

Supplementary information

Table S1. Electronic configuration states by B3LYP/TZVP//B3LYP/aug-cc-pVTZ

Mol.	Inner-valence	Outer-valence
CH ₄	$(2a_1)^2$	$(1t_2)^6$
C ₂ H ₆	$(2a_{1g})^2(2a_{2u})^2$	$(1e_u)^4(3a_{1g})^2(1e_g)^4$
C ₃ H ₈	$(3a_1)^2(2b_2)^2(4a_1)^2$	$(1b_1)^2(5a_1)^2(3b_2)^2$ $(1a_2)^2(4b_2)^2(6a_1)^2(2b_1)^2$
nC ₄ H ₁₀	$(3a_g)^2(3b_u)^2(4a_g)^2(4b_u)^2$	$(1a_u)^2(5a_g)^2(5b_u)^2(1b_g)^2$ $(6b_u)^2(2a_u)^2(6a_g)^2(7a_g)^2(2b_g)^2$
isoC ₄ H ₁₀	$(3a_1)^2(2e)^4(4a_1)^2$ $(4a_1)^2(3b_2)^2$	$(5a_1)^2(3e)^4(4e)^4(1a_2)^2(5e)^4(6a_1)^2$ $(1b_1)^2(5b_2)^2(1a_2)^2(7a_1)^2(8a_1)^2$
nC ₅ H ₁₂	$(5a_1)^2(4b_2)^2(6a_1)^2$	$(2b_1)^2(6b_2)^2(2a_2)^2(9a_1)^2(3b_1)^2(7b_2)^2$
isoC ₅ H ₁₂	$(6a)^2(7a)^2(8a)^2(9a)^2(10a)^2$	$(11a)^2(12a)^2(13a)^2(14a)^2(15a)^2$ $(16a)^2(17a)^2(18a)^2(19a)^2(20a)^2(21a)^2$
neoC ₅ H ₁₂	$(3a_1)^2(2t_2)^6(4a_1)^2$	$(3t_2)^6(1e)^4(1t_1)^6(4t_2)^6$
nC ₆ H ₁₄	$(4a_g)^2(4b_u)^2(5a_g)^2$ $(5b_u)^2(6a_g)^2(6b_u)^2$	$(1a_u)^2(1b_g)^2(7a_g)^2(7b_u)^2(2a_u)^2(8b_u)^2$ $(8a_g)^2(2b_g)^2(9b_u)^2(3a_u)^2(9a_g)^2(3b_g)^2$ $(10a_g)^2$
isoC ₆ H ₁₄	$(7a)^2(8a)^2(9a)^2$ $(10a)^2(11a)^2(12a)^2$	$(13a)^2(14a)^2(15a)^2(16a)^2(17a)^2(18a)^2$ $(19a)^2(20a)^2(21a)^2(22a)^2(23a)^2(24a)^2(25a)^2$

3-methyl C ₅ H ₁₂	$(5a')^2(3a'')^2(6a')^2$	$(9a')^2(5a'')^2(6a'')^2(10a')^2(11a')^2(12a')^2$
	$(7a')^2(4a'')^2(8a')^2$	$(7a'')^2(13a')^2(8a'')^2(9a'')^2(14a')^2(15a')^2$ $(10a'')^2$
2,3-dime -thylC ₄ H ₁₀	$(4a_g)^2(4a_u)^2(5a_u)^2$	$(7a_u)^2(7a_g)^2(8a_g)^2(8a_u)^2(9a_u)^2(9a_g)^2$
	$(5a_g)^2(6a_g)^2(6a_u)^2$	$(10a_u)^2(10a_g)^2(11a_u)^2(12a_u)^2(11a_g)^2$ $(12a_g)^2(13a_g)^2$
2,2-dime -thylC ₄ H ₁₀	$(6a')^2(7a')^2(2a'')^2$	$(11a')^2(3a'')^2(12a')^2(4a'')^2(13a')^2(14a')^2$
	$(8a')^2(9a')^2(10a')^2$	$(5a'')^2(6a'')^2(15a')^2(7a'')^2(8a'')^2(16a')^2(17a')^2$
