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Investigation of soot precursor molecules during inception by acetylene pyrolysis using reactive molecular dynamics

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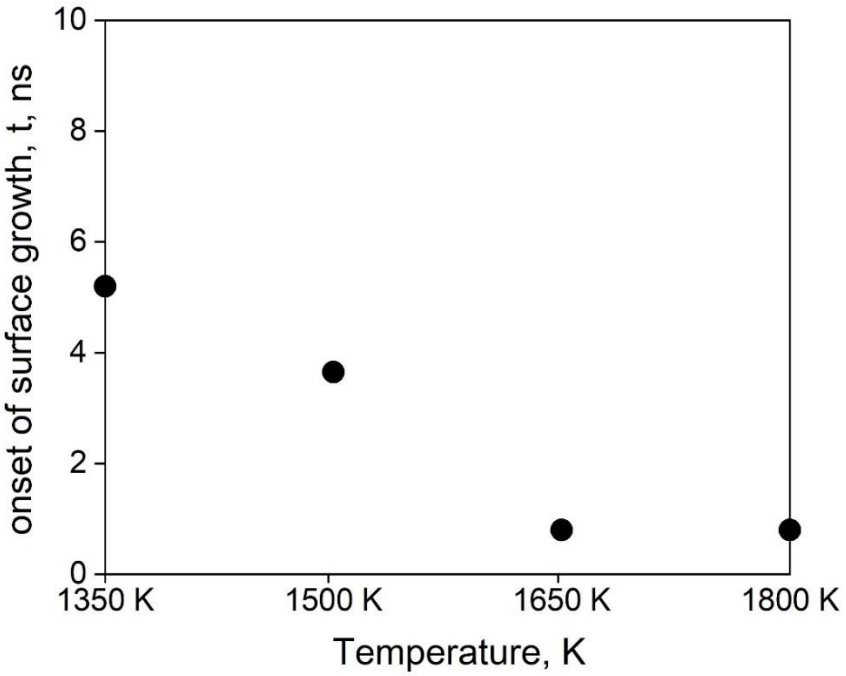


Figure S1. The onset of surface growth at 1350, 1500, 1650 and 1800 K denoted by the formation of soot clusters with $M_w \geq 202$ g/mol for the simulations of Figure 2.

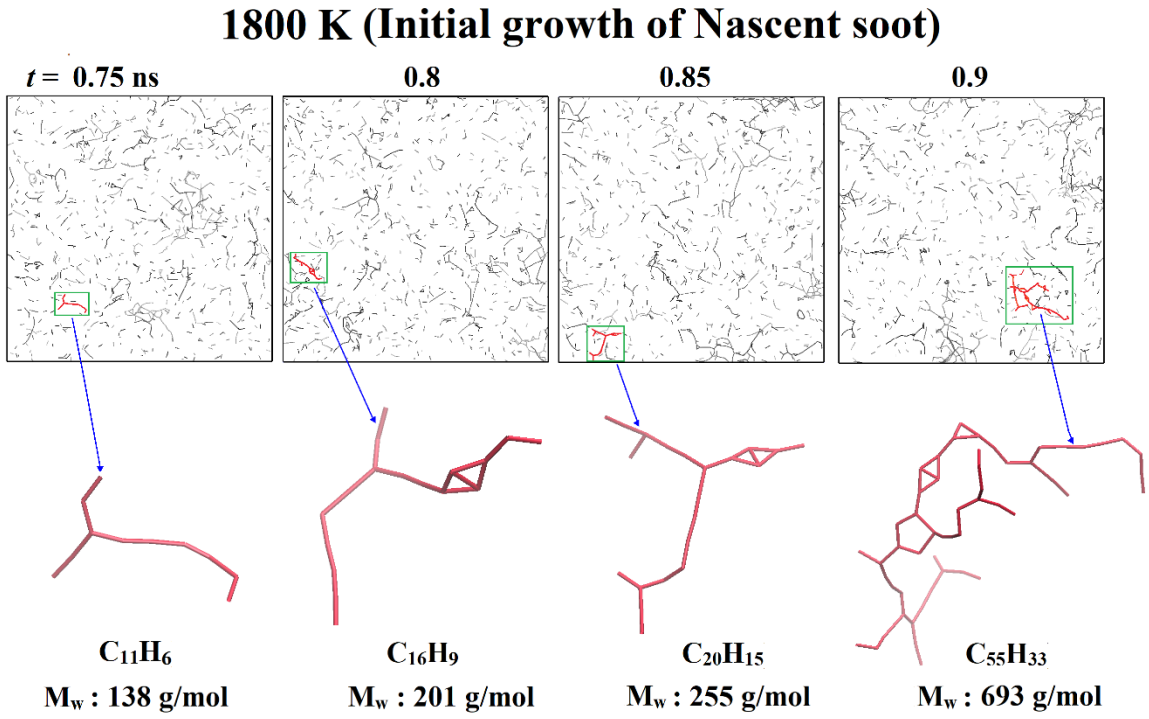


Figure S2. Snapshots of the growth of the largest cluster (hydrogen atoms are omitted) formed by acetylene pyrolysis at 1800 K at t = 0.75-0.9 ns.

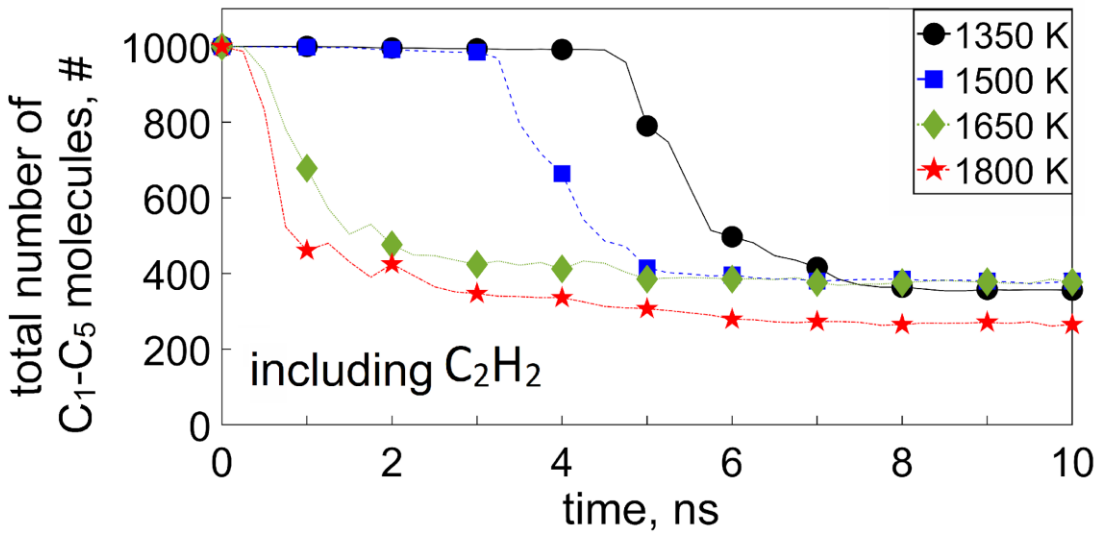


Figure S3. Temporal evolution of the total number of C_1-C_5 (including C_2H_2) molecules during acetylene pyrolysis at 1350 (circles), 1500 (squares), 1650 (diamonds) and 1800 K (stars).

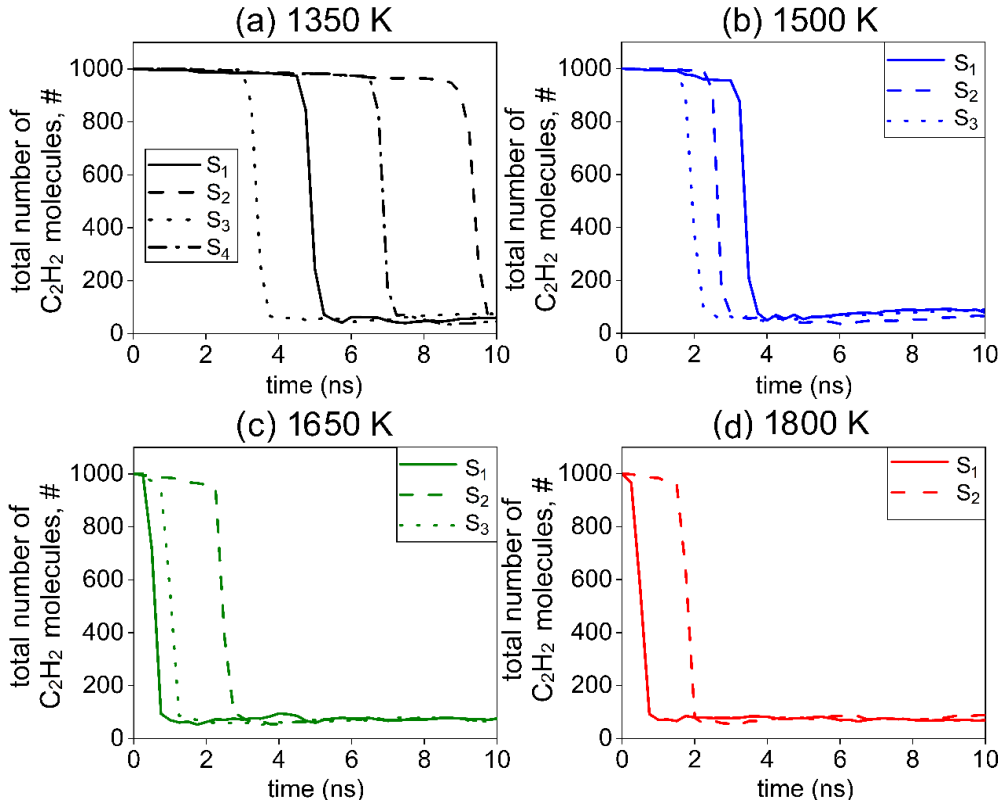


Figure S4. Temporal evolution of the total number of acetylene molecules during pyrolysis at (a) 1350, (b) 1500, (c) 1650 and (d) 1800 K for different simulations (S_1 – S_4).

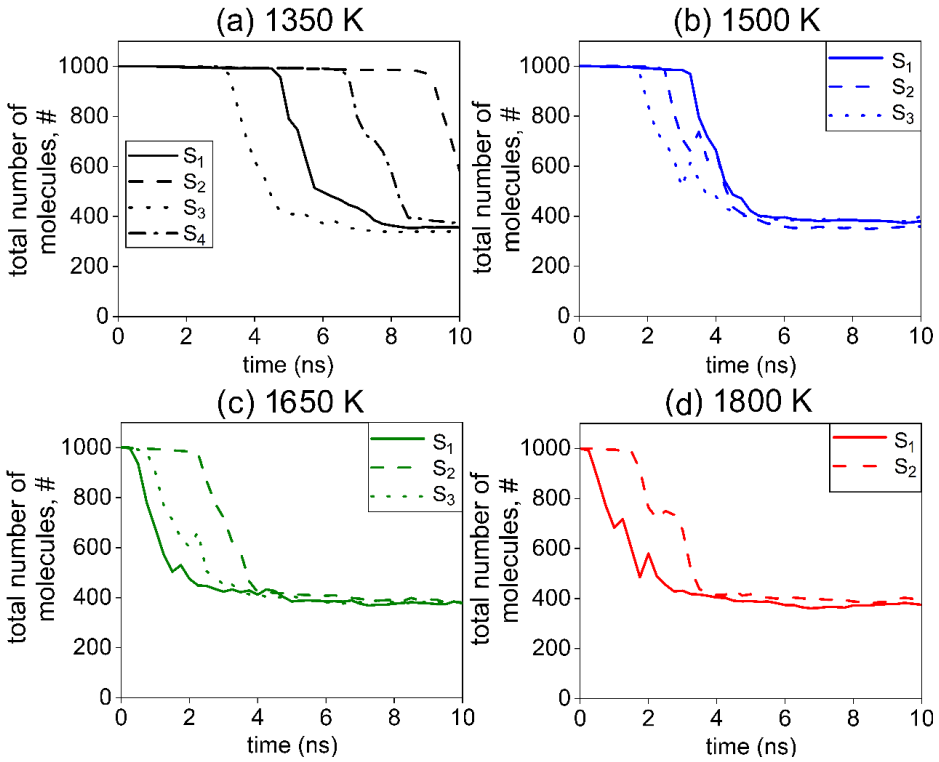


Figure S5. Temporal evolution of the total number of molecules during acetylene pyrolysis at (a) 1350, (b) 1500, (c) 1650 and (d) 1800 K for different simulations (S_1 – S_4).

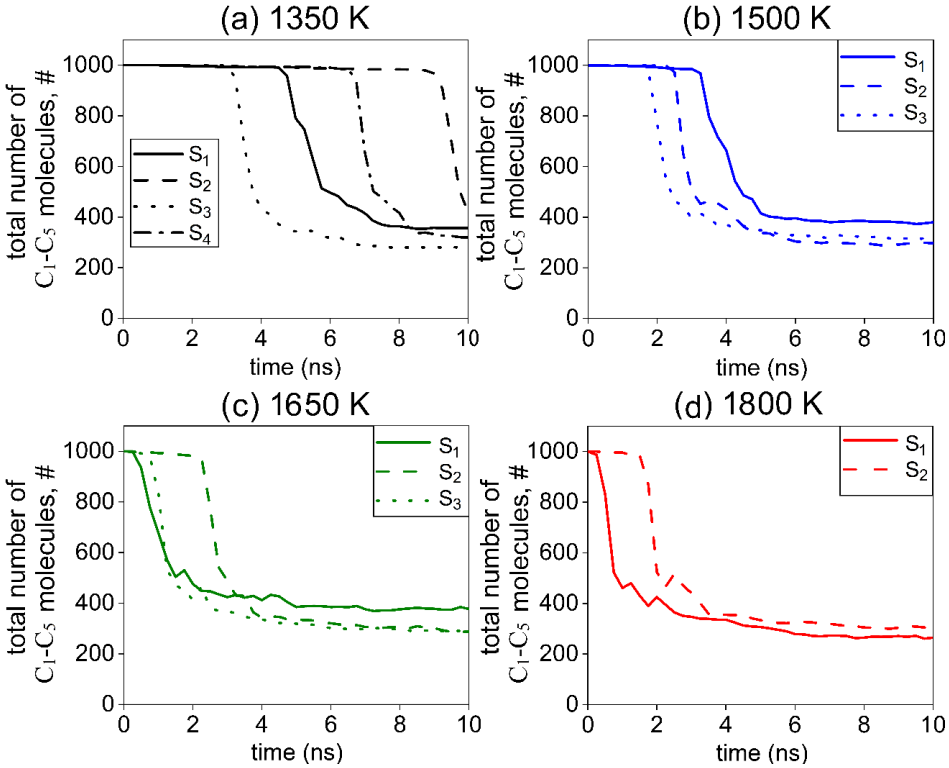


Figure S6. Temporal evolution of the C_1-C_5 molecules (including C_2H_2) during acetylene pyrolysis at (a) 1350, (b) 1500, (c) 1650 and (d) 1800 K for different simulations (S_1 – S_4).

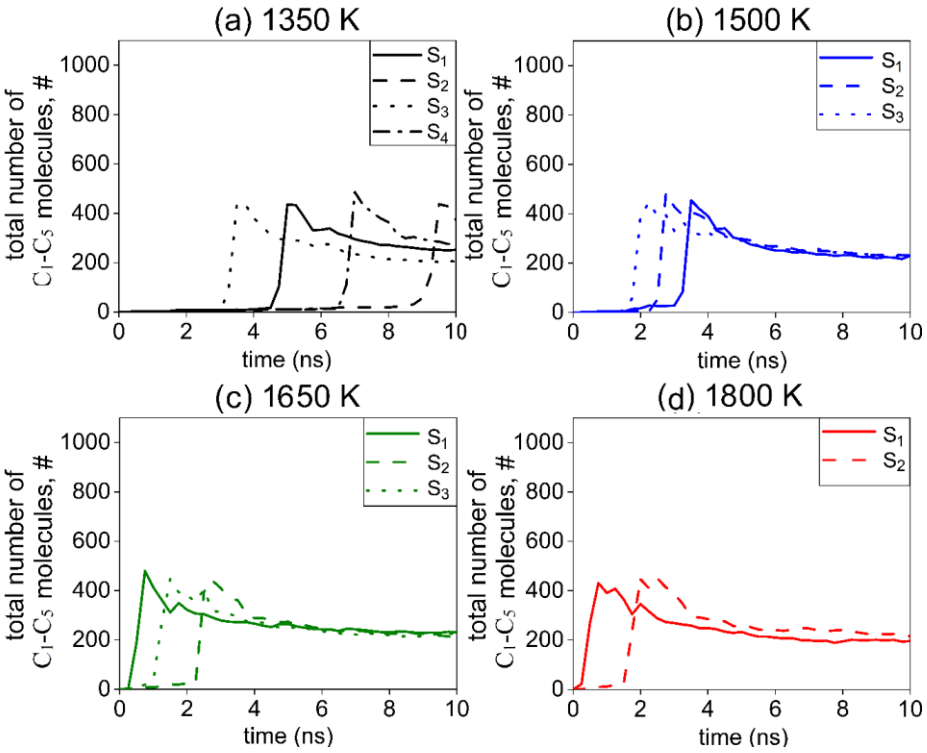


Figure S7. Temporal evolution of the C_1-C_5 molecules (excluding C_2H_2) during acetylene pyrolysis at (a) 1350, (b) 1500, (c) 1650 and (d) 1800 K for different simulations (S_1 – S_4).

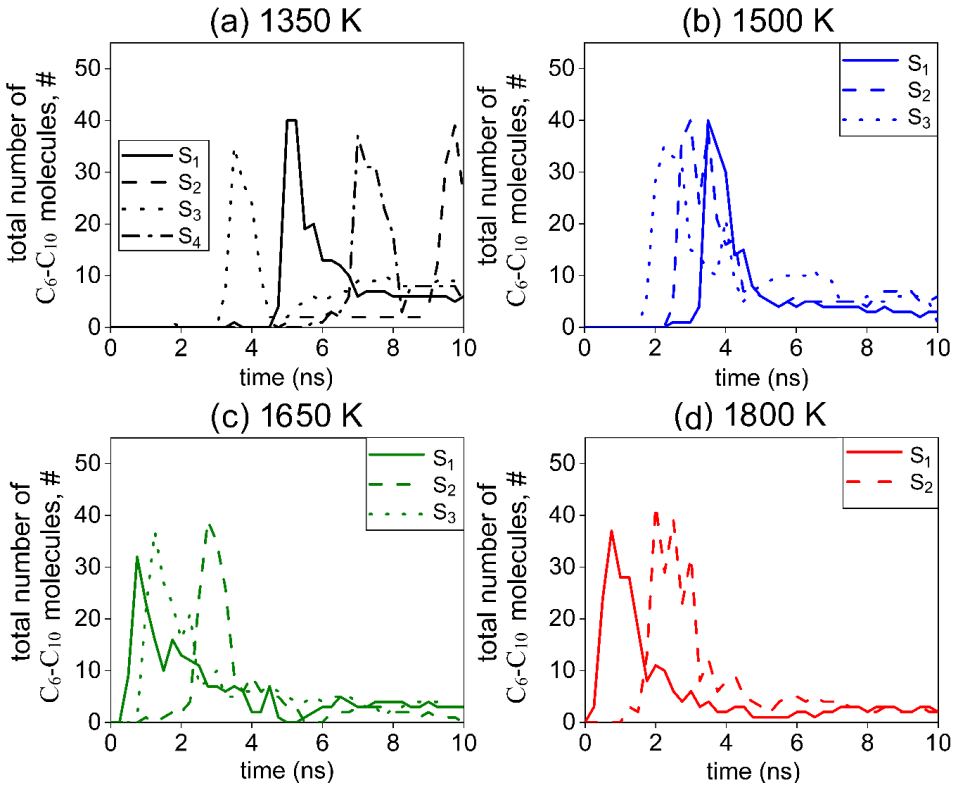


Figure S8. Temporal evolution of the C_6-C_{10} molecules during acetylene pyrolysis at (a) 1350, (b) 1500, (c) 1650 and (d) 1800 K for different simulations (S_1 – S_4).

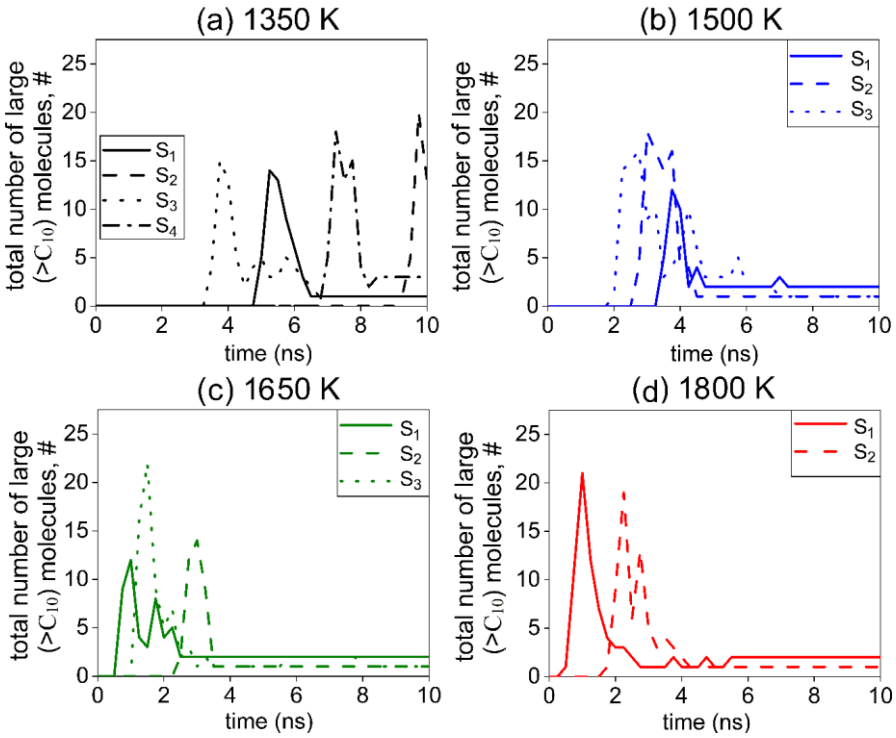


Figure S9. Temporal evolution of large (> C_{10}) molecules during acetylene pyrolysis at (a) 1350, (b) 1500, (c) 1650 and (d) 1800 K for different simulations (S_1 – S_4).

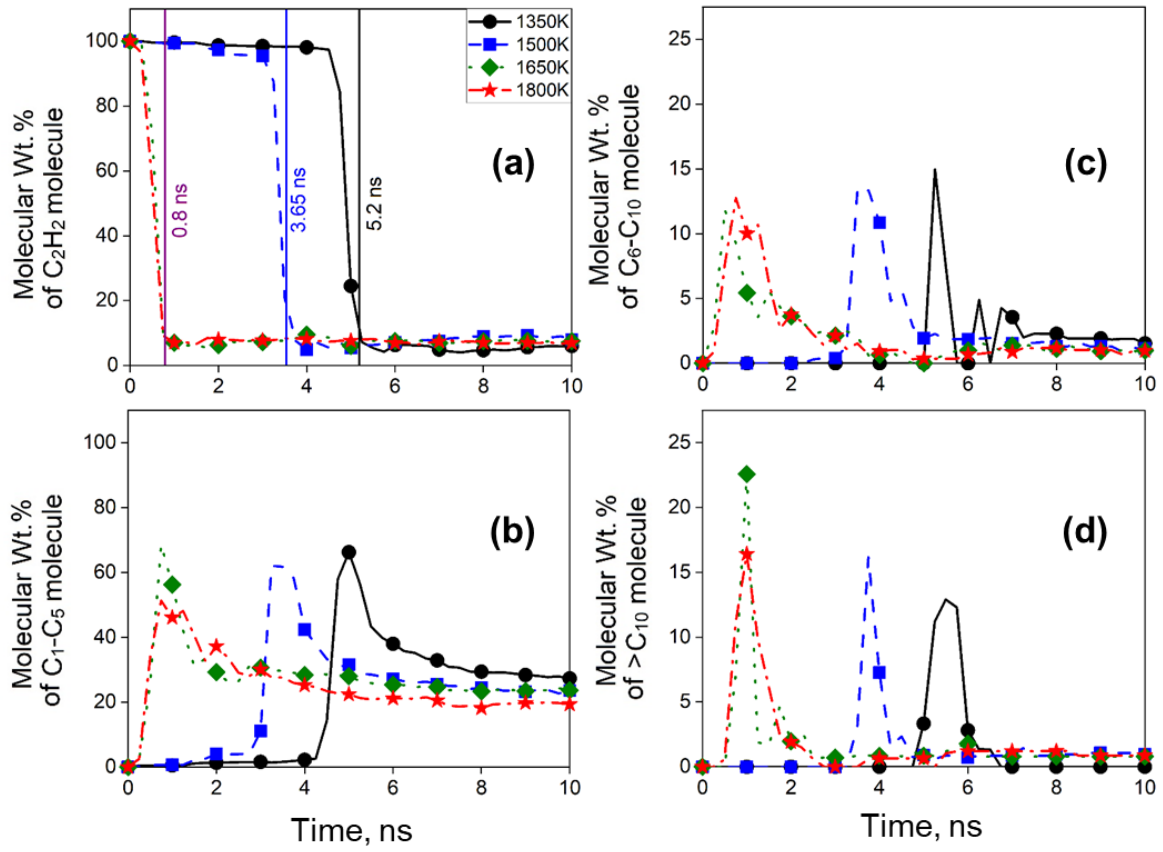


Figure S10. Temporal evolution of the molecular wt% of (a) acetylene (C_2H_2), (b) C_1-C_5 (excluding C_2H_2), (c) C_6-C_{10} and (d) > C_{10} molecules during acetylene pyrolysis at 1350 (circles), 1500 (squares), 1650 (diamonds) and 1800 K (stars). The vertical lines in Fig. S10a indicate the onset of surface growth for the respective temperatures.

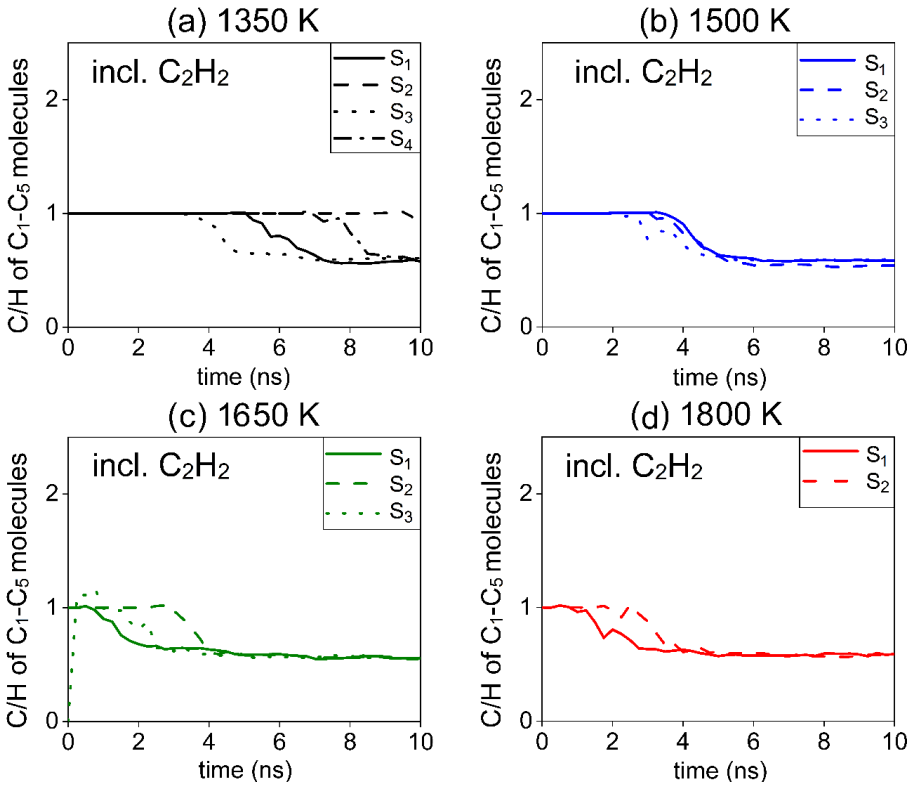


Figure S11. Temporal evolution of the C/H ratio of C_1-C_5 molecules (including C_2H_2) during acetylene pyrolysis at (a) 1350, (b) 1500, (c) 1650 and (d) 1800 K for different simulations (S_1 – S_4).

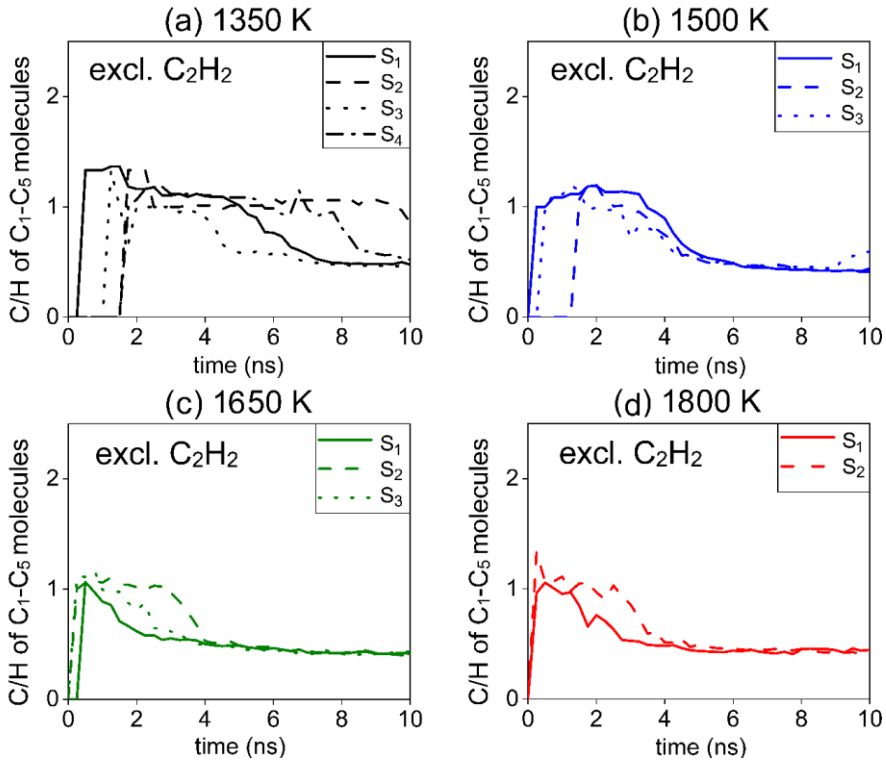


Figure S12. Temporal evolution of the C/H ratio of C_1-C_5 molecules (excluding C_2H_2) during acetylene pyrolysis at (a) 1350, (b) 1500, (c) 1650 and (d) 1800 K for different simulations (S_1 – S_4).

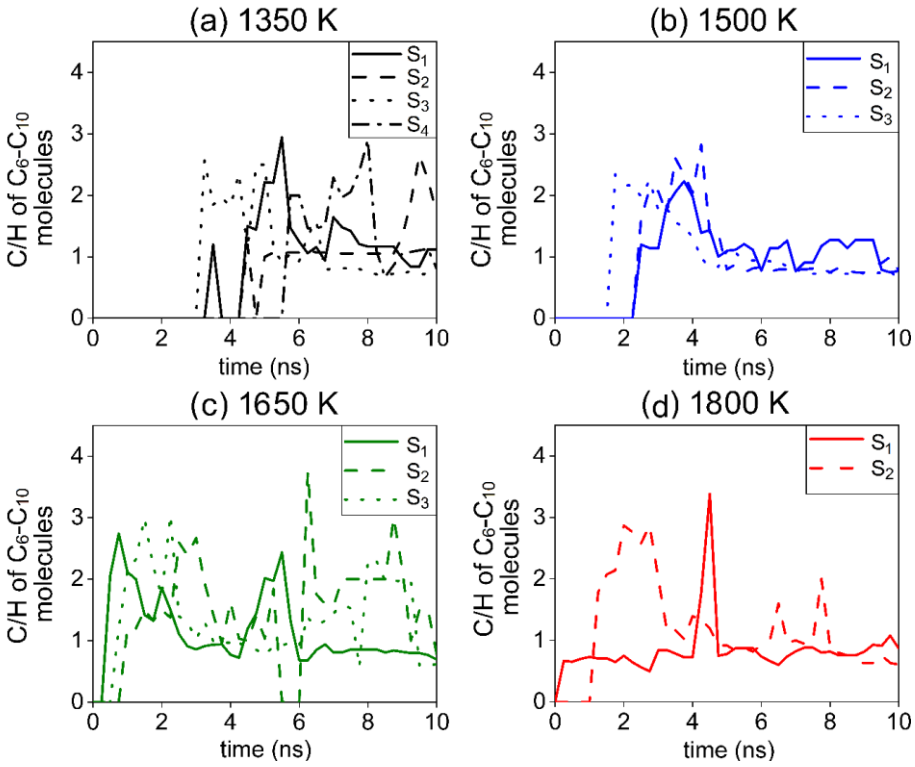


Figure S13. Temporal evolution of the C/H ratio of C_6-C_{10} molecules during acetylene pyrolysis at (a) 1350, (b) 1500, (c) 1650 and (d) 1800 K for different simulations (S_1 – S_4).

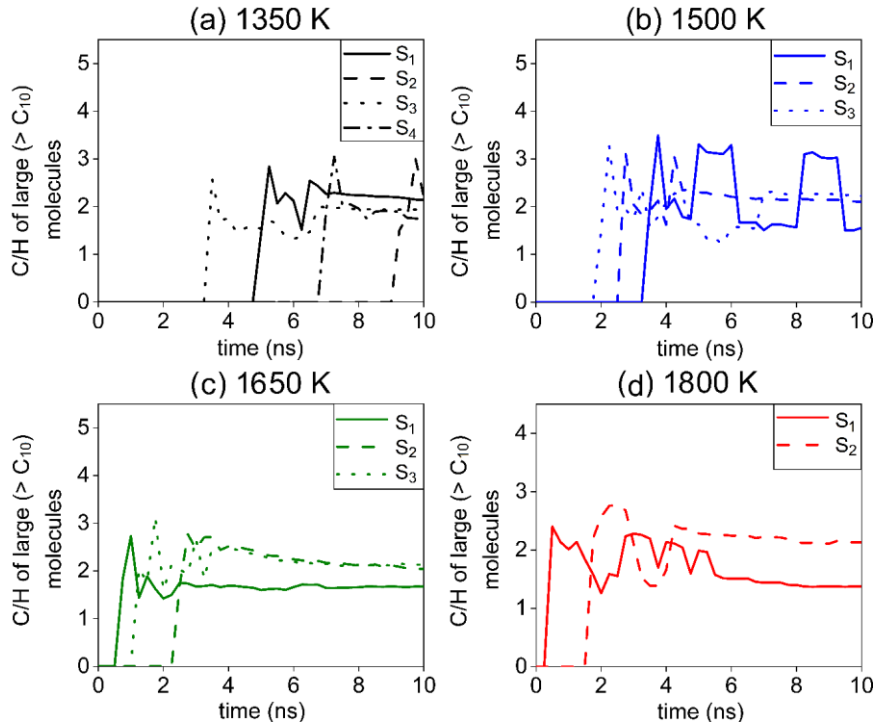


Figure S14. Temporal evolution of the C/H ratio of large (> C_{10}) molecules during acetylene pyrolysis at (a) 1350, (b) 1500, (c) 1650 and (d) 1800 K for different simulations (S_1 – S_4).

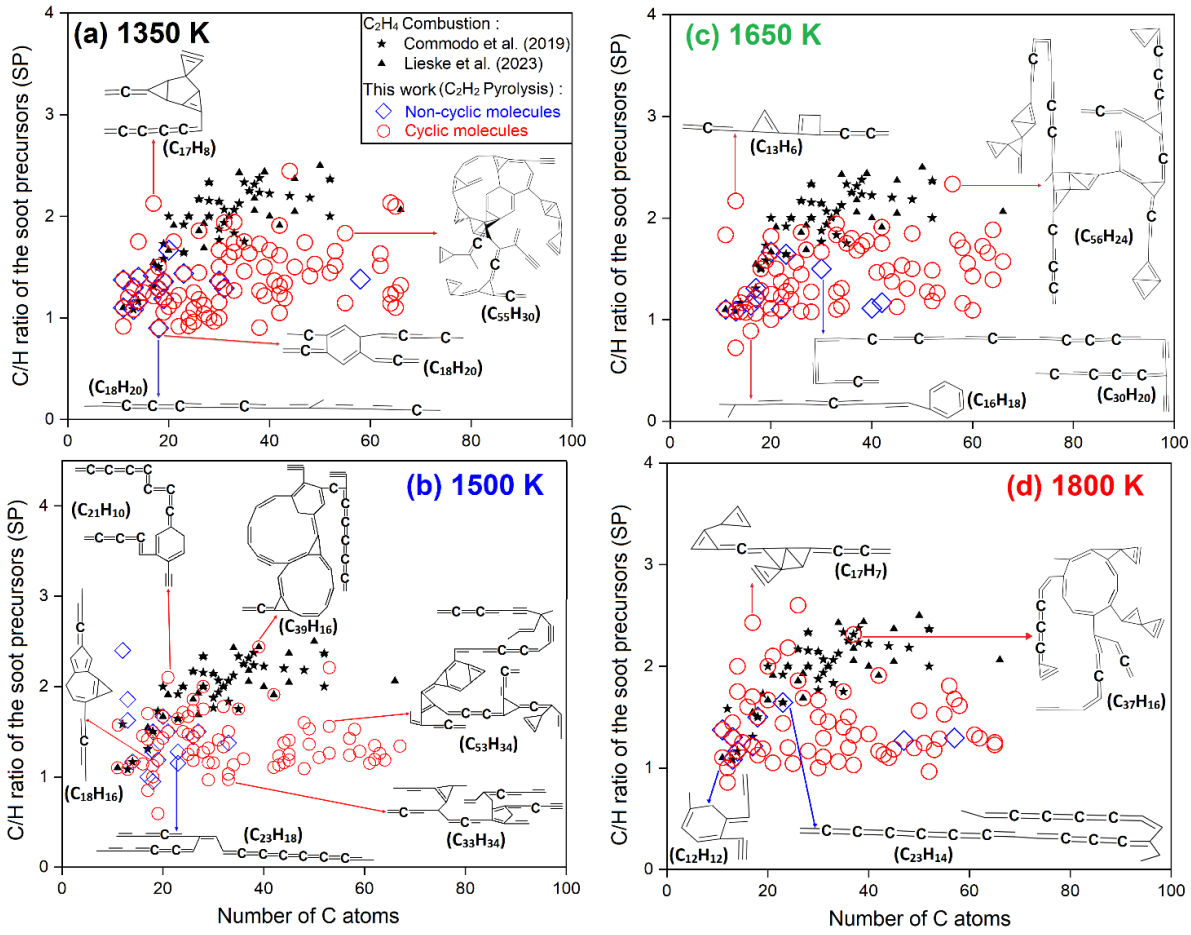


Figure S15. MD-obtained C/H ratio as a function of the number of C atoms per molecules formed at (a) 1350, (b) 1500, (c) 1650 and (c) 1800 K. The MD results are compared with AFM experiments (Lieske et al., 2023; Commodo et al., 2019).

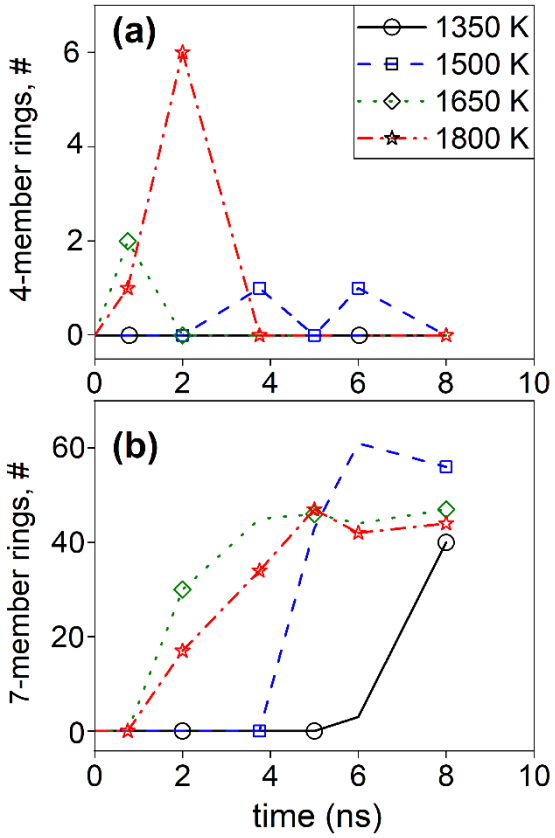


Figure S16. Temporal evolution of (a) 4- and (b) 7-member rings at 1350 (circles), 1500 (squares), 1650 (diamonds), and 1800 K (stars). A negligible number of 4-member rings is formed transiently, indicating that these structures are rather unstable and practically disappear over time. In contrast, a considerable number of 7-member rings is formed, comparable to that of 5-member rings (Fig. 6b). All 7-member rings appear after the onset of surface growth and belong to the incipient soot nanoparticle.

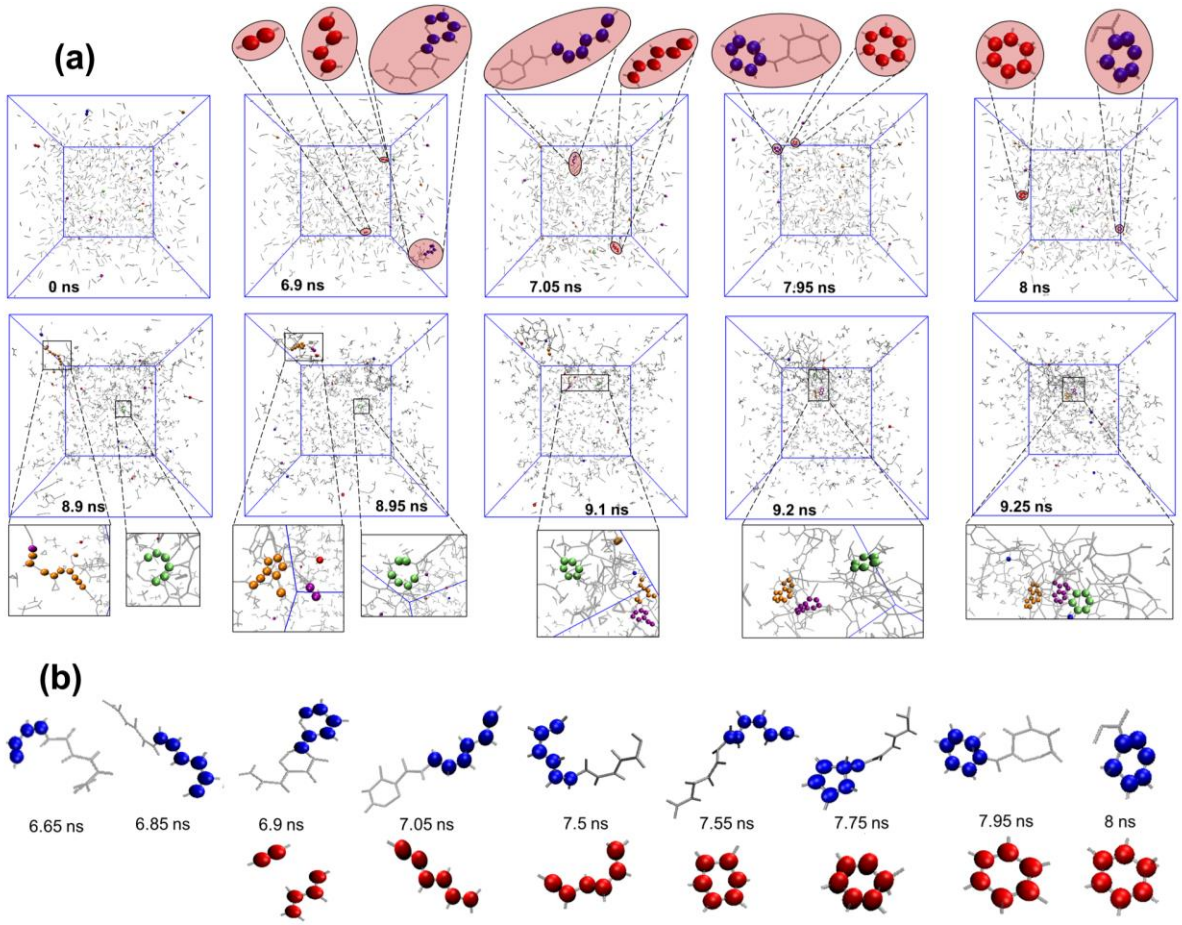


Figure S17. (a) Snapshots of a 1500 K acetylene pyrolysis simulation. Top row: The formation of two 6-member rings is tracked exemplarily at t = 6.9 – 8 ns (blue and red atoms belong to two distinguished 6-member rings formed at t = 7.95 ns). Bottom row: Ring formation within the incipient soot cluster is highlighted at t = 8.9 – 9.25 ns (orange, green and purple molecules). (b) Isolated cyclic molecule formation corresponding to Fig. S17a (top row).

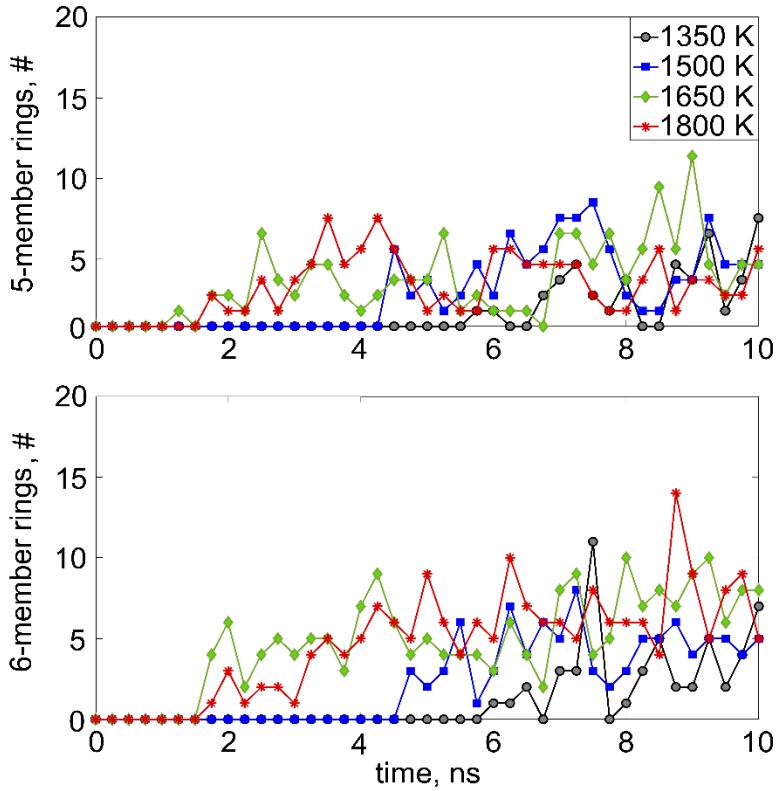


Figure S18. Temporal evolution of the number of *aromatic* (a) 5-, and (b) 6-member rings during acetylene pyrolysis at 1350 (circles), 1500 (squares), 1650 (diamonds) and 1800 K (stars).

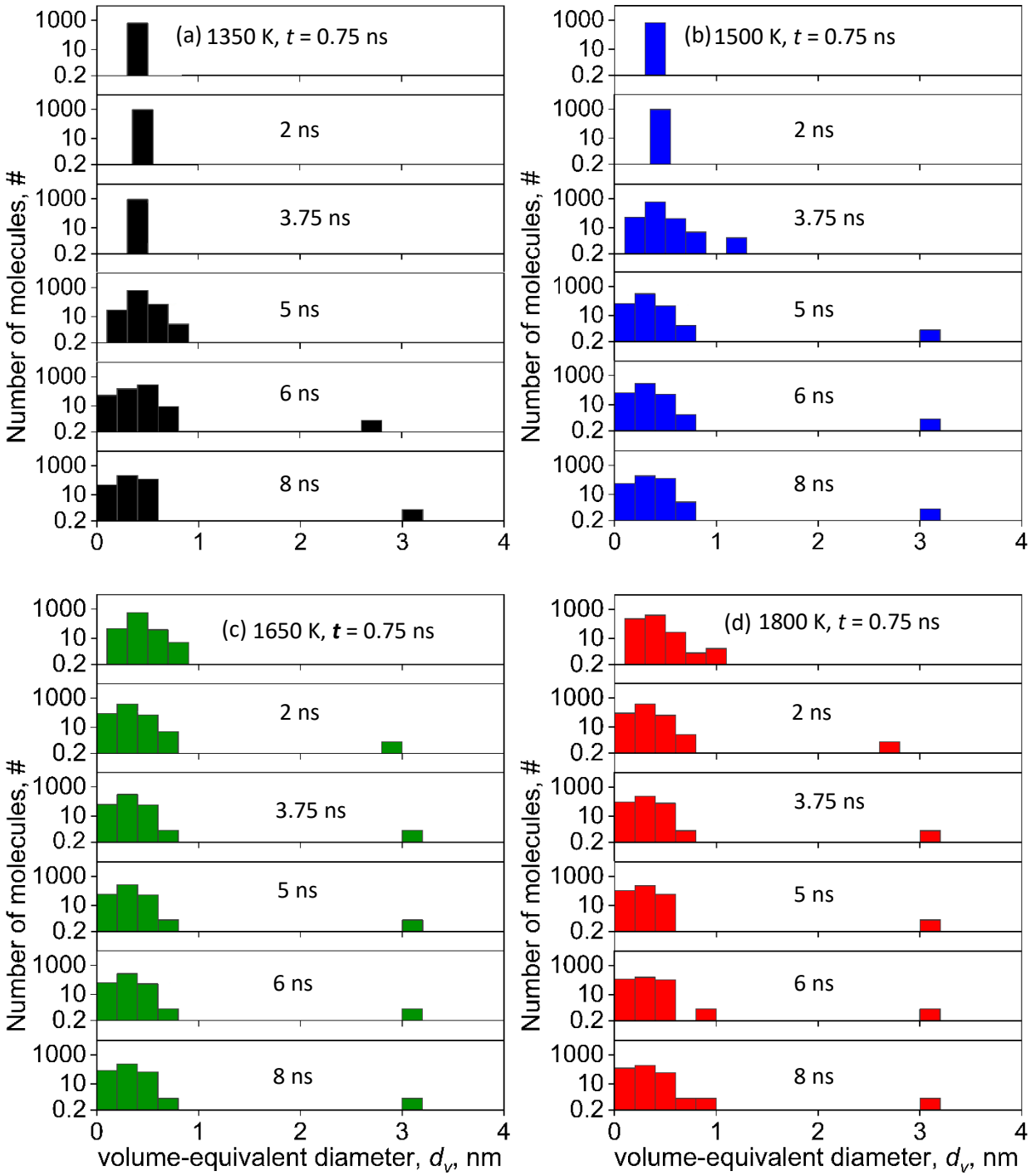


Figure S19. Size distributions of molecules formed during acetylene pyrolysis as a function of volume-equivalent diameter, d_v, nm at 0.75, 2, 3.75, 5, 6 and 8 ns at (a) 1350, (b) 1500, (c) 1650, and (d) 1800 K.

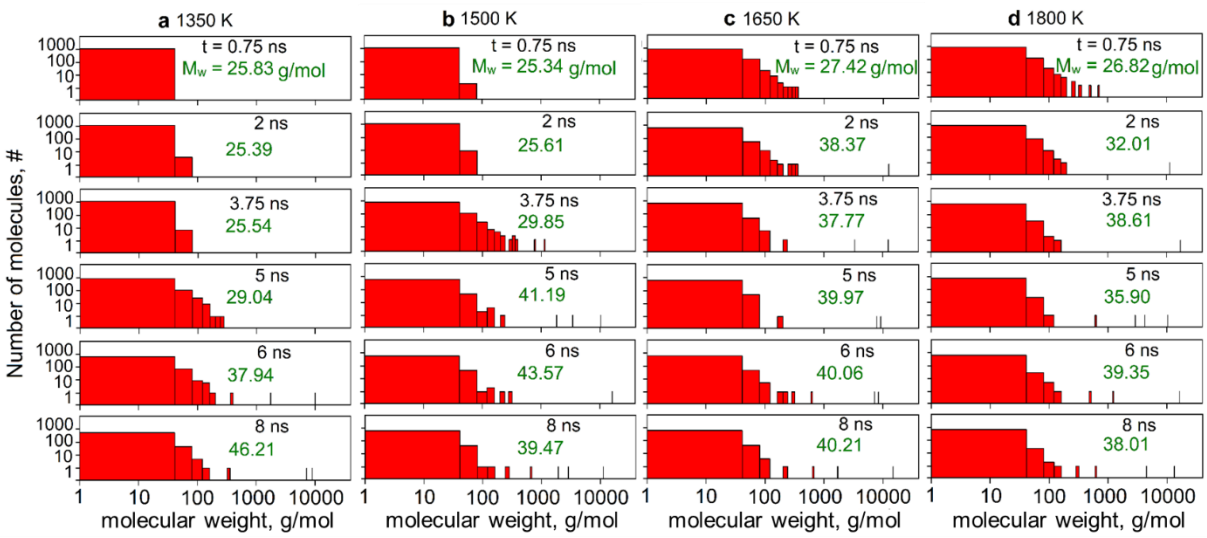


Figure S20. Molecular weight distributions of all molecules formed at 0.75, 2, 3.75, 5, 6 and 8 ns during C_2H_2 pyrolysis at (a) 1350, (b) 1500, (c) 1650 and (d) 1800 K.

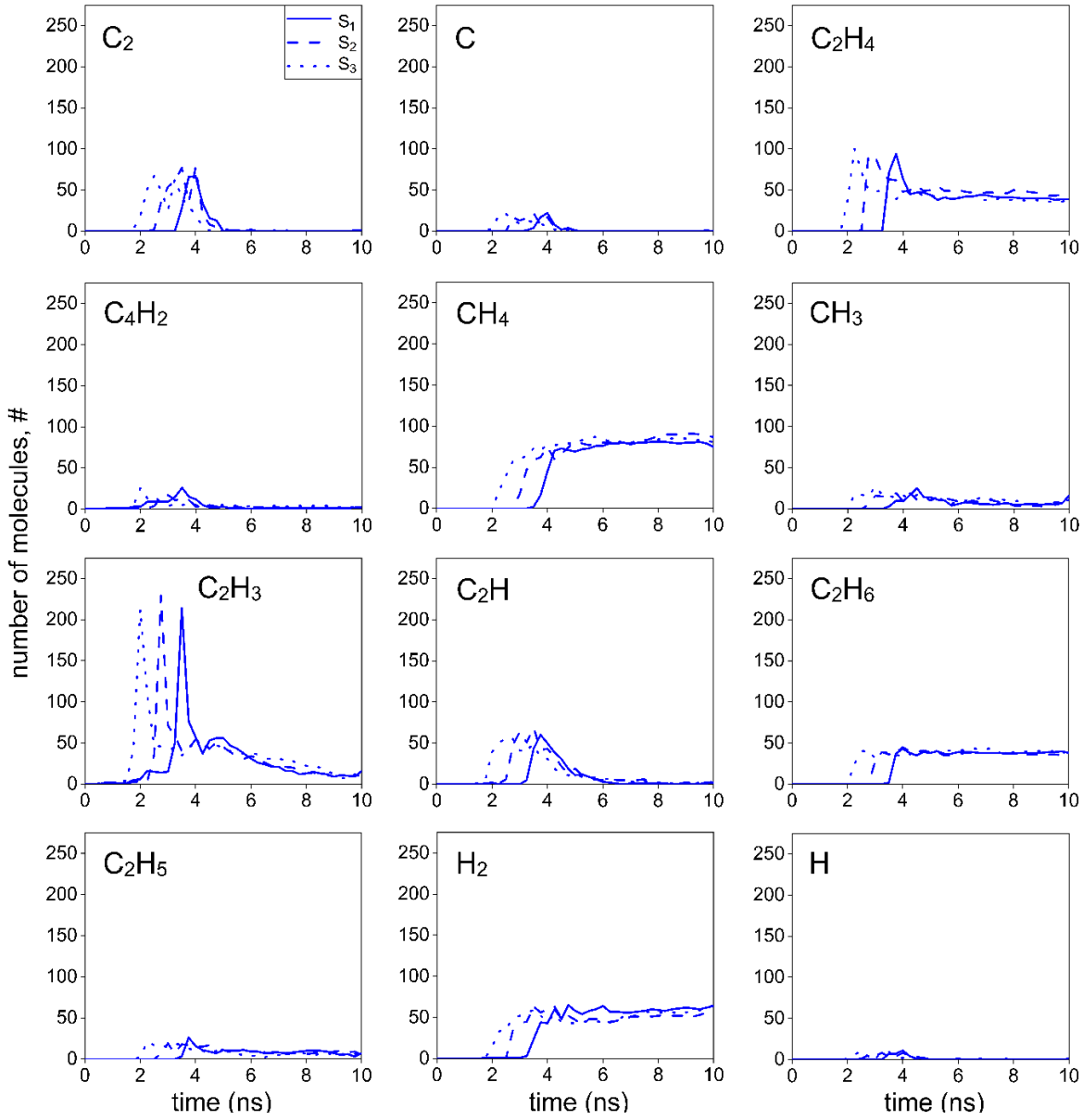


Figure S21. Temporal evolution of the number of (a) C_2, (b) C, (c) C_2H_4, (d) C_4H_2, (e) CH_4, (f) CH_3, (g) C_2H_3 (h) C_2H, (i) C_2H_6, (j) C_2H_5, (k) H_2 and (l) H during acetylene pyrolysis at 1500 K for different simulations (S_1 – S_3).

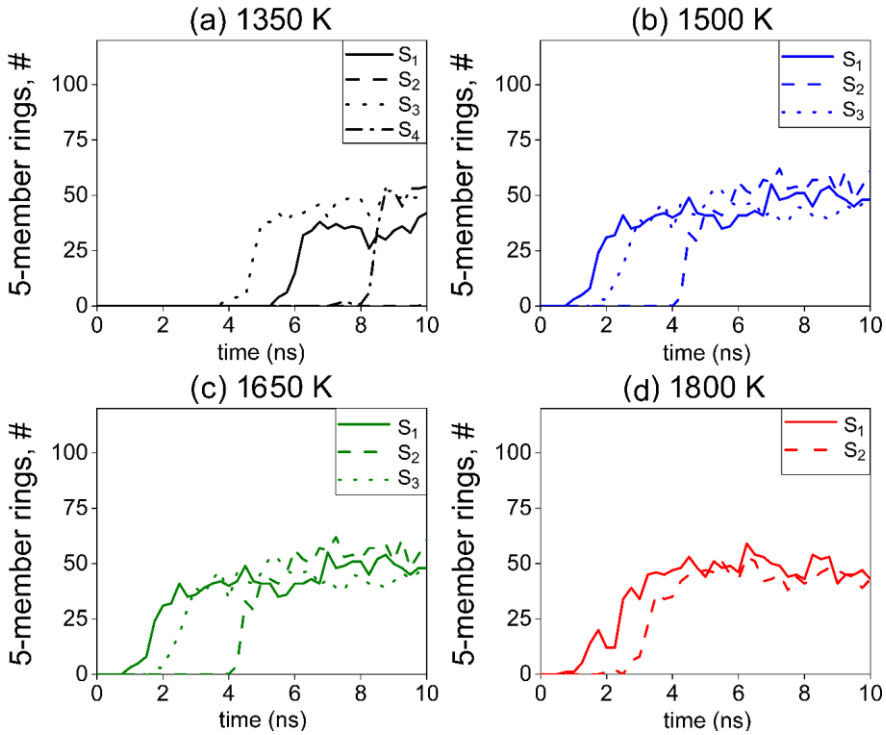


Figure S22. Temporal evolution of the number of 5-member *aliphatic* and *aromatic* rings during acetylene pyrolysis at (a) 1350, (b) 1500, (c) 1650 and (d) 1800 K for different simulations (S_1 – S_4).

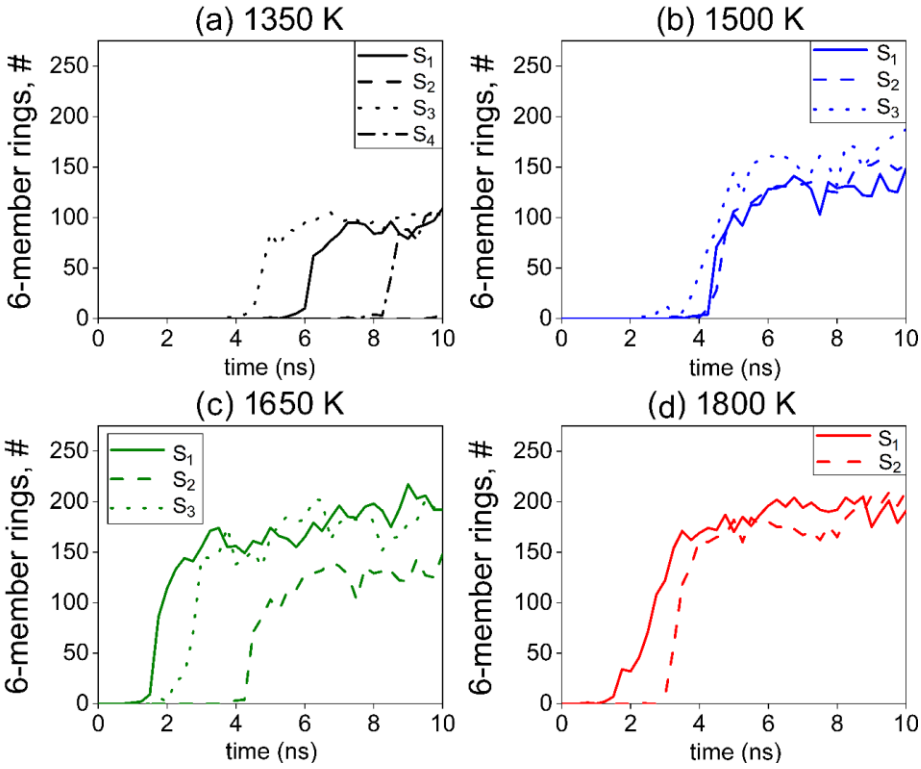


Figure S23. Temporal evolution of the number of 6-member *aliphatic* and *aromatic* rings during acetylene pyrolysis at (a) 1350, (b) 1500, (c) 1650 and (d) 1800 K for different simulations (S_1 – S_4).

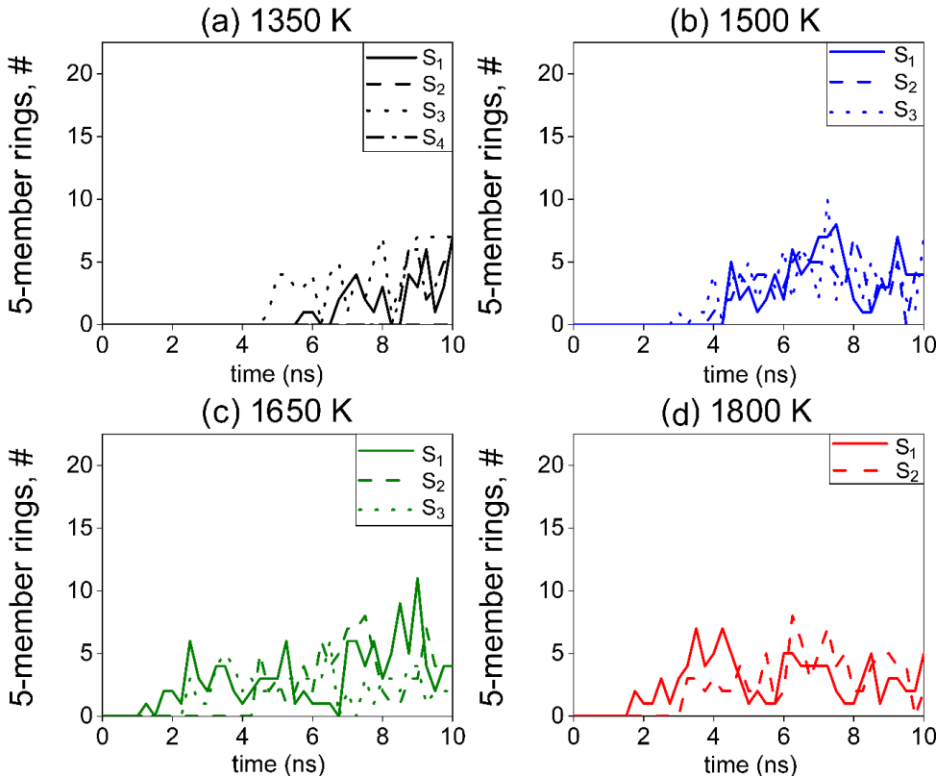


Figure S24. Temporal evolution of the number of 5-member *aromatic* rings during acetylene pyrolysis at (a) 1350, (b) 1500, (c) 1650 and (d) 1800 K for different simulations (S_1 – S_4).

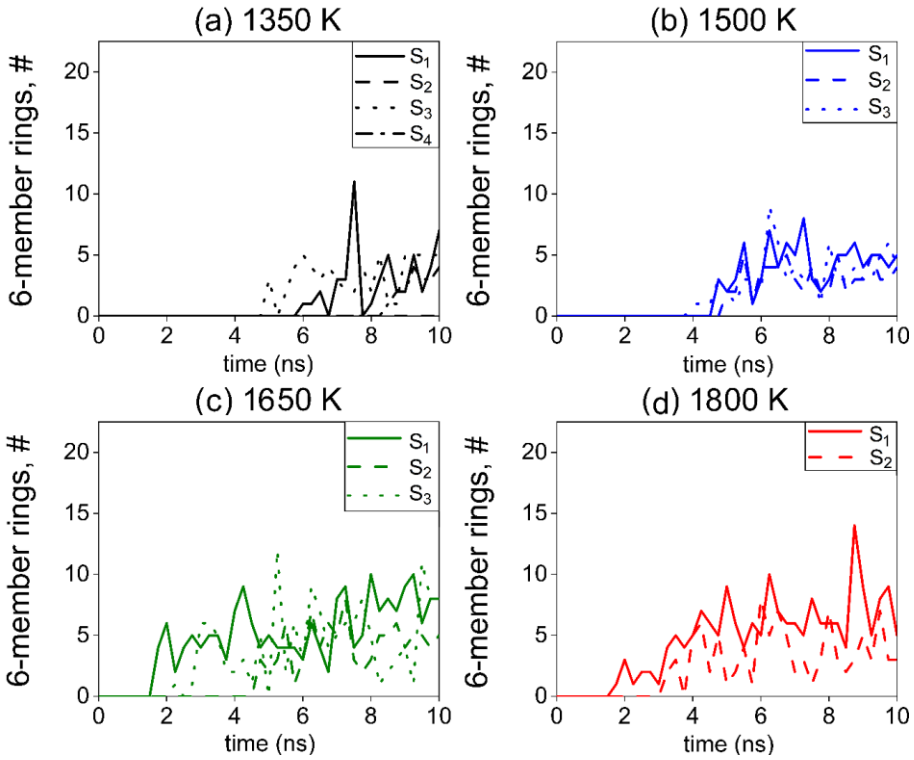


Figure S25. Temporal evolution of the number of 6-member *aromatic* rings during acetylene pyrolysis at (a) 1350, (b) 1500, (c) 1650 and (d) 1800 K for different simulations (S_1 – S_4).

Table S1. Chemical structures of incipient soot formed at the onset of surface growth at 1350-1800 K from various simulations.

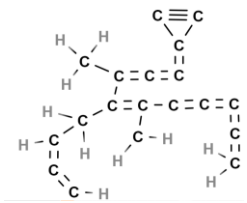
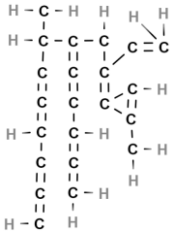
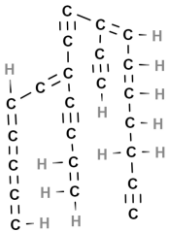
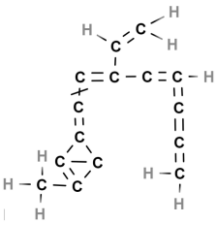
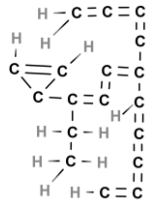
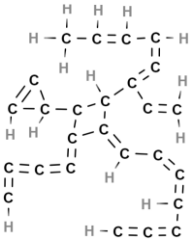
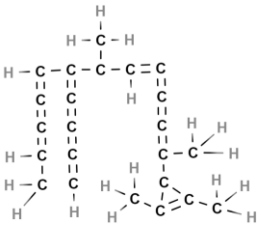
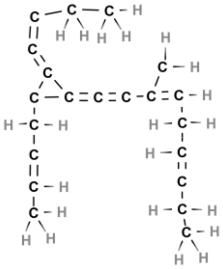
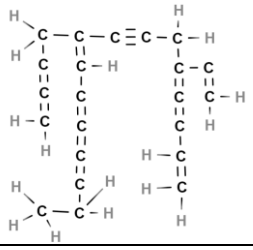
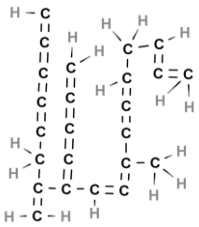
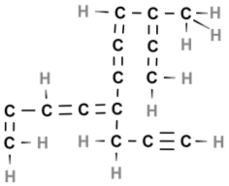
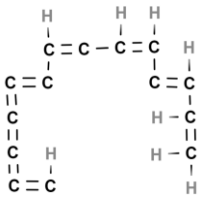
***T* (K)**	**1350**	**1500**	**1650**	**1800**
Simulation 1	5.2 ns $C_{19}H_{11}$ 	3.65 ns $C_{22}H_{14}$ 	0.8 ns $C_{23}H_{11}$ 	0.8 ns $C_{16}H_{9}$ 
Simulation 2	9.8 ns $C_{18}H_{11}$ 	3.5 ns $C_{26}H_{15}$ 	2.75 ns $C_{23}H_{18}$ 	2.55 ns $C_{20}H_{22}$ 
Simulation 3	3.7 ns $C_{22}H_{17}$ 	2.65 ns $C_{24}H_{17}$ 	1.35 ns $C_{15}H_{12}$ 	–
Simulation 4	7.15 ns $C_{14}H_{8}$ 	–	–	–

Table S2. Chemical structure of 84 and 87 C molecules formed during acetylene pyrolysis at 3.75 ns at 1500 K.

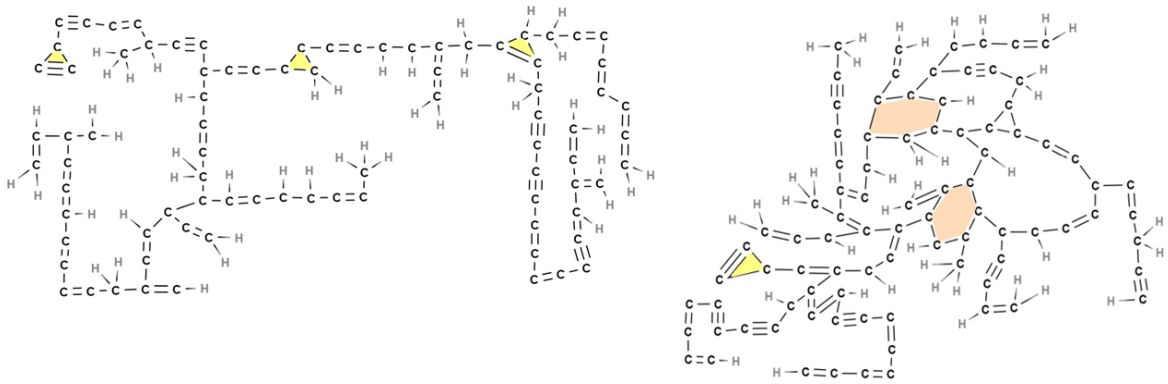


Table S3. Chemical structures of molecules formed during acetylene pyrolysis at 1350 K, at *t* = 0.75 ns, 2 and 3.75 ns.

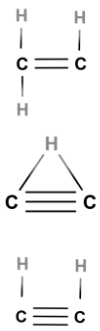
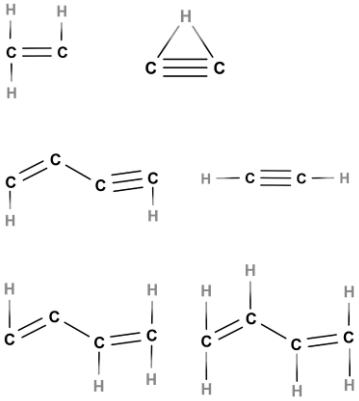
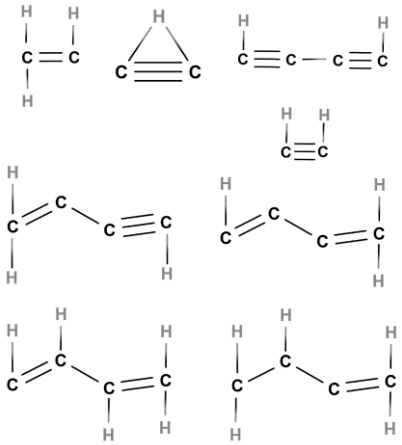
t, ns	0.75	2	3.75
C_1-C_5			
C_6-C_{10}	-	-	-
> C_{10}	-	-	-

Table S4. Chemical structures of all molecules formed during acetylene pyrolysis at 1350 K at *t* = 5 ns.

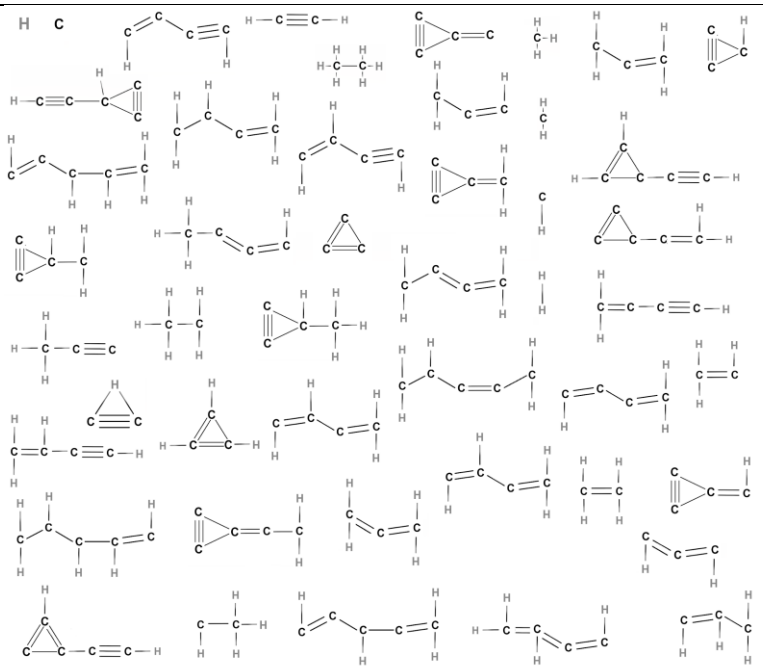
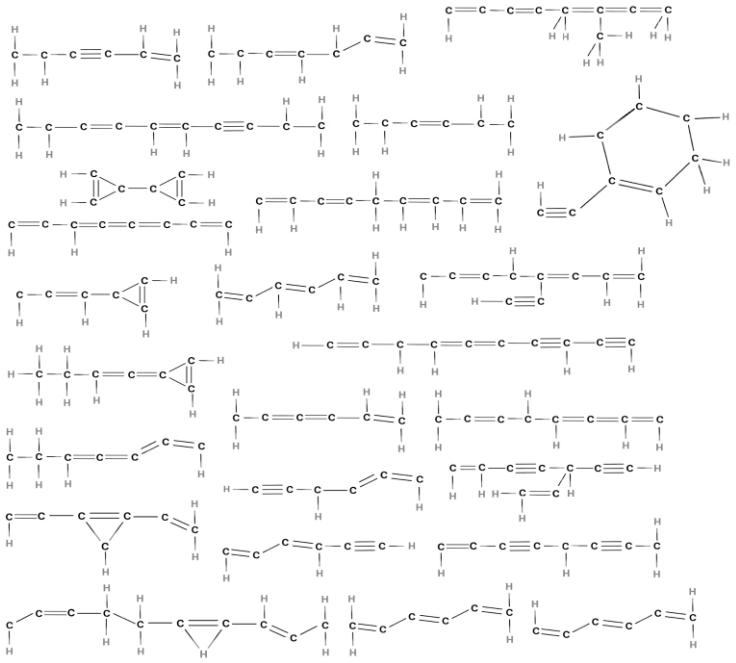
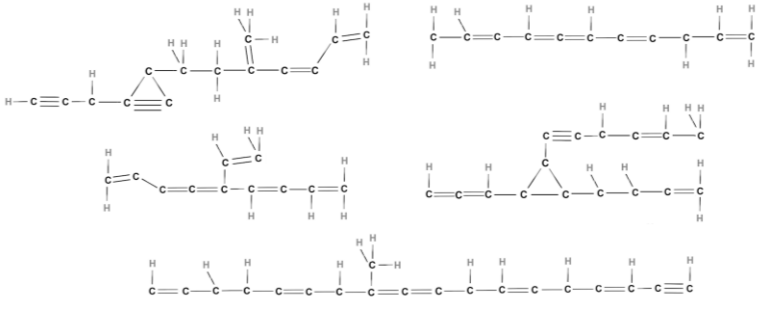
t, ns	5
C_1-C_5	
C_6-C_{10}	
> C_{10}	

Table S5. Chemical structure of molecules formed during acetylene pyrolysis at 1350 K at *t* = 6 ns, excluding the incipient soot (consisting of 947 C atoms).

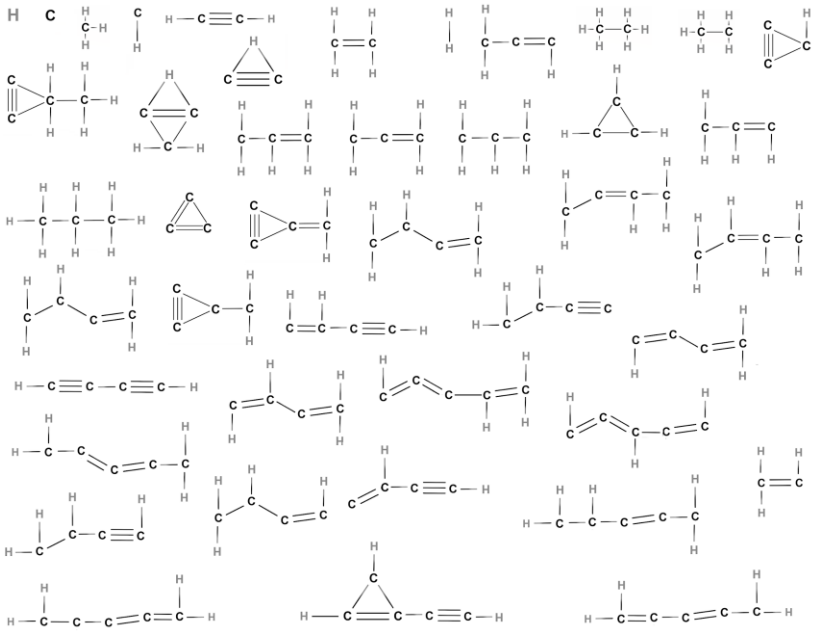
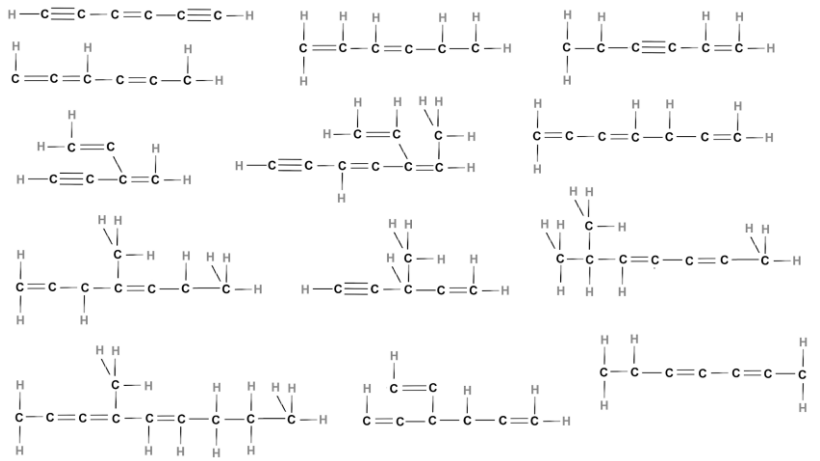
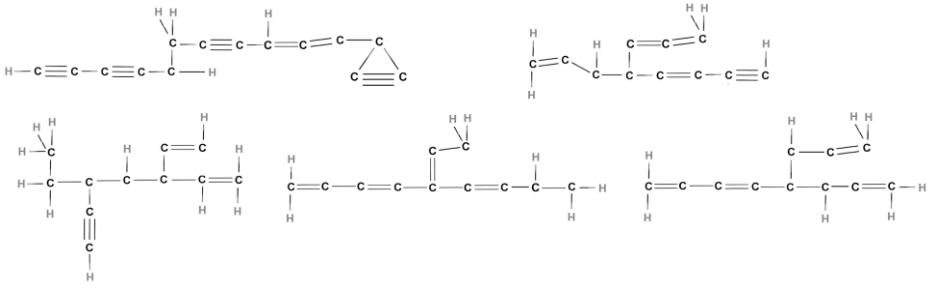
t, ns	6
C_1-C_5	
C_6-C_{10}	
> C_{10}	

Table S6. Chemical structure of molecules formed during acetylene pyrolysis at 1350 K, at t = 8 ns, excluding the incipient soot (consisting of 1080 C atoms).

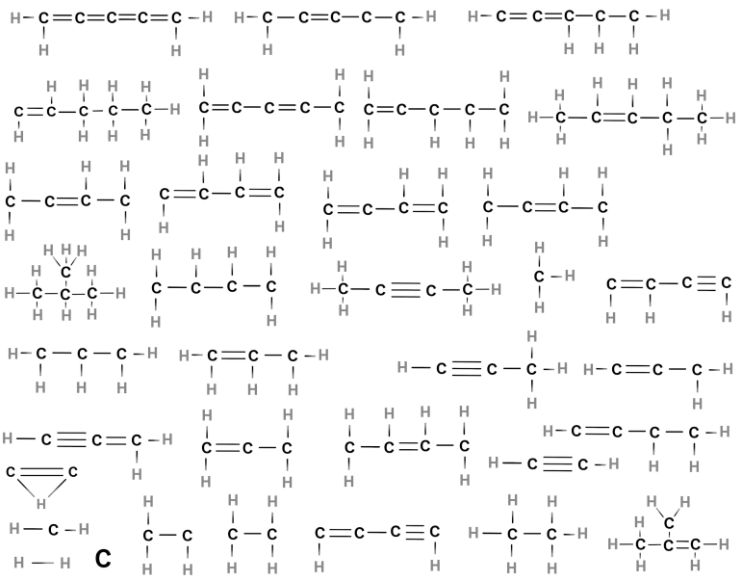
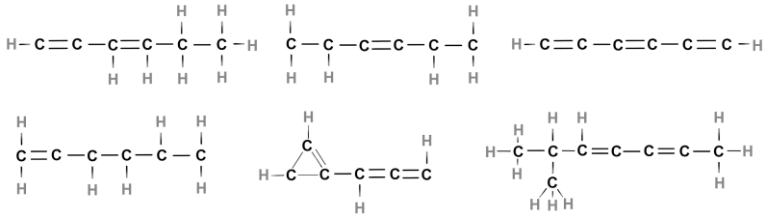
t, ns	8
C_1-C_5	
C_6-C_{10}	
> C_{10}	–

Table S7a. Chemical structure of C_1-C_5 molecules formed during acetylene pyrolysis at 1650 K at 0.75 ns.

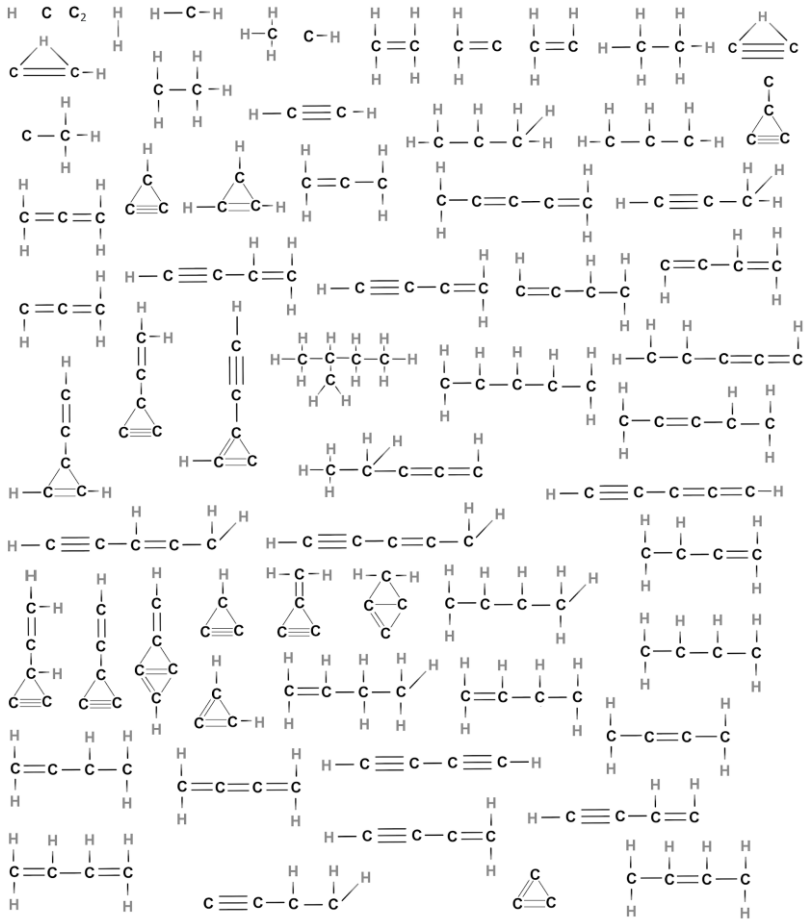
t, ns	0.75
C_1-C_5	

Table S7b. Chemical structure of > C_5 molecules formed during acetylene pyrolysis at 0.75 ns at 1650 K.

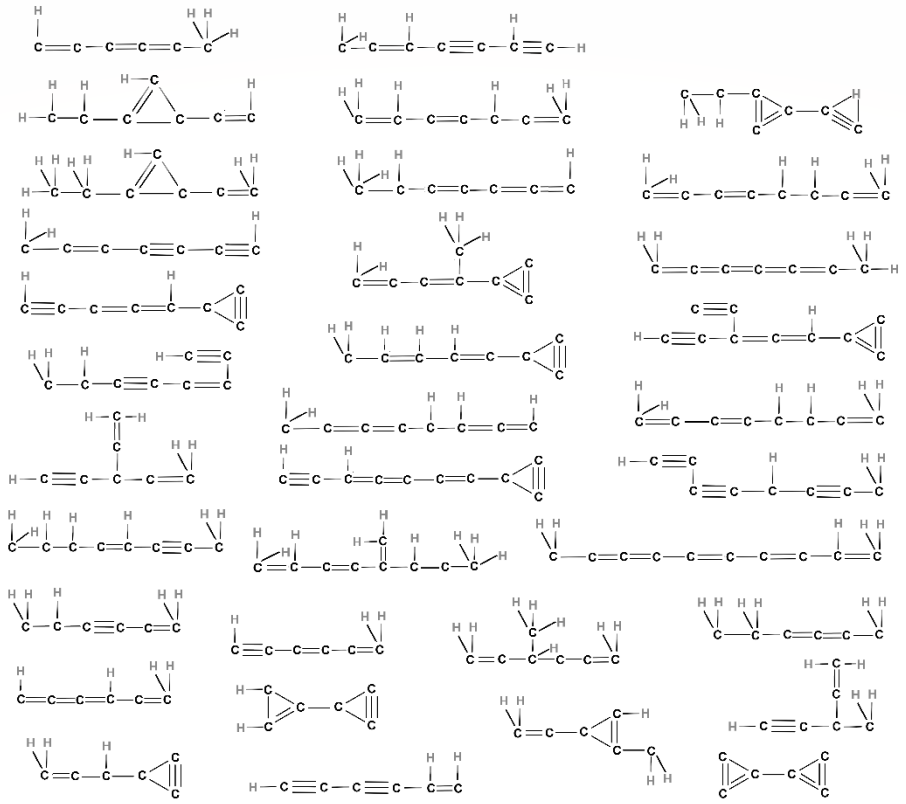
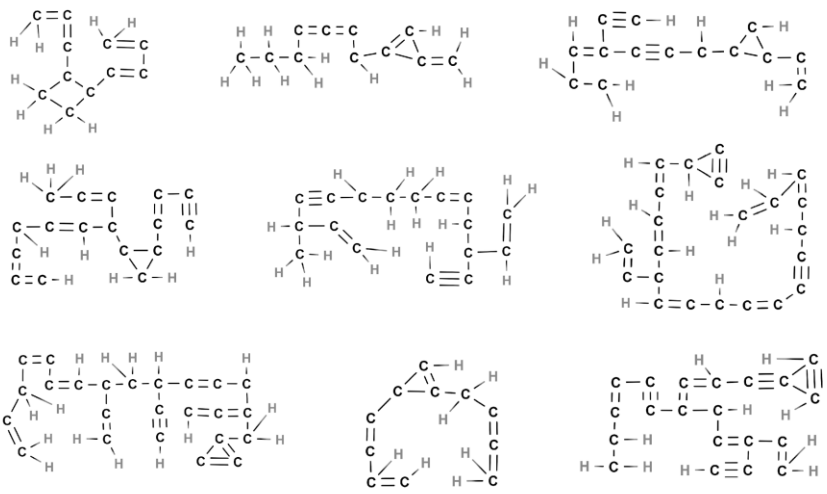
t, ns	0.75
C_6-C_{10}	
> C_{10}	

Table S8. Chemical structure of molecules formed during acetylene pyrolysis at 2 ns at 1650 K, excluding the incipient soot (consisting of 866 C atoms).

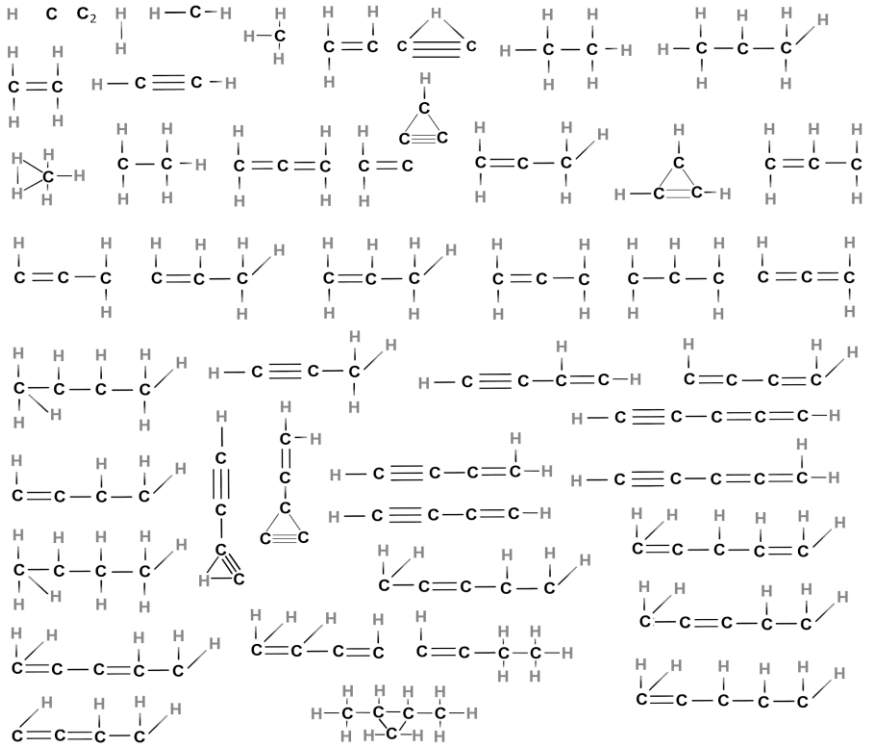
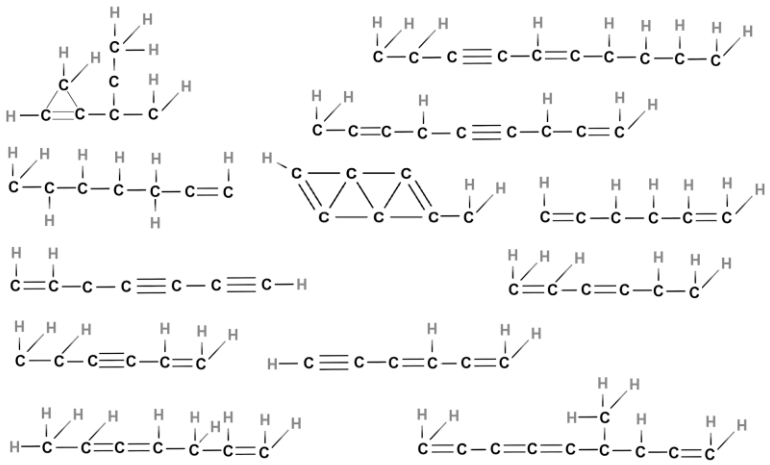
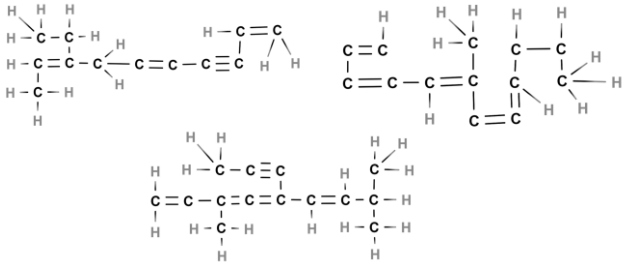
t, ns	2
C_1-C_5	
C_6-C_{10}	
> C_{10}	

Table S9. Chemical structure of molecules formed during acetylene pyrolysis at 3.75 ns at 1650 K, excluding the incipient soot (consisting of 1012 C atoms).

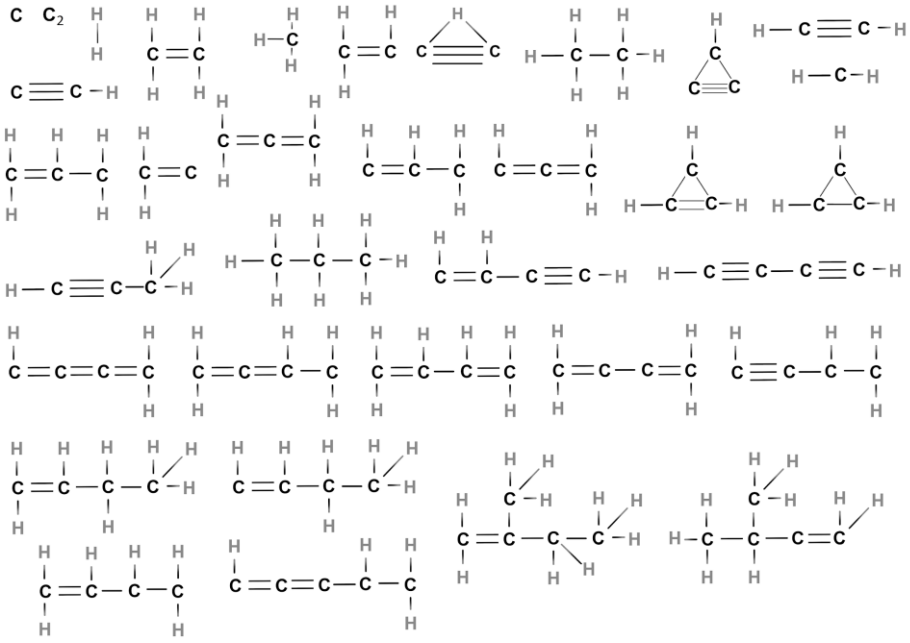
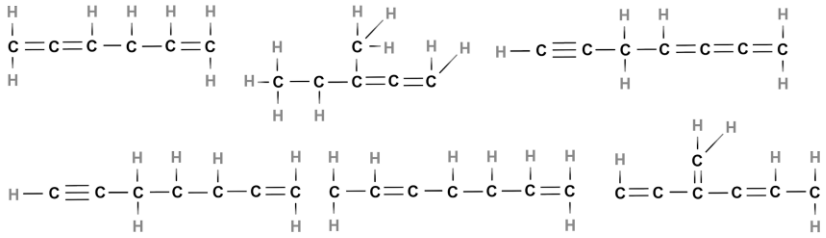
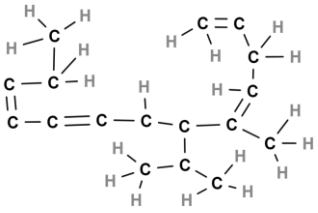
t, ns	3.75
C_1-C_5	
C_6-C_{10}	
> C_{10}	

Table S10. Chemical structure of molecules formed during acetylene pyrolysis at *t* = 5 and 6 ns at 1650 K, excluding the incipient soot (consisting of 1353 C at 5 ns and 1350 C atoms at 6 ns).

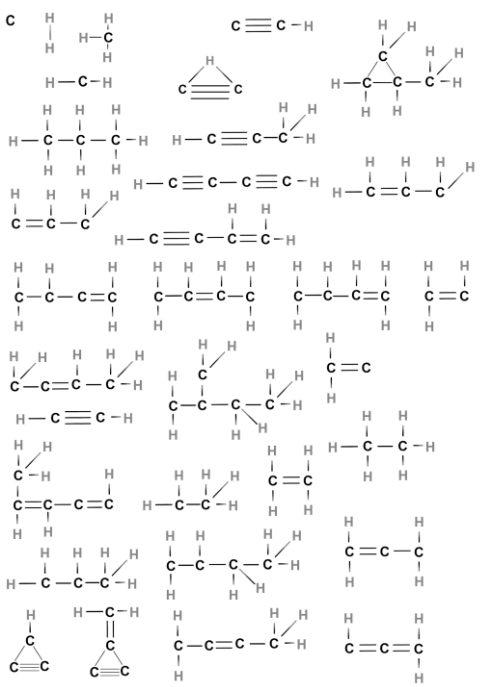
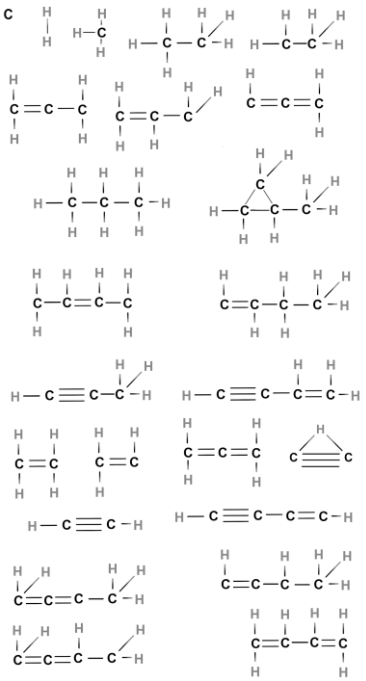
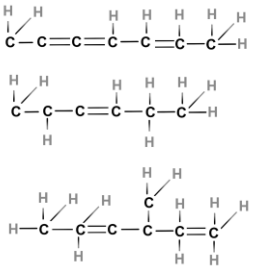
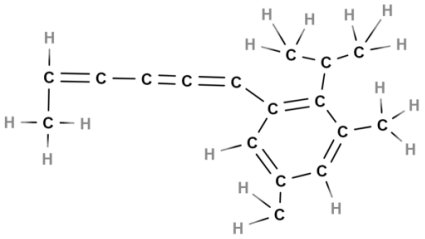
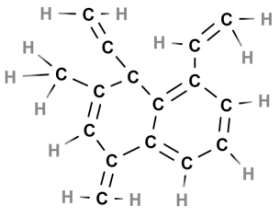
t, ns	5	6
C_1-C_5		
C_6-C_{10}		
> C_{10}		

Table S11. Chemical structure of molecules formed during acetylene pyrolysis at 8 ns at 1650 K, excluding the incipient soot (consisting of 1378 C atoms).

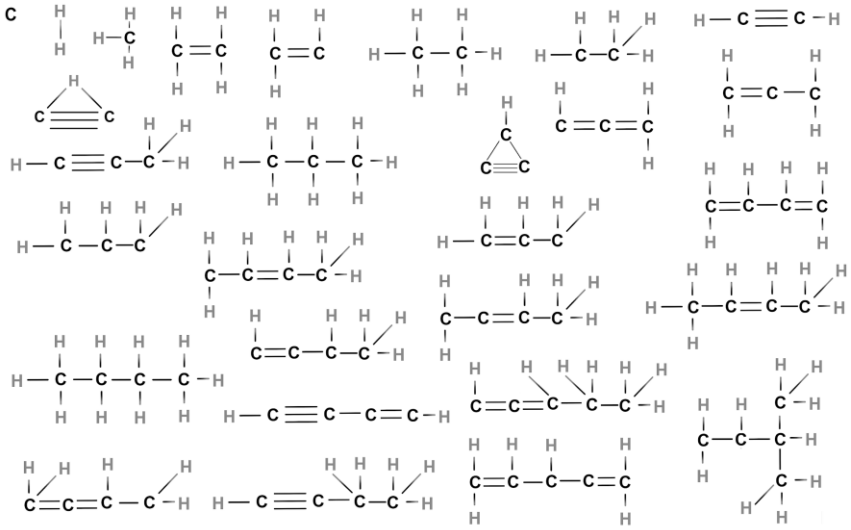
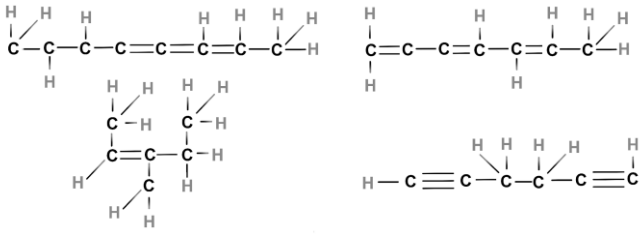
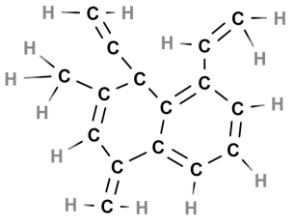
t, ns	8
C_1-C_5	
C_6-C_{10}	
> C_{10}	

Table S12a. Chemical structure of C_1-C_5 molecules formed during acetylene pyrolysis at 0.75 ns at 1800 K.

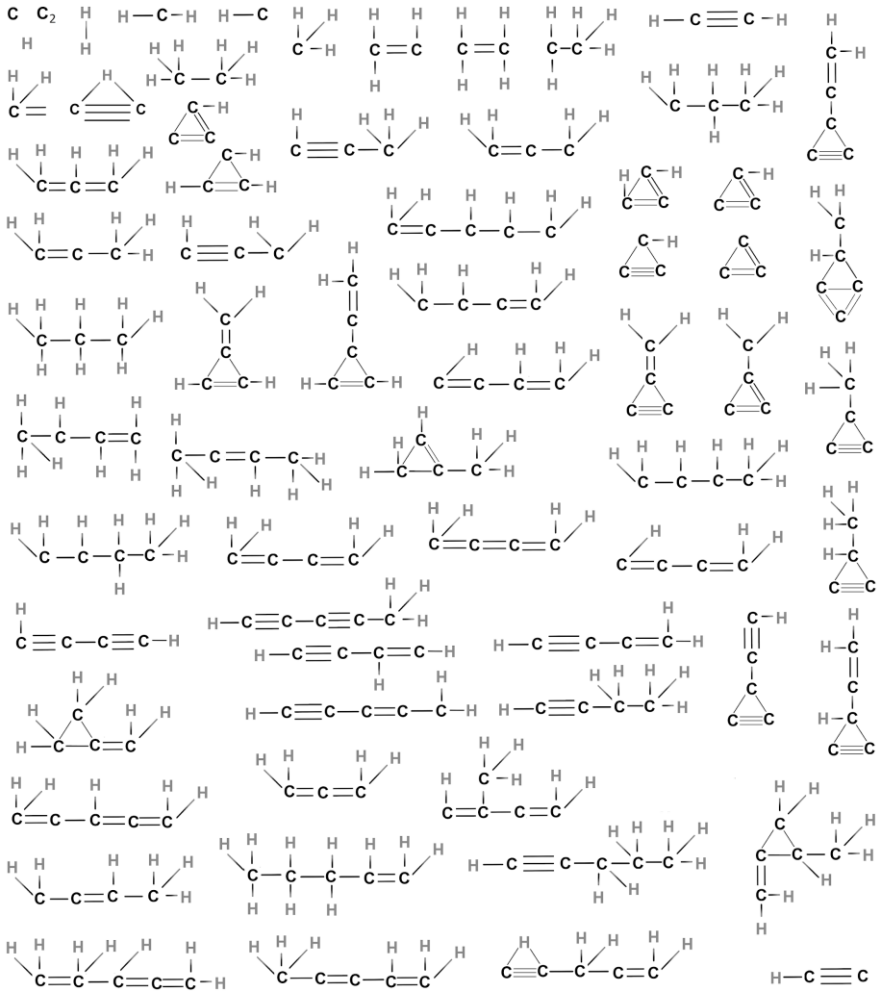
t, ns	0.75
C_1-C_5	

Table S12b. Chemical structure of > C_5 molecules formed during acetylene pyrolysis at 0.75 ns at 1800 K.

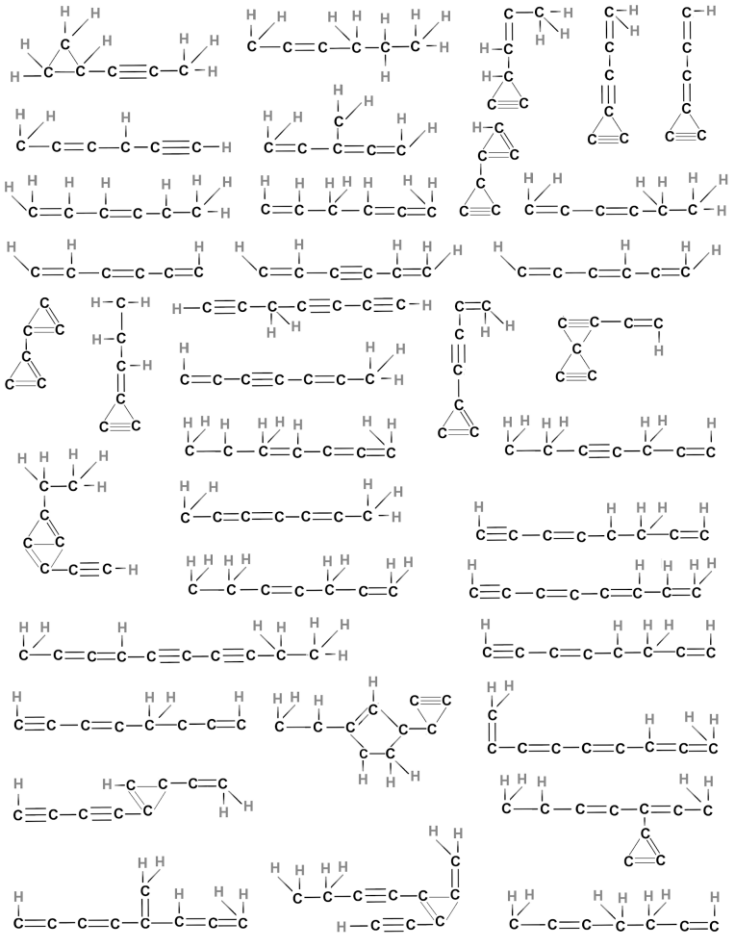
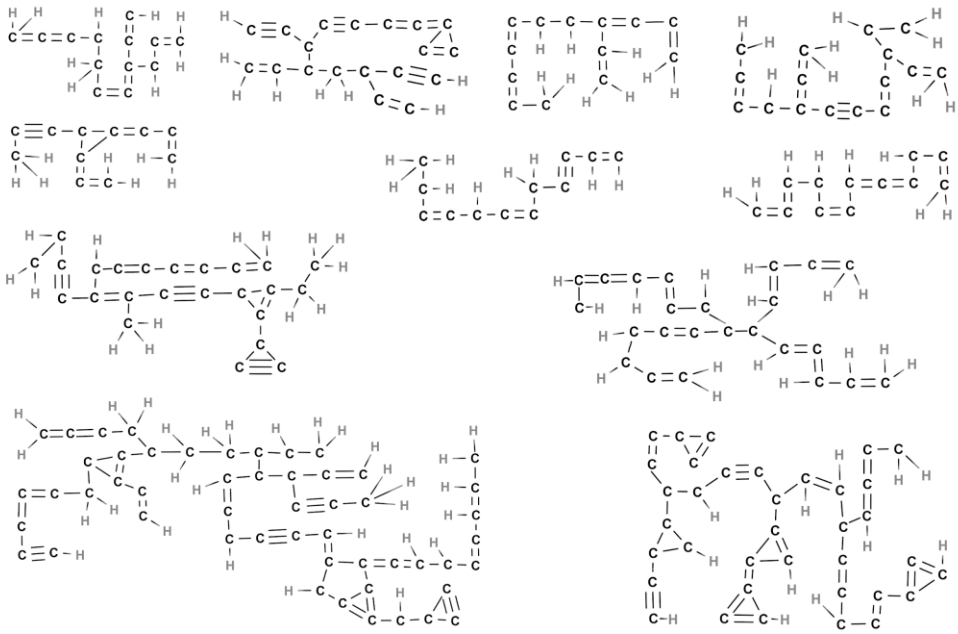
t, ns	0.75
C_6-C_{10}	
> C_{10}	

Table S13. Chemical structure of molecules formed during acetylene pyrolysis at *t* = 2 ns at 1800 K, excluding the incipient soot (consisting of 881 C atoms).

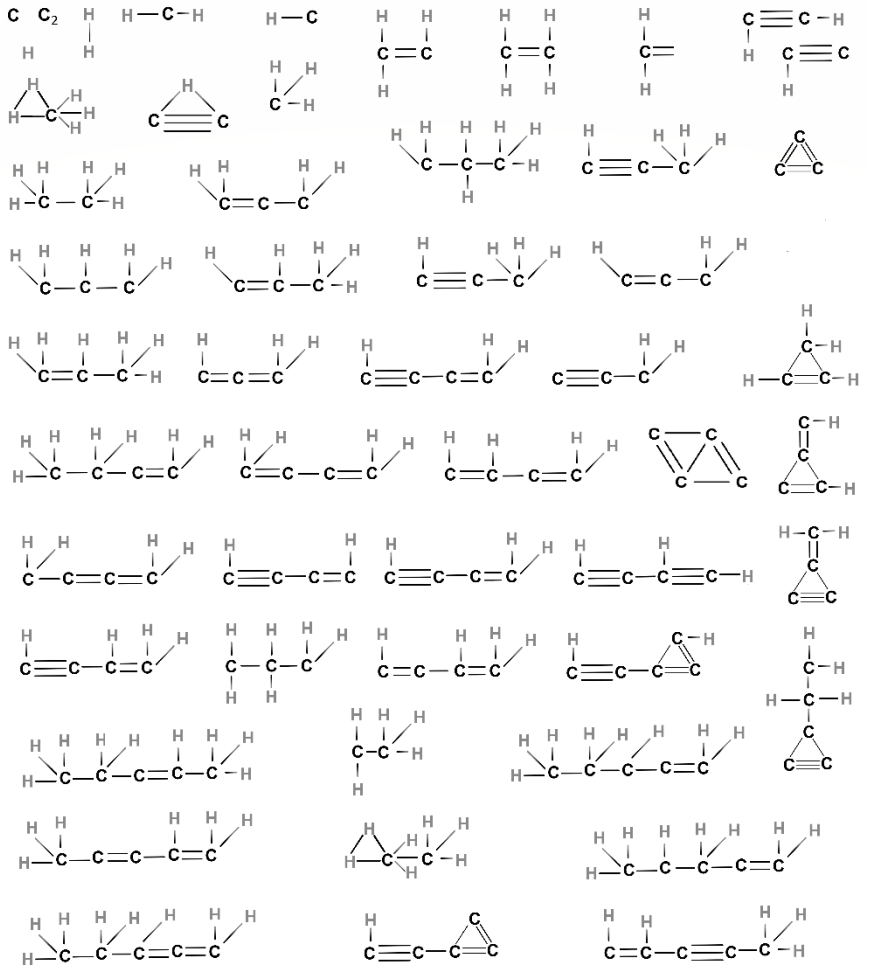
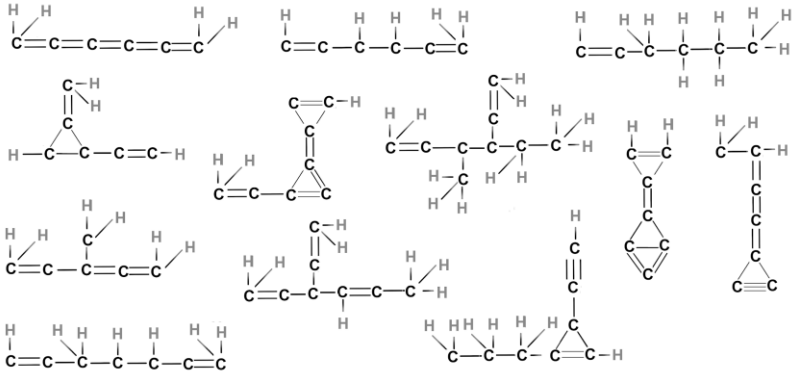
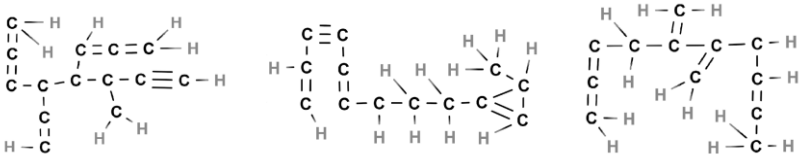
t, ns	2
C_1-C_5	
C_6-C_{10}	
> C_{10}	

Table S14. Chemical structure of molecules formed during acetylene pyrolysis at *t* = 3.75 and 5 ns at 1800 K, excluding the incipient soot (consisting of 1338 C atoms at 3.75 ns and 1439 C atoms at 5 ns).

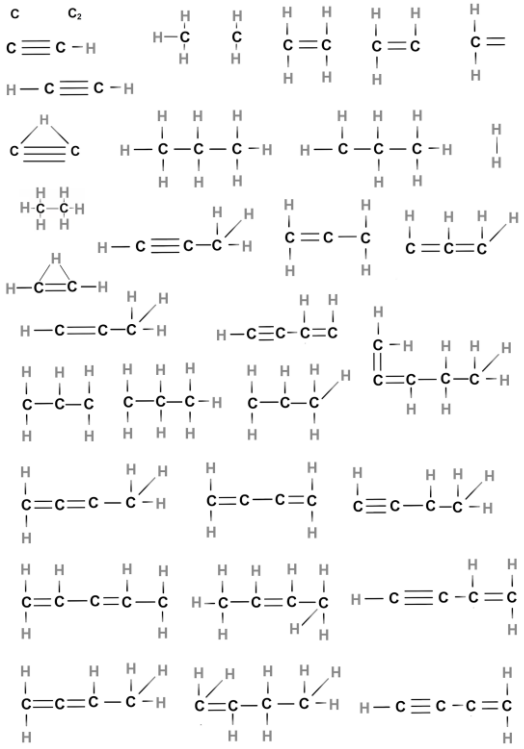
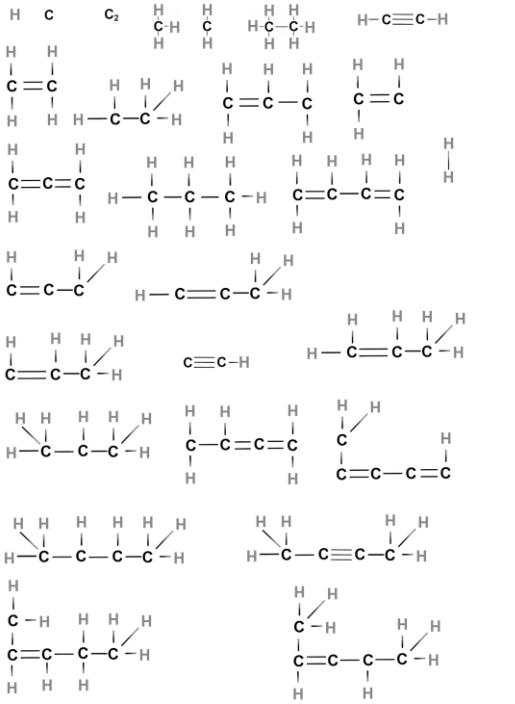
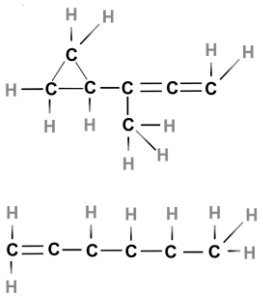
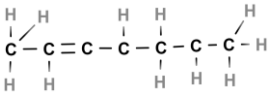
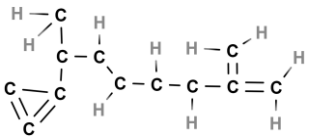
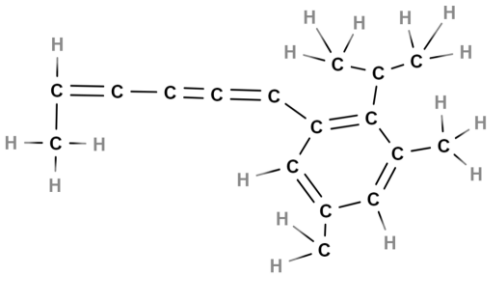
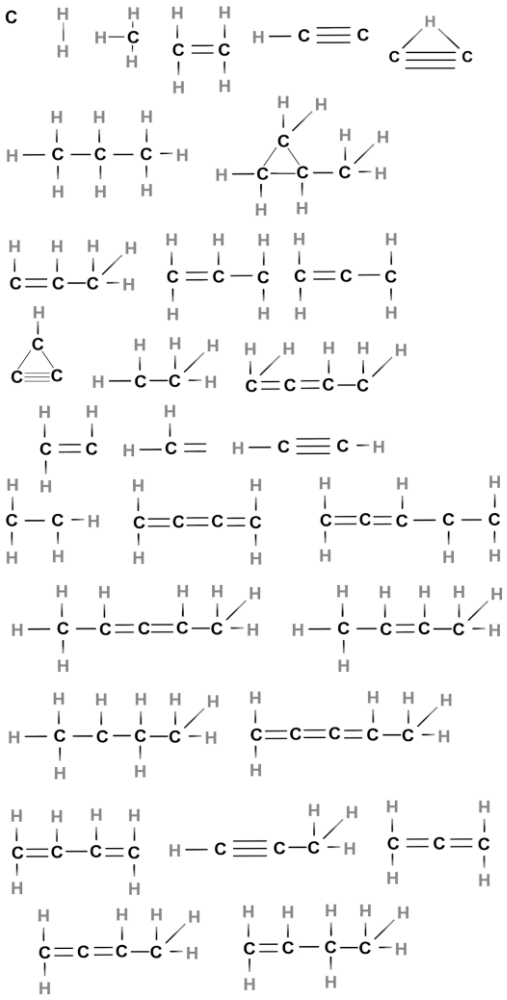
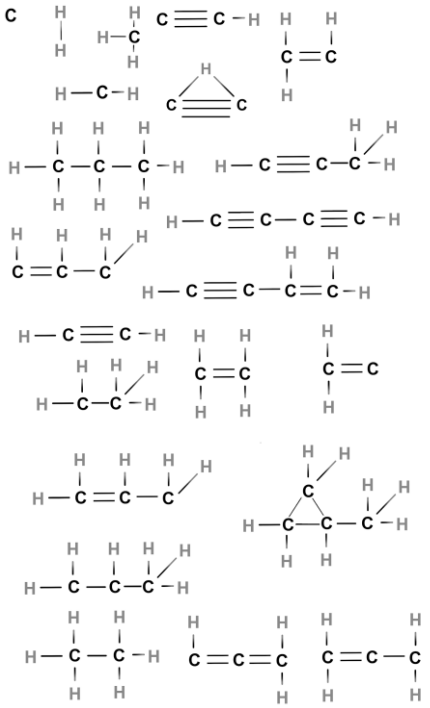
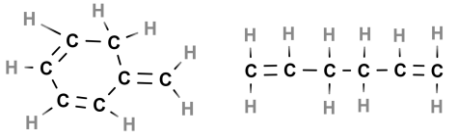
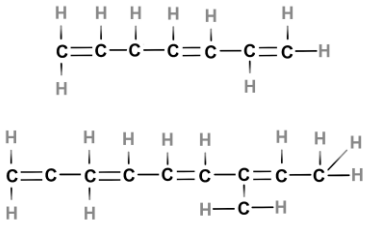
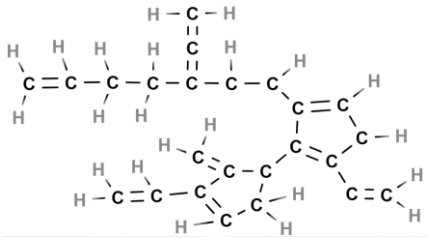
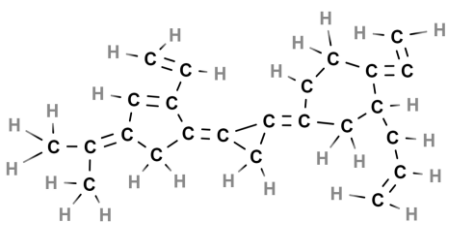
t, ns	3.75	5
C_1-C_5		
C_6-C_{10}		
> C_{10}		

Table S15. Chemical structure of molecules formed during acetylene pyrolysis at *t* = 6 and 8 ns at 1800 K, excluding the incipient soot (consisting of 1442 C atoms at 6 ns and 1460 C atoms at 8 ns).

t, ns	6	8
C_1-C_5		
C_6-C_{10}		
> C_{10}		

References

Commodo, M., Kaiser, K., De Falco, G., Minutolo, P., Schulz, F., D'Anna, A., and Gross, L.: On the early stages of soot formation: Molecular structure elucidation by high-resolution atomic force microscopy, Combustion and Flame, 205, 154-164, https://doi.org/10.1016/j.combustflame.2019.03.042, 2019.

Lieske, L.-A., Commodo, M., Martin, J. W., Kaiser, K., Benekou, V., Minutolo, P., D'Anna, A., and Gross, L.: Portraits of Soot Molecules Reveal Pathways to Large Aromatics, Five-/Seven-Membered Rings, and Inception through π-Radical Localization, ACS Nano, https://doi.org/10.1021/acsnano.3c02194, 2023.