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Six low-lying isomers of $C_{11}H_8$ are unidentified in the laboratory - A theoretical study†

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The potential energy surface of $C_{11}H_8$ has been theoretically examined using density functional theory and coupled-cluster methods. The current investigation reveals that 2*a*H-cyclopenta[cd]indene (**2**), 7-ethynyl-1H-indene (**6**), 4-ethynyl-1H-indene (**7**), 6-ethynyl-1H-indene (**8**), 5-ethynyl-1H-indene (**9**), and 7bH-cyclopenta[cd]indene (**10**) remain elusive to date in the laboratory. The puckered low-lying isomer **2** lies at 11 kJ mol^{-1} below the experimentally known molecule, cyclobuta[de]naphthalene (**3**), at the fc-CCSD(T)/cc-pVTZ//fc-CCSD(T)/cc-pVDZ level of theory. **2** lies at 35 kJ mol^{-1} above the thermodynamically most stable and experimentally known isomer, 1H-cyclopenta[cd]indene (**1**), at the same level. It is identified that 1,2-H transfer from **1** yields 2H-cyclopenta[cd]indene (**14**) and subsequent 1,2-H shift from **14** yields **2**. Appropriate transition states have been identified and intrinsic reaction coordinate calculations have been done at the B3LYP/6-311+G(d,p) level of theory. Recently, 1-ethynyl-1H-indene (**11**) has been detected using synchrotron based vacuum ultraviolet ionization mass spectrometry. 2-ethynyl-1H-indene (**4**) and 3-ethynyl-1H-indene (**5**) have been synthetically characterized in the past. While the derivatives of 7bH-cyclopenta[cd]indene (**10**) have been isolated elsewhere, the parent compound remains unidentified to date in the laboratory. Although $C_{11}H_8$ is a key elemental composition in reactive intermediates chemistry and most of its isomers are having a non-zero dipole moment ($\mu \neq 0$), to the best of our knowledge, none of them have been characterized by rotational spectroscopy. Therefore, energetic and spectroscopic properties have been computed and the present investigation necessitates new synthetic studies on $C_{11}H_8$, in particular **2**, **6**-**10**, and also rotational spectroscopic studies on all low-lying isomers.

1 Introduction

$C_{11}H_8$ is a prototypical elemental composition for organic chemists as it encompasses a diverge set of structural isomers.[1–13] The most stable isomer, 1H-cyclopenta[cd]indene (**1**; see figure 1) was isolated by different groups in the early 1970s.[1,2] Wentrup and co-workers have synthesized **1** by flash vacuum pyrolysis of 1-(2-diazoethylidene)indene at 600 °C. Another experimentally well-known low-lying isomer for $C_{11}H_8$ is cyclobuta[de]naphthalene (**3**).[5,6,11,12,14–16] For a long time, **3** has been considered as the global minimum isomer[7,8] on the PES of $C_{11}H_8$ instead of **1**.[1,9,11,12] Within 1H-indene system, 2-ethynyl-1H-indene (**4**)[17] and 3-ethynyl-1H-indene (**5**)[18,19] have been synthetically characterized in the past but only recently, using a synchrotron based vacuum ultraviolet ionization mass spectrometry, 1-ethynyl-1H-indene (**11**; see Figure 1) has been detected by Kaiser and co-workers.[20] A bimolecular reaction between the 1-indenyl ($C_9H_7^{\bullet}$) radical and acetylene (C_2H_2) has been carried out at 1500±10 K and 300 Torr pressure. This highly endothermic reaction produces **11** and hydrogen. It had been pointed out by Kaiser and co-workers[20] that none of the photoionization efficiency curves of the remaining 2- to 7-ethynyl-1H-indene isomers (**4**-**9**) are able to replicate the experimental data except **11**. Thus, it was concluded that **11** alone has been detected in their experiments.[20] Therefore, 7-ethynyl-1H-indene (**6**), 4-ethynyl-1H-indene (**7**), 5-ethynyl-1H-indene (**8**), and 6-ethynyl-1H-indene (**9**) should be considered as elusive molecules.

Attempts to synthesize the second most stable isomer, 2*a*H-cyclopenta[cd]indene (**2**) or its derivatives, have not been successful to date.[1,9] This indirectly indicates that mere thermodynamic stability is not the only governing factor in the successful identification of molecules in the laboratory.[10,20–27] One of the main reasons we have studied isomerization pathways relevant

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† Electronic Supplementary Information (ESI) is available: [Cartesian coordinates of the optimized geometries, total electronic energies, zero-point vibrational energies (ZPVEs), dipole moments, rotational constants, NICS (1 Å) values, and T_1 diagnostic values calculated at different levels are given].

to isomer **2** through other experimentally known molecules such as **1** and **3** is to assess the kinetic stability of **2**. While several derivatives of 7bH-cyclopenta[cd]indene (**10**) have been isolated elsewhere,[28–31] the parent molecule remains elusive, which outlines that it is the kinetic control that governs the formation of a particular molecule in the the laboratory. Other low-lying neutral molecules of $C_{11}H_8$ that are synthetically characterized are as follows: 1H-cyclopropa[b]naphthalene (**12**; see Figure 2),[32,33] 1H-cyclopropa[a]naphthalene (**13**),[34] penta-1,3-diyn-1-ylbenzene (**15**),[35,36] 1-(buta-1,3-diyn-1-yl)-4-methylbenzene (**20**),[37,38] 1-(buta-1,3-diyn-1-yl)-2-methylbenzene (**22**),[39,40] 1-ethynyl-2-(prop-1-yn-1-yl)benzene (**28**; see Figure 3),[41,42] 1,4-diethynyl-2-methylbenzene (**31**),[43] 1,3-diethynyl-5-methylbenzene (**33**),[44] 1,2-diethynyl-4-methylbenzene (**36**),[45] and 1,2-diethynyl-3-methylbenzene (**37**).[46]

On the contrary, on the high-energy side, reactive intermediates such as 1-naphthylcarbene (**52**; see Figure 5) and 2-naphthylcarbene (**51**) have been trapped by matrix isolation within their triplet ground electronic state.[4,8,11] Though attempts have been made to trap 1-azulenylcarbene (**56**) with styrenes by Saito and co-workers,[47] the first successful trapping was done by Sanders and co-workers in 2012.[10] Through irradiation of 1-azulenyldiazomethane at low temperatures in argon matrices, **56** has been synthesized in its singlet ground electronic state.[10] This metastable carbene undergoing quantum chemical tunneling even at lowest temperatures (3-10 K) and rearranging to 8-methylenebicyclo[5.3.0]deca-1,3,5,6,9-pentaene (**55**) has also been observed.[10] Using falling solid flash vacuum pyrolysis, Wentrup and co-workers have studied the isomerizations of both azulenylcarbenes and naphthylcarbenes.[11,13] Among the four regio-isomers (2-, 4-, 5-, and 6-azulenylcarbene) of **56**, three of them in their triplet ground electronic state (2-, 5-, and 6-azulenylcarbene) have also been trapped by Sanders and co-workers in 2016.[12] 4-azulenylcarbene is yet to be synthetically characterized in the laboratory. Perhaps, for **56**, it was concluded that the singlet electronic state is stabilized by the high electron density at the 1-position of the azulenyl system along with a favorable C...H interaction between the carbene carbon and the neighboring H-atom at the seven-membered ring.[12]

Although enormous amount of experimental activity has been done in the past on $C_{11}H_8$, the current theoretical study delineates that the following isomers (apart from **2**, **6**-**10**) are remaining elusive, which all lie energetically below the experimentally known carbene molecule, **56**. They are, 2H-cyclopenta[cd]indene (**14**, see Figure 2), 1-ethynyl-2H-indene (**16**), 6H-cyclopenta[cd]indene (**17**), 4-ethynyl-2H-indene (**18**), 2H-cyclopenta[3,4]cyclobuta[1,2]benzene (**19**),[48] 5-ethynyl-2H-indene (**21**), 1-(buta-1,3-diyn-1-yl)-3-methylbenzene (**23**), 7H-cyclopenta[cd]indene (**24**), 1-ethynyl-4-(prop-1-yn-1-yl)benzene (**25**), 7aH-cyclopenta[cd]indene (**26**), 1-ethynyl-3-(prop-1-yn-1-yl)benzene (**27**; see Figure 3), 4H-cyclobuta[f]indene (**29**), 5H-cyclobuta[e]indene (**30**), 5H-cyclobuta[f]indene (**34**), 1,3-diethynyl-2-methylbenzene (**35**), 2-ethynyl-2H-indene (**38**), 5-ethynyl-5H-indene (**39**), 4-ethynyl-4H-indene (**40**), 1H-cyclopenta[3,4]cyclobuta[1,2]benzene (**41**; see Figure 4), 7aH-cyclobuta[a]indene (**42**), 2-ethynyl-8-methylbicyclo-[4.2.0]octa-1,3,5,7-tetraene (**43**), 2-(prop-1-yn-1-yl)bicyclo-[4.2.0]octa-1,3,5,7-tetraene (**44**), 2-ethynyl-7-methylbicyclo-[4.2.0]octa-1,3,5,7-tetraene (**45**), and 2-ethynyl-5-methylbicyclo-[4.2.0]octa-1,3,5,7-tetraene (**46**). Isomers energetically lying above **56** are listed in the ESI†.

Overall, though the potential energy surface of $C_{11}H_8$ has been examined before by quantum chemical studies, most of the attention was given to either naphthylcarbenes[6,7] or azulenylcarbenes[10,12] or ethynyl-1H-indenes[20] or the derivatives of 7bH-cyclopenta[cd]indene.[9] A comprehensive theoretical account on the low-lying isomers of $C_{11}H_8$ has been missing in the literature for quite sometime. Therefore, in this work, our major attention was given to the low-lying PES of $C_{11}H_8$. The present investigation further reveals that potential rearrangements have been playing a crucial role with multiple number of 1,2 H-shifts among **1**, **2** and **14**. Appropriate transition states have been identified and intrinsic reaction coordinate calculations have been done using density functional theory (DFT). While the entire PES has been explored with DFT, high-level coupled cluster calculations have been done only for the low-lying isomers. Furthermore, to the best of our knowledge, rotational spectra have not been reported for any isomer of $C_{11}H_8$ though they are polar with non-zero net dipole moments ($\mu \neq 0$). Hence, to aid experimental studies along this direction, rotational and centrifugal distortion constants have been calculated for the eleven low-lying isomers (**1**-**11**) of $C_{11}H_8$. It is also noted here that in the present work the PES of $C_{11}H_8$ has been explored based on prior experimental studies and our chemical intuition. More number of structural isomers are certainly possible than what has been reported here. In the future, the surface will be explored based on search algorithms.[49–56] However, we leave this discussion with a caveat that no search algorithm to date guarantees all possible isomers for a given elemental composition.[54,56,57]

2 Computational Details

Initially, geometry optimization and frequency calculations for all isomers of $C_{11}H_8$ considered in this work have been carried out using DFT at the B3LYP[58,59]/6-311+G(d,p)[60,61] level of theory. For the low-lying eleven isomers (**1**-**11**), ab initio calculations have also been done using coupled-cluster singles and doubles (CCSD),[62] and CCSD with quasiperturbative triple excitations (CCSD(T))[63,64] methods to incorporate higher-level treatment of electron-correlation effects. In all CCSD and CCSD(T) calculations, correlation-consistent polarized valence double zeta basis set of Dunning's (cc-pVDZ) has been used.[65] For $C_{11}H_8$, the latter basis set consists of 194 basis functions. The carbon 1*s* orbitals are frozen in all these calculations. The force constant matrix obtained at lower levels had subsequently been used at higher levels to facilitate geometry optimizations. For all stationary points obtained at the CCSD(T)/cc-pVDZ level, harmonic vibrational frequencies were determined by analytic calculation of second derivatives.[66] Nuclear independent chemical shift (NICS) values[67–69] for all ring isomers have been calculated at the B3LYP/6-311+G(d,p) level of theory at 1 Å above the plane of the rings. To assess the multi-reference character of $C_{11}H_8$ isomers, T_1 diagnostic values[70] have been calculated

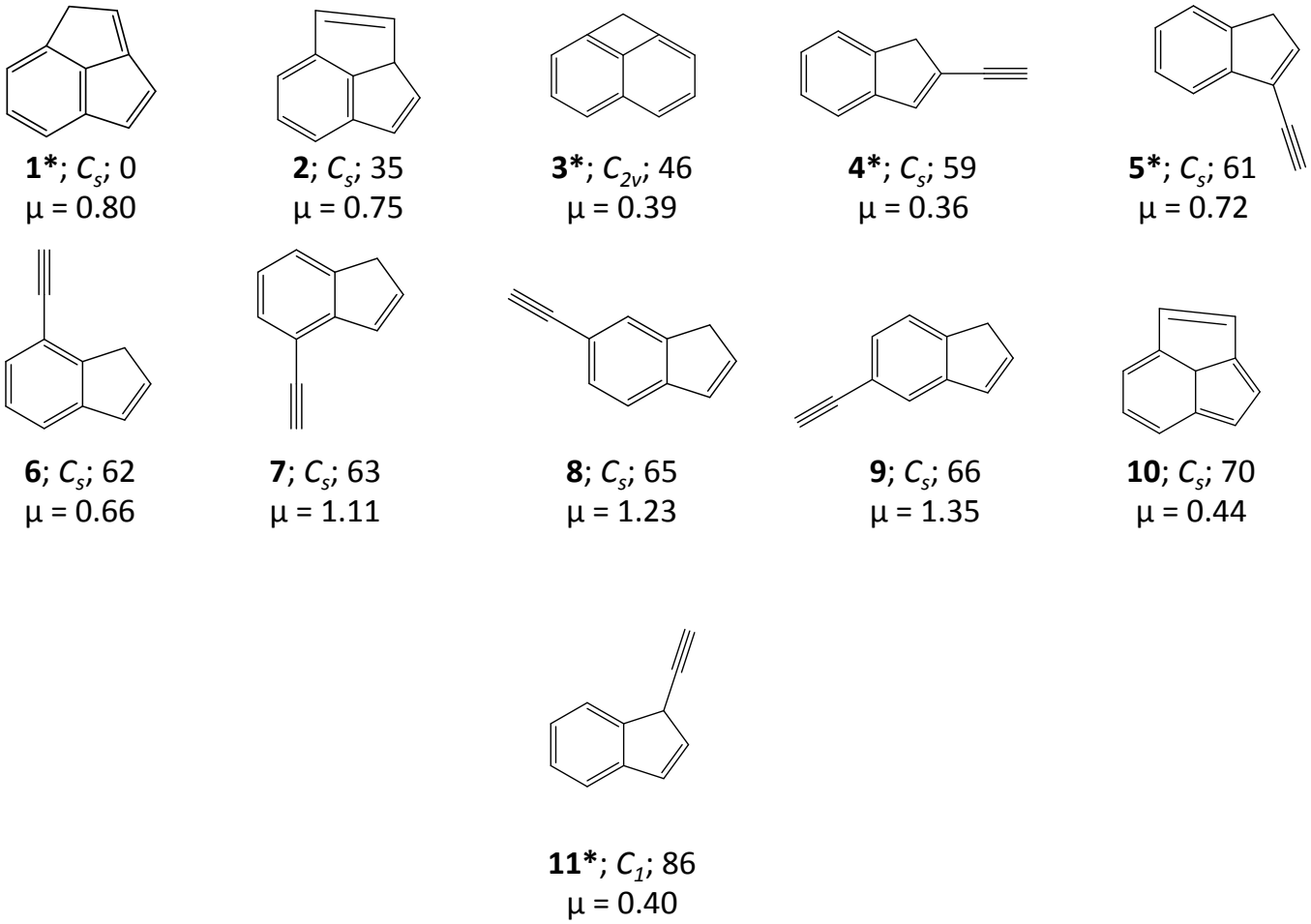

Fig. 1 Eleven low-lying isomers of $C_{11}H_8$. Relative energies (in kJ mol^{-1}) are calculated at the fc-CCSD(T)/cc-pVTZ//fc-CCSD(T)/cc-pVDZ level of theory. Absolute dipole moment values (in Debye) are calculated at the fc-CCSD(T)/cc-pVDZ level of theory. Experimentally detected isomers are marked with an asterisk symbol.

at the CCSD/6-311+G(d,p)//B3LYP/6-311+G(d,p) level of theory. All triplet electronic states are optimized at the UB3LYP/6-311+G(d,p) level of theory. All ab initio calculations have been carried out using the CFOUR program package.[71] All DFT calculations have been done using the Gaussian suite of program.[72]

3 Results and Discussion

Eighty-one stationary points of $C_{11}H_8$ spanning from 0 to 517 kJ mol^{-1} have been theoretically studied here at the B3LYP/6-311+G(d,p) level of theory. The valence bond structures of sixty-three isomers (excluding transition states and higher-order saddle-point) are shown in Figures 1-5 along with zero-point vibrational energy (ZPVE) corrected relative energy (with respect to **1**), point group symmetry, and permanent dipole moment. Experimentally detected isomers are represented with an asterisk symbol. In Table 1, relative energies of eleven low-lying isomers calculated at both B3LYP/6-311+G(d,p) and fc-CCSD(T)/cc-pVDZ levels are shown along with singlet-triplet energy gaps, NICS (1Å) values, and T_1 diagnostic numbers. Rotational constants, inertial axis dipole moment components, absolute dipole moments, and centrifugal distortion constants computed at the fc-CCSD(T)/cc-pVDZ level of theory for isomers **1**-**11** are shown in Table 2. For brevity, total energies, ZPVEs, rotational constants, singlet-triplet energy gaps, NICS (1Å) and T_1 diagnostic values calculated using DFT for all isomers, and final optimized Cartesian coordinates are given in the ESI†.

3.1 Energetics

Unequivocally, the global minimum geometry for $C_{11}H_8$ is the singlet ground electronic state of **1**.[1,9,11,12] For quite sometime, isomer **3** had been considered as the most stable geometry in the literature.[7,8] Isomers **2** and **3** lie 35 and 46 kJ mol^{-1}, respectively, above **1** at the fc-CCSD(T)/cc-pVTZ//fc-CCSD(T)/cc-pVDZ level of theory (see Table 1). Though **2** lies 11 kJ mol^{-1} below **3**, this puckered aromatic molecule remains elusive to date.[1] Isomer **3** has been prepared from 1- and 2-naphthylcarbenes or its derivatives through ther-

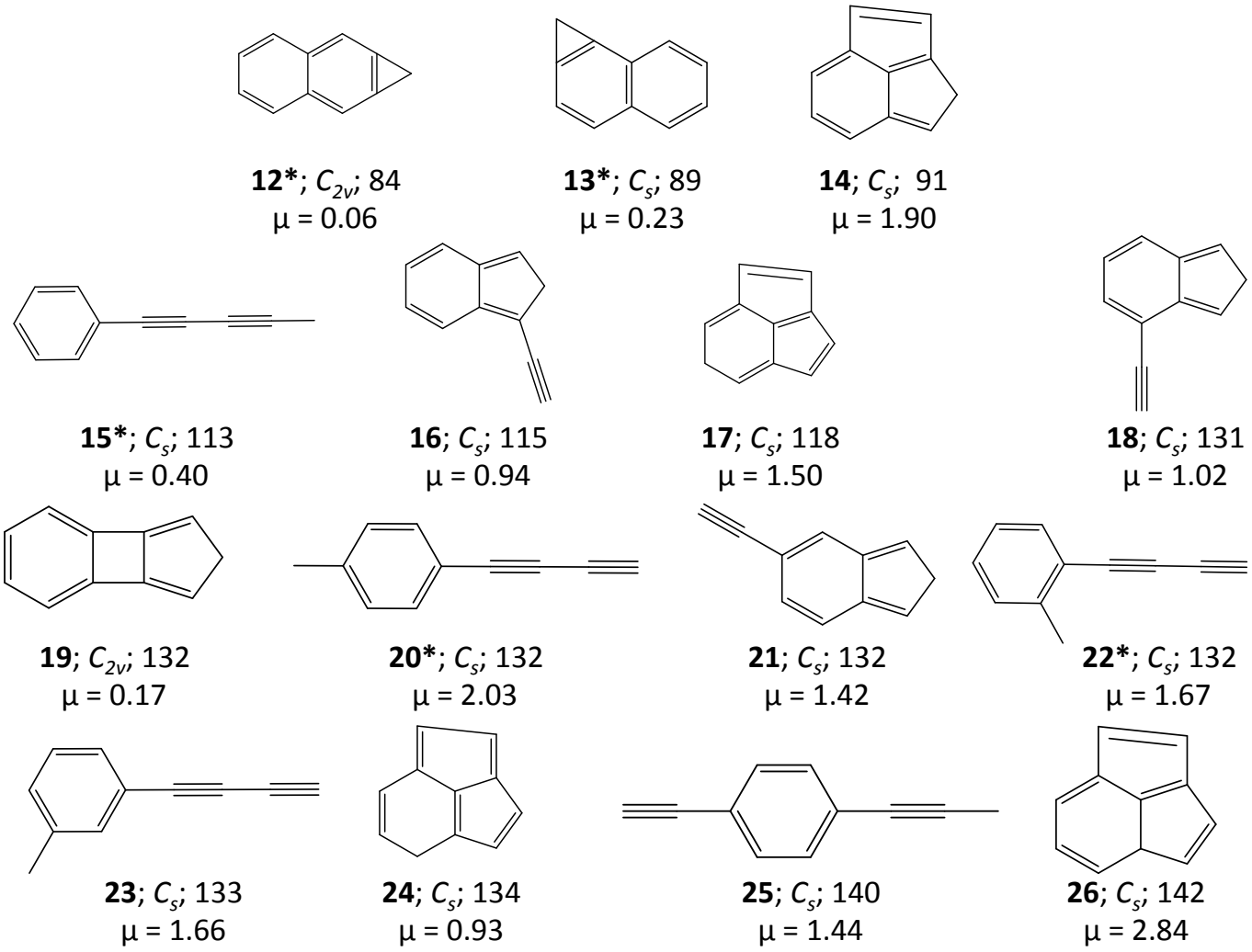

Fig. 2 Isomers **12-26** of $C_{11}H_8$. ZPVE-corrected relative energies (in kJ mol^{-1}) and absolute dipole moment values (in Debye) are calculated at the B3LYP/6-311+G(d,p) level of theory. Experimentally detected isomers are marked with an asterisk symbol.

mal rearrangements.[5,6] Wentrup and co-workers synthesized **3** from 1-azulenylcarbene using Falling Solid Flash Vacuum Pyrolysis (FS-FVP).[11] Another route to the syntheses of **3** and its derivatives have been achieved by vacuum thermolyses of [methoxy(trimethylsilyl)methyl]naphthalenes.[14,15] Synthesis and characterization of isomer **1** have been documented elsewhere by several research groups.[1–3,11,12,73] Isomers **4**[17] and **5**[18,19], that energetically lie 59 and 61 kJ mol^{-1} above **1**, respectively, at the fc-CCSD(T)/cc-pVTZ//fc-CCSD(T)/cc-pVDZ level have also been synthetically characterized. Within 1H-indene system, isomers **6**, **7**, **8**, and **9** that lie 62, 63, 65, and 66 kJ mol^{-1} above **1**, respectively, at the former level remain elusive to date. Kaiser and coworkers had detected isomer **11** recently, which lies 86 kJ mol^{-1} above **1**, using a synchrotron based vacuum ultraviolet ionization mass spectrometry (see Figure 1). The photoionization efficiency curves of their experiment, using the reactants 1-indenyl ($C_9H_7^{\bullet}$) radical and acetylene (C_2H_2), unequivocally confirms that **11** alone has been detected.[20]

Isomer **2**, **10**, **14**, **17**, **24** and **26** (see Figures 1-2) are prototropic tautomers of 1H-cyclopenta[cd]indene (**1**). The most stable hydrocarbon tautomer among them is **1**. While derivatives of 7bH-cyclopenta[cd]indene (**10**) have been reported in the literature,[28–31] for isomer **2** neither the parent molecule nor its derivatives have been characterized yet. Other tautomers of **1**, which remain elusive are: 2H-cyclopenta[cd]indene (**14**, 91 kJ mol^{-1}), 6H-cyclopenta[cd]indene (**17**, 118 kJ mol^{-1}), 7H-cyclopenta[cd]indene (**24**, 134 kJ mol^{-1}), 7aH-cyclopenta[cd]indene (**26**, 142 kJ mol^{-1}). All the tautomers contain a rigid tricyclic structure with one sp^3 carbon atom (tertiary or secondary). As active hydrogen atoms are present in all of them, it was suggested by theoretical calculations that the polycyanated derivatives of these prototropic tautomers can act as powerful Brønsted superacids.[9]

4 Rearrangement Schemes

In this work, we propose a low energy thermal rearrangement scheme (see Figure 6) for the formation of the most stable isomer **1** from the experimentally identified 1-azulenylcarbene (**56**, 252

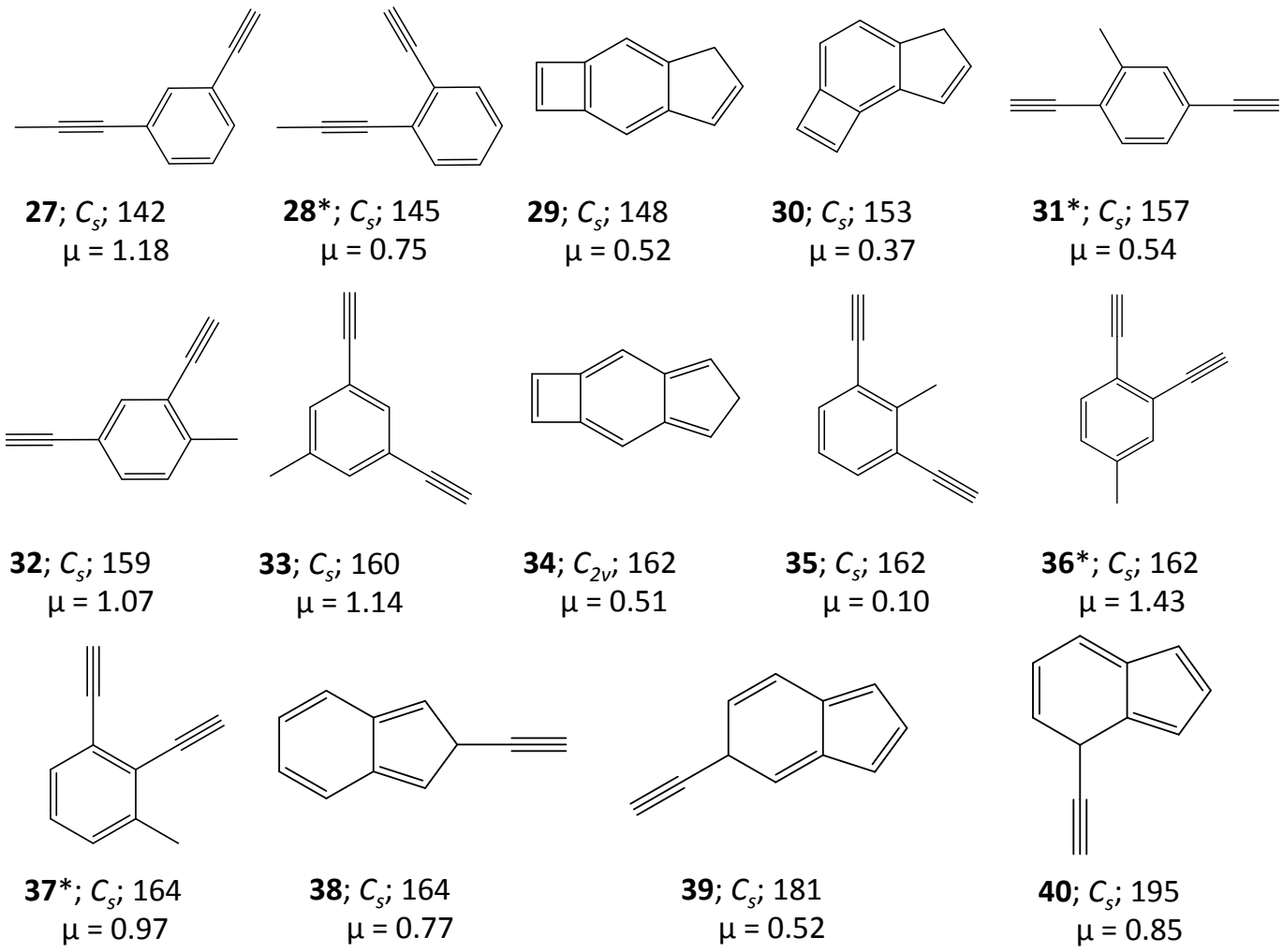

Fig. 3 Isomers **27**-**40** of $C_{11}H_8$. ZPVE-corrected relative energies (in kJ mol^{-1}) and absolute dipole moment values (in Debye) are calculated at the B3LYP/6-311+G(d,p) level of theory. Experimentally detected isomers are marked with an asterisk symbol.

kJ mol^{-1}) based on thermodynamically favorable energy considerations. Depending upon the cyclization process of **56**, this rearrangement can proceed in two pathways as depicted in Figures 7 and 8 as Scheme-I and Scheme-II, respectively. We have identified the appropriate transition states and intermediates involved in the rearrangement process and the corresponding activation energies are shown in the form of relative potential energy diagram. All the transition states reported in this study have been identified after several trial calculations and verified through the Intrinsic Reaction Coordinate (IRC) calculations[74,75] as implemented in Gaussian 16 software.[72] The transition states connect the reactants to the products through the IRCs in the potential energy surface.

4.1 Scheme I

In this rearrangement Scheme I (see Figure 7), a hydrogen transfer rearrangement takes place from the 8th position of 1-azulenylcarbene (**56**) to form 8-methylene-bicyclo[5.3.0]deca-1,3,5,6,9-pentaene (**55**) which is 38 kJ mol^{-1} lower in energy than **56**. This reaction goes through the transition state (**Tsa1**) with an activation energy (E_a) of 153 kJ mol^{-1}. **Tsa1** has one imaginary frequency (ν_i) at 1606.31i cm^{-1}, which corresponds to the hydrogen transfer from the 8th position of **56** to form **55**. Following this, a ring closing reaction takes place to form 1H-cyclobuta[cd]azulene (**64**) which is 10 kJ mol^{-1} lower in energy compared to **55**. The E_a required to complete the ring closing rearrangement is relatively high (526 kJ mol^{-1}, through **Tsa2**, ν_i = 500.47i cm^{-1}) which is likely to be the reason that both **55** and **64** were not isolated in the FVP experiments performed by Wentrup and co-workers.[11] Our theoretical calculations at the B3LYP/6-311+G(d,p) level of theory shows that **64** is about 166 kJ mol^{-1} higher in energy than that of **3**.

8-azulenylcarbene (**66**) is formed after ring opening reaction takes place from 1aH-cyclobuta[cd]azulene (**65**) following transfer of a hydrogen atom from **64**. The hydrogen transfer reaction goes through the transition state **Tsa3** (E_a = 198 kJ mol^{-1}, ν_i = 1103.51i cm^{-1}) and the ring opening reaction goes through the transition state **Tsa4** (E_a = 87 kJ mol^{-1}, ν_i

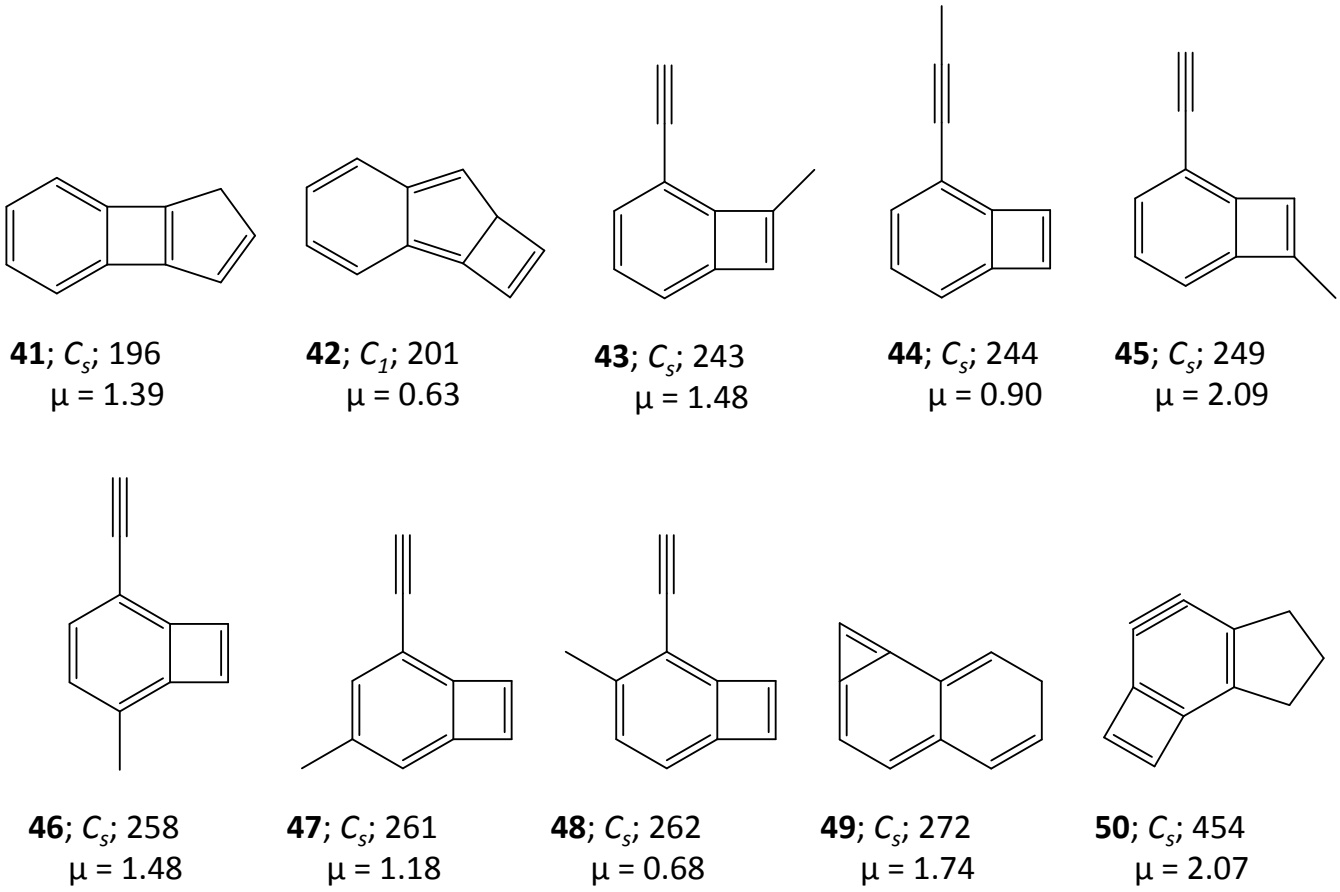

Fig. 4 Isomers **41**-**50** of $C_{11}H_8$. ZPVE-corrected relative energies (in kJ mol^{-1}) and absolute dipole moment values (in Debye) are calculated at the B3LYP/6-311+G(d,p) level of theory. Experimentally detected isomers are marked with an asterisk symbol.

= 284.91i cm^{-1}). From **66**, the rearrangement can proceed through two possible pathways: (i) ring closing and hydrogen transfer reaction to form relatively more stable (89 kJ mol^{-1}) isomer 1H-cyclopropa[e]azulene (**68**) through transition state **Tsa6**, (E_a = 185 kJ mol^{-1}, ν_i = 255.85i cm^{-1}) or, (ii) only ring closing reaction without any hydrogen transfer to form 1aH-cyclopropa[e]azulene (**67**) which requires relatively low activation energy (**Tsa5**, E_a = 27 kJ mol^{-1}, ν_i = 973.09i cm^{-1}).

The ring expansion of **67** to form an eight-membered ring can give bicyclo[6.3.0]undeca-1,2,4,6,8,10-hexaene (**69**) which is 47 kJ mol^{-1} lower in energy than **67**. 224 kJ mol^{-1} activation energy is needed for this conversion through the transition state **Tsa7** (ν_i = 528.58i cm^{-1}). Again, from **69** the rearrangement can proceed through two possible pathways: a ring closing reaction within the eight-membered ring which ultimately converts into three five-membered rings containing isomer 6aH-cyclopenta[a]pentalene (**70**) which would convert to 7H-cyclopenta[a]pentalene (**71**) through a hydrogen shifting reaction. **Tsa8** (E_a = 340 kJ mol^{-1}, ν_i = 653.48i cm^{-1}) and **Tsa9** (E_a = 327 kJ mol^{-1}, ν_i = 1965.63i cm^{-1}) have been identified as the transition states for these rearrangements, respectively. It is noted here that derivatives of **71** have been identified experimentally elsewhere.[76] Another ring closing reaction within the eight membered ring leads to the formation of 3bH-cyclopenta[3,4]cyclobuta[1,2]benzene (**72**) containing a six-membered, a four-membered and a five-membered fused ring system. **Tsa10** (E_a = 332 kJ mol^{-1}, ν_i = 619.98i cm^{-1}) can act as the transition state for this ring closing reaction. Isomer **72** could possibly convert to a carbene isomer bicyclo[5.4.0]undeca-1,3,5,7,9-pentaene-11-ylidene (**73**) which is 30 kJ mol^{-1} lower in energy. This can occur through a puckered transition state **Tsa11** (E_a = 591 kJ mol^{-1}, ν_i = 281.95i cm^{-1}) via simultaneous ring opening and ring closing rearrangement. A hydrogen transfer rearrangement can take place to form bicyclo[5.4.0]undeca-1,2,4,6,8,10-hexaene (**76**) (which is 68 kJ mol^{-1} lower in energy than **73**) through **Tsa12** (E_a = 206 kJ mol^{-1}, ν_i = 1741.06i cm^{-1}). The formation of the most stable isomer **1** from bicyclo[5.4.0]undeca-2,4,6,8,10,11-hexaene (**75**)

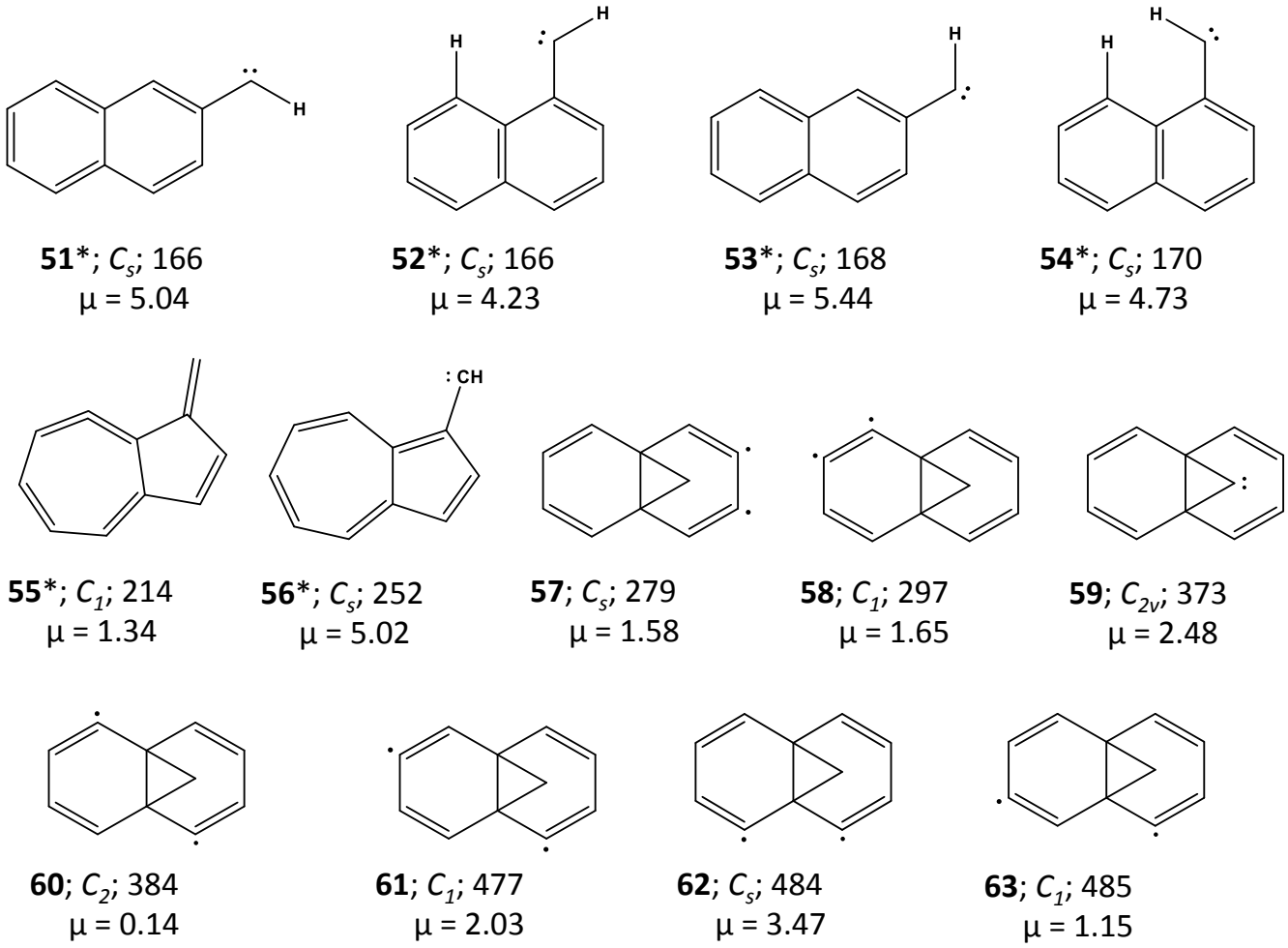

Fig. 5 Isomers **51**-**63** of $C_{11}H_8$. ZPVE-corrected relative energies (in kJ mol^{-1}) and absolute dipole moment values (in Debye) are calculated at the B3LYP/6-311+G(d,p) level of theory. Experimentally detected isomers are marked with an asterisk symbol.

is discussed in detail in Scheme II.

4.2 Scheme II

Another low-energy pathway to reach isomer **1** of $C_{11}H_8$ from the experimentally known molecule **56** is shown in Scheme II (see Figure 8). While the thermal rearrangement scheme outlined here has briefly been discussed elsewhere,[10] we have identified the appropriate transition states and reactive intermediates for each step and they are verified through IRC calculations.

A thermal ring closing reaction from experimentally identified 1-azulenylcarbene (**56**) can form 7aH-cyclopropa[a]azulene (**74**) through **Tsb1** (E_a = 130 kJ mol^{-1}, ν_i = 736.31i cm^{-1}). Although **74** is 65 kJ mol^{-1} higher in energy than **56**, it rearranges quickly to bicyclo[5.4.0]undeca-1,2,4,6,8,10-hexaene (**76**) via **75**. Isomer **76** is 167 kJ mol^{-1} lower in energy compared to **74**. A ring expansion followed by hydrogen transfer reaction leads to the formation of **76** through **Tsb2** (E_a = 48 kJ mol^{-1}, ν_i = 496.53i cm^{-1}) and **Tsb3** (E_a = 48 kJ mol^{-1}, ν_i = 1741.05i cm^{-1}), respectively. **76** has a seven-membered allene like structure which is quite unstable and a ring contraction rearrangement takes place through **Tsb4** (E_a = 27 kJ mol^{-1}, ν_i = 217.64i cm^{-1}) to form 1aH-cyclopropa[a]naphthalene (**77**) containing a fused six- and three-membered ring system. But, the puckered three membered ring of **77** leads to the ring opening rearrangement to form the experimentally detected carbene isomer (Z)-1-naphthylcarbene (**54**) via **Tsb5** (E_a = 155 kJ mol^{-1}, ν_i = 324.20i cm^{-1}). A hydrogen transfer followed by a ring closing rearrangement could possibly take place to form the experimentally observed 1H-cyclobuta[de]naphthalene (**3**) through **Tsb6** (E_a = 155 kJ mol^{-1}, ν_i = 1698.44i cm^{-1}) and **Tsb7** (E_a = 23 kJ mol^{-1}, ν_i = 336.88i cm^{-1}), respectively.

4.3 1,2-H Shifting Rearrangement

In this section, we have studied the final step of the rearrangement scheme from **3** to **1** in detail, which would occur through two possible pathways dominated by 1,2-H shifting rearrangement.

In first step, the conversion of **3** to 2,2a-dihydro-1H-

Table 1 Computed relative energies (in kJ mol^{-1}), singlet-triplet energy gaps (ΔE_{ST}; in kJ mol^{-1}), NICS (1Å) (in ppm) values, and T_1 diagnostic values of eleven low-lying isomers of $C_{11}H_8$ calculated at different levels

isomer		Relative energies				B3LYP/6-311+G(d,p)		
	state	ΔE+ZPVE[a]	ΔE+ZPVE[b]	ΔE[c]	ΔG[f]	ΔE_{ST}[d]	NICS (1Å)	T_1[e]
1; C_s	$\widetilde{X}^1A'$	0	0	0	0	181	-14.90	0.011
2; C_s	$\widetilde{X}^1A'$	40	34	35	41	246	-10.60	0.011
3; C_{2v}	$\widetilde{X}^1A_1$	38	45	46	39	251	-13.92	0.011
4; C_s	$\widetilde{X}^1A'$	35	55	59	31	204	-14.59	0.012
5; C_s	$\widetilde{X}^1A'$	42	57	61	38	220	-14.68	0.012
6; C_s	$\widetilde{X}^1A'$	44	59	62	40	253	-14.11	0.011
7; C_s	$\widetilde{X}^1A'$	44	59	63	40	243	-14.42	0.012
8; C_s	$\widetilde{X}^1A'$	44	61	65	41	232	-13.44	0.012
9; C_s	$\widetilde{X}^1A'$	46	62	66	42	253	-13.47	0.011
10; C_s	$\widetilde{X}^1A'$	60	66	70	61	259	-15.15	0.012
11; C_1	$\widetilde{X}^1A$	72	82	86	68	249	-17.63	0.012

[a] Calculated at the B3LYP/6-311+G(d,p) level of theory. [b] Calculated at the fc-CCSD(T)/cc-pVDZ level of theory. [c] Calculated at the fc-CCSD(T)/cc-pVTZ//fc-CCSD(T)/cc-pVDZ level of theory. [d] Positive value indicates that singlet electronic state is more stable than the triplet. [e] Calculated at the CCSD/6-311+G(d,p)//B3LYP/6-311+G(d,p) level of theory. [f] Calculated at the B3LYP/6-311+G(d,p) level of theory at 298.15 K.

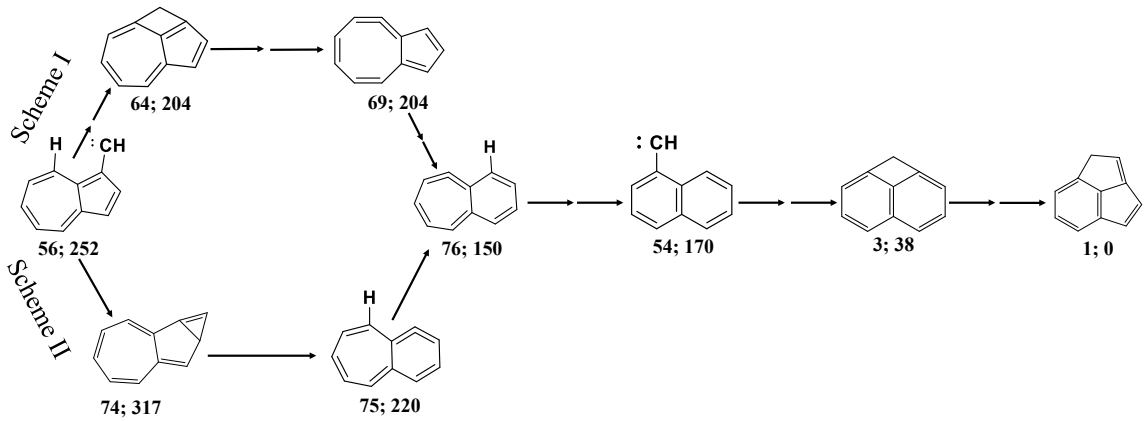

Fig. 6 Low energy thermal rearrangement schemes for the formation of **1** from **56**.

cyclopenta[cd]indenylidene (**79**) goes through **TS1**, where bond elongation and contraction takes place simultaneously (electrocyclization reaction). In this step, formation of relatively less stable five-membered ring takes place from more stable six-membered ring and therefore, this process goes through a high activation energy (> 418 kJ mol^{-1}) barrier. As soon as **79** is formed, 1,2-H shifting rearrangement reaction proceeds to form the most stable isomer **1** in two different pathways: Path-a and Path-b as indicated in the rearrangement Scheme (see Figure 9). There are two different active hydrogens present in **79**, one hydrogen is present in secondary carbon atom and another one is in tertiary carbon atom, so 1,2-H shifting reaction takes place in two ways involving those two active hydrogen atoms. In Path-a, 1,2-H shifting reaction takes place from secondary carbon atom to form **2** with very low activation energy (E_a = 24 kJ mol^{-1}) through **TS2** (336 kJ mol^{-1}). To form the most stable isomer (**1**), the reaction goes through a relatively high energy isomer (**14**; 91 kJ mol^{-1}). Conversion of **2** to **14** goes through another transition state (**TS3**, E_a = 139 kJ mol^{-1}, ν_i = 1222.62i cm^{-1}) with an activation energy of 139 kJ mol^{-1}. This reaction also

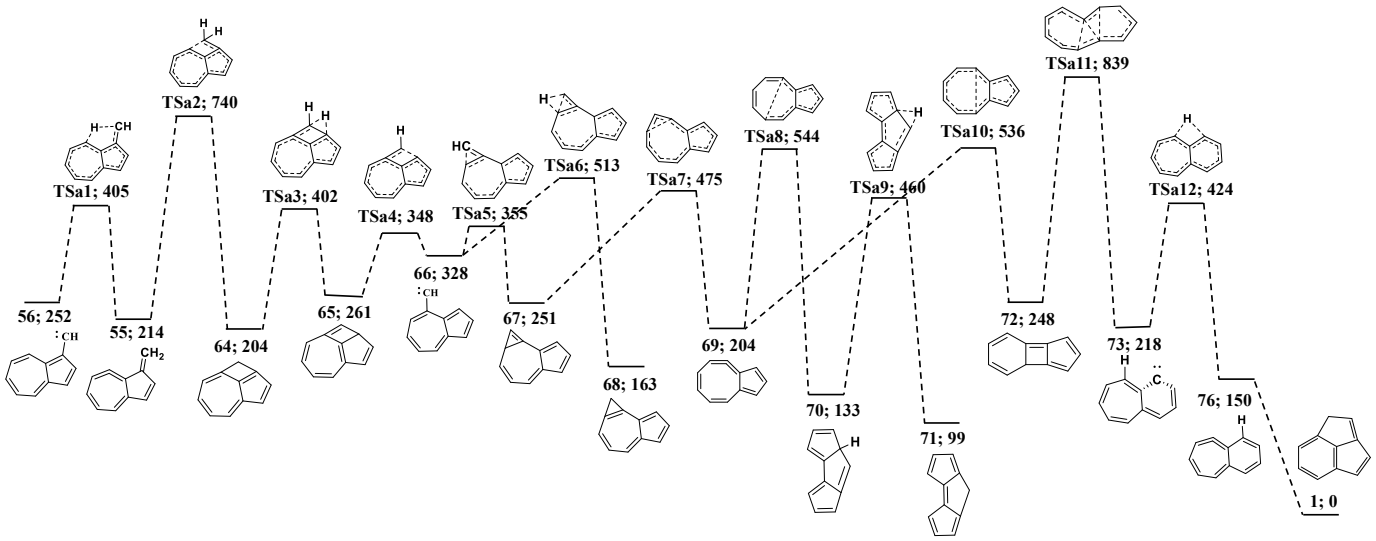

Fig. 7 Rearrangement scheme I for the formation of **1** from **56**.

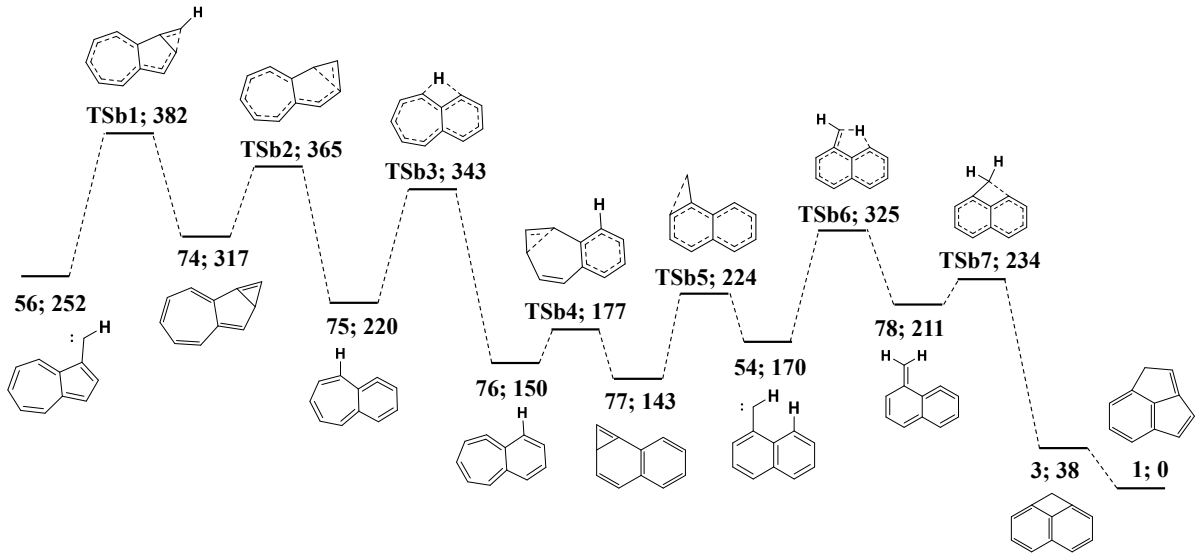

Fig. 8 Rearrangement scheme II for the formation of **1** from **56**.

proceeds through 1,2-H shifting mechanism, where the H-shifting takes place from the tertiary carbon atom. Again, very low activation energy (E_a = 68 kJ mol^{-1}) is required for the rearrangement of **14** to form the most stable isomer **1**. H-shifting for this process takes place from the secondary carbon atom via transition state **TS4** (ν_i = 1203.78i cm^{-1}). To form the lowest energy isomer **1** from **79**, Path-a involves higher energy isomers **2** and **14** with three different transition states **TS2**, **TS3**, and **TS4**, whereas, Path-b proceeds through a single step conversion involving only one transition state (**TS5**, ν_i = 643.08i cm^{-1}). As very low activation energy ($E_a \sim$ 4.4 kJ mol^{-1}) is required for Path-b, this pathway might clearly be much more faster than Path-a. Previ-

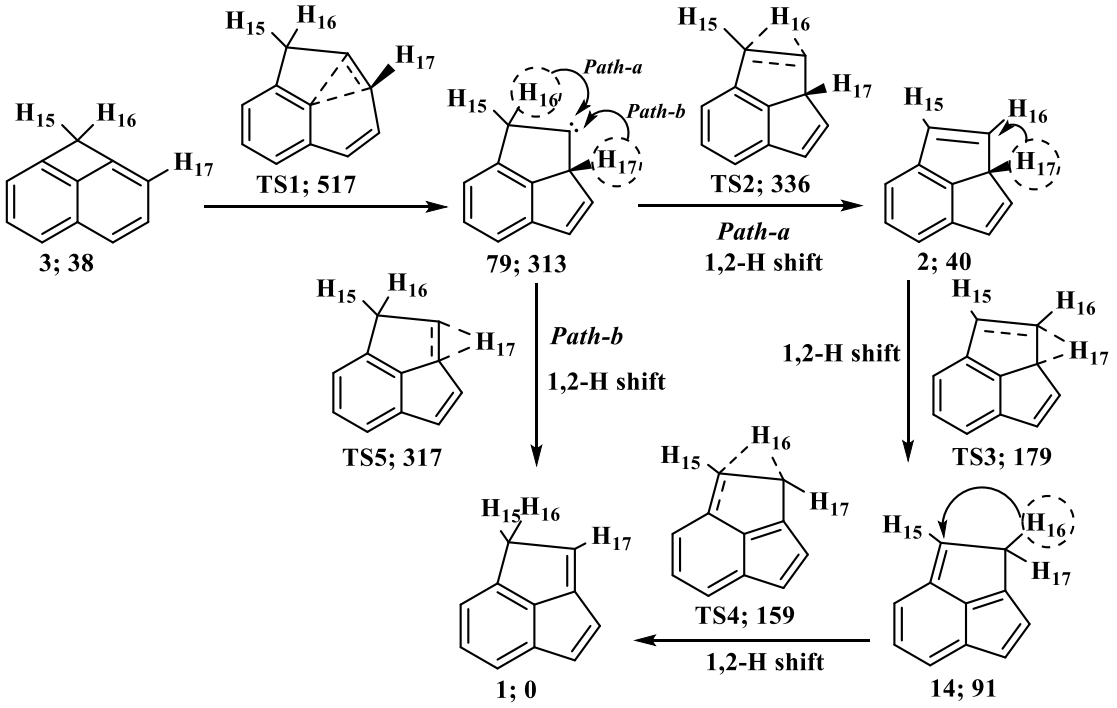

Fig. 9 1,2-H shifting rearrangement from **3** to **1**.

ous studies on similar rearrangement suggest that Path-a might go through quantum mechanical tunneling mechanism.[10] However, this process needs to be studied in detail and would be the attention of our future work.

4.4 Spectroscopic Parameters

Despite decades of experimental activity on $C_{11}H_8$, to the best of our knowledge, experimentally observed rotational constants (A_0, B_0, and C_0) are not available for any isomer. Theoretical rotational constants (A_e, B_e, and C_e) obtained from the optimized equilibrium geometries for isomers **1**-**11** calculated at the CCSD(T)/cc-pVDZ level of theory are given in Table 2. Centrifugal distortion constants have also been calculated for these low-lying isomers to aid their experimental identification. Since experimental values are unavailable at the moment, percentage errors cannot be calculated. Nevertheless, prior experience of some of us in comparison of experimental results with theoretical spectroscopic parameters in C_nH_2 (here n = 5,[77,78] 7,[79–81] and 9[82,83]) and SiC_4H_2[24] isomers suggest that the percentage error for coupled-cluster values lie within 2-3 % of experimental accuracy. The later scenario has been proven for other systems as well elsewhere in the literature.[84,85] Perhaps, by incorporating core-valence correlation, higher-order basis set effects, higher-order electron correlation effects, and corrections from the zero-point vibrational motion, one could improve the accuracy of spectroscopic parameters.[86,87] However, it is noted here that for a system of this size, such an exercise is computationally highly demanding and not viable with our current resources. The harmonic vibrational frequencies and infrared intensities calculated at the CCSD(T)/cc-pVDZ level of theory for isomers **1**-**11** are given in the ESI†. This would be helpful to infrared spectroscopists in assigning the corresponding vibrational transitions of low-lying isomers. While we certainly do not underestimate the importance of anharmonic vibrational corrections, it would be a computationally demanding task for a system of this size as each molecule contains 51 vibrational degrees of freedom (3N-6; here N = 19; 11 carbons and 8 hydrogens). Therefore, we have not done anharmonic corrections in the present study.

4.5 Aromatic Characteristics

To evaluate the aromatic stability of $C_{11}H_8$ isomers, NICS values have been calculated at 1 Å above the plane of the ring at the B3LYP/6-311+G(d,p) level of theory. These calculations have been done using the optimized equilibrium geometries at the same level. All values obtained have been found to be negative indicating their aromatic nature (see Table 1). Among the low-lying isomers, the highest value (-17.63 ppm) has been obtained for isomer **11**, which has been identified recently.[20] While some of the derivatives of **10** had been synthetically characterized in the laboratory,[28–31] which shows the second highest value (-15.15 ppm), the parent molecule remains elusive to date. Among the first eleven isomers, **1**, **2**, **3**, and **10** can be considered as molecules with 10 π electrons inside the ring. The least value (-10.60 ppm) has been obtained for isomer **2**, whose geometry is slightly puckered similar to **10**. It is noted here that aromatic stability is a response property whereas energetic stability is a state

property.[67] Therefore, one cannot arrive to a conclusion about the synthetic viability of a particular molecule based on aromatic characteristics alone. Furthermore, to assess the multireference character of $C_{11}H_8$ isomers, T_1 diagnostic values recommended by Lee and co-workers[70] have been calculated at the CCSD/6-311+G(d,p)//B3LYP/6-311+G(d,p) level of theory. For all low-lying isomers, the T_1 diagnostic value is below 0.02 (see Table 1). Therefore, we have not done multireference CC calculations for these molecules.

5 Conclusions

In summary, the PES of $C_{11}H_8$ has been computationally characterized using DFT and CC methods. All the stationary points spanning from 0 to 523 kJ mol^{-1} have been obtained initially at the B3LYP/6-311+G(d,p) level of theory. High-level electron correlation effects have been incorporated through CC methods for the low-lying eleven isomers at the CCSD(T)/cc-pVDZ level of theory. Rotational and centrifugal distortion constants for isomers **1**-**11** are obtained at the latter level. While isomers **1** and **3** are experimentally characterized already, **2**, and **6**-**10** remain elusive in the laboratory though they lie on the low-energy side. It is noted here that rotational spectra are unavailable for all isomers of $C_{11}H_8$ including **1** and **3**. It is also found through this work that 1,2-H transfer from **1** yields **14** and subsequent 1,2-H shift from **14** yields **2**. Appropriate transition states have been identified and intrinsic reaction coordinate calculations have been carried out for this conversion at the B3LYP/6-311+G(d,p) level of theory. It is believed that the current theoretical investigation may motivate and assist experimentalists in identifying the unknown molecules, especially the ones, which lie on the low-energy side.

Conflicts of Interest

There are no conflicts of interest to declare.

Acknowledgments

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Notes and references

1 B. L. McDowell and H. Rapoport, *J. Org. Chem.*, 1972, **37**, 3261–3265.
2 P. Eilbracht and K. Hafner, *Angew. Chem., Int. Ed.*, 1971, **10**, 751–752.
3 C. Wentrup and J. Benedikt, *J. Org. Chem.*, 1980, **45**, 1407–1409.
4 R. L. Barcus, L. M. Hadel, L. J. Johnston, M. S. Platz, T. G. Savino and J. C. Scaiano, *J. Am. Chem. Soc.*, 1986, **108**, 3928–3937.
5 R. J. Bailey, P. Card and H. Shechter, *J. Am. Chem. Soc.*, 1983, **105**, 6096–6103.
6 P. A. Bonvallet and R. J. McMahon, *J. Am. Chem. Soc.*, 1999, **121**, 10496–10503.
7 Y. Xie, P. R. Schreiner, P. v. R. Schleyer and H. F. Schaefer, *J. Am. Chem. Soc.*, 1997, **119**, 1370–1377.

Table 2 Rotational constants (in MHz), inertial axis dipole moment components, absolute dipole moments (in Debye), and centrifugal distortion constants (in MHz) of $C_{11}H_8$ isomers calculated at the CCSD(T)/cc-pVDZ level of theory

isomer	A_e	B_e	C_e	μ_a	μ_b	μ_c	$\|\mu\|$	D_J	D_K	D_{JK}	d_1	d_2
1	1769.57	1461.74	804.58	-0.55	-0.59	–	0.80	0.2038×10^{-4}	0.1859×10^{-4}	0.1129×10^{-4}	0.7895×10^{-5}	0.2549×10^{-4}
2	1824.23	1456.73	835.83	-0.33	-0.68	–	0.75	0.2578×10^{-4}	0.3735×10^{-4}	0.2194×10^{-4}	0.7630×10^{-5}	0.3432×10^{-4}
3	2017.00	1272.57	784.26	0.39	–	–	0.39	0.1216×10^{-4}	0.2428×10^{-4}	0.4356×10^{-4}	-0.5748×10^{-5}	-0.1904×10^{-5}
4	3694.04	660.54	562.35	0.20	0.30	–	0.36	0.4519×10^{-5}	0.2066×10^{-3}	0.1076×10^{-3}	-0.8242×10^{-6}	-0.2673×10^{-6}
5	2072.00	938.27	648.47	0.23	0.68	–	0.72	0.4802×10^{-4}	0.6580×10^{-3}	-0.2602×10^{-3}	-0.2061×10^{-4}	-0.1252×10^{-5}
6	1678.24	1126.69	677.00	-0.51	0.42	–	0.66	0.6304×10^{-4}	0.2908×10^{-3}	-0.1676×10^{-3}	-0.3091×10^{-4}	-0.3150×10^{-5}
7	1690.75	1113.22	674.12	-1.11	-0.06	–	1.11	0.5694×10^{-4}	0.2863×10^{-3}	-0.1537×10^{-3}	-0.2784×10^{-4}	-0.2858×10^{-5}
8	3178.42	711.30	583.38	-1.19	0.32	–	1.23	0.7511×10^{-5}	0.7395×10^{-3}	0.1358×10^{-4}	-0.2104×10^{-5}	-0.3525×10^{-6}
9	3196.34	709.11	582.50	-1.32	0.29	–	1.35	0.7260×10^{-5}	0.7305×10^{-3}	0.1883×10^{-4}	-0.2004×10^{-4}	-0.3473×10^{-6}
10	1828.24	1484.37	846.86	-0.21	0.00	-0.39	0.44	0.2488×10^{-4}	0.4507×10^{-5}	0.4844×10^{-4}	0.7732×10^{-5}	0.4882×10^{-4}
11	2058.99	950.62	694.95	-0.14	-0.28	0.24	0.40	0.7128×10^{-4}	0.7320×10^{-3}	-0.2259×10^{-3}	-0.1864×10^{-3}	-0.2987×10^{-5}

[a] Centrifugal distortion constants for isomers **1**, **2**, and **10** are from the A-reduced Hamiltonian, whereas for all other isomers they are from the S-reduced Hamiltonian, considering the fact that they are approaching close to the prolate limit.

8 P. A. Bonvallet, E. M. Todd, Y. S. Kim and R. J. McMahon, *J. Org. Chem.*, 2002, **67**, 9031–9042.
9 R. Vianello and Z. B. Maksić, *New J. Chem.*, 2008, **32**, 413–427.
10 S. Henkel, Y.-a. Huynh, P. Neuhaus, M. Winkler and W. Sander, *J. Am. Chem. Soc.*, 2012, **134**, 13204–13207.
11 D. Kvaskoff, J. Becker and C. Wentrup, *J. Org. Chem.*, 2015, **80**, 5030–5034.
12 S. Henkel, C. H. Pollok, T. Schleif and W. Sander, *Chem. Eur. J*, 2016, **22**, 12479–12486.
13 C. Wentrup, *Angew. Chem., Int. Ed.*, 2018, **57**, 11508–11521.
14 J. Becker and C. Wentrup, *J. Chem. Soc., Chem. Commun.*, 1980, 190–191.
15 T. A. Engler and H. Shechter, *J. Org. Chem*, 1999, **64**, 4247–4254.
16 C. Wentrup, C. Mayor, J. Becker and H. J. Lindner, *Tetrahedron*, 1985, **41**, 1601 – 1612.
17 J. G. M. Morton, H. Al-Shammari, Y. Sun, J. Zhu and D. W. Stephan, *Dalton Trans.*, 2014, **43**, 13219–13231.
18 A. Padwa, D. J. Austin, Y. Gareau, J. M. Kassir and S. L. Xu, *J. Am. Chem. Soc.*, 1993, **115**, 2637–2647.
19 A. Padwa, Y. Gareau and S. L. Xu, *Tetrahedron Lett.*, 1991, **32**, 983 – 986.
20 L. Zhao, M. B. Prendergast, R. I. Kaiser, B. Xu, W. Lu, U. Ablikim, M. Ahmed, A. D. Oleinikov, V. N. Azyazov, A. M. Mebel, A. H. Howlader and S. F. Wnuk, *ChemPhysChem*, 2019, **20**, 1437–1447.
21 J. Fulara, A. Nagy, K. Filipkowski, V. S. Thimmakondu, J. F. Stanton and J. P. Maier, *J. Phys. Chem. A*, 2013, **117**, 13605–13615.
22 V. S. Thimmakondu, *Chem. Phys.*, 2020, **538**, 110899.
23 A. P. Pandey, U. K. Padidela, L. K. Thulasiraman, R. Sethu, P. Vairaprakash and V. S. Thimmakondu, *J. Phys. Chem. A*, 2020, **124**, 7518–7525.
24 N. Job, A. Karton, K. Thirumoorthy, A. L. Cooksy and V. S. Thimmakondu, *J. Phys. Chem. A*, 2020, **124**, 987–1002.
25 L. Zhao, R. I. Kaiser, W. Lu, O. Kostko, M. Ahmed, M. M. Evseev, E. K. Bashkirov, A. D. Oleinikov, V. N. Azyazov, A. M. Mebel, A. H. Howlader and S. F. Wnuk, *Phys. Chem. Chem. Phys.*, 2020, **22**, 22493–22500.
26 C. He, G. R. Galimova, Y. Luo, L. Zhao, A. K. Eckhardt, R. Sun, A. M. Mebel and R. I. Kaiser, *Proc. Natl Acad. Sci.*, 2020, **117**, 30142–30150.
27 L. Zhao, M. Prendergast, R. I. Kaiser, B. Xu, U. Ablikim, W. Lu, M. Ahmed, A. D. Oleinikov, V. N. Azyazov, A. H. Howlader, S. F. Wnuk and A. M. Mebel, *Phys. Chem. Chem. Phys.*, 2019, **21**, 16737–16750.
28 T. L. Gilchrist, C. W. Rees, D. Tuddenham and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1980, 691–692.
29 H. C. Gibbard, C. J. Moody and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1985, 723–729.
30 Z. Lidert, R. McCague, C. J. Moody and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1985, 383–389.
31 T. Nishinaga, *Science of Synthesis*, Thieme Chemistry, 2010, vol. 45, p. 407.
32 P. Müller and D. Rodriguez, *Hel. Chim. Acta*, 1985, **68**, 975–980.
33 P. Müller and J.-P. Schaller, *Hel. Chim. Acta*, 1989, **72**, 1608–1617.
34 P. Müller, G. Bernardinelli and H. C. G.-N. Thi, *Hel. Chim. Acta*, 1989, **72**, 1627–1638.
35 E. Métay, Q. Hu and E.-i. Negishi, *Org. Lett.*, 2006, **8**, 5773–5776.
36 F. Esteban, L. Boughani, J. L. García Ruano, A. Fraile and J. Alemán, *Org. Biomol. Chem.*, 2017, **15**, 3901–3908.
37 R. Singha and J. K. Ray, *RSC Adv.*, 2014, **4**, 44052–44055.
38 Y.-X. Xue, Y.-Y. Zhu, L.-M. Gao, X.-Y. He, N. Liu, W.-Y. Zhang, J. Yin, Y. Ding, H. Zhou and Z.-Q. Wu, *J. Am. Chem. Soc.*, 2014, **136**, 4706–4713.
39 H. Bel Abed and S. A. Blum, *Org. Lett.*, 2018, **20**, 6673–6677.
40 R. A. Aitken and S. Seth, *J. Chem. Soc., Perkin Trans. 1*, 1994, 2461–2466.
41 A. Odedra, C.-J. Wu, T. B. Pratap, C.-W. Huang, Y.-F. Ran and R.-S. Liu, *J. Am. Chem. Soc.*, 2005, **127**, 3406–3412.
42 A. Das, H.-K. Chang, C.-H. Yang and R.-S. Liu, *Org. Lett.*, 2008, **10**, 4061–4064.
43 X. H. Wu, S. Jin, J. H. Liang, Z. Y. Li, G.-a. Yu and S. H. Liu, *Organometallics*, 2009, **28**, 2450–2459.
44 J. L. A. E. V. Höger, S.; Weber, *Beilstein J. Org. Chem.*, 2008, **4**, year.
45 C. Shu, C.-Y. Shi, Q. Sun, B. Zhou, T.-Y. Li, Q. He, X. Lu, R.-S. Liu and L.-W. Ye, *ACS Catalysis*, 2019, **9**, 1019–1025.
46 T. Watanabe, D. Hirose, D. P. Curran and T. Taniguchi, *Chem. Eur. J.*, 2017, **23**, 5404–5409.
47 K. Saito, H. Fushihara, K. Tominaga, K. Kumagai, K. Kondo, Satoru Fujimori, N. Abe and K. Takahashi, *Heterocycles*, 1993, **36**, 1997–2004.
48 M. P. Cava, K. Narasimhan, W. Zeiger, L. J. Radonovich and M. D. Glick, *J. Am. Chem. Soc.*, 1969, **91**, 2378–2379.
49 S. Stepanenko and B. Engels, *J. Comput. Chem.*, 2007, **28**, 601–611.
50 C. Grebner, J. Kästner, W. Thiel and B. Engels, *J. Chem. Theory Comput.*, 2013, **9**, 814–821.
51 S. Nandi, S. R. McAnanama-Brereton, M. P. Waller and A. Anoop, *Comput. Theor. Chem*, 2017, **1111**, 69 – 81.
52 S. Nandi, D. Bhattacharyya and A. Anoop, *Chem. Eur. J.*, 2018, **24**, 4885–4894.
53 M. Khatun, R. S. Majumdar and A. Anoop, *Front. Chem.*, 2019, **7**, 644.
54 P. P. Bera, K. W. Sattelmeyer, M. Saunders, H. F. Schaefer and P. v. R. Schleyer, *J. Phys. Chem. A*, 2006, **110**, 4287–4290.
55 O. Yañez, R. Báez-Grez, D. Inostroza, W. A. Rabanal-León, R. Pino-Rios, J. Garza and W. Tiznado, *J. Chem. Theory Comput.*, 2019, **15**, 1463–1475.
56 K. Thirumoorthy, A. L. Cooksy and V. S. Thimmakondu, *Phys. Chem. Chem. Phys.*, 2020, **22**, 5865–5872.
57 K. Thirumoorthy, V. Chandrasekaran, A. L. Cooksy and V. S. Thimmakondu, *Chemistry*, 2021, **3**, 13–27.
58 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785–789.
59 A. D. Becke, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1988, **38**, 3098–3100.
60 R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650–654.
61 T. Clark, J. Chandrasekhar, G. W. Spitznagel and P. V. R. Schleyer, *J. Comput. Chem.*, 1983, **4**, 294–301.
62 G. D. Purvis and R. J. Bartlett, *J. Chem. Phys.*, 1982, **76**, 1910–1918.
63 K. Raghavachari, G. W. Trucks, J. A. Pople and M. Head-Gordon, *Chem. Phys. Lett.*, 1989, **157**, 479–483.
64 R. J. Bartlett, J. Watts, S. Kucharski and J. Noga, *Chem. Phys. Lett.*, 1990, **165**, 513–522.
65 K. A. Peterson and T. H. Dunning, *J. Chem. Phys.*, 2002, **117**, 10548–10560.
66 J. Gauss and J. F. Stanton, *Chem. Phys. Lett.*, 1997, **276**, 70–77.
67 Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta and P. v. R. Schleyer, *Chem. Rev.*, 2005, **105**, 3842–3888.
68 H. Fallah-Bagher-Shaidaei, C. S. Wannere, C. Corminboeuf, R. Puchta and P. v. R. Schleyer, *Org. Lett.*, 2006, **8**, 863–866.
69 P. Seal and S. Chakrabarti, *J. Phys. Chem. A*, 2007, **111**, 9988–9994.
70 T. J. Lee and P. R. Taylor, *Int. J. Quantum Chem.*, 1989, **36**, 199–207.
71 J. F. Stanton, J. Gauss, L. Cheng, M. E. Harding, D. A. Matthews and P. G. Szalay, *CFOUR, Coupled-Cluster techniques for Computational Chemistry, a quantum-chemical program package*, With contributions from A.A. Auer, R.J. Bartlett, U. Benedikt, C. Berger, D.E. Bernholdt, Y.J. Bomble, O. Christiansen, F. Engel, R. Faber, M. Heckert, O. Heun, M. Hilgenberg, C. Huber, T.-C. Jagau, D. Jonsson, J. Jusélius, T. Kirsch, K. Klein, W.J. Lauderdale, F. Lipparini, T. Metzroth, L.A. Mück, D.P. O'Neill, D.R. Price, E. Prochnow, C. Puzzarini, K. Ruud, F. Schiffmann, W. Schwalbach, C. Simmons, S. Stopkowicz, A. Tajti, J. Vázquez, F. Wang, J.D. Watts and the integral packages MOLECULE (J. Almlöf and P.R. Taylor), PROPS (P.R. Taylor), ABACUS (T. Helgaker, H.J. Aa. Jensen, P. Jørgensen, and J. Olsen), and ECP routines by A. V. Mitin and C. van Wüllen. For the current version, see http://www.cfour.de.
72 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 16 Revision B.01*, 2016, Gaussian Inc. Wallingford CT.
73 E. F. Brown RFC, Coulston KJ and S. S, *Aus. J. Chem.*, 1987, **40**, 107–120.
74 K. Fukui, *Acc. Chem. Res.*, 1981, **14**, 363–368.
75 H. P. Hratchian and H. B. Schlegel, *Theory and Applications of Computational Chemistry*, Elsevier, Amsterdam, 2005, pp. 195 – 249.
76 G. I. Fray, G. M. Hearn and J. C. Petts, *Tetrahedron Lett.*, 1984, **25**, 2923 – 2924.
77 V. S. Thimmakondu and A. Karton, *Chem. Phys.*, 2018, **515**, 411 – 417.
78 V. S. Thimmakondu, I. Ulusoy, A. K. Wilson and A. Karton, *J. Phys. Chem. A*, 2019, **123**, 6618–6627.
79 V. S. Thimmakondu, *Comput. Theor. Chem*, 2016, **1079**, 1 – 10.
80 V. S. Thimmakondu and A. Karton, *Phys. Chem. Chem. Phys.*, 2017, **19**, 17685–17697.
81 K. Thirumoorthy, A. Karton and V. S. Thimmakondu, *J. Phys. Chem. A*, 2018, **122**, 9054–9064.
82 V. S. Thimmakondu and B. Sekar, *Comput. Theor. Chem.*, 2017, **1101**, 1 – 7.
83 K. Thirumoorthy, M. Viji, A. P. Pandey, T. G. Netke, B. Sekar, G. Yadav, S. Deshpande and V. S. Thimmakondu, *Chem. Phys.*, 2019, **527**, 110496.
84 S. L. Johansen, M.-A. Martin-Drumel and K. N. Crabtree, *J. Phys. Chem. A*, 2019, **123**, 5171–5177.
85 C. C. Womack, K. N. Crabtree, L. McCaslin, O. Martinez Jr., R. W. Field, J. F. Stanton and M. C. McCarthy, *Angew. Chem., Int. Ed.*, 2014, **53**, 4089–4092.
86 C. Puzzarini, M. Heckert and J. Gauss, *J. Chem. Phys.*, 2008, **128**, 194108.
87 C. Puzzarini, J. F. Stanton and J. Gauss, *Int. Rev. Phys. Chem.*, 2010, **29**, 273–367.

Supporting Information For:

Six low-lying isomers of $C_{11}H_8$ are unidentified in the laboratory - A theoretical study

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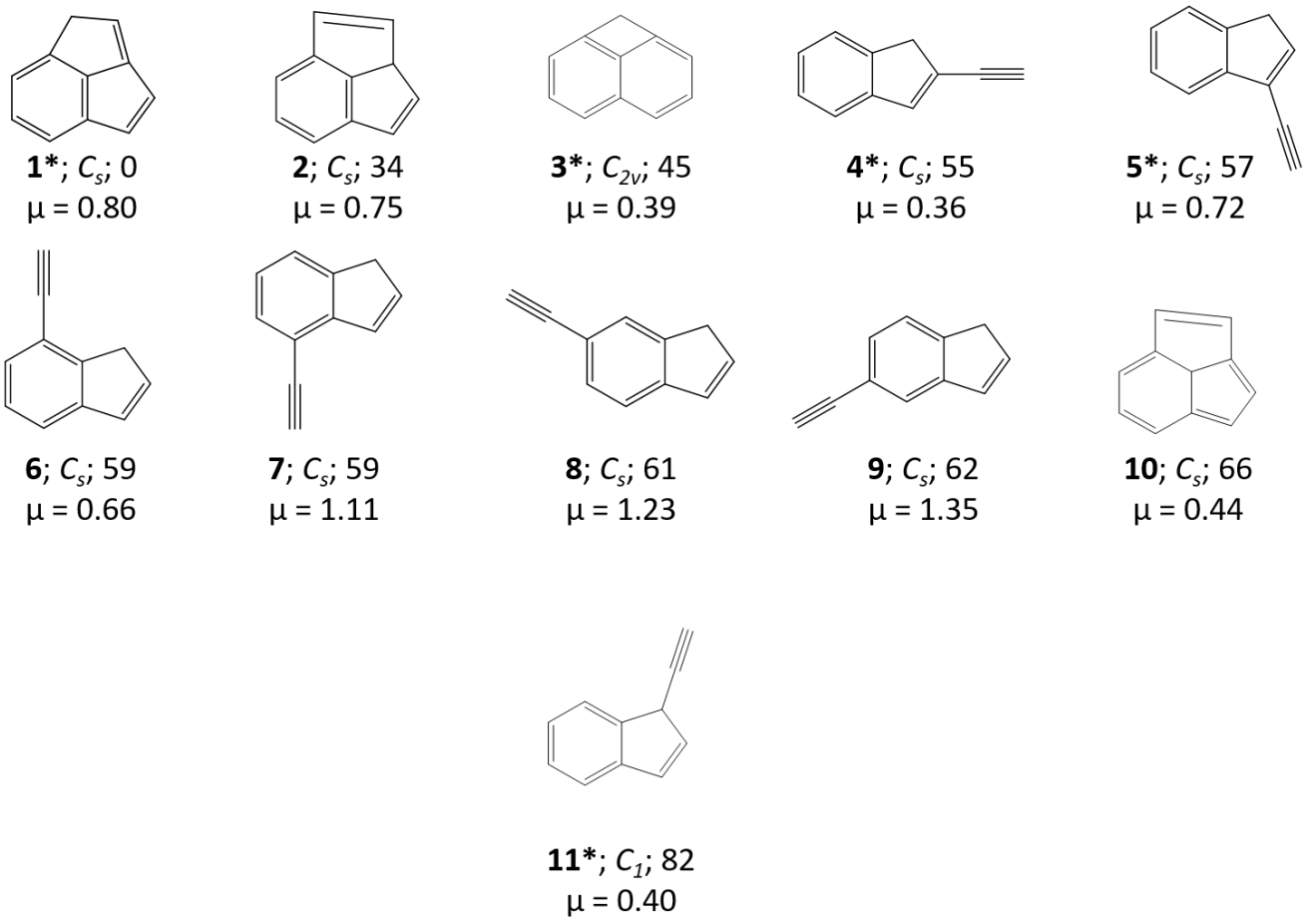


Figure S1: Isomers **1-11** of $C_{11}H_8$. ZPVE-corrected relative energies (in kJ mol^{-1}) and net dipole moments (in Debye) are obtained at the CCSD(T)/cc-pVDZ level. Experimentally detected isomers are marked with asterisk symbol.

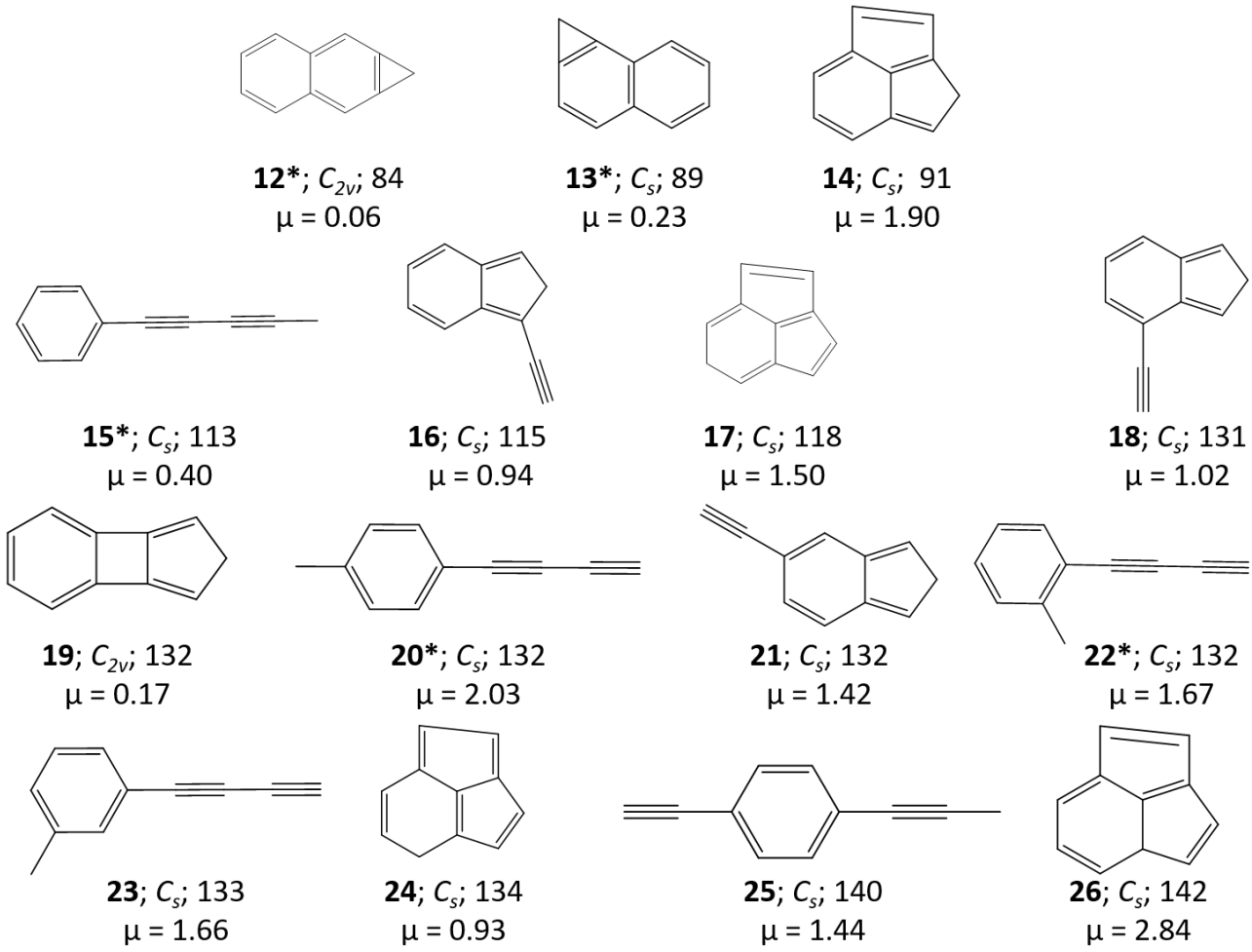


Figure S2: Isomers **12-26** of $C_{11}H_8$. ZPVE-corrected relative energies (in kJ mol^{-1}) and net dipole moments (in Debye) are obtained at the B3LYP/6-311+G(D,P) level. Experimentally detected isomers are marked with asterisk symbol.

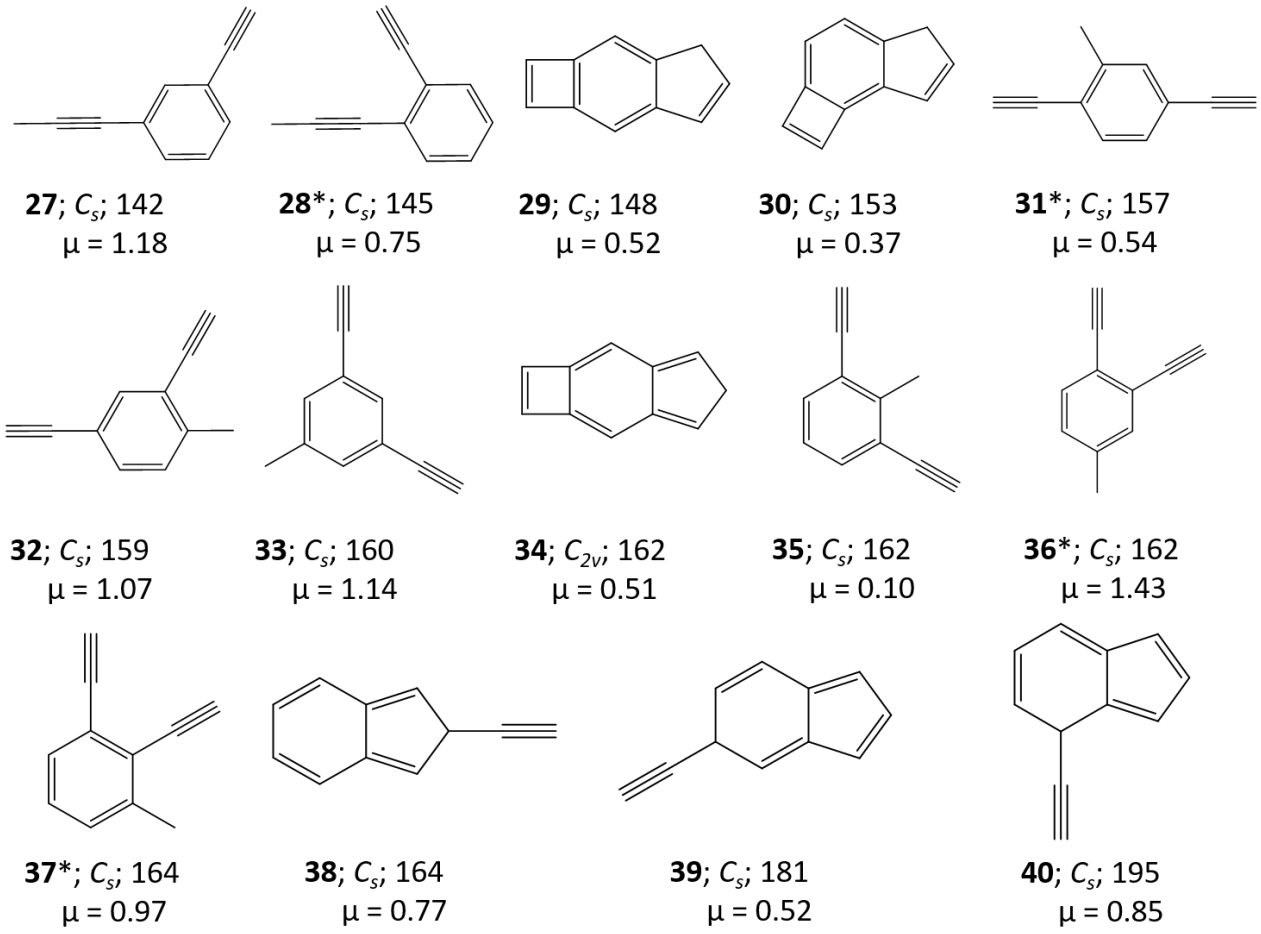


Figure S3: Isomers **27**-**40** of $C_{11}H_8$. ZPVE-corrected relative energies (in kJ mol^{-1}) and net dipole moments (in Debye) are obtained at the B3LYP/6-311+G(D,P) level. Experimentally detected isomers are marked with asterisk symbol.

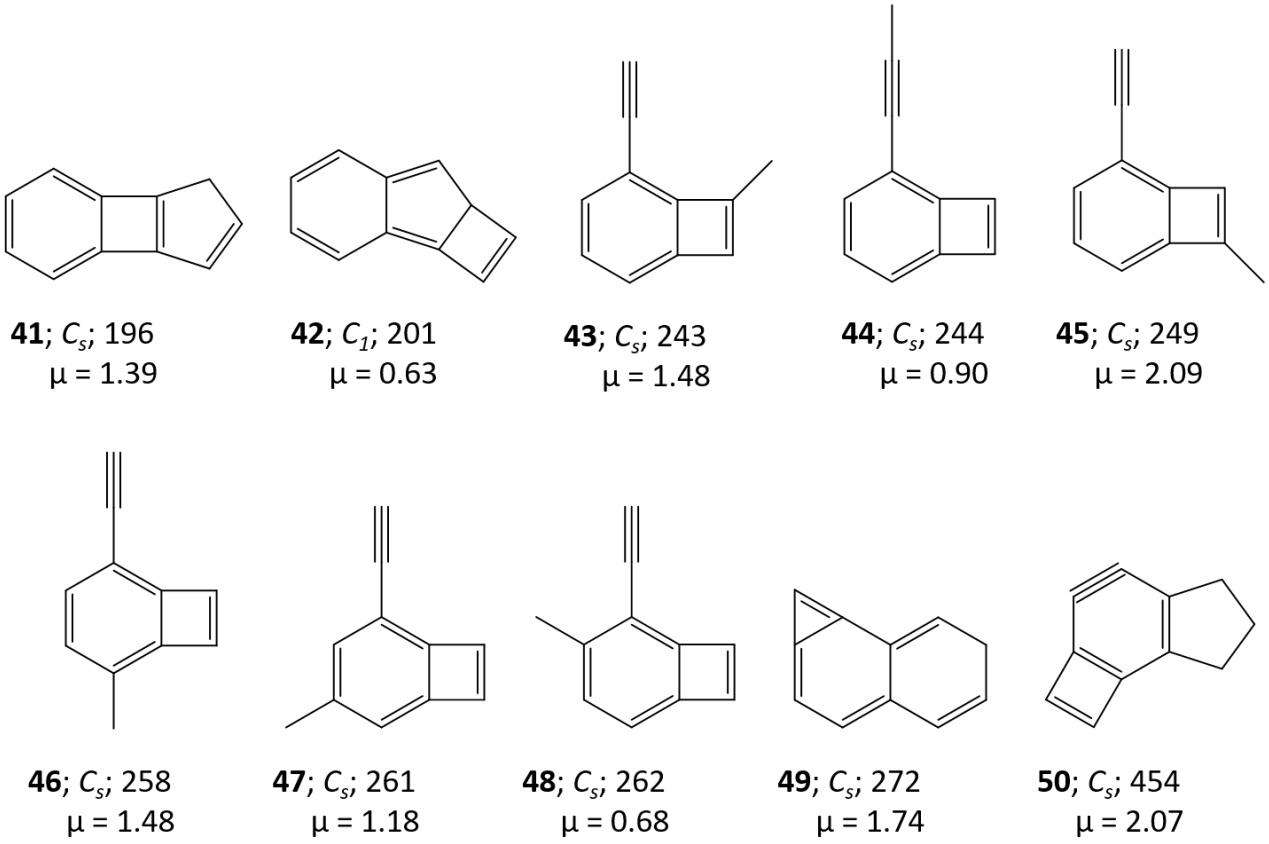


Figure S4: Isomers **41-50** of $C_{11}H_8$. ZPVE-corrected relative energies (in kJ mol^{-1}) and net dipole moments (in Debye) are obtained at the B3LYP/6-311+G(D,P) level. Experimentally detected isomers are marked with asterisk symbol.

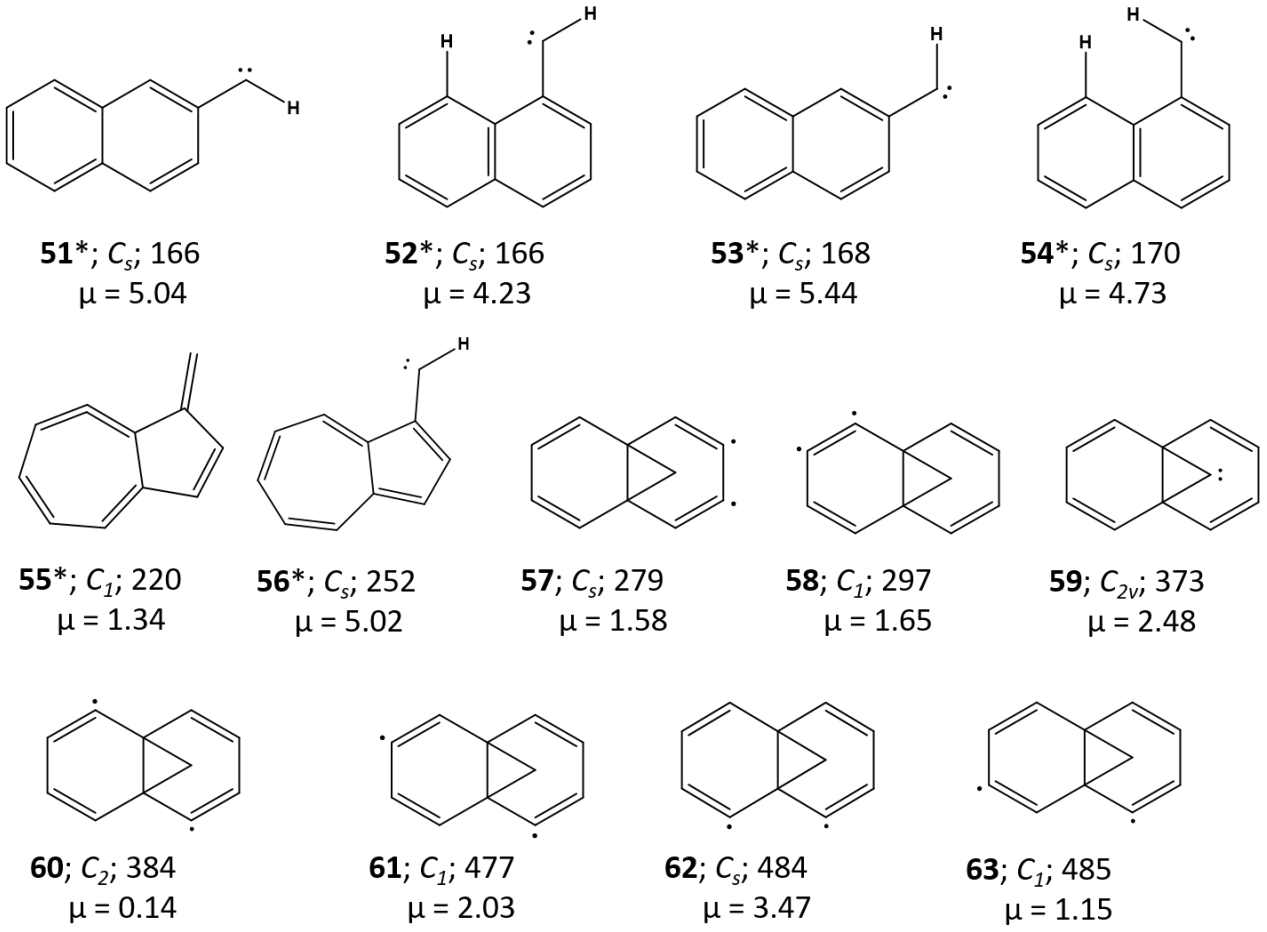


Figure S5: Isomers **51-63** of $C_{11}H_8$. ZPVE-corrected relative energies (in kJ mol^{-1}) and net dipole moments (in Debye) are obtained at the B3LYP/6-311+G(D,P) level. Experimentally detected isomers are marked with asterisk symbol.

Table S1: IUPAC or common names of $C_{11}H_8$ isomers of **1-39** in this work.

Isomer	Point group	IUPAC name
1	C_s	1H-cyclopenta[cd]indene
2	C_s	2aH-cyclopenta[cd]indene
3	C_{2v}	1H-cyclobuta[de]naphthalene
4	C_s	2-ethynyl-1H-indene
5	C_s	3-ethynyl-1H-indene
6	C_s	7-ethynyl-1H-indene
7	C_s	4-ethynyl-1H-indene
8	C_s	6-ethynyl-1H-indene
9	C_s	5-ethynyl-1H-indene
10	C_s	7bH-cyclopenta[cd]indene
11	C_1	1-ethynyl-1H-indene
12	C_{2v}	1H-cyclopropa[b]naphthalene
13	Cs	1H-cyclopropa[a]naphthalene
14	C_s	2H-cyclopenta[cd]indene
15	C_s	penta-1,3-diyn-1-ylbenzene
16	C_s	1-ethynyl-2H-indene
17	C_s	6H-cyclopenta[cd]indene
18	C_s	4-ethynyl-2H-indene
19	C_{2v}	2H-cyclopenta[3,4]cyclobuta[1,2]benzene
20	C_s	1-(buta-1,3-diyn-1-yl)-4-methylbenzene
21	C_s	5-ethynyl-2H-indene
22	C_s	1-(buta-1,3-diyn-1-yl)-2-methylbenzene
23	C_s	1-(buta-1,3-diyn-1-yl)-3-methylbenzene
24	C_1	7H-cyclopenta[cd]indene
25	C_s	1-ethynyl-4-(prop-1-yn-1-yl)benzene
26	C_s	7aH-cyclopenta[cd]indene
27	C_s	1-ethynyl-3-(prop-1-yn-1-yl)benzene
28	C_s	1-ethynyl-2-(prop-1-yn-1-yl)benzene
29	C_s	4H-cyclobuta[f]indene
30	C_s	5H-cyclobuta[e]indene
31	C_s	1,4-diethynyl-2-methylbenzene
32	C_s	2,4-diethynyl-1-methylbenzene
33	C_s	1,3-diethynyl-5-methylbenzene
34	C_{2v}	5H-cyclobuta[f]indene
35	C_s	1,3-diethynyl-2-methylbenzene
36	C_s	1,2-diethynyl-4-methylbenzene
37	C_s	1,2-diethynyl-3-methylbenzene
38	C_s	2-ethynyl-2H-indene
39	C_1	5-ethynyl-5H-indene

Table S2: IUPAC or common names of $C_{11}H_8$ isomers of **40-78** in this work.

Isomer	Point Group	IUPAC name
40	C_1	4-ethynyl-4H-indene
41	C_s	1H-cyclopenta[3,4]cyclobuta[1,2]benzene
42	C_1	7aH-cyclobuta[a]indene
43	C_s	2-ethynyl-8-methylbicyclo-[4.2.0]octa-1,3,5,7-tetraene
44	C_s	2-(prop-1-yn-1-yl)bicyclo-[4.2.0]octa-1,3,5,7-tetraene
45	C_s	2-ethynyl-7-methylbicyclo-[4.2.0]octa-1,3,5,7-tetraene
46	C_s	2-ethynyl-5-methylbicyclo-[4.2.0]octa-1,3,5,7-tetraene
47	C_s	2-ethynyl-4-methylbicyclo-[4.2.0]octa-1,3,5,7-tetraene
48	C_s	2-ethynyl-3-methylbicyclo-[4.2.0]octa-1,3,5,7-tetraene
49	C_s	6H-cyclopropa[a]naphthalene
50	C_1	6,7-dihydro-5H-cyclobuta[e]indenyl-4-carbyne
51	C_s	(E)-2-naphthylcarbene
52	C_s	(E)-1-naphthylcarbene
53	C_s	(Z)-2-naphthylcarbene
54	C_s	(Z)-1-naphthylcarbene
55	C_1	8-methylene-bicyclo[5.3.0]deca-1,3,5,6,9-pentaene
56	C_s	1-Azulenylcarbene
57	C_s	bicyclo[4.4.1]undeca-1,5,7,9-tetraen-3-yne
58	C_1	bicyclo[4.4.1]undeca-1,3,5,9-tetraen-7-yne
59	C_{2v}	bicyclo[4.4.1]undeca-1,3,5,7,9-pentaen-11-ylidene
60	C_2	2,7-didehydro-bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene
61	C_1	2,8-didehydro-bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene
62	C_s	2,10-didehydro-bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene
63	C_1	2,9-didehydro-bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene
64	C_1	1H-cyclobuta[cd]azulene
65	C_1	1aH-cyclobuta[cd]azulene
66	C_1	8-azulenylcarbene
67	C_1	1aH-cyclopropa[e]azulene
68	C_1	1H-cyclopropa[e]azulene
69	C_1	Bicyclo[6.3.0]undeca-1,2,4,6,8,10-hexaene
70	C_1	6aH-cyclopenta[a]pentalene
71	C_s	7H-cyclopenta[a]pentalene
72	C_1	3bH-cyclopenta[3,4]cyclobuta[1,2]benzene
73	C_1	Bicyclo[5.4.0]undeca-1,3,5,7,9-pentaene-11-ylidene
74	C_1	7aH-cyclopropa[a]azulene
75	C_1	Bicyclo[5.4.0]undeca-2,4,6,8,10,11-hexaene
76	C_1	Bicyclo[5.4.0]undeca-1,2,4,6,8,10-hexaene
77	C_1	1aH-cyclopropa[a]naphthalene
78	C_1	2-methylene-bicyclo[4.4.0]deca-3,5,7,9,10-pentaene
79	C_1	2,2a-dihydro-1Hcyclopenta[cd]indenylidene

Table S3: Electronic energies (in a.u), relative energies (ΔE; in kJ mol^{-1}), rotational constants (*Ae*, *Be*, and *Ce*; in MHz), inertial axis dipole moment components (μ_a and μ_b; in Debye) , and absolute dipole moments (|μ|; in Debye) of first **Eleven** low-lying isomers of $C_{11}H_8$ in their ground singlet electronic states calculated at the CCSD/cc-pVDZ level of theory.

Isomer	E (a.u.)	ΔE (kJ mol^{-1})	*Ae* (MHz)	*Be* (MHz)	*Ce* (MHz)	μ_a (Debye)	μ_b (Debye)	|μ| (Debye)
1	-422.6676932	0	1780.18	1469.49	809.1	-0.55	-0.55	0.78
2	-422.6551561	32	1832.48	1464.99	839.49	-0.32	-0.69	0.76
3	-422.6499683	45	2030.12	1280.56	789.26	0.4	-----	0.4
4	-422.6455859	56	3719.58	663.65	565.18	0.19	0.3	0.36
5	-422.6446007	58	2089.02	940.64	651.26	0.22	0.69	0.72
6	-422.6439397	60	1689.75	1130.98	680.41	-0.52	0.41	0.66
7	-422.643646	61	1700.87	1118.53	677.67	-1.1	-0.05	1.1
8	-422.6431217	62	3200.75	714.68	586.4	-1.19	0.32	1.23
9	-422.6428258	63	3216.09	712.67	585.55	-1.32	0.29	1.35
10	-422.6362527	79	1839.28	1495.18	851.93	-0.23	-0.37	0.44
11	-422.6360117	80	2072.57	954.21	697.83	-0.05	-0.11	0.09

Table S4: Single Point Energy (SPE; in a.u), relative energies (ΔE; in kJ mol^{-1}) of first **Eleven** low-lying isomers of $C_{11}H_8$ in their ground singlet electronic states calculated at the fc-CCSD(T)/cc-pVTZ//fc-CCSD(T)/cc-pVDZ level of theory.

Isomer	SPE	ΔE (kJ mol^{-1})
1	-423.13316490	0
2	-423.11979210	35
3	-423.11582430	46
4	-423.11082460	59
5	-423.10982850	61
6	-423.10935049	63
7	-423.10902503	63
8	-423.10830283	65
9	-423.10794298	66
10	-423.10649930	70
11	-423.10032200	86

Table S5: Computed energies of $C_{11}H_8$ isomers of **1-32** in their ground electronic states calculated at the B3LYP/6-311+G(D,P) level of theory.

Isomer	Point group	E (a.u.)	ZPVE (a.u.)	E+ZPVE (a.u.)	ΔE ($kJmol^{-1}$)	ΔE + ZPVE ($kJ\ mol^{-1}$)
1	C_s	-424.0375772	0.151674	-423.885903	0	0
2	C_s	-424.0222984	0.151621	-423.870678	40	35
3	C_{2v}	-424.0234022	0.15192	-423.871482	37	38
4	C_s	-424.0217755	0.149052	-423.872724	41	40
5	C_s	-424.0190519	0.148959	-423.870093	49	42
6	C_s	-424.0179758	0.14886	-423.869116	51	44
7	C_s	-424.0179818	0.148881	-423.869101	52	44
8	C_s	-424.0178194	0.148818	-423.869002	52	44
9	C_s	-424.0171975	0.148818	-423.86838	54	46
10	C_s	-424.0144219	0.151226	-423.863196	61	60
11	C_1	-424.0075011	0.149182	-423.858319	79	72
12	C_{2v}	-424.0047913	0.150774	-423.854018	86	84
13	C_s	-424.002932	0.150877	-423.852055	91	89
14	C_s	-424.0014978	0.150221	-423.851276	95	91
15	C_s	-423.9906357	0.147585	-423.843051	123	113
16	C_s	-423.9897916	0.147754	-423.842038	125	115
17	C_s	-423.9911873	0.150095	-423.841092	122	118
18	C_s	-423.9833963	0.147541	-423.835855	142	131
19	C_{2v}	-423.9862837	0.150476	-423.835808	135	132
20	C_s	-423.9820254	0.146432	-423.835593	146	132
21	C_s	-423.9828205	0.147368	-423.835453	144	132
22	C_s	-423.9820799	0.146633	-423.835447	146	132
23	C_1	-423.981681	0.14645	-423.835231	147	133
24	C_1	-423.9846049	0.149794	-423.834811	139	134
25	C_s	-423.978754	0.146217	-423.832537	154	140
26	C_s	-423.9825043	0.150499	-423.832005	145	142
27	C_s	-423.977884	0.146189	-423.831695	157	142
28	C_s	-423.9767107	0.146101	-423.83061	160	145
29	C_s	-423.978669	0.149242	-423.829427	155	148
30	C_s	-423.9773871	0.149621	-423.827766	158	153
31	C_s	-423.9713885	0.145429	-423.825959	174	157
32	C_s	-423.9707916	0.145477	-423.825315	175	159

Table S6: Computed energies of $C_{11}H_8$ isomers of **33-63** in their ground electronic states calculated at the B3LYP/6-311+G(D,P) level of theory.

Isomer	Point Group	E (a.u.)	ZPVE (a.u.)	E+ZPVE (a.u.)	ΔE (kJ mol^{-1})	ΔE + ZPVE (kJ mol^{-1})
33	C_s	-423.9702129	0.145268	-423.824945	177	160
34	C_{2v}	-423.9733269	0.149133	-423.824194	169	162
35	C_s	-423.9695026	0.145384	-423.824119	179	162
36	C_s	-423.9690752	0.145026	-423.824049	180	162
37	C_s	-423.968852	0.145317	-423.823535	180	164
38	C_s	-423.9714043	0.147946	-423.823458	174	164
39	C_1	-423.9650429	0.148091	-423.816952	190	181
40	C_1	-423.9597983	0.147996	-423.811803	204	195
41	C_s	-423.9606609	0.149501	-423.81116	202	196
42	C_1	-423.9589267	0.149454	-423.809473	206	201
43	C_s	-423.9398756	0.146361	-423.793515	256	243
44	C_s	-423.939899	0.146847	-423.793052	256	244
45	C_s	-423.9372062	0.146041	-423.791165	264	249
46	C_s	-423.9335588	0.145979	-423.78758	273	258
47	C_s	-423.9327106	0.14606	-423.786651	275	261
48	C_s	-423.9324176	0.14616	-423.786257	276	262
49	C_s	-423.9310783	0.148616	-423.782462	280	272
50	C_1	-423.8615557	0.148499	-423.713056	462	454
51	C_s	-423.9716171	0.148859	-423.822758	173	166
52	C_s	-423.9716262	0.148952	-423.822674	173	166
53	C_s	-423.9706353	0.148747	-423.821888	176	168
54	C_s	-423.9699361	0.148926	-423.82101	178	170
55	C_1	-423.9467347	0.148096	-423.804357	214	238
56	C_s	-423.9385996	0.148666	-423.789934	260	252
57	C_s	-423.9294775	0.150027	-423.77945	284	279
58	C_1	-423.9224745	0.149759	-423.772716	302	297
59	C_{2v}	-423.8897451	0.145946	-423.743799	388	373
60	C_2	-423.8887296	0.148977	-423.739753	391	384
61	C_1	-423.8508767	0.146612	-423.704265	490	477
62	C_s	-423.849082	0.147373	-423.701709	495	484
63	C_1	-423.848391	0.147375	-423.701016	497	485
. **.**						

Table S7: Singlet-Triplet energy gaps of $C_{11}H_8$ isomers of **1-18** calculated at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer	Point Group	Singlet			Triplet			ΔE_{T-S} (kJ mol^{-1})
		E (a.u.)	ZPVE (a.u.)	E+ZPVE (a.u.)	E (a.u.)	ZPVE (a.u.)	E+ZPVE (a.u.)	
1	C_s	-424.0375772	0.151674	-423.885903	-423.9641732	0.147234	-423.816939	181
2	C_s	-424.0222984	0.151621	-423.870678	-423.9214642	0.144418	-423.777047	204
3	C_{2v}	-424.0234022	0.15192	-423.871482	-423.9224321	0.146647	-423.775785	251
4	C_s	-424.0217755	0.149052	-423.872724	-423.9397501	0.144764	-423.794987	246
5	C_s	-424.0190519	0.148959	-423.870093	-423.9300112	0.143785	-423.786226	220
6	C_s	-424.0179758	0.14886	-423.869116	-423.9161867	0.143555	-423.772632	253
7	C_s	-424.0179818	0.148881	-423.869101	-423.9204973	0.143853	-423.776645	243
8	C_s	-424.0178194	0.148818	-423.869002	-423.9247264	0.144105	-423.780621	232
9	C_s	-424.0171975	0.148818	-423.86838	-423.9154455	0.143557	-423.771888	253
10	C_s	-424.0144219	0.151226	-423.863196	-423.914996	0.150581	-423.764415	259
11	C_1	-424.0075011	0.149182	-423.858319	-423.9077122	0.144105	-423.763607	249
12	C_{2v}	-424.0047913	0.150774	-423.854018	-423.902617	0.145082	-423.757535	253
13	Cs	-424.002932	0.150877	-423.852055	-423.9085282	0.145467	-423.763062	234
14	C_s	-424.0014978	0.150221	-423.851276	-423.9799623	0.148427	-423.831536	52
15	C_s	-423.9906357	0.147585	-423.843051	-423.8915066	0.142728	-423.748779	248
16	C_s	-423.9897916	0.147754	-423.842038	-423.9554977	0.14542	-423.810078	84
17	C_s	-423.9911873	0.150095	-423.841092	-423.9493943	0.146452	-423.802942	100
18	C_s	-423.9833963	0.147541	-423.835855	-423.9438441	0.144965	-423.798879	97

Table S8: Singlet-Triplet energy gaps of $C_{11}H_8$ isomers of **19-36** calculated at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer	Point Group	Singlet			Triplet			ΔE_{T-S} (kJ mol^{-1})
		E (a.u.)	ZPVE (a.u.)	E+ZPVE (a.u.)	E (a.u.)	ZPVE (a.u.)	E+ZPVE (a.u.)	
19	C_{2v}	-423.9862837	0.150476	-423.835808	-423.8628865	0.146646	-423.71624	314
20	Cs	-423.9820254	0.146432	-423.835593	-423.8835931	0.141078	-423.742515	244
21	Cs	-423.9828205	0.147368	-423.835453	-423.9424513	0.144857	-423.797594	99
22	Cs	-423.9820799	0.146633	-423.835447	-423.8838995	0.141482	-423.742418	244
23	C_1	-423.981681	0.14645	-423.835231	-423.883129	0.141381	-423.741748	245
24	C_1	-423.9846049	0.149794	-423.834811	-423.9631543	0.148441	-423.814714	53
25	C_s	-423.978754	0.146217	-423.832537	-423.8806603	0.141269	-423.739391	245
26	C_s	-423.9825043	0.150499	-423.832005	-423.9439138	0.147555	-423.796359	94
27	C_s	-423.977884	0.146189	-423.831695	-423.867667	0.139451	-423.728216	272
28	C_s	-423.9767107	0.146101	-423.83061	-423.8721791	0.140346	-423.731833	259
29	C_s	-423.978669	0.149242	-423.829427	-423.9401847	0.14707	-423.793115	95
30	C_s	-423.9773871	0.149621	-423.827766	-423.9355798	0.14695	-423.78863	103
31	C_s	-423.9713885	0.145429	-423.825959	-423.873893	0.140438	-423.733455	243
32	C_s	-423.9707916	0.145477	-423.825315	-423.8617299	0.138954	-423.722776	269
33	C_s	-423.9702129	0.145268	-423.824945	-423.8594892	0.138249	-423.72124	272
34	C_{2v}	-423.9733269	0.149133	-423.824194	-423.8871198	0.147291	-423.739829	222
35	C_s	-423.9695026	0.145384	-423.824119	-423.8591456	0.13856	-423.720586	272
36	C_s	-423.9690752	0.145026	-423.824049	-423.8665777	0.139529	-423.727048	255

Table S9: Singlet-Triplet energy gaps of $C_{11}H_8$ isomers of **37**-**54** calculated at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer	Point Group	Singlet			Triplet			ΔE_{T-S} (kJ mol^{-1})
		E (a.u.)	ZPVE (a.u.)	E+ZPVE (a.u.)	E (a.u.)	ZPVE (a.u.)	E+ZPVE (a.u.)	
37	C_s	-423.968852	0.145317	-423.823535	-423.864378	0.139484	-423.724894	259
38	C_s	-423.9714043	0.147946	-423.823458	-423.9320166	0.145363	-423.786653	97
39	C_1	-423.9650429	0.148091	-423.816952	-423.9159473	0.144924	-423.771024	121
40	C_1	-423.9597983	0.147996	-423.811803	-423.9153324	0.144929	-423.770403	109
41	C_s	-423.9606609	0.149501	-423.81116	-423.9235727	0.147572	-423.776001	92
42	C_1	-423.9589267	0.149454	-423.809473	-423.9299274	0.147233	-423.782694	70
43	C_s	-423.9398756	0.146361	-423.793515	-423.8948276	0.143675	-423.751152	111
44	C_s	-423.939899	0.146847	-423.793052	-423.8974135	0.144353	-423.75306	105
45	C_s	-423.9372062	0.146041	-423.791165	-423.8953746	0.143868	-423.751507	104
46	C_s	-423.9335588	0.145979	-423.78758	-423.8905266	0.143314	-423.747212	106
47	C_s	-423.9327106	0.14606	-423.786651	-423.8896813	0.1433	-423.746381	106
48	C_s	-423.9324176	0.14616	-423.786257	-423.8900261	0.143486	-423.74654	104
49	C_s	-423.9310783	0.148616	-423.782462	-423.8952216	0.144427	-423.750795	83
50	C_1	-423.8615557	0.148499	-423.713056	-423.8188956	0.147491	-423.671405	109
51	C_s	-423.9716171	0.148859	-423.822758	-423.9793603	0.148072	-423.831288	-22
52	C_s	-423.9716262	0.148952	-423.822674	-423.9805198	0.148095	-423.832425	-26
53	C_s	-423.9706353	0.148747	-423.821888	-423.9793814	0.148142	-423.831239	-25
54	C_s	-423.9699361	0.148926	-423.82101	-423.9791855	0.148044	-423.831142	-27

Table S10: Singlet-Triplet Energy gaps of $C_{11}H_8$ isomers of **55**-**63** calculated at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer	Point Group	Singlet			Triplet			ΔE_{T-S} (kJ mol^{-1})
		E (a.u.)	ZPVE (a.u.)	E+ZPVE (a.u.)	E (a.u.)	ZPVE (a.u.)	E+ZPVE (a.u.)	
55	C_1	-423.9467347	0.148096	-423.804357	-423.9399362	0.146225	-423.793711	-28
56	C_s	-423.9385996	0.148666	-423.789934	-423.9353531	0.146296	-423.789057	2
57	C_s	-423.9294775	0.150027	-423.77945	-423.8475051	0.144341	-423.703164	200
58	C_1	-423.9224745	0.149759	-423.772716	-423.8635652	0.148236	-423.715329	151
59	C_{2v}	-423.8897451	0.145946	-423.743799	-423.8880799	0.148215	-423.739865	10
60	C_2	-423.8887296	0.148977	-423.739753	-423.8713361	0.147878	-423.723459	43
61	C_1	-423.8508767	0.146612	-423.704265	-423.8740306	0.147688	-423.726342	-58
62	C_s	-423.849082	0.147373	-423.701709	-423.8747058	0.147712	-423.726994	-66
63	C_1	-423.848391	0.147375	-423.701016	-423.8717258	0.1 47822	-423.723904	-60

Table S11: Dipole moments (in Debye) and rotational constants (in GHz) of $C_{11}H_8$ isomers of **1-32** in their ground electronic states calculated at the B3LYP/6-311+G(D,P) level of theory.

Isomer	Point Group	ΔE + ZPVE (kJ mol^{-1})	|μ| (in Debye)	Rotational Constants (in GHz)		
				A_e	B_e	C_e
1	C_s	0	1.01	1.80935	1.49057	0.8214
2	C_s	35	0.83	1.8567	1.48846	0.85184
3	C_{2v}	38	0.49	2.05879	1.30006	0.80091
4	C_s	40	0.54	3.77607	0.67602	0.57541
5	C_s	42	1.00	2.12888	0.95615	0.6625
6	C_s	44	0.80	1.72278	1.14641	0.69127
7	C_s	44	1.46	1.73162	1.13648	0.68906
8	C_s	44	1.55	3.25294	0.72745	0.59669
9	C_s	46	1.72	3.26608	0.72562	0.59589
10	C_s	60	0.52	1.86262	1.51744	0.86432
11	C_1	72	0.51	2.12181	0.96248	0.70393
12	C_{2v}	84	0.06	3.08552	0.89258	0.69549
13	C_s	89	0.23	2.46019	1.01211	0.72052
14	C_s	91	1.89	1.76928	1.51035	0.81888
15	C_s	113	0.4	5.49699	0.36288	0.34113
16	C_s	115	0.94	2.15961	0.94662	0.6608
17	C_s	118	1.50	1.76101	1.50621	0.81577
18	C_s	131	1.02	1.73445	1.12386	0.68482
19	C_{2v}	132	0.17	3.36921	0.82112	0.6629
20	C_s	132	2.03	5.53305	0.42554	0.39612
21	C_s	132	1.42	3.22995	0.72828	0.59645
22	C_s	132	1.67	2.79636	0.57094	0.47552
23	C_1	133	1.66	3.07228	0.48564	0.42045
24	C_1	134	0.93	1.81627	1.46831	0.81593
25	C_s	140	1.44	5.50292	0.45326	0.41986
26	C_s	142	2.84	1.79887	1.48159	0.81244
27	C_s	142	1.18	2.28421	0.57143	0.45839
28	C_s	145	0.75	1.71444	0.81665	0.55507
29	C_s	148	0.52	3.39444	0.84606	0.68009
30	C_s	153	0.37	2.46625	1.01931	0.72444
31	C_s	157	0.54	2.86791	0.67603	0.54892
32	C_s	159	1.07	2.09663	0.76841	0.56427

Table S12: Dipole moments (in Debye) and rotational constants (in GHz) of $C_{11}H_8$ isomers of **33-63** in their ground electronic states calculated at the B3LYP/6-311+G(D,P) level of theory.

Isomer	Point Group	ΔE + ZPVE (kJ mol^{-1})	|μ| (in Debye)	Rotational Constants (in GHz)		
				A_e	B_e	C_e
33	C_s	160	1.14	1.39261	0.90195	0.54928
34	C_{2v}	162	0.51	3.28097	0.86657	0.6884
35	C_s	162	0.1	1.98382	0.88648	0.61501
36	C_s	162	1.43	1.87422	0.86985	0.59631
37	C_s	164	0.97	1.49709	1.16356	0.65735
38	C_s	164	0.77	3.1439	0.7242	0.62523
39	C_1	181	0.52	2.75987	0.78399	0.64947
40	C_1	195	0.85	1.7499	1.11733	0.71465
41	C_s	196	1.39	3.41132	0.7995	0.65029
42	C_1	201	0.63	2.76454	0.97712	0.75948
43	C_s	243	1.48	1.33897	1.31408	0.66592
44	C_s	244	0.9	2.1916	0.72565	0.54701
45	C_s	249	2.09	1.95403	0.89128	0.61442
46	C_s	258	1.48	2.07419	0.92019	0.63993
47	C_s	261	1.18	1.45326	1.12792	0.63755
48	C_s	262	0.68	1.70604	1.13024	0.6827
49	C_s	272	1.74	2.48014	0.99991	0.71567
50	C_1	454	2.07	2.64117	0.97093	0.72384
51	C_s	166	5.04	2.83522	0.88065	0.67194
52	C_s	166	4.23	2.05468	1.13925	0.73289
53	C_s	168	5.44	2.832	0.88056	0.67171
54	C_s	170	4.73	2.03363	1.15865	0.73811
55	C_s	220	1.34	2.20453	1.02886	0.70148
56	C_s	252	5.02	2.19733	1.04085	0.70629
57	C_s	279	1.58	2.07009	1.31232	0.89797
58	C_1	297	1.65	2.19764	1.22439	0.8932
59	C_{2v}	373	2.48	2.24459	1.18985	0.83305
60	C_2	384	0.14	2.22115	1.16391	0.91473
61	C_1	477	2.03	2.05235	1.28852	0.92556
62	C_s	484	3.47	2.28951	1.17049	0.86033
63	C_1	485	1.15	2.08064	1.2423	0.92368

Table S13: NICS (1Å) (in ppm) values of $C_{11}H_8$ isomers of **1-36** in their ground electronic states calculated B3LYP/6-311+G(D,P) level of theory.

Isomer	Point group	Isotropic shift (in ppm)
1	C_s	-14.9
2	C_s	-10.6
3	C_{2v}	-13.92
4	C_s	-14.59
5	C_s	-14.68
6	C_s	-14.11
7	C_s	-14.42
8	C_s	-13.44
9	C_s	-13.47
10	C_s	-15.15
11	C_1	-17.63
12	C_{2v}	-15.59
13	C_s	-16.40
14	C_s	-12.34
15	C_s	-5.13
16	C_s	-11.02
17	C_s	-12.39
18	C_s	-7.75
19	C_{2v}	-1.38
20	C_s	-15.01
21	C_s	-3.10
22	C_s	-8.58
23	C_1	-12.28
24	C_1	-11.41
25	C_s	-12.33
26	C_s	-15.07
27	C_s	-14.97
28	C_s	-9.51
29	C_s	-3.51
30	C_s	-7.04
31	C_s	-10.54
32	C_s	-11.78
33	C_s	-9.86
34	C_{2v}	-1.05
35	C_s	-15.16
36	C_s	-13.21

Table S14: NICS (1Å) (in ppm) values of $C_{11}H_8$ isomers of **37-63** in their ground electronic states calculated B3LYP/6-311+G(D,P) level of theory.

Isomer	Point Group	Isotropic shift (ppm)
37	C_s	-14.95
38	C_s	-4.51
39	C_1	-3.86
40	C_1	-12.79
41	C_s	11.61
42	C_1	-16.59
43	C_s	-10.31
44	C_s	-11.91
45	C_s	-6.79
46	C_s	-5.16
47	C_s	-4.52
48	C_s	-8.34
49	C_s	-2.43
50	C_1	-12.45
51	C_s	-15.63
52	C_s	-13.98
53	C_s	-15.68
54	C_s	-16.49
55	C_s	-13.98
56	C_s	-14.08
57	C_s	-29.39
58	C_1	-39.38
59	C_{2v}	115.94
60	C_2	-47.83
61	C_1	-34.46
62	C_s	-68.28
63	C_1	-40.65

Table S15: T_1 Diagnostic values of $C_{11}H_8$ isomers of **1-32** in their ground electronic states calculated CCSD/6-311+G(D,P)//B3LYP/6-311+G(D,P) level of theory.

Isomer	Point group	T_1 Diagnostic
1	C_s	0.011
2	C_s	0.011
3	C_{2v}	0.011
4	C_s	0.012
5	C_s	0.012
6	C_s	0.011
7	C_s	0.012
8	C_s	0.012
9	C_s	0.011
10	C_s	0.012
11	C_1	0.012
12	C_{2v}	0.012
13	C_s	0.011
14	C_s	0.013
15	C_s	0.013
16	C_s	0.015
17	C_s	0.013
18	C_s	0.013
19	C_{2v}	0.011
20	C_s	0.012
21	C_s	0.013
22	C_s	0.013
23	C_1	0.001
24	C_1	0.014
25	C_s	0.012
26	C_s	0.013
27	C_s	0.012
28	C_s	0.012
29	C_s	0.013
30	C_s	0.012
31	C_s	0.012
32	C_s	0.012

Table S16: T_1 diagnostic values of $C_{11}H_8$ isomers of **33-63** in their ground electronic states calculated CCSD/6-311+G(D,P)//B3LYP/6-311+G(D,P) level of theory.

Isomer	Point Group	T_1 Diagnostic
33	C_s	0.012
34	C_{2v}	0.013
35	C_s	0.013
36	C_s	0.012
37	C_s	0.012
38	C_s	0.012
39	C_1	0.012
40	C_1	0.012
41	C_s	0.012
42	C_1	0.013
43	C_s	0.015
44	C_s	0.012
45	C_s	0.015
46	C_s	0.012
47	C_s	0.012
48	C_s	0.012
49	C_s	0.018
50	C_1	0.015
51	C_s	0.013
52	C_s	0.015
53	C_s	0.013
54	C_s	0.013
55	C_s	0.013
56	C_s	0.014
57	C_s	0.014
58	C_1	0.015
59	C_{2v}	0.014
60	C_2	0.027
61	C_1	0.025
62	C_s	0.035
63	C_1	0.070

Table S17: Optimized geometries of the singlet and triplet ground electronic state of 1H-cyclopenta[cd]indene (**1**) and 2aH-cyclopenta[cd]indene (**2**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-1

	Singlet				Triplet		
C	-0.274920	-2.478917	0.000000	C	-0.480906	-2.453809	0.000000
H	-0.384534	-3.558161	0.000000	H	-0.651989	-3.524880	0.000000
C	-1.308678	-0.303294	0.000000	C	-1.362887	-0.197458	0.000000
C	-1.450179	-1.695433	0.000000	C	-1.588389	-1.609519	0.000000
H	-2.416827	-2.187578	0.000000	H	-2.587495	-2.030657	0.000000
C	1.176118	-0.555403	0.000000	C	1.117608	-0.619178	0.000000
C	0.000000	0.140753	0.000000	C	0.000000	0.164802	0.000000
C	-2.097883	0.952681	0.000000	C	-2.057334	1.022348	0.000000
C	0.125000	1.571185	0.000000	C	0.235930	1.581409	0.000000
C	1.033397	-1.948327	0.000000	C	0.872974	-2.001787	0.000000
H	1.880661	-2.625694	0.000000	H	1.671721	-2.735648	0.000000
C	-1.265828	2.045859	0.000000	C	-1.035823	2.152320	0.000000
H	-1.595473	3.075336	0.000000	H	-1.305462	3.199621	0.000000
H	-3.179366	1.009745	0.000000	H	-3.127733	1.177753	0.000000
C	1.455943	1.839419	0.000000	C	1.642898	1.744092	0.000000
C	2.260029	0.523431	0.000000	C	2.304559	0.353493	0.000000
H	2.916394	0.464114	0.877133	H	2.950237	0.214337	0.877008
H	1.944757	2.806393	0.000000	H	2.208703	2.664854	0.000000
H	2.916394	0.464114	-0.877133	H	2.950237	0.214337	-0.877008

Isomer-2

	Singlet				Triplet		
C	0.420264	0.208306	0.000000	C	0.509977	0.255289	0.000000
C	0.223653	-0.404606	1.226278	C	0.259426	-0.359651	1.222535
C	0.223653	-1.806552	1.234564	C	0.259426	-1.844601	1.230303
C	0.287632	-2.476775	0.000000	C	0.236898	-2.507537	0.000000
C	0.223653	-1.806552	-1.234564	C	0.259426	-1.844601	-1.230303
C	0.223653	-0.404606	-1.226278	C	0.259426	-0.359651	-1.222535
C	-0.285066	0.666649	-2.111277	C	-0.352847	0.626193	-2.057436
C	-0.473356	1.807651	-1.402887	C	-0.509834	1.822651	-1.371653
C	0.112392	1.655245	0.000000	C	0.140045	1.699967	0.000000
C	-0.473356	1.807651	1.402887	C	-0.509834	1.822651	1.371653
C	-0.285066	0.666649	2.111277	C	-0.352847	0.626193	2.057436
H	0.094103	-2.376217	2.148226	H	0.299926	-2.403265	2.157309
H	0.279597	-3.561548	0.000000	H	0.245807	-3.592911	0.000000
H	0.094103	-2.376217	-2.148226	H	0.299926	-2.403265	-2.157309
H	-0.524159	0.543884	-3.160877	H	-0.678616	0.459974	-3.077838
H	-0.823698	2.745335	-1.815566	H	-0.857157	2.752713	-1.802328
H	1.039578	2.257186	0.000000	H	1.030332	2.352650	0.000000
H	-0.823698	2.745335	1.815566	H	-0.857157	2.752713	1.802328
H	-0.524159	0.543884	3.160877	H	-0.678616	0.459974	3.077838

Table S18: Optimized geometries of the singlet and triplet ground electronic state of 1H-cyclobuta[de]naphthalene (**3**) and 2-ethynyl-1H-indene (**4**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-3

	Singlet				Triplet		
C	0.000000	0.000000	0.226419	C	0.000000	0.000000	0.235284
C	0.000000	0.000000	-1.157440	C	0.000000	0.000000	-1.163597
C	0.000000	1.328222	-1.681702	C	0.000000	1.314880	-1.686594
C	0.000000	2.412400	-0.806900	C	0.000000	2.466903	-0.774708
C	0.000000	2.324081	0.629360	C	0.000000	2.377400	0.601685
C	0.000000	1.049132	1.139700	C	0.000000	1.046230	1.139213
C	0.000000	0.000000	2.312437	C	0.000000	0.000000	2.312811
C	0.000000	-1.049132	1.139700	C	0.000000	-1.046230	1.139213
C	0.000000	-2.324081	0.629360	C	0.000000	-2.377400	0.601685
C	0.000000	-2.412400	-0.806900	C	0.000000	-2.466903	-0.774708
C	0.000000	-1.328222	-1.681702	C	0.000000	-1.314880	-1.686594
H	0.000000	1.512999	-2.750767	H	0.000000	1.505611	-2.753959
H	0.000000	3.407032	-1.241296	H	0.000000	3.450008	-1.232006
H	0.000000	3.232399	1.221258	H	0.000000	3.274640	1.209741
H	0.891575	0.000000	2.943805	H	0.891528	0.000000	2.945148
H	-0.891575	0.000000	2.943805	H	-0.891528	0.000000	2.945148
H	0.000000	-3.232399	1.221258	H	0.000000	-3.274640	1.209741
H	0.000000	-3.407032	-1.241296	H	0.000000	-3.450008	-1.232006
H	0.000000	-1.512999	-2.750767	H	0.000000	-1.505611	-2.753959

Isomer-4

	Singlet				Triplet		
C	-1.902652	2.342129	0.000000	C	2.927539	-0.739404	0.000016
H	-2.323853	3.341230	0.000000	H	3.871088	-1.274044	-0.000007
C	0.000000	0.879157	0.000000	C	0.505784	-0.726647	0.000032
C	-0.517905	2.175788	0.000000	C	1.742991	-1.444690	0.000018
H	0.140710	3.037484	0.000000	H	1.740458	-2.528739	-0.000019
C	-2.238164	-0.065355	0.000000	C	1.728774	1.396549	-0.000027
H	-2.908280	-0.918886	0.000000	H	1.752048	2.481594	-0.000043
C	-0.862317	-0.237557	0.000000	C	0.532652	0.718527	-0.000012
C	1.392656	-0.958909	0.000000	C	-1.723698	-0.009165	0.000159
C	1.375096	0.398402	0.000000	C	-0.800975	-1.180611	-0.000060
H	2.252760	1.031507	0.000000	H	-1.133197	-2.208710	-0.000138
C	-0.030789	-1.495388	0.000000	C	-0.883727	1.260268	-0.000002
H	-0.217390	-2.121705	0.879961	H	-1.091342	1.884455	0.878866
H	-0.217390	-2.121705	-0.879961	H	-1.091438	1.884382	-0.878896
C	2.528237	-1.798802	0.000000	C	-3.082300	-0.059212	-0.000125
C	3.475499	-2.547140	0.000000	C	-4.310837	-0.103303	0.000033
H	4.316471	-3.196379	0.000000	H	-5.372425	-0.142349	0.000076
C	-2.755331	1.234869	0.000000	C	2.937457	0.671447	0.000000
H	-3.829005	1.385292	0.000000	H	3.882845	1.200856	-0.000024

Table S19: Optimized geometries of the singlet and triplet ground electronic state of 3-ethynyl-1H-indene (**5**) and 7-ethynyl-1H-indene (**6**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-5

	Singlet				Triplet		
C	2.738714	0.653882	0.000000	C	2.787909	0.364812	0.000000
C	1.855816	1.736750	0.000000	C	2.027515	1.547985	0.000000
H	3.807936	0.833544	0.000000	H	3.870246	0.423273	0.000000
H	2.248577	2.747392	0.000000	H	2.534549	2.506386	0.000000
C	-2.542543	0.512573	0.000000	C	-2.444589	0.802007	0.000000
C	0.000000	0.223195	0.000000	C	0.000000	0.241572	0.000000
C	0.885684	-0.869271	0.000000	C	0.778051	-0.955783	0.000000
C	2.257474	-0.659415	0.000000	C	2.158425	-0.888818	0.000000
H	2.950127	-1.494822	0.000000	H	2.756305	-1.794466	0.000000
C	-3.507168	1.235298	0.000000	C	-3.404718	1.556493	0.000000
H	-4.365591	1.861443	0.000000	H	-4.236608	2.217172	0.000000
C	-1.380646	-0.303014	0.000000	C	-1.381482	-0.073151	0.000000
C	0.084779	-2.149221	0.000000	C	-0.119416	-2.182928	0.000000
H	0.297372	-2.772243	0.878408	H	0.063159	-2.824440	0.876712
C	-1.337724	-1.657025	0.000000	C	-1.493118	-1.579898	0.000000
H	0.297372	-2.772243	-0.878408	H	0.063159	-2.824440	-0.876712
H	-2.201214	-2.307992	0.000000	H	-2.427761	-2.120182	0.000000
C	0.475253	1.532038	0.000000	C	0.645077	1.501962	0.000000
H	-0.212417	2.370182	0.000000	H	0.055020	2.411181	0.000000

Isomer-6

	Singlet				Triplet		
C	0.574398	-1.943145	0.000000	C	1.123224	-1.681177	-0.000036
C	-0.777492	-2.275595	0.000000	C	-0.080792	-2.419924	0.000012
H	-1.065659	-3.320775	0.000000	H	-0.025095	-3.502978	0.000016
C	2.373492	-0.253877	0.000000	C	2.329992	0.482894	-0.000098
C	3.541678	0.043421	0.000000	C	3.365696	1.099885	0.000098
H	4.573132	0.298270	0.000000	H	4.279493	1.641967	-0.000021
C	-1.365347	0.051234	0.000000	C	-1.359360	-0.356852	0.000023
C	-1.762492	-1.285124	0.000000	C	-1.306623	-1.800854	0.000041
H	-2.813032	-1.554390	0.000000	H	-2.224996	-2.376143	0.000068
C	0.987093	-0.594432	0.000000	C	1.104194	-0.247364	-0.000044
C	0.000000	0.394392	0.000000	C	-0.111982	0.397783	0.000004
C	-1.311784	2.349489	0.000000	C	-1.920232	1.900966	-0.000058
H	-1.605568	3.390865	0.000000	H	-2.534004	2.789591	-0.000105
C	-2.144690	1.293013	0.000000	C	-2.421252	0.510304	-0.000006
H	-3.226595	1.333835	0.000000	H	-3.466895	0.233403	-0.000009
C	0.127780	1.895760	0.000000	C	-0.414308	1.884842	0.000044
H	0.677360	2.261645	0.876255	H	0.021398	2.391562	0.874637
H	0.677360	2.261645	-0.876255	H	0.021545	2.391673	-0.874404
H	1.327179	-2.721920	0.000000	H	2.077209	-2.192100	-0.000062

Table S20: Optimized geometries of the singlet and triplet ground electronic state of 4-ethynyl-1H-indene (**7**) and 6-ethynyl-1H-indene (**8**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-7

Singlet				Triplet			
C	-0.632423	-2.303947	0.000000	C	-0.530126	-2.316645	0.000000
C	1.044633	-0.535251	0.000000	C	1.111072	-0.510791	0.000000
C	0.699197	-1.900042	0.000000	C	0.792675	-1.870918	0.000000
H	-0.866747	-3.362301	0.000000	H	-0.730983	-3.381255	0.000000
H	1.490808	-2.639573	0.000000	H	1.600421	-2.593379	0.000000
C	2.410906	-0.126348	0.000000	C	2.443717	-0.057787	0.000000
C	0.000000	0.405735	0.000000	C	0.000000	0.447021	0.000000
C	-1.344222	-0.014337	0.000000	C	-1.372724	-0.058641	0.000000
C	-1.668567	-1.361717	0.000000	C	-1.626031	-1.393620	0.000000
H	-2.703254	-1.688358	0.000000	H	-2.642374	-1.773241	0.000000
C	3.565099	0.222241	0.000000	C	3.579374	0.362217	0.000000
H	4.583408	0.525153	0.000000	H	4.580523	0.717786	0.000000
C	0.028273	1.868113	0.000000	C	-0.007962	1.813789	0.000000
H	0.935371	2.457314	0.000000	H	0.868488	2.447188	0.000000
C	-2.229437	1.209638	0.000000	C	-2.331302	1.122787	0.000000
H	-2.885968	1.243649	0.878465	H	-2.995716	1.112667	0.876825
C	-1.231782	2.341770	0.000000	C	-1.390724	2.299439	0.000000
H	-2.885968	1.243649	-0.878465	H	-2.995716	1.112667	-0.876825
H	-1.517709	3.385339	0.000000	H	-1.692455	3.336462	0.000000

Isomer-8

Singlet				Triplet			
C	-0.138392	2.481208	0.000000	C	0.172361	2.510387	0.000000
C	-1.635424	2.676446	0.000000	C	1.674950	2.657057	0.000000
C	-2.271656	1.490083	0.000000	C	2.291967	1.361995	0.000000
C	-1.289925	0.404816	0.000000	C	1.430982	-1.067472	0.000000
C	-1.444816	-0.981726	0.000000	C	0.298851	-1.813233	0.000000
C	-0.309995	-1.786766	0.000000	C	-1.020511	-1.200485	0.000000
C	0.980620	-1.223778	0.000000	C	-1.122719	0.244869	0.000000
C	1.128949	0.179011	0.000000	C	0.000000	0.999104	0.000000
C	0.000000	0.976668	0.000000	C	1.333858	0.378363	0.000000
C	2.131778	-2.067049	0.000000	C	-2.162683	-1.995910	0.000000
C	3.105310	-2.778434	0.000000	C	-3.161128	-2.693040	0.000000
H	0.332511	2.939788	0.878417	H	-0.295073	2.980164	0.877204
H	0.332511	2.939788	-0.878417	H	-0.295073	2.980164	-0.877204
H	-2.106850	3.650378	0.000000	H	2.198565	3.602339	0.000000
H	-3.344427	1.343804	0.000000	H	3.361628	1.194395	0.000000
H	-2.431281	-1.432300	0.000000	H	2.406056	-1.541748	0.000000
H	-0.408202	-2.865575	0.000000	H	0.351459	-2.895416	0.000000
H	2.124815	0.607571	0.000000	H	-2.110864	0.691399	0.000000
H	3.962221	-3.406335	0.000000	H	-4.032257	-3.301110	0.000000

Table S21: Optimized geometries of the singlet and triplet ground electronic state of 5-ethynyl-1H-indene (**9**) and 7bH-cyclopenta[cd]indene (**10**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-9

Singlet				Triplet			
C	-1.027533	-1.192764	0.000000	C	-1.083558	-1.145767	0.000000
C	0.251337	-1.780840	0.000000	C	0.210779	-1.773066	0.000000
H	0.330686	-2.861015	0.000000	H	0.265126	-2.853797	0.000000
C	-2.194122	-2.017449	0.000000	C	-2.250305	-1.968502	0.000000
C	-3.178555	-2.712868	0.000000	C	-3.223538	-2.679749	0.000000
H	-4.046039	-3.326121	0.000000	H	-4.084928	-3.301709	0.000000
C	1.276677	0.388309	0.000000	C	1.306221	0.370717	0.000000
C	1.402932	-0.992983	0.000000	C	1.387584	-0.998112	0.000000
H	2.379417	-1.466059	0.000000	H	2.350420	-1.498953	0.000000
C	-1.151744	0.208333	0.000000	C	-1.191491	0.228108	0.000000
H	-2.137226	0.659001	0.000000	H	-2.166973	0.698897	0.000000
C	0.000000	0.987781	0.000000	C	0.000000	1.032156	0.000000
C	0.178656	2.442902	0.000000	C	0.169911	2.391752	0.000000
H	-0.634209	3.157982	0.000000	H	-0.618151	3.132415	0.000000
C	1.491214	2.737161	0.000000	C	1.613341	2.701418	0.000000
H	1.919657	3.730735	0.000000	H	2.039434	3.694249	0.000000
C	2.322958	1.476599	0.000000	C	2.407382	1.419616	0.000000
H	2.978400	1.420194	0.878267	H	3.068555	1.328735	0.876549
H	2.978400	1.420194	-0.878267	H	3.068555	1.328735	-0.876549

Isomer-10

Singlet				Triplet			
C	0.237227	-2.430121	0.000000	C	0.214497	-2.426321	0.000000
H	0.202271	-3.514982	0.000000	H	0.151906	-3.511794	0.000000
C	0.165710	-0.387939	1.282257	C	0.189663	-0.388196	1.289902
C	0.165710	-1.780738	1.255182	C	0.189663	-1.798158	1.271521
H	-0.011770	-2.377634	2.143854	H	0.032109	-2.397367	2.159200
C	0.165710	-0.387939	-1.282257	C	0.189663	-0.388196	-1.289902
C	0.546963	0.248499	0.000000	C	0.535308	0.248292	0.000000
C	-0.253233	0.679835	2.103004	C	-0.230611	0.682963	2.117634
C	-0.030886	1.610138	0.000000	C	-0.124861	1.587998	0.000000
C	0.165710	-1.780738	-1.255182	C	0.189663	-1.798158	-1.271521
H	-0.011770	-2.377634	-2.143854	H	0.032109	-2.397367	-2.159200
C	-0.385168	1.868951	1.335693	C	-0.402358	1.888165	1.360170
H	-0.814293	2.785220	1.722581	H	-0.784376	2.817189	1.756848
H	-0.517420	0.607982	3.151405	H	-0.490576	0.592120	3.165673
C	-0.385168	1.868951	-1.335693	C	-0.402358	1.888165	-1.360170
H	-0.814293	2.785220	-1.722581	H	-0.784376	2.817189	-1.756848
C	-0.253233	0.679835	-2.103004	C	-0.230611	0.682963	-2.117634
H	-0.517420	0.607982	-3.151405	H	-0.490576	0.592120	-3.165673
H	1.648640	0.351445	0.000000	H	1.627832	0.410795	0.000000

Table S22: Optimized geometries of the singlet and triplet ground electronic state of 1-ethynyl-1H-indene (**11**) and 1H-cyclopropa[b]naphthalene (**12**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-11

	Singlet				Triplet		
C	2.757342	-0.375159	-0.274903	C	2.756902	-0.469304	-0.242905
H	3.815935	-0.443924	-0.499401	H	3.814949	-0.605706	-0.438309
C	0.747136	0.921174	-0.081221	C	0.802356	0.952782	-0.055183
C	2.109547	0.858032	-0.370156	C	2.209689	0.787182	-0.310012
H	2.657193	1.746079	-0.666641	H	2.816925	1.648279	-0.564941
C	0.690565	-1.461447	0.396166	C	0.586119	-1.468517	0.332088
H	0.147662	-2.356260	0.680696	H	-0.010416	-2.342835	0.569803
C	0.049563	-0.237626	0.305683	C	0.017608	-0.221306	0.296212
C	-1.419991	1.623098	0.251055	C	-1.402523	1.662130	0.185397
C	-0.196153	2.043484	-0.105085	C	-0.004473	2.062482	-0.105321
H	0.069366	3.057851	-0.375406	H	0.307609	3.071029	-0.338865
C	-1.401026	0.137000	0.589916	C	-1.427021	0.199050	0.596798
H	-1.590076	0.025377	1.669032	H	-1.615240	0.104253	1.681987
C	-2.398770	-0.656509	-0.125076	C	-2.447452	-0.597814	-0.088166
C	-3.228757	-1.309742	-0.699487	C	-3.292975	-1.248801	-0.643566
H	-3.957166	-1.885893	-1.215562	H	-4.036317	-1.822001	-1.141393
C	2.057331	-1.523574	0.101180	C	1.965273	-1.605198	0.069888
H	2.577171	-2.472917	0.162676	H	2.428666	-2.583176	0.118240
H	-2.320812	2.217293	0.316173	H	-2.287192	2.214050	-0.097893

Isomer-12

	Singlet				Triplet		
C	0.000000	-1.396349	-1.553318	C	0.000000	1.392248	-1.550794
C	0.000000	1.396349	-1.553318	C	0.000000	-1.392248	-1.550794
H	0.000000	-2.481661	-1.554411	H	0.000000	2.476776	-1.562280
H	0.000000	2.481661	-1.554411	H	0.000000	-2.476776	-1.562280
C	0.000000	0.722236	-0.306774	C	0.000000	-0.731828	-0.309475
C	0.000000	-0.722236	-0.306774	C	0.000000	0.731828	-0.309475
C	0.000000	0.684305	2.043685	C	0.000000	-0.657589	2.084090
C	0.000000	-0.684305	2.043685	C	0.000000	0.657589	2.084090
C	0.000000	1.458477	0.930055	C	0.000000	-1.467537	0.913677
H	0.000000	2.543577	0.915548	H	0.000000	-2.550540	0.908487
C	0.000000	-1.458477	0.930055	C	0.000000	1.467537	0.913677
H	0.000000	-2.543577	0.915548	H	0.000000	2.550540	0.908487
C	0.000000	-0.705309	-2.744134	C	0.000000	0.680637	-2.799260
H	0.000000	-1.244303	-3.684891	H	0.000000	1.239268	-3.727791
C	0.000000	0.705309	-2.744134	C	0.000000	-0.680637	-2.799260
H	0.000000	1.244303	-3.684891	H	0.000000	-1.239268	-3.727791
C	0.000000	0.000000	3.377098	C	0.000000	0.000000	3.436394
H	0.910734	0.000000	3.975381	H	-0.910069	0.000000	4.042973
H	-0.910734	0.000000	3.975381	H	0.910069	0.000000	4.042973

Table S23: Optimized geometries of the singlet and triplet ground electronic state of 1H-cyclopropa[a]naphthalene (**13**) and 2H-cyclopenta[cd]indene (**14**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-13

	Singlet				Triplet		
C	0.000000	0.618707	0.000000	C	0.000000	0.628012	0.000000
C	-0.878369	1.730786	0.000000	C	-0.863815	1.733385	0.000000
H	-0.459381	2.730615	0.000000	H	-0.445202	2.732719	0.000000
C	1.401231	0.631038	0.000000	C	1.394079	0.627910	0.000000
C	-0.538670	-0.724061	0.000000	C	-0.549190	-0.729091	0.000000
C	1.707789	-1.767125	0.000000	C	1.773560	-1.769966	0.000000
H	2.340081	-2.647151	0.000000	H	2.389757	-2.661177	0.000000
C	0.324092	-1.865147	0.000000	C	0.316559	-1.865682	0.000000
H	-0.142187	-2.845376	0.000000	H	-0.143504	-2.847938	0.000000
C	-1.951441	-0.870321	0.000000	C	-1.945068	-0.861562	0.000000
H	-2.373792	-1.870084	0.000000	H	-2.385087	-1.852633	0.000000
C	-2.778890	0.228072	0.000000	C	-2.808064	0.288126	0.000000
C	-3.854853	0.094647	0.000000	H	-3.881668	0.137849	0.000000
C	2.174668	-0.448671	0.000000	C	2.214132	-0.498174	0.000000
C	-2.239452	1.537109	0.000000	C	-2.286367	1.549489	0.000000
H	-2.909060	2.389998	0.000000	H	-2.935385	2.417273	0.000000
C	2.887163	0.878114	0.000000	C	2.867826	0.844622	0.000000
H	3.375232	1.228172	0.910678	H	3.359588	1.195748	0.909324
H	3.375232	1.228172	-0.910678	H	3.359588	1.195748	-0.909324

Isomer-14

	Singlet				Triplet		
C	0.000000	0.176649	0.000000	C	0.000000	0.138252	0.000000
C	-1.338434	-0.313447	0.000000	C	-1.346899	-0.189234	0.000000
C	-1.428025	-1.677596	0.000000	C	-1.616693	-1.573926	0.000000
C	-0.201937	-2.475494	0.000000	C	-0.514614	-2.461845	0.000000
C	1.074968	-1.969301	0.000000	C	0.833443	-2.066615	0.000000
C	1.232433	-0.532487	0.000000	C	1.126358	-0.672142	0.000000
C	2.216866	0.429833	0.000000	C	2.238400	0.222301	0.000000
C	1.570394	1.820151	0.000000	C	1.764057	1.690444	0.000000
C	0.088741	1.522045	0.000000	C	0.251824	1.546652	0.000000
C	-1.302318	1.998229	0.000000	C	-0.993449	2.154462	0.000000
C	-2.154986	0.911276	0.000000	C	-1.998342	1.110176	0.000000
H	-2.375602	-2.207745	0.000000	H	-2.624122	-1.974292	0.000000
H	-0.326610	-3.553404	0.000000	H	-0.726939	-3.525843	0.000000
H	1.926168	-2.640636	0.000000	H	1.613299	-2.819167	0.000000
H	3.289194	0.281968	0.000000	H	3.285962	-0.050359	0.000000
H	1.901207	2.395365	-0.875876	H	2.137965	2.237440	0.876127
H	1.901207	2.395365	0.875876	H	2.137965	2.237440	-0.876127
H	-1.627354	3.030593	0.000000	H	-1.222812	3.210929	0.000000
H	-3.234426	0.959352	0.000000	H	-3.065834	1.292702	0.000000

Table S24: Optimized geometries of the singlet and triplet ground electronic state of penta-1,3-diyn-1-ylbenzene (**15**) and 1-ethynyl-2H-indene (**16**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-15

	Singlet				Triplet		
C	-0.009755	-3.893787	0.000000	C	0.003512	-3.893188	0.000000
C	-1.214825	-3.190981	0.000000	C	-1.223729	-3.179233	0.000000
C	-1.216836	-1.800899	0.000000	C	-1.248887	-1.813872	0.000000
C	-0.003343	-1.087575	0.000000	C	0.001074	-1.045294	0.000000
C	1.206875	-1.806458	0.000000	C	1.252349	-1.811739	0.000000
C	1.198525	-3.196507	0.000000	C	1.229535	-3.177135	0.000000
H	-0.012234	-4.977789	0.000000	H	0.004439	-4.975813	0.000000
H	-2.156640	-3.728031	0.000000	H	-2.158167	-3.730082	0.000000
H	-2.151331	-1.253002	0.000000	H	-2.184710	-1.269119	0.000000
H	2.143859	-1.262830	0.000000	H	2.187233	-1.265377	0.000000
H	2.137877	-3.737855	0.000000	H	2.164917	-3.726380	0.000000
C	0.000000	0.333800	0.000000	C	0.000000	0.297349	0.000000
C	0.003222	1.548440	0.000000	C	-0.000888	1.564894	0.000000
C	0.007274	2.909290	0.000000	C	-0.001570	2.882187	0.000000
C	0.011002	4.120944	0.000000	C	-0.000169	4.119939	0.000000
C	0.015724	5.573797	0.000000	C	-0.007866	5.567986	0.000000
H	-0.493673	5.968315	0.884649	H	-0.522729	5.964368	0.883532
H	1.038638	5.962483	0.000000	H	1.011578	5.966673	0.000000
H	-0.493673	5.968315	-0.884649	H	-0.522729	5.964368	-0.883532

Isomer-16

	Singlet				Triplet		
C	2.816655	0.217252	0.000000	C	2.750223	0.722060	0.000000
C	2.071543	1.458371	0.000000	C	1.852550	1.783324	0.000000
H	3.899907	0.267716	0.000000	H	3.815934	0.921568	0.000000
H	2.625934	2.390411	0.000000	H	2.222525	2.802030	0.000000
C	-2.414374	0.875251	0.000000	C	-2.515443	0.450210	0.000000
C	0.000000	0.233598	0.000000	C	0.000000	0.242777	0.000000
C	0.752896	-1.032235	0.000000	C	0.921523	-0.859698	0.000000
C	2.192537	-0.989283	0.000000	C	2.297438	-0.608778	0.000000
H	2.759351	-1.913802	0.000000	H	3.006966	-1.428739	0.000000
C	-3.342659	1.650755	0.000000	C	-3.550948	1.092271	0.000000
H	-4.155317	2.334864	0.000000	H	-4.453387	1.653043	0.000000
C	-1.349707	-0.041012	0.000000	C	-1.348578	-0.286048	0.000000
C	-0.122989	-2.076626	0.000000	C	0.192040	-2.075851	0.000000
H	0.123566	-3.129574	0.000000	H	0.626794	-3.066540	0.000000
C	-1.520217	-1.541886	0.000000	C	-1.289069	-1.807596	0.000000
H	-2.091309	-1.878183	0.875993	H	-1.800678	-2.235180	0.876074
H	-2.091309	-1.878183	-0.875993	H	-1.800678	-2.235180	-0.876074
C	0.711150	1.478309	0.000000	C	0.460254	1.549025	0.000000
H	0.160171	2.411778	0.000000	H	-0.237415	2.378822	0.000000

Table S25: Optimized geometries of the singlet and triplet ground electronic state of 6H-cyclopenta[cd]indene (**17**) and 4-ethynyl-2H-indene (**18**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-17

	Singlet				Triplet		
C	0.000000	0.000000	-2.484637	C	0.032020	-2.544558	0.000000
H	0.000000	-0.863310	-3.169566	H	0.916891	-3.206241	0.000000
C	-1.298632	0.000000	-0.370453	C	0.009987	-0.381071	1.273438
C	-1.313815	0.000000	-1.723435	C	0.009987	-1.756311	1.314005
H	-2.222038	0.000000	-2.319217	H	-0.002717	-2.327427	2.235936
C	1.298632	0.000000	-0.370453	C	0.009987	-0.381071	-1.273438
C	0.000000	0.000000	0.213070	C	0.020997	0.189802	0.000000
C	-2.201536	0.000000	0.802938	C	-0.014812	0.806074	2.148327
C	0.000000	0.000000	1.562102	C	-0.006334	1.634626	0.000000
C	1.313815	0.000000	-1.723435	C	0.009987	-1.756311	-1.314005
C	-1.427356	0.000000	1.940149	C	-0.024338	1.988333	1.371949
H	-1.823421	0.000000	2.947717	H	-0.046425	2.985180	1.791196
H	-3.281650	0.000000	0.774251	H	-0.028469	0.791680	3.230945
C	1.427356	0.000000	1.940149	C	-0.024338	1.988333	-1.371949
C	2.201536	0.000000	0.802938	C	-0.014812	0.806074	-2.148327
H	3.281650	0.000000	0.774251	H	-0.028469	0.791680	-3.230945
H	1.823421	0.000000	2.947717	H	-0.046425	2.985180	-1.791196
H	2.222038	0.000000	-2.319217	H	-0.002717	-2.327427	-2.235936
H	0.000000	0.863310	-3.169566	H	-0.811646	-3.256150	0.000000

Isomer-18

	Singlet				Triplet		
C	-0.631135	-2.308364	0.000000	C	-0.590094	-2.332366	0.000000
C	1.075917	-0.532938	0.000000	C	1.054297	-0.517242	0.000000
C	0.740040	-1.860502	0.000000	C	0.720433	-1.912597	0.000000
H	-0.816198	-3.376709	0.000000	H	-0.808298	-3.394203	0.000000
H	1.528453	-2.603875	0.000000	C	1.527280	-2.634931	0.000000
C	2.432301	-0.103021	0.000000	C	2.409048	-0.103949	0.000000
C	0.000000	0.446416	0.000000	C	0.000000	0.416189	0.000000
C	-1.403372	-0.023311	0.000000	C	-1.378649	-0.042672	0.000000
C	-1.673939	-1.436280	0.000000	C	-1.664581	-1.402668	0.000000
H	-2.698839	-1.790672	0.000000	H	-2.689853	-1.754485	0.000000
C	3.573537	0.286793	0.000000	C	3.565494	0.245858	0.000000
H	4.582429	0.619807	0.000000	H	4.583437	0.549839	0.000000
C	0.019003	1.804534	0.000000	C	0.008703	1.821772	0.000000
H	0.893577	2.439116	0.000000	H	0.897080	2.438361	0.000000
C	-2.231334	1.057625	0.000000	C	-2.222615	1.093692	0.000000
H	-3.312610	1.046778	0.000000	H	-3.304355	1.069048	0.000000
C	-1.395424	2.301694	0.000000	C	-1.400573	2.356498	0.000000
H	-1.605187	2.934838	0.874391	H	-1.607030	2.995641	0.874443
H	-1.605187	2.934838	-0.874391	H	-1.607030	2.995641	-0.874443

Table S26: Optimized geometries of the singlet and triplet ground electronic state of 2H-cyclopenta[3,4]cyclobuta[1,2]benzene (**19**) and 1-(buta-1,3-diyn-1-yl)-4-methylbenzene (**20**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-19

Singlet				Triplet			
C	0.000000	0.712315	-0.491342	C	0.000000	0.737556	-0.478259
C	0.000000	1.445301	-1.663014	C	0.000000	1.489257	-1.652967
C	0.000000	-1.445301	-1.663014	C	0.000000	-1.489257	-1.652967
C	0.000000	-0.712315	-0.491342	C	0.000000	-0.737556	-0.478259
H	0.000000	2.528821	-1.682660	H	0.000000	2.569529	-1.677851
H	0.000000	-2.528821	-1.682660	H	0.000000	-2.569529	-1.677851
C	0.000000	-0.699651	-2.854556	C	0.000000	-0.704153	-2.837663
C	0.000000	0.699651	-2.854556	C	0.000000	0.704153	-2.837663
C	0.000000	0.737198	1.000749	C	0.000000	0.732483	0.964949
C	0.000000	-0.737198	1.000749	C	0.000000	-0.732483	0.964949
C	0.000000	-1.213975	2.253575	C	0.000000	-1.221899	2.255451
C	0.000000	1.213975	2.253575	C	0.000000	1.221899	2.255451
H	0.000000	2.236141	2.606725	H	0.000000	2.242447	2.608286
C	0.000000	0.000000	3.186455	C	0.000000	0.000000	3.168261
H	-0.876978	0.000000	3.849166	H	-0.868544	0.000000	3.854746
H	0.000000	-1.221641	-3.805062	H	0.000000	-1.206535	-3.799029
H	0.000000	1.221641	-3.805062	H	0.000000	1.206535	-3.799029
H	0.876978	0.000000	3.849166	H	0.868544	0.000000	3.854746
H	0.000000	-2.236141	2.606725	H	0.000000	-2.242447	2.608286

Isomer-20

Singlet				Triplet			
C	0.001046	-2.681069	0.000000	C	0.007646	-2.682233	0.000000
C	0.003082	0.148598	0.000000	C	0.006559	0.189197	0.000000
C	0.004251	-0.571325	1.208517	C	0.009179	-0.582164	1.248402
C	0.004251	-1.959969	1.200143	C	0.009179	-1.944621	1.221947
H	0.008493	-0.030783	2.147376	H	0.014090	-0.040167	2.185694
H	0.008932	-2.495109	2.144228	H	0.012406	-2.491550	2.159898
C	0.005456	1.568796	0.000000	C	0.004504	1.531089	0.000000
C	0.006418	2.783041	0.000000	C	0.004316	2.796263	0.000000
C	0.007750	4.143841	0.000000	C	0.004576	4.115402	0.000000
C	0.008877	5.353262	0.000000	C	0.004675	5.349722	0.000000
H	0.009865	6.415567	0.000000	H	0.004639	6.411970	0.000000
C	0.004251	-0.571325	-1.208517	C	0.009179	-0.582164	-1.248402
H	0.008493	-0.030783	-2.147376	H	0.014090	-0.040167	-2.185694
C	-0.032888	-4.188915	0.000000	C	-0.044736	-4.180233	0.000000
H	-1.065557	-4.555276	0.000000	H	-1.082333	-4.543547	0.000000
H	0.460188	-4.599155	-0.884460	H	0.439584	-4.599405	-0.886071
H	0.460188	-4.599155	0.884460	H	0.439584	-4.599405	0.886071
C	0.004251	-1.959969	-1.200143	C	0.009179	-1.944621	-1.221947
H	0.008932	-2.495109	-2.144228	H	0.012406	-2.491550	-2.159898

Table S27: Optimized geometries of the singlet and triplet ground electronic state of 5-ethynyl-2H-indene (**21**) and 1-(buta-1,3-diyn-1-yl)-2-methylbenzene (**22**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-21

Singlet				Triplet			
C	-1.055646	-1.148832	0.000000	C	-1.031187	-1.214190	0.000000
C	0.266081	-1.778691	0.000000	C	0.234536	-1.806057	0.000000
H	0.301715	-2.861425	0.000000	H	0.306129	-2.886855	0.000000
C	-2.204510	-1.993237	0.000000	C	-2.203921	-2.016310	0.000000
C	-3.158640	-2.730636	0.000000	C	-3.209112	-2.685228	0.000000
H	-4.004699	-3.373254	0.000000	H	-4.090653	-3.278057	0.000000
C	1.332631	0.388235	0.000000	C	1.307281	0.364395	0.000000
C	1.407913	-1.051098	0.000000	C	1.405711	-1.029637	0.000000
H	2.375178	-1.541622	0.000000	H	2.375129	-1.515062	0.000000
C	-1.179289	0.213678	0.000000	C	-1.146675	0.214495	0.000000
H	-2.160911	0.672804	0.000000	H	-2.131598	0.665436	0.000000
C	0.000000	1.031874	0.000000	C	0.000000	0.990226	0.000000
C	2.292510	1.351479	0.000000	C	2.292023	1.372940	0.000000
H	3.363506	1.202152	0.000000	H	3.360947	1.203356	0.000000
C	0.159274	2.385187	0.000000	C	0.182385	2.401906	0.000000
H	-0.623026	3.131676	0.000000	H	-0.612725	3.135636	0.000000
C	1.625882	2.695147	0.000000	C	1.651882	2.739051	0.000000
H	1.915499	3.295515	0.875015	H	1.947617	3.343000	0.874330
H	1.915499	3.295515	-0.875015	H	1.947617	3.343000	-0.874330

Isomer-22

Singlet				Triplet			
C	1.661594	2.702679	0.000000	C	1.766081	2.633669	0.000000
C	2.210062	1.421148	0.000000	C	2.278925	1.313714	0.000000
C	1.405662	0.280873	0.000000	C	1.467524	0.209029	0.000000
C	0.000000	0.455904	0.000000	C	0.000000	0.411592	0.000000
C	-0.547356	1.752289	0.000000	C	-0.502316	1.791648	0.000000
C	0.277876	2.869004	0.000000	C	0.361153	2.845571	0.000000
H	2.314575	3.568191	0.000000	H	2.444213	3.477737	0.000000
H	3.288362	1.301320	0.000000	H	3.354904	1.170440	0.000000
H	-1.624822	1.865072	0.000000	H	-1.574708	1.940690	0.000000
H	-0.155720	3.862251	0.000000	H	-0.026610	3.858296	0.000000
C	-0.867743	-0.669178	0.000000	C	-0.857884	-0.621183	0.000000
C	-1.610145	-1.630415	0.000000	C	-1.695201	-1.570760	0.000000
C	-2.442641	-2.706813	0.000000	C	-2.557965	-2.567595	0.000000
C	2.013471	-1.097356	0.000000	C	2.009878	-1.187772	0.000000
H	1.698581	-1.669107	0.878003	H	1.665565	-1.746174	0.877575
H	1.698581	-1.669107	-0.878003	H	1.665565	-1.746174	-0.877575
H	3.103308	-1.042346	0.000000	H	3.101076	-1.184158	0.000000
C	-3.182396	-3.663630	0.000000	C	-3.365074	-3.502177	0.000000
H	-3.833170	-4.503292	0.000000	H	-4.060729	-4.305068	0.000000

Table S28: Optimized geometries of the singlet and triplet ground electronic state of 1-(buta-1,3-diyn-1-yl)-3-methylbenzene (**23**) and 7H-cyclopenta[cd]indene (**24**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-23

	Singlet				Triplet		
C	-2.752764	0.676450	-0.005774	C	-2.747456	0.688394	-0.000042
C	-2.243310	-0.628833	-0.007810	C	-2.229096	-0.648164	0.000027
C	0.014142	0.302239	0.000619	C	0.057739	0.284957	-0.000038
C	-0.521013	1.601555	0.005384	C	-0.516858	1.637004	0.000058
C	-1.899897	1.777744	0.001673	C	-1.872310	1.801836	0.000012
H	-3.827149	0.829983	-0.011476	H	-3.819998	0.844260	-0.000168
H	0.146734	2.454107	0.009031	H	0.157346	2.483819	0.000104
H	-2.312709	2.780260	0.002000	H	-2.289619	2.802971	0.000016
C	1.421066	0.101308	0.000171	C	1.386283	0.094481	-0.000072
C	2.622975	-0.070134	0.000313	C	2.639331	-0.080372	-0.000020
C	3.970365	-0.261154	0.000239	C	3.945615	-0.263070	-0.000028
C	5.167789	-0.430541	0.000138	C	5.168027	-0.433210	0.000054
H	6.219660	-0.579152	-0.000018	H	6.220146	-0.579835	-0.000060
C	-3.173456	-1.818256	0.006517	C	-3.194026	-1.805713	0.000000
H	-2.644507	-2.741022	-0.239025	H	-2.670958	-2.763384	-0.000602
H	-3.627106	-1.948222	0.994612	H	-3.843556	-1.772494	0.880920
H	-3.988031	-1.693006	-0.711755	H	-3.844368	-1.771843	-0.880306
C	-0.860358	-0.800844	-0.006584	C	-0.878207	-0.842779	0.000047
H	-0.440124	-1.800157	-0.012678	H	-0.463232	-1.843679	0.000101

Isomer-24

	Singlet				Triplet		
C	2.465147	-0.082234	-0.003682	C	2.470239	0.228266	0.000177
H	3.547800	-0.165451	-0.008775	H	3.553144	0.304344	0.000233
C	0.474142	1.289404	0.006510	C	0.301448	1.295912	0.000007
C	1.910364	1.162744	0.000732	C	1.739455	1.380848	0.000300
H	2.556767	2.034404	-0.002797	H	2.253277	2.336631	0.000471
C	0.239877	-1.243469	0.005299	C	0.421073	-1.229915	-0.000028
C	-0.202156	0.019926	0.017575	C	-0.191408	-0.005547	-0.000207
C	-0.540199	2.225662	-0.004684	C	-0.883197	2.111152	-0.000136
C	-1.608799	0.143283	0.009254	C	-1.636462	-0.072754	-0.000132
C	1.722903	-1.411517	-0.004257	C	1.925474	-1.202363	-0.000298
H	2.050085	-1.999548	-0.876197	H	2.341825	-1.734480	-0.869908
C	-1.838524	1.503895	-0.005700	C	-2.049026	1.292019	-0.000071
H	-2.794412	2.015097	-0.021884	H	-3.059153	1.676911	0.000099
H	-0.449908	3.303043	-0.015596	H	-0.908789	3.194058	0.000027
C	-2.092078	-1.258706	-0.002481	C	-1.929255	-1.449708	0.000159
C	-1.000414	-2.086613	-0.004623	C	-0.673330	-2.160081	0.000191
H	-1.030391	-3.167579	-0.010747	H	-0.594695	-3.240896	0.000460
H	-3.121824	-1.588311	-0.007118	H	-2.898053	-1.928199	0.000394
H	2.060299	-2.005913	0.859453	H	2.342372	-1.735357	0.868457

Table S29: Optimized geometries of the singlet and triplet ground electronic state of 1-ethynyl-4-(prop-1-yn-1-yl)benzene (**25**) and 7aH-cyclopenta[cd]indene (**26**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-25

	Singlet				Triplet		
C	0.001030	-2.027713	0.000000	C	0.001007	-2.050122	0.000000
C	-1.208084	-1.310732	0.000000	C	-1.253456	-1.290284	0.000000
C	-1.208089	0.075793	0.000000	C	-1.252976	0.057535	0.000000
C	0.000000	0.796370	0.000000	C	0.000000	0.821287	0.000000
C	1.209608	-1.309859	0.000000	C	1.255031	-1.289162	0.000000
H	-2.145544	-1.853494	0.000000	H	-2.184573	-1.843922	0.000000
H	-2.146268	0.617240	0.000000	H	-2.185195	0.609663	0.000000
C	-0.000724	2.222448	0.000000	C	-0.001113	2.195442	0.000000
C	-0.002156	3.429846	0.000000	C	-0.005356	3.423608	0.000000
C	-0.002737	4.885997	0.000000	C	-0.001854	4.875605	0.000000
H	0.507656	5.279606	0.884263	H	0.513516	5.271461	0.882701
H	0.507656	5.279606	-0.884263	H	0.513516	5.271461	-0.882701
H	-1.023550	5.278407	0.000000	H	-1.021003	5.272459	0.000000
C	0.001465	-3.453958	0.000000	C	0.001547	-3.425118	0.000000
C	0.001769	-4.659323	0.000000	C	0.002002	-4.650425	0.000000
H	0.001992	-5.721811	0.000000	H	0.002350	-5.712826	0.000000
C	1.208624	0.076710	0.000000	C	1.253435	0.058670	0.000000
H	2.146370	0.618913	0.000000	H	2.185216	0.611563	0.000000
H	2.147453	-1.851954	0.000000	H	2.186569	-1.842078	0.000000

Isomer-26

	Singlet				Triplet		
C	2.381848	0.334111	-0.240300	C	2.407001	0.248423	-0.274298
H	3.413967	0.513537	-0.524567	H	3.433863	0.362255	-0.608910
C	0.214574	1.326105	0.267994	C	0.267339	1.289868	0.225534
C	1.512682	1.501107	-0.108323	C	1.656445	1.440700	-0.054746
H	1.887495	2.462048	-0.446761	H	2.111710	2.405483	-0.242925
C	-0.207195	-0.023357	0.496720	C	-0.179913	0.016319	0.470013
C	-1.026102	2.078671	-0.010086	C	-0.954128	2.060097	-0.042555
C	-1.503997	-0.174574	0.112652	C	-1.586696	-0.113662	0.121491
C	1.961946	-0.949515	-0.112913	C	1.919557	-1.034200	-0.134615
H	2.667296	-1.762536	-0.252843	H	2.563553	-1.883925	-0.333401
C	-2.044666	1.175103	-0.134477	C	-2.063550	1.195130	-0.113369
H	-3.065453	1.413789	-0.401948	H	-3.067066	1.491382	-0.382230
H	-1.096097	3.149002	-0.143427	H	-0.990564	3.124633	-0.238845
C	-1.671273	-1.576947	-0.267245	C	-1.752972	-1.481446	-0.257681
C	-0.471730	-2.217791	-0.187479	C	-0.547122	-2.145384	-0.167983
H	-0.315292	-3.281298	-0.319862	H	-0.388024	-3.175160	-0.465838
H	-2.596124	-2.047561	-0.577787	H	-2.659508	-1.925304	-0.650533
C	0.578221	-1.265021	0.394093	C	0.549562	-1.267037	0.466070
H	0.758351	-1.694342	1.403386	H	0.702899	-1.652219	1.495510

Table S30: Optimized geometries of the singlet and triplet ground electronic state of 1-ethynyl-3-(prop-1-yn-1-yl)benzene (**27**) and 1-ethynyl-2-(prop-1-yn-1-yl)benzene (**28**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-27

Singlet				Triplet			
C	-2.027450	-1.228954	0.000000	C	-1.905265	-1.437643	0.000000
C	-2.352771	0.123354	0.000000	C	-2.361579	-0.127758	0.000000
C	-1.354783	1.092285	0.000000	C	-1.485806	0.943060	0.000000
C	0.000000	0.715798	0.000000	C	0.000000	0.689471	0.000000
C	-0.679630	-1.626253	0.000000	C	-0.424428	-1.711520	0.000000
H	-2.804240	-1.983511	0.000000	H	-2.583900	-2.279432	0.000000
H	-3.393996	0.425078	0.000000	H	-3.430316	0.060002	0.000000
H	-1.611208	2.144620	0.000000	H	-1.832114	1.967358	0.000000
C	1.031148	1.703943	0.000000	C	0.867514	1.773686	0.000000
C	1.901822	2.539743	0.000000	C	1.589124	2.759254	0.000000
C	2.955640	3.544920	0.000000	C	2.469304	3.914683	0.000000
H	2.535923	4.554830	0.000000	H	1.897431	4.846854	0.000000
H	3.593000	3.446281	0.883897	H	3.118081	3.916707	0.882872
H	3.593000	3.446281	-0.883897	H	3.118081	3.916707	-0.882872
C	-0.333962	-3.012401	0.000000	C	0.019126	-3.032896	0.000000
C	-0.045626	-4.182224	0.000000	C	0.360818	-4.200997	0.000000
H	0.209802	-5.213549	0.000000	H	0.674453	-5.216019	0.000000
C	0.324558	-0.648498	0.000000	C	0.456943	-0.634246	0.000000
H	1.364046	-0.950309	0.000000	H	1.523773	-0.822739	0.000000

Isomer-28

Singlet				Triplet			
C	-2.779020	0.950833	0.000000	C	-2.857439	0.677114	0.000000
C	-1.897173	2.032552	0.000000	C	-2.034765	1.894362	0.000000
C	-0.525859	1.811576	0.000000	C	-0.678414	1.808132	0.000000
C	0.000000	0.508656	0.000000	C	0.000000	0.545526	0.000000
C	-0.898958	-0.590173	0.000000	C	-0.859113	-0.718813	0.000000
C	-2.281918	-0.346057	0.000000	C	-2.277234	-0.555940	0.000000
H	-3.849883	1.117822	0.000000	H	-3.936657	0.771008	0.000000
H	-2.278375	3.047300	0.000000	H	-2.523511	2.860863	0.000000
H	0.163093	2.647404	0.000000	H	-0.069570	2.705016	0.000000
H	-2.958103	-1.192284	0.000000	H	-2.889174	-1.450580	0.000000
C	1.410697	0.311350	0.000000	C	1.371541	0.465592	0.000000
C	2.607935	0.159738	0.000000	C	2.595772	0.383519	0.000000
C	4.049968	-0.037493	0.000000	C	4.043669	0.286541	0.000000
H	4.509478	0.415451	0.883798	H	4.474791	0.772693	0.882803
H	4.298359	-1.102617	0.000000	H	4.366075	-0.758586	0.000000
H	4.509478	0.415451	-0.883798	H	4.474791	0.772693	-0.882803
C	-0.422144	-1.933632	0.000000	C	-0.283498	-1.970797	0.000000
C	-0.045235	-3.078091	0.000000	C	0.220476	-3.085178	0.000000
H	0.296193	-4.084082	0.000000	H	0.657283	-4.053451	0.000000

Table S31: Optimized geometries of the singlet and triplet ground electronic state of 4H-cyclobuta[f]indene (**29**) and 5H-cyclobuta[e]indene (**30**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-29

	Singlet				Triplet		
C	0.390954	-1.627209	0.000000	C	0.442091	-1.651135	0.000000
C	-0.905561	-1.217141	0.000000	C	-0.887814	-1.256846	0.000000
C	1.351018	0.630288	0.000000	C	1.329667	0.705561	0.000000
C	1.496385	-0.725620	0.000000	C	1.553616	-0.678597	0.000000
H	-1.755036	-1.891149	0.000000	H	-1.718479	-1.954166	0.000000
H	2.184093	1.325208	0.000000	H	2.134856	1.432927	0.000000
C	0.000000	1.086520	0.000000	C	0.000000	1.085265	0.000000
C	-1.082031	0.207313	0.000000	C	-1.093125	0.128490	0.000000
C	-2.316405	0.993565	0.000000	C	-2.329815	0.882453	0.000000
H	-3.311116	0.564692	0.000000	H	-3.313374	0.428994	0.000000
C	-2.022450	2.308778	0.000000	C	-2.078363	2.211160	0.000000
H	-2.731297	3.125705	0.000000	H	-2.822982	2.996250	0.000000
C	1.384452	-2.783883	0.000000	C	1.394127	-2.722565	0.000000
H	1.296345	-3.861417	0.000000	H	1.335950	-3.801002	0.000000
C	2.429277	-1.928119	0.000000	C	2.491392	-1.747287	0.000000
H	3.503002	-2.056097	0.000000	H	3.569097	-1.820411	0.000000
C	-0.526798	2.499289	0.000000	C	-0.592320	2.476998	0.000000
H	-0.189523	3.065187	0.878589	H	-0.280906	3.058216	0.877837
H	-0.189523	3.065187	-0.878589	H	-0.280906	3.058216	-0.877837

Isomer-30

	Singlet				Triplet		
C	-1.094178	-1.427137	0.000000	C	-1.115073	-1.464056	0.000000
C	-1.142045	-0.002841	0.000000	C	-1.180162	0.006778	0.000000
C	1.286536	-1.370125	0.000000	C	1.260861	-1.382125	0.000000
C	0.066003	-2.136159	0.000000	C	0.094499	-2.156509	0.000000
H	2.236710	-1.894242	0.000000	H	2.227812	-1.874589	0.000000
C	1.248919	-0.001682	0.000000	C	1.207221	0.031708	0.000000
C	0.000000	0.738564	0.000000	C	0.000000	0.758608	0.000000
C	0.322197	2.164622	0.000000	C	0.309864	2.185622	0.000000
H	-0.413451	2.958601	0.000000	H	-0.430743	2.974697	0.000000
C	1.656757	2.331044	0.000000	C	1.647202	2.354319	0.000000
H	2.171491	3.283432	0.000000	H	2.169811	3.301583	0.000000
C	-2.618660	-1.438324	0.000000	C	-2.543525	-1.526391	0.000000
H	-3.373649	-2.212227	0.000000	H	-3.280490	-2.315756	0.000000
C	2.382060	1.004262	0.000000	C	2.348969	1.017945	0.000000
H	3.031279	0.899356	0.878087	H	2.998260	0.899679	0.877781
H	3.031279	0.899356	-0.878087	H	2.998260	0.899679	-0.877781
C	-2.661238	-0.087527	0.000000	C	-2.601648	-0.046996	0.000000
H	-3.463745	0.636972	0.000000	H	-3.399963	0.680365	0.000000
H	0.101973	-3.219434	0.000000	H	0.147807	-3.239077	0.000000

Table S32: Optimized geometries of the singlet and triplet ground electronic state of 1,4-diethynyl-2-methylbenzene (**31**) and 2,4-diethynyl-1-methylbenzene (**32**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-31

	Singlet				Triplet		
C	-1.221189	-1.034191	0.000000	C	-1.616623	-0.139094	0.000008
C	-0.005308	-1.736313	0.000000	C	-0.981114	-1.460515	0.000075
C	1.193582	-1.042294	0.000000	C	0.359636	-1.578943	0.000093
C	1.216803	0.362772	0.000000	C	1.230774	-0.399017	0.000008
C	-1.194696	0.370257	0.000000	C	-0.748563	1.035501	0.000002
H	-0.011887	-2.819110	0.000000	H	-1.617937	-2.336666	0.000103
H	2.133001	-1.581610	0.000000	H	0.830742	-2.554313	0.000143
C	2.468796	1.046206	0.000000	C	2.596117	-0.556999	-0.000081
C	-2.464959	-1.732854	0.000000	C	-2.986971	-0.012796	-0.000039
C	-3.515793	-2.323030	0.000000	C	-4.206691	0.097046	-0.000085
H	-4.442087	-2.843583	0.000000	H	-5.264897	0.192430	-0.000130
C	0.000000	1.084823	0.000000	C	0.600285	0.943481	0.000027
H	-2.135285	0.908817	0.000000	H	-1.223976	2.009738	-0.000018
C	-0.005912	2.591447	0.000000	C	1.483640	2.156477	0.000060
H	0.512545	2.987333	0.878059	H	2.138310	2.165339	0.877810
H	0.512545	2.987333	-0.878059	H	2.138484	2.165291	-0.877559
H	-1.026310	2.977585	0.000000	H	0.890584	3.072155	-0.000022
C	3.527767	1.622532	0.000000	C	3.810391	-0.726095	-0.000102
H	4.462924	2.127110	0.000000	H	4.863403	-0.868250	-0.000131

Isomer-32

	Singlet				Triplet		
C	-0.661705	-1.750559	0.000000	C	-0.612739	-1.800960	0.000000
C	-1.658502	-0.782374	0.000000	C	-1.646961	-0.884158	0.000000
C	-1.361851	0.582317	0.000000	C	-1.437610	0.491077	0.000000
C	0.000000	0.964984	0.000000	C	0.000000	0.989977	0.000000
C	0.690511	-1.373794	0.000000	C	0.807101	-1.312004	0.000000
H	-0.921157	-2.802196	0.000000	H	-0.792293	-2.866871	0.000000
H	-2.697628	-1.093631	0.000000	H	-2.669845	-1.248869	0.000000
C	0.365568	2.345829	0.000000	C	0.270295	2.355280	0.000000
C	1.724445	-2.358409	0.000000	C	1.847472	-2.239363	0.000000
C	2.595026	-3.191381	0.000000	C	2.723134	-3.083940	0.000000
H	3.363798	-3.924777	0.000000	H	3.499637	-3.809277	0.000000
C	0.671634	3.511483	0.000000	C	0.504310	3.551029	0.000000
H	0.946980	4.537782	0.000000	H	0.715255	4.592365	0.000000
C	-2.457747	1.614191	0.000000	C	-2.550109	1.482015	0.000000
H	-2.388472	2.263752	0.877639	H	-2.499692	2.142102	0.875598
H	-2.388472	2.263752	-0.877639	H	-2.499692	2.142102	-0.875598
H	-3.440563	1.140086	0.000000	H	-3.520888	0.983150	0.000000
C	1.006283	-0.009718	0.000000	C	1.045176	0.058874	0.000000
H	2.043552	0.299822	0.000000	H	2.067108	0.418327	0.000000

Table S33: Optimized geometries of the singlet and triplet ground electronic state of 2,4-diethynyl-1-methylbenzene (**33**) and 5H-cyclobuta[f]indene (**34**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-33

Singlet				Triplet			
C	-0.952509	0.009822	1.200363	C	0.987014	-0.016447	1.200621
C	-1.664643	0.011824	0.000000	C	1.686655	-0.012712	0.000000
C	0.451944	-0.000375	-1.213053	C	-0.518506	-0.005100	-1.213253
C	0.451944	-0.000375	1.213053	C	-0.518506	-0.005100	1.213253
H	-1.484253	0.018195	2.144988	H	1.501138	-0.027754	2.152792
C	1.161133	-0.000845	-2.453227	C	-1.180320	0.002966	-2.437006
C	1.161133	-0.000845	2.453227	C	-1.180320	0.002966	2.437006
C	1.756256	-0.001880	3.500728	C	-1.717384	0.009255	3.530043
H	2.283258	-0.002754	4.423347	H	-2.200757	0.013977	4.476277
C	1.756256	-0.001880	-3.500728	C	-1.717384	0.009255	-3.530043
H	2.283258	-0.002754	-4.423347	H	-2.200757	0.013977	-4.476277
C	1.151618	-0.006285	0.000000	C	-1.206302	-0.000847	0.000000
H	2.233619	-0.011302	0.000000	H	-2.289216	0.007227	0.000000
C	-3.174610	-0.010651	0.000000	C	3.197791	0.019053	0.000000
H	-3.579780	0.485285	-0.884804	H	3.603825	-0.475988	-0.884782
H	-3.548138	-1.040152	0.000000	H	3.562289	1.051264	0.000000
H	-3.579780	0.485285	0.884804	H	3.603825	-0.475988	0.884782
C	-0.952509	0.009822	-1.200363	C	0.987014	-0.016447	-1.200621
H	-1.484253	0.018195	-2.144988	H	1.501138	-0.027754	-2.152792

Isomer-34

Singlet				Triplet			
C	-0.000314	1.504554	0.743056	C	-0.000052	1.543464	0.742835
C	-0.000023	0.393052	1.496080	C	-0.000028	0.368764	1.492126
C	-0.000023	0.393052	-1.496080	C	-0.000028	0.368764	-1.492126
C	-0.000314	1.504554	-0.743056	C	-0.000052	1.543464	-0.742835
H	0.000152	0.389351	2.580632	H	-0.000031	0.352208	2.575716
H	0.000152	0.389351	-2.580632	H	-0.000031	0.352208	-2.575716
C	-0.000173	-0.858111	-0.747920	C	-0.000021	-0.826046	-0.741910
C	-0.000173	-0.858111	0.747920	C	-0.000021	-0.826046	0.741910
C	0.000024	-2.141275	1.180039	C	0.000011	-2.152297	1.166506
H	0.000010	-2.470259	2.210946	H	0.000015	-2.472277	2.200791
C	0.000191	2.981107	0.685242	C	0.000048	2.972635	0.725049
H	0.000569	3.764865	1.430562	H	0.000089	3.736904	1.487278
C	0.000191	2.981107	-0.685242	C	0.000048	2.972635	-0.725049
H	0.000569	3.764865	-1.430562	H	0.000089	3.736904	-1.487278
C	0.000024	-2.141275	-1.180039	C	0.000011	-2.152297	-1.166506
H	0.000010	-2.470259	-2.210946	H	0.000015	-2.472277	-2.200791
C	0.000237	-3.073934	0.000000	C	0.000038	-3.097447	0.000000
H	0.876692	-3.737947	0.000000	H	0.875838	-3.763585	0.000000
H	-0.876025	-3.738289	0.000000	H	-0.875714	-3.763646	0.000000

Table S34: Optimized geometries of the singlet and triplet ground electronic state of 1,3-diethynyl-2-methylbenzene (**35**) and 1,2-diethynyl-4-methylbenzene (**36**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-35

	Singlet				Triplet		
C	-1.199220	-1.612585	0.000000	C	-1.241581	-1.612151	0.000000
C	0.000507	-2.310173	0.000000	C	-0.049444	-2.338472	0.000000
C	1.202737	-1.613626	0.000000	C	1.162565	-1.696859	0.000000
C	1.211106	-0.210227	0.000000	C	1.214280	-0.190795	0.000000
C	-1.211332	-0.206123	0.000000	C	-1.208128	-0.112384	0.000000
H	-2.143768	-2.142556	0.000000	H	-2.206484	-2.099573	0.000000
H	-0.000471	-3.393770	0.000000	H	-0.085992	-3.422533	0.000000
H	2.147333	-2.143659	0.000000	H	2.100595	-2.235058	0.000000
C	2.463878	0.476676	0.000000	C	2.453108	0.416360	0.000000
C	-2.475595	0.462214	0.000000	C	-2.448697	0.545879	0.000000
C	-3.556828	0.994512	0.000000	C	-3.555203	1.043998	0.000000
H	-4.508646	1.466833	0.000000	H	-4.516443	1.496841	0.000000
C	0.000000	0.517920	0.000000	C	0.000000	0.564859	0.000000
C	3.524390	1.049216	0.000000	C	3.575215	0.904910	0.000000
H	4.460365	1.552244	0.000000	H	4.543961	1.341561	0.000000
C	0.025385	2.022716	0.000000	C	0.072770	2.067041	0.000000
H	0.558075	2.400176	0.877802	H	0.617696	2.425556	0.878477
H	0.558075	2.400176	-0.877802	H	0.617696	2.425556	-0.878477
H	-0.981132	2.437438	0.000000	H	-0.920343	2.513341	0.000000

Isomer-36

	Singlet				Triplet		
C	1.795589	-0.930327	0.000000	C	1.845471	-0.820280	0.000000
C	0.824725	-1.942034	0.000000	C	0.865533	-1.929020	0.000000
C	-0.527313	-1.635120	0.000000	C	-0.473159	-1.691340	0.000000
C	-0.968902	-0.301742	0.000000	C	-0.999293	-0.363212	0.000000
C	0.000000	0.731240	0.000000	C	0.000000	0.790496	0.000000
C	1.363541	0.393362	0.000000	C	1.387851	0.466684	0.000000
H	1.133896	-2.982275	0.000000	H	1.237878	-2.947231	0.000000
H	-1.266260	-2.427105	0.000000	H	-1.177825	-2.514895	0.000000
C	-2.364572	-0.016291	0.000000	C	-2.356101	-0.133094	0.000000
C	-0.381924	2.104424	0.000000	C	-0.433133	2.099304	0.000000
C	-0.681958	3.271132	0.000000	C	-0.816324	3.260047	0.000000
H	-0.958721	4.296885	0.000000	H	-1.152363	4.267794	0.000000
C	-3.549688	0.200610	0.000000	C	-3.562752	0.067085	0.000000
H	-4.592668	0.402795	0.000000	H	-4.610138	0.245355	0.000000
C	3.264992	-1.272718	0.000000	C	3.301318	-1.167074	0.000000
H	3.531382	-1.864659	0.881028	H	3.560789	-1.771629	0.878620
H	3.531382	-1.864659	-0.881028	H	3.560789	-1.771629	-0.878620
H	3.883742	-0.373691	0.000000	H	3.930888	-0.275762	0.000000
H	2.090307	1.197490	0.000000	H	2.093517	1.290419	0.000000

Table S35: Optimized geometries of the singlet and triplet ground electronic state of 1,2-diethynyl-3-methylbenzene (**37**) and 2-ethynyl-2H-indene (**38**) in Cartesian coordinates (in Angstrom units) obtained at (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-37

Singlet				Triplet			
C	-2.128616	-0.718423	0.000000	C	-2.139892	-0.662185	0.000000
C	-1.479428	-1.952066	0.000000	C	-1.466000	-1.964076	0.000000
C	-0.093088	-2.009423	0.000000	C	-0.104611	-2.047209	0.000000
C	0.663501	-0.828489	0.000000	C	0.703168	-0.878034	0.000000
C	0.000000	0.425864	0.000000	C	0.000000	0.481035	0.000000
C	-1.412750	0.478665	0.000000	C	-1.448939	0.510264	0.000000
H	-3.212633	-0.682604	0.000000	H	-3.223828	-0.643536	0.000000
H	-2.057905	-2.868785	0.000000	H	-2.068601	-2.864202	0.000000
H	0.422170	-2.961725	0.000000	H	0.391450	-3.010515	0.000000
C	2.086909	-0.908229	0.000000	C	2.080139	-0.958283	0.000000
C	0.753439	1.635461	0.000000	C	0.741524	1.635368	0.000000
C	1.370830	2.670376	0.000000	C	1.411326	2.662150	0.000000
H	1.929349	3.574222	0.000000	H	1.994655	3.550144	0.000000
C	3.287750	-1.004021	0.000000	C	3.299606	-1.035394	0.000000
H	4.347751	-1.075782	0.000000	H	4.360019	-1.100033	0.000000
C	-2.130588	1.803413	0.000000	C	-2.153488	1.839864	0.000000
H	-1.862151	2.398467	0.877646	H	-1.877265	2.431229	0.878227
H	-1.862151	2.398467	-0.877646	H	-1.877265	2.431229	-0.878227
H	-3.212187	1.658969	0.000000	H	-3.236165	1.704688	0.000000

Isomer-38

Singlet				Triplet			
C	-0.246970	-2.827240	0.725986	C	0.333085	-2.845610	0.692873
H	-0.247145	-3.783295	1.237830	H	0.532972	-3.765122	1.230929
C	-0.242312	-0.414041	0.741295	C	-0.178531	-0.480953	0.723143
C	-0.246970	-1.675115	1.441863	C	0.077209	-1.658973	1.418614
H	-0.247274	-1.688884	2.526156	H	0.082693	-1.670738	2.502784
C	-0.246970	-1.675115	-1.441863	C	0.077209	-1.658973	-1.418614
H	-0.247274	-1.688884	-2.526156	H	0.082693	-1.670738	-2.502784
C	-0.242312	-0.414041	-0.741295	C	-0.178531	-0.480953	-0.723143
C	-0.276880	1.799609	0.000000	C	-0.687594	1.765735	0.000000
C	-0.234521	0.866462	1.190881	C	-0.465794	0.831480	1.178486
H	-0.222411	1.212115	2.214550	H	-0.510164	1.157125	2.208554
C	-0.234521	0.866462	-1.190881	C	-0.465794	0.831480	-1.178486
H	-0.222411	1.212115	-2.214550	H	-0.510164	1.157125	-2.208554
C	0.733865	2.855424	0.000000	C	0.205823	2.933086	0.000000
C	1.554457	3.734057	0.000000	C	0.936978	3.888537	0.000000
H	2.286488	4.504028	0.000000	H	1.588406	4.728003	0.000000
C	-0.246970	-2.827240	-0.725986	C	0.333085	-2.845610	-0.692873
H	-0.247145	-3.783295	-1.237830	H	0.532972	-3.765122	-1.230929
H	-1.272198	2.280780	0.000000	H	-1.722280	2.153990	0.000000

Table S36: Optimized geometries of the singlet and triplet ground electronic state of 5-ethynyl-5H-indene (**39**) and 4-ethynyl-4H-indene (**40**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-39

	Singlet				Triplet		
C	-1.131354	1.443613	-0.288797	C	1.125907	1.414693	0.331090
H	-1.906891	2.199337	-0.324710	H	1.875246	2.197231	0.368777
C	1.155231	0.741419	0.074234	C	-1.139050	0.700800	-0.059645
C	0.140280	1.759615	0.015521	C	-0.172472	1.714869	0.006310
H	0.408622	2.789995	0.227015	H	-0.444137	2.744850	-0.204098
C	-0.475920	-1.013235	-0.490481	C	0.514935	-1.039928	0.540203
H	-0.762745	-2.044248	-0.671922	H	0.790683	-2.070776	0.725711
C	0.785459	-0.666899	-0.187871	C	-0.775784	-0.676972	0.205185
C	3.007190	-0.597399	0.278581	C	-3.048210	-0.535573	-0.314942
C	2.490245	0.768483	0.351562	C	-2.567705	0.740128	-0.379510
H	3.081144	1.642474	0.590978	H	-3.127389	1.632427	-0.622840
C	2.002297	-1.458442	-0.040314	C	-1.965755	-1.436112	0.043042
H	2.072135	-2.529123	-0.166145	H	-2.055775	-2.507405	0.163080
C	-2.755559	-0.363026	0.156262	C	2.774923	-0.331398	-0.183596
C	-3.730214	-0.684041	0.782147	C	3.726541	-0.612005	-0.863756
H	-4.589197	-0.965101	1.340962	C	4.562663	-0.863124	-1.469382
C	-1.566189	0.028399	-0.613503	C	1.607472	0.009146	0.650049
H	-1.871652	0.023971	-1.676071	H	1.981951	0.023835	1.691682
H	4.039783	-0.868223	0.455842	H	-4.068049	-0.842930	-0.499509

Isomer-40

	Singlet				Triplet		
C	0.318877	2.306320	-0.088725	C	0.391665	2.323182	-0.067111
H	0.499151	3.362099	-0.259518	H	0.638512	3.369473	-0.216500
C	-1.299712	0.485003	-0.082557	C	-1.246938	0.530235	-0.129831
C	-1.035372	1.802665	-0.250631	C	-0.939829	1.900903	-0.298876
H	-1.821466	2.497652	-0.528764	H	-1.697349	2.608094	-0.612793
C	1.167898	0.027945	0.553695	C	1.153600	-0.007111	0.594888
H	1.329431	-0.054202	1.643818	H	1.312643	-0.191620	1.675812
C	-0.230424	-0.465020	0.263577	C	-0.260579	-0.406529	0.272965
C	-2.204866	-1.591634	-0.028804	C	-2.186546	-1.604633	0.006226
C	-2.522760	-0.286112	-0.244389	C	-2.447157	-0.202064	-0.297022
H	-3.489285	0.121176	-0.503380	H	-3.402662	0.206043	-0.600214
C	-0.776196	-1.707102	0.286796	C	-0.872617	-1.733687	0.347183
H	-0.260863	-2.636516	0.488271	H	-0.354724	-2.642586	0.617829
C	2.219674	-0.774578	-0.080907	C	2.136479	-0.851063	-0.104793
C	3.090620	-1.427983	-0.589984	C	2.947089	-1.532513	-0.674359
H	3.853153	-2.009744	-1.047242	H	3.662157	-2.131160	-1.183639
C	1.343501	1.505579	0.251324	C	1.386067	1.473601	0.330207
H	2.347498	1.900060	0.357067	H	2.395493	1.835033	0.483943
H	-2.885056	-2.431018	-0.086618	H	-2.921481	-2.395200	-0.041296

Table S37: Optimized geometries of the singlet and triplet ground electronic state of 1H-cyclopenta[3,4]cyclobuta[1,2]benzene (**41**) and 7aH-cyclobuta[a]indene (**42**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-41

Singlet				Triplet			
C	0.851399	-0.278025	0.000000	C	0.813036	-0.371884	0.000000
C	2.206591	-0.185456	0.000000	C	2.197040	-0.330453	0.000000
C	0.494246	2.143216	0.000000	C	0.598830	2.116772	0.000000
C	0.000000	0.874777	0.000000	C	0.000000	0.850613	0.000000
H	2.865584	-1.045748	0.000000	H	2.814740	-1.221257	0.000000
H	-0.129960	3.029073	0.000000	H	0.028262	3.038295	0.000000
C	1.924981	2.255710	0.000000	C	1.992081	2.131925	0.000000
C	2.741420	1.147930	0.000000	C	2.773024	0.947719	0.000000
C	-0.403753	-1.149483	0.000000	C	-0.406521	-1.166749	0.000000
C	-1.199272	-0.053742	0.000000	C	-1.194658	0.068205	0.000000
C	-2.635771	-0.458423	0.000000	C	-2.656725	-0.258270	0.000000
H	-3.190437	-0.104719	0.878457	H	-3.199169	0.124122	0.877220
H	-3.190437	-0.104719	-0.878457	H	-3.199169	0.124122	-0.877220
C	-1.199940	-2.363805	0.000000	C	-1.266348	-2.271118	0.000000
H	-0.841385	-3.383839	0.000000	H	-1.002026	-3.320492	0.000000
C	-2.503592	-1.978371	0.000000	C	-2.574348	-1.792368	0.000000
H	-3.359588	-2.639808	0.000000	H	-3.457332	-2.419013	0.000000
H	2.370825	3.244099	0.000000	H	2.509348	3.085168	0.000000
H	3.817539	1.279697	0.000000	H	3.852881	1.042713	0.000000

Isomer-42

Singlet				Triplet			
C	2.453909	-1.063826	-0.094618	C	2.566958	-0.983668	-0.026018
H	3.259850	-1.782982	-0.189361	H	3.394470	-1.683372	-0.047889
C	0.145280	-0.527547	0.327233	C	0.213164	-0.558383	0.251832
C	1.184074	-1.491966	0.168594	C	1.260122	-1.458029	0.214801
H	0.968706	-2.547135	0.297120	H	1.084682	-2.516381	0.372345
C	1.793098	1.292595	-0.158559	C	1.751459	1.297450	-0.218563
H	2.037666	2.343446	-0.270012	H	1.942653	2.347771	-0.410241
C	0.430607	0.894356	0.070132	C	0.445338	0.851838	0.040913
C	-1.219795	-0.644701	0.524334	C	-1.227534	-0.712664	0.403058
C	-0.738217	1.625295	0.032738	C	-0.777927	1.582894	0.087309
H	-0.794705	2.703392	-0.052754	H	-0.862091	2.649009	-0.082823
C	-2.293911	-1.234436	-0.285909	C	-2.307730	-1.194966	-0.413463
H	-2.496500	-2.237171	-0.637058	H	-2.502444	-2.146160	-0.893945
C	-2.792886	-0.013927	-0.572221	C	-2.945004	0.021160	-0.441866
H	-3.523663	0.363695	-1.274761	H	-3.856972	0.385321	-0.899531
C	2.760257	0.336356	-0.234337	C	2.801368	0.372232	-0.240308
H	3.791510	0.623885	-0.408429	H	3.811884	0.716596	-0.430262
C	-1.862144	0.737440	0.425900	C	-1.894745	0.667845	0.495763
H	-2.404496	1.075028	1.315526	H	-2.324997	0.932966	1.471608

Table S38: Optimized geometries of the singlet and triplet ground electronic state of 2-ethynyl-8-methylbicyclo-[4.2.0]octa-1,3,5,7-tetraene (**43**) and 2-(prop-1-yn-1-yl)bicyclo-[4.2.0]octa-1,3,5,7-tetraene(**44**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-43

Singlet				Triplet			
C	0.337156	-1.024975	0.000000	C	0.435685	-1.002596	0.000000
C	1.678999	-1.505626	0.000000	C	1.809363	-1.369812	0.000000
C	0.000000	0.301716	0.000000	C	0.000000	0.339075	0.000000
C	-1.344615	0.757496	0.000000	C	-1.424956	0.684021	0.000000
C	2.808293	-1.927664	0.000000	C	2.977061	-1.673353	0.000000
H	3.803812	-2.298641	0.000000	H	4.004178	-1.944798	0.000000
C	0.464014	1.755556	0.000000	C	0.355564	1.717180	0.000000
C	-0.821880	2.184337	0.000000	C	-1.089533	2.070573	0.000000
H	-1.283219	3.162472	0.000000	H	-1.643155	2.998666	0.000000
C	-2.406070	-0.091587	0.000000	C	-2.415455	-0.292168	0.000000
H	-3.439215	0.235099	0.000000	H	-3.474062	-0.059886	0.000000
C	-2.081119	-1.490955	0.000000	C	-1.967389	-1.616266	0.000000
H	-2.887985	-2.215266	0.000000	H	-2.692037	-2.422463	0.000000
C	1.800917	2.393726	0.000000	C	1.618433	2.494946	0.000000
H	2.377667	2.083016	0.878092	H	2.231616	2.262732	0.878844
H	2.377667	2.083016	-0.878092	H	2.231616	2.262732	-0.878844
H	1.720363	3.482688	0.000000	H	1.417576	3.568192	0.000000
C	-0.784428	-1.940217	0.000000	C	-0.591606	-1.960885	0.000000
H	-0.576686	-3.003217	0.000000	H	-0.318734	-3.009466	0.000000

Isomer-44

Singlet				Triplet			
C	0.000000	0.493704	0.000000	C	0.000000	0.521913	0.000000
C	-1.240075	1.195602	0.000000	C	-1.237176	1.221921	0.000000
C	0.112245	-0.870132	0.000000	C	0.080977	-0.885666	0.000000
C	1.362828	-1.545630	0.000000	C	1.367957	-1.589887	0.000000
C	-2.283870	1.802505	0.000000	C	-2.296613	1.802699	0.000000
C	-0.584395	-2.219080	0.000000	C	-0.614256	-2.122642	0.000000
C	0.601685	-2.866876	0.000000	C	0.680881	-2.843494	0.000000
C	2.552890	-0.891436	0.000000	C	2.577270	-0.902744	0.000000
H	3.515537	-1.388927	0.000000	H	3.541105	-1.398061	0.000000
C	2.468060	0.543265	0.000000	C	2.4810 86	0.491365	0.000000
H	3.384899	1.122061	0.000000	H	3.388701	1.084613	0.000000
C	1.264055	1.201779	0.000000	C	1.240776	1.180637	0.000000
H	1.239492	2.284853	0.000000	H	1.250018	2.264058	0.000000
H	-1.617163	-2.537358	0.000000	H	-1.652017	-2.420068	0.000000
C	-3.545386	2.530605	0.000000	C	-3.572356	2.504420	0.000000
H	-4.142472	2.285778	0.883880	H	-4.164009	2.246470	0.883788
H	-3.375148	3.611014	0.000000	H	-3.424991	3.588175	0.000000
H	-4.142472	2.285778	-0.883880	H	-4.164009	2.246470	-0.883788
H	0.889098	-3.909038	0.000000	H	0.973927	-3.882786	0.000000

Table S39: Optimized geometries of the singlet and triplet ground electronic state of 2-ethynyl-7-methylbicyclo-[4.2.0]octa-1,3,5,7-tetraene (**45**) and 2-ethynyl-5-methylbicyclo-[4.2.0]octa-1,3,5,7-tetraene (**46**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-45

Singlet				Triplet			
C	1.349782	0.196395	0.000000	C	1.375564	0.168794	0.000000
C	2.328375	1.231694	0.000000	C	2.376768	1.178476	0.000000
C	0.000000	0.422412	0.000000	C	0.000000	0.463316	0.000000
C	-0.953814	-0.629882	0.000000	C	-1.016577	-0.591826	0.000000
C	3.164245	2.100511	0.000000	C	3.215915	2.044785	0.000000
H	3.899245	2.867531	0.000000	H	3.957859	2.805187	0.000000
C	-1.134771	1.421877	0.000000	C	-1.009896	1.458757	0.000000
C	-2.059268	0.428574	0.000000	C	-2.052853	0.395289	0.000000
C	-0.606721	-1.942488	0.000000	C	-0.668528	-1.940693	0.000000
H	-1.322136	-2.756734	0.000000	H	-1.397506	-2.742628	0.000000
C	0.806780	-2.209672	0.000000	C	0.701947	-2.214782	0.000000
H	1.146123	-3.239267	0.000000	H	1.034592	-3.246802	0.000000
C	1.735360	-1.200485	0.000000	C	1.692963	-1.201136	0.000000
H	2.792672	-1.436326	0.000000	H	2.736396	-1.491890	0.000000
C	-3.547108	0.355115	0.000000	C	-3.533736	0.394434	0.000000
H	-3.967132	0.849787	0.881550	H	-3.935389	0.914148	0.879660
H	-3.967132	0.849787	-0.881550	H	-3.935389	0.914148	-0.879660
H	-3.890391	-0.680629	0.000000	H	-3.928273	-0.623728	0.000000
H	-1.188408	2.501547	0.000000	H	-1.021690	2.539078	0.000000

Isomer-46

Singlet				Triplet			
C	0.099247	-1.902194	0.000000	C	0.058975	-1.883449	0.000000
C	1.247721	0.278335	0.000000	C	1.273291	0.277986	0.000000
C	1.257467	-1.170603	0.000000	C	1.256375	-1.126614	0.000000
H	0.165598	-2.985749	0.000000	H	0.150428	-2.965221	0.000000
H	2.216432	-1.674591	0.000000	H	2.202249	-1.655178	0.000000
C	2.459270	1.026806	0.000000	C	2.481876	1.025459	0.000000
C	0.000000	0.835953	0.000000	C	0.000000	0.878047	0.000000
C	-1.194225	0.062625	0.000000	C	-1.229975	0.079284	0.000000
C	-1.212530	-1.297010	0.000000	C	-1.223419	-1.314869	0.000000
C	3.491971	1.648733	0.000000	C	3.500590	1.671357	0.000000
H	4.400457	2.199453	0.000000	H	4.399384	2.237791	0.000000
C	-0.843143	2.095448	0.000000	C	-0.758866	2.075614	0.000000
H	-0.621804	3.152975	0.000000	H	-0.527304	3.130087	0.000000
C	-1.983078	1.368944	0.000000	C	-2.009550	1.279295	0.000000
H	-3.033450	1.625326	0.000000	H	-3.062289	1.518762	0.000000
C	-2.454949	-2.145993	0.000000	C	-2.475385	-2.152250	0.000000
H	-2.487858	-2.795363	0.880946	H	-2.518184	-2.799340	0.881623
H	-3.358021	-1.532941	0.000000	H	-3.369574	-1.526724	0.000000
H	-2.487858	-2.795363	-0.880946	H	-2.518184	-2.799340	-0.881623

Table S40: Optimized geometries of the singlet and triplet ground electronic state of 2-ethynyl-4-methylbicyclo-[4.2.0]octa-1,3,5,7-tetraene (**47**) and 2-ethynyl-3-methylbicyclo-[4.2.0]octa-1,3,5,7-tetraene (**48**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-47

Singlet				Triplet			
C	1.537889	-0.913993	0.000000	C	1.516323	-0.933072	0.000000
C	0.000000	1.031939	0.000000	C	0.000000	1.049951	0.000000
C	1.324972	0.443698	0.000000	C	1.279489	0.470582	0.000000
H	2.173220	1.118425	0.000000	H	2.137652	1.132893	0.000000
C	-0.173494	2.446042	0.000000	C	-0.191494	2.458294	0.000000
C	-1.031298	0.136541	0.000000	C	-1.069731	0.134199	0.000000
C	-0.818202	-1.269917	0.000000	C	-0.831236	-1.313069	0.000000
C	-0.307453	3.644036	0.000000	C	-0.368197	3.651484	0.000000
H	-0.428139	4.699555	0.000000	H	-0.521242	4.702831	0.000000
C	-2.525081	-0.116964	0.000000	C	-2.470622	-0.076389	0.000000
H	-3.399645	0.517866	0.000000	H	-3.342292	0.560258	0.000000
C	-2.330745	-1.455121	0.000000	C	-2.243130	-1.541627	0.000000
H	-2.991499	-2.310678	0.000000	H	-2.882683	-2.411686	0.000000
C	0.417037	-1.827634	0.000000	C	0.448907	-1.846015	0.000000
H	0.589737	-2.898604	0.000000	H	0.638164	-2.914365	0.000000
C	2.933652	-1.485453	0.000000	C	2.937134	-1.441662	0.000000
H	3.102341	-2.114440	0.880687	H	3.133982	-2.061840	0.880603
H	3.102341	-2.114440	-0.880687	H	3.133982	-2.061840	-0.880603
H	3.687987	-0.696728	0.000000	H	3.657781	-0.622302	0.000000

Isomer-48

Singlet				Triplet			
C	0.000000	0.699705	0.000000	C	0.000000	0.722567	0.000000
C	-1.389319	0.251962	0.000000	C	-1.342214	0.279788	0.000000
C	0.337855	2.084176	0.000000	C	0.343479	2.102098	0.000000
C	0.942897	-0.290020	0.000000	C	0.981135	-0.284762	0.000000
C	0.621408	-1.673317	0.000000	C	0.638726	-1.709212	0.000000
C	0.622356	3.255820	0.000000	C	0.647226	3.269776	0.000000
H	0.876721	4.287345	0.000000	H	0.916291	4.297606	0.000000
C	2.415116	-0.657292	0.000000	C	2.364015	-0.603610	0.000000
H	3.335800	-0.091852	0.000000	H	3.281667	-0.034749	0.000000
C	2.114905	-1.975410	0.000000	C	2.026895	-2.046813	0.000000
H	2.706906	-2.880119	0.000000	H	2.597863	-2.962965	0.000000
C	-0.660863	-2.115473	0.000000	C	-0.687138	-2.127842	0.000000
H	-0.939229	-3.162897	0.000000	H	-0.981128	-3.171005	0.000000
C	-1.672527	-1.095050	0.000000	C	-1.646513	-1.113621	0.000000
H	-2.712652	-1.403136	0.000000	H	-2.695515	-1.389871	0.000000
C	-2.489624	1.279702	0.000000	C	-2.467197	1.280235	0.000000
H	-2.425309	1.930649	0.877653	H	-2.415609	1.933045	0.877261
H	-2.425309	1.930649	-0.877653	H	-2.415609	1.933045	-0.877261
H	-3.470149	0.800548	0.000000	H	-3.438437	0.783278	0.000000

Table S41: Optimized geometries of the singlet and triplet ground electronic state of 6H-cyclopropa[a]naphthalene (**49**) and 6,7-dihydro-5H-cyclobuta[e]indenyl-4-carbyne (**50**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-49

	Singlet				Triplet		
C	0.000000	0.638604	0.000000	C	0.000000	0.650969	0.000000
C	0.919260	1.633318	0.000000	C	1.049767	1.609761	0.000000
H	0.586772	2.666468	0.000000	H	0.805077	2.665145	0.000000
C	-1.424749	0.809849	0.000000	C	-1.362311	0.882433	0.000000
C	0.360438	-0.799444	0.000000	C	0.317911	-0.776886	0.000000
C	-2.729496	1.094359	0.000000	C	-2.760563	1.209116	0.000000
H	-3.512807	1.837346	0.000000	H	-3.549300	1.939577	0.000000
C	-2.026153	-1.578990	0.000000	C	-2.068719	-1.474385	0.000000
H	-2.723090	-2.405562	0.000000	H	-2.818847	-2.254698	0.000000
C	-0.590841	-1.793032	0.000000	C	-0.695828	-1.760142	0.000000
H	-0.234505	-2.819704	0.000000	H	-0.380363	-2.799285	0.000000
C	1.787253	-1.075846	0.000000	C	1.706809	-1.170737	0.000000
H	2.097488	-2.116944	0.000000	H	1.931033	-2.233392	0.000000
C	2.719242	-0.108532	0.000000	C	2.715065	-0.273246	0.000000
H	3.770702	-0.379112	0.000000	H	3.744496	-0.617341	0.000000
C	-2.365454	-0.269641	0.000000	C	-2.347026	-0.102343	0.000000
C	2.397606	1.366150	0.000000	C	2.485669	1.206196	0.000000
H	2.866400	1.858369	0.867917	H	3.011625	1.647786	0.865542
H	2.866400	1.858369	-0.867917	H	3.011625	1.647786	-0.865542

Isomer-50

	Singlet				Triplet		
C	-1.864378	0.628585	0.029848	C	1.820593	0.597630	-0.160774
C	-1.007930	-0.532152	-0.033747	C	0.977846	-0.592653	-0.093262
C	0.061696	1.868785	-0.000736	C	-0.071653	1.944313	0.143349
C	-1.205671	1.809392	0.043216	C	1.313213	1.843234	-0.087919
C	0.982145	0.879042	-0.053677	C	-0.898316	0.852262	0.120683
C	0.348706	-0.451685	-0.073604	C	-0.362669	-0.496037	0.101320
C	1.445001	-1.492985	-0.151749	C	-1.488248	-1.496212	0.198108
H	1.242977	-2.369081	0.468823	H	-1.307908	-2.407550	-0.375901
C	2.717798	-0.729417	0.292988	C	-2.705692	-0.685864	-0.318633
H	2.812920	-0.792769	1.380975	H	-2.757212	-0.773421	-1.407803
C	-3.077424	-0.289039	0.057174	C	3.013752	-0.312692	-0.016244
H	-4.145724	-0.135142	0.105712	H	4.073100	-0.138710	0.113159
C	2.480379	0.746285	-0.111173	C	-2.410251	0.784673	0.065744
H	2.836140	0.934004	-1.132375	H	-2.812935	1.023406	1.058246
H	2.993839	1.454368	0.542848	H	-2.841307	1.507412	-0.630767
C	-2.286425	-1.379916	-0.001888	C	2.229736	-1.421488	0.009426
H	-2.480059	-2.443252	-0.017867	H	2.430296	-2.475391	0.142898
H	1.547535	-1.845452	-1.185555	H	-1.640180	-1.793219	1.243439
H	3.628987	-1.144043	-0.142470	H	-3.653719	-1.045528	0.085952

Table S42: Optimized geometries of the singlet and triplet ground electronic state of (E)-2-naphthylcarbene (**51**) and (E)-1-naphthylcarbene (**52**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-51

Singlet				Triplet			
C	-0.667478	-0.593611	-0.000000	C	-0.669759	-0.582820	0.000000
C	0.000000	0.675854	0.000000	C	0.000000	0.684180	-0.000000
C	-0.773023	1.869347	0.000000	C	-0.786715	1.868887	-0.000000
C	-2.145053	1.814183	0.000000	C	-2.161106	1.803750	0.000000
C	-2.801810	0.560900	0.000000	C	-2.816494	0.552567	0.000000
C	-2.082685	-0.613505	-0.000000	C	-2.080612	-0.615272	0.000000
C	0.110501	-1.789321	-0.000000	C	0.122919	-1.772495	0.000000
C	1.475727	-1.734221	-0.000000	C	1.483877	-1.724240	-0.000000
C	2.176871	-0.475147	-0.000000	C	2.186734	-0.455799	-0.000000
C	1.409032	0.698302	0.000000	C	1.409901	0.722701	-0.000000
C	3.602021	-0.317275	-0.000000	C	3.570293	-0.421087	-0.000000
H	4.045591	-1.334414	-0.000000	H	4.363644	-1.154496	-0.000000
H	1.943060	1.642517	0.000000	H	1.913932	1.682693	-0.000000
H	2.061907	-2.646980	-0.000000	H	2.064884	-2.639272	-0.000000
H	-0.406256	-2.743583	-0.000000	H	-0.383647	-2.732527	0.000000
H	-0.257582	2.823625	0.000000	H	-0.283212	2.829931	-0.000000
H	-2.729990	2.726374	0.000000	H	-2.747141	2.715933	0.000000
H	-3.885663	0.528531	0.000000	H	-3.899744	0.512732	0.000000
H	-2.595680	-1.569108	-0.000000	H	-2.582945	-1.577237	0.000000

Isomer-52

Singlet				Triplet			
C	0.358741	-0.883209	-0.000000	C	0.366125	-0.882764	-0.000000
C	0.000000	0.502093	0.000000	C	0.000000	0.495128	0.000000
C	1.033174	1.465849	0.000000	C	1.018580	1.470640	-0.000000
C	2.354507	1.075648	0.000000	C	2.350476	1.109266	-0.000000
C	2.709497	-0.292462	0.000000	C	2.715701	-0.251848	-0.000000
C	1.729423	-1.254948	0.000000	C	1.742022	-1.225438	-0.000000
C	-0.668128	-1.858803	-0.000000	C	-0.648124	-1.882583	-0.000000
C	-2.005260	-1.510820	-0.000000	C	-1.985486	-1.529781	0.000000
C	-2.362525	-0.157526	-0.000000	C	-2.374493	-0.188911	0.000000
C	-1.406604	0.876183	-0.000000	C	-1.413649	0.860494	0.000000
C	-1.773064	2.258071	-0.000000	C	-1.825951	2.173920	0.000000
H	-2.878930	2.296671	-0.000000	H	-2.778090	2.684246	0.000000
H	-3.411590	0.119330	-0.000000	H	-3.427445	0.067513	0.000000
H	-2.769079	-2.279723	-0.000000	H	-2.747941	-2.301065	0.000000
H	-0.383963	-2.906969	-0.000000	H	-0.354895	-2.926585	-0.000000
H	0.745255	2.509240	0.000000	H	0.737764	2.518025	0.000000
H	3.135843	1.827778	0.000000	H	3.118960	1.873955	-0.000000
H	3.755184	-0.578364	0.000000	H	3.763690	-0.529696	-0.000000
H	1.988706	-2.308419	0.000000	H	2.016752	-2.275133	-0.000000

Table S43: Optimized geometries of the singlet and triplet ground electronic state of (Z)-2-naphthylcarbene (**53**) and (Z)-1-naphthylcarbene (**54**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-53

	Singlet				Triplet		
C	-0.664574	-0.607754	-0.000000	C	-0.668861	-0.603375	0.000000
C	0.000000	0.664459	0.000000	C	0.000000	0.664028	0.000000
C	-0.777445	1.856418	0.000000	C	-0.786693	1.848710	0.000000
C	-2.148372	1.797872	0.000000	C	-2.161148	1.783219	0.000000
C	-2.802612	0.542038	0.000000	C	-2.816031	0.531931	0.000000
C	-2.080975	-0.629616	0.000000	C	-2.079701	-0.635710	0.000000
C	0.114803	-1.800242	-0.000000	C	0.124271	-1.792999	-0.000000
C	1.480868	-1.742193	-0.000000	C	1.485021	-1.744134	-0.000000
C	2.177918	-0.485188	-0.000000	C	2.187154	-0.480256	-0.000000
C	1.408491	0.689243	-0.000000	C	1.410461	0.702623	-0.000000
C	3.613618	-0.494803	-0.000000	C	3.570493	-0.439218	-0.000000
H	3.942052	0.564637	-0.000000	H	4.324495	0.334755	-0.000000
H	1.918829	1.647958	0.000000	H	1.910263	1.665363	-0.000000
H	2.086761	-2.640404	-0.000000	H	2.070358	-2.655878	-0.000000
H	-0.399042	-2.755750	-0.000000	H	-0.382763	-2.752566	-0.000000
H	-0.265660	2.812892	0.000000	H	-0.283779	2.810130	0.000000
H	-2.735747	2.708535	0.000000	H	-2.747340	2.695315	0.000000
H	-3.886373	0.507402	0.000000	H	-3.899263	0.491751	0.000000
H	-2.591147	-1.586678	0.000000	H	-2.581766	-1.597780	0.000000

Isomer-54

	Singlet				Triplet		
C	0.329878	-0.883617	0.000000	C	0.319218	-0.894821	0.000000
C	0.000000	0.509621	0.000000	C	0.000000	0.496370	0.000000
C	1.066208	1.436245	0.000000	C	1.057012	1.430445	0.000000
C	2.378966	1.014574	0.000000	C	2.375428	1.020844	0.000000
C	2.698763	-0.359299	0.000000	C	2.691961	-0.351371	0.000000
C	1.689196	-1.291327	0.000000	C	1.682012	-1.286790	0.000000
C	-0.714276	-1.845296	-0.000000	C	-0.724298	-1.863558	-0.000000
C	-2.042646	-1.477266	-0.000000	C	-2.050286	-1.470618	-0.000000
C	-2.375168	-0.116022	-0.000000	C	-2.395957	-0.119431	-0.000000
C	-1.407376	0.904434	-0.000000	C	-1.410260	0.904030	-0.000000
C	-1.939483	2.231950	-0.000000	C	-1.803508	2.221678	-0.000000
H	-1.107347	2.960638	-0.000000	H	-1.359386	3.204044	-0.000000
H	-3.410111	0.204449	-0.000000	H	-3.438647	0.174464	-0.000000
H	-2.820589	-2.231540	-0.000000	H	-2.835594	-2.218347	-0.000000
H	-0.443153	-2.896839	-0.000000	H	-0.461447	-2.915586	-0.000000
H	0.846436	2.496044	0.000000	H	0.831853	2.490097	0.000000
H	3.177012	1.748681	0.000000	H	3.169877	1.758479	0.000000
H	3.736015	-0.673390	0.000000	H	3.728919	-0.667613	0.000000
H	1.917353	-2.352028	0.000000	H	1.916494	-2.346211	0.000000

Table S44: Optimized geometries of the singlet and triplet ground electronic state of 8-methylene-bicyclo[5.3.0]deca-1,3,5,6,9-pentaene (**55**) and 1-Azulenylcarbene (**56**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-55

Singlet				Triplet			
C	-0.553578	-1.339644	0.384399	C	-0.423754	-1.451816	0.000322
C	0.396626	-0.431704	0.133948	C	0.455614	-0.425553	0.000052
C	-1.876805	-1.449948	0.490450	C	-1.791099	-1.640956	-0.000111
C	0.070790	0.984518	0.259324	C	0.028139	1.004419	0.000078
C	-2.676602	-0.556394	-0.329706	C	-2.720046	-0.586006	-0.000153
C	-1.178931	1.489238	-0.013127	C	-1.261432	1.491422	0.000207
C	-2.342702	0.766483	-0.454437	C	-2.489342	0.786932	0.000005
C	1.340455	1.709847	0.288607	C	1.232375	1.776352	-0.000064
C	1.848913	-0.521540	-0.145245	C	1.908957	-0.446289	-0.000029
C	2.351023	0.850610	0.011345	C	2.320779	0.942195	-0.000200
C	2.576054	-1.618426	-0.411360	C	2.728036	-1.546216	0.000056
H	2.113380	-2.596479	-0.471409	H	2.321970	-2.549650	0.000353
H	-2.355499	-2.105741	1.215303	H	-2.177947	-2.655424	-0.000382
H	-3.612525	-0.896431	-0.767513	H	-3.765160	-0.886230	-0.000577
H	-3.082597	1.390148	-0.951156	H	-3.377788	1.409813	-0.000114
H	-1.269465	2.571560	-0.052932	H	-1.350469	2.575317	0.000408
H	1.434656	2.780797	0.414700	H	1.258696	2.858140	0.000038
H	3.393304	1.117411	-0.106717	H	3.355997	1.258185	-0.000524
H	3.647280	-1.559508	-0.565460	H	3.805348	-1.437050	-0.000177

Isomer-56

Singlet				Triplet			
C	1.378925	0.741546	0.000000	C	1.369601	0.783311	0.000000
C	0.000000	0.615012	0.000000	C	0.000000	0.629978	0.000000
C	2.341730	-0.273368	0.000000	C	2.369323	-0.204705	0.000000
C	-0.805636	-0.601782	0.000000	C	-0.773170	-0.635726	0.000000
C	2.153053	-1.651884	0.000000	C	2.212801	-1.595075	0.000000
C	-0.350662	-1.923348	0.000000	C	-0.288222	-1.926266	0.000000
C	0.959966	-2.385828	0.000000	C	1.052687	-2.364349	0.000000
C	-2.172970	-0.199089	0.000000	C	-2.153516	-0.271425	0.000000
C	-0.908370	1.749255	0.000000	C	-0.964334	1.720663	0.000000
C	-2.232508	1.178895	0.000000	C	-2.277493	1.095615	0.000000
C	-0.464810	3.074233	0.000000	C	-0.707681	3.052066	0.000000
H	1.717713	1.775645	0.000000	H	1.722543	1.812030	0.000000
H	3.375607	0.059135	0.000000	H	3.391814	0.157966	0.000000
H	3.061344	-2.247731	0.000000	H	3.140616	-2.161560	0.000000
H	1.077164	-3.465196	0.000000	H	1.196110	-3.439948	0.000000
H	-1.124163	-2.687648	0.000000	H	-1.040387	-2.711797	0.000000
H	-3.010574	-0.883777	0.000000	H	-2.970509	-0.980800	0.000000
H	-3.139788	1.769963	0.000000	H	-3.206413	1.649497	0.000000
H	-1.349600	3.737767	0.000000	H	-1.273744	3.970088	0.000000

Table S45: Optimized geometries of the singlet and triplet ground electronic state of bicyclo[4.4.1]undeca-1,5,7,9-tetraen-3-yne (**57**) and bicyclo[4.4.1]undeca-1,3,5,9-tetraen-7-yne (**58**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-57

	Singlet				Triplet		
C	1.197224	-0.161827	-0.000000	C	1.175832	-0.137540	0.000000
C	0.284844	-0.129482	1.199526	C	0.259411	-0.121219	1.203312
C	-0.138575	1.155093	1.598072	C	-0.247070	1.125742	1.555864
C	-0.203185	2.228503	0.712977	C	-0.143048	2.296973	0.681296
C	-0.203185	2.228503	-0.712977	C	-0.143048	2.296973	-0.681296
C	-0.138575	1.155093	-1.598072	C	-0.247070	1.125742	-1.555864
C	0.284844	-0.129482	-1.199526	C	0.259411	-0.121219	-1.203312
C	-0.274225	-1.354156	-1.633973	C	-0.227171	-1.372835	-1.673765
C	-0.261380	-2.295753	-0.624588	C	-0.220270	-2.341980	-0.612887
C	-0.261380	-2.295753	0.624588	C	-0.220270	-2.341980	0.612887
C	-0.274225	-1.354156	1.633973	C	-0.227171	-1.372835	1.673765
H	1.841356	0.716682	0.000000	H	1.802686	0.754000	-0.000000
H	1.811500	-1.061697	-0.000000	H	1.813353	-1.019448	0.000000
H	-0.544059	1.298515	2.596073	H	-0.859287	1.229157	2.447714
H	-0.544059	1.298515	-2.596073	H	-0.859287	1.229157	-2.447714
H	-0.833030	-1.446595	-2.558023	H	-0.831543	-1.470637	-2.566179
H	-0.833030	-1.446595	2.558023	H	-0.831543	-1.470637	2.566179
H	-0.485883	3.180838	1.152786	H	-0.175800	3.266743	1.172615
H	-0.485883	3.180838	-1.152786	H	-0.175800	3.266743	-1.172615

Isomer-58

	Singlet				Triplet		
C	0.015368	-0.162915	1.278383	C	0.097728	-0.115950	1.268036
C	-0.167112	-1.276775	0.266903	C	0.020461	-1.234225	0.264625
C	-1.427787	-1.450814	-0.282953	C	-1.275900	-1.533324	-0.256836
C	-2.377456	-0.410093	-0.301562	C	-2.304834	-0.620738	-0.306248
C	-2.138205	0.974368	-0.219284	C	-2.249484	0.815586	-0.198817
C	-0.895417	1.630063	-0.110330	C	-1.134598	1.604132	-0.052159
C	0.254995	1.015099	0.378687	C	0.136383	1.062101	0.327255
C	1.577249	1.319728	-0.101529	C	1.341420	1.418857	-0.254670
C	2.539470	0.365854	-0.398309	C	2.453786	0.522437	-0.321739
C	2.113964	-0.968626	-0.308507	C	2.340551	-0.852373	-0.325589
C	1.103183	-1.671223	-0.208863	C	1.237027	-1.654797	-0.212969
H	-0.886532	-0.009622	1.870643	C	-0.780484	-0.082864	1.911911
H	0.859386	-0.365957	1.935171	C	1.004439	-0.174928	1.868219
H	-1.649620	-2.354008	-0.843276	C	-1.436604	-2.517463	-0.683819
H	-0.817990	2.620122	-0.553790	C	-1.196945	2.649745	-0.341397
H	1.783484	2.340826	-0.414337	C	1.427032	2.381528	-0.754040
H	-3.377217	-0.682495	-0.627797	C	-3.261111	-1.004136	-0.650164
H	-2.984922	1.600457	-0.485584	C	-3.172751	1.322765	-0.462300
H	3.483895	0.662676	-0.836833	C	3.441181	0.955129	-0.473751

Table S46: Optimized geometries of the singlet and triplet ground electronic state bicyclo[4.4.1]undeca-1,3,5,7,9-pentaen-11-ylidene (**59**) and 2,7-didehydro-bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**60**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-59

Singlet				Triplet			
C	0.000000	0.000000	1.182799	C	0.000000	0.000000	1.122285
C	0.000000	1.119238	0.251732	C	0.000000	1.187595	0.350370
C	1.277034	1.561061	-0.138606	C	1.280152	1.613116	-0.090908
C	2.380766	0.710450	-0.139992	C	2.339313	0.715290	-0.201057
C	2.380766	-0.710450	-0.139992	C	2.339313	-0.715290	-0.201057
C	1.277034	-1.561061	-0.138606	C	1.280152	-1.613116	-0.090908
C	-0.000000	-1.119238	0.251732	C	-0.000000	-1.187595	0.350370
C	-1.277034	-1.561061	-0.138606	C	-1.280152	-1.613116	-0.090908
C	-2.380766	-0.710450	-0.139992	C	-2.339313	-0.715290	-0.201057
C	-2.380766	0.710450	-0.139992	C	-2.339313	0.715290	-0.201057
C	-1.277034	1.561061	-0.138606	C	-1.280152	1.613116	-0.090908
H	1.387600	2.576975	-0.504247	H	1.425158	2.623460	-0.465727
H	1.387600	-2.576975	-0.504247	H	1.425158	-2.623460	-0.465727
H	-1.387600	-2.576975	-0.504247	H	-1.425158	-2.623460	-0.465727
H	-1.387600	2.576975	-0.504247	H	-1.425158	2.623460	-0.465727
H	3.341669	1.168150	-0.353564	H	3.284370	1.148591	-0.517025
H	3.341669	-1.168150	-0.353564	H	3.284370	-1.148591	-0.517025
H	-3.341669	-1.168150	-0.353564	H	-3.284370	-1.148591	-0.517025
H	-3.341669	1.168150	-0.353564	H	-3.284370	1.148591	-0.517025

Isomer-60

Singlet				Triplet			
C	0.000000	0.000000	1.456818	C	0.000000	0.000000	1.289271
C	-1.086177	0.346290	0.422668	C	-1.090232	0.342384	0.301722
C	-1.084452	1.626804	-0.307796	C	-1.121383	1.654962	-0.226199
C	0.000000	2.388237	-0.597492	C	0.000000	2.465814	-0.334970
C	1.393870	2.045458	-0.267513	C	1.376122	2.062945	-0.278925
C	1.653297	0.778784	0.015053	C	1.785668	0.774298	-0.109605
C	1.086177	-0.346290	0.422668	C	1.090232	-0.342384	0.301722
C	1.084452	-1.626804	-0.307796	C	1.121383	-1.654962	-0.226199
C	-0.000000	-2.388237	-0.597492	C	-0.000000	-2.465814	-0.334970
C	-1.393870	-2.045458	-0.267513	C	-1.376122	-2.062945	-0.278925
C	-1.653297	-0.778784	0.015053	C	-1.785668	-0.774298	-0.109605
H	0.314721	0.835874	2.078264	H	0.262723	0.853677	1.912629
H	-0.314721	-0.835874	2.078264	H	-0.262723	-0.853677	1.912629
H	-2.047421	1.949571	-0.688833	H	-2.047826	2.007924	-0.668963
H	2.047421	-1.949571	-0.688833	H	2.047826	-2.007924	-0.668963
H	-0.166007	3.324737	-1.121888	H	-0.164558	3.483379	-0.676906
H	2.137289	2.835638	-0.227517	H	2.108162	2.820357	-0.546711
H	0.166007	-3.324737	-1.121888	H	0.164558	-3.483379	-0.676906
H	-2.137289	-2.835638	-0.227517	H	-2.108162	-2.820357	-0.546711

Table S47: Optimized geometries of the singlet and triplet ground electronic state of 2,8-didehydro-bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**61**) and 2,10-didehydro-bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**62**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-61

Singlet				Triplet			
C	-0.129381	-0.055855	1.349640	C	-0.075398	-0.041718	1.266333
C	-0.101100	1.136935	0.457541	C	0.082560	1.118848	0.335045
C	1.094438	1.460095	-0.274652	C	1.379432	1.420528	-0.156061
C	2.197033	0.659896	-0.473241	C	2.389042	0.482558	-0.297985
C	2.344744	-0.760657	-0.215311	C	2.265739	-0.951409	-0.258588
C	1.251410	-1.515453	0.004151	C	1.078281	-1.598962	-0.145417
C	-0.005987	-1.208328	0.323874	C	-0.166967	-1.168940	0.257867
C	-1.206876	-1.601241	-0.360920	C	-1.439960	-1.457945	-0.278538
C	-2.260754	-0.708882	-0.477950	C	-2.462514	-0.498298	-0.310719
C	-2.030716	0.647928	-0.350840	C	-2.228144	0.869403	-0.236804
C	-1.357694	1.725763	0.001628	C	-1.108672	1.662672	-0.190278
H	0.742825	-0.074734	2.003406	H	0.790234	-0.160618	1.915572
H	-1.042698	-0.103067	1.941572	H	-0.984215	0.040870	1.862479
H	1.108913	2.447553	-0.730937	H	1.555642	2.415195	-0.558052
H	-1.287127	-2.601021	-0.772350	H	-1.616642	-2.425092	-0.738856
H	-1.448185	2.734905	-0.388568	H	-1.089700	2.607247	-0.729061
H	3.057635	1.146999	-0.927067	H	3.358557	0.852078	-0.620361
H	3.346798	-1.178495	-0.258012	H	3.168776	-1.520698	-0.462463
H	-3.248864	-1.053345	-0.771564	H	-3.463033	-0.829400	-0.578396

Isomer-62

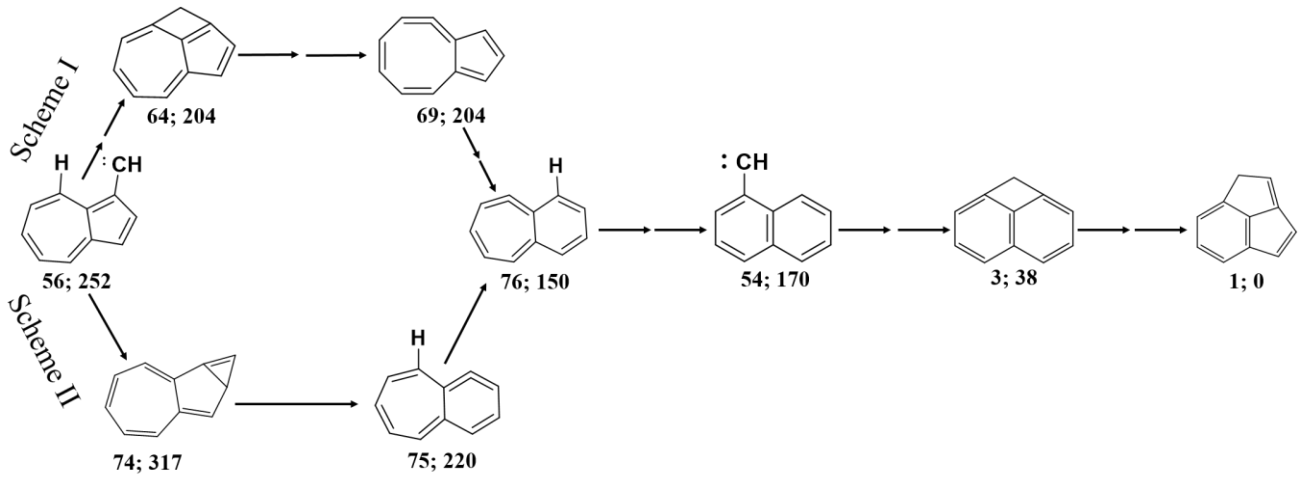
Singlet				Triplet			
C	-1.233445	0.026165	-0.000000	C	-1.310797	0.150976	0.000000
C	-0.103679	1.042646	0.000000	C	-0.130499	1.075187	-0.000000
C	0.415093	1.442011	1.239940	C	0.461597	1.406911	1.243318
C	0.415093	0.617953	2.365474	C	0.461597	0.573910	2.352340
C	0.157745	-0.780731	2.390534	C	0.146201	-0.830595	2.379408
C	-0.158731	-1.563182	1.310809	C	-0.135033	-1.546172	1.263511
C	-0.372249	-1.257602	-0.000000	C	-0.535519	-1.166126	0.000000
C	-0.158731	-1.563182	-1.310809	C	-0.135033	-1.546172	-1.263511
C	0.157745	-0.780731	-2.390534	C	0.146201	-0.830595	-2.379408
C	0.415093	0.617953	-2.365474	C	0.461597	0.573910	-2.352340
C	0.415093	1.442011	-1.239940	C	0.461597	1.406911	-1.243318
H	-1.856407	0.113426	0.889191	H	-1.921049	0.264464	0.894661
H	-1.856407	0.113426	-0.889191	H	-1.921049	0.264464	-0.894661
H	0.987758	2.364817	1.292851	H	1.073244	2.305161	1.291719
H	0.987758	2.364817	-1.292851	H	1.073244	2.305161	-1.291719
H	0.759930	1.056337	3.298731	H	0.895047	0.968801	3.266750
H	0.261636	-1.264514	3.359611	H	0.277026	-1.342862	3.328639
H	0.261636	-1.264514	-3.359611	H	0.277026	-1.342862	-3.328639
H	0.759930	1.056337	-3.298731	H	0.895047	0.968801	-3.266750

Table S48: Optimized geometries of the singlet and triplet ground electronic state of 2,9-didehydro-bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**63**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-63

Singlet				Triplet			
C	-0.067492	-0.335386	1.348218	C	-0.065135	-0.119320	1.258316
C	0.083153	0.984565	0.617514	C	-0.059362	1.060023	0.331345
C	1.399441	1.374700	0.130437	C	1.189961	1.520579	-0.143048
C	2.340922	0.510443	-0.369318	C	2.314855	0.716095	-0.275816
C	2.176389	-0.925548	-0.507390	C	2.365399	-0.717702	-0.275801
C	0.951047	-1.460984	-0.425702	C	1.267931	-1.515189	-0.160443
C	-0.205258	-1.333000	0.159092	C	-0.013940	-1.244702	0.254160
C	-1.678338	-1.492037	-0.136666	C	-1.256313	-1.646478	-0.311148
C	-2.269261	-0.365981	-0.460461	C	-2.284725	-0.748619	-0.309789
C	-2.122143	0.958621	-0.577569	C	-2.403415	0.639927	-0.264613
C	-0.981683	1.629397	0.024432	C	-1.310747	1.506082	-0.136410
H	0.818995	-0.542690	1.946699	H	0.809882	-0.120095	1.906200
H	-0.946975	-0.339103	1.991580	H	-0.975263	-0.157801	1.856855
H	1.591119	2.440148	0.022273	H	1.246650	2.528807	-0.546716
H	-2.186922	-2.326554	0.340383	H	-1.334557	-2.582812	-0.855311
H	-0.782484	2.607114	-0.410073	H	-1.409597	2.516909	-0.524420
H	3.286509	0.932930	-0.697685	H	3.235369	1.206979	-0.578408
H	3.063416	-1.542353	-0.623497	H	3.324607	-1.166184	-0.521023
H	-2.604324	1.501772	-1.385200	H	-3.364149	1.070020	-0.537697

Figure S6: Probable rearrangement scheme of $C_{11}H_8$ isomers at their ground energy state and their potential energy diagram calculated at B3LYP/6-311+G(D,P) level of theory.



Scheme-I (Detailed)

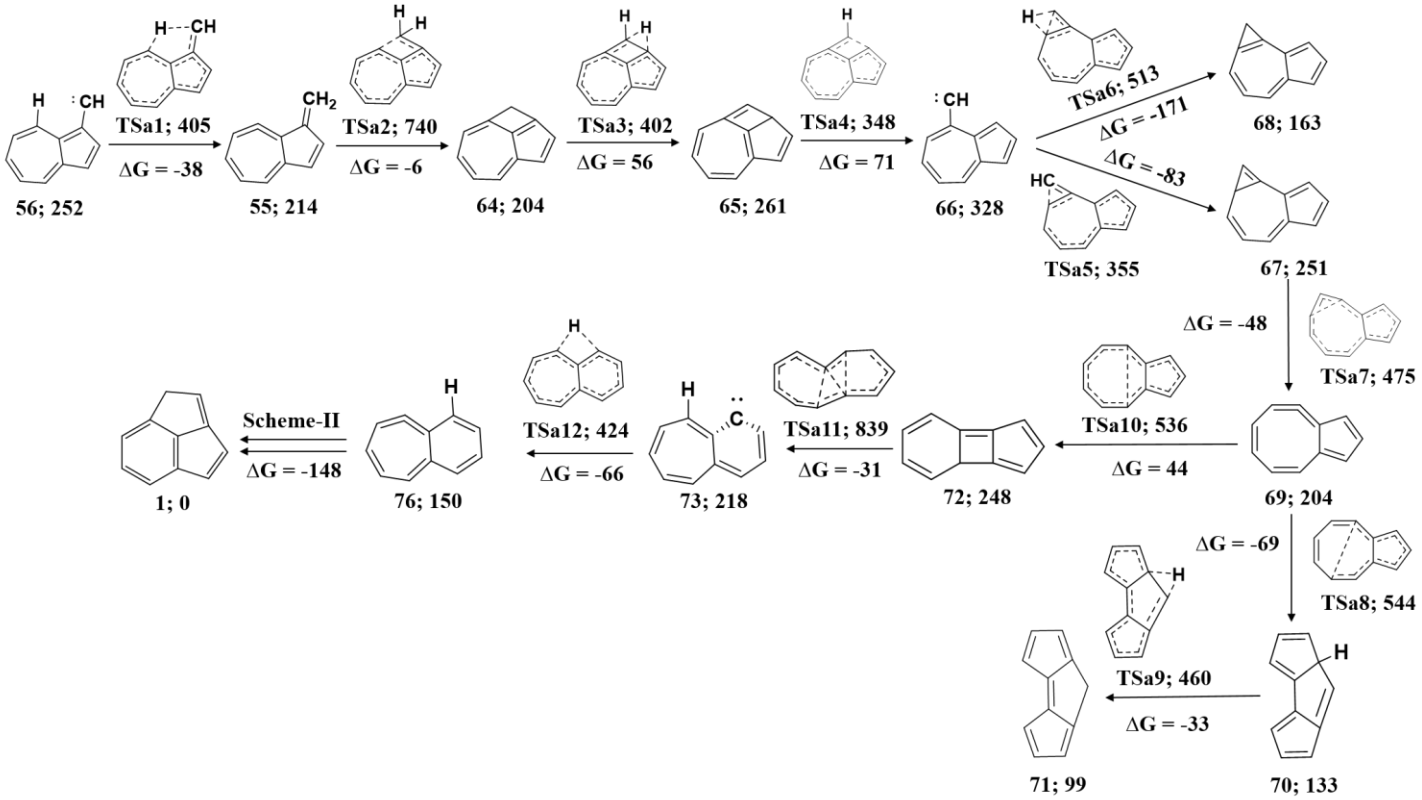


Figure S7: Probable rearrangement scheme of $C_{11}H_8$ isomers at their ground energy state and their potential energy diagram calculated at B3LYP/6-311+G(D,P) level of theory.

Scheme-II (Detailed)

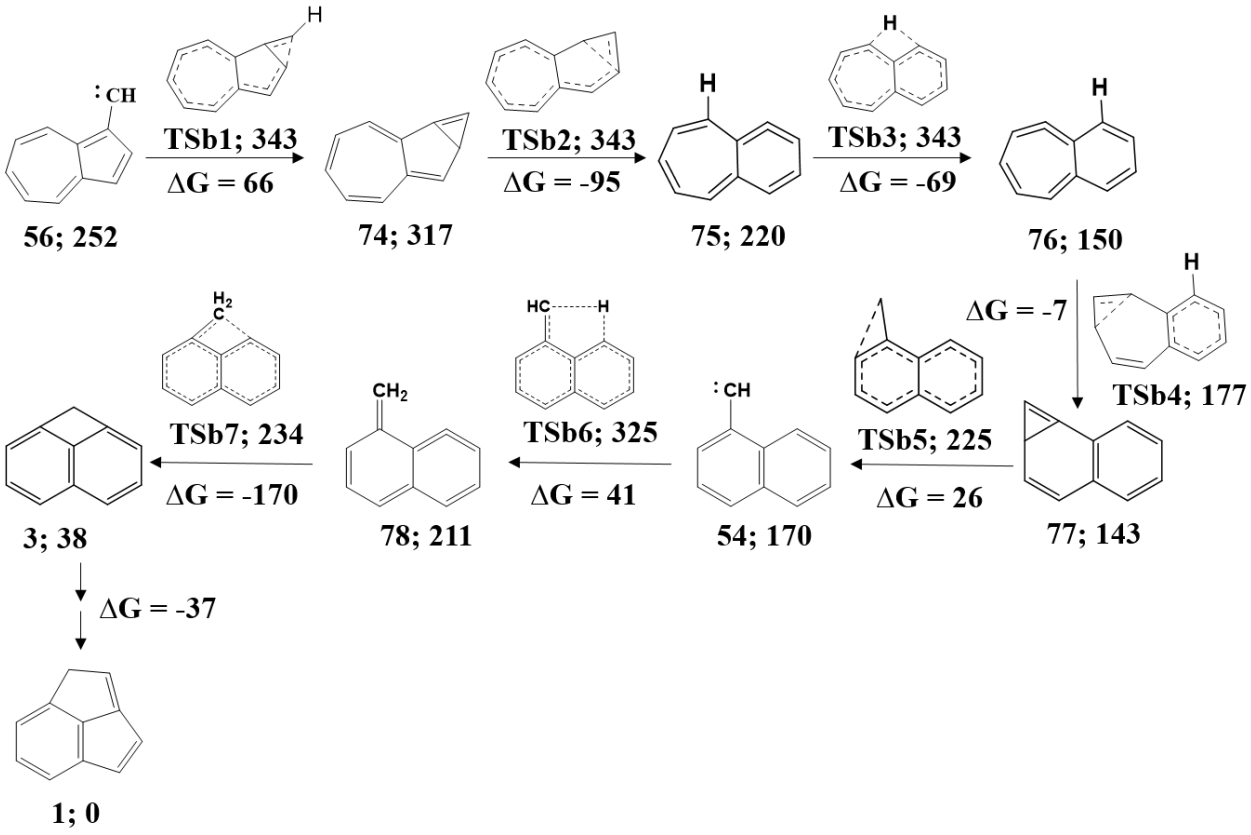


Figure S8: Potential Energy Surface of rearrangement scheme (**Scheme-I**) of $C_{11}H_8$ isomers at their ground energy state and their potential energy diagram calculated at B3LYP/6-311+G(D,P) level of theory.

PES-I

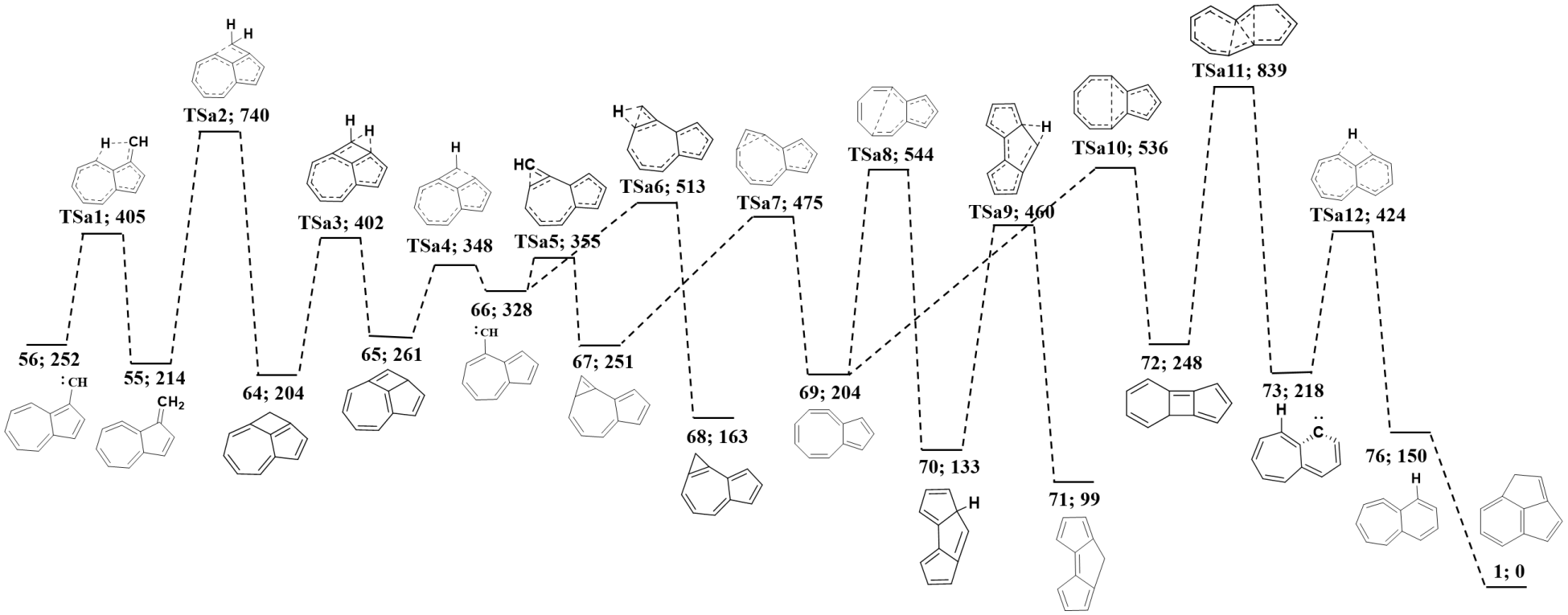


Figure S9: Potential Energy Surface of rearrangement scheme (**Scheme-II**) of $C_{11}H_8$ isomers at their ground energy state and their potential energy diagram calculated at B3LYP/6-311+G(D,P) level of theory

PES-II

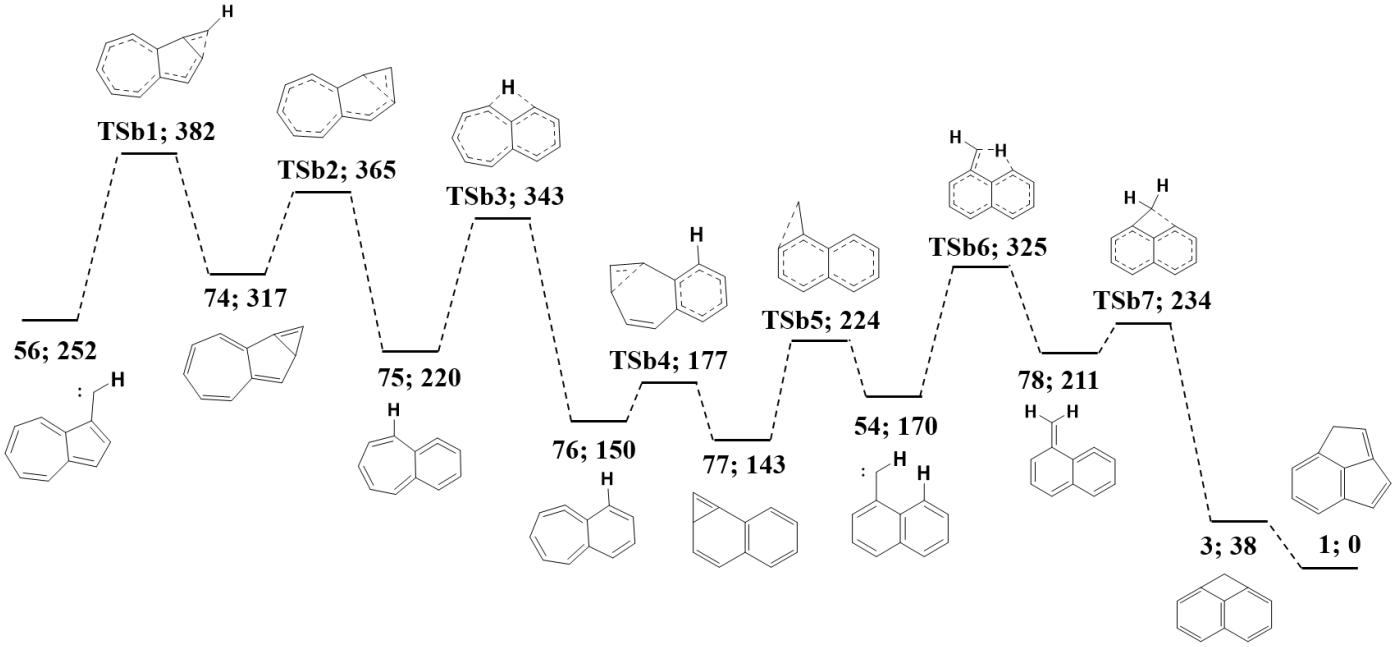


Table S49: Computed energies of probable rearrangement schemes (**Scheme-I**) of $C_{11}H_8$ isomers in their ground electronic states calculated at the B3LYP/6-311+G(D,P) level of theory.

Scheme-I

Isomer	Point group	E (a.u.)	ZPVE (a.u.)	E+ZPVE (a.u.)	ΔE + ZPVE (kJ mol^{-1})	Nimag	Imaginary Frequency (cm^{-1})
56	C_s	-423.9385996	0.148666	-423.789934	252	0	
TSa1	C_1	-423.9021339	0.142557	-423.731747	404	1	*i*1606.31
55	C_1	-423.9467347	0.148096	-423.804357	214	0	
TSa2	C_1	-423.903775	0.13916	-423.603875	740	1	*i*500.47
64	C_s	-423.9586568	0.150236	-423.808338	204	0	
TSa3	C_1	-423.8716207	0.142714	-423.732657	402	1	*i*1103.51
65	C_1	-423.9361824	0.149705	-423.786478	261	0	
TSa4	C_1	-423.8990368	0.145979	-423.753061	349	1	*i*284.91
66	C_1	-423.9079077	0.146875	-423.761033	328	0	
TSa5	C_1	-423.904192	0.146626	-423.750394	356	1	*i*255.85
67	C_1	-423.938662	0.148538	-423.790123	251	0	
66	C_1	-423.9079077	0.146875	-423.761033	328	0	
TSa6	C_1	-423.877081	0.141511	-423.690431	513	1	*i*973.09
68	C_s	-423.9733919	0.149465	-423.823927	163	0	
67	C_1	-423.938662	0.148538	-423.790123	251	0	
TSa7	C_1	-423.928876	0.141898	-423.70512	474	1	*i*528.58
69	C_1	-423.957115	0.148836	-423.80828	204	0	
TSa8	C_1	-423.901658	0.13938	-423.678755	544	1	*i*653.48
70	C_1	-423.981062	0.150078	-423.835224	133	0	
TSa9	C_1	-423.905048	0.140105	-423.710789	460	1	*i*1965.63
71	C_s	-423.998635	0.150434	-423.848201	99	0	
69	C_1	-423.957115	0.148836	-423.80828	204	0	
TSa10	C_1	-423.896578	0.145966	-423.681686	536	1	*i*619.98
72	C_1	-423.941321	0.149834	-423.791487	248	0	
TSa11	C_1	-423.870298	0.14117	-423.566487	839	1	*i*281.95
73	C_1	-423.952256	0.149458	-423.802797	218	0	
TSa12	C_1	-423.900104	0.141207	-423.724555	424	1	*i*1741.06
76	C_1	-423.9781734	0.149541	-423.828632	150	0	

Table S50: Computed energies of probable rearrangement schemes (**Scheme-II**) of $C_{11}H_8$ isomers in their ground electronic states calculated at the B3LYP/6-311+G(D,P) level of theory.

Scheme-II

Isomer	Point group	E (a.u.)	ZPVE (a.u.)	E+ZPVE (a.u.)	ΔE +ZPVE (kJ mol^{-1})	Nimag	Imaginary Frequency (cm^{-1})
56	C_s	-423.9385996	0.148666	-423.789934	252	0	
TSb1	C_1	-423.8826476	0.146894	-423.742409	377	1	*i*736.31
74	C_1	-423.9135058	0.148614	-423.764892	318	0	
TSb2	C_1	-423.9047809	0.14636	-423.746826	365	1	*i*496.53
75	C_1	-423.9518192	0.149094	-423.802216	220	0	
TSb3	C_1	-423.900104	0.14499	-423.755114	343	1	*i*1741.05
76	C_1	-423.9781734	0.149541	-423.828632	150	0	
TSb4	C_1	-423.9666231	0.15414	-423.818477	177	1	*i*217.64
77	C_1	-423.9814159	0.149831	-423.831585	143	0	
TSb5	C_1	-423.9567484	0.147684	-423.800266	225	1	*i*324.20
54	C_s	-423.9699908	0.148982	-423.821009	170	0	
TSb6	C_1	-423.9208997	0.143672	-423.76203	325	1	*i*1698.44
78	C_s	-423.9539591	0.148613	-423.805346	211	0	
TSb7	C_1	-423.9493914	0.14832	-423.79661	234	1	*i*336.88
3	C_{2v}	-424.0234022	0.15192	-423.871482	38	0	
1	C_s	-424.0375772	0.151674	-423.885903	0	0	

Figure S10: Rearrangement process and mechanism of $C_{11}H_8$ isomers from 1H-cyclobuta[de]naphthalene (**3**) to 1H-cyclopenta[cd]indene (**1**) through 1,2-H shifting calculated at B3LYP/6-311+G(D,P) level of theory.

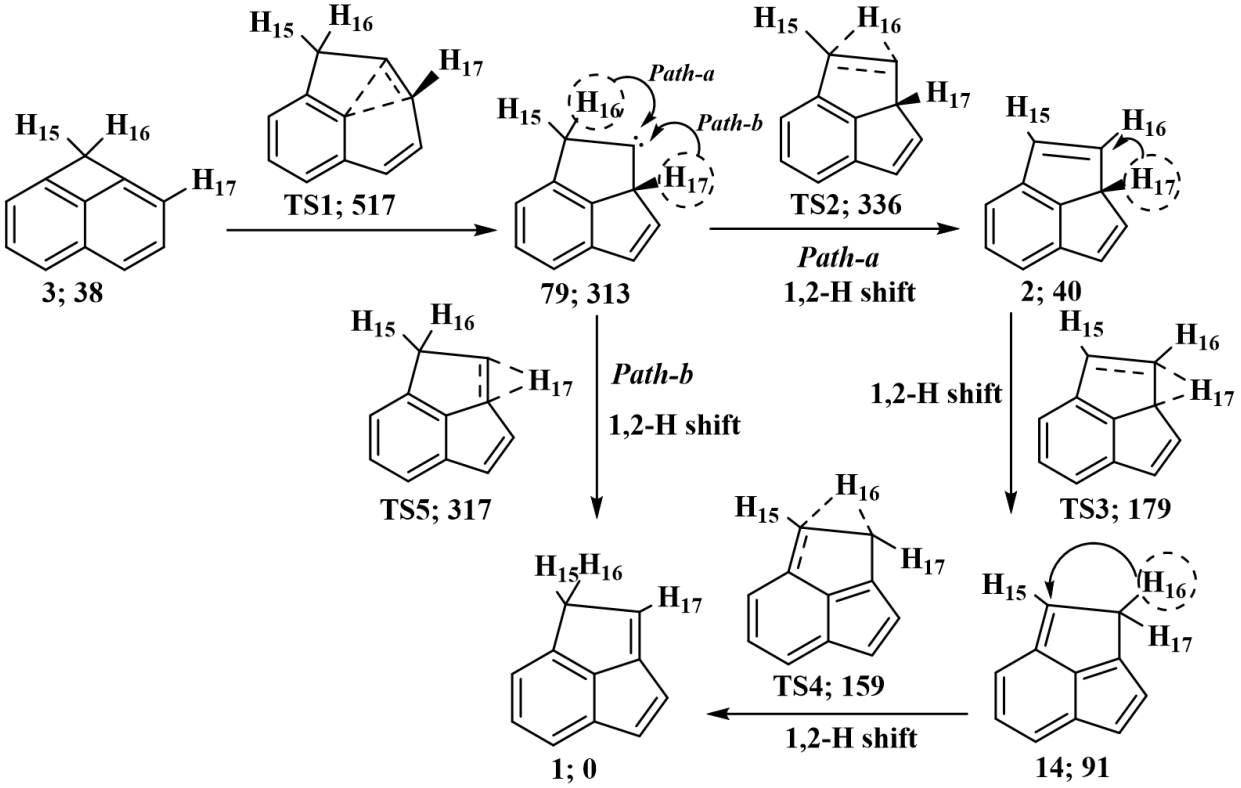


Table S51: Computed energies of rearrangement process of $C_{11}H_8$ isomers from 1H-cyclobuta[de]naphthalene (**3**) to 1H-cyclopenta[cd]indene (**1**) through 1,2-H shifting calculated at B3LYP/6-311+G(D,P) level of theory.

Isomer	Point group	E (a.u.)	ZPVE (a.u.)	E+ZPVE (a.u.)	ΔE + ZPVE (kJ mol^{-1})	Nimag	Imaginary Frequency (cm^{-1})
3	C_{2v}	-424.0234022	0.15192	-423.871482	38	0	
TS1	C_1	-423.835519	0.146703	-423.688817	517	1	*i*622.89
79	C_s	-423.914486	0.147625	-423.766862	313	0	
TS2	C_1	-423.903958	0.146154	-423.757805	336	1	*i*768.54
2	C_s	-424.0222984	0.151621	-423.870678	40	0	
TS3	C_1	-423.9663483	0.146129	-423.817632	179	1	*i*1222.62
14	C_s	-424.0014978	0.150221	-423.851276	91	0	
TS4	C_1	-423.9728516	0.1475	-423.825351	159	1	*i*1203.78
1	C_s	-424.0375772	0.151674	-423.885903	0	0	
TS5	C_1	-423.911029	0.145839	-423.76519	317	1	*i*643.08

Figure S11: Potential energy diagram of $C_{11}H_8$ isomers from 1H-cyclobuta[de]naphthalene (**3**) to 1H-cyclopenta[cd]indene (**1**) through 1,2-H shifting calculated at B3LYP/6-311+G(D,P) level of theory.

PES-IIa

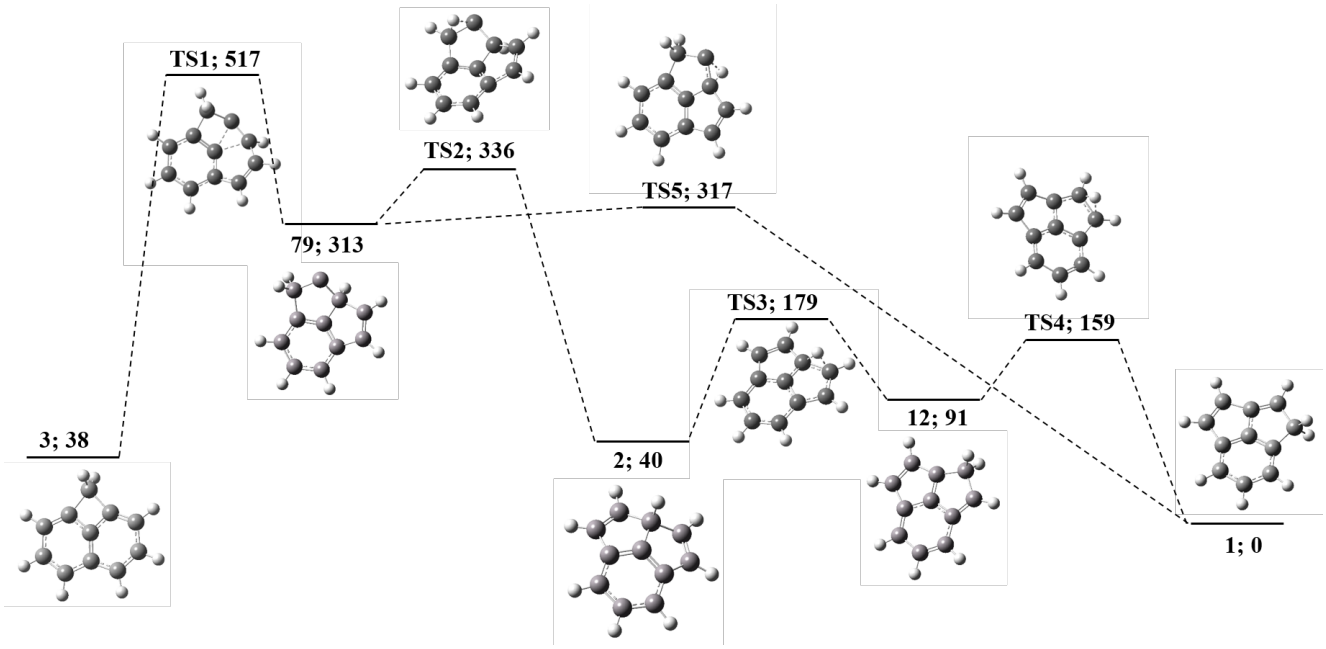


Table S52: Optimized geometries of the singlet and triplet ground electronic state of 1H-cyclobuta[cd]azulene (**64**) and 1aH-cyclobuta[cd]azulene (**65**) (in **Scheme I**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-64

Singlet				Triplet			
C	-0.294677	1.369086	0.008147	C	0.242685	1.382957	-0.132785
C	0.400601	0.185934	0.024832	C	-0.400538	0.139189	-0.368407
C	-1.682104	1.452852	-0.008978	C	1.578220	1.500909	0.117492
C	0.342609	-1.251631	0.009819	C	-0.272007	-1.213435	-0.175246
C	-2.455589	0.273804	-0.006872	C	2.460245	0.360251	0.080816
C	-0.922946	-1.832606	0.003306	C	1.024017	-1.807904	-0.043796
C	-2.134863	-1.105557	0.000958	C	2.190066	-1.030981	0.031713
C	1.714383	-1.610874	-0.008372	C	-1.658669	-1.625820	0.105779
C	1.676169	0.693304	0.011804	C	-1.715612	0.616613	-0.111785
C	2.531407	-0.427444	-0.011926	C	-2.522127	-0.499001	0.181176
C	1.076976	2.147202	-0.002417	C	-1.161851	2.066741	0.036261
H	-2.203357	2.403597	-0.024541	H	2.022918	2.458102	0.375342
H	-3.528325	0.451809	-0.015459	H	3.512742	0.600714	0.188382
H	-3.017827	-1.738404	-0.002432	H	3.097266	-1.626550	0.113447
H	-1.019746	-2.915732	-0.004904	H	1.130724	-2.883545	0.039592
H	2.109712	-2.617524	-0.020321	H	-1.972570	-2.645775	0.295425
H	3.613800	-0.451230	-0.033101	H	-3.572828	-0.539402	0.428493
H	1.270121	2.762275	0.880721	H	-1.451796	2.751009	-0.766756
H	1.263824	2.740796	-0.901770	H	-1.353023	2.548328	0.998766

Isomer-65

Singlet				Triplet			
C	-0.249736	1.343306	0.089852	C	0.224847	-1.317377	0.056837
C	0.445030	0.191868	0.652563	C	-0.416007	-0.200492	0.726870
C	0.331824	-1.107520	0.258999	C	-0.267732	1.126921	0.189825
C	-0.956312	-1.740203	0.043094	C	0.959232	1.698165	-0.036669
C	-2.150191	-1.094905	-0.053748	C	2.217408	0.998525	0.087283
C	-2.480754	0.329631	-0.088814	C	2.487632	-0.357185	-0.031013
C	-1.684088	1.429811	-0.080550	C	1.590675	-1.442070	-0.232658
C	1.803480	0.770611	0.359692	C	-1.816603	-0.730705	0.441848
C	2.470714	-0.401922	-0.306083	C	-2.450983	0.454414	-0.250932
C	1.651605	-1.489222	-0.254580	C	-1.595953	1.505482	-0.300948
C	0.927796	1.878979	-0.336521	C	-1.027650	-1.838774	-0.307982
H	-2.140778	2.399875	-0.250261	H	1.985179	-2.371399	-0.629234
H	-3.541908	0.518553	-0.227374	H	3.543943	-0.609928	-0.080372
H	-3.017252	-1.735957	-0.185257	H	3.095426	1.638171	0.123573
H	-0.972023	-2.822622	-0.056863	H	1.009552	2.719019	-0.405992
H	1.908129	-2.481636	-0.609324	H	-1.827548	2.472107	-0.734277
H	3.509686	-0.423382	-0.611903	H	-3.477672	0.481418	-0.597353
H	2.384088	1.168442	1.198449	H	-2.417573	-1.105634	1.278251
H	1.213850	2.714131	-0.960893	H	-1.340490	-2.605169	-1.009360

Table S53: Optimized geometries of the singlet and triplet ground electronic state of 8-azulenylcarbene (**66**) and 1aH-cyclopropa[e]azulene (**67**) (in **Scheme I**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer-66

	Singlet				Triplet		
C	-0.576780	-1.813093	-0.155898	C	0.261242	-1.905222	0.000149
C	0.545183	-0.962180	-0.118058	C	-0.711455	-0.910723	0.000181
C	0.556637	0.484157	0.163392	C	-0.534102	0.574138	-0.000088
C	-1.907921	-1.499417	0.014543	C	1.646220	-1.769211	-0.000094
C	-0.549020	1.363719	0.043386	C	0.700954	1.312331	0.000049
C	-2.498846	-0.219097	0.165204	C	2.410009	-0.589176	-0.000137
C	-1.934448	1.033748	0.137240	C	2.017031	0.734702	-0.000041
H	-3.583053	-0.228538	0.244471	H	3.486008	-0.741636	-0.000241
H	-0.348656	-2.865949	-0.306091	H	-0.116909	-2.924773	0.000230
H	-2.603344	-2.331930	-0.000238	H	2.215025	-2.693692	-0.000236
H	-2.616366	1.877962	0.147797	H	2.825363	1.459297	0.000002
C	1.927975	0.880283	0.310403	C	-1.807294	1.127348	-0.000221
H	2.254580	1.872674	0.575371	H	-2.031487	2.184325	-0.000390
C	1.887262	-1.358336	-0.164420	C	-2.103296	-1.150795	0.000116
H	2.224150	-2.380408	-0.278532	H	-2.562465	-2.129222	0.000191
C	2.718637	-0.241356	0.091803	C	-2.762198	0.077612	-0.000098
H	3.797508	-0.269988	0.157842	H	-3.835517	0.215690	-0.000183
C	0.024423	2.569092	-0.352118	C	0.654571	2.690213	0.000257
H	-0.283428	2.901052	-1.353485	H	1.389889	3.482711	0.000190

Isomer 67

	Singlet				Triplet		
C	-0.670943	-1.230289	-0.002628	C	-0.608077	-1.224246	0.075658
C	0.657811	-0.722058	0.029108	C	0.658408	-0.654448	0.042568
C	-2.000978	-0.724561	0.522947	C	-1.970388	-0.728724	0.470656
C	0.848818	0.743148	-0.003487	C	0.815123	0.787295	0.092209
C	-2.400694	0.648373	0.140724	C	-2.432433	0.574590	-0.082575
C	-0.100824	1.716132	-0.122997	C	-0.193035	1.781965	-0.003515
C	-1.552112	1.662180	-0.162005	C	-1.600647	1.661894	-0.187121
C	2.290841	0.959061	0.005081	C	2.204803	1.013469	0.048110
C	1.890408	-1.307388	0.058680	C	1.983129	-1.264334	-0.064998
C	2.902045	-0.257245	0.053230	C	2.903071	-0.258832	-0.034138
H	-3.463339	0.887393	0.166689	H	-3.489577	0.711112	-0.294952
H	-2.012458	2.618040	-0.398123	H	-2.086458	2.599270	-0.451486
H	0.291595	2.728206	-0.203594	H	0.184214	2.800276	-0.037669
H	2.766365	1.929090	-0.030895	H	2.679519	1.985981	0.037034
H	3.968792	-0.435482	0.068297	H	3.977665	-0.372698	-0.064733
H	2.090159	-2.369426	0.087496	H	2.171713	-2.326846	-0.111649
C	-1.718173	-1.801689	-0.508756	C	-1.627317	-1.980358	-0.299414
H	-2.165572	-2.431806	-1.258223	H	-1.988262	-2.767295	-0.941435
H	-2.352735	-1.040005	1.508974	H	-2.244634	-0.879426	1.520255

Table S54: Optimized geometries of the singlet and triplet ground electronic state of 1H-cyclopropa[e]azulne (**68**) and Bicyclo[6.3.0]undeca-1,2,4,6,8,10-hexaene (**69**) (in **Scheme I**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer 68

Singlet				Triplet			
C	-0.690410	-1.130499	0.001727	C	0.705472	-1.139148	-0.001551
C	0.614387	-0.714786	0.000855	C	-0.616309	-0.660528	-0.000594
C	-1.897331	-0.531200	0.002228	C	1.898242	-0.543332	-0.000864
C	0.872326	0.768634	0.000893	C	-0.851635	0.732675	-0.000459
C	-2.368876	0.757338	-0.000447	C	2.409377	0.753374	0.000419
C	-0.064551	1.814928	0.000183	C	0.086913	1.822909	-0.000388
C	-1.465815	1.837236	-0.000606	C	1.480342	1.826112	0.000186
C	2.268811	0.911479	-0. 000091	C	-2.294166	0.894734	0.000119
C	1.856509	-1.361765	-0.000070	C	-1.900646	-1.329766	-0.000124
C	2.850728	-0.369150	-0.000913	C	-2.912886	-0.364356	0.000446
H	-3.433412	0.970181	-0.001862	H	3.471439	0.960511	0.001354
H	-1.910703	2.827800	-0.001804	H	1.924121	2.819579	0.000819
H	0.392301	2.802736	-0.000545	H	-0.372382	2.807141	-0.000348
H	2.803615	1.851138	-0.000537	H	-2.801689	1.851348	0.000478
H	3.915979	-0.562454	-0.001840	H	-3.975797	-0.552786	0.000979
H	2.014669	-2.430074	-0.000014	H	-2.036248	-2.403119	-0.000172
C	-1.890668	-2.034190	-0.001519	C	1.900151	-2.045950	0.001416
H	-2.145429	-2.571120	-0.915748	H	2.179643	-2.580043	0.913710
H	-2.147688	-2.576361	0.908915	H	2.181781	-2.582974	-0.908451

Isomer 69

Singlet				Triplet			
C	0.375735	-1.344302	0.358207	C	-0.375301	-1.345996	0.355609
C	-0.774409	-0.761633	0.072918	C	0.774887	-0.761865	0.073041
C	-0.903140	0.704888	0.269136	C	0.902671	0.704518	0.269487
C	0.192898	1.636464	0.359507	C	-0.193237	1.636066	0.359460
C	1.513237	1.559531	0.015153	C	-1.513680	1.559534	0.014919
C	2.402591	0.549904	-0.562330	C	-2.403170	0.549902	-0.561632
C	2.534129	-0.781152	-0.362063	C	-2.534313	-0.781298	-0.361491
C	1.651321	-1.497380	0.577834	C	-1.650747	-1.497204	0.577827
C	-2.226742	1.008172	0.059217	C	2.074873	-1.257283	-0.339480
C	-2.938559	-0.198740	-0.306380	C	2.938750	-0.197644	-0.306334
C	-2.074036	-1.257729	-0.339955	C	2.226226	1.008622	0.059273
H	-0.126392	2.635843	0.649338	H	0.126257	2.635613	0.648506
H	2.021777	2.519454	0.082833	H	-2.021549	2.519851	0.081744
H	3.161774	0.994012	-1.205532	H	-3.163224	0.993741	-1.204015
H	3.341172	-1.314736	-0.856377	H	-3.341783	-1.314765	-0.855233
H	2.049090	-2.004423	1.453706	H	-2.047384	-2.003384	1.454713
H	-2.308024	-2.292694	-0.539314	H	2.309531	-2.292247	-0.538033
H	-3.998164	-0.245341	-0.519783	H	3.998388	-0.243497	-0.519759
H	-2.659384	1.999746	0.087670	H	2.658004	2.000564	0.088002

Table S55: Optimized geometries of the singlet and triplet ground electronic state of 6aH-cyclopenta[a]pentalene (**70**) 7H-cyclopenta[a]pentalene (**71**) (in **Scheme I**)in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer 70

	Singlet				Triplet		
C	-1.734270	-1.395286	-0.122680	C	-1.761481	-1.419088	0.006879
C	-0.701456	-0.637048	0.324557	C	-0.666819	-0.575577	0.300539
C	-1.181516	0.799475	0.478564	C	-1.175220	0.859047	0.377810
C	-2.565303	0.770646	-0.122452	C	-2.557627	0.746465	-0.208714
C	-2.884905	-0.521547	-0.368735	C	-2.875696	-0.592523	-0.312771
C	0.736431	-0.604956	0.218154	C	0.704987	-0.544474	0.180883
C	1.877123	-1.345730	0.167048	C	1.885691	-1.380571	0.060256
C	1.098025	0.809589	-0.064598	C	1.122336	0.851493	-0.003613
C	2.980809	-0.430022	-0.146748	C	2.956004	-0.538002	-0.152826
C	2.529521	0.851142	-0.298891	C	2.523929	0.837068	-0.198738
C	0.009540	1.610355	-0.001501	C	0.023319	1.701366	-0.014745
H	-3.235948	1.617780	-0.173769	H	-3.239537	1.571747	-0.363368
H	-3.847396	-0.873703	-0.719878	H	-3.845655	-0.972336	-0.610226
H	-1.688744	-2.438166	-0.408326	H	-1.739415	-2.496923	-0.075835
H	1.985966	-2.410338	0.319744	H	1.925704	-2.456622	0.146576
H	4.012181	-0.744464	-0.246817	H	3.982637	-0.856636	-0.277696
H	3.121283	1.722979	-0.534963	H	3.166206	1.685925	-0.387688
H	-0.018491	2.680681	-0.169043	H	0.025470	2.779426	-0.093380
H	-1.312844	1.005527	1.556746	H	-1.351947	1.074198	1.451853

Isomer 71

	Singlet				Triplet		
C	0.000000	1.839928	-1.442174	C	0.000000	1.838278	-1.420572
C	0.000000	0.679934	-0.570933	C	0.000000	0.713403	-0.614829
C	0.000000	1.164492	0.829992	C	0.000000	1.169281	0.784009
C	0.000000	2.513679	0.802572	C	0.000000	2.563684	0.807680
C	0.000000	2.927905	-0.622849	C	0.000000	2.985296	-0.537310
C	0.000000	-0.679934	-0.570933	C	0.000000	-0.713403	-0.614829
C	0.000000	-1.839928	-1.442174	C	0.000000	-1.838278	-1.420572
C	0.000000	-1.164492	0.829992	C	0.000000	-1.169281	0.784009
C	0.000000	-2.927905	-0.622849	C	0.000000	-2.985296	-0.537310
C	0.000000	-2.513679	0.802572	C	0.000000	-2.563684	0.807680
C	0.000000	0.000000	1.800551	C	0.000000	0.000000	1.729035
H	0.000000	3.201442	1.637107	H	0.000000	3.208740	1.674077
H	0.000000	3.960536	-0.949149	H	0.000000	4.015479	-0.869398
H	0.000000	1.836151	-2.521399	H	0.000000	1.881666	-2.499818
H	0.000000	-1.836151	-2.521399	H	0.000000	-1.881666	-2.499818
H	0.000000	-3.960536	-0.949149	H	0.000000	-4.015479	-0.869398
H	0.000000	-3.201442	1.637107	H	0.000000	-3.208740	1.674077
H	0.880227	0.000000	2.452139	H	0.875304	0.000000	2.394162
H	-0.880227	0.000000	2.452139	H	-0.875304	0.000000	2.394162

Table S56: Optimized geometries of the singlet and triplet ground electronic state of 3bH-cyclopenta[3,4]cyclobuta[1,2]benzene (**72**) and Bicyclo[5.4.0]undeca-1,3,5,7,9-pentaene-11-ylidene (**73**) (in **Scheme-I**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer 72

	Singlet				Triplet		
C	2.565483	-0.652692	-0.530882	C	2.726548	-0.689439	-0.329766
C	2.580328	0.799222	-0.365623	C	2.756891	0.731458	-0.181245
C	1.519904	1.491459	0.130879	C	1.571859	1.465890	0.058157
C	0.379528	0.710247	0.504810	C	0.437269	0.754630	0.344806
C	0.484109	-0.807468	0.760188	C	0.444672	-0.770293	0.548020
C	1.577520	-1.433768	-0.047712	C	1.613900	-1.448789	-0.088801
C	-0.988550	0.708434	0.340288	C	-1.006112	0.744728	0.145566
C	-1.009885	-0.748683	0.342425	C	-1.037725	-0.694380	0.140615
C	-2.165484	-1.177964	-0.224564	C	-2.356287	-1.157262	-0.125673
C	-2.948274	0.044726	-0.483301	C	-3.113357	-0.006614	-0.283542
C	-2.249687	1.187282	-0.156470	C	-2.272926	1.211965	-0.113371
H	3.400262	-1.101667	-1.058648	H	3.629045	-1.178844	-0.682877
H	3.446478	1.338547	-0.734363	H	3.680656	1.257750	-0.389665
H	1.494082	2.575395	0.125067	H	1.552404	2.539211	-0.100632
H	1.618406	-2.513050	-0.157394	H	1.619556	-2.522971	-0.236577
H	-2.487025	-2.179937	-0.471566	H	-2.713066	-2.172987	-0.205645
H	-3.953654	0.034417	-0.887774	H	-4.172327	0.021784	-0.506301
H	-2.597278	2.204533	-0.252703	H	-2.638628	2.225886	-0.195003
H	0.608779	-1.082999	1.817162	H	0.453960	-1.021193	1.628103

Isomer 73

	Singlet				Triplet		
C	2.791167	0.000196	-0.032064	C	2.831659	0.026041	-0.000298
C	2.186599	-1.243334	0.198746	C	2.235874	-1.247142	0.000131
C	0.837944	-1.561062	0.149016	C	0.904327	-1.594841	0.000153
C	-0.313431	-0.767020	-0.075683	C	-0.280341	-0.757086	-0.000018
C	0.821296	1.543673	-0.092599	C	0.828808	1.560675	0.000281
C	2.183336	1.239703	-0.173544	C	2.170223	1.273004	-0.000143
C	-1.524875	-1.480747	-0.240123	C	-1.518518	-1.380573	0.000027
C	-0.301296	0.708272	-0.032238	C	-0.331100	0.681887	0.000038
C	-1.561116	1.336322	0.184610	C	-1.594843	1.300066	0.000043
C	-2.726950	0.606455	0.202938	C	-2.792901	0.587887	-0.000091
C	-2.703879	-0.765827	-0.172035	C	-2.766447	-0.811694	-0.000129
H	3.877139	-0.001292	-0.068231	H	3.915642	0.054722	-0.000616
H	2.863265	-2.074480	0.369945	H	2.929190	-2.084321	0.000366
H	0.585867	-2.614473	0.245818	H	0.683873	-2.656982	0.000311
H	2.849632	2.089433	-0.284196	H	2.825167	2.140711	-0.000329
H	-1.587397	2.412343	0.319180	H	-1.630958	2.383851	0.000094
H	-3.669424	1.110358	0.401896	H	-3.740404	1.115819	-0.000037
H	-3.649117	-1.228981	-0.450789	H	-3.677075	-1.399447	-0.000449
H	0.597260	2.607301	-0.035757	H	0.574109	2.616299	0.000691

Table S57: Optimized geometries of the singlet and triplet ground electronic state of 7aH-cyclopropa[a]azulene (**74**) and Bicyclo[5.4.0]undeca-2,4,6,8,10,11-hexaene (**75**) (in **Scheme II**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer 74

	Singlet				Triplet		
C	-0.690912	-1.584721	0.179210	C	0.677867	-1.606373	-0.117817
C	0.318893	-0.680184	0.131831	C	-0.342396	-0.604855	-0.212277
C	-2.104163	-1.355745	0.060905	C	2.025799	-1.423445	-0.017710
C	0.276227	0.821202	0.022902	C	-0.217304	0.836171	-0.056217
C	-2.765556	-0.173977	-0.074810	C	2.776188	-0.195301	0.045601
C	-0.941097	1.582607	-0.100827	C	0.985251	1.584481	0.098059
C	-2.233604	1.160701	-0.132321	C	2.303553	1.102375	0.109300
C	1.526474	1.374487	0.113173	C	-1.496646	1.423982	-0.001330
C	1.743098	-0.942108	0.150507	C	-1.744460	-0.856943	-0.235021
C	2.553255	0.325916	0.378072	C	-2.550718	0.429280	-0.246812
C	2.767734	-0.764717	-0.651315	C	-2.828916	-0.877780	0.518566
H	-0.394339	-2.620954	0.309285	H	0.322195	-2.631463	-0.155612
H	-2.715683	-2.252794	0.077478	H	2.625901	-2.327917	0.021040
H	-3.847323	-0.236739	-0.148950	H	3.854157	-0.314014	0.078653
H	-2.982142	1.942702	-0.220241	H	3.068813	1.869712	0.195559
H	-0.786906	2.656971	-0.165223	H	0.858648	2.655550	0.217140
H	1.706224	2.442634	0.134084	H	-1.656505	2.496346	-0.004609
H	3.083678	-0.944789	-1.669585	H	-3.337074	-1.291589	1.375767
H	3.234395	0.432206	1.219188	H	-3.265446	0.673831	-1.033986

Isomer 75

	Singlet				Triplet		
C	0.839874	-1.561246	0.078303	C	-0.904392	-1.594886	-0.000265
C	-0.320469	-0.761805	0.068002	C	0.280378	-0.757024	-0.000201
C	2.204527	-1.250627	0.006575	C	-2.235800	-1.247236	0.000151
C	-0.311166	0.708727	0.084586	C	0.331078	0.681938	-0.000178
C	2.801121	-0.003360	-0.050563	C	-2.831640	0.026131	0.000368
C	0.831077	1.546940	-0.014791	C	-0.828791	1.560706	-0.000310
C	2.179031	1.255810	-0.067410	C	-2.170306	1.272948	0.000014
C	-1.560335	1.355473	0.098652	C	1.594874	1.300088	0.000056
C	-1.534263	-1.529519	-0.006738	C	1.518483	-1.380564	-0.000139
C	-2.734922	0.627038	-0.013528	C	2.792902	0.587855	0.000252
C	-2.703999	-0.772864	-0.140188	C	2.766461	-0.811712	0.000141
H	0.590833	-2.616799	0.126338	H	-0.683781	-2.656997	-0.000493
H	2.877556	-2.102450	0.007124	H	-2.929241	-2.084309	0.000261
H	3.886885	0.007851	-0.087895	H	-3.915627	0.054653	0.000684
H	2.844463	2.110450	-0.138015	H	-2.825207	2.140695	-0.000032
H	0.594771	2.607442	-0.074261	H	-0.574146	2.616336	-0.000604
H	-1.593307	2.437844	0.159464	H	1.631062	2.383868	0.000070
H	-3.686580	1.152563	0.014766	H	3.740399	1.115811	0.000448
H	-3.657468	-1.284296	-0.264918	H	3.677054	-1.399516	0.000329

Table S58: Optimized geometries of the singlet and triplet ground electronic state of Bicyclo[5.4.0]undeca-1,2,4,6,8,10-hexaene (**76**) and 1aH-cyclopropa[a]naphthalene (**77**) (in **Scheme II**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer 76

Singlet				Triplet			
C	1.178063	-1.085359	0.047945	C	-1.208946	-1.115781	-0.329544
C	-0.194985	-0.653092	0.062003	C	0.130410	-0.594345	-0.166085
C	2.283762	-1.335419	-0.583397	C	-2.171765	-1.386087	0.692452
C	-0.305317	0.760455	-0.063674	C	0.339275	0.805732	-0.017777
C	2.378662	-0.251095	0.471843	C	-2.400438	-0.172421	-0.228065
C	0.891499	1.605965	-0.122234	C	-0.808584	1.690664	0.041242
C	2.146915	1.176876	0.144473	C	-2.079923	1.246702	-0.055316
C	-1.592237	1.315487	-0.126741	C	1.649226	1.294826	0.107741
C	-1.334173	-1.455060	0.145071	C	1.242465	-1.454444	-0.148463
C	-2.724077	0.511973	-0.046276	C	2.735647	0.431536	0.103363
C	-2.597179	-0.872712	0.092246	C	2.527854	-0.948254	-0.018747
H	2.742990	-1.727472	-1.476301	H	-2.908305	-2.185453	0.714026
H	2.959654	1.896408	0.203413	H	-2.900932	1.955435	-0.097730
H	0.721184	2.658596	-0.329581	H	-0.618388	2.753948	0.149451
H	-1.697928	2.390720	-0.229890	H	1.804183	2.362900	0.222727
H	-3.708984	0.962826	-0.091064	H	3.741270	0.823182	0.204189
H	-3.482169	-1.496105	0.149034	H	3.374513	-1.625615	-0.011201
H	-1.225239	-2.528849	0.243720	H	1.080831	-2.521130	-0.253968
H	2.904899	-0.464244	1.403125	H	-3.304485	-0.352041	-0.812303

Isomer 77

Singlet				Triplet			
C	1.178063	-1.085359	0.047945	C	-1.208946	-1.115781	-0.329544
C	-0.194985	-0.653092	0.062003	C	0.130410	-0.594345	-0.166085
C	2.283762	-1.335419	-0.583397	C	-2.171765	-1.386087	0.692452
C	-0.305317	0.760455	-0.063674	C	0.339275	0.805732	-0.017777
C	2.378662	-0.251095	0.471843	C	-2.400438	-0.172421	-0.228065
C	0.891499	1.605965	-0.122234	C	-0.808584	1.690664	0.041242
C	2.146915	1.176876	0.144473	C	-2.079923	1.246702	-0.055316
C	-1.592237	1.315487	-0.126741	C	1.649226	1.294826	0.107741
C	-1.334173	-1.455060	0.145071	C	1.242465	-1.454444	-0.148463
C	-2.724077	0.511973	-0.046276	C	2.735647	0.431536	0.103363
C	-2.597179	-0.872712	0.092246	C	2.527854	-0.948254	-0.018747
H	2.742990	-1.727472	-1.476301	H	-2.908305	-2.185453	0.714026
H	2.959654	1.896408	0.203413	H	-2.900932	1.955435	-0.097730
H	0.721184	2.658596	-0.329581	H	-0.618388	2.753948	0.149451
H	-1.697928	2.390720	-0.229890	H	1.804183	2.362900	0.222727
H	-3.708984	0.962826	-0.091064	H	3.741270	0.823182	0.204189
H	-3.482169	-1.496105	0.149034	H	3.374513	-1.625615	-0.011201
H	-1.225239	-2.528849	0.243720	H	1.080831	-2.521130	-0.253968
H	2.904899	-0.464244	1.403125	H	-3.304485	-0.352041	-0.812303

Table S59: Optimized geometries of the singlet and triplet ground electronic state of 2-methylene-bicyclo[4.4.0]deca-3,5,7,9,10-pentaene (**78**) 2,2a-dihydro-1Hcyclopenta[cd]indenylidene **79** (in **1,2 H Shifting Rearrangement**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

Isomer 78

	Singlet				Triplet		
C	-1.399261	0.834722	-0.033577	C	-1.399261	0.834722	-0.033577
C	0.018069	0.503252	0.086397	C	0.018069	0.503252	0.086397
C	0.409517	-0.883838	0.198413	C	0.409517	-0.883838	0.198413
C	-0.581898	-1.868322	0.096384	C	-0.581898	-1.868322	0.096384
C	-1.943825	-1.542237	-0.050994	C	-1.943825	-1.542237	-0.050994
C	-2.345829	-0.230918	-0.162021	C	-2.345829	-0.230918	-0.162021
C	-1.797946	2.138185	0.100618	C	-1.797946	2.138185	0.100618
C	1.000104	1.463517	-0.054720	C	1.000104	1.463517	-0.054720
C	2.329355	1.143682	-0.076357	C	2.329355	1.143682	-0.076357
C	2.729757	-0.225569	-0.141512	C	2.729757	-0.225569	-0.141512
C	1.795268	-1.208188	0.070413	C	1.795268	-1.208188	0.070413
H	-2.830749	2.430019	-0.054128	H	-2.830749	2.430019	-0.054128
H	-3.389419	0.011860	-0.330212	H	-3.389419	0.011860	-0.330212
H	-2.671141	-2.340666	-0.145110	H	-2.671141	-2.340666	-0.145110
H	-0.278105	-2.905469	-0.011552	H	-0.278105	-2.905469	-0.011552
H	2.093880	-2.250106	0.119966	H	2.093880	-2.250106	0.119966
H	3.779962	-0.482019	-0.243098	H	3.779962	-0.482019	-0.243098
H	3.098289	1.901915	0.055393	H	3.098289	1.901915	0.055393
H	-1.082570	2.888745	0.410481	H	-1.082570	2.888745	0.410481

Isomer-79

	Singlet				Triplet		
C	-0.791491	-1.602552	-0.000214	C	-0.801178	-1.514924	0.000135
C	0.264772	-0.656795	-0.000337	C	0.254455	-0.560110	0.000443
C	-2.172095	-1.318608	0.000303	C	-2.152331	-1.382019	-0.000278
C	0.295691	0.780553	-0.000154	C	0.321012	0.841975	-0.000006
C	-2.776521	-0.071392	0.000202	C	-2.783498	-0.104381	-0.000274
C	-0.868564	1.592171	-0.000137	C	-0.889702	1.641756	0.000354
C	-2.195988	1.218745	-0.000095	C	-2.197049	1.189408	0.000188
C	1.574810	1.379463	0.000060	C	1.629493	1.353815	-0.000428
C	1.443562	-1.472724	-0.000252	C	1.362120	-1.382399	0.000147
C	2.721906	0.598022	0.000232	C	2.755059	0.511435	-0.000221
C	2.669825	-0.813009	0.000147	C	2.658528	-0.892019	0.000154
H	0.363085	-2.456073	-0.000158	H	0.337719	-2.420163	0.000248
H	-2.849856	-2.169808	0.000590	H	-2.791421	-2.259284	-0.000838
H	-3.865303	-0.070801	0.000356	H	-3.868526	-0.119386	-0.000682
H	-2.908691	2.038086	-0.000181	H	-2.935376	1.987967	0.000413
H	-0.684283	2.664523	-0.000097	H	-0.750777	2.718625	0.000789
H	1.656824	2.461345	0.000206	H	1.782257	2.428168	-0.000837
H	3.687914	1.095880	0.000430	H	3.741202	0.964371	-0.000496
H	3.604871	-1.366397	0.000330	H	3.543467	-1.515522	0.000126

Table S60: Optimized geometries of the singlet ground electronic state of **TSa1**, **TSa2**, **TSa3** and **TSa4** (in **Scheme-I**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

TSa1

C	0.292447	1.533291	-0.000091
C	-0.406669	0.336874	-0.000062
C	1.694867	1.589828	-0.000174
C	-0.088792	-1.054242	-0.000103
C	2.606446	0.531113	0.000137
C	1.206596	-1.582295	-0.000043
C	2.394208	-0.859786	0.000165
C	-1.345668	-1.771493	-0.000101
C	-1.875390	0.467744	0.000027
C	-2.393325	-0.881978	0.000050
C	-2.292092	1.764840	0.000122
H	-0.933700	2.286685	-0.000130
H	2.152725	2.578602	-0.000486
H	3.655537	0.820961	0.000345
H	3.300540	-1.458606	0.000354
H	1.300504	-2.665581	-0.000113
H	-1.430357	-2.850392	-0.000176
H	-3.441490	-1.150834	0.000164
H	-3.359529	1.995797	0.000490

TSa2

C	-0.244112	1.461138	-0.122382
C	0.432347	0.268371	-0.247227
C	-1.609317	1.629546	-0.008188
C	0.094150	-1.145657	-0.238756
C	-2.523684	0.566175	0.175159
C	-1.203426	-1.609483	-0.084684
C	-2.356509	-0.821077	0.099676
C	1.346151	-1.807246	-0.018570
C	1.796586	0.435913	-0.003787
C	2.353815	-0.857076	0.198468
C	2.045008	1.845516	0.070082
H	1.863104	2.465030	-0.792778
H	-2.036229	2.627520	-0.064274
H	-3.550943	0.877846	0.356022
H	-3.271511	-1.388621	0.242320
H	-1.348574	-2.685108	-0.012058
H	1.473538	-2.878270	0.070865
H	3.376522	-1.092719	0.462285
H	2.708035	2.277607	0.818861

TSa3

C	-0.310163	1.369877	0.096688
C	0.486214	0.256085	0.431822
C	0.378336	-1.135360	0.129663
C	-0.851123	-1.805202	0.018863
C	-2.104558	-1.207814	0.024857
C	-2.462790	0.164187	-0.058401
C	-1.705576	1.326292	-0.098693
C	1.819022	0.666707	0.330464
C	2.565343	-0.409119	-0.199449
C	1.712018	-1.528867	-0.210412
C	0.687241	2.361722	-0.123819
H	-2.224703	2.252203	-0.322925
H	-3.530823	0.323175	-0.185486
H	-2.946895	-1.890146	-0.030196
H	-0.826393	-2.880883	-0.139156
H	2.039513	-2.550844	-0.361788
H	3.626269	-0.431149	-0.406194
H	1.736178	2.006976	0.493549
H	0.843079	2.819617	-1.097295

TSa4

C	0.449132	1.365260	-0.027025
C	-0.502161	0.353711	-0.396483
C	-0.449568	-1.011335	-0.008265
C	0.735647	-1.767459	0.115293
C	2.034385	-1.315140	-0.011039
C	2.523012	0.017406	-0.109266
C	1.861842	1.225698	-0.062983
C	-1.869365	0.790382	-0.370018
C	-2.651524	-0.339502	0.013967
C	-1.808265	-1.424512	0.196264
C	-0.400600	2.219540	0.622081
H	2.459571	2.123058	0.061427
H	3.607511	0.091158	-0.128694
H	2.806951	-2.075729	0.039702
H	0.611176	-2.829902	0.310559
H	-2.122932	-2.441324	0.393877
H	-3.731725	-0.369485	0.051551
H	-2.255781	1.687762	-0.830958
H	-0.909980	3.130173	0.327372

Table S61: Optimized geometries of the singlet ground electronic state of **TSa5**, **TSa6**, **TSa7** and **TSa8** (in **Scheme-I**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

TSa5

C	0.810689	0.788486	-0.004905	C	-0.676122	-1.189592	0.127226
C	-0.116561	1.786150	-0.190852	C	0.592661	-0.666184	0.043854
C	-1.540761	1.737022	-0.161003	C	-1.901219	-0.569285	0.107284
C	-2.364597	0.685907	0.178710	C	0.811985	0.806168	0.057644
C	-1.978545	-0.644914	0.480490	C	-2.385259	0.689873	-0.104007
C	-0.722831	-1.243817	0.066815	C	-0.143463	1.842490	0.032379
C	0.585820	-0.661051	0.105247	C	-1.531986	1.819084	-0.040412
C	1.810090	-1.276197	0.140183	C	2.202900	0.986291	0.001566
C	2.839123	-0.258406	0.077348	C	1.852820	-1.285165	-0.036724
C	2.247161	0.971250	-0.027397	C	2.824674	-0.276079	-0.055469
C	-1.342294	-2.130434	-0.712217	H	-3.447106	0.849152	-0.256151
H	0.296601	2.778622	-0.356920	H	-2.027351	2.784157	-0.068221
H	-2.032834	2.689099	-0.334227	H	0.291394	2.839719	0.037876
H	-3.414145	0.927794	0.330435	H	2.707702	1.942621	-0.010761
H	-2.662673	-1.246447	1.062356	H	3.892895	-0.441639	-0.101888
H	-2.178237	-2.803919	-0.595263	H	2.033380	-2.350385	-0.046463
H	1.982274	-2.341758	0.201198	C	-1.516003	-2.367555	0.048809
H	3.902458	-0.455706	0.088846	H	-1.626063	-2.756750	-0.974216
H	2.742780	1.928344	-0.110934	H	-2.610784	-1.607156	0.326924

TSa7

C	-0.556698	-1.287090	-0.223663	C	-0.644781	-0.806003	0.564771
C	0.694035	-0.745568	0.008839	C	0.669235	-0.607886	0.290821
C	0.850475	0.717274	-0.191803	C	1.079209	0.808389	0.119594
C	-0.160199	1.658791	-0.309609	C	0.034301	1.711617	0.294779
C	-1.551925	1.606314	-0.042708	C	-1.305249	1.254388	0.358035
C	-2.346103	0.589154	0.472712	C	-2.248033	0.668982	-0.650420
C	-2.155860	-0.812882	0.468102	C	-2.618230	-0.624341	-0.537432
C	-1.693960	-1.562691	-0.735730	C	-1.816458	-1.421632	0.389519
C	2.249181	0.974687	-0.090386	C	1.781931	-1.407076	-0.064970
C	2.889303	-0.214944	0.219990	C	2.842179	-0.531972	-0.344119
C	1.942174	-1.279300	0.287830	C	2.431547	0.816617	-0.237312
H	0.199579	2.668388	-0.499352	H	0.253416	2.733211	0.601706
H	-2.022541	2.585492	-0.037309	H	-1.897851	1.844322	1.072525
H	-3.212734	0.931553	1.040487	H	-2.748176	1.344766	-1.339346
H	-2.584602	-1.384291	1.289098	H	-3.416166	-1.068790	-1.123119
H	-2.168078	-1.957666	-1.622006	H	-2.129885	-2.367469	0.815450
H	2.163013	-2.321780	0.463170	H	1.828941	-2.485522	-0.044932
H	3.954141	-0.332469	0.372247	H	3.842826	-0.849657	-0.609370
H	2.708687	1.948298	-0.187784	H	3.032991	1.682644	-0.472504

Table S62: Optimized geometries of the singlet ground electronic state of **TSa9**, **TSa10**, **TSa11** and **TSa12** (in **Scheme-I**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

TSa9

C	-1.807549	-1.428519	0.023788
C	-0.686830	-0.643345	0.020554
C	-1.178176	0.794298	0.002600
C	-2.616616	0.794777	-0.029111
C	-2.968830	-0.536127	-0.017829
C	0.735034	-0.571269	-0.062658
C	1.922196	-1.360051	0.010104
C	1.137579	0.786816	-0.094628
C	3.025260	-0.486689	0.027240
C	2.550583	0.844761	-0.015757
C	-0.018334	1.650757	-0.013069
H	-3.272315	1.649346	-0.074195
H	-3.991094	-0.892482	-0.069031
H	-1.863107	-2.506182	0.000994
H	1.976142	-2.440119	0.039614
H	4.063997	-0.782265	0.050162
H	3.166789	1.734130	-0.004649
H	-0.055901	2.724010	-0.160440
H	-0.590416	1.441112	1.110142

TSa10

C	-0.376622	-0.920511	0.685163
C	0.936124	-0.709169	0.476608
C	0.946862	0.728876	0.424752
C	-0.428365	1.192661	0.838558
C	-1.539063	1.460418	0.007624
C	-2.250001	0.566290	-0.795897
C	-2.336424	-0.823358	-0.585883
C	-1.546315	-1.530301	0.322057
C	2.123193	-1.210011	-0.183027
C	2.789621	-0.085065	-0.603946
C	2.034654	1.131352	-0.288970
H	-0.433152	1.776083	1.763872
H	-2.048169	2.412473	0.170720
H	-3.028889	0.993884	-1.420407
H	-3.183167	-1.335936	-1.031923
H	-1.896912	-2.456147	0.771445
H	2.446161	-2.235544	-0.276671
H	3.740868	-0.086698	-1.122081
H	2.281275	2.124796	-0.637188

TSa11

C	-2.702127	0.418024	-0.238527
C	-2.347175	-0.954288	-0.531552
C	-1.135838	-1.463816	-0.227211
C	-0.044145	-0.621547	0.261997
C	-0.490033	0.901641	0.791256
C	-1.881365	1.241053	0.448340
C	1.243659	-1.068829	0.594790
C	0.482288	0.677626	-0.247372
C	1.722899	1.112250	-0.742224
C	2.820057	0.337854	-0.463114
C	2.535648	-0.772638	0.425101
H	-3.708176	0.747756	-0.473394
H	-3.117514	-1.607778	-0.926113
H	-0.923824	-2.525372	-0.298792
H	-2.249682	2.192450	0.822170
H	1.791813	2.059683	-1.265825
H	3.799135	0.499194	-0.900462
H	3.329084	-1.394879	0.826533
H	-0.144043	1.184965	1.786973

TSa12

C	-0.791457	-1.602578	-0.000078
C	0.264785	-0.656807	0.000078
C	-2.172086	-1.318616	-0.000241
C	0.295679	0.780548	-0.000024
C	-2.776516	-0.071413	0.000024
C	-0.868585	1.592175	0.000076
C	-2.195990	1.218758	0.000169
C	1.574778	1.379462	-0.000170
C	1.443576	-1.472718	0.000224
C	2.721894	0.598037	-0.000137
C	2.669835	-0.812983	0.000119
H	0.363098	-2.456060	0.000097
H	-2.849846	-2.169816	-0.000472
H	-3.865297	-0.070839	0.000083
H	-2.908699	2.038093	0.000304
H	-0.684297	2.664526	0.000095
H	1.656782	2.461345	-0.000308
H	3.687889	1.095919	-0.000274
H	3.604886	-1.366361	0.000231

Table S63: Optimized geometries of the singlet ground electronic state of **TSb1**, **TSb2**, **TSb3** and **TSb4** (in **Scheme-II**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

TSb1

C	0.709420	-1.587682	-0.155697
C	-0.317001	-0.703171	-0.001857
C	2.116444	-1.331755	-0.190789
C	-0.263799	0.803503	-0.013199
C	2.768893	-0.147064	0.000780
C	0.928428	1.568570	0.213625
C	2.231530	1.162277	0.216034
C	-1.490297	1.340533	-0.290237
C	-1.674002	-1.087731	0.171672
C	-2.576847	0.368930	-0.453523
C	-2.830920	-0.625011	0.572376
H	0.419211	-2.631831	-0.220750
H	2.739521	-2.208855	-0.334033
H	3.854213	-0.197085	-0.010749
H	2.972009	1.940586	0.373109
H	0.762069	2.633450	0.356658
H	-1.633723	2.393706	-0.506196
H	-3.140259	0.362793	-1.387800
H	-3.584141	-0.861158	1.314646

TSb2

C	0.709486	-1.587728	-0.155371
C	-0.316990	-0.703274	-0.001362
C	2.116430	-1.331599	-0.191360
C	-0.263773	0.803388	-0.013359
C	2.768843	-0.146883	0.000326
C	0.928295	1.568492	0.214132
C	2.231429	1.162264	0.216526
C	-1.490063	1.340329	-0.291268
C	-1.673848	-1.088171	0.172589
C	-2.576935	0.369025	-0.453843
C	-2.831050	-0.624503	0.572216
H	0.419385	-2.631949	-0.219792
H	2.739540	-2.208577	-0.335210
H	3.854164	-0.196756	-0.011840
H	2.971863	1.940518	0.374088
H	0.761853	2.633317	0.357495
H	-1.633529	2.393697	-0.506258
H	-3.139903	0.362073	-1.388385
H	-3.584314	-0.860360	1.314552

TSb3

C	-0.928096	-1.369571	0.358009
C	0.233583	-0.737375	0.033207
C	-2.232110	-1.159826	0.519409
C	0.289432	0.714150	0.211567
C	-2.787989	-0.105499	-0.303285
C	-0.841693	1.495473	-0.010854
C	-2.136401	1.096656	-0.446471
C	1.587434	1.309683	0.386918
C	1.431014	-1.417476	-0.374513
C	2.711216	0.588806	0.106392
C	2.631121	-0.770635	-0.342438
H	1.364094	-2.472164	-0.616921
H	-2.851841	-1.728297	1.209135
H	-3.764323	-0.225552	-0.769224
H	-2.705733	1.882736	-0.937806
H	-0.675487	2.569853	0.002295
H	1.658241	2.350748	0.684568
H	3.687207	1.051790	0.204065
H	3.542775	-1.295428	-0.603756

TSb4

C	1.059881	-1.215633	-0.216832
C	-0.210806	-0.691700	-0.014009
C	2.286315	-1.185951	-0.615485
C	-0.289899	0.732175	-0.193370
C	2.565247	-0.207496	0.448328
C	0.876369	1.554175	-0.099880
C	2.110992	1.131722	0.357170
C	-1.587075	1.304938	-0.270161
C	-1.377167	-1.443906	0.272410
C	-2.713931	0.543434	-0.056386
C	-2.610090	-0.833749	0.247898
H	-1.284305	-2.508264	0.453688
H	-3.506903	-1.413680	0.432322
H	-3.693244	1.006523	-0.104502
H	-1.676777	2.369393	-0.461410
H	0.707954	2.624888	-0.162848
H	2.748789	1.889253	0.811546
H	3.175867	-0.498275	1.302918
H	2.869605	-1.597897	-1.429815

Table S64: Optimized geometries of the singlet ground electronic state of **TSb5**, **TSb6**, **TSb7** and **TSb8** (in **Scheme-II**) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

TSb5

C	-1.284764	-0.985748	-0.176770
C	0.098162	-0.558848	-0.118742
C	-2.123162	-1.826603	0.469485
C	0.322175	0.836971	0.031014
C	-2.356547	-0.057386	-0.361937
C	-0.806232	1.736155	0.135349
C	-2.091592	1.318648	-0.037378
C	1.648972	1.301669	0.111324
C	1.184572	-1.442261	-0.165967
C	2.714161	0.417767	0.052537
C	2.482192	-0.958588	-0.080369
H	-1.823271	-2.172461	1.464944
H	-3.279833	-0.344542	-0.834423
H	-2.906517	2.034118	-0.027560
H	-0.597206	2.786557	0.311446
H	1.829947	2.366393	0.216064
H	3.730319	0.790361	0.113039
H	3.319259	-1.646527	-0.114888
H	0.999683	-2.504553	-0.279896

TSb6

C	1.320493	0.925264	0.019551
C	-0.029969	0.407898	-0.062821
C	-0.307069	-0.979952	-0.096895
C	0.807680	-1.849166	-0.052073
C	2.115750	-1.359512	0.009532
C	2.388216	0.008156	0.103616
C	1.325199	2.315946	-0.119568
C	-1.015834	1.394877	0.002407
C	-2.331927	1.001160	0.048014
C	-2.649980	-0.391117	0.082645
C	-1.676270	-1.361746	-0.020257
H	2.165702	2.881498	0.294153
H	3.409067	0.356528	0.214460
H	2.936863	-2.066531	0.049947
H	0.643949	-2.921006	0.009938
H	-1.945468	-2.412654	-0.026479
H	-3.692645	-0.689158	0.136882
H	-3.147354	1.717761	0.008313
H	-0.047859	2.462714	-0.172113

TSb7

C	-1.328954	0.869232	0.013288
C	0.010304	0.407236	0.132367
C	0.346316	-0.972624	0.196189
C	-0.733450	-1.881339	0.086140
C	-2.041490	-1.429004	-0.085371
C	-2.356090	-0.064950	-0.172502
C	-1.407676	2.277126	0.114231
C	0.973940	1.390988	-0.062418
C	2.300002	1.072518	-0.139029
C	2.662651	-0.312621	-0.117284
C	1.726593	-1.303921	0.085320
H	-2.212477	2.844433	-0.345382
H	-3.378240	0.252224	-0.346674
H	-2.834905	-2.158649	-0.204428
H	-0.526688	-2.944238	0.007967
H	2.033099	-2.344139	0.118999
H	3.711538	-0.578247	-0.211220
H	3.084700	1.822742	-0.158064
H	-0.789899	2.790027	0.833209

Table S65: Optimized geometries of the singlet ground electronic state of **TS1**, **TS2**, **TS3** and **TS4** (in 1,2-H shifting rearrangement) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

TS1

C	0.145144	0.189946	-0.431117
C	-0.031980	-1.174593	-0.209929
C	-1.369352	-1.610509	-0.114886
C	-2.406503	-0.681010	-0.052811
C	-2.139984	0.697938	0.079229
C	-0.823169	1.110576	-0.041742
C	0.085070	2.218000	0.421329
C	1.260449	1.609123	-0.330043
C	2.011765	0.413789	-0.323242
C	2.205346	-0.906987	0.364062
C	1.187795	-1.787080	0.289410
H	-1.581255	-2.667077	0.011073
H	-3.428783	-1.033135	0.023419
H	-2.929874	1.390307	0.348027
H	-0.122316	3.242536	0.107268
H	0.143820	2.178887	1.517773
H	2.714306	0.406039	-1.175823
H	3.217508	-1.175619	0.645431
H	1.239114	-2.817087	0.621279

TS2

C	-0.149706	0.005554	0.413160
C	0.372558	-1.249580	0.148376
C	1.759312	-1.309299	-0.046851
C	2.485958	-0.103851	-0.060626
C	1.871415	1.160867	-0.004858
C	0.485378	1.204851	0.193061
C	-0.654113	2.133186	-0.157158
C	-1.947595	1.498273	-0.175899
C	-1.619585	0.074263	0.313354
C	-1.934718	-1.329862	-0.178300
C	-0.807288	-2.087331	-0.169138
H	2.270270	-2.241019	-0.264348
H	3.557705	-0.150329	-0.220636
H	2.462061	2.053608	-0.178111
H	-0.550175	3.210742	-0.265150
H	-1.129400	1.825776	-1.259908
H	-2.075270	0.158478	1.321888
H	-2.933780	-1.697116	-0.373368
H	-0.771110	-3.142561	-0.411090

TS3

C	0.152959	0.021675	0.079380
C	-0.539858	1.246769	0.037705
C	-1.957264	1.107977	0.030941
C	-2.488904	-0.187587	0.007903
C	-1.733984	-1.383595	-0.029881
C	-0.316097	-1.277543	-0.027404
C	0.869586	-2.093513	-0.079634
C	2.032562	-1.272212	-0.046096
C	1.591106	0.147887	0.098992
C	1.811236	1.553027	-0.110924
C	0.471467	2.221711	-0.053318
H	-2.620275	1.964750	0.024002
H	-3.570000	-0.284589	-0.005270
H	-2.244280	-2.337575	-0.085227
H	0.907172	-3.173700	-0.119230
H	3.060279	-1.604529	-0.075750
H	2.016200	-0.438490	1.155198
H	2.752978	2.074833	-0.192280
H	0.341069	3.291725	-0.147418

TS4

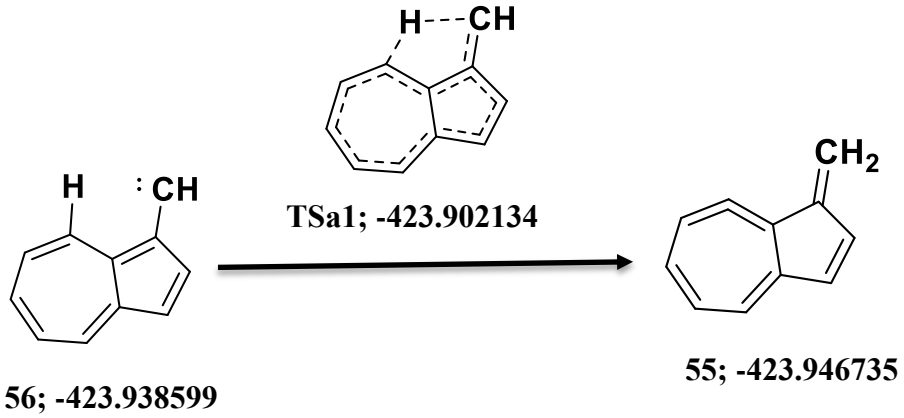
C	0.156954	0.042223	-0.045306
C	-0.594579	1.234792	-0.006063
C	-2.005149	1.038408	0.012082
C	-2.486104	-0.280180	0.009438
C	-1.677235	-1.439154	-0.004972
C	-0.264575	-1.273044	-0.036130
C	0.960569	-2.054632	-0.014171
C	2.139188	-1.086845	-0.016241
C	1.573686	0.241582	-0.034108
C	1.755387	1.616486	-0.000872
C	0.381132	2.250793	0.010626
H	-2.703831	1.866597	0.028824
H	-3.561554	-0.424376	0.021531
H	-2.144930	-2.416683	-0.000391
H	1.081285	-3.111471	-0.207458
H	1.645422	-1.747272	1.039836
H	3.155319	-1.409234	-0.186265
H	2.677353	2.179914	0.015911
H	0.215292	3.319933	0.042308

Table S66: Optimized geometries of the singlet ground electronic state of **TS5** (in 1,2-H shifting rearrangement) in Cartesian coordinates (in Angstrom units) obtained at the (U)B3LYP/6-311+G(D,P) level of theory.

TS5

C	0.130479	-0.003965	0.176041
C	-0.393903	1.267050	0.075869
C	-1.786809	1.319724	-0.020340
C	-2.489136	0.092754	-0.032896
C	-1.871378	-1.172976	-0.007782
C	-0.470065	-1.223049	0.077568
C	0.703492	-2.209365	-0.057249
C	2.025606	-1.396421	-0.187725
C	1.577693	-0.046621	0.065994
C	1.951288	1.400407	-0.068397
C	0.807154	2.140859	-0.050816
H	-2.335713	2.249765	-0.118957
H	-3.570905	0.129263	-0.107204
H	-2.485132	-2.064052	-0.082905
H	0.782247	-2.937297	0.758519
H	0.635337	-2.815294	-0.970144
H	2.131532	-0.579004	1.009642
H	2.956329	1.787324	-0.158385
H	0.779779	3.218910	-0.152177

Figure S12: Intrinsic Reaction Coordinate for the rearrangement from **56** to **55** in **Scheme-I** calculated at B3LYP/6-311+G(D,P) level of theory.



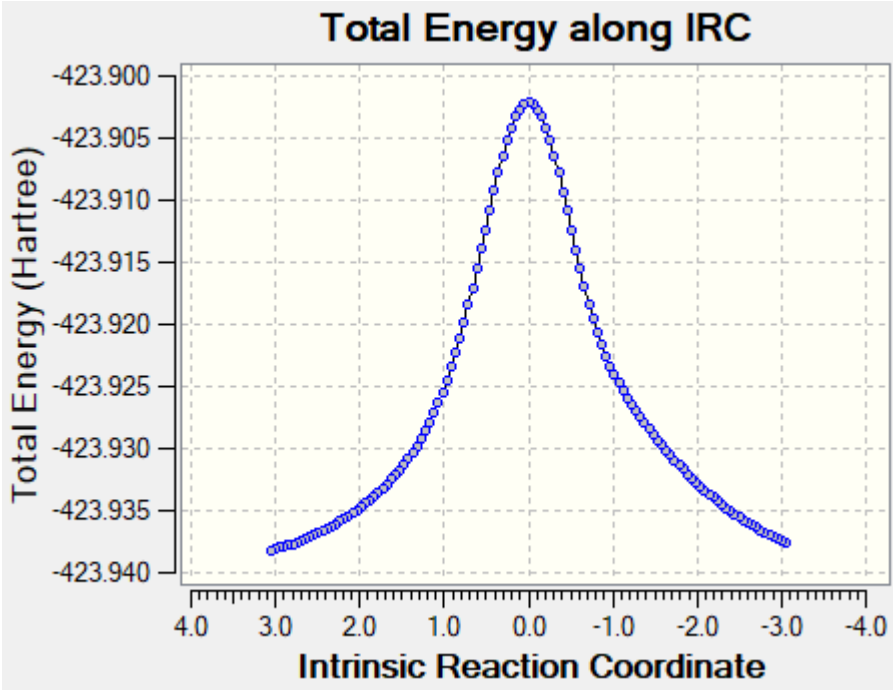
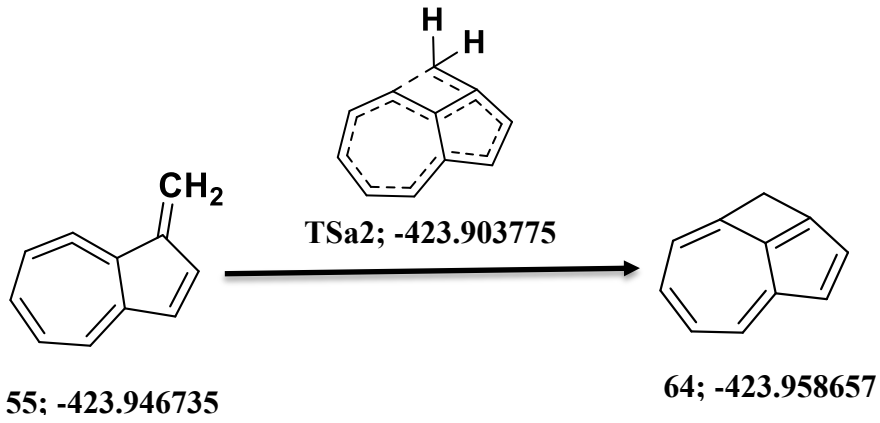


Figure S13: Intrinsic Reaction Coordinate for the rearrangement from **55** to **64** in **Scheme-I** calculated at B3LYP/6-311+G(D,P) level of theory.



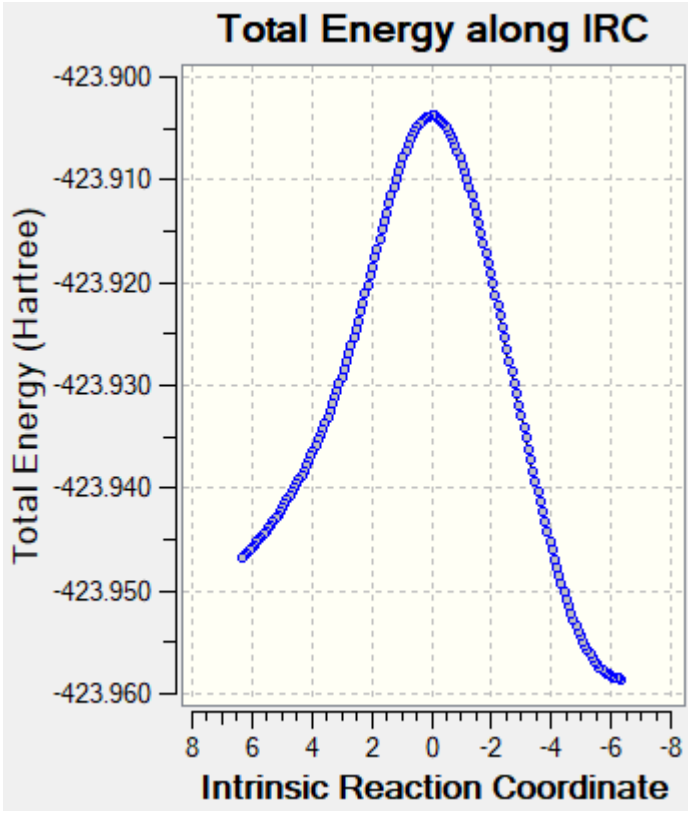
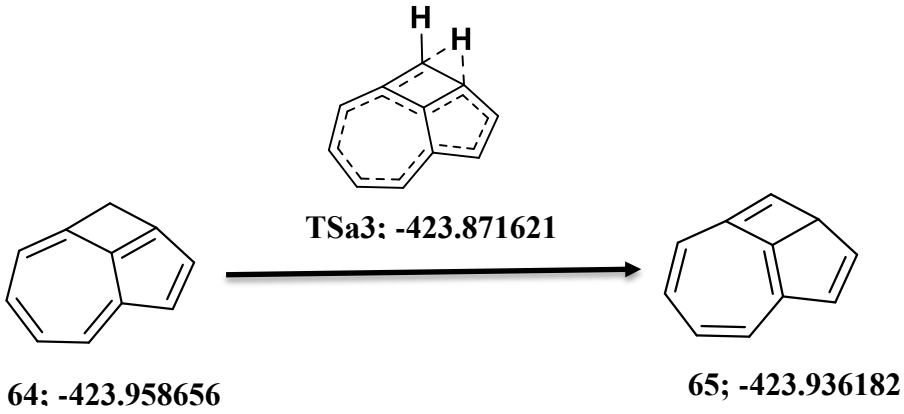


Figure S14: Intrinsic Reaction Coordinate for the rearrangement from **64** to **65** in **Scheme-I** calculated at B3LYP/6-311+G(D,P) level of theory.



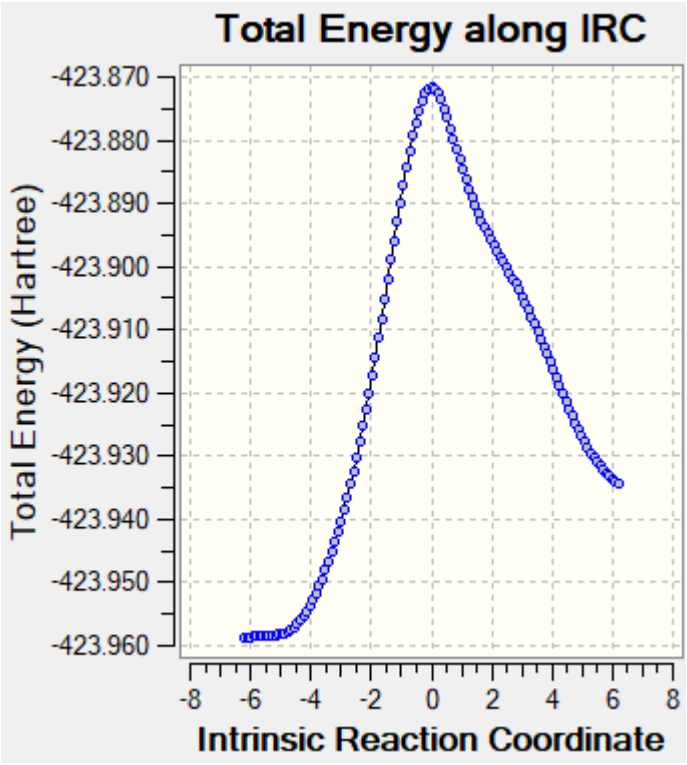
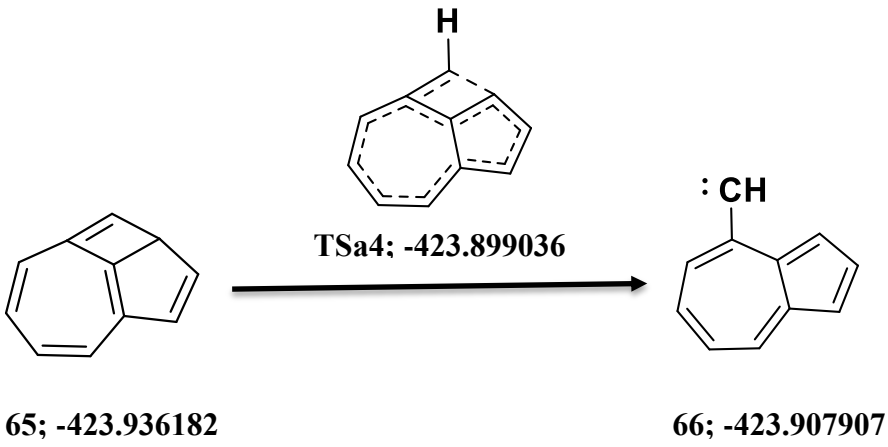


Figure S15: Intrinsic Reaction Coordinate for the rearrangement from **65** to **66** in **Scheme-I** calculated at B3LYP/6-311+G(D,P) level of theory.



65; -423.936182 **66; -423.907907**

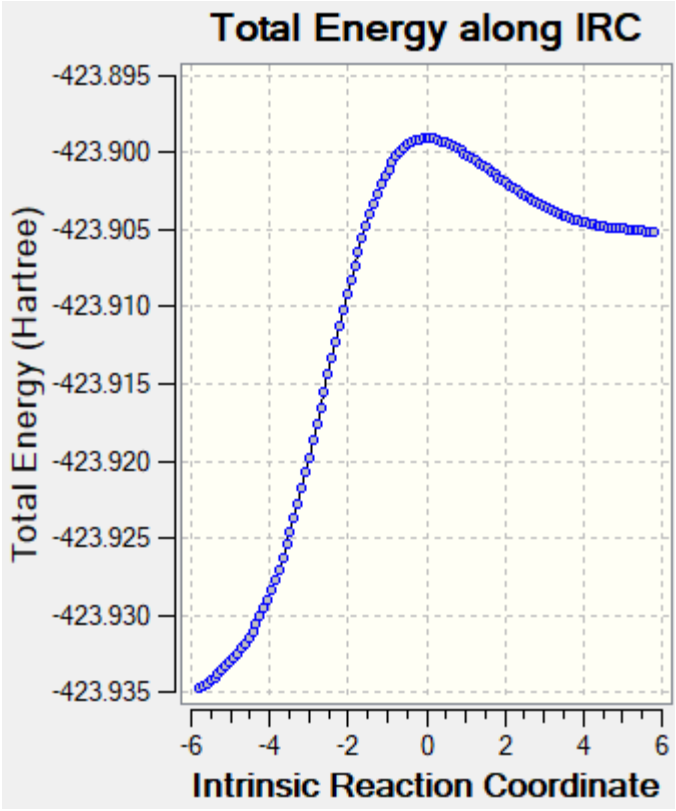
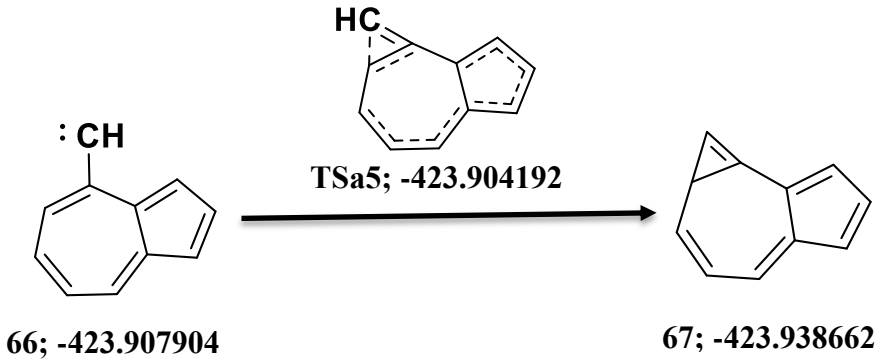


Figure S16: Intrinsic Reaction Coordinate for the rearrangement from **66** to **67** in **Scheme-I** calculated at B3LYP/6-311+G(D,P) level of theory.



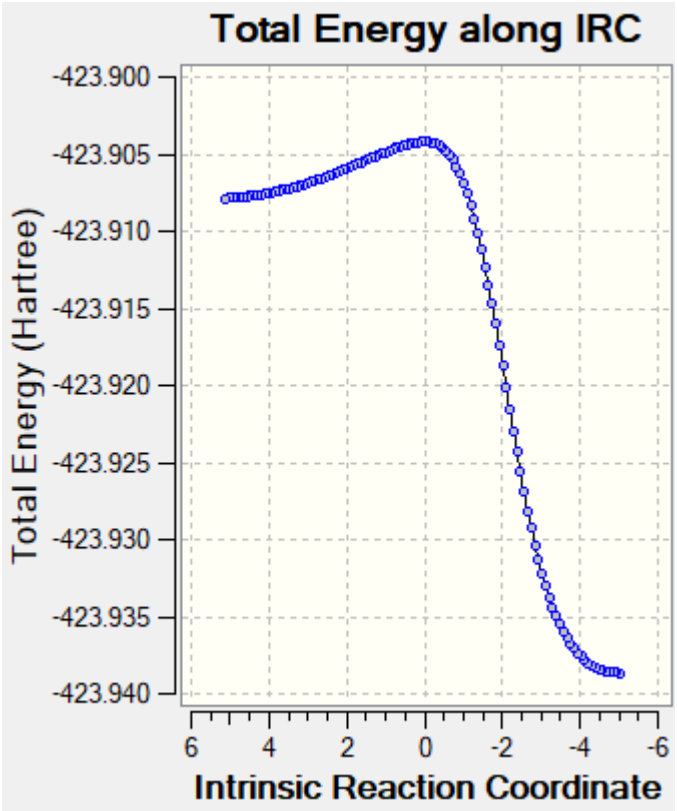
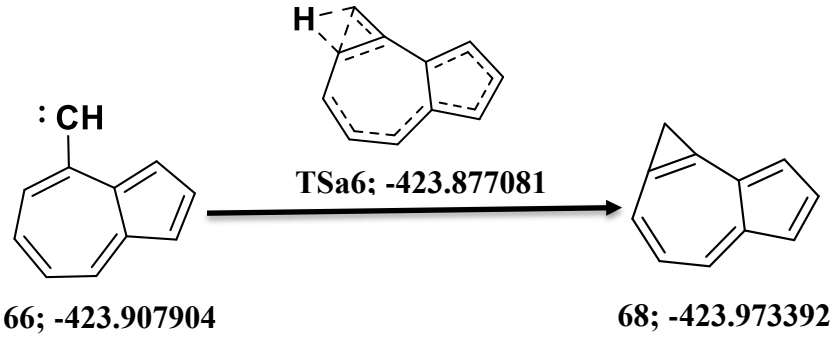


Figure S17: Intrinsic Reaction Coordinate for the rearrangement from **66** to **68** in **Scheme-I** calculated at B3LYP/6-311+G(D,P) level of theory.



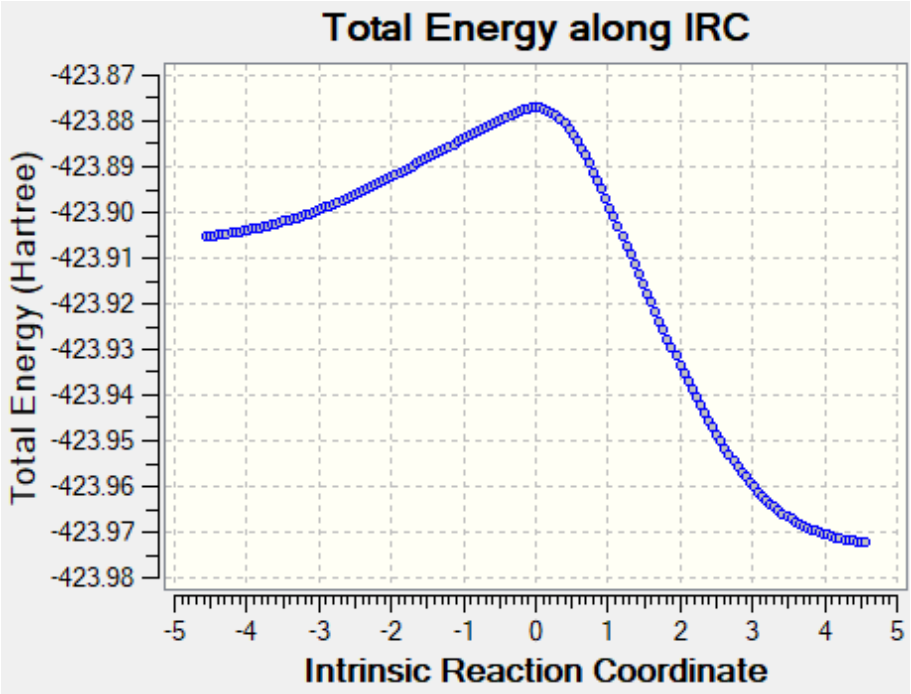
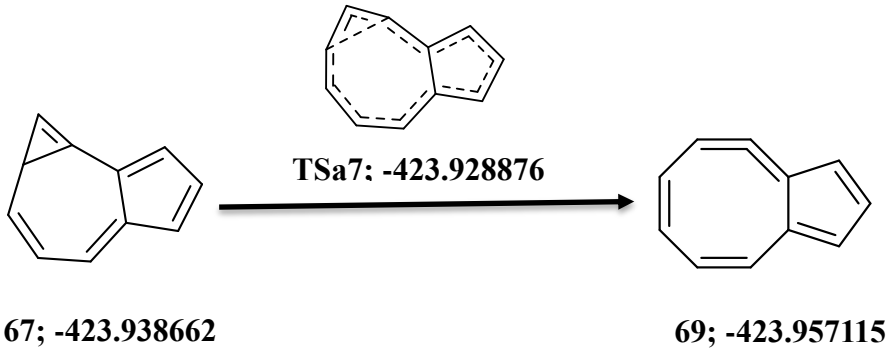


Figure S18: Intrinsic Reaction Coordinate for the rearrangement from **67** to **69** in **Scheme-I** calculated at B3LYP/6-311+G(D,P) level of theory.



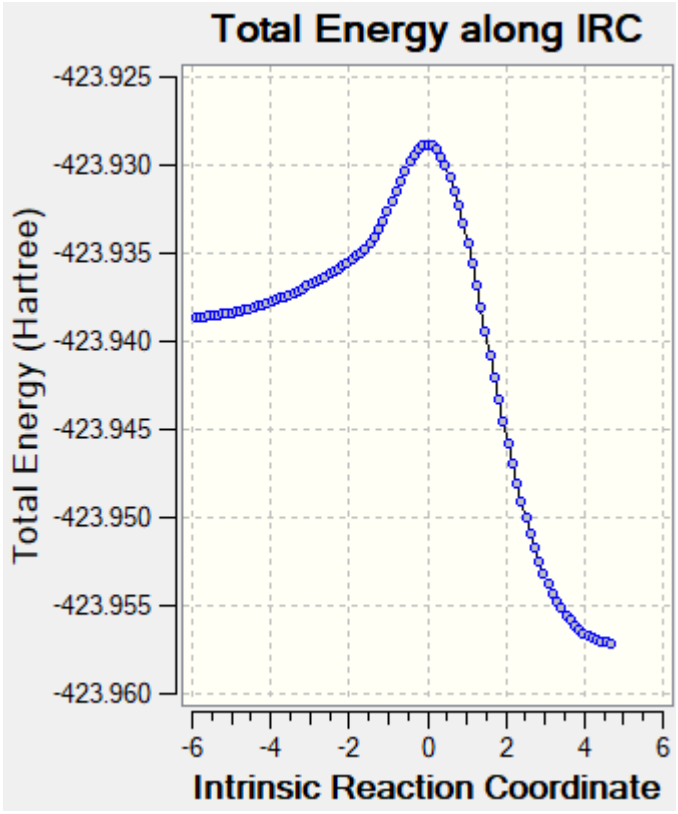
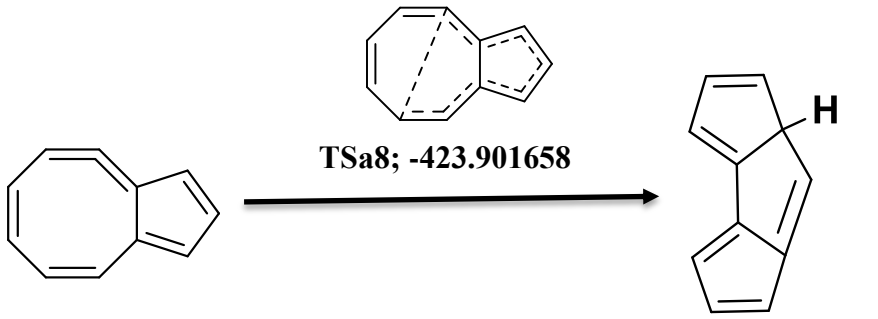


Figure S19: Intrinsic Reaction Coordinate for the rearrangement from **69** to **70** in **Scheme-I** calculated at B3LYP/6-311+G(D,P) level of theory.



TSa8; -423.901658

69; -423.957115

70; -423.981062

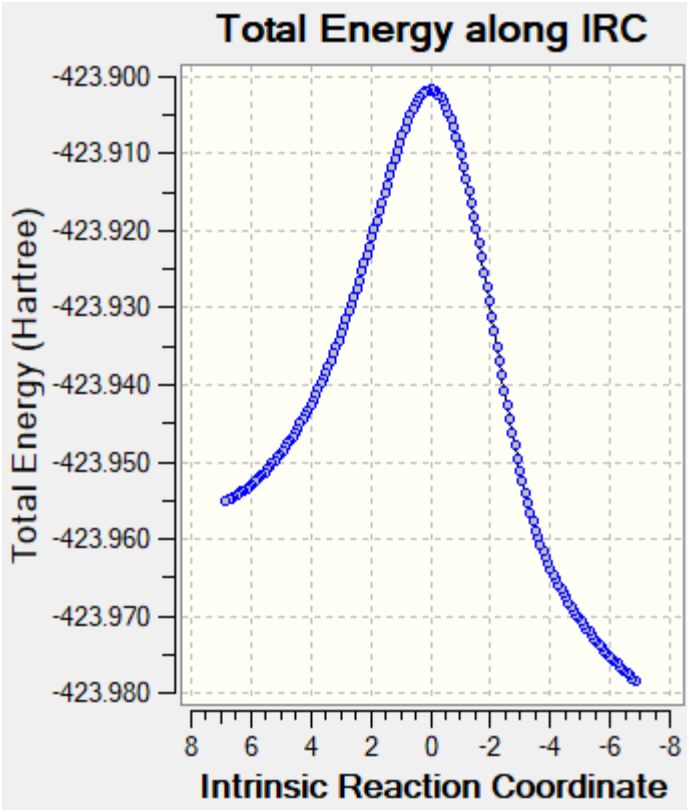
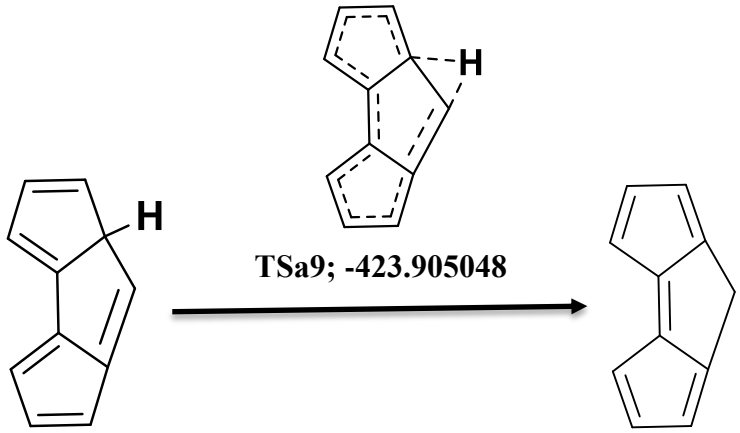


Figure S20: Intrinsic Reaction Coordinate for the rearrangement from **70** to **71** in **Scheme-I** calculated at B3LYP/6-311+G(D,P) level of theory.



70; -423.981062

71; -423.998635

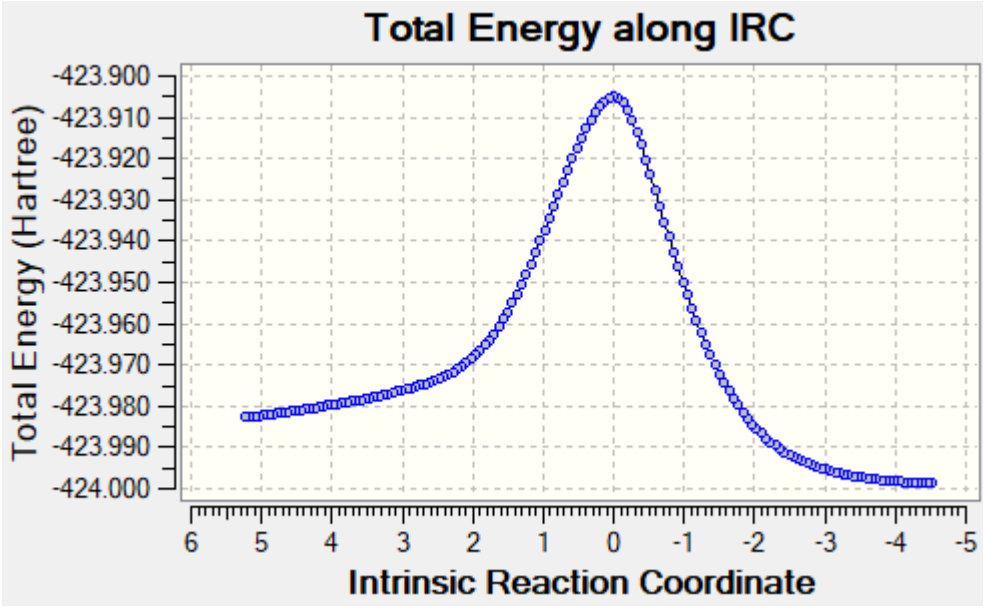
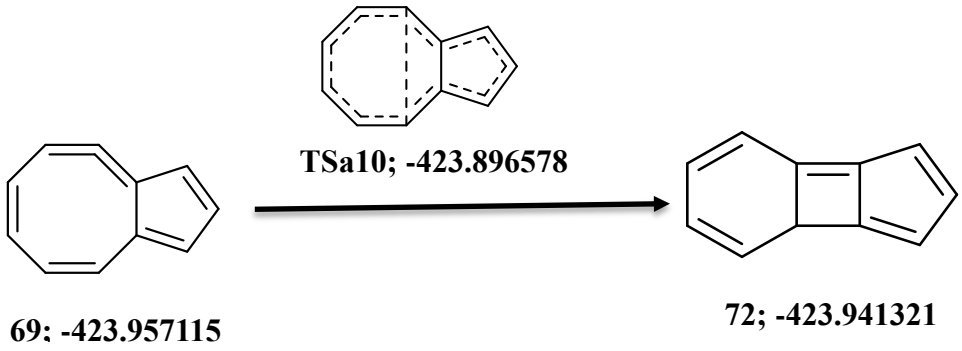


Figure S21: Intrinsic Reaction Coordinate for the rearrangement from **71** to **72** in **Scheme-I** calculated at B3LYP/6-311+G(D,P) level of theory.



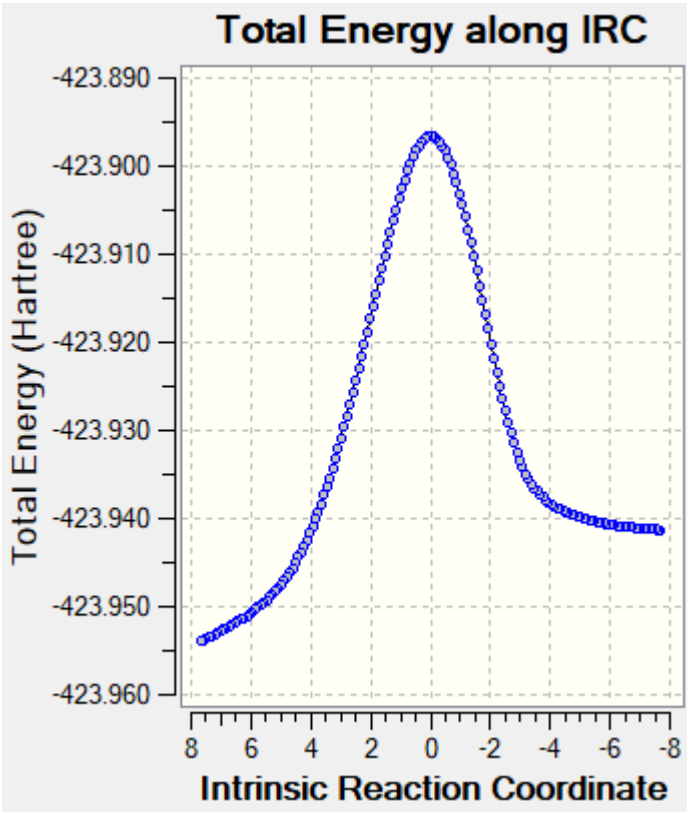
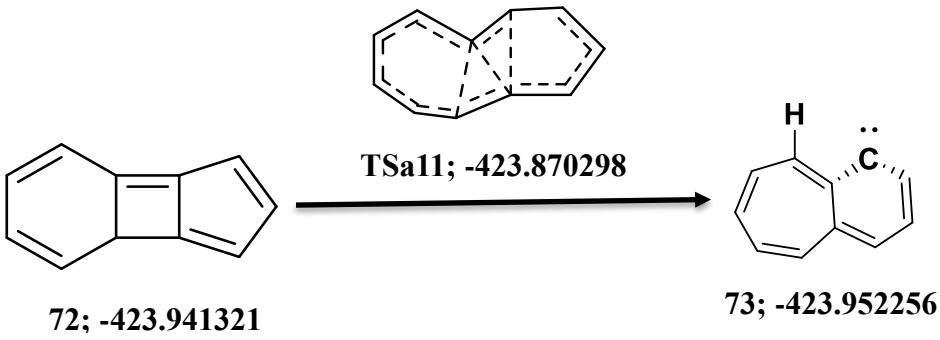


Figure S22: Intrinsic Reaction Coordinate for the rearrangement from **72** to **73** in **Scheme-I** calculated at B3LYP/6-311+G(D,P) level of theory.



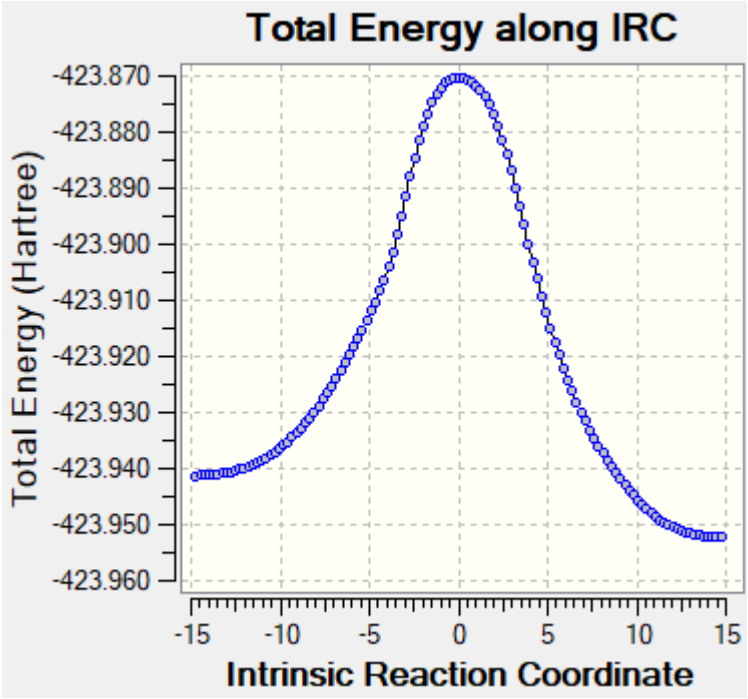
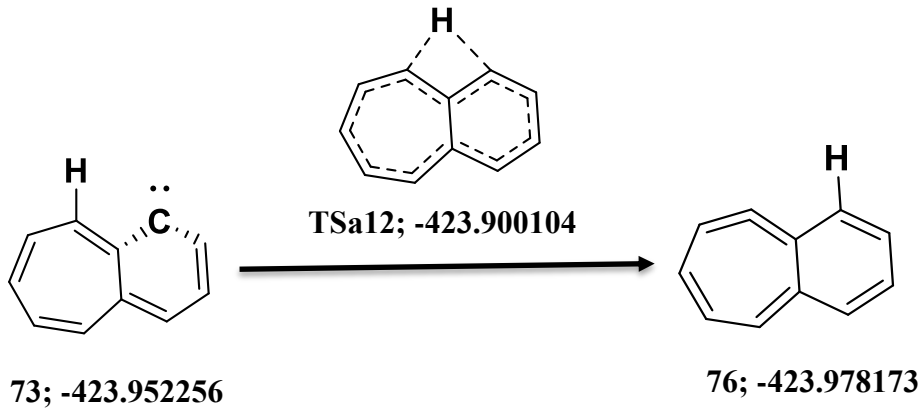


Figure S23: Intrinsic Reaction Coordinate for the rearrangement from **73** to **76** in **Scheme-I** calculated at B3LYP/6-311+G(D,P) level of theory.



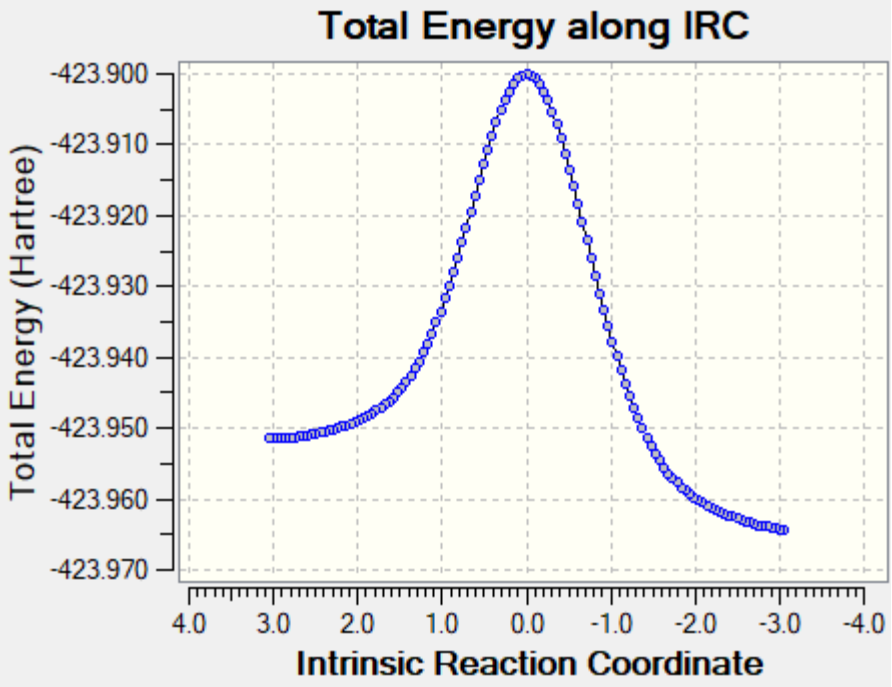
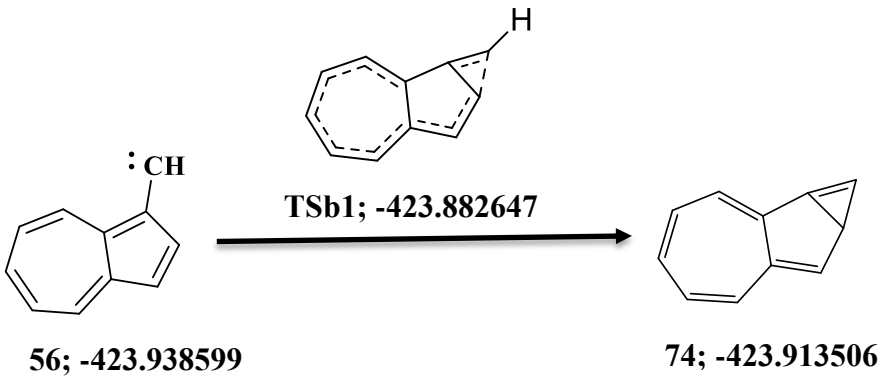


Figure S24: Intrinsic Reaction Coordinate for the rearrangement from **56** to **74** in **Scheme-II** calculated at B3LYP/6-311+G(D,P) level of theory.



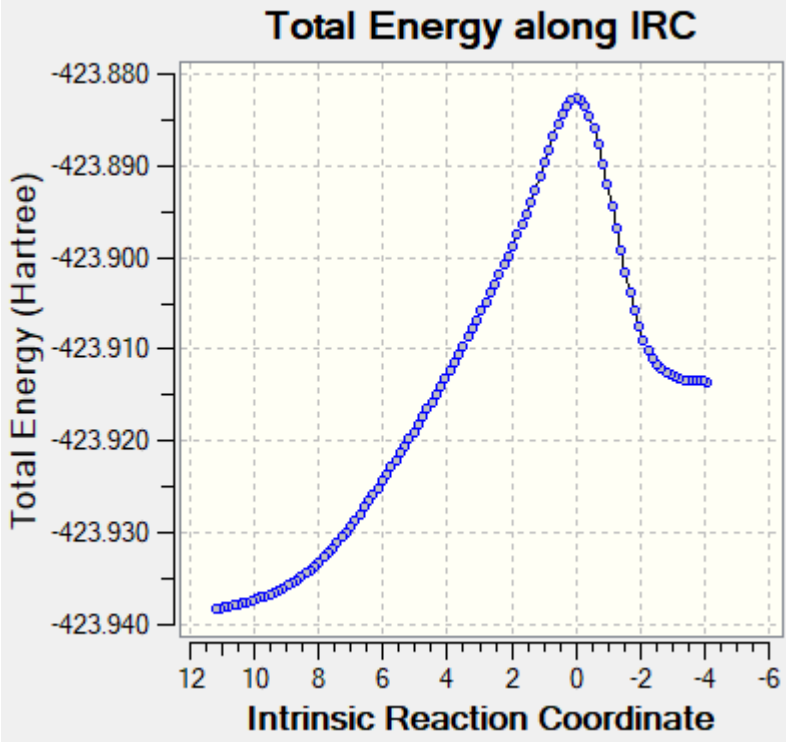
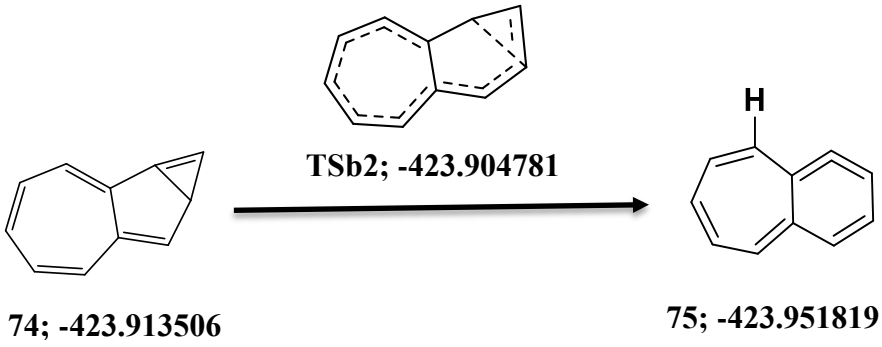


Figure S25: Intrinsic Reaction Coordinate for the rearrangement from **74** to **75** in **Scheme-II** calculated at B3LYP/6-311+G(D,P) level of theory.



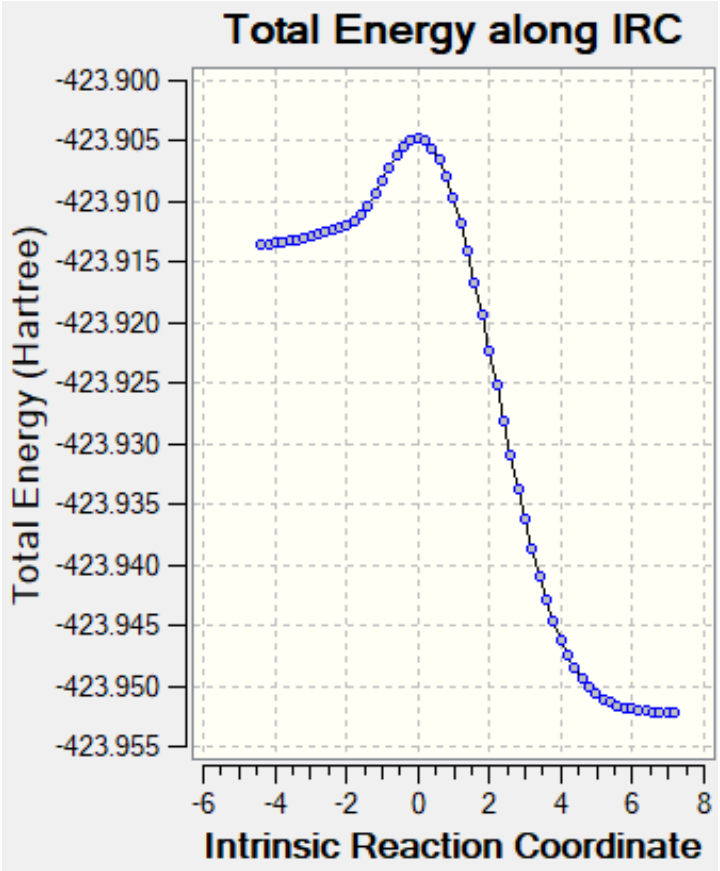
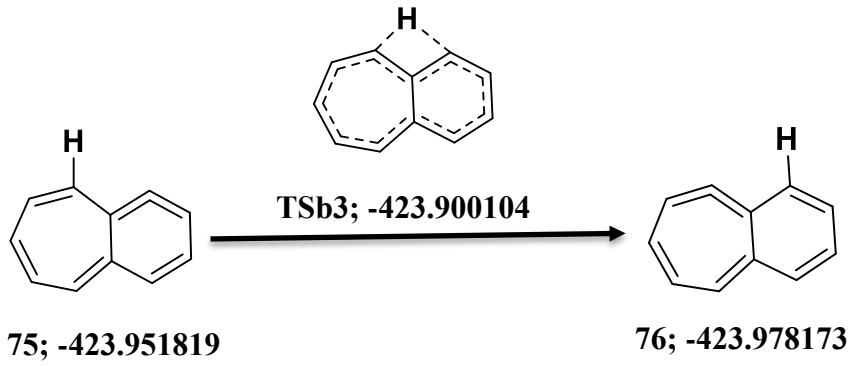


Figure S26: Intrinsic Reaction Coordinate for the rearrangement from **75 to 76** in **Scheme-II** calculated at B3LYP/6-311+G(D,P) level of theory.



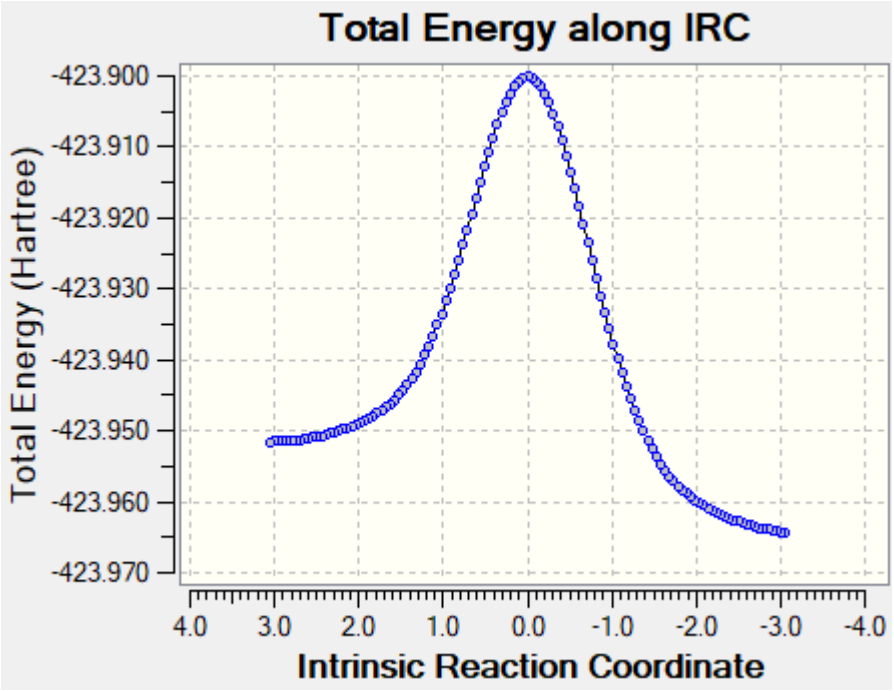
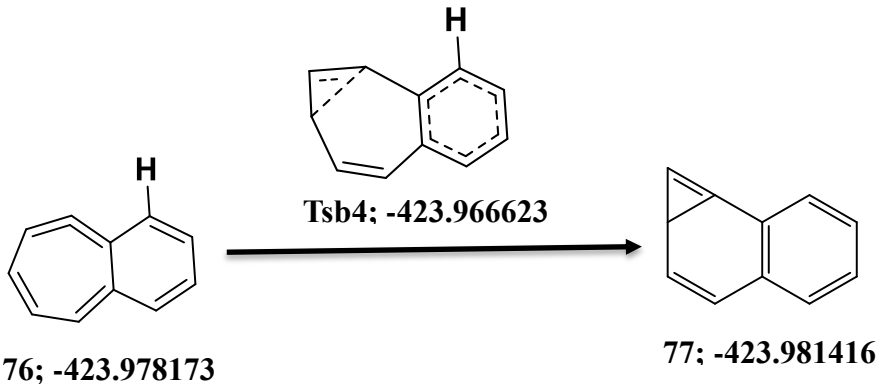


Figure S27: Intrinsic Reaction Coordinate for the rearrangement from **76 to 77** in **Scheme-II** calculated at B3LYP/6-311+G(D,P) level of theory.



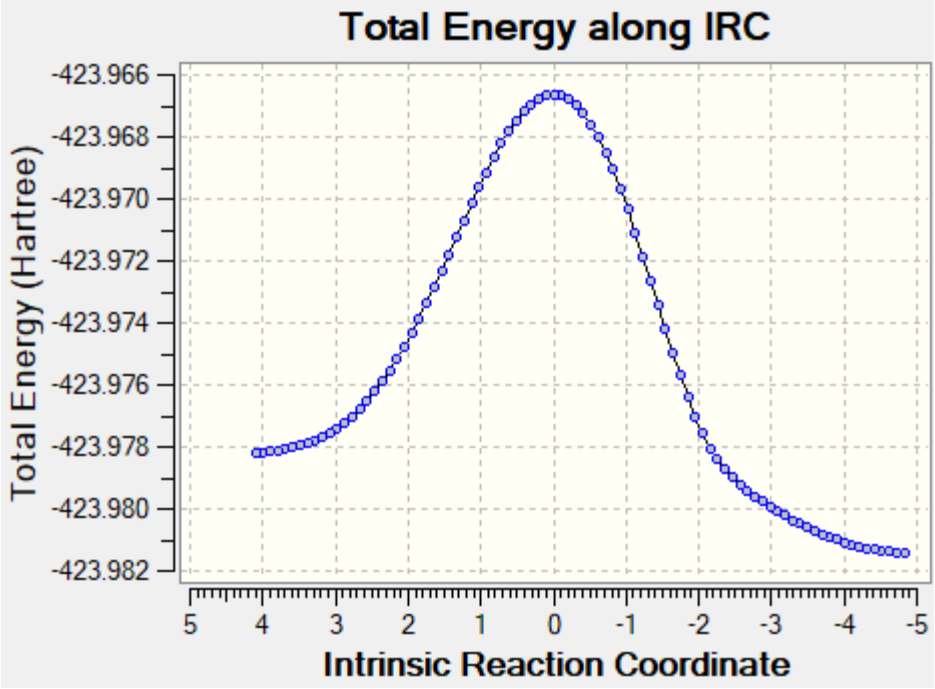
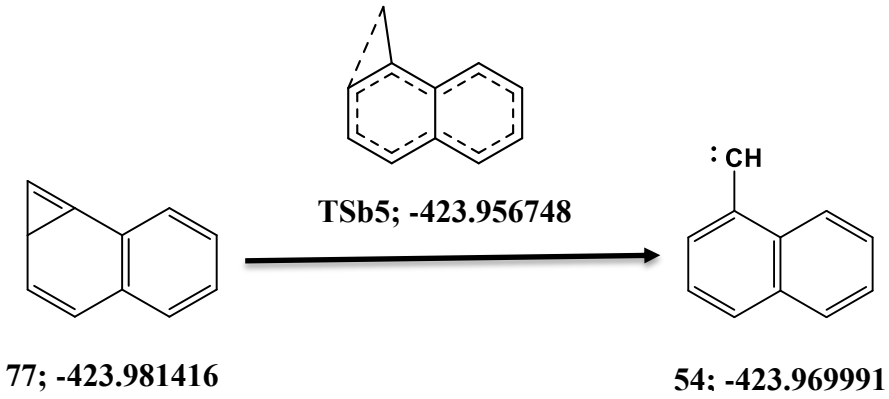


Figure S28: Intrinsic Reaction Coordinate for the rearrangement from **77 to 54** in **Scheme-II** calculated at B3LYP/6-311+G(D,P) level of theory.



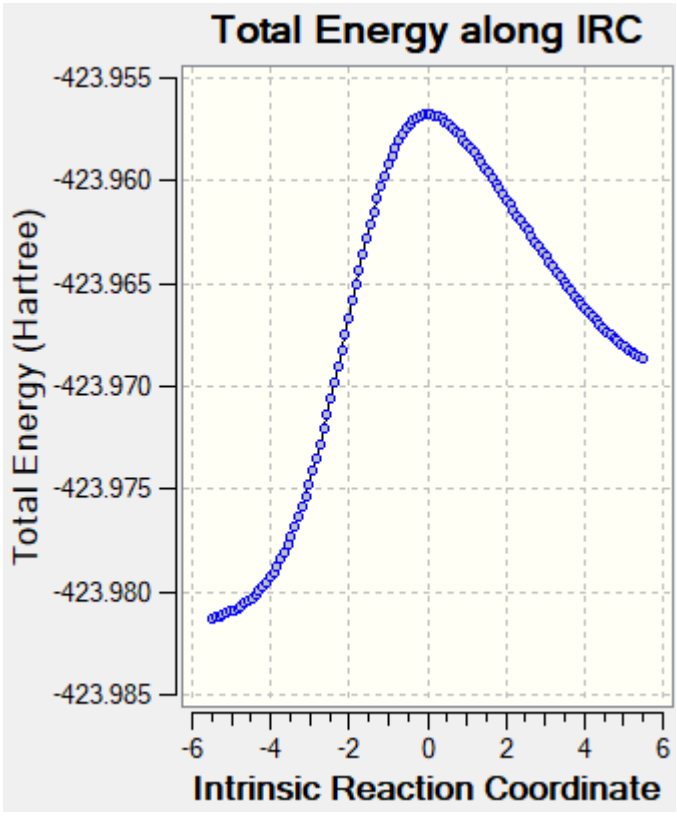
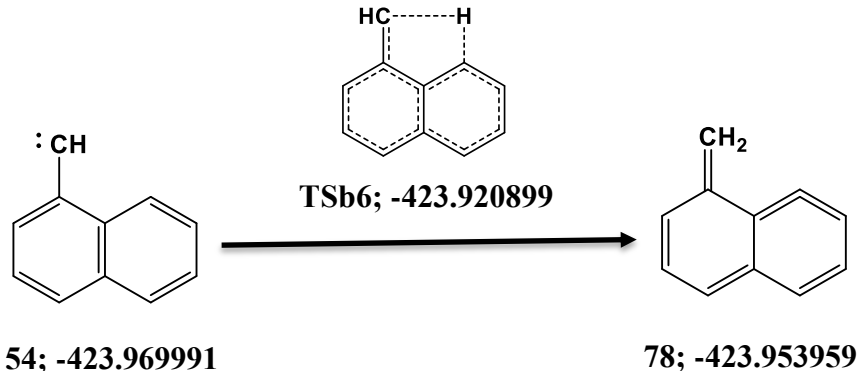


Figure S29: Intrinsic Reaction Coordinate for the rearrangement from **54** to **78** in **Scheme-II** calculated at B3LYP/6-311+G(D,P) level of theory.



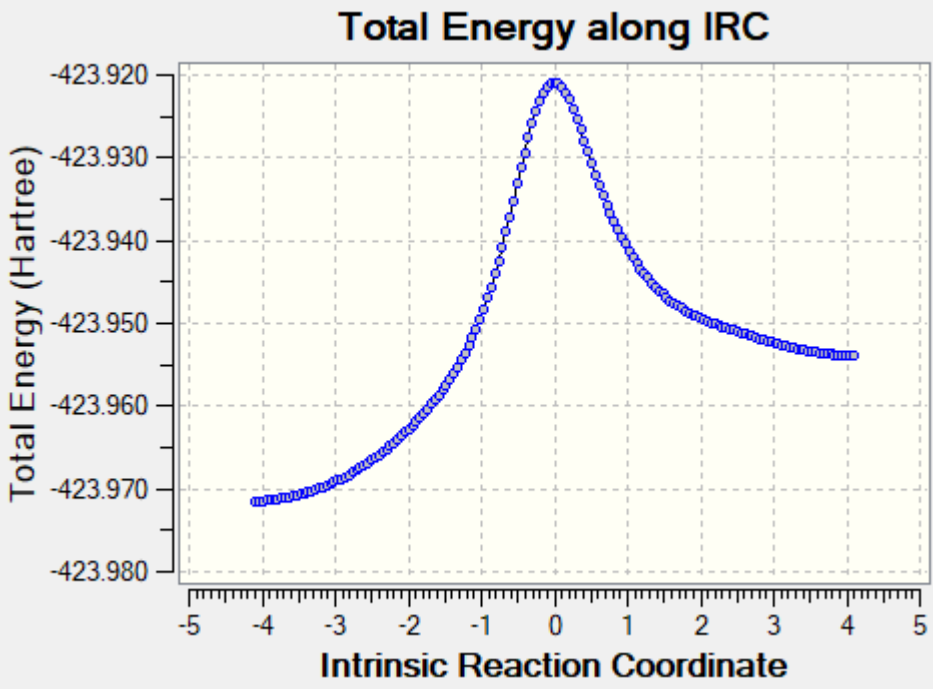
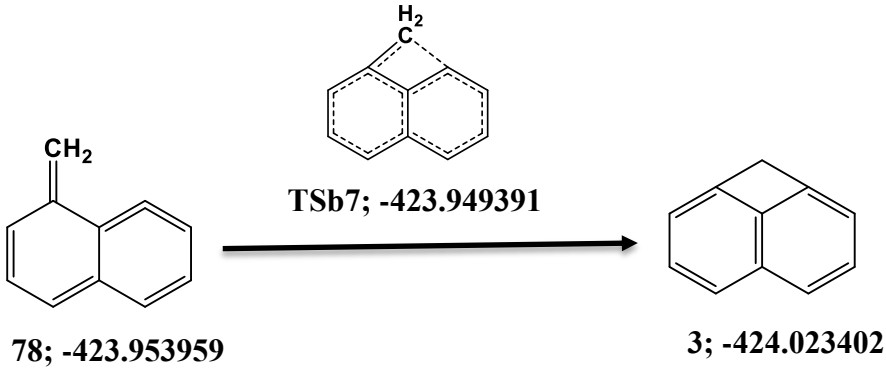


Figure S30: Intrinsic Reaction Coordinate for the rearrangement from **78** to **3** in **Scheme-II** calculated at B3LYP/6-311+G(D,P) level of theory.



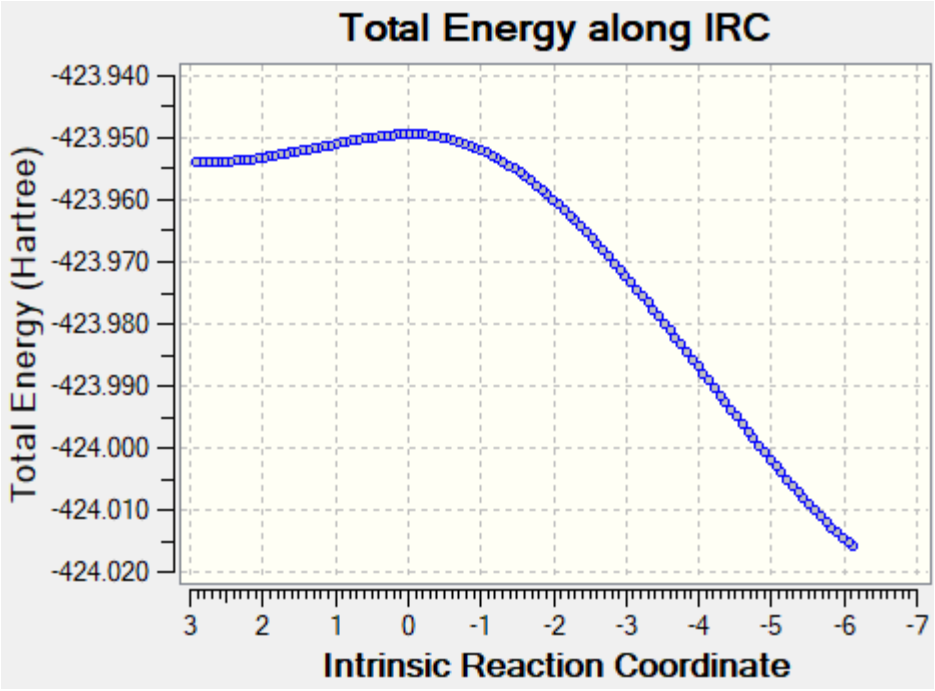
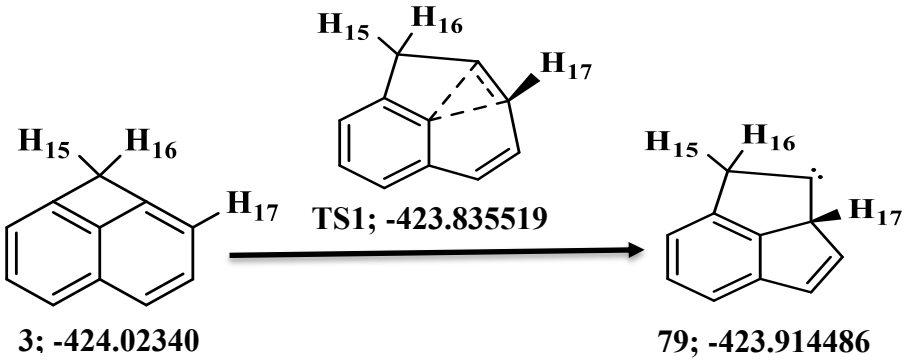


Figure S31: Intrinsic Reaction Coordinate for the rearrangement from 1H-cyclobuta[de]naphthalene (**3**) to 2,2a-dihydro-1H-cyclopenta[cd]inden-1ylidene (**79**) calculated at B3LYP/6-311+G(D,P) level of theory



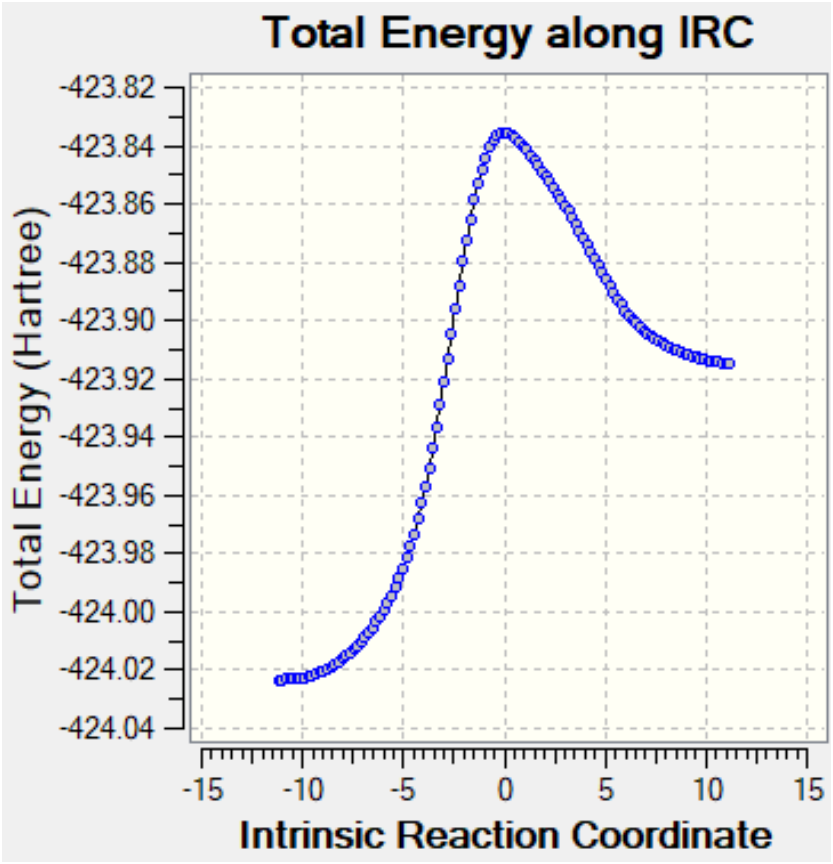
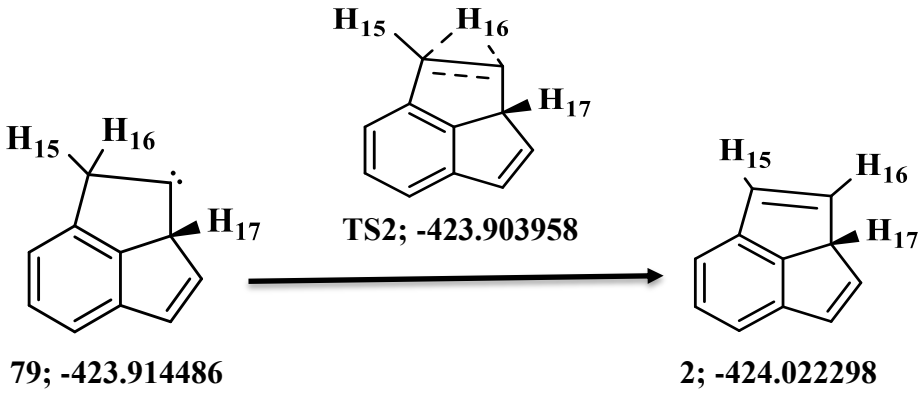


Figure S32: Intrinsic Reaction Coordinate for the rearrangement from 2,2a-dihydro-1H-cyclopenta[cd]inden-1ylidene (**72**) to 2aH-cyclopenta[cd]indene (**2**) through 1,2-H shifting calculated at B3LYP/6-311+G(D,P) level of theory.



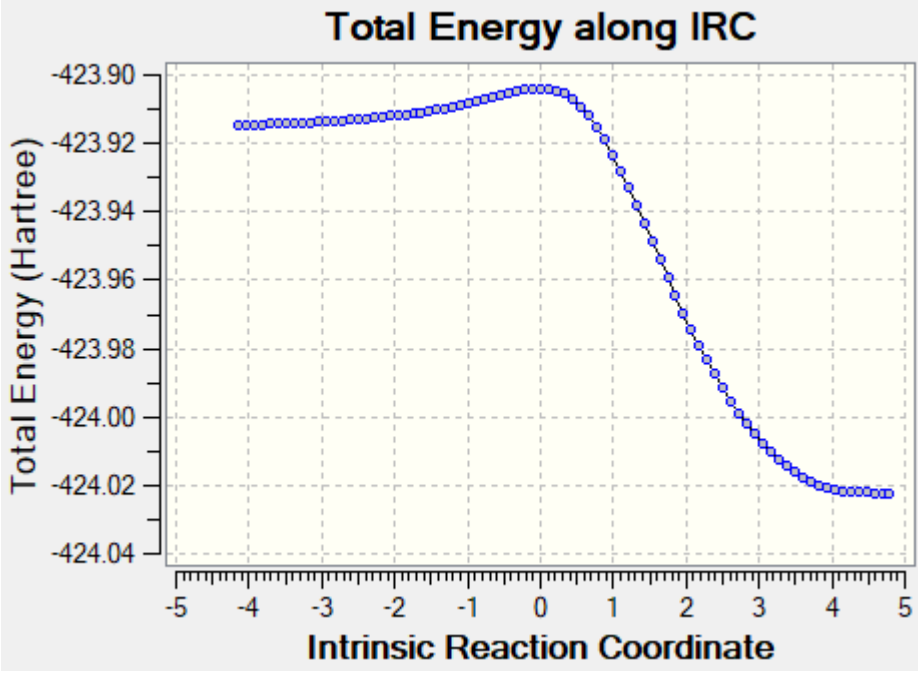
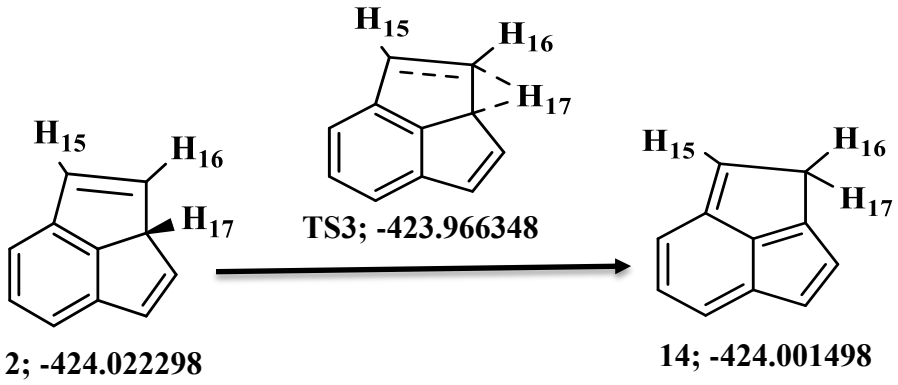


Figure S33: Intrinsic Reaction Coordinate for the rearrangement from 2aH-cyclopenta[cd]indene (**2**) to 2H-cyclopenta[cd]indene (**14**) through 1,2-H shifting calculated at B3LYP/6-311+G(D,P) level of theory.



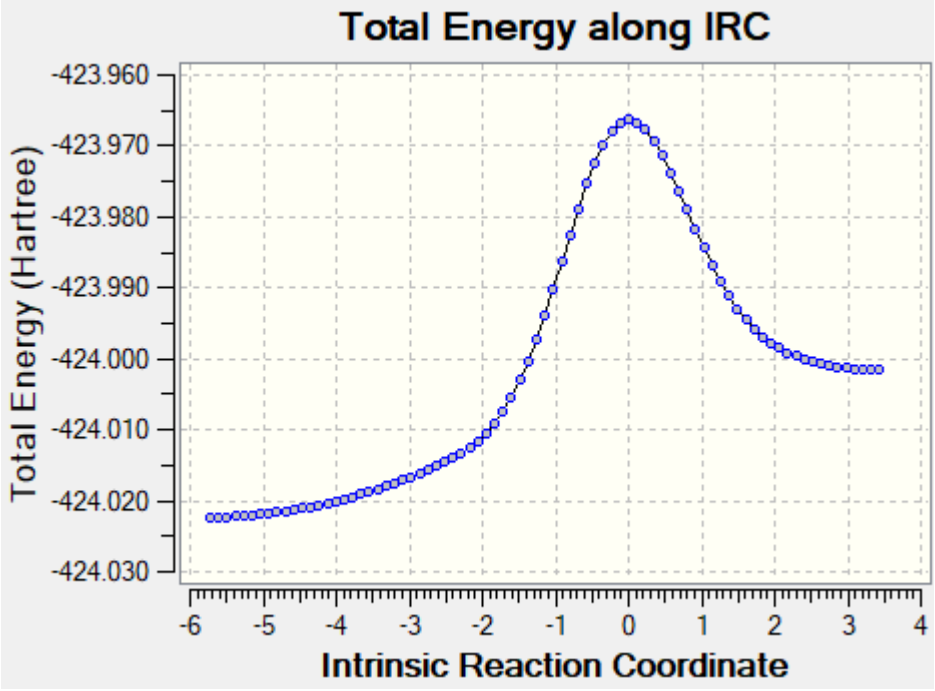
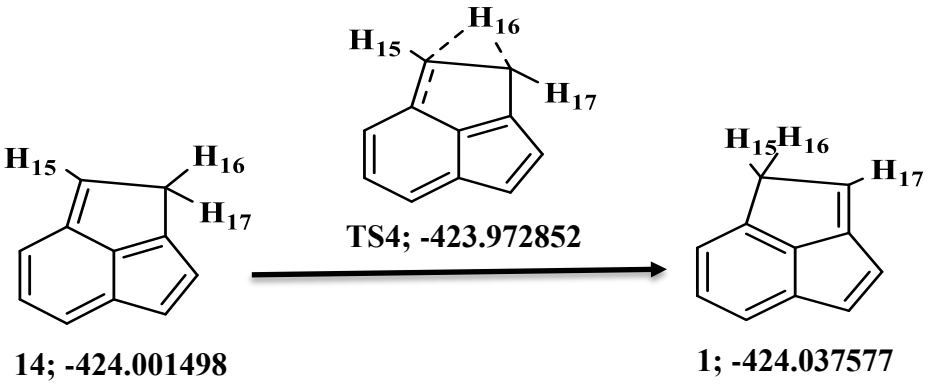


Figure S34: Intrinsic Reaction Coordinate for the rearrangement from 2H-cyclopenta[cd]indene (**14**) to 1H-cyclopenta[cd]indene (**1**) through 1,2-H shifting calculated at B3LYP/6-311+G(D,P) level of theory.



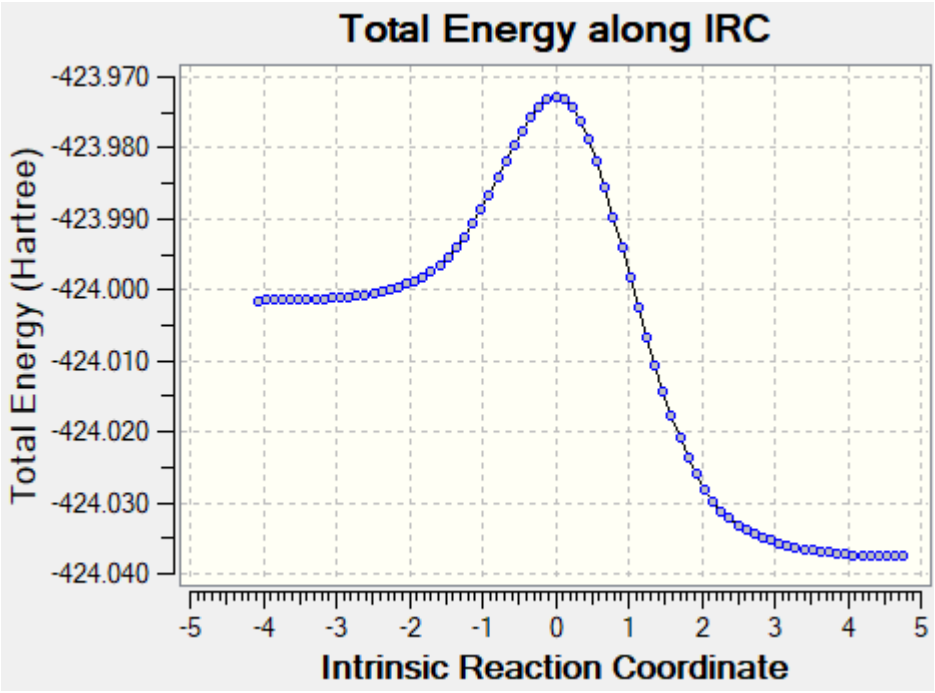


Figure S35: Intrinsic Reaction Coordinate for the rearrangement from 2,2a-dihydro-1H-cyclopenta[cd]inden-1ylidene (**72**) to 1H-cyclopenta[cd]indene (**1**) through 1,2-H shifting calculated at B3LYP/6-311+G(D,P) level of theory.