SUPPLEMENTARY MATERIALS

On the Dynamics of the Carbon-Bromine Bond Dissociation in the 1-Bromo-2-Methylnaphthalene Radical Anion

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Index

1) Path A PES

2) Path B PES

3) Path C PES

4) Path B DRC

5) Path C DRC

6) Theoretical UV-VIS, IR and CD spectra

1) Path A PES

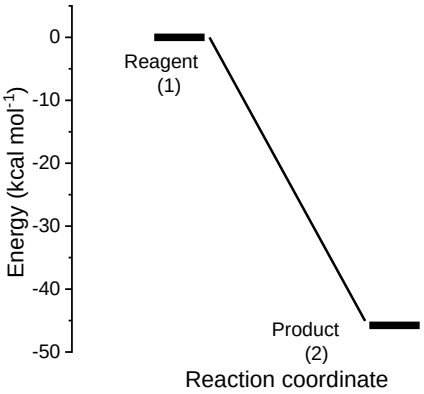


Figure S1. Potential energy surface for reaction path A, at the B3LYP/cc-pVTZ level of theory. Gibbs free energy of reagents (**1**), final products (**2**). The energy levels have been normalized to the energy of state (**1**), which corresponds to a 1882041.187849 kcal mol^{-1} absolute value.

2) Path B PES

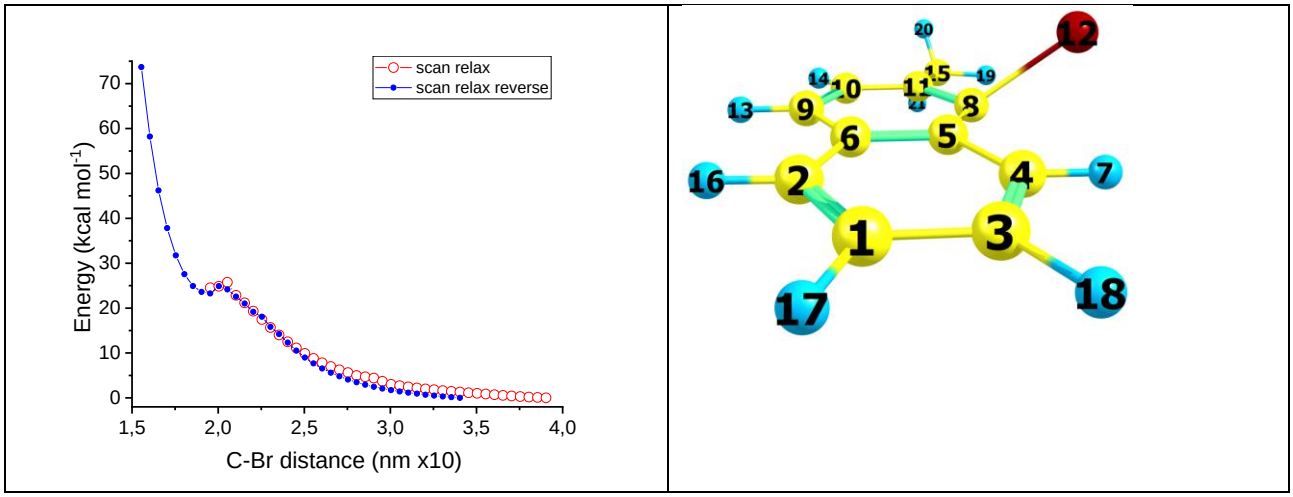


Figure S2. Molecular potential energy vs $C_8 - Br_{12}$ distance for the 1-bromo-2-methylnaphthalene radical anion (2) UB3LYP/cc-pVTZ level of theory, using the Barone and Cossi's polarizable conductor model (CPCM) scan relax.

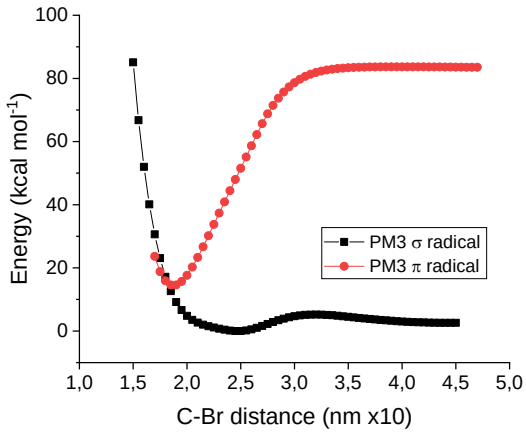


Figure S3. Molecular potential energy vs $C_8 - Br_{12}$ distance, unrelax scan, for the 1-bromo-2-methylnaphthalene radical anion (2). PM3 level of theory, using the Barone and Cossi's polarizable conductor model (CPCM).

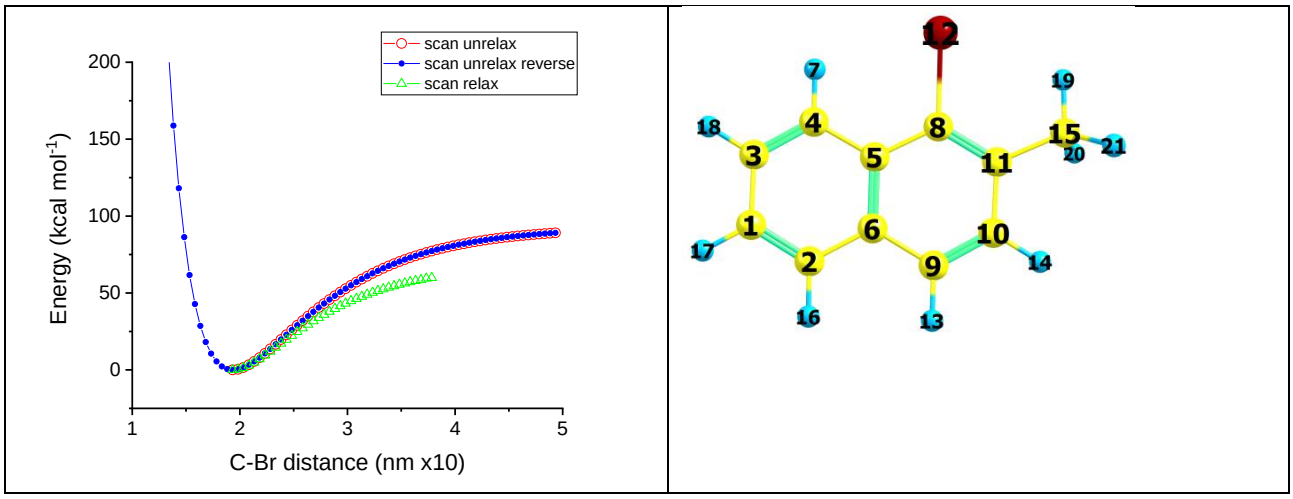


Figure S4. Molecular potential energy vs $C_8 - Br_{12}$ distance for the 1-bromo-2-methylnaphthalene neutral parent species (1), UB3LYP/cc-pVTZ level of theory, using the Barone and Cossi's polarizable conductor model (CPCM)

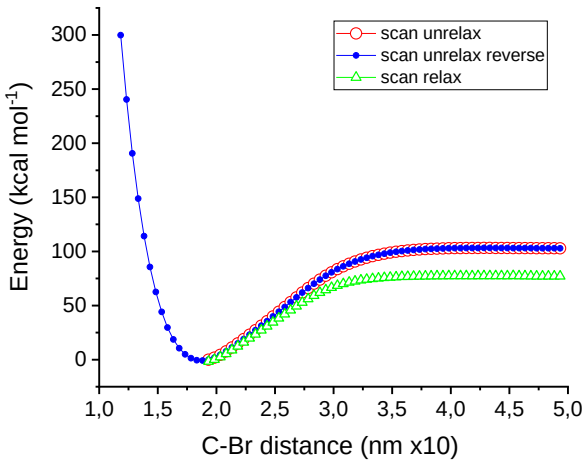
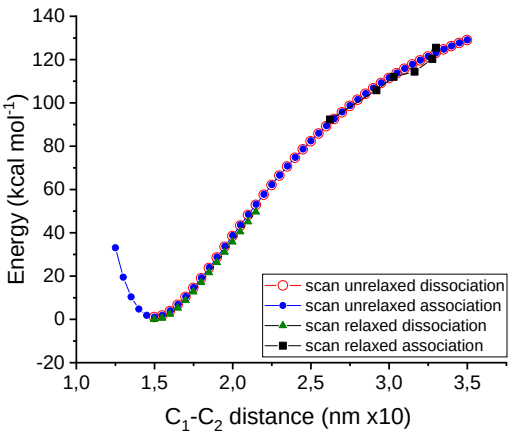


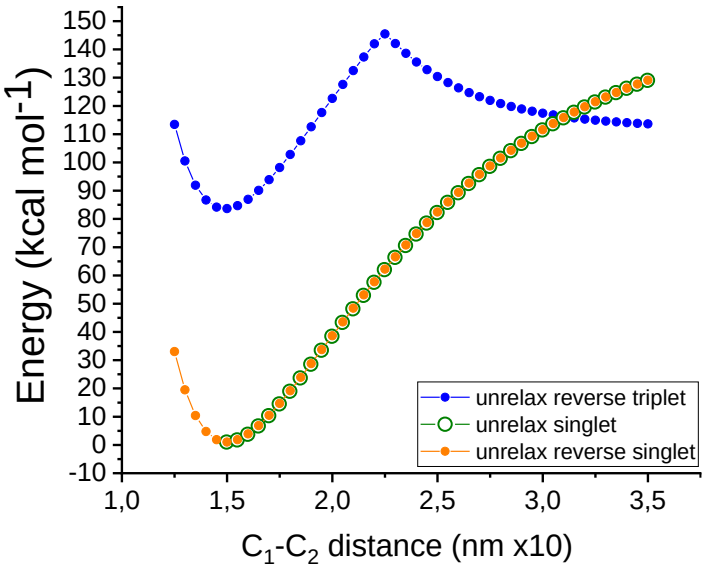
Figure S5. Molecular potential energy vs $C_8 - Br_{12}$ distance for the 1-bromo-2-methylnaphthalene neutral parent species (1) PM3 level of theory, using the Barone and Cossi's polarizable conductor model (CPCM).

3) Path C PES

a)



b)



c)

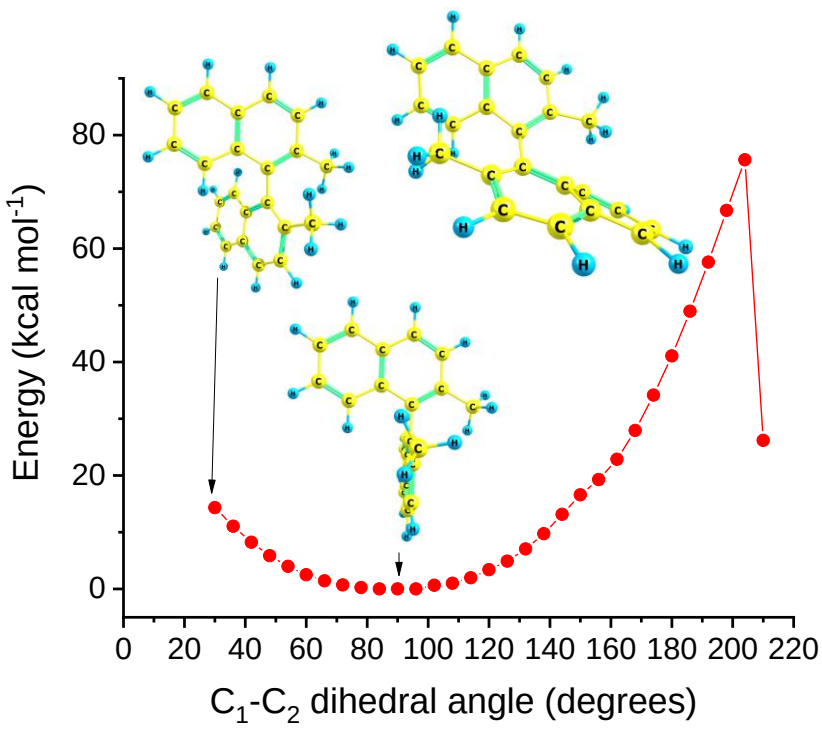


Figure S6. a) Molecular potential energy vs $C_1 - C_2$ distance for the neutral closed shell dimer 1,1'-binaphthalene, 2,2'-dimethyl (4), unrelaxed potential energy surface for the C-C association (UB3LYP/cc-pVTZ level of theory) vs relaxed potential energy surface b) Molecular potential energy vs $C_1 - C_2$ distance for the dimer 1,1'-binaphthyl (4) in the case of spin multiplicity equal to three (triplet state). UB3LYP/cc-pVTZ level of theory, using the Barone and Cossi's polarizable conductor model (CPCM). Overlay of triplet and singlet state curves. c) Molecular potential energy vs $C_1 - C_2$ dihedral angle for the dimer.

4) Path B DRC

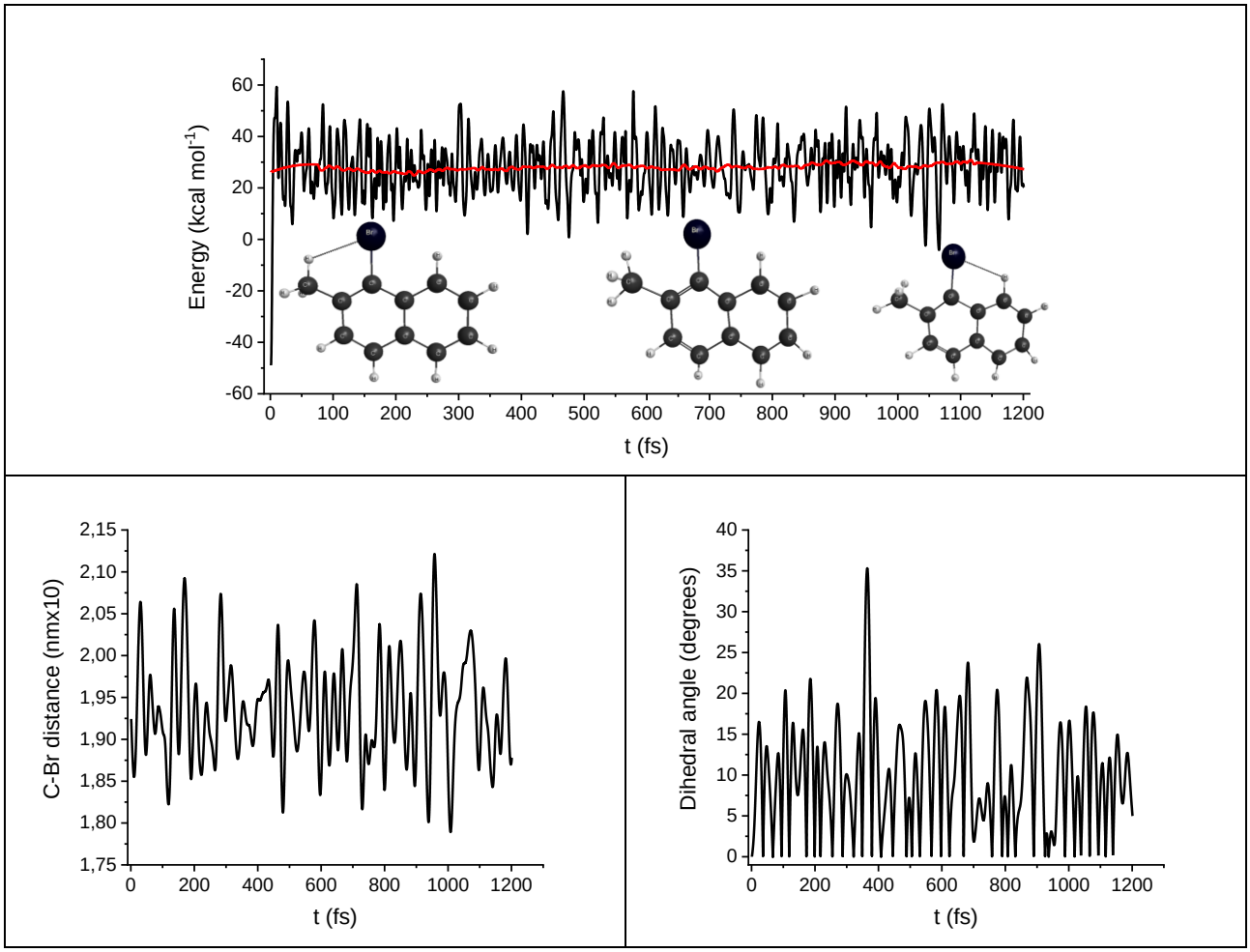


Figure S7. Path B DRC results, B3LYP/6-31G(d), DRC trajectory for the 1-bromo-2-methylnaphthalene neutral parent species (1). a) molecular electronic potential energy vs time b) Carbon bromine distance as a function of time c) dihedral angle between the dissociating $C - Br$ bond as a function of time.

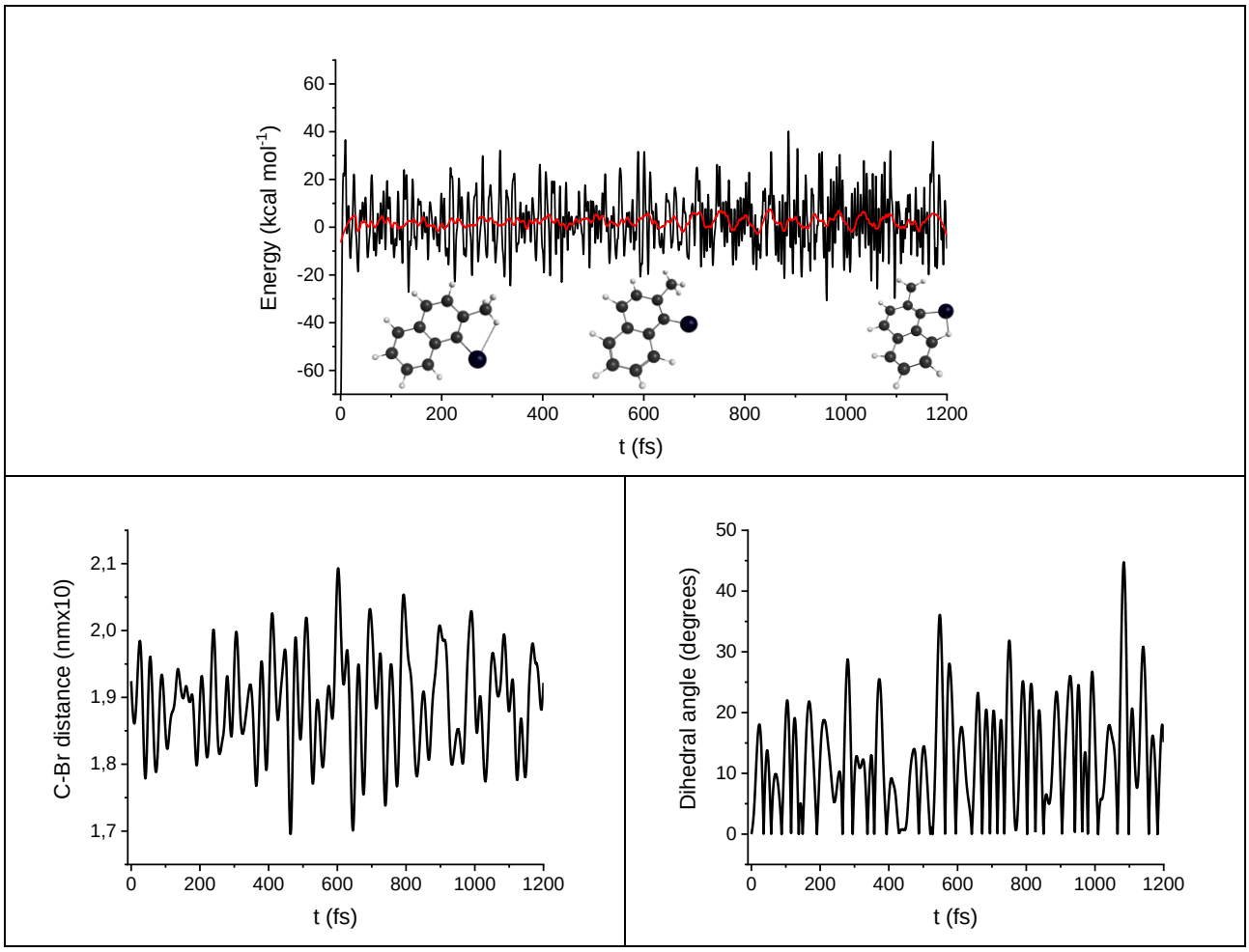


Figure S8. Path B DRC results, PM3 level of theory, DRC trajectory for the 1-bromo-2-methylnaphthalene neutral parent species (1). a) molecular electronic potential energy vs time b) Carbon bromine distance as a function of time c) dihedral angle between the dissociating $C - Br$ bond as a function of time.

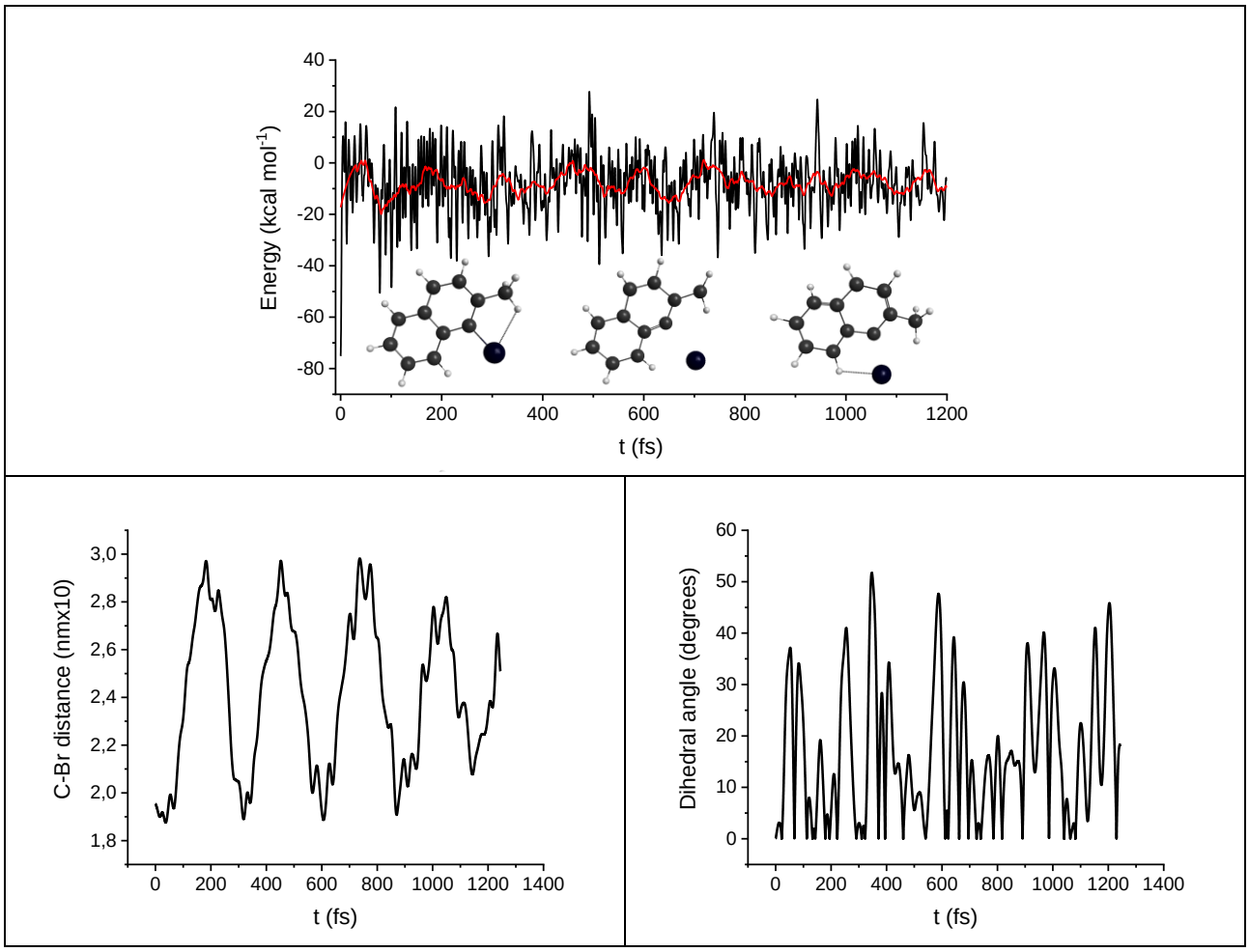


Figure S9. Path B DRC results, PM3 level of theory 1-bromo-2-methylnaphthalene DRC trajectory for the doublet radical anion. a) molecular electronic potential energy vs time b) Carbon bromine distance as a function of time c) dihedral angle between the dissociating $C - Br$ bond as a function of time.

5) Path C DRC

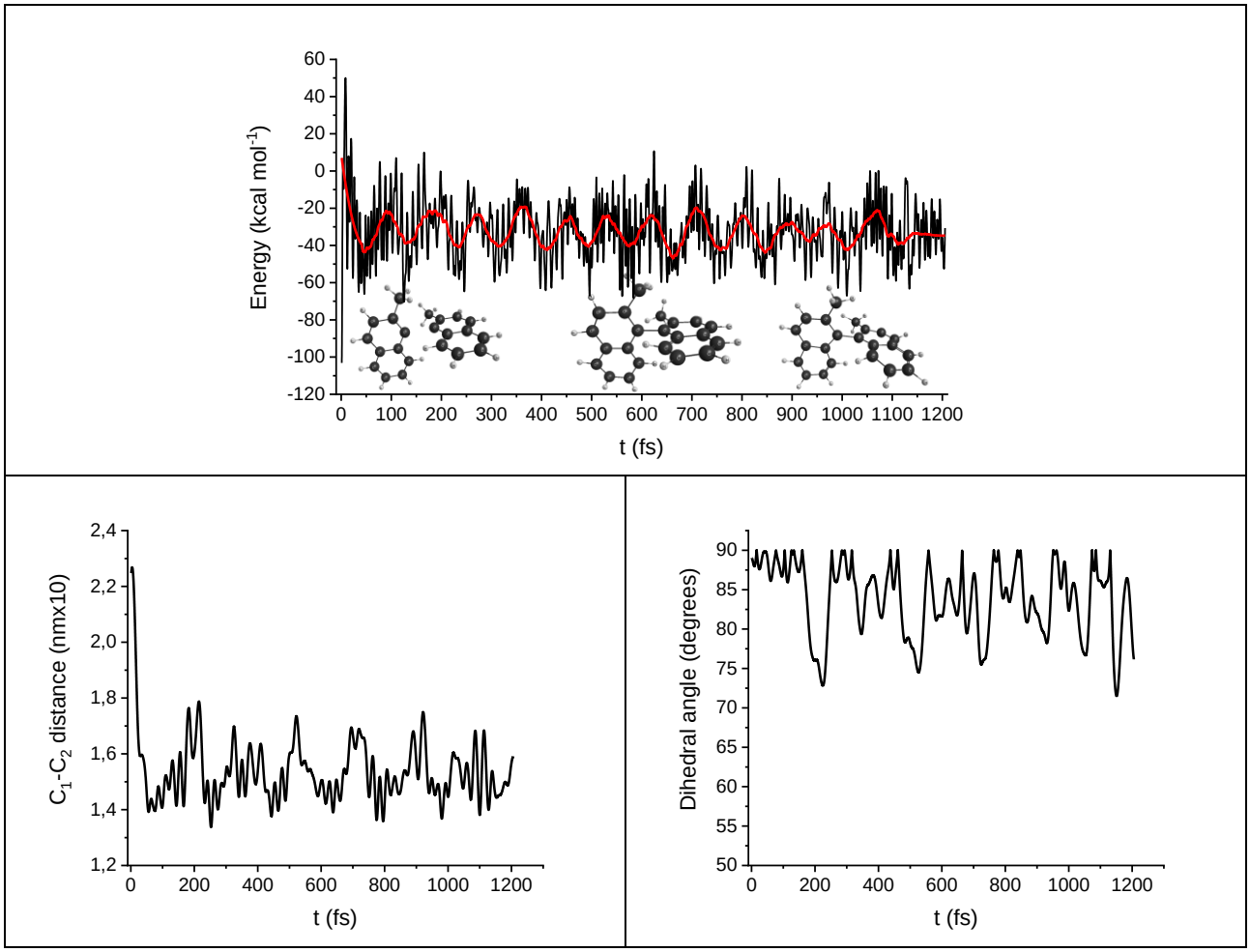


Figure S10. Path C DRC results, B3LYP/6-31G(d) DRC trajectory for the coupling of two 1-Methylnaphthalene (3) radical forming 1,1'-Binaphthalene, 2,2'-dimethyl (4) from a distances of 2.5 Amstrong. a) molecular electronic potential energy vs time, b) $C - C$ bond between the two aromatic rings distance as a function of time c) dihedral angle between the dissociating $C - Br$ bond as a function of time.

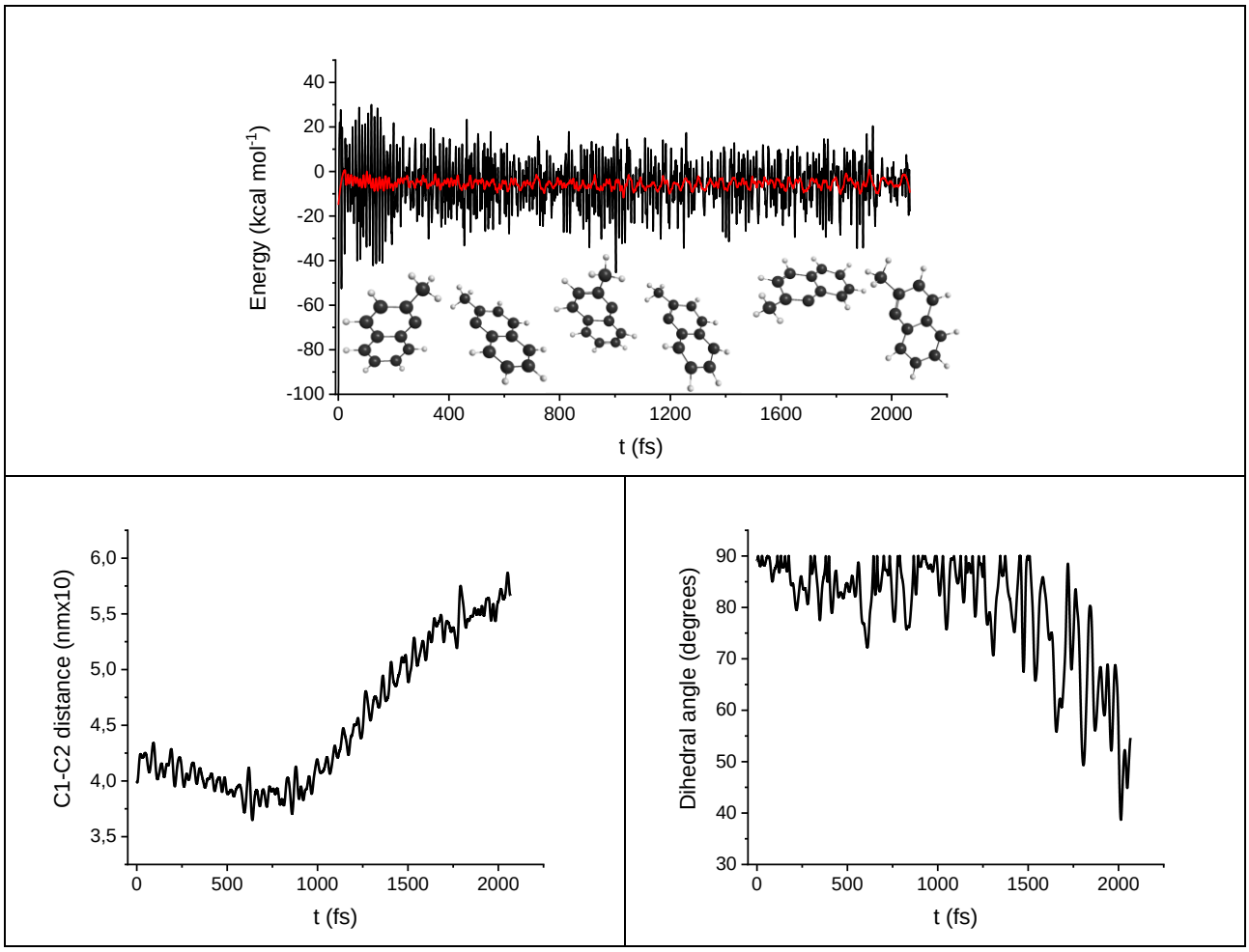


Figure S11. Path C DRC results, B3LYP/6-31G(d) DRC trajectory for the coupling of two 1-Methylnaphthalene (3) radical forming 1,1'-binaphthalene, 2,2'-dimethyl (4). $(3)^{\alpha\cdot} + (3)^{\alpha\cdot} \rightarrow (4)$. a) molecular electronic potential energy vs time, b) $C - C$ bond between the two aromatic rings distance as a function of time c) dihedral angle between the dissociating $C - Br$ bond as a function of time.

6) Theoretical UV-VIS, IR and CD spectra

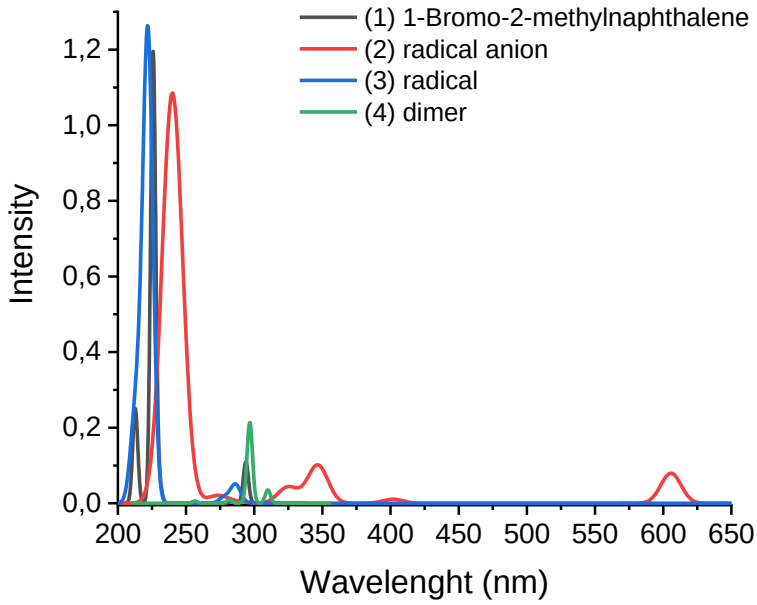


Figure S12. UV-VIS spectra calculated at the cc-pVTZ level of theory, in the wavelength range between 200 and 650 nm of all the species under study (1)-(4).

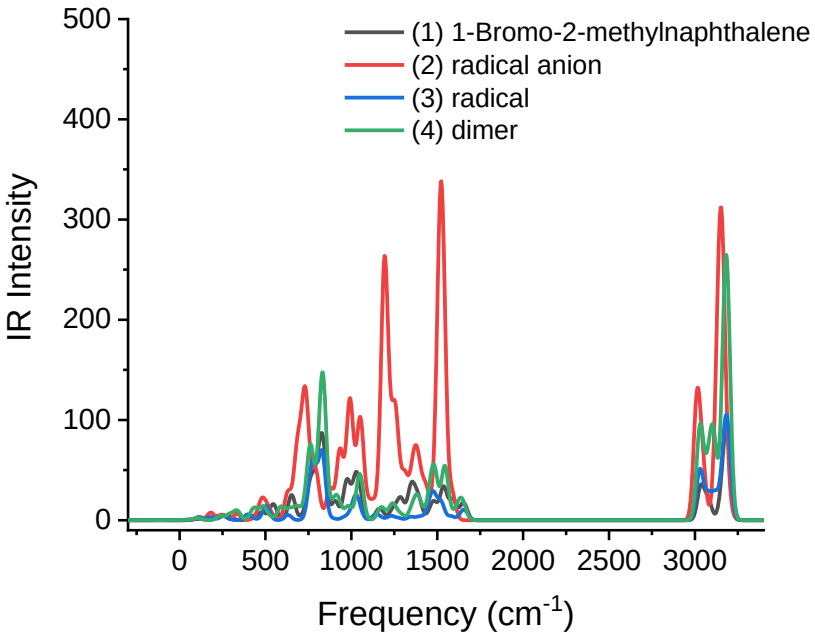


Figure S13. IR spectra calculated at the cc-pVTZ level of theory, in the wavelength range between 0 and 3500 cm^{-1} of all the species under study (1)-(4).

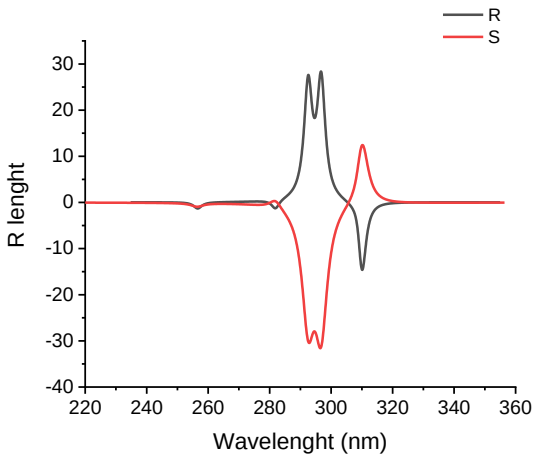


Figure S14. CD spectra calculated at the cc-pVTZ level of theory, in the wavelength range between 220 and 360 nm of (4)-R and (4)-S structures.

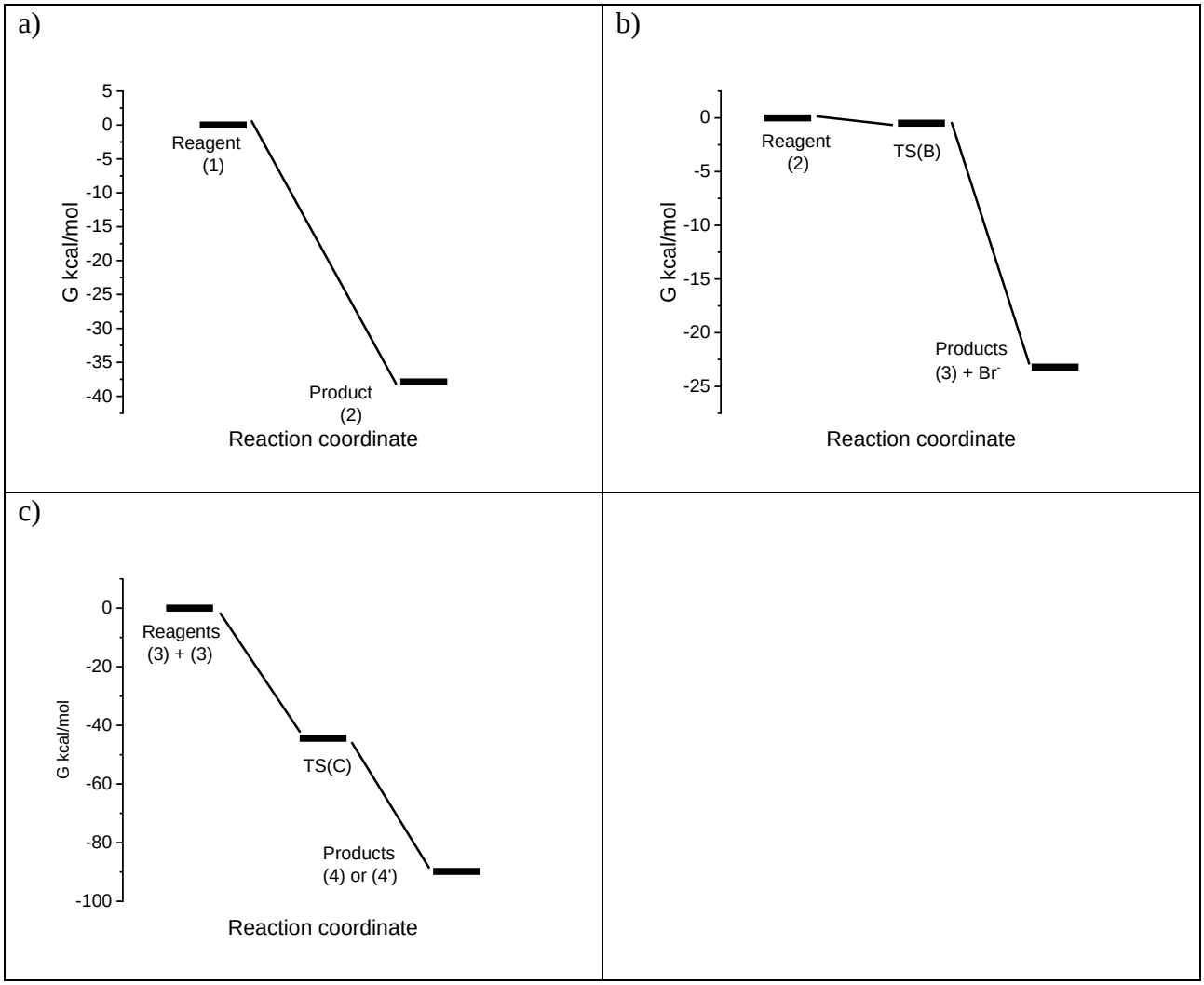


Figure S15. a) Potential energy surface for reaction path A, at the B3LYP/6-31G(d) level of theory. Gibbs free energy of reagents (**1**), final products (**2**). b) Potential energy surface for reaction path B, at the UB3LYP/6-31G(d) level of theory. Gibbs free energy of reagents (2), final products ($3 + Br^{-}$) and transition state ($TS(B)$) c) Potential energy surface for reaction path C, at the UB3LYP/6-31G(d) level of theory. Gibbs free energy of reagents (3), final products (4) and transition state ($TS(C)$).