1.61468700
C	1.66676400	-1.76935900	-0.39195400
H	1.92222700	-2.67191500	-0.95548600
H	1.87249200	-0.89609800	-1.01847000

$Me_2HC–I$
E = -1210.04
H = -1149.06
G = -1172.25
N_{imag} = 0

C	0.22577200	-2.06575800	-0.16946300
H	-0.12835600	-2.24127200	0.84670200
H	0.22194300	-3.04772600	-2.11023700
H	2.31082500	-2.40472000	0.17008600
I	-1.12014400	-0.36521100	-0.78648600
C	1.66923400	-1.58437900	-0.18263800
H	1.99139700	-1.31472500	-1.19396200
H	1.82145900	-0.72567300	0.47658800
C	-0.04436100	-3.26230200	-1.06989000
H	0.57805800	-4.10123600	-0.72670100
H	-1.09064900	-3.57677600	-1.03156200

$Me_3C–I$
E = -1578.79
H = -1500.02
G = -1524.96
N_{imag} = 0

C	0.21770400	-2.08449900	-0.13525100
H	0.39050000	-3.18661000	1.69146200
H	0.26952900	-3.03278600	-2.10136400
H	2.31960300	-2.35465200	0.16639200
I	-1.12104800	-0.38628400	-0.90477300
C	1.65065700	-1.56094900	-0.19749400
H	1.94724100	-1.31024200	-1.21971900
H	1.78999900	-0.68248000	0.43862200
C	-0.01177200	-3.26870700	-1.07134600
H	0.61934300	-4.10161200	-0.72803700
H	-1.05265300	-3.60352800	-1.05492200
C	-0.23570100	-2.37447900	1.29363800
H	-0.11348100	-1.50345100	1.94333800
H	-1.27840700	-2.70191500	1.33039600

$H_3C–H$
E = -537.16
H = -507.63
G = -520.90
N_{imag} = 0

C	0.00000000	0.00000000	0.00000000
H	0.63162900	-0.63162900	0.63162900
H	-0.63162900	-0.63162900	-0.63162900
H	0.63162900	0.63162900	-0.63162900
H	-0.63162900	0.63162900	0.63162900

$MeH_2C–H$
E = -901.84
H = -853.74
G = -870.02
N_{imag} = 0

C	0.00000000	0.00000000	0.76921100
H	0.00000000	1.02198700	1.16679100
H	0.88506700	-0.51099400	1.16679100
H	0.88506700	0.51099400	-1.16679100
H	-0.88506700	-0.51099400	1.16679100
C	0.00000000	0.00000000	-0.76921100
H	0.00000000	-1.02198700	-1.16679100
H	-0.88506700	0.51099400	-1.16679100

$Me_2HC–H$
E = -1268.49
H = -1202.26
G = -1221.46
N_{imag} = 0

C	0.00000000	0.00000000	-1.13402500
H	0.87899300	0.00000000	-0.47488300
H	-0.88582600	-1.32204500	-2.63247300
H	0.88582600	1.32204500	-2.63247300
H	-0.87899300	0.00000000	-0.47488300
C	0.00000000	1.28111100	-1.98553400
H	-0.88582600	1.32204500	-2.63247300
H	0.00000000	2.18080800	-1.35865100
C	0.00000000	-1.28111100	-1.98553400
H	0.88582600	-1.32204500	-2.63247300
H	0.00000000	-2.18080800	-1.35865100

$Me_3C–H$
E = -1636.37
H = -1552.28
G = -1573.24
N_{imag} = 0

C	0.00000000	0.00000000	1.57986100
H	-1.51805700	0.00000000	3.14959400
H	1.76866300	-1.28834600	1.69103800
H	0.75902800	1.31467600	3.14959400

H	0.00000000	0.00000000	0.47934400
C	0.73311900	1.26980000	2.05220200
H	1.76866300	1.28834600	1.69103800
H	0.23140900	2.17588000	1.69103800
C	0.73311900	-1.26980000	2.05220200
H	0.75902800	-1.31467600	3.14959400
H	0.23140900	-2.17588000	1.69103800
C	-1.46623900	0.00000000	2.05220200
H	-2.00007200	0.88753300	1.69103800
H	-2.00007200	-0.88753300	1.69103800

$H_3C–CH_3$
E = -901.84
H = -853.74
G = -870.02
N_{imag} = 0

C	0.00000000	0.00000000	0.76921000
H	0.00000000	1.02198700	1.16679100
H	0.88506700	-0.51099300	1.16679100
H	0.88506700	0.51099300	-1.16679100
H	-0.88506700	-0.51099300	1.16679100
C	0.00000000	0.00000000	-0.76921000
H	0.00000000	-1.02198700	-1.16679100
H	-0.88506700	0.51099300	-1.16679100

$MeH_2C–CH_3$
E = -1268.49
H = -1202.26
G = -1221.46
N_{imag} = 0

C	0.00000000	0.00000000	-1.13402500
H	0.87899300	0.00000000	-0.47488300
H	-0.88582600	-1.32204500	-2.63247300
H	0.88582600	1.32204500	-2.63247300
H	-0.87899300	0.00000000	-0.47488300
C	0.00000000	1.28111100	-1.98553400
H	-0.88582600	1.32204500	-2.63247300
H	0.00000000	2.18080800	-1.35865100
C	0.00000000	-1.28111100	-1.98553400
H	0.88582600	-1.32204500	-2.63247300
H	0.00000000	-2.18080800	-1.35865100

$Me_2HC–CH_3$
E = -1636.37
H = -1552.28
G = -1573.24
N_{imag} = 0

C	0.00000000	0.00000000	1.57986100
H	-1.51805700	0.00000000	3.14959400
H	1.76866300	-1.28834600	1.69103800
H	0.75902800	1.31467600	3.14959400

H	0.00000000	0.00000000	0.47934400
C	0.73311900	1.26980000	2.05220200
H	1.76866300	1.28834600	1.69103800
H	0.23140900	2.17588000	1.69103800
C	0.73311900	-1.26980000	2.05220200
H	0.75902800	-1.31467600	3.14959400
H	0.23140900	-2.17588000	1.69103800
C	-1.46623900	0.00000000	2.05220200
H	-2.00007200	0.88753300	1.69103800
H	-2.00007200	-0.88753300	1.69103800

$Me_3C–CH_3$
E = -2004.68
H = -1902.86
G = -1925.35
N_{imag} = 0

C	0.00000100	0.00001400	1.55709500
H	-1.24516100	0.80833100	3.16891900
H	0.78162800	-2.04066000	1.71897900
H	1.32221400	0.67446200	3.16903100
H	0.05378000	1.02362300	-0.37961600
C	1.29783500	0.66132100	2.07217100
H	2.18204900	0.11528000	1.72027800
H	1.37664100	1.69717300	1.71910800
C	-0.07610800	-1.45462500	2.07209800
H	-0.07675600	-1.48231600	3.16894700
H	-0.99107300	-1.94748100	1.72029200
C	-1.22176300	0.79319500	2.07207100
H	-1.19158000	1.83178600	1.71954200
H	-2.15809600	0.34284700	1.71948200
C	0.00003800	0.00014000	0.01208000
H	0.85948700	-0.55807000	-0.37978100
H	-0.91313700	-0.46502000	-0.37980500

F^-
E = -194.37
H = -193.48
G = -201.23
N_{imag} = 0

Cl^-
E = -160.58
H = -159.69
G = -167.44
N_{imag} = 0

Br^-
E = -147.55
H = -146.66
G = -154.41
N_{imag} = 0

I^-
E = -132.18
H = -131.29
G = -139.04
N_{imag} = 0

H^-
E = -120.29
H = -119.40
G = -127.15
N_{imag} = 0

H_3C^-
E = -479.02
H = -458.93
G = -472.70
N_{imag} = 0

C	0.00000000	0.00000000	-1.03533400
H	-0.51066800	0.88450400	-0.61146600
H	-0.51066800	-0.88450400	-0.61146600
H	1.02133700	0.00000000	-0.61146600

H_3C^+
E = -265.12
H = -243.48
G = -256.78
N_{imag} = 0

C	0.00000000	0.00000000	0.00000000
H	-0.54357600	0.94150100	0.00000000
H	-0.54357600	-0.94150100	0.00000000
H	1.08715100	0.00000000	0.00000000

MeH_2C^+
E = -662.05
H = -622.77
G = -639.19
N_{imag} = 0

C	0.00000000	-0.68963100	1.05189900
H	0.93462300	1.24161400	1.05782700
H	-0.93462300	1.24161400	1.05782700
C	0.00000000	0.68963100	1.05189900
H	0.93462300	-1.24161400	1.05782700
H	0.00000000	0.00000000	-0.07178200
H	-0.93462300	-1.24161400	1.05782700

Me_2HC^+
E = -1044.98
H = -987.55
G = -1007.54
N_{imag} = 0

C	0.00000000	0.00000000	-0.54878100

H	-0.45660600	1.16957600	1.18400300
H	-1.69510600	0.94755700	-0.09592200
H	1.69510600	-0.94755700	-0.09592200
C	0.61057400	-1.12193600	0.10666200
H	0.45660600	-1.16957600	1.18400300
H	0.41837900	-2.06441700	-0.42087900
H	0.00000000	0.00000000	-1.63878900
C	-0.61057400	1.12193600	0.10666200
H	-0.41837900	2.06441700	-0.42087900

Me_3C^+
E = -1424.52
H = -1348.99
G = -1372.57
N_{imag} = 0

C	0.91408900	-1.43620900	0.45642600
H	0.86193800	0.71070900	0.59286300
H	0.59819000	-3.06245900	1.65019600
H	2.35203200	-1.00462900	-0.95797100
C	2.31738100	-1.45100200	0.05319600
H	2.89269600	-0.74776300	0.67043500
H	2.76623600	-2.44306000	0.03131700
C	0.20432600	-2.69086200	0.68298700
H	-0.87707300	-2.58422800	0.76572500
H	0.50315000	-3.45518700	-0.04350100
C	0.21496000	-0.16463300	0.62693100
H	-0.52768500	-0.11333300	-0.19051500
H	-0.39825900	-0.19025600	1.53800100

•••CF
E = -98.64
H = -94.95
G = -109.39
N_{imag} = 0

C	0.00000000	0.00000000	-4.33522800
F	0.00000000	0.00000000	-2.98616500

•••CCl
E = -77.86
H = -74.59
G = -89.81
N_{imag} = 0

C	0.00000000	0.00000000	-4.64152400
Cl	0.00000000	0.00000000	-2.96726700

•••CBr
E = -68.08
H = -65.00
G = -81.07
N_{imag} = 0

C	0.00000000	0.00000000	-4.86732600

Br	0.00000000	0.00000000	-3.01406700

•••CI

E = -65.90
H = -62.92
G = -79.57
N_{imag} = 0

C	0.00000000	0.00000000	-5.03717800
I	0.00000000	0.00000000	-2.98398000

•••CH

E = -116.20
H = -109.98
G = -122.17
N_{imag} = 0

C	0.00000000	0.00000000	-0.57527900
H	0.00000000	0.00000000	-1.68080800

•••CMe

E = -489.49
H = -464.57
G = -480.27
N_{imag} = 0

C	0.00000000	0.00000000	-4.65331500
H	0.51737600	-0.89612200	-2.77144400
C	0.00000000	0.00000000	-3.14341000
H	0.51737600	0.89612200	-2.77144400
H	-1.03475300	0.00000000	-2.77144400

•H

E = -22.09
H = -21.20
G = -28.95
N_{imag} = 0

•Me

E = -405.10
H = -384.47
G = -398.98
N_{imag} = 0

C	0.00914600	-0.00248000	-0.72628800
H	-0.02001400	-0.00789200	-1.80979900
H	-0.58351300	-0.71532300	-0.16459800
H	0.63097100	0.71577800	-0.20444400

•••C^+

E = 258.87
H = 259.76
G = 252.01
N_{imag} = 0

Table S11. Cartesian coordinates (in Å), energies (*E*, *H* and *G*, in kcal mol^{-1}), and number of imaginary vibrational frequencies (N_{imag}) of all stationary points and transition states in the gas phase, computed at ZORA-(U)PB86-D3(BJ)/QZ4P.

H_3C-F
E = -549.94
H = -523.69
G = -539.58
$\boldsymbol{N_{imag}}$ = 0

C	0.00000000	0.00000000	0.13772800
H	-0.51966700	0.90008900	0.49061100
H	-0.51966700	-0.90008900	0.49061100
H	1.03933300	0.00000000	0.49061100
F	0.00000000	0.00000000	-1.26203200

MeH_2C-F
E = -932.41
H = -888.11
G = -906.99
$\boldsymbol{N_{imag}}$ = 0

C	0.20822000	-1.79703400	0.07764700
H	-0.05835900	-0.88770100	0.63542300
H	-0.00111500	-2.67477200	0.70599200
H	2.31880000	-1.71444600	0.47316600
F	-0.66361600	-1.86877100	-1.03052600
C	1.64577200	-1.76956200	-0.39353600
H	1.88869700	-2.67640700	-0.96038400
H	1.83211900	-0.89594900	-1.02974800

Me_2HC-F
E = -1315.21
H = -1253.14
G = -1274.14
$\boldsymbol{N_{imag}}$ = 0

C	0.92837800	-1.38055100	0.00000000
H	0.10677100	-2.11419600	0.00000000
H	2.54587500	-0.75055200	-1.28723900
H	2.20172700	-2.49707800	1.33735900
F	0.29424700	-0.10550700	0.00000000
C	1.74464200	-1.50071900	1.27335100
H	2.54587500	-0.75055200	1.28723900
H	1.11040200	-1.35472100	2.15546700
C	1.74464200	-1.50071900	-1.27335100
H	2.20172700	-2.49707800	-1.33735900
H	1.11040200	-1.35472100	-2.15546700

Me_3C-F
E = -1697.71
H = -1618.02
G = -1640.93
$\boldsymbol{N_{imag}}$ = 0

C	0.17409400	-1.90244300	0.00000000
H	0.47151400	-3.58457800	1.33211700
H	0.02998500	-2.06872300	-2.15432400
H	2.31935400	-2.20335500	0.00000000
F	-0.68592800	-0.75179000	0.00000000
C	1.60229300	-1.37217900	0.00000000
H	1.78267700	-0.75872600	-0.89097700
H	1.78267700	-0.75872600	0.89097700
C	-0.15349000	-2.68459600	-1.26564700
H	0.47151400	-3.58457800	-1.33211700
H	-1.20595200	-2.99283400	-1.26336600
C	-0.15349000	-2.68459600	1.26564700
H	0.02998500	-2.06872300	2.15432400
H	-1.20595200	-2.99283400	1.26336600

$H_3C–Cl$
E = -512.00
H = -486.53
G = -503.24
N_{imag} = 0

C	0.00000000	0.00000000	0.12308400
H	-0.51844700	0.89797700	0.46703100
H	-0.51844700	-0.89797700	0.46703100
H	1.03689400	0.00000000	0.46703100
Cl	0.00000000	0.00000000	-1.67364300

$MeH_2C–Cl$
E = -893.11
H = -849.45
G = -869.10
N_{imag} = 0

C	0.21804200	-1.79947900	0.07382000
H	-0.05639800	-0.90860500	0.64731900
H	-0.01232400	-2.68972200	0.66730900
H	1.87168700	-0.87987900	-0.98324300
Cl	-0.91534000	-1.84379100	-1.34248200
C	1.66508500	-1.76872700	-0.37599800
H	2.32116200	-1.74485000	0.50608700
H	1.91433500	-2.65776200	-0.96673900

$Me_2HC–Cl$
E = -1274.71
H = -1213.16
G = -1234.85
N_{imag} = 0

C	0.62494800	-1.53777600	0.00000000
H	0.61712300	-0.44147000	0.00000000
H	2.32377100	-1.76178500	1.30043300
H	0.76911800	-1.67276800	-2.16420200
Cl	-1.15393500	-1.98149700	0.00000000
C	1.26746400	-2.06595800	-1.27147100

H	2.32377100	-1.76178500	-1.30043300
H	1.22349200	-3.16186600	-1.30150300
C	1.26746400	-2.06595800	1.27147100
H	0.76911800	-1.67276800	2.16420200
H	1.22349200	-3.16186600	1.30150300

$Me_3C–Cl$
E = -1656.17
H = -1576.93
G = -1600.39
N_{imag} = 0

C	0.19886200	-1.79100600	0.10142800
H	0.52284900	-0.39146000	1.70668500
H	0.58098700	-2.98796300	1.85152700
H	1.79312500	-0.93033000	-1.10052000
Cl	-0.93684800	-1.89900100	-1.35972700
C	-0.13228900	-0.49248200	0.82907300
H	0.02548500	0.37501300	0.17811900
H	-1.17317000	-0.48763900	1.17215100
C	1.62396200	-1.78926500	-0.44111900
H	2.33166800	-1.72691900	0.39844500
H	1.83284500	-2.70730000	-1.00212900
C	-0.07608300	-3.01382900	0.96995400
H	-1.11652700	-3.02616600	1.31420500
H	0.12087100	-3.94041200	0.41875300

$H_3C–Br$
E = -498.86
H = -473.70
G = -491.24
N_{imag} = 0

C	0.00000000	0.00000000	1.08319800
H	-1.04001700	0.00000000	1.41220400
H	0.52000800	-0.90068100	1.41220400
H	0.52000800	0.90068100	1.41220400
Br	0.00000000	0.00000000	-0.87736400

$MeH_2C–Br$
E = -879.84
H = -836.46
G = -856.95
N_{imag} = 0

C	0.16621300	0.01815000	0.00000000
H	-0.11047000	0.58440500	-0.89301200
H	-0.11047000	0.58440500	0.89301200
H	2.25933200	0.48355500	0.00000000
Br	-1.04944800	-1.54657400	0.00000000
C	1.61744800	-0.41036000	0.00000000
H	1.85836700	-1.00448300	0.88894500
H	1.85836700	-1.00448300	-0.88894500

Me_2HC-Br

E = -1261.37
H = -1200.07
G = -1222.59
N_{imag} = 0

C	0.93254700	-1.36729300	0.00000000
H	0.08370000	-2.05900800	0.00000000
H	2.54846400	-0.75364500	-1.30590900
H	2.21030700	-2.50086600	1.29952800
Br	0.02424400	0.41923800	0.00000000
C	1.74741900	-1.50254100	1.27225000
H	2.54846400	-0.75364500	1.30590900
H	1.12502000	-1.38697200	2.16595700
C	1.74741900	-1.50254100	-1.27225000
H	2.21030700	-2.50086600	-1.29952800
H	1.12502000	-1.38697200	-2.16595700

Me_3C-Br

E = -1642.80
H = -1563.77
G = -1587.40
N_{imag} = 0

C	0.00000000	0.00000000	1.61645500
H	-0.75099100	1.30075400	3.15236600
H	-0.22123000	-2.16329000	1.68793200
H	1.50198100	0.00000000	3.15236600
Br	0.00000000	0.00000000	-0.41229100
C	1.45879300	0.00000000	2.05209400
H	1.98407900	-0.89005400	1.68793200
H	1.98407900	0.89005400	1.68793200
C	-0.72939700	-1.26335200	2.05209400
H	-0.75099100	-1.30075400	3.15236600
H	-1.76284900	-1.27323600	1.68793200
C	-0.72939700	1.26335200	2.05209400
H	-0.22123000	2.16329000	1.68793200
H	-1.76284900	1.27323600	1.68793200

H_3C-I

E = -487.44
H = -462.56
G = -480.68
N_{imag} = 0

C	0.00000000	0.00000000	1.08553200
H	-1.04070100	0.00000000	1.41054300
H	0.52035000	-0.90127300	1.41054300
H	0.52035000	0.90127300	1.41054300
I	0.00000000	0.00000000	-1.07386600

$MeH_2C–I$
E = -867.79
H = -824.63
G = -845.71
N_{imag} = 0

C	0.21919800	-1.79361600	0.07359700
H	-0.07239800	-0.88986300	0.61394400
H	-0.02319200	-2.67361700	0.67416000
H	2.32363500	-1.71922800	0.48683400
I	-1.17681800	-1.88805100	-1.60233800
C	1.66071300	-1.76950700	-0.39081100
H	1.91610400	-2.67160000	-0.95852300
H	1.86593600	-0.89747900	-1.02226300

$Me_2HC–I$
E = -1248.84
H = -1187.73
G = -1210.83
N_{imag} = 0

C	0.21976800	-2.05842800	-0.17161500
H	-0.12795700	-2.24329900	0.84973400
H	0.22199300	-3.03880900	-2.10775100
H	2.30930000	-2.40625700	0.16938600
I	-1.09446500	-0.39193300	-0.78626100
C	1.66248500	-1.58688600	-0.18263300
H	1.98250200	-1.31462200	-1.19612200
H	1.81659500	-0.72298800	0.47261300
C	-0.04284200	-3.25666900	-1.06559900
H	0.57951600	-4.09978800	-0.72583700
H	-1.09171800	-3.57009600	-1.03347700

$Me_3C–I$
E = -1629.97
H = -1551.10
G = -1575.95
N_{imag} = 0

C	0.20988200	-2.07462200	-0.13974400
H	0.39391900	-3.18722700	1.68549000
H	0.26809300	-3.02748300	-2.09967500
H	2.31439600	-2.35920700	0.16695400
I	-1.09592000	-0.41850400	-0.89064900
C	1.64351300	-1.56386500	-0.19703500
H	1.94133100	-1.30846200	-1.22015000
H	1.78440900	-0.68203500	0.43796100
C	-0.01035300	-3.26301500	-1.06640600
H	0.62198600	-4.09798900	-0.72271700
H	-1.05359600	-3.59799300	-1.05367800
C	-0.23319400	-2.37315200	1.28646800
H	-0.11403100	-1.50050400	1.93835500
H	-1.27892200	-2.69813600	1.32576400

$H_3C–H$
E = -550.33
H = -520.64
G = -533.92
N_{imag} = 0

C	0.00000000	0.00000000	0.00000000
H	0.63209400	-0.63209400	0.63209400
H	-0.63209400	-0.63209400	-0.63209400
H	0.63209400	0.63209400	-0.63209400
H	-0.63209400	0.63209400	0.63209400

$MeH_2C–H$
E = -927.08
H = -878.79
G = -895.06
N_{imag} = 0

C	0.00000000	0.00000000	0.76502600
H	0.00000000	1.02207100	1.16618300
H	0.88513900	-0.51103600	1.16618300
H	0.88513900	0.51103600	-1.16618300
H	-0.88513900	-0.51103600	1.16618300
C	0.00000000	0.00000000	-0.76502600
H	0.00000000	-1.02207100	-1.16618300
H	-0.88513900	0.51103600	-1.16618300

$Me_2HC–H$
E = -1305.77
H = -1239.33
G = -1258.54
N_{imag} = 0

C	0.00000000	0.00000000	-1.13589400
H	0.87877700	0.00000000	-0.47322500
H	-0.88581400	-1.31645300	-2.63313600
H	0.88581400	1.31645300	-2.63313600
H	-0.87877700	0.00000000	-0.47322500
C	0.00000000	1.27429600	-1.98370500
H	-0.88581400	1.31645300	-2.63313600
H	0.00000000	2.17771400	-1.35987900
C	0.00000000	-1.27429600	-1.98370500
H	0.88581400	-1.31645300	-2.63313600
H	0.00000000	-2.17771400	-1.35987900

$Me_3C–H$
E = -1685.72
H = -1601.44
G = -1622.42
N_{imag} = 0

C	0.00000000	0.00000000	1.57919300
H	-1.50957300	0.00000000	3.14986700
H	1.76731600	-1.28457600	1.69227400
H	0.75478700	1.30732900	3.14986700

H	0.00000000	0.00000000	0.47615800
C	0.72923700	1.26307600	2.05074000
H	1.76731600	1.28457600	1.69227400
H	0.22881800	2.17282900	1.69227400
C	0.72923700	-1.26307600	2.05074000
H	0.75478700	-1.30732900	3.14986700
H	0.22881800	-2.17282900	1.69227400
C	-1.45847400	0.00000000	2.05074000
H	-1.99613400	0.88825200	1.69227400
H	-1.99613400	-0.88825200	1.69227400

$H_3C–CH_3$
E = -927.08
H = -878.79
G = -895.06
N_{imag} = 0

C	0.00000000	0.00000000	0.76502600
H	0.00000000	1.02207100	1.16618300
H	0.88513900	-0.51103600	1.16618300
H	0.88513900	0.51103600	-1.16618300
H	-0.88513900	-0.51103600	1.16618300
C	0.00000000	0.00000000	-0.76502600
H	0.00000000	-1.02207100	-1.16618300
H	-0.88513900	0.51103600	-1.16618300

$MeH_2C–CH_3$
E = -1305.77
H = -1239.33
G = -1258.54
N_{imag} = 0

C	0.00000000	0.00000000	-1.13589400
H	0.87877700	0.00000000	-0.47322500
H	-0.88581400	-1.31645300	-2.63313600
H	0.88581400	1.31645300	-2.63313600
H	-0.87877700	0.00000000	-0.47322500
C	0.00000000	1.27429600	-1.98370500
H	-0.88581400	1.31645300	-2.63313600
H	0.00000000	2.17771400	-1.35987900
C	0.00000000	-1.27429600	-1.98370500
H	0.88581400	-1.31645300	-2.63313600
H	0.00000000	-2.17771400	-1.35987900

$Me_2HC–CH_3$
E = -1685.72
H = -1601.44
G = -1622.42
N_{imag} = 0

C	0.00000000	0.00000000	1.57919300
H	-1.50957300	0.00000000	3.14986700
H	1.76731600	-1.28457600	1.69227400
H	0.75478700	1.30732900	3.14986700

H	0.00000000	0.00000000	0.47615800
C	0.72923700	1.26307600	2.05074000
H	1.76731600	1.28457600	1.69227400
H	0.22881800	2.17282900	1.69227400
C	0.72923700	-1.26307600	2.05074000
H	0.75478700	-1.30732900	3.14986700
H	0.22881800	-2.17282900	1.69227400
C	-1.45847400	0.00000000	2.05074000
H	-1.99613400	0.88825200	1.69227400
H	-1.99613400	-0.88825200	1.69227400

$Me_3C–CH_3$
E = -2066.20
H = -1964.24
G = -1986.13
N_{imag} = 0

C	0.00000000	0.00000000	0.00000000
H	-1.53410200	1.53410200	-0.27782900
H	-0.27782900	-1.53410200	1.53410200
H	0.27782900	1.53410200	1.53410200
H	1.53410200	-0.27782900	-1.53410200
C	0.88752200	0.88752200	0.88752200
H	1.53410200	0.27782900	1.53410200
H	1.53410200	1.53410200	0.27782900
C	-0.88752200	-0.88752200	0.88752200
H	-1.53410200	-0.27782900	1.53410200
H	-1.53410200	-1.53410200	0.27782900
C	-0.88752200	0.88752200	-0.88752200
H	-0.27782900	1.53410200	-1.53410200
H	-1.53410200	0.27782900	-1.53410200
C	0.88752200	-0.88752200	-0.88752200
H	1.53410200	-1.53410200	-0.27782900
H	0.27782900	-1.53410200	-1.53410200

F^-
E = -97.28
H = -96.39
G = -104.14
N_{imag} = 0

Cl^-
E = -93.09
H = -92.20
G = -99.95
N_{imag} = 0

Br^-
E = -87.15
H = -86.26
G = -94.01
N_{imag} = 0

I^-
E = -81.76
H = -80.87
G = -88.62
N_{imag} = 0

H^-
E = -42.98
H = -42.09
G = -49.84
N_{imag} = 0

H_3C^-
E = -419.03
H = -399.20
G = -412.99
N_{imag} = 0

C	0.00000000	0.00000000	-1.03063500
H	-0.51576500	0.89333100	-0.61303300
H	-0.51576500	-0.89333100	-0.61303300
H	1.03153000	0.00000000	-0.61303300

H_3C^+
E = -183.64
H = -162.18
G = -175.49
N_{imag} = 0

C	0.00000000	0.00000000	0.00000000
H	-0.54956200	0.95186900	0.00000000
H	-0.54956200	-0.95186900	0.00000000
H	1.09912400	0.00000000	0.00000000

MeH_2C^+
E = -609.09
H = -569.67
G = -586.01
N_{imag} = 0

C	0.00000000	-0.69188400	1.05348500
H	0.93964800	1.25060500	1.05805300
H	-0.93964800	1.25060500	1.05805300
C	0.00000000	0.69188400	1.05348500
H	0.93964800	-1.25060500	1.05805300
H	0.00000000	0.00000000	-0.07585600
H	-0.93964800	-1.25060500	1.05805300

Me_2HC^+
E = -1011.07
H = -953.78
G = -973.69
N_{imag} = 0

C	0.00000000	0.00000000	-0.53741400

H	-1.15081800	0.54084500	1.19696300
H	-1.94956100	-0.35100200	-0.15646400
H	1.94956100	0.35100200	-0.15646400
C	1.20078500	-0.44061700	0.11036200
H	1.15081800	-0.54084500	1.19696300
H	1.64556200	-1.31353800	-0.40108900
H	0.00000000	0.00000000	-1.63549300
C	-1.20078500	0.44061700	0.11036200
H	-1.64556200	1.31353800	-0.40108900

Me_3C^+
E = -1408.22
H = -1332.74
G = -1356.37
N_{imag} = 0

C	0.91348300	-1.43371100	0.45488600
H	0.84852600	0.72470300	0.52465300
H	0.61210300	-3.10684000	1.61444900
H	2.37783400	-1.02632900	-0.94750700
C	2.32190000	-1.45392400	0.07664300
H	2.89574800	-0.72753400	0.67586500
H	2.78378600	-2.44402500	0.07717900
C	0.19848900	-2.68627200	0.67140100
H	-0.88440500	-2.58526800	0.77823400
H	0.47755100	-3.44148900	-0.08044400
C	0.21630100	-0.16140800	0.61296000
H	-0.59205300	-0.13020400	-0.14551100
H	-0.34728100	-0.16061200	1.56328100

•••CF
E = -111.58
H = -107.78
G = -122.20
N_{imag} = 0

C	0.00000000	0.00000000	-4.32811800
F	0.00000000	0.00000000	-2.99327500

•••CCl
E = -91.53
H = -88.18
G = -103.37
N_{imag} = 0

C	0.00000000	0.00000000	-4.63306100
Cl	0.00000000	0.00000000	-2.97573000

•••CBr
E = -80.25
H = -77.10
G = -93.13
N_{imag} = 0

C	0.00000000	0.00000000	-4.85412600

Br	0.00000000	0.00000000	-3.02726700

•••CI

E = -75.32
H = -72.28
G = -88.87
N_{imag} = 0

C	0.00000000	0.00000000	-5.02040800
I	0.00000000	0.00000000	-3.00075000

•••CH

E = -126.94
H = -120.57
G = -132.75
N_{imag} = 0

C	0.00000000	0.00000000	-0.57846000
H	0.00000000	0.00000000	-1.67762700

•••CMe

E = -511.65
H = -486.54
G = -502.20
N_{imag} = 0

C	0.00000000	0.00000000	-4.64492800
H	0.51643300	-0.89448800	-2.76998400
C	0.00000000	0.00000000	-3.15617600
H	0.51643300	0.89448800	-2.76998400
H	-1.03286500	0.00000000	-2.76998400

•H

E = -21.89
H = -21.00
G = -28.75
N_{imag} = 0

•Me

E = -416.15
H = -395.44
G = -409.95
N_{imag} = 0

C	0.00914600	-0.00248100	-0.72628300
H	-0.02004900	-0.00789800	-1.81113100
H	-0.58424500	-0.71620300	-0.16391000
H	0.63173800	0.71666400	-0.20380600

•••C^+

E = 353.42
H = 354.31
G = 346.56
N_{imag} = 0

Table S12. Cartesian coordinates (in Å), energies (*E*, *H* and *G*, in kcal mol^{-1}), and number of imaginary vibrational frequencies (N_{imag}) of all stationary points and transition states in the gas phase, computed at COSMO(H_2O)-ZORA-(U)B86-D3(BJ)/QZ4P.

H_3C-F
E = -552.61
H = -526.44
G = -542.36
$\boldsymbol{N_{imag}}$ = 0

C	0.00000000	0.00000000	0.15001800
H	-0.52043200	0.90141400	0.48927900
H	-0.52043200	-0.90141400	0.48927900
H	1.04086400	0.00000000	0.48927900
F	0.00000000	0.00000000	-1.27032400

MeH_2C-F
E = -935.10
H = -890.96
G = -909.86
$\boldsymbol{N_{imag}}$ = 0

C	0.15907400	0.02124200	0.00000000
H	-0.10522700	0.59539400	-0.89611000
H	-0.10522700	0.59539400	0.89611000
H	2.24533800	0.47409600	0.00000000
F	-0.69712800	-1.13113200	0.00000000
C	1.60244900	-0.41645700	0.00000000
H	1.83709000	-1.00682400	0.89408400
H	1.83709000	-1.00682400	-0.89408400

Me_2HC-F
E = -1317.91
H = -1256.07
G = -1277.08
$\boldsymbol{N_{imag}}$ = 0

C	0.93493600	-1.39143900	0.00000000
H	0.10600000	-2.11221000	0.00000000
H	2.54915800	-0.75121500	-1.28590700
H	2.20043200	-2.49551100	1.33469400
F	0.28510100	-0.09503400	0.00000000
C	1.74515800	-1.49860000	1.27341300
H	2.54915800	-0.75121500	1.28590700
H	1.10957800	-1.35853000	2.15569500
C	1.74515800	-1.49860000	-1.27341300
H	2.20043200	-2.49551100	-1.33469400
H	1.10957800	-1.35853000	-2.15569500

Me_3C-F
E = -1700.43
H = -1621.01
G = -1643.92
$\boldsymbol{N_{imag}}$ = 0

C	0.18162700	-1.91252700	0.00000000
H	0.47101000	-3.58260200	1.33048500
H	0.03348900	-2.06901200	-2.15481500
H	2.31678600	-2.20283800	0.00000000
F	-0.69501400	-0.73969300	0.00000000
C	1.60154500	-1.37065400	0.00000000
H	1.78324700	-0.76096000	-0.89343700
H	1.78324700	-0.76096000	0.89343700
C	-0.15457000	-2.68339800	-1.26591400
H	0.47101000	-3.58260200	-1.33048500
H	-1.20601000	-2.99551200	-1.26145100
C	-0.15457000	-2.68339800	1.26591400
H	0.03348900	-2.06901200	2.15481500
H	-1.20601000	-2.99551200	1.26145100

$H_3C–Cl$
E = -513.93
H = -488.53
G = -505.25
N_{imag} = 0

C	0.00000000	0.00000000	0.13196900
H	-0.51942700	0.89967500	0.46528700
H	-0.51942700	-0.89967500	0.46528700
H	1.03885500	0.00000000	0.46528700
Cl	0.00000000	0.00000000	-1.67729600

$MeH_2C–Cl$
E = -871.15
H = -851.46
G = -894.99
N_{imag} = 0

C	0.22499400	-1.79924000	0.08059600
H	-0.05626600	-0.90690300	0.64544300
H	-0.01208300	-2.69157400	0.66533000
H	1.87447900	-0.87726300	-0.98192400
Cl	-0.92423200	-1.84391500	-1.34522900
C	1.66554000	-1.76874400	-0.37914200
H	2.31649500	-1.74483600	0.50615500
H	1.91732300	-2.66033600	-0.96515800

$Me_2HC–Cl$
E = -1276.56
H = -1215.21
G = -1236.95
N_{imag} = 0

C	0.24067500	-1.82145900	0.09861200
H	-0.01361800	-0.89677600	0.62637400
H	0.57566600	-3.02283000	1.83668700
H	1.84469800	-0.89502300	-1.03846300
Cl	-0.91642600	-1.79697000	-1.35191500
C	1.66636500	-1.77884900	-0.41629300

H	2.35036600	-1.73887400	0.44307600
H	1.90020100	-2.67866000	-0.99917200
C	-0.07311200	-3.03673000	0.94964400
H	-1.11548000	-3.03533000	1.28656700
H	0.12189400	-3.96416600	0.39653400

$Me_3C–Cl$
E = -1658.02
H = -1579.02
G = -1602.53
N_{imag} = 0

C	0.20608900	-1.79030300	0.11073000
H	0.52240500	-0.39274200	1.70464900
H	0.58008100	-2.98673200	1.84955900
H	1.79444300	-0.92784300	-1.09880000
Cl	-0.94633600	-1.89979800	-1.37195000
C	-0.13371300	-0.49149000	0.82820700
H	0.02846700	0.37625100	0.17858900
H	-1.17321400	-0.48884700	1.17560500
C	1.62397800	-1.78939100	-0.44308200
H	2.32934500	-1.72696000	0.39771300
H	1.83426400	-2.70967400	-0.99995500
C	-0.07752400	-3.01497400	0.96914700
H	-1.11683200	-3.02482800	1.31703400
H	0.12428400	-3.94142600	0.41940000

$H_3C–Br$
E = -500.62
H = -475.52
G = -493.08
N_{imag} = 0

C	0.00000000	0.00000000	1.09075300
H	-1.04188500	0.00000000	1.41043400
H	0.52094200	-0.90229900	1.41043400
H	0.52094200	0.90229900	1.41043400
Br	0.00000000	0.00000000	-0.87960700

$MeH_2C–Br$
E = -881.57
H = -838.32
G = -858.84
N_{imag} = 0

C	0.17240800	0.02395800	0.00000000
H	-0.10993200	0.58233300	-0.89477200
H	-0.10993200	0.58233300	0.89477200
H	2.25408800	0.48393600	0.00000000
Br	-1.05802600	-1.54862000	0.00000000
C	1.61787700	-0.41353900	0.00000000
H	1.86142800	-1.00289400	0.89153100
H	1.86142800	-1.00289400	-0.89153100

Me_2HC-Br

E = -1263.08
H = -1201.97
G = -1224.55
N_{imag} = 0

C	0.93788100	-1.37554000	0.00000000
H	0.08290400	-2.05753600	0.00000000
H	2.55323000	-0.75506300	-1.30510000
H	2.20777200	-2.49945100	1.29649600
Br	0.01387500	0.42699900	0.00000000
C	1.74833900	-1.50001200	1.27291300
H	2.55323000	-0.75506300	1.30510000
H	1.12493500	-1.38968100	2.16663000
C	1.74833900	-1.50001200	-1.27291300
H	2.20777200	-2.49945100	-1.29649600
H	1.12493500	-1.38968100	-2.16663000

Me_3C-Br

E = -1644.52
H = -1565.74
G = -1590.08
N_{imag} = 0

C	0.00000200	-0.00000000	1.62860300
H	-1.29616100	0.75704900	3.15039600
H	0.88221300	-1.98837100	1.68979000
H	1.30352800	0.74409000	3.15051300
Br	0.00000000	-0.00000400	-0.42806100
C	1.26815100	0.72359700	2.05070900
H	2.16531800	0.20772900	1.69056700
H	1.28078800	1.75826800	1.69005500
C	-0.00743200	-1.46008200	2.05061100
H	-0.00715000	-1.50103800	3.15040800
H	-0.90283900	-1.97908400	1.69055700
C	-1.26072800	0.73649900	2.05061000
H	-1.26261800	1.77135000	1.69026500
H	-2.16307400	0.22999800	1.69011000

H_3C-I

E = -488.91
H = -464.11
G = -482.24
N_{imag} = 0

C	0.00000000	0.00000000	1.08989300
H	-1.04203000	0.00000000	1.40891800
H	0.52101500	-0.90242400	1.40891800
H	0.52101500	0.90242400	1.40891800
I	0.00000000	0.00000000	-1.07335500

$MeH_2C–I$

E = -869.12
H = -826.11
G = -847.21
N_{imag} = 0

C	0.22286400	-1.79329400	0.07695200
H	-0.07191700	-0.88841300	0.61217800
H	-0.02259200	-2.67481600	0.67269000
H	2.31930500	-1.71973200	0.48728800
I	-1.18139900	-1.88859000	-1.60259700
C	1.66076400	-1.76957000	-0.39322200
H	1.91805100	-2.67342000	-0.95768800
H	1.86810400	-0.89512600	-1.02100000

$Me_2HC–I$

E = -1250.09
H = -1189.18
G = -1212.32
N_{imag} = 0

C	0.22351900	-2.06284600	-0.17054200
H	-0.12860400	-2.24234700	0.84924200
H	0.22483700	-3.04017600	-2.10942800
H	2.30518400	-2.40705700	0.16903100
I	-1.10050500	-0.38624200	-0.78505000
C	1.66257400	-1.58556400	-0.18420000
H	1.98487200	-1.31690400	-1.19810300
H	1.81759700	-0.72442300	0.47467200
C	-0.04326900	-3.25584600	-1.06748200
H	0.58020300	-4.09603600	-0.72412000
H	-1.09123000	-3.57233700	-1.03158400

$Me_3C–I$

E = -1631.18
H = -1552.54
G = -1577.44
N_{imag} = 0

C	0.21463600	-2.08061600	-0.13701600
H	0.39363800	-3.18610900	1.68381100
H	0.27065900	-3.02796300	-2.10010000
H	2.31244500	-2.35866800	0.16685600
I	-1.10233400	-0.40998100	-0.89435200
C	1.64373700	-1.56245800	-0.19753300
H	1.94238500	-1.31104200	-1.22148400
H	1.78498300	-0.68267500	0.44037300
C	-0.01134700	-3.26280200	-1.06754200
H	0.62156900	-4.09598100	-0.72236300
H	-1.05394700	-3.59991300	-1.05140700
C	-0.23434800	-2.37238200	1.28700100
H	-0.11151200	-1.50054100	1.93943000
H	-1.27905100	-2.70106200	1.32526800

$H_3C–H$
E = -550.20
H = -520.70
G = -533.98
N_{imag} = 0

C	0.00000000	0.00000000	0.00000000
H	0.63235500	-0.63235500	0.63235500
H	-0.63235500	-0.63235500	-0.63235500
H	0.63235500	0.63235500	-0.63235500
H	-0.63235500	0.63235500	0.63235500

$MeH_2C–H$
E = -926.81
H = -878.74
G = -895.02
N_{imag} = 0

C	0.00000000	0.00000000	0.76534400
H	0.00000000	1.02278000	1.16545700
H	0.88575300	-0.51139000	1.16545700
H	0.88575300	0.51139000	-1.16545700
H	-0.88575300	-0.51139000	1.16545700
C	0.00000000	0.00000000	-0.76534400
H	0.00000000	-1.02278000	-1.16545700
H	-0.88575300	0.51139000	-1.16545700

$Me_2HC–H$
E = -1305.42
H = -1239.26
G = -1258.46
N_{imag} = 0

C	0.00000000	0.00000000	-1.13567100
H	0.87954400	0.00000000	-0.47388700
H	-0.88663700	-1.31537500	-2.63295800
H	0.88663700	1.31537500	-2.63295800
H	-0.87954400	0.00000000	-0.47388700
C	0.00000000	1.27441400	-1.98407500
H	-0.88663700	1.31537500	-2.63295800
H	0.00000000	2.17757300	-1.35931200
C	0.00000000	-1.27441400	-1.98407500
H	0.88663700	-1.31537500	-2.63295800
H	0.00000000	-2.17757300	-1.35931200

$Me_3C–H$
E = -1685.35
H = -1601.38
G = -1622.35
N_{imag} = 0

C	0.00000000	0.00000000	1.57921900
H	-1.50846300	0.00000000	3.15062300
H	1.76742100	-1.28359100	1.69168200
H	0.75423200	1.30636700	3.15062300

H	0.00000000	0.00000000	0.47631600
C	0.72935000	1.26327100	2.05110900
H	1.76742100	1.28359100	1.69168200
H	0.22791200	2.17242700	1.69168200
C	0.72935000	-1.26327100	2.05110900
H	0.75423200	-1.30636700	3.15062300
H	0.22791200	-2.17242700	1.69168200
C	-1.45869900	0.00000000	2.05110900
H	-1.99533300	0.88883600	1.69168200
H	-1.99533300	-0.88883600	1.69168200

$H_3C–CH_3$
E = -926.81
H = -878.74
G = -895.02
N_{imag} = 0

C	0.00000000	0.00000000	0.76534200
H	0.00000000	1.02277900	1.16546100
H	0.88575300	-0.51138900	1.16546100
H	0.88575300	0.51138900	-1.16546100
H	-0.88575300	-0.51138900	1.16546100
C	0.00000000	0.00000000	-0.76534200
H	0.00000000	-1.02277900	-1.16546100
H	-0.88575300	0.51138900	-1.16546100

$MeH_2C–CH_3$
E = -1305.42
H = -1239.26
G = -1258.46
N_{imag} = 0

C	0.00000000	0.00000000	-1.13567100
H	0.87954200	0.00000000	-0.47388600
H	-0.88663500	-1.31537600	-2.63295900
H	0.88663500	1.31537600	-2.63295900
H	-0.87954200	0.00000000	-0.47388600
C	0.00000000	1.27441400	-1.98407500
H	-0.88663500	1.31537600	-2.63295900
H	0.00000000	2.17757300	-1.35931200
C	0.00000000	-1.27441400	-1.98407500
H	0.88663500	-1.31537600	-2.63295900
H	0.00000000	-2.17757300	-1.35931200

$Me_2HC–CH_3$
E = -1685.35
H = -1601.38
G = -1622.35
N_{imag} = 0

C	0.00000000	0.00000000	1.57921900
H	-1.50846300	0.00000000	3.15062300
H	1.76742100	-1.28359100	1.69168200
H	0.75423200	1.30636700	3.15062300

H	0.00000000	0.00000000	0.47631600
C	0.72935000	1.26327100	2.05110900
H	1.76742100	1.28359100	1.69168200
H	0.22791200	2.17242700	1.69168200
C	0.72935000	-1.26327100	2.05110900
H	0.75423200	-1.30636700	3.15062300
H	0.22791200	-2.17242700	1.69168200
C	-1.45869900	0.00000000	2.05110900
H	-1.99533300	0.88883600	1.69168200
H	-1.99533300	-0.88883600	1.69168200

$Me_3C–CH_3$
E = -2065.84
H = -1964.21
G = -1987.15
N_{imag} = 0

C	0.00000000	0.00000000	0.89899600
H	-1.81942000	1.18090800	0.62243800
H	0.04844700	-1.55764300	2.43280800
H	-0.04844700	1.55764300	2.43280800
H	1.55731200	0.04838900	-0.63514900
C	0.68367600	1.05276200	1.78664900
H	1.44272800	0.58922900	2.43272800
H	1.18135300	1.81913400	1.17556600
C	-0.68367600	-1.05276200	1.78664900
H	-1.44272800	-0.58922900	2.43272800
H	-1.18135300	-1.81913400	1.17556600
C	-1.05277100	0.68367000	0.01134800
H	-0.58933400	1.44308100	-0.63438000
H	-1.55731200	-0.04838900	-0.63514900
C	1.05277100	-0.68367000	0.01134800
H	1.81942000	-1.18090800	0.62243800
H	0.58933400	-1.44308100	-0.63438000

F^-
E = -197.72
H = -196.83
G = -204.58
N_{imag} = 0

Cl^-
E = -166.80
H = -165.91
G = -173.66
N_{imag} = 0

Br^-
E = -154.40
H = -153.51
G = -161.26
N_{imag} = 0

I^-
E = -139.73
H = -138.84
G = -146.59
N_{imag} = 0

H^-
E = -124.21
H = -123.32
G = -131.07
N_{imag} = 0

H_3C^-
E = -494.09
H = -474.02
G = -487.79
N_{imag} = 0

C	0.00000000	0.00000000	-1.03928500
H	-0.51065300	0.88447700	-0.61014900
H	-0.51065300	-0.88447700	-0.61014900
H	1.02130700	0.00000000	-0.61014900

H_3C^+
E = -269.43
H = -247.83
G = -261.13
N_{imag} = 0

C	0.00000000	0.00000000	0.00000000
H	-0.54473700	0.94351100	0.00000000
H	-0.54473700	-0.94351100	0.00000000
H	1.08947300	0.00000000	0.00000000

MeH_2C^+
E = -680.88
H = -641.46
G = -657.80
N_{imag} = 0

C	0.00000000	-0.68864000	1.05316000
H	0.93700100	1.24124100	1.05564600
H	-0.93700100	1.24124100	1.05564600
C	0.00000000	0.68864000	1.05316000
H	0.93700100	-1.24124100	1.05564600
H	0.00000000	0.00000000	-0.06558200
H	-0.93700100	-1.24124100	1.05564600

Me_2HC^+
E = -1074.79
H = -1017.53
G = -1037.64
N_{imag} = 0

C	0.00000000	0.00000000	-0.54981500

H	-1.10136500	0.60120100	1.18342100
H	-1.88845000	-0.38191300	-0.09737700
H	1.88845000	0.38191300	-0.09737700
C	1.18428500	-0.46496000	0.10409800
H	1.10136500	-0.60120100	1.18342100
H	1.66215500	-1.29665400	-0.43051900
H	0.00000000	0.00000000	-1.64279200
C	-1.18428500	0.46496000	0.10409800
H	-1.66215500	1.29665400	-0.43051900

Me_3C^+
E = -1466.67
H = -1391.28
G = -1414.11
N_{imag} = 0

C	0.91587900	-1.43684100	0.46137300
H	0.87360900	0.70411700	0.66199200
H	0.58362800	-3.03281900	1.66888900
H	2.32111200	-1.02265300	-0.97801100
C	2.30997100	-1.45118000	0.04410600
H	2.89506400	-0.73156300	0.63446900
H	2.76283700	-2.44366700	0.02367600
C	0.20776700	-2.68696600	0.68185200
H	-0.87721000	-2.58372800	0.74870500
H	0.52788700	-3.46779900	-0.01902100
C	0.22158500	-0.17046000	0.64570200
H	-0.47349600	-0.09368800	-0.21470200
H	-0.44665500	-0.21566600	1.51705900

•••CF
E = -111.95
H = -108.19
G = -122.61
N_{imag} = 0

C	0.00000000	0.00000000	-4.32996500
F	0.00000000	0.00000000	-2.99142700

•••CCl
E = -92.10
H = -88.76
G = -103.95
N_{imag} = 0

C	0.00000000	0.00000000	-4.63410400
Cl	0.00000000	0.00000000	-2.97468700

•••CBr
E = -81.43
H = -80.54
G = -88.29
N_{imag} = 0

C	0.00000000	0.00000000	-4.85576400

Br	0.00000000	0.00000000	-3.02562900

•••CI

E = -77.93
H = -74.90
G = -91.50
N_{imag} = 0

C	0.00000000	0.00000000	-5.02337600
I	0.00000000	0.00000000	-2.99778200

•••CH

E = -127.77
H = -121.46
G = -133.64
N_{imag} = 0

C	0.00000000	0.00000000	-0.57668400
H	0.00000000	0.00000000	-1.67940300

•••CMe

E = -512.48
H = -487.47
G = -503.15
N_{imag} = 0

C	0.00000000	0.00000000	-4.64615600
H	0.51705000	-0.89555700	-2.77131400
C	0.00000000	0.00000000	-3.15096000
H	0.51705000	0.89555700	-2.77131400
H	-1.03410100	0.00000000	-2.77131400

•H

E = -21.82
H = -20.93
G = -28.68
N_{imag} = 0

•Me

E = -416.40
H = -395.78
G = -410.29
N_{imag} = 0

C	0.00914500	-0.00248100	-0.72628600
H	-0.02007000	-0.00790000	-1.81193100
H	-0.58468000	-0.71672600	-0.16349200
H	0.63219300	0.71719000	-0.20342000

•••C^+

E = 254.60
H = 255.49
G = 247.74
N_{imag} = 0

Table S13. Cartesian coordinates (in Å), energies (*E*, *H* and *G*, in kcal mol^{-1}), and number of imaginary vibrational frequencies (N_{imag}) of all stationary points and transition states in the gas phase, computed at COSMO(DMSO)-ZORA-(U)M06-2X/QZ4P.

H_3C-F
E = -796.77
H = -769.58
G = -785.45
$\boldsymbol{N_{imag}}$ = 0

C	0.00000000	0.00000000	0.14534500
H	-0.51544800	0.89278100	0.48493400
H	-0.51544800	-0.89278100	0.48493400
H	1.03089500	0.00000000	0.48493400
F	0.00000000	0.00000000	-1.25261900

MeH_2C-F
E = -1307.96
H = -1262.21
G = -1281.02
$\boldsymbol{N_{imag}}$ = 0

C	0.21509200	-1.79658300	0.08329400
H	-0.05323500	-0.89437800	0.62729900
H	0.00407600	-2.66767200	0.69865600
H	2.30827700	-1.71589500	0.46670000
F	-0.64721700	-1.86876100	-1.02663900
C	1.64312400	-1.76962200	-0.39356800
H	1.87811200	-2.67143900	-0.95499500
H	1.82228900	-0.90028900	-1.02271500

Me_2HC-F
E = -1819.68
H = -1755.70
G = -1776.58
$\boldsymbol{N_{imag}}$ = 0

C	0.92836800	-1.38556000	0.00000000
H	0.10978100	-2.10385200	0.00000000
H	2.53600400	-0.75269500	-1.27061800
H	2.19871300	-2.48787200	1.31831200
F	0.30810900	-0.11210600	0.00000000
C	1.74377000	-1.50037500	1.26521100
H	2.53600400	-0.75269500	1.27061800
H	1.11572800	-1.36149600	2.14230900
C	1.74377000	-1.50037500	-1.26521100
H	2.19871300	-2.48787200	-1.31831200
H	1.11572800	-1.36149600	-2.14230900

Me_3C-F
E = -2331.41
H = -2249.32
G = -2271.98
$\boldsymbol{N_{imag}}$ = 0

C	0.17501400	-1.90364000	0.00000000
H	0.47304700	-3.57063300	1.31518000
H	0.03494500	-2.06994200	-2.14060100
H	2.29756400	-2.20674200	0.00000000
F	-0.67861600	-0.76191000	0.00000000
C	1.59514700	-1.37495700	0.00000000
H	1.77425000	-0.76972400	-0.88682700
H	1.77425000	-0.76972400	0.88682700
C	-0.15169900	-2.68079100	-1.25919600
H	0.47304700	-3.57063300	-1.31518000
H	-1.19545900	-2.98962800	-1.25381000
C	-0.15169900	-2.68079100	1.25919600
H	0.03494500	-2.06994200	2.14060100
H	-1.19545900	-2.98962800	1.25381000

$H_3C–Cl$
E = -722.64
H = -696.37
G = -713.05
N_{imag} = 0

C	0.00000000	0.00000000	0.12905900
H	-0.51492500	0.89187600	0.46105300
H	-0.51492500	-0.89187600	0.46105300
H	1.02985000	0.00000000	0.46105300
Cl	0.00000000	0.00000000	-1.66168200

$MeH_2C–Cl$
E = -1232.17
H = -1187.17
G = -1206.75
N_{imag} = 0

C	0.22291200	-1.79950600	0.07926200
H	-0.05121800	-0.91478800	0.64193900
H	-0.00763000	-2.68441400	0.66090900
H	1.86078700	-0.88507400	-0.97884500
Cl	-0.89621100	-1.84206700	-1.33795800
C	1.66269700	-1.76885100	-0.37685300
H	2.31078700	-1.74410600	0.49834100
H	1.90412700	-2.65400800	-0.96072400

$Me_2HC–Cl$
E = -1742.47
H = -1679.09
G = -1700.65
N_{imag} = 0

C	0.23499500	-1.81738200	0.09516200
H	-0.01099100	-0.90241700	0.62465600
H	0.57810500	-3.01755100	1.82401900
H	1.83894500	-0.90635600	-1.03187500
Cl	-0.89533800	-1.80770200	-1.33501000
C	1.66110000	-1.78092700	-0.41141800

H	2.33766900	-1.74526100	0.44217700
H	1.88182900	-2.67675100	-0.99000200
C	-0.06842300	-3.03157200	0.94685400
H	-1.10346000	-3.03389700	1.27878100
H	0.12679700	-3.94584700	0.38830800

$Me_3C–Cl$
E = -2252.80
H = -2171.21
G = -2194.45
N_{imag} = 0

C	0.19897300	-1.79092700	0.10153500
H	0.52313300	-0.40684200	1.69417200
H	0.58119500	-2.97378300	1.83711800
H	1.78612000	-0.93415200	-1.08994000
Cl	-0.92890500	-1.89744900	-1.34944300
C	-0.13092800	-0.49761300	0.82645000
H	0.03004000	0.36266100	0.18020400
H	-1.16334800	-0.49623400	1.16955500
C	1.61848000	-1.78941400	-0.43875800
H	2.31175000	-1.72755600	0.40059400
H	1.82528900	-2.70315200	-0.99187800
C	-0.07466900	-3.00890100	0.96673800
H	-1.10668000	-3.01769800	1.31099200
H	0.12528700	-3.92769900	0.41950400

$H_3C–Br$
E = -702.76
H = -676.83
G = -694.33
N_{imag} = 0

C	0.00000000	0.00000000	1.08516800
H	-1.03204400	0.00000000	1.40722900
H	0.51602200	-0.89377600	1.40722900
H	0.51602200	0.89377600	1.40722900
Br	0.00000000	0.00000000	-0.86440700

$MeH_2C–Br$
E = -1211.95
H = -1167.25
G = -1187.65
N_{imag} = 0

C	0.16857700	0.01973400	0.00000000
H	-0.10325800	0.57868400	-0.88660700
H	-0.10325800	0.57868400	0.88660700
H	2.24594700	0.47709300	0.00000000
Br	-1.03374900	-1.53907800	0.00000000
C	1.61514400	-0.41217800	0.00000000
H	1.84996800	-0.99916400	0.88462400
H	1.84996800	-0.99916400	-0.88462400

$Me_2HC–Br$

E = -1721.88
H = -1658.74
G = -1681.08
N_{imag} = 0

C	0.21860200	-2.06141100	-0.16348600
H	-0.11648700	-2.25497600	0.84946300
H	0.22993700	-3.01790500	-2.09251700
H	2.29238500	-2.40485500	0.16267000
Br	-0.95715100	-0.56009000	-0.73027800
C	1.65579500	-1.59034100	-0.18554800
H	1.95858400	-1.32784100	-1.19794200
H	1.80767900	-0.73226500	0.46362600
C	-0.03946400	-3.24955800	-1.06330300
H	0.58062600	-4.08089200	-0.72522700
H	-1.08028600	-3.56002000	-1.03057800

$Me_3C–Br$

E = -2231.90
H = -2150.53
G = -2174.57
N_{imag} = 0

C	0.00000700	0.00001600	1.61041200
H	-1.27615400	0.74634200	3.14140600
H	0.87614000	-1.97702200	1.69346500
H	1.28369700	0.73326400	3.14141300
Br	-0.00002800	0.00012300	-0.40207700
C	1.26138900	0.71976900	2.05016300
H	2.15244800	0.20741200	1.69454100
H	1.27434900	1.74714000	1.69335300
C	-0.00742000	-1.45235500	2.04985700
H	-0.00753900	-1.47881500	3.14110100
H	-0.89631800	-1.96793900	1.69349000
C	-1.25395800	0.73261700	2.05015800
H	-1.25641700	1.76005900	1.69333100
H	-2.15019600	0.22938800	1.69452300

$H_3C–I$

E = -685.05
H = -659.43
G = -677.49
N_{imag} = 0

C	0.00000000	0.00000000	1.08371300
H	-1.03242900	0.00000000	1.40395800
H	0.51621500	-0.89411000	1.40395800
H	0.51621500	0.89411000	1.40395800
I	0.00000000	0.00000000	-1.05229400

$MeH_2C–I$

E = -1193.33
H = -1148.86
G = -1169.83
N_{imag} = 0

C	0.21852500	-1.79357300	0.07285500
H	-0.06569000	-0.89637200	0.60826700
H	-0.01686300	-2.66658600	0.66860800
H	2.30963200	-1.72054500	0.47996300
I	-1.15182000	-1.88750900	-1.59013000
C	1.65725900	-1.76965500	-0.39272200
H	1.90586400	-2.66675000	-0.95490400
H	1.85627300	-0.90197100	-1.01733500

$Me_2HC–I$

E = -1702.55
H = -1639.59
G = -1662.49
N_{imag} = 0

C	0.21446900	-2.05439200	-0.16901700
H	-0.12436600	-2.24387200	0.84347700
H	0.22981700	-3.02628800	-2.09505700
H	2.28758200	-2.41011600	0.16174400
I	-1.07807900	-0.40935500	-0.78475400
C	1.65626100	-1.59025300	-0.18591600
H	1.96667500	-1.32645700	-1.19581300
H	1.81494700	-0.73449400	0.46488200
C	-0.03899100	-3.25006500	-1.06379100
H	0.58488700	-4.07744800	-0.72054600
H	-1.07802600	-3.56703900	-1.03277200

$Me_3C–I$

E = -2212.08
H = -2130.85
G = -2155.42
N_{imag} = 0

C	0.20379100	-2.06686000	-0.14327600
H	0.39788300	-3.17998600	1.66011900
H	0.27246300	-3.02607000	-2.08711300
H	2.28807700	-2.36427000	0.16669900
I	-1.08497000	-0.43406300	-0.88337600
C	1.63683000	-1.56583800	-0.19692100
H	1.93495300	-1.31756400	-1.21312600
H	1.77871300	-0.69356900	0.43729800
C	-0.00932000	-3.25746200	-1.06229200
H	0.62308800	-4.07524700	-0.70853300
H	-1.04365400	-3.59377000	-1.04634000
C	-0.23128000	-2.37163500	1.27987500
H	-0.10695500	-1.50761400	1.92888600
H	-1.26810400	-2.69824400	1.31904100

$H_3C–H$

E = -734.78
H = -704.37
G = -717.63
N_{imag} = 0

C	0.00000000	0.00000000	0.00000000
H	0.62729400	-0.62729400	0.62729400
H	-0.62729400	-0.62729400	-0.62729400
H	0.62729400	0.62729400	-0.62729400
H	-0.62729400	0.62729400	0.62729400

$MeH_2C–H$

E = -1240.32
H = -1190.69
G = -1206.92
N_{imag} = 0

C	0.00000000	0.00000000	0.76281900
H	0.00000000	1.01540100	1.15607200
H	0.87936300	-0.50770100	1.15607200
H	0.87936300	0.50770100	-1.15607200
H	-0.87936300	-0.50770100	1.15607200
C	0.00000000	0.00000000	-0.76281900
H	0.00000000	-1.01540100	-1.15607200
H	-0.87936300	0.50770100	-1.15607200

$Me_2HC–H$

E = -1698.63
H = -1679.51
G = -1747.84
N_{imag} = 0

C	0.00000000	0.00000000	-1.13128400
H	0.87387400	0.00000000	-0.47826800
H	-0.88023800	-1.29616300	-2.62671700
H	0.88023800	1.29616300	-2.62671700
H	-0.87387400	0.00000000	-0.47826800
C	0.00000000	1.26482800	-1.98382100
H	-0.88023800	1.29616300	-2.62671700
H	0.00000000	2.16418800	-1.36986100
C	0.00000000	-1.26482800	-1.98382100
H	0.88023800	-1.29616300	-2.62671700
H	0.00000000	-2.16418800	-1.36986100

$Me_3C–H$

E = -2256.72
H = -2170.01
G = -2190.86
N_{imag} = 0

C	0.00000000	0.00000000	1.57256700
H	-1.48670500	0.00000000	3.14166200
H	1.75595500	-1.27566000	1.69712200
H	0.74335300	1.28752500	3.14166200

H	0.00000000	0.00000000	0.47976600
C	0.72505800	1.25583700	2.05025500
H	1.75595500	1.27566000	1.69712200
H	0.22677700	2.15853200	1.69712200
C	0.72505800	-1.25583700	2.05025500
H	0.74335300	-1.28752500	3.14166200
H	0.22677700	-2.15853200	1.69712200
C	-1.45011600	0.00000000	2.05025500
H	-1.98273200	0.88287200	1.69712200
H	-1.98273200	-0.88287200	1.69712200

$H_3C–CH_3$
E = -1240.32
H = -1190.69
G = -1206.92
N_{imag} = 0

C	0.00000000	0.00000000	0.76281900
H	0.00000000	1.01540100	1.15607200
H	0.87936300	-0.50770100	1.15607200
H	0.87936300	0.50770100	-1.15607200
H	-0.87936300	-0.50770100	1.15607200
C	0.00000000	0.00000000	-0.76281900
H	0.00000000	-1.01540100	-1.15607200
H	-0.87936300	0.50770100	-1.15607200

$MeH_2C–CH_3$
E = -1747.84
H = -1679.51
G = -1698.63
N_{imag} = 0

C	0.00000000	0.00000000	-1.13128400
H	0.87387400	0.00000000	-0.47826800
H	-0.88023800	-1.29616300	-2.62671700
H	0.88023800	1.29616300	-2.62671700
H	-0.87387400	0.00000000	-0.47826800
C	0.00000000	1.26482800	-1.98382100
H	-0.88023800	1.29616300	-2.62671700
H	0.00000000	2.16418800	-1.36986100
C	0.00000000	-1.26482800	-1.98382100
H	0.88023800	-1.29616300	-2.62671700
H	0.00000000	-2.16418800	-1.36986100

$Me_2HC–CH_3$
E = -2256.72
H = -2170.01
G = -2190.86
N_{imag} = 0

C	0.00000000	0.00000000	1.57256700
H	-1.48670500	0.00000000	3.14166200
H	1.75595500	-1.27566000	1.69712200
H	0.74335300	1.28752500	3.14166200

H	0.00000000	0.00000000	0.47976600
C	0.72505800	1.25583700	2.05025500
H	1.75595500	1.27566000	1.69712200
H	0.22677700	2.15853200	1.69712200
C	0.72505800	-1.25583700	2.05025500
H	0.74335300	-1.28752500	3.14166200
H	0.22677700	-2.15853200	1.69712200
C	-1.45011600	0.00000000	2.05025500
H	-1.98273200	0.88287200	1.69712200
H	-1.98273200	-0.88287200	1.69712200

$Me_3C–CH_3$
E = -2766.43
H = -2661.46
G = -2683.09
N_{imag} = 0

C	-0.00002800	-0.00002300	1.55711800
H	-1.23132400	0.79934700	3.15774400
H	0.77716500	-2.02194200	1.71473100
H	1.30782100	0.66667000	3.15776000
H	0.05342700	1.01839300	-0.36046100
C	1.28569000	0.65451700	2.06719200
H	2.16322300	0.10977100	1.71627800
H	1.36234200	1.68407500	1.71490900
C	-0.07602400	-1.44073800	2.06720200
H	-0.07635300	-1.46602200	3.15776500
H	-0.98661300	-1.92833100	1.71642700
C	-1.20967700	0.78625300	2.06718400
H	-1.17665900	1.81856700	1.71618700
H	-2.13962100	0.33784200	1.71489400
C	0.00000600	0.00002300	0.02688300
H	0.85521900	-0.55547100	-0.36038700
H	-0.90859400	-0.46293100	-0.36053600

F^-
E = -280.80
H = -279.91
G = -287.66
N_{imag} = 0

Cl^-
E = -218.61
H = -217.72
G = -225.47
N_{imag} = 0

Br^-
E = -201.56
H = -200.67
G = -208.42
N_{imag} = 0

I^-
E = -182.99
H = -182.10
G = -189.85
N_{imag} = 0

H^-
E = -146.50
H = -145.61
G = -153.36
N_{imag} = 0

H_3C^-
E = -647.11
H = -626.34
G = -640.09
N_{imag} = 0

C	-0.00004200	0.00000700	-1.02955400
H	-0.50728900	0.87869700	-0.61340000
H	-0.50726500	-0.87868800	-0.61339700
H	1.01459700	-0.00001600	-0.61338200

H_3C^+
E = -431.36
H = -408.97
G = -422.25
N_{imag} = 0

C	0.00000000	0.00000000	0.00000000
H	-0.53998900	0.93528900	0.00000000
H	-0.53998900	-0.93528900	0.00000000
H	1.07997900	0.00000000	0.00000000

MeH_2C^+
E = -965.78
H = -924.73
G = -940.97
N_{imag} = 0

C	0.00000000	-0.68527000	1.05228500
H	0.93104600	1.23148400	1.05297800
H	-0.93104600	1.23148400	1.05297800
C	0.00000000	0.68527000	1.05228500
H	0.93104600	-1.23148400	1.05297800
H	0.00000000	0.00000000	-0.05315900
H	-0.93104600	-1.23148400	1.05297800

Me_2HC^+
E = -1484.38
H = -1425.25
G = -1444.85
N_{imag} = 0

C	0.00000000	0.00000000	-0.56903200

H	-0.80119800	-0.94894100	1.15428500
H	0.18164600	-1.85577600	-0.01325900
H	-0.18164600	1.85577600	-0.01325900
C	0.62725900	1.10097100	0.09589600
H	0.80119800	0.94894100	1.15428500
H	1.46749000	1.51464000	-0.45303100
H	0.00000000	0.00000000	-1.65244800
C	-0.62725900	-1.10097100	0.09589600
H	-1.46749000	-1.51464000	-0.45303100

Me_3C^+
E = -2004.32
H = -1927.14
G = -1948.53
N_{imag} = 91,15*i* (spurious imaginary frequency associated with free methyl-group rotation)

C	0.92600600	-1.42859500	0.48410900
H	0.89142200	0.65444300	0.94694900
H	0.47692600	-2.95233700	1.69556900
H	2.18018200	-1.32106100	-1.07968200
C	2.30038600	-1.42866700	0.01146400
H	2.86996800	-0.57237500	0.35484800
H	2.80196300	-2.37659500	0.17709500
C	0.22331800	-2.68777700	0.65452600
H	-0.85554800	-2.58775800	0.60295800
H	0.61857000	-3.48105400	0.02790200
C	0.22988100	-0.17759300	0.73926800
H	-0.28211200	0.02088500	-0.21645500
H	-0.55897900	-0.29442500	1.47753500

•••CF
E = -270.56
H = -266.68
G = -281.09
N_{imag} = 0

C	0.00000000	0.00000000	-4.32172600
F	0.00000000	0.00000000	-2.99966700

•••CCl
E = -216.02
H = -212.63
G = -227.82
N_{imag} = 0

C	0.00000000	0.00000000	-4.63092900
Cl	0.00000000	0.00000000	-2.97786200

•••CBr
E = -199.00
H = -195.83
G = -211.85
N_{imag} = 0

C	0.00000000	0.00000000	-4.85229400
Br	0.00000000	0.00000000	-3.02909900

•••CI
E = -189.61
H = -186.61
G = -203.24
N_{imag} = 0

C	0.00000000	0.00000000	-5.02855400
I	0.00000000	0.00000000	-2.99260400

•••CH
E = -228.94
H = -222.43
G = -234.60
N_{imag} = 0

C	0.00000000	0.00000000	-0.58165600
H	0.00000000	0.00000000	-1.67443100

•••CMe
E = -741.66
H = -715.73
G = -731.38
N_{imag} = 0

C	0.00000000	0.00000000	-4.64150000
H	0.51265600	-0.88794600	-2.77420000
C	0.00000000	0.00000000	-3.14695600
H	0.51265600	0.88794600	-2.77420000
H	-1.02531100	0.00000000	-2.77420000

•H
E = -51.62
H = -50.73
G = -58.48
N_{imag} = 0

•Me
E = -571.72
H = -550.64
G = -564.18
N_{imag} = 0

C	0.00914500	-0.00248200	-0.72628000
H	-0.01981300	-0.00785400	-1.80226800
H	-0.57940600	-0.71038300	-0.16850700
H	0.62666300	0.71080200	-0.20807400

•••C^+
E = 182.01
H = 182.90
G = 175.15
N_{imag} = 0

Table S14. Cartesian coordinates (in Å), energies (*E*, *H* and *G*, in kcal mol^{-1}), and number of imaginary vibrational frequencies (N_{imag}) of all stationary points and transition states in the gas phase, computed at COSMO(DCM)-ZORA-(U)M06-2X/QZ4P.

H_3C-F
E = -796.45
H = -769.25
G = -785.12
$\boldsymbol{N_{imag}}$ = 0

C	0.00000000	0.00000000	0.14414500
H	-0.51536500	0.89263800	0.48502400
H	-0.51536500	-0.89263800	0.48502400
H	1.03072900	0.00000000	0.48502400
F	0.00000000	0.00000000	-1.25168800

MeH_2C-F
E = -1307.66
H = -1261.89
G = -1280.70
$\boldsymbol{N_{imag}}$ = 0

C	0.21427800	-1.79664200	0.08241700
H	-0.05328800	-0.89450900	0.62740900
H	0.00403100	-2.66753700	0.69874900
H	2.30864100	-1.71588300	0.46677700
F	-0.64627300	-1.86870900	-1.02601800
C	1.64312600	-1.76960700	-0.39327100
H	1.87789500	-2.67116500	-0.95516300
H	1.82210800	-0.90058900	-1.02286500

Me_2HC-F
E = -1819.39
H = -1755.38
G = -1776.26
$\boldsymbol{N_{imag}}$ = 0

C	0.92781800	-1.38457900	0.00000000
H	0.10983500	-2.10392300	0.00000000
H	2.53562900	-0.75260200	-1.27075700
H	2.19888200	-2.48805200	1.31850100
F	0.30898400	-0.11304800	0.00000000
C	1.74373400	-1.50060600	1.26518400
H	2.53562900	-0.75260200	1.27075700
H	1.11578100	-1.36116300	2.14223100
C	1.74373400	-1.50060600	-1.26518400
H	2.19888200	-2.48805200	-1.31850100
H	1.11578100	-1.36116300	-2.14223100

Me_3C-F
E = -2331.13
H = -2249.01
G = -2271.66
$\boldsymbol{N_{imag}}$ = 0

C	0.17439200	-1.90280500	0.00000000
H	0.47311300	-3.57085600	1.31530700
H	0.03461100	-2.06988000	-2.14049700
H	2.29781700	-2.20682200	0.00000000
F	-0.67779900	-0.76300000	0.00000000
C	1.59521900	-1.37512900	0.00000000
H	1.77411800	-0.76950300	-0.88657500
H	1.77411800	-0.76950300	0.88657500
C	-0.15157100	-2.68092400	-1.25915500
H	0.47311300	-3.57085600	-1.31530700
H	-1.19544600	-2.98930000	-1.25395500
C	-0.15157100	-2.68092400	1.25915500
H	0.03461100	-2.06988000	2.14049700
H	-1.19544600	-2.98930000	1.25395500

$H_3C–Cl$
E = -722.43
H = -696.14
G = -712.82
N_{imag} = 0

C	0.00000000	0.00000000	0.12812400
H	-0.51481500	0.89168600	0.46121600
H	-0.51481500	-0.89168600	0.46121600
H	1.02963100	0.00000000	0.46121600
Cl	0.00000000	0.00000000	-1.66123600

$MeH_2C–Cl$
E = -1231.96
H = -1186.95
G = -1206.53
N_{imag} = 0

C	0.22222000	-1.79952900	0.07856200
H	-0.05120100	-0.91495000	0.64206700
H	-0.00761900	-2.68423100	0.66105500
H	1.86051400	-0.88535200	-0.97896200
Cl	-0.89538400	-1.84206200	-1.33763300
C	1.66264500	-1.76884900	-0.37651100
H	2.31124900	-1.74411300	0.49837200
H	1.90382800	-2.65372900	-0.96087800

$Me_2HC–Cl$
E = -1742.27
H = -1678.86
G = -1700.42
N_{imag} = 0

C	0.23432200	-1.81730200	0.09437900
H	-0.01087500	-0.90247100	0.62475600
H	0.57816300	-3.01779400	1.82429600
H	1.83876500	-0.90658000	-1.03210700
Cl	-0.89448900	-1.80808200	-1.33428000
C	1.66107700	-1.78082500	-0.41115300

H	2.33803400	-1.74522500	0.44221600
H	1.88156200	-2.67645100	-0.99010800
C	-0.06829900	-3.03136700	0.94699800
H	-1.10348200	-3.03399600	1.27845700
H	0.12645000	-3.94557000	0.38819700

$Me_3C–Cl$
E = -2252.60
H = -2170.98
G = -2194.22
N_{imag} = 0

C	0.19826200	-1.79099000	0.10062400
H	0.52322600	-0.40675800	1.69438200
H	0.58130100	-2.97384400	1.83732500
H	1.78597100	-0.93443300	-1.09012300
Cl	-0.92806900	-1.89735400	-1.34834400
C	-0.13076200	-0.49773500	0.82654800
H	0.02974700	0.36251200	0.18015900
H	-1.16332300	-0.49613400	1.16921900
C	1.61846000	-1.78940300	-0.43853200
H	2.31195100	-1.72753000	0.40071900
H	1.82512300	-2.70293100	-0.99204600
C	-0.07450500	-3.00876100	0.96681400
H	-1.10664200	-3.01783500	1.31067000
H	0.12499600	-3.92756200	0.41943000

$H_3C–Br$
E = -702.57
H = -676.63
G = -694.13
N_{imag} = 0

C	0.00000000	0.00000000	1.08433000
H	-1.03182800	0.00000000	1.40741100
H	0.51591400	-0.89358900	1.40741100
H	0.51591400	0.89358900	1.40741100
Br	0.00000000	0.00000000	-0.86411600

$MeH_2C–Br$
E = -1211.77
H = -1167.05
G = -1187.45
N_{imag} = 0

C	0.16792200	0.01906900	0.00000000
H	-0.10325100	0.57884400	-0.88642200
H	-0.10325100	0.57884400	0.88642200
H	2.24644400	0.47710600	0.00000000
Br	-1.03301100	-1.53881600	0.00000000
C	1.61508900	-0.41183600	0.00000000
H	1.84969900	-0.99929900	0.88435000
H	1.84969900	-0.99929900	-0.88435000

$Me_2HC–Br$

E = -1721.70
H = -1658.53
G = -1680.87
N_{imag} = 0

C	0.21790700	-2.06056700	-0.16373700
H	-0.11641100	-2.25501500	0.84942100
H	0.22955600	-3.01778600	-2.09229900
H	2.29273200	-2.40500300	0.16247400
Br	-0.95630400	-0.56086000	-0.73049000
C	1.65574100	-1.59056000	-0.18536800
H	1.95825400	-1.32738400	-1.19765900
H	1.80761300	-0.73229100	0.46355300
C	-0.03935100	-3.24964600	-1.06301200
H	0.58075100	-4.08120100	-0.72529400
H	-1.08026700	-3.55984100	-1.03070800

$Me_3C–Br$

E = -2231.71
H = -2150.31
G = -2174.35
N_{imag} = 0

C	0.00000600	0.00001800	1.60907800
H	-1.27615200	0.74626700	3.14161400
H	0.87587500	-1.97703600	1.69326400
H	1.28366800	0.73325900	3.14161600
Br	-0.00001400	0.00013900	-0.40063800
C	1.26122900	0.71967800	2.05030700
H	2.15232800	0.20763000	1.69433900
H	1.27449100	1.74691800	1.69313200
C	-0.00741900	-1.45216500	2.05001600
H	-0.00751600	-1.47876000	3.14131900
H	-0.89607500	-1.96794600	1.69332700
C	-1.25380300	0.73251600	2.05030700
H	-1.25654200	1.75985400	1.69317900
H	-2.15007800	0.22962800	1.69427400

$H_3C–I$

E = -684.91
H = -659.28
G = -677.34
N_{imag} = 0

C	0.00000000	0.00000000	1.08323200
H	-1.03228600	0.00000000	1.40411200
H	0.51614300	-0.89398600	1.40411200
H	0.51614300	0.89398600	1.40411200
I	0.00000000	0.00000000	-1.05227700

$MeH_2C–I$
E = -1193.20
H = -1148.71
G = -1169.67
N_{imag} = 0

C	0.21812900	-1.79360000	0.07245500
H	-0.06569200	-0.89647300	0.60833900
H	-0.01688900	-2.66642600	0.66876000
H	2.31003800	-1.72059600	0.47997400
I	-1.15141600	-1.88754500	-1.59003100
C	1.65724800	-1.76964900	-0.39246300
H	1.90566400	-2.66650800	-0.95506500
H	1.85609900	-0.90216500	-1.01736800

$Me_2HC–I$
E = -1702.40
H = -1639.42
G = -1662.31
N_{imag} = 0

C	0.21406800	-2.05389100	-0.16916700
H	-0.12420700	-2.24393800	0.84349200
H	0.22966700	-3.02619500	-2.09487000
H	2.28791500	-2.41009100	0.16180000
I	-1.07763600	-0.40994900	-0.78471300
C	1.65623800	-1.59040000	-0.18579400
H	1.96649200	-1.32628900	-1.19563700
H	1.81485000	-0.73434200	0.46461500
C	-0.03891900	-3.25012800	-1.06359800
H	0.58478200	-4.07782300	-0.72061000
H	-1.07807300	-3.56673300	-1.03308000

$Me_3C–I$
E = -2211.95
H = -2130.70
G = -2155.25
N_{imag} = 0

C	0.20327200	-2.06619900	-0.14357500
H	0.39799200	-3.18009000	1.66022400
H	0.27219100	-3.02601200	-2.08705700
H	2.28821300	-2.36437700	0.16676300
I	-1.08434400	-0.43485100	-0.88302000
C	1.63678700	-1.56601000	-0.19686100
H	1.93485100	-1.31736300	-1.21298500
H	1.77864200	-0.69351000	0.43703500
C	-0.00921200	-3.25746000	-1.06215000
H	0.62316600	-4.07540100	-0.70851200
H	-1.04360900	-3.59356900	-1.04653200
C	-0.23114200	-2.37172500	1.27978900
H	-0.10723400	-1.50762000	1.92875900
H	-1.26805800	-2.69800600	1.31906300

$H_3C–H$
E = -734.79
H = -704.36
G = -717.62
N_{imag} = 0

C	0.00000000	0.00000000	0.00000000
H	0.62726900	-0.62726900	0.62726900
H	-0.62726900	-0.62726900	-0.62726900
H	0.62726900	0.62726900	-0.62726900
H	-0.62726900	0.62726900	0.62726900

$MeH_2C–H$
E -1240.34
H = -1190.69
G = -1206.92
N_{imag} = 0

C	0.00000000	0.00000000	0.76279700
H	0.00000000	1.01533300	1.15615200
H	0.87930400	-0.50766700	1.15615200
H	0.87930400	0.50766700	-1.15615200
H	-0.87930400	-0.50766700	1.15615200
C	0.00000000	0.00000000	-0.76279700
H	0.00000000	-1.01533300	-1.15615200
H	-0.87930400	0.50766700	-1.15615200

$Me_2HC–H$
E = -1747.87
H = -1679.51
G = -1698.63
N_{imag} = 0

C	0.00000000	0.00000000	-1.13130500
H	0.87380700	0.00000000	-0.47821300
H	-0.88016300	-1.29627900	-2.62673500
H	0.88016300	1.29627900	-2.62673500
H	-0.87380700	0.00000000	-0.47821300
C	0.00000000	1.26482600	-1.98378900
H	-0.88016300	1.29627900	-2.62673500
H	0.00000000	2.16419900	-1.36990100
C	0.00000000	-1.26482600	-1.98378900
H	0.88016300	-1.29627900	-2.62673500
H	0.00000000	-2.16419900	-1.36990100

$Me_3C–H$
E = -2256.76
H = -2170.02
G = -2190.86
N_{imag} = 0

C	0.00000000	0.00000000	1.57256700
H	-1.48683000	0.00000000	3.14159600
H	1.75594900	-1.27575400	1.69717300
H	0.74341500	1.28763300	3.14159600

H	0.00000000	0.00000000	0.47975300
C	0.72505200	1.25582700	2.05022300
H	1.75594900	1.27575400	1.69717300
H	0.22686100	2.15857300	1.69717300
C	0.72505200	-1.25582700	2.05022300
H	0.74341500	-1.28763300	3.14159600
H	0.22686100	-2.15857300	1.69717300
C	-1.45010400	0.00000000	2.05022300
H	-1.98281000	0.88281900	1.69717300
H	-1.98281000	-0.88281900	1.69717300

$H_3C–CH_3$
E = -1240.34
H = -1190.69
G = -1206.92
N_{imag} = 0

C	0.00000000	0.00000000	0.76279700
H	0.00000000	1.01533300	1.15615200
H	0.87930400	-0.50766700	1.15615200
H	0.87930400	0.50766700	-1.15615200
H	-0.87930400	-0.50766700	1.15615200
C	0.00000000	0.00000000	-0.76279700
H	0.00000000	-1.01533300	-1.15615200
H	-0.87930400	0.50766700	-1.15615200

$MeH_2C–CH_3$
E = -1747.87
H = -1679.51
G = -1698.63
N_{imag} = 0

C	0.00000000	0.00000000	-1.13130500
H	0.87380700	0.00000000	-0.47821300
H	-0.88016300	-1.29627900	-2.62673600
H	0.88016300	1.29627900	-2.62673600
H	-0.87380700	0.00000000	-0.47821300
C	0.00000000	1.26482600	-1.98378900
H	-0.88016300	1.29627900	-2.62673600
H	0.00000000	2.16419900	-1.36990100
C	0.00000000	-1.26482600	-1.98378900
H	0.88016300	-1.29627900	-2.62673600
H	0.00000000	-2.16419900	-1.36990100

$Me_2HC–CH_3$
E = -2256.76
H = -2170.02
G = -2190.86
N_{imag} = 0

C	0.00000000	0.00000000	1.57256600
H	-1.48682900	0.00000000	3.14159600
H	1.75594900	-1.27575400	1.69717400
H	0.74341500	1.28763200	3.14159600

H	0.00000000	0.00000000	0.47975300
C	0.72505200	1.25582700	2.05022300
H	1.75594900	1.27575400	1.69717400
H	0.22686100	2.15857300	1.69717400
C	0.72505200	-1.25582700	2.05022300
H	0.74341500	-1.28763200	3.14159600
H	0.22686100	-2.15857300	1.69717400
C	-1.45010400	0.00000000	2.05022300
H	-1.98281000	0.88281900	1.69717400
H	-1.98281000	-0.88281900	1.69717400

$Me_3C–CH_3$
E = -2766.47
H = -2661.47
G = -2683.10
N_{imag} = 0

C	-0.00002600	-0.00002500	1.55711700
H	-1.23143800	0.79940200	3.15770900
H	0.77709700	-2.02203900	1.71478100
H	1.30792000	0.66674600	3.15773000
H	0.05340900	1.01831900	-0.36057100
C	1.28567000	0.65452400	2.06718800
H	2.16328100	0.10989600	1.71635800
H	1.36243400	1.68407400	1.71498200
C	-0.07601100	-1.44072500	2.06719700
H	-0.07632100	-1.46615200	3.15773200
H	-0.98655200	-1.92842600	1.71652200
C	-1.20967000	0.78623200	2.06717700
H	-1.17678200	1.81855200	1.71625800
H	-2.13966500	0.33792700	1.71496000
C	0.00000800	0.00002200	0.02689800
H	0.85516800	-0.55542000	-0.36050000
H	-0.90852100	-0.46290900	-0.36064600

F^-
E = -271.39
H = -270.50
G = -278.25
N_{imag} = 0

Cl^-
E = -211.49
H = -210.60
G = -218.35
N_{imag} = 0

Br^-
E = -195.05
H = -194.16
G = -201.91
N_{imag} = 0

I^-
E = -177.26
H = -176.37
G = -184.12
N_{imag} = 0

H^-
E = -138.08
H = -137.19
G = -144.94
N_{imag} = 0

H_3C^-
E = -639.53
H = -618.77
G = -632.52
N_{imag} = 0

C	-0.00004000	0.00000600	-1.02862100
H	-0.50782600	0.87962900	-0.61371000
H	-0.50780800	-0.87962200	-0.61370800
H	1.01567400	-0.00001200	-0.61369300

H_3C^+
E = -423.42
H = -401.06
G = -414.34
N_{imag} = 0

C	0.00000000	0.00000000	0.00000000
H	-0.54039100	0.93598500	0.00000000
H	-0.54039100	-0.93598500	0.00000000
H	1.08078200	0.00000000	0.00000000

MeH_2C^+
E = -959.07
H = -918.04
G = -934.28
N_{imag} = 0

C	0.00000000	-0.68551300	1.05173600
H	0.93108500	1.23233800	1.05377500
H	-0.93108500	1.23233800	1.05377500
C	0.00000000	0.68551300	1.05173600
H	0.93108500	-1.23233800	1.05377500
H	0.00000000	0.00000000	-0.05524700
H	-0.93108500	-1.23233800	1.05377500

Me_2HC^+
E = -1478.65
H = -1419.52
G = -1439.13
N_{imag} = 0

C	0.00000000	0.00000000	-0.57009500

H	-1.04364600	0.67510000	1.15351500
H	-1.82234600	-0.40783900	-0.01865200
H	1.82234600	0.40783900	-0.01865200
C	1.17071900	-0.48629500	0.09421400
H	1.04364600	-0.67510000	1.15351500
H	1.68392400	-1.27098500	-0.45370900
H	0.00000000	0.00000000	-1.65400200
C	-1.17071900	0.48629500	0.09421400
H	-1.68392400	1.27098500	-0.45370900

Me_3C^+
E = -1999.11
H = -1921.92
G = -1943.28
N_{imag} = 83.88*i* (spurious imaginary frequency associated with free methyl-group rotation)

C	0.92607900	-1.42859200	0.48342800
H	0.89029800	0.65757000	0.93769900
H	0.47772200	-2.95452300	1.69451700
H	2.18473000	-1.31507600	-1.07787000
C	2.30160000	-1.42925900	0.01323900
H	2.87226600	-0.57532000	0.36142000
H	2.80210800	-2.37853200	0.17491800
C	0.22270200	-2.68774600	0.65412300
H	-0.85640000	-2.58803200	0.60433900
H	0.61663400	-3.48125400	0.02659900
C	0.22964400	-0.17705000	0.73719900
H	-0.29105200	0.01705200	-0.21487900
H	-0.55434800	-0.29214900	1.48135600

•••CF
E = -270.50
H = -266.62
G = -281.02
N_{imag} = 0

C	0.00000000	0.00000000	-4.32146400
F	0.00000000	0.00000000	-2.99992900

•••CCl
E = -215.97
H = -212.58
G = -227.77
N_{imag} = 0

C	0.00000000	0.00000000	-4.63082100
Cl	0.00000000	0.00000000	-2.97796900

•••CBr
E = -198.88
H = -195.72
G = -211.74
N_{imag} = 0

C	0.00000000	0.00000000	-4.85208500
Br	0.00000000	0.00000000	-3.02930700

•••CI
E = -189.28
H = -186.28
G = -202.90
N_{imag} = 0

C	0.00000000	0.00000000	-5.02773800
I	0.00000000	0.00000000	-2.99342100

•••CH
E = -228.85
H = -222.34
G = -234.51
N_{imag} = 0

C	0.00000000	0.00000000	-0.58183700
H	0.00000000	0.00000000	-1.67425000

•••CMe
E = -741.58
H = -715.64
G = -731.29
N_{imag} = 0

C	0.00000000	0.00000000	-4.64132800
H	0.51260400	-0.88785700	-2.77411800
C	0.00000000	0.00000000	-3.14737500
H	0.51260400	0.88785700	-2.77411800
H	-1.02520900	0.00000000	-2.77411800

•H
E = -51.63
H = -50.74
G = -58.49
N_{imag} = 0

•Me
E = -571.70
H = -550.60
G = -564.14
N_{imag} = 0

C	0.00914500	-0.00248200	-0.72628000
H	-0.01981000	-0.00785400	-1.80218700
H	-0.57936200	-0.71033000	-0.16854900
H	0.62661700	0.71074900	-0.20811400

•••C^+
E = 190.87
H = 191.76
G = 184.01
N_{imag} = 0

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