

## Supporting Information

*for*

# Functionalized Corannulene Cations: Detailed Theoretical Survey

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Properties of *hub*-isomers of {R-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup>

**Table S1.** Absolute energies for {R-*hub*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> at different levels of theory.

| Compound                       | PBE0/cc-pVTZ     | MP2/cc-pVTZ      | RIJCOSX-<br>PBE0/cc-pVTZ | RIJCOSX-<br>MP2/cc-pVTZ* |
|--------------------------------|------------------|------------------|--------------------------|--------------------------|
| H- <i>hub</i>                  | -767.82728187086 | -766.8410809680  | -767.828278226           | -766.841263097           |
| CH <sub>3</sub> - <i>hub</i>   | -807.1064061814  | -806.0737270304  | -807.107483199           | -806.074063530           |
| CH <sub>2</sub> Cl- <i>hub</i> | -1266.5691757961 | -1265.1855694990 | -1266.570359670          | -1265.185615262          |
| CHCl <sub>2</sub> - <i>hub</i> | -1726.0295569687 | -1720.6438677223 | -1726.030549170          | -1724.294434517          |
| CCl <sub>3</sub> - <i>hub</i>  | -2185.4830305621 | -2183.4034229234 | -2185.484025454          | -2183.401077248          |

\* Energy at the RIJCOSX-MP2/cc-pVTZ level of theory was obtained as result of single-point calculations for RIJCOSX-PBE0/cc-pVTZ optimized geometries.

**Table S2.** Cartesian coordinates for {H-*hub*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | -0.593080000 | -0.955720000 | -0.702520000 |
| C | -0.593220000 | -0.945820000 | 0.715840000  |
| C | -0.646940000 | 0.344430000  | -1.154329999 |
| C | -0.837180000 | 1.252639999  | -0.008650000 |
| C | -0.053000000 | -1.999999999 | -1.446359999 |
| C | -0.053620000 | -1.979679999 | 1.474299999  |
| C | -0.646850000 | 0.360440000  | 1.149399999  |
| C | 0.309440000  | -3.138769999 | -0.673800000 |
| H | 0.713030000  | -4.012449998 | -1.172949999 |
| C | -0.004210000 | 2.465719999  | -0.017160000 |
| C | 0.375570000  | 2.920239999  | -1.293389999 |
| H | 0.854380000  | 3.886849998  | -1.398089999 |
| C | 0.317660000  | 2.124999999  | 2.385449999  |
| H | 0.751250000  | 2.515789999  | 3.300259998  |
| C | 0.309100000  | -3.128989999 | 0.717750000  |
| H | 0.712390000  | -3.995719998 | 1.229019999  |
| C | 0.290940000  | -1.661879999 | -2.794319999 |
| H | 0.663410000  | -2.429359999 | -3.462149998 |
| C | -0.094250000 | 0.724010000  | -2.357169999 |
| C | 0.376660000  | 2.937369999  | 1.252289999  |
| H | 0.856090000  | 3.904989998  | 1.343309999  |
| C | -0.093870000 | 0.756730000  | 2.346669999  |
| C | 0.287930000  | -0.308730000 | 3.230169999  |
| H | 0.666360000  | -0.070980000 | 4.217209998  |
| C | 0.316330000  | 2.092269999  | -2.415259999 |
| H | 0.749130000  | 2.470739999  | -3.335699998 |
| C | 0.289840000  | -1.622949999 | 2.817519999  |
| H | 0.661590000  | -2.381149999 | 3.496229998  |
| C | 0.288260000  | -0.353510000 | -3.225599999 |
| H | 0.666770000  | -0.129290000 | -4.215879998 |
| H | -1.878569999 | 1.637189999  | -0.011290000 |

**Table S3.** Cartesian coordinates for {CH<sub>3</sub>-*hub*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 0.066590000  | -2.083709999 | -1.461299999 |
| C | -0.215350000 | -3.249659999 | 0.695310000  |
| H | -0.557300000 | -4.146339998 | 1.199839999  |
| C | 0.496540000  | 0.295540000  | 1.147919999  |
| C | -0.592710000 | 1.972829999  | -2.398819999 |
| H | -1.055910000 | 2.324979999  | -3.314829999 |
| C | -0.296570000 | -1.763019999 | -2.808349999 |
| H | -0.610890000 | -2.550119999 | -3.483089998 |
| C | -0.711740000 | 2.780359999  | -1.267179999 |
| H | -1.266009999 | 3.707369998  | -1.357839999 |
| C | -0.384690000 | -0.454730000 | -3.227729999 |
| H | -0.775710000 | -0.248500000 | -4.217049998 |
| C | 0.066660000  | -2.084479999 | 1.460239999  |
| C | -0.290990000 | 2.341539999  | 0.000590000  |
| C | -0.592800000 | 1.971559999  | 2.399809999  |
| H | -1.056110000 | 2.323199999  | 3.315959998  |
| C | 0.496540000  | 0.296130000  | -1.147749999 |
| C | 0.531490000  | -1.008610000 | -0.709710000 |
| C | -0.081130000 | 0.640520000  | -2.349289999 |
| C | -0.384740000 | -0.456430000 | 3.227479999  |
| H | -0.775810000 | -0.250720000 | 4.216899998  |
| C | -0.215380000 | -3.249289999 | -0.696970000 |
| H | -0.557180000 | -4.145759998 | -1.201979999 |
| C | 0.531510000  | -1.008980000 | 0.709190000  |
| C | -0.081170000 | 0.639290000  | 2.349619999  |
| C | -0.711770000 | 2.779709999  | 1.268589999  |
| H | -1.266039999 | 3.706659998  | 1.359709999  |
| C | -0.296450000 | -1.764509999 | 2.807469999  |
| H | -0.610800000 | -2.551959999 | 3.481799998  |
| C | 0.664640000  | 1.215379999  | 0.000320000  |
| C | 2.103889999  | 1.844069999  | 0.000490000  |
| H | 2.236089999  | 2.458989999  | -0.888280000 |
| H | 2.235739999  | 2.459269999  | 0.889130000  |
| H | 2.840099999  | 1.041570000  | 0.000750000  |

**Table S4.** Cartesian coordinates for {CH<sub>2</sub>Cl-*hub*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | -0.006350000 | -2.192339999 | -1.464119999 |
| C | -0.109910000 | -3.388479998 | 0.692430000  |
| H | -0.316210000 | -4.326749998 | 1.195069999  |
| C | 0.076010000  | 0.219170000  | 1.150459999  |
| C | -1.256219999 | 1.720529999  | -2.396539999 |
| H | -1.767339999 | 2.002149999  | -3.311459998 |
| C | -0.411880000 | -1.927419999 | -2.811239999 |
| H | -0.606660000 | -2.751669999 | -3.486709998 |
| C | -1.498559999 | 2.494939999  | -1.259869999 |
| H | -2.190759999 | 3.324609998  | -1.346679999 |
| C | -0.690980000 | -0.646080000 | -3.229199999 |
| H | -1.108089999 | -0.497880000 | -4.218249998 |
| C | -0.001530000 | -2.197039999 | 1.458639999  |
| C | -1.016360000 | 2.122559999  | 0.006320000  |
| C | -1.245179999 | 1.714509999  | 2.409169999  |
| H | -1.751179999 | 1.994539999  | 3.327459998  |

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 0.072080000  | 0.223000000  | -1.148329999 |
| C  | 0.296370000  | -1.060670000 | -0.711430000 |
| C  | -0.551450000 | 0.480940000  | -2.349119999 |
| C  | -0.680940000 | -0.656330000 | 3.230919999  |
| H  | -1.095270000 | -0.511300000 | 4.221649998  |
| C  | -0.112410000 | -3.386149998 | -0.701350000 |
| H  | -0.320190000 | -4.322889998 | -1.206199999 |
| C  | 0.298730000  | -1.063030000 | 0.708510000  |
| C  | -0.542820000 | 0.473510000  | 2.354439999  |
| C  | -1.491399999 | 2.492709999  | 1.276049999  |
| H  | -2.181669999 | 3.323419998  | 1.368579999  |
| C  | -0.403350000 | -1.936419999 | 2.807839999  |
| H  | -0.597310000 | -2.762829999 | 3.480939998  |
| C  | 0.103710000  | 1.154189999  | 0.002480000  |
| C  | 1.404189999  | 2.046199999  | 0.002370000  |
| H  | 1.397579999  | 2.675829999  | -0.884510000 |
| H  | 1.405309999  | 2.663939999  | 0.897610000  |
| Cl | 2.891439999  | 1.098910000  | -0.010690000 |

**Table S5.** Cartesian coordinates for {CHCl<sub>2</sub>-*hub*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 0.243010000  | -1.959879999 | -2.063109999 |
| C  | 0.433470000  | -3.749249998 | -0.373210000 |
| H  | 0.424000000  | -4.816669998 | -0.183520000 |
| C  | -0.035100000 | -0.480520000 | 1.159559999  |
| C  | -1.767949999 | 1.715829999  | -1.791609999 |
| H  | -2.374239999 | 2.135619999  | -2.587719999 |
| C  | -0.251850000 | -1.385159999 | -3.275819999 |
| H  | -0.315420000 | -1.989459999 | -4.172649998 |
| C  | -2.110409999 | 2.046639999  | -0.477540000 |
| H  | -2.963679999 | 2.696259999  | -0.320920000 |
| C  | -0.783690000 | -0.115740000 | -3.289519998 |
| H  | -1.264369999 | 0.241170000  | -4.192549998 |
| C  | 0.341870000  | -2.845869999 | 0.719870000  |
| C  | -1.495389999 | 1.437999999  | 0.623460000  |
| C  | -1.542109999 | 0.306730000  | 2.795129999  |
| H  | -2.045619999 | 0.207220000  | 3.751059998  |
| C  | -0.100470000 | 0.225960000  | -1.031330000 |
| C  | 0.359260000  | -1.069650000 | -0.997480000 |
| C  | -0.820290000 | 0.699270000  | -2.107829999 |
| C  | -0.537260000 | -2.062259999 | 2.862229999  |
| H  | -0.931280000 | -2.300979999 | 3.842929998  |
| C  | 0.385340000  | -3.326289998 | -1.699809999 |
| H  | 0.339800000  | -4.087469998 | -2.470399999 |
| C  | 0.400340000  | -1.503899999 | 0.354340000  |
| C  | -0.638510000 | -0.715980000 | 2.373649999  |
| C  | -1.972569999 | 1.322509999  | 1.941799999  |
| H  | -2.798089999 | 1.945489999  | 2.266459999  |
| C  | -0.049720000 | -3.081929999 | 2.075639999  |
| H  | -0.064110000 | -4.093339998 | 2.463509999  |
| C  | -0.207370000 | 0.754780000  | 0.351010000  |
| C  | 0.954240000  | 1.776539999  | 0.730870000  |
| Cl | 0.889720000  | 3.265629999  | -0.206140000 |
| H  | 0.819760000  | 2.046289999  | 1.774669999  |
| Cl | 2.543189999  | 1.031200000  | 0.580620000  |

**Table S6.** Cartesian coordinates for {CCl<sub>3</sub>-*hub*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 0.251160000  | -2.038399999 | -1.941119999 |
| C  | 0.445840000  | -0.358860000 | -3.736689998 |
| H  | 0.439950000  | -0.173230000 | -4.804849998 |
| C  | -0.027740000 | 1.195009999  | -0.471520000 |
| C  | -1.768779999 | -1.764889999 | 1.729349999  |
| H  | -2.375389999 | -2.561719999 | 2.146809999  |
| C  | -0.241690000 | -3.249939999 | -1.365099999 |
| H  | -0.300070000 | -4.148919998 | -1.966609999 |
| C  | -2.111529999 | -0.451940000 | 2.054649999  |
| H  | -2.972909999 | -0.292200000 | 2.692819999  |
| C  | -0.778670000 | -3.259459999 | -0.097940000 |
| H  | -1.259499999 | -4.161579998 | 0.261060000  |
| C  | 0.343910000  | 0.737450000  | -2.839729999 |
| C  | -1.499719999 | 0.650580000  | 1.441179999  |
| C  | -1.614429999 | 2.788659999  | 0.255920000  |
| H  | -2.162529999 | 3.714499998  | 0.116200000  |
| C  | -0.101400000 | -0.999200000 | 0.238870000  |
| C  | 0.359210000  | -0.968040000 | -1.054770000 |
| C  | -0.819220000 | -2.076589999 | 0.713300000  |
| C  | -0.572540000 | 2.866339999  | -2.080609999 |
| H  | -0.990490000 | 3.835079998  | -2.327389999 |
| C  | 0.401540000  | -1.683249999 | -3.307919998 |
| H  | 0.363400000  | -2.458389999 | -4.064829998 |
| C  | 0.404280000  | 0.384410000  | -1.492679999 |
| C  | -0.668580000 | 2.387559999  | -0.731570000 |
| C  | -2.030319999 | 1.938599999  | 1.281009999  |
| H  | -2.887189999 | 2.235719999  | 1.874759999  |
| C  | -0.062890000 | 2.083959999  | -3.091599999 |
| H  | -0.079100000 | 2.462029999  | -4.106639998 |
| C  | -0.196200000 | 0.390440000  | 0.773130000  |
| C  | 1.019660000  | 0.681830000  | 1.800249999  |
| Cl | 0.911130000  | -0.365040000 | 3.216989999  |
| Cl | 1.003450000  | 2.364499999  | 2.333009999  |
| Cl | 2.558459999  | 0.367730000  | 0.990330000  |

**Table S7.** Cartesian coordinates for {H-*hub*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (RIJCOSX-PBE0/cc-pVTZ).

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 0.769558000  | -2.236923000 | -1.469177000 |
| C | 0.733496000  | -3.447632000 | 0.680487000  |
| H | 0.581861000  | -4.397070000 | 1.181308000  |
| C | 0.719590000  | 0.165263000  | 1.156783000  |
| C | -0.687469000 | 1.619837000  | -2.385681000 |
| H | -1.208272000 | 1.880974000  | -3.301122000 |
| C | 0.342809000  | -1.986916000 | -2.812758000 |
| H | 0.187086000  | -2.818016000 | -3.490286000 |
| C | -0.961258000 | 2.388445000  | -1.252900000 |
| H | -1.679512000 | 3.194812000  | -1.345348000 |
| C | -0.008270000 | -0.720766000 | -3.227528000 |
| H | -0.437838000 | -0.595159000 | -4.214112000 |
| C | 0.777984000  | -2.252528000 | 1.451610000  |
| C | -0.469163000 | 2.035849000  | 0.017503000  |
| C | -0.674480000 | 1.593782000  | 2.417223000  |
| H | -1.190561000 | 1.844913000  | 3.338123000  |

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 0.713123000  | 0.177599000  | -1.148179000 |
| C | 1.012436000  | -1.094804000 | -0.712665000 |
| C | 0.073675000  | 0.409730000  | -2.345680000 |
| C | 0.009882000  | -0.755441000 | 3.230429000  |
| H | -0.414132000 | -0.640332000 | 4.220673000  |
| C | 0.729482000  | -3.440226000 | -0.710654000 |
| H | 0.574956000  | -4.384267000 | -1.220685000 |
| C | 1.016520000  | -1.102392000 | 0.705964000  |
| C | 0.086740000  | 0.384425000  | 2.360218000  |
| C | -0.954492000 | 2.374530000  | 1.294251000  |
| H | -1.672462000 | 3.179622000  | 1.399215000  |
| C | 0.358837000  | -2.017019000 | 2.800206000  |
| H | 0.207084000  | -2.855346000 | 3.469678000  |
| C | 0.657820000  | 1.089769000  | 0.009389000  |
| H | 1.557250000  | 1.740281000  | 0.010364000  |

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**Table S8.** Cartesian coordinates for {CH<sub>3</sub>-*hub*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (RIJCOSX-PBE0/cc-pVTZ).

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 0.765567000  | -2.237579000 | -1.469117000 |
| C | 0.724761000  | -3.447200000 | 0.680846000  |
| H | 0.568965000  | -4.396127000 | 1.181443000  |
| C | 0.724876000  | 0.166892000  | 1.153049000  |
| C | -0.683785000 | 1.615181000  | -2.384538000 |
| H | -1.209011000 | 1.874252000  | -3.298060000 |
| C | 0.341406000  | -1.988578000 | -2.813681000 |
| H | 0.184365000  | -2.819594000 | -3.490921000 |
| C | -0.955832000 | 2.378602000  | -1.247922000 |
| H | -1.679779000 | 3.180893000  | -1.333120000 |
| C | -0.005533000 | -0.721615000 | -3.226322000 |
| H | -0.435120000 | -0.592621000 | -4.212539000 |
| C | 0.773944000  | -2.253186000 | 1.451509000  |
| C | -0.454492000 | 2.023683000  | 0.017352000  |
| C | -0.670680000 | 1.589407000  | 2.415939000  |
| H | -1.190931000 | 1.838877000  | 3.334961000  |
| C | 0.719056000  | 0.179340000  | -1.144704000 |
| C | 1.012451000  | -1.095248000 | -0.713090000 |
| C | 0.079968000  | 0.408540000  | -2.343083000 |
| C | 0.012708000  | -0.756179000 | 3.229169000  |
| H | -0.411045000 | -0.637690000 | 4.219204000  |
| C | 0.720721000  | -3.439760000 | -0.710965000 |
| H | 0.561991000  | -4.383279000 | -1.220765000 |
| C | 1.016328000  | -1.102881000 | 0.706217000  |
| C | 0.092787000  | 0.383356000  | 2.357484000  |
| C | -0.948900000 | 2.364974000  | 1.289040000  |
| H | -1.672386000 | 3.166244000  | 1.386786000  |
| C | 0.357543000  | -2.018582000 | 2.801084000  |
| H | 0.204673000  | -2.856758000 | 3.470400000  |
| C | 0.704722000  | 1.107622000  | 0.009191000  |
| C | 1.990032000  | 2.011189000  | 0.012332000  |
| H | 1.998414000  | 2.634841000  | 0.905415000  |
| H | 2.870711000  | 1.370630000  | 0.006251000  |
| H | 1.994868000  | 2.646539000  | -0.872516000 |

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**Table S9.** Cartesian coordinates for {CH<sub>2</sub>Cl-*hub*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (RIJCOSX-PBE0/cc-pVTZ).

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | -0.006674000 | -2.193990000 | -1.464192000 |
| C  | -0.110615000 | -3.390100000 | 0.692080000  |
| H  | -0.316088000 | -4.328135000 | 1.195289000  |
| C  | 0.075719000  | 0.217535000  | 1.151192000  |
| C  | -1.252886000 | 1.722110000  | -2.398420000 |
| H  | -1.759062000 | 2.006783000  | -3.314974000 |
| C  | -0.412645000 | -1.929167000 | -2.811287000 |
| H  | -0.609626000 | -2.753741000 | -3.485866000 |
| C  | -1.496062000 | 2.497117000  | -1.261525000 |
| H  | -2.183002000 | 3.330896000  | -1.350328000 |
| C  | -0.692101000 | -0.647889000 | -3.230123000 |
| H  | -1.110836000 | -0.500467000 | -4.218392000 |
| C  | -0.000790000 | -2.198792000 | 1.458455000  |
| C  | -1.019078000 | 2.121360000  | 0.006124000  |
| C  | -1.243686000 | 1.714094000  | 2.410295000  |
| H  | -1.746257000 | 1.995862000  | 3.329721000  |
| C  | 0.071534000  | 0.221402000  | -1.149344000 |
| C  | 0.296511000  | -1.062205000 | -0.711741000 |
| C  | -0.551408000 | 0.479687000  | -2.350594000 |
| C  | -0.679221000 | -0.658584000 | 3.232248000  |
| H  | -1.093785000 | -0.514387000 | 4.222744000  |
| C  | -0.113452000 | -3.387818000 | -0.701292000 |
| H  | -0.320990000 | -4.324205000 | -1.206709000 |
| C  | 0.299248000  | -1.064552000 | 0.708472000  |
| C  | -0.542393000 | 0.471838000  | 2.355737000  |
| C  | -1.491221000 | 2.492846000  | 1.276877000  |
| H  | -2.177781000 | 3.326349000  | 1.371068000  |
| C  | -0.401234000 | -1.938446000 | 2.808094000  |
| H  | -0.595156000 | -2.765230000 | 3.480848000  |
| C  | 0.100869000  | 1.152761000  | 0.002464000  |
| C  | 1.398701000  | 2.050012000  | 0.002156000  |
| H  | 1.392916000  | 2.674954000  | -0.888263000 |
| H  | 1.393810000  | 2.673892000  | 0.893318000  |
| Cl | 2.888144000  | 1.106592000  | 0.001110000  |

**Table S10.** Cartesian coordinates for {CHCl<sub>2</sub>-*hub*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (RIJCOSX-PBE0/cc-pVTZ).

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 0.243287000  | -1.960242000 | -2.063459000 |
| C | 0.435034000  | -3.749625000 | -0.372222000 |
| H | 0.425362000  | -4.817009000 | -0.181148000 |
| C | -0.035158000 | -0.481033000 | 1.158887000  |
| C | -1.764750000 | 1.718151000  | -1.793048000 |
| H | -2.368734000 | 2.139346000  | -2.589975000 |
| C | -0.254799000 | -1.386532000 | -3.275605000 |
| H | -0.322034000 | -1.992560000 | -4.171204000 |
| C | -2.108218000 | 2.049075000  | -0.479345000 |
| H | -2.959570000 | 2.701746000  | -0.322980000 |
| C | -0.785322000 | -0.116394000 | -3.290167000 |
| H | -1.267698000 | 0.238956000  | -4.192929000 |
| C | 0.344740000  | -2.845387000 | 0.720610000  |
| C | -1.496022000 | 1.437590000  | 0.621851000  |
| C | -1.544444000 | 0.306052000  | 2.792903000  |
| H | -2.048335000 | 0.205852000  | 3.748543000  |

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | -0.099268000 | 0.225850000  | -1.032755000 |
| C  | 0.361545000  | -1.069255000 | -0.998319000 |
| C  | -0.818823000 | 0.699757000  | -2.109045000 |
| C  | -0.536476000 | -2.061036000 | 2.863162000  |
| H  | -0.929921000 | -2.299934000 | 3.843960000  |
| C  | 0.385152000  | -3.327069000 | -1.699392000 |
| H  | 0.337144000  | -4.088562000 | -2.469489000 |
| C  | 0.403078000  | -1.503442000 | 0.353914000  |
| C  | -0.638868000 | -0.715214000 | 2.373099000  |
| C  | -1.974614000 | 1.321490000  | 1.939310000  |
| H  | -2.800489000 | 1.944961000  | 2.263055000  |
| C  | -0.047636000 | -3.080586000 | 2.076786000  |
| H  | -0.060820000 | -4.091888000 | 2.465014000  |
| C  | -0.208604000 | 0.753591000  | 0.350356000  |
| C  | 0.952725000  | 1.774444000  | 0.734749000  |
| Cl | 0.880547000  | 3.271911000  | -0.188245000 |
| H  | 0.824441000  | 2.034207000  | 1.782012000  |
| Cl | 2.542047000  | 1.033577000  | 0.566765000  |

**Table S11.** Cartesian coordinates for {CCl<sub>3</sub>-*hub*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (RIJCOSX-PBE0/cc-pVTZ).

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 0.250455000  | -2.038741000 | -1.941482000 |
| C  | 0.449591000  | -0.358199000 | -3.737135000 |
| H  | 0.446300000  | -0.171523000 | -4.805314000 |
| C  | -0.029281000 | 1.194832000  | -0.472541000 |
| C  | -1.766462000 | -1.765029000 | 1.733085000  |
| H  | -2.369983000 | -2.562429000 | 2.153609000  |
| C  | -0.244693000 | -3.249782000 | -1.365563000 |
| H  | -0.304722000 | -4.148394000 | -1.967773000 |
| C  | -2.109603000 | -0.452177000 | 2.058561000  |
| H  | -2.968415000 | -0.292398000 | 2.700697000  |
| C  | -0.780967000 | -3.259864000 | -0.097804000 |
| H  | -1.261951000 | -4.162238000 | 0.260386000  |
| C  | 0.346682000  | 0.738373000  | -2.839988000 |
| C  | -1.501021000 | 0.650339000  | 1.441350000  |
| C  | -1.616475000 | 2.787390000  | 0.255238000  |
| H  | -2.164067000 | 3.713661000  | 0.115553000  |
| C  | -0.103481000 | -0.999848000 | 0.237677000  |
| C  | 0.359129000  | -0.968318000 | -1.055027000 |
| C  | -0.820153000 | -2.076985000 | 0.713711000  |
| C  | -0.572769000 | 2.867366000  | -2.080831000 |
| H  | -0.990263000 | 3.836077000  | -2.328257000 |
| C  | 0.403211000  | -1.683131000 | -3.308590000 |
| H  | 0.365399000  | -2.458028000 | -4.065741000 |
| C  | 0.405433000  | 0.384371000  | -1.492827000 |
| C  | -0.670338000 | 2.387286000  | -0.732086000 |
| C  | -2.032128000 | 1.937728000  | 1.280438000  |
| H  | -2.888410000 | 2.235476000  | 1.875199000  |
| C  | -0.060961000 | 2.085290000  | -3.091411000 |
| H  | -0.075394000 | 2.463726000  | -4.106365000 |
| C  | -0.199019000 | 0.390028000  | 0.771285000  |
| C  | 1.017739000  | 0.681685000  | 1.797481000  |
| Cl | 0.909975000  | -0.363665000 | 3.215390000  |
| Cl | 1.002024000  | 2.364174000  | 2.329722000  |
| Cl | 2.555721000  | 0.365695000  | 0.987426000  |



**Table S12.** Cartesian coordinates for C<sub>20</sub>H<sub>10</sub> (PBE0/cc-pVTZ, C<sub>5v</sub>).

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 3.166060000  | 0.280300000  | 0.689780000  |
| H | 4.048410000  | 0.646250000  | 1.203900000  |
| C | -0.763300000 | -0.072170000 | 2.349210000  |
| C | -1.198320000 | -0.596900000 | 0.000000000  |
| C | 3.166060000  | 0.280300000  | -0.689780000 |
| H | 4.048410000  | 0.646250000  | -1.203900000 |
| C | 0.322340000  | 0.280300000  | 3.224260000  |
| C | 0.969460000  | -0.596900000 | -0.704360000 |
| C | 1.634390000  | 0.280300000  | 2.797950000  |
| H | 2.396010000  | 0.646250000  | 3.478240000  |
| C | -2.470100000 | -0.072170000 | 0.000000000  |
| C | 0.969460000  | -0.596900000 | 0.704360000  |
| C | -0.370300000 | -0.596900000 | 1.139670000  |
| C | -2.966840000 | 0.280300000  | 1.302920000  |
| H | -3.982870000 | 0.646250000  | 1.405620000  |
| C | -0.763300000 | -0.072170000 | -2.349210000 |
| C | -2.155950000 | 0.280300000  | 2.419010000  |
| C | 1.998360000  | -0.072170000 | 1.451890000  |
| C | -2.155950000 | 0.280300000  | -2.419010000 |
| H | -2.567600000 | 0.646250000  | -3.353570000 |
| C | -2.966840000 | 0.280300000  | -1.302920000 |
| H | -3.982870000 | 0.646250000  | -1.405620000 |
| C | 1.998360000  | -0.072170000 | -1.451890000 |
| C | -0.370300000 | -0.596900000 | -1.139670000 |
| C | 1.634390000  | 0.280300000  | -2.797950000 |
| H | 2.396010000  | 0.646250000  | -3.478240000 |
| C | 0.322340000  | 0.280300000  | -3.224260000 |
| H | 0.106050000  | 0.646250000  | -4.222290000 |
| H | -2.567600000 | 0.646250000  | 3.353570000  |
| H | 0.106050000  | 0.646250000  | 4.222290000  |

**Table S13.** Cartesian coordinates for C<sub>20</sub>H<sub>10</sub> (RIJCOSX-PBE0/cc-pVTZ, C<sub>5v</sub>).

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | -3.168206000 | 0.276973000  | 0.689747000  |
| C | -1.634466000 | 0.284276000  | -2.797406000 |
| C | 2.156948000  | 0.281186000  | -2.419205000 |
| C | 2.967959000  | 0.278767000  | 1.303315000  |
| C | -0.322339000 | 0.285434000  | 3.223637000  |
| H | -4.052590000 | 0.637002000  | 1.204332000  |
| H | -2.395995000 | 0.650210000  | -3.477510000 |
| H | 2.569294000  | 0.645578000  | -3.354046000 |
| H | 3.984809000  | 0.641316000  | 1.406495000  |
| H | -0.105913000 | 0.652933000  | 4.221101000  |
| C | -1.998514000 | -0.069301000 | -1.451585000 |
| C | 0.763507000  | -0.067928000 | -2.349113000 |
| C | 2.470520000  | -0.071849000 | 0.000031000  |
| C | 0.763543000  | -0.068271000 | 2.349159000  |
| C | -1.998601000 | -0.069734000 | 1.451667000  |
| C | -0.969177000 | -0.592810000 | -0.704305000 |
| C | 0.370216000  | -0.592549000 | -1.139592000 |
| C | 1.198039000  | -0.593923000 | -0.000033000 |
| C | 0.370228000  | -0.592747000 | 1.139564000  |
| C | -0.969170000 | -0.592905000 | 0.704334000  |

|   |              |             |              |
|---|--------------|-------------|--------------|
| C | -3.168090000 | 0.277397000 | -0.689626000 |
| C | -0.322382000 | 0.285226000 | -3.223812000 |
| C | 2.967934000  | 0.278999000 | -1.303227000 |
| C | 2.157036000  | 0.280602000 | 2.419347000  |
| C | -1.634460000 | 0.284266000 | 2.797352000  |
| H | -4.052420000 | 0.637663000 | -1.204150000 |
| H | -0.106001000 | 0.652074000 | -4.221519000 |
| H | 3.984889000  | 0.641246000 | -1.406406000 |
| H | 2.569315000  | 0.645117000 | 3.354165000  |
| H | -2.395913000 | 0.650665000 | 3.477287000  |

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**NBO analysis for {R-*hub*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup>**

**Table S14.** Full set of NBO atomic charges for {R-*hub*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ). For comparison, charge distribution in unperturbed molecules of corannulene, C<sub>20</sub>H<sub>10</sub>, is also presented.

| Atom         | CH <sub>3</sub> <sup>+</sup> | CH <sub>2</sub> Cl <sup>+</sup> | CHCl <sub>2</sub> <sup>+</sup> | CCl <sub>3</sub> <sup>+</sup> | C <sub>20</sub> H <sub>10</sub> |
|--------------|------------------------------|---------------------------------|--------------------------------|-------------------------------|---------------------------------|
| <b>C(1)</b>  | <b>-0.530</b>                | <b>-0.312</b>                   | <b>-0.157</b>                  | <b>-0.060</b>                 | -                               |
| <b>C(2)</b>  | <b>-0.142</b>                | <b>-0.157</b>                   | <b>-0.167</b>                  | <b>-0.176</b>                 | <b>-0.015</b>                   |
| <b>C(3)</b>  | <b>+0.133</b>                | <b>+0.116</b>                   | <b>+0.109</b>                  | <b>+0.099</b>                 | <b>-0.043</b>                   |
| C(4)         | -0.226                       | -0.224                          | -0.224                         | -0.207                        | -0.181                          |
| C(5)         | -0.048                       | -0.050                          | -0.055                         | -0.040                        | -0.181                          |
| C(6)         | -0.084                       | -0.082                          | -0.086                         | -0.079                        | -0.043                          |
| C(7)         | -0.156                       | -0.155                          | -0.155                         | -0.154                        | -0.181                          |
| C(8)         | -0.163                       | -0.160                          | -0.160                         | -0.159                        | -0.181                          |
| C(9)         | -0.022                       | -0.023                          | -0.027                         | -0.029                        | -0.043                          |
| C(10)        | -0.138                       | -0.133                          | -0.132                         | -0.134                        | -0.181                          |
| C(11)        | -0.138                       | -0.134                          | -0.135                         | -0.133                        | -0.181                          |
| C(12)        | -0.022                       | -0.023                          | -0.024                         | -0.029                        | -0.043                          |
| C(13)        | -0.163                       | -0.160                          | -0.159                         | -0.159                        | -0.181                          |
| C(14)        | -0.156                       | -0.155                          | -0.154                         | -0.154                        | -0.181                          |
| C(15)        | -0.084                       | -0.082                          | -0.075                         | -0.079                        | -0.043                          |
| C(16)        | -0.048                       | -0.050                          | -0.034                         | -0.040                        | -0.181                          |
| C(17)        | -0.226                       | -0.224                          | -0.209                         | -0.207                        | -0.181                          |
| <b>C(18)</b> | <b>+0.109</b>                | <b>+0.104</b>                   | <b>+0.098</b>                  | <b>+0.091</b>                 | <b>-0.015</b>                   |
| C(19)        | -0.020                       | -0.006                          | -0.004                         | -0.001                        | -0.015                          |
| C(20)        | -0.020                       | -0.006                          | -0.003                         | -0.001                        | -0.015                          |
| <b>C(21)</b> | <b>+0.109</b>                | <b>+0.105</b>                   | <b>+0.095</b>                  | <b>+0.091</b>                 | <b>-0.015</b>                   |

Atoms surrounding the C(2) atom (atom of attachment) are highlighted by bold.

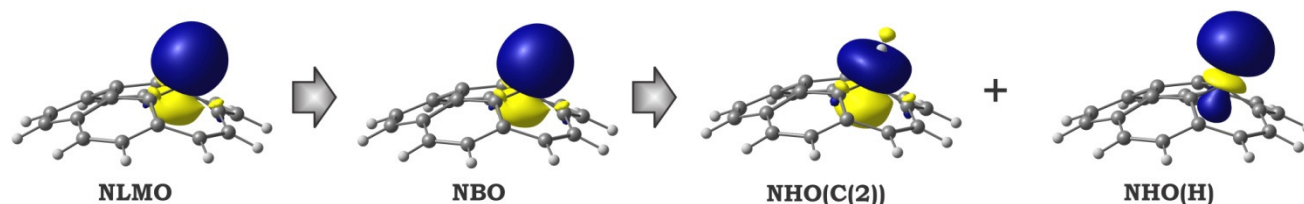
**Table S15.** The full set of Wiberg bond indexes (bond orders) for {R-*hub*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ). For comparison, the same set of indexes is presented for unperturbed corannulene, C<sub>20</sub>H<sub>10</sub>.

| Bond                | Order                        |                                 |                                |                               |                                 |
|---------------------|------------------------------|---------------------------------|--------------------------------|-------------------------------|---------------------------------|
|                     | CH <sub>3</sub> <sup>+</sup> | CH <sub>2</sub> Cl <sup>+</sup> | CHCl <sub>2</sub> <sup>+</sup> | CCl <sub>3</sub> <sup>+</sup> | C <sub>20</sub> H <sub>10</sub> |
| <b>C(1) – C(2)</b>  | <b>0.930</b>                 | <b>0.884</b>                    | <b>0.872</b>                   | <b>0.857</b>                  | -                               |
| <b>C(2) – C(3)</b>  | <b>0.990</b>                 | <b>0.981</b>                    | <b>0.980</b>                   | <b>0.979</b>                  | <b>1.340</b>                    |
| C(3) – C(4)         | 1.349                        | 1.353                           | 1.343                          | 1.363                         | 1.216                           |
| C(4) – C(5)         | 1.491                        | 1.484                           | 1.493                          | 1.469                         | 1.633                           |
| C(5) – C(6)         | 1.241                        | 1.245                           | 1.235                          | 1.242                         | 1.216                           |
| C(6) – C(7)         | 1.207                        | 1.206                           | 1.208                          | 1.209                         | 1.216                           |
| C(7) – C(8)         | 1.624                        | 1.625                           | 1.621                          | 1.617                         | 1.633                           |
| C(8) – C(9)         | 1.230                        | 1.229                           | 1.232                          | 1.235                         | 1.216                           |
| C(9) – C(10)        | 1.280                        | 1.285                           | 1.282                          | 1.283                         | 1.216                           |
| C(10) – C(11)       | 1.531                        | 1.520                           | 1.522                          | 1.519                         | 1.633                           |
| C(11) – C(12)       | 1.280                        | 1.285                           | 1.284                          | 1.283                         | 1.216                           |
| C(12) – C(13)       | 1.230                        | 1.229                           | 1.233                          | 1.235                         | 1.216                           |
| C(13) – C(14)       | 1.624                        | 1.625                           | 1.621                          | 1.617                         | 1.633                           |
| C(14) – C(15)       | 1.207                        | 1.205                           | 1.207                          | 1.209                         | 1.216                           |
| C(15) – C(16)       | 1.241                        | 1.245                           | 1.248                          | 1.242                         | 1.216                           |
| C(16) – C(17)       | 1.491                        | 1.483                           | 1.462                          | 1.469                         | 1.633                           |
| C(17) – C(3)        | 1.349                        | 1.354                           | 1.372                          | 1.363                         | 1.216                           |
| <b>C(2) – C(18)</b> | <b>0.984</b>                 | <b>0.983</b>                    | <b>0.973</b>                   | <b>0.972</b>                  | <b>1.185</b>                    |
| C(18) – C(19)       | 1.342                        | 1.351                           | 1.351                          | 1.362                         | 1.185                           |
| C(19) – C(20)       | 1.130                        | 1.124                           | 1.120                          | 1.113                         | 1.185                           |
| C(20) – C(21)       | 1.342                        | 1.351                           | 1.357                          | 1.362                         | 1.185                           |
| <b>C(21) – C(2)</b> | <b>0.984</b>                 | <b>0.983</b>                    | <b>0.983</b>                   | <b>1.972</b>                  | <b>1.185</b>                    |
| C(18) – C(6)        | 1.329                        | 1.325                           | 1.328                          | 1.322                         | 1.340                           |
| C(19) – C(9)        | 1.249                        | 1.244                           | 1.244                          | 1.239                         | 1.340                           |
| C(20) – C(12)       | 1.249                        | 1.244                           | 1.242                          | 1.239                         | 1.340                           |
| C(21) – C(15)       | 1.329                        | 1.325                           | 1.322                          | 1.322                         | 1.340                           |

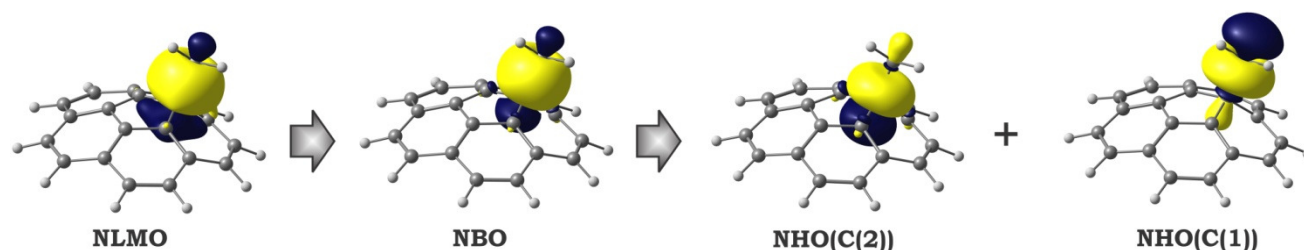
In terms of NBO analysis, molecular orbitals can be represented at different degree of localization, from fully delocalized canonical MOs to strongly localized natural atomic orbitals (NAOs). From chemical point of view three types localization have the highest interest. First of all, this is natural bond orbitals (NBOs), which correspond to Lewis structure of molecule under investigation. Increasing a degree of localization one can obtain natural hybrid orbitals (NHOs), which are the primer components of NBOs. Chemically they are very important because of showing what target NBO consists from in terms of molecular fragments. If one decrease the level of localization in comparison with NBOs, it is possible to obtain natural localized MOs (NLMOs). This type of orbitals a little less delocalized than canonical MOs. However, usually they have one-to-one correspondence to canonical MOs. At the same time, NLMOs usually have high correspondence towards NBOs as well (for systems, where Lewis structure, one or several, describes the electronic structure successfully). In most cases, NLMOs already show the electronic structure of molecule quite

clear. The next step of localization (from NKMOs to NBOs) is usually undertaken to get the picture of target bond in terms of molecular fragments (in terms of NHOs).

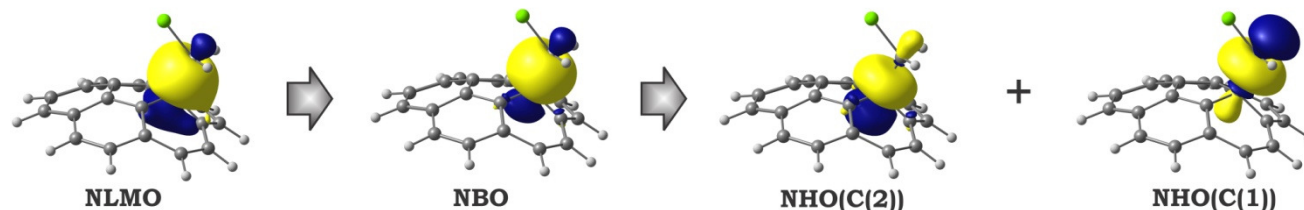
Here we present these three steps of localization of orbitals for systems considered. High relation between NLMOs and NBOs is supported by the fact that NBO describing the target bond corresponds to >90% of NLMO in all cases.



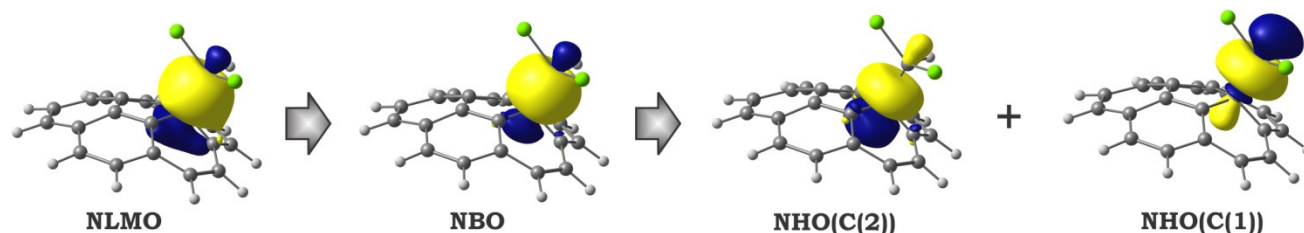
**Figure S1.** NLMO, NBO and two NHOs taking part in the formation of a given NBO corresponding to the C(2)–H bond in  $\{\text{H-hub-C}_{20}\text{H}_{10}\}^+$ .



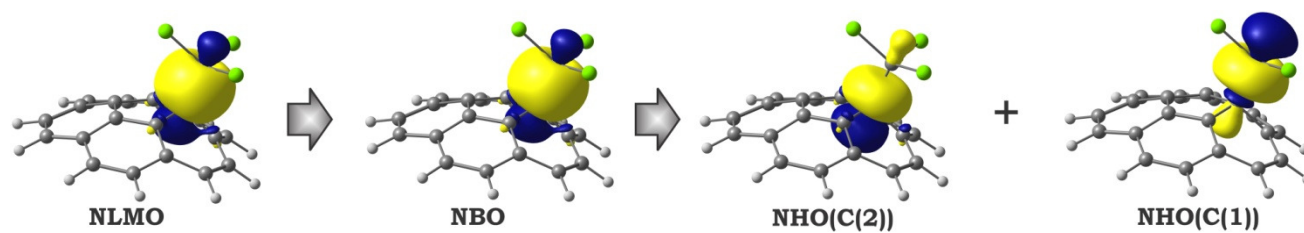
**Figure S2.** NLMO, NBO and two NHOs taking part in the formation of a given NBO corresponding to the C(1)–C(2) bond in  $\{\text{CH}_3\text{-hub-C}_{20}\text{H}_{10}\}^+$ .



**Figure S3.** NLMO, NBO and two NHOs taking part in the formation of a given NBO corresponding to the C(1)–C(2) bond in  $\{\text{CH}_2\text{Cl-hub-C}_{20}\text{H}_{10}\}^+$ .



**Figure S4.** NLMO, NBO and two NHOs taking part in the formation of a given NBO corresponding to the C(1)–C(2) bond in  $\{\text{CHCl}_2\text{-hub-C}_{20}\text{H}_{10}\}^+$ .



**Figure S5.** NLMO, NBO and two NHOs taking part in the formation of a given NBO corresponding to the C(1)–C(2) bond in  $\{\text{CCl}_3\text{-hub-C}_{20}\text{H}_{10}\}^+$ .

Properties of *rimi* and *spoke*-isomers of {R-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup>

**Table S16.** Absolute energies for {R-*rim*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> and {R-*spoke*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> at different levels of theory.

| Compound                         | PBE0/cc-pVTZ     | MP2/cc-pVTZ      | RIJCOSX-<br>PBE0/cc-pVTZ | RIJCOSX-<br>MP2/cc-pVTZ* |
|----------------------------------|------------------|------------------|--------------------------|--------------------------|
| H- <i>rim</i>                    | -767.8248099927  | -766.8349927129  | -767.825812121           | -766.834347870           |
| CH <sub>3</sub> - <i>rim</i>     | -807.1026827780  | -806.0609484537  | -807.103716245           | -806.060234255           |
| CH <sub>2</sub> Cl- <i>rim</i>   | -1266.5668993423 | -1265.1716445232 | -1266.567930473          | -1265.170044942          |
| CHCl <sub>2</sub> - <i>rim</i>   | -1726.0290875520 | -1724.2817545302 | -1726.030092328          | -1724.279746593          |
| CCl <sub>3</sub> - <i>rim</i>    | -2185.4865841596 | -2183.3887260234 | -2185.487555189          | -2183.386582214          |
| H- <i>spoke</i>                  | -767.8052554193  | -763.7362546507  | -767.806276412           | -766.814529616           |
| CH <sub>3</sub> - <i>spoke</i>   | -807.0814084993  | -802.7828048021  | -807.082544833           | -806.042326028           |
| CH <sub>2</sub> Cl- <i>spoke</i> | -1266.5432216300 | -1265.1538089591 | -1266.544372136          | -1265.151638946          |
| CHCl <sub>2</sub> - <i>spoke</i> | -1726.0015623180 | -1724.2617693868 | -1726.002567749          | -1724.261664751          |
| CCl <sub>3</sub> - <i>spoke</i>  | -2185.4576053248 | -2183.3686475683 | -2185.458601494          | -2183.367899662          |

\* Energy at the RIJCOSX-MP2/cc-pVTZ level of theory was obtained as result of single-point calculations for RIJCOSX-PBE0/cc-pVTZ optimized geometries.

**Table S17.** Cartesian coordinates for {H-*rim*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | -0.588500000 | -0.851140000 | -0.833050000 |
| C | -0.601030000 | -1.072349999 | 0.557410000  |
| C | -0.541650000 | 0.525690000  | -1.039790000 |
| C | -0.581500000 | 1.177749999  | 0.217580000  |
| C | -0.063580000 | -1.750899999 | -1.743229999 |
| C | -0.069850000 | -2.200279999 | 1.130649999  |
| C | -0.605760000 | 0.179370000  | 1.204669999  |
| C | 0.283980000  | -3.018219999 | -1.183409999 |
| H | 0.646970000  | -3.810319998 | -1.827129999 |
| C | -0.066160000 | 2.423779999  | 0.427120000  |
| C | 0.244060000  | 3.187609999  | -0.825120000 |
| H | 1.193599999  | 3.732739998  | -0.737160000 |
| C | 0.279580000  | 1.728719999  | 2.749489999  |
| H | 0.644250000  | 1.986099999  | 3.737579998  |
| C | 0.280620000  | -3.229149999 | 0.184590000  |
| H | 0.641220000  | -4.184339998 | 0.550440000  |
| C | 0.247820000  | -1.204279999 | -3.048069999 |
| H | 0.563120000  | -1.873289999 | -3.839929998 |
| C | -0.048700000 | 1.092060000  | -2.225759999 |
| C | 0.288970000  | 2.713369999  | 1.776649999  |
| H | 0.658520000  | 3.696489998  | 2.043559999  |
| C | -0.078510000 | 0.366670000  | 2.459869999  |
| C | 0.271330000  | -0.842780000 | 3.153849999  |
| H | 0.628760000  | -0.789920000 | 4.175489998  |
| C | 0.289070000  | 2.421299999  | -2.110489999 |
| H | 0.670010000  | 2.969879999  | -2.967369999 |
| C | 0.277670000  | -2.066869999 | 2.519219999  |
| H | 0.640030000  | -2.929529999 | 3.065859999  |
| C | 0.248710000  | 0.141550000  | -3.285909999 |
| H | 0.553310000  | 0.509270000  | -4.258079998 |
| H | -0.483720000 | 4.006669998  | -0.971130000 |

**Table S18.** Cartesian coordinates for {H-*spoke*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | -0.649380000 | -0.989470000 | -0.707530000 |
| C | -0.649520000 | -0.993520000 | 0.701940000  |
| C | -0.637840000 | 0.354170000  | -1.136559999 |
| C | -0.652910000 | 1.169909999  | 0.003380000  |
| C | -0.089370000 | -2.008289999 | -1.440809999 |
| C | -0.089570000 | -2.016549999 | 1.429349999  |
| C | -0.638370000 | 0.347650000  | 1.138779999  |
| C | 0.267860000  | -3.180369999 | -0.698610000 |
| H | 0.643440000  | -4.052259998 | -1.221039999 |
| C | -0.256210000 | 2.556959999  | 0.007360000  |
| C | 0.321450000  | 2.964139999  | -1.322869999 |
| H | 0.648940000  | 3.991709998  | -1.427029999 |
| C | 0.370820000  | 2.121169999  | 2.404189999  |
| H | 0.795270000  | 2.490229999  | 3.330749998  |
| C | 0.267820000  | -3.184239999 | 0.680270000  |
| H | 0.643130000  | -4.059189998 | 1.197829999  |
| C | 0.306820000  | -1.637309999 | -2.775509999 |
| H | 0.683910000  | -2.399209999 | -3.448699998 |
| C | -0.026630000 | 0.743230000  | -2.314189999 |
| C | 0.322750000  | 2.956049999  | 1.339449999  |
| H | 0.651480000  | 3.982729998  | 1.449039999  |
| C | -0.026860000 | 0.729730000  | 2.318429999  |
| C | 0.345690000  | -0.341280000 | 3.187819999  |
| H | 0.759000000  | -0.118340000 | 4.163969998  |
| C | 0.369450000  | 2.135489999  | -2.392519999 |
| H | 0.792880000  | 2.509979999  | -3.317429998 |
| C | 0.306820000  | -1.653449999 | 2.766269999  |
| H | 0.684020000  | -2.419399999 | 3.434769998  |
| C | 0.346810000  | -0.322670000 | -3.189259999 |
| H | 0.759970000  | -0.094580000 | -4.164259998 |
| H | -1.218619999 | 3.131389999  | 0.009820000  |

**Table S19.** Cartesian coordinates for {CH<sub>3</sub>-*rim*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 0.083330000  | -1.561129999 | -2.093319999 |
| C | -0.188170000 | -3.445529998 | -0.545680000 |
| H | -0.509480000 | -4.471679998 | -0.403450000 |
| C | 0.576720000  | -0.319470000 | 1.211699999  |
| C | -0.416650000 | 2.572579999  | -1.510109999 |
| H | -0.817760000 | 3.287309999  | -2.224409999 |
| C | -0.260920000 | -0.747940000 | -3.241279999 |
| H | -0.560010000 | -1.233379999 | -4.162689998 |
| C | -0.393710000 | 3.052859999  | -0.087210000 |
| H | -1.427069999 | 3.390239998  | 0.095370000  |
| C | -0.313580000 | 0.616190000  | -3.170359999 |
| H | -0.642460000 | 1.180329999  | -4.034559998 |
| C | 0.129990000  | -2.641799999 | 0.607300000  |
| C | -0.048080000 | 2.021489999  | 0.952740000  |
| C | -0.350630000 | 0.810890000  | 3.062959999  |
| H | -0.715760000 | 0.828510000  | 4.083619998  |
| C | 0.483640000  | 0.515810000  | -0.897540000 |
| C | 0.582480000  | -0.869340000 | -1.004560000 |
| C | -0.040530000 | 1.315089999  | -1.924439999 |
| C | -0.245530000 | -1.784829999 | 2.882259999  |
| H | -0.596500000 | -1.975359999 | 3.889729998  |

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | -0.210760000 | -2.934269999 | -1.831619999 |
| H | -0.548970000 | -3.575879998 | -2.636239999 |
| C | 0.613160000  | -1.394649999 | 0.301290000  |
| C | 0.053340000  | -0.438200000 | 2.476859999  |
| C | -0.401990000 | 1.986519999  | 2.333389999  |
| H | -0.804220000 | 2.870499999  | 2.814859999  |
| C | -0.210270000 | -2.835829999 | 1.990359999  |
| H | -0.535150000 | -3.812109998 | 2.330289999  |
| C | 0.509400000  | 0.873130000  | 0.472990000  |
| C | 0.476880000  | 4.333799998  | 0.021400000  |
| H | 0.151830000  | 5.082589998  | -0.700120000 |
| H | 0.379210000  | 4.753649998  | 1.021330000  |
| H | 1.524959999  | 4.097639998  | -0.158340000 |

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**Table S20.** Cartesian coordinates for {CH<sub>3</sub>-*spoke*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 0.170390000  | -2.188909999 | -1.433979999 |
| C | -0.091490000 | -3.384329998 | 0.689000000  |
| H | -0.395510000 | -4.284919998 | 1.209389999  |
| C | 0.530880000  | 0.212070000  | 1.137470000  |
| C | -0.640810000 | 1.899109999  | -2.381039999 |
| H | -1.116619999 | 2.231939999  | -3.296189999 |
| C | -0.258800000 | -1.853989999 | -2.767849999 |
| H | -0.573740000 | -2.645279999 | -3.439109998 |
| C | -0.631850000 | 2.730139999  | -1.314679999 |
| H | -1.044630000 | 3.727899998  | -1.416959999 |
| C | -0.409950000 | -0.547430000 | -3.181659999 |
| H | -0.848220000 | -0.355230000 | -4.153479998 |
| C | 0.170420000  | -2.189279999 | 1.433569999  |
| C | 0.035120000  | 2.406139999  | 0.000290000  |
| C | -0.640390000 | 1.898819999  | 2.381709999  |
| H | -1.115649999 | 2.231769999  | 3.297139999  |
| C | 0.531100000  | 0.212340000  | -1.137389999 |
| C | 0.648050000  | -1.125919999 | -0.705060000 |
| C | -0.121930000 | 0.545820000  | -2.309309999 |
| C | -0.410230000 | -0.548130000 | 3.181529999  |
| H | -0.848400000 | -0.356200000 | 4.153479998  |
| C | -0.091610000 | -3.384099998 | -0.689680000 |
| H | -0.395750000 | -4.284509998 | -1.210269999 |
| C | 0.647960000  | -1.126089999 | 0.704850000  |
| C | -0.122040000 | 0.545360000  | 2.309539999  |
| C | -0.630490000 | 2.730459999  | 1.315799999  |
| H | -1.043260000 | 3.728189998  | 1.418339999  |
| C | -0.258540000 | -1.854629999 | 2.767609999  |
| H | -0.573600000 | -2.646069999 | 3.438669998  |
| C | 0.485600000  | 1.032120000  | 0.000160000  |
| C | 1.345159999  | 3.323599998  | -0.000740000 |
| H | 1.033760000  | 4.366549998  | -0.001280000 |
| H | 1.932569999  | 3.116589999  | 0.891150000  |
| H | 1.931929999  | 3.115489999  | -0.892800000 |

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**Table S21.** Cartesian coordinates for {CH<sub>2</sub>Cl-*rim*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 0.132730000  | -1.921259999 | -2.162169999 |
| C  | 0.195830000  | -3.902409998 | -0.716300000 |
| H  | 0.046550000  | -4.973029998 | -0.627330000 |
| C  | 0.475140000  | -0.790310000 | 1.202029999  |
| C  | -1.014390000 | 2.040279999  | -1.357829999 |
| H  | -1.532969999 | 2.719739999  | -2.029719999 |
| C  | -0.357160000 | -1.116460000 | -3.262799998 |
| H  | -0.585870000 | -1.595839999 | -4.207249998 |
| C  | -1.048780000 | 2.439089999  | 0.095030000  |
| H  | -2.122519999 | 2.585889999  | 0.304460000  |
| C  | -0.629570000 | 0.214330000  | -3.118059999 |
| H  | -1.057230000 | 0.763070000  | -3.948149998 |
| C  | 0.400730000  | -3.119179999 | 0.476210000  |
| C  | -0.520530000 | 1.427079999  | 1.078620000  |
| C  | -0.588150000 | 0.075510000  | 3.120819999  |
| H  | -0.932980000 | -0.019520000 | 4.144299998  |
| C  | 0.211230000  | 0.126810000  | -0.858160000 |
| C  | 0.532050000  | -1.214859999 | -1.041400000 |
| C  | -0.453690000 | 0.882410000  | -1.837559999 |
| C  | -0.066510000 | -2.455069999 | 2.798509999  |
| H  | -0.362300000 | -2.752729999 | 3.797579998  |
| C  | 0.068170000  | -3.335019999 | -1.972719999 |
| H  | -0.177070000 | -3.980119998 | -2.807709999 |
| C  | 0.669890000  | -1.796129999 | 0.233940000  |
| C  | 0.002220000  | -1.058080000 | 2.464119999  |
| C  | -0.842330000 | 1.263819999  | 2.456589999  |
| H  | -1.374509999 | 2.042909999  | 2.990379999  |
| C  | 0.121110000  | -3.437859998 | 1.850129999  |
| H  | -0.034670000 | -4.470429998 | 2.139469999  |
| C  | 0.202530000  | 0.411300000  | 0.530400000  |
| C  | -0.452290000 | 3.852529998  | 0.276250000  |
| H  | -0.953580000 | 4.562849998  | -0.378020000 |
| H  | -0.573960000 | 4.171639998  | 1.308649999  |
| Cl | 1.278089999  | 3.893669998  | -0.106140000 |

**Table S22.** Cartesian coordinates for {CH<sub>2</sub>Cl-*spoke*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 0.234320000  | -2.128589999 | -1.900439999 |
| C | 0.392980000  | -3.837149998 | -0.151430000 |
| H | 0.307240000  | -4.879729998 | 0.130990000  |
| C | 0.393710000  | -0.411540000 | 1.184149999  |
| C | -1.392829999 | 1.820759999  | -1.721759999 |
| H | -2.006119999 | 2.262039999  | -2.498629999 |
| C | -0.371440000 | -1.567899999 | -3.082169999 |
| H | -0.598620000 | -2.216539999 | -3.921019998 |
| C | -1.432479999 | 2.352409999  | -0.481720000 |
| H | -2.026789999 | 3.241969999  | -0.303480000 |
| C | -0.796420000 | -0.256730000 | -3.135979999 |
| H | -1.351949999 | 0.076810000  | -4.003959998 |
| C | 0.504010000  | -2.833979999 | 0.864390000  |
| C | -0.596260000 | 1.854249999  | 0.670890000  |
| C | -0.958950000 | 0.644690000  | 2.862709999  |
| H | -1.411789999 | 0.635520000  | 3.847459998  |
| C | 0.181420000  | 0.148310000  | -1.009340000 |
| C | 0.579840000  | -1.204289999 | -0.944170000 |

|       |              |              |              |
|-------|--------------|--------------|--------------|
| C     | -0.629130000 | 0.623420000  | -2.025209999 |
| C     | -0.203770000 | -1.822929999 | 2.999769999  |
| H     | -0.580250000 | -1.966159999 | 4.005379998  |
| C     | 0.262830000  | -3.497769998 | -1.481439999 |
| H     | 0.079070000  | -4.284159998 | -2.203969999 |
| C     | 0.713210000  | -1.550999999 | 0.416170000  |
| C     | -0.199720000 | -0.515570000 | 2.427379999  |
| C     | -1.202519999 | 1.695229999  | 2.049419999  |
| H     | -1.794089999 | 2.526409999  | 2.417199999  |
| C     | 0.145990000  | -2.930729999 | 2.256409999  |
| H     | 0.043740000  | -3.909279998 | 2.712479999  |
| C     | 0.095830000  | 0.637080000  | 0.298530000  |
| C     | 0.503440000  | 2.988639999  | 0.946790000  |
| H     | -0.023360000 | 3.891909998  | 1.245189999  |
| H     | 1.148749999  | 2.648719999  | 1.752049999  |
| Cl    | 1.512789999  | 3.373989998  | -0.443740000 |
| ----- |              |              |              |

**Table S23.** Cartesian coordinates for {CHCl<sub>2</sub>-rim-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|       |              |              |              |
|-------|--------------|--------------|--------------|
| C     | 0.024210000  | -2.755879999 | -1.894199999 |
| C     | 0.070450000  | -4.460599998 | -0.131330000 |
| H     | -0.110880000 | -5.493549997 | 0.144880000  |
| C     | 0.522970000  | -1.078850000 | 1.212769999  |
| C     | -0.948720000 | 1.328379999  | -1.757399999 |
| H     | -1.467659999 | 1.901249999  | -2.521769999 |
| C     | -0.476390000 | -2.132849999 | -3.103569999 |
| H     | -0.753880000 | -2.757849999 | -3.943919998 |
| C     | -0.900200000 | 1.984179999  | -0.395500000 |
| H     | -1.945939999 | 2.254649999  | -0.181800000 |
| C     | -0.698830000 | -0.787990000 | -3.182319999 |
| H     | -1.137220000 | -0.372660000 | -4.081449998 |
| C     | 0.342270000  | -3.493489998 | 0.902170000  |
| C     | -0.385870000 | 1.131469999  | 0.740400000  |
| C     | -0.445030000 | 0.141320000  | 2.982039999  |
| H     | -0.763320000 | 0.234690000  | 4.014229998  |
| C     | 0.220960000  | -0.519390000 | -0.964570000 |
| C     | 0.486800000  | -1.884149999 | -0.923650000 |
| C     | -0.452500000 | 0.082830000  | -2.041779999 |
| C     | -0.021960000 | -2.424569999 | 3.086799999  |
| H     | -0.294050000 | -2.533929999 | 4.130079998  |
| C     | -0.081990000 | -4.112199998 | -1.463099999 |
| H     | -0.377430000 | -4.880629998 | -2.167089999 |
| C     | 0.648120000  | -2.243329999 | 0.428100000  |
| C     | 0.083890000  | -1.109259999 | 2.514679999  |
| C     | -0.675800000 | 1.211769999  | 2.133079999  |
| H     | -1.158149999 | 2.092519999  | 2.536149999  |
| C     | 0.099040000  | -3.561929998 | 2.317539999  |
| H     | -0.082070000 | -4.522849998 | 2.784339999  |
| C     | 0.272710000  | 0.001590000  | 0.352770000  |
| C     | -0.194590000 | 3.357219998  | -0.558290000 |
| H     | -0.636650000 | 3.899509998  | -1.389259999 |
| Cl    | -0.420550000 | 4.367379998  | 0.871680000  |
| Cl    | 1.519189999  | 3.146989999  | -0.938740000 |
| ----- |              |              |              |

**Table S24.** Cartesian coordinates for {CHCl<sub>2</sub>-*spoke*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 0.502840000  | -2.828219999 | -1.430899999 |
| C  | 0.590250000  | -4.049889998 | 0.688590000  |
| H  | 0.551010000  | -4.999079998 | 1.209999999  |
| C  | 0.183690000  | -0.420100000 | 1.136139999  |
| C  | -1.457899999 | 0.849510000  | -2.354159999 |
| H  | -2.038359999 | 1.013390000  | -3.254669999 |
| C  | -0.021500000 | -2.631939999 | -2.758819999 |
| H  | -0.107610000 | -3.481699998 | -3.427019998 |
| C  | -1.649219999 | 1.669159999  | -1.301729999 |
| H  | -2.332109999 | 2.506499999  | -1.395719999 |
| C  | -0.548290000 | -1.423669999 | -3.163799999 |
| H  | -1.044620000 | -1.365629999 | -4.124929998 |
| C  | 0.502900000  | -2.828989999 | 1.429819999  |
| C  | -0.881860000 | 1.566909999  | 0.000690000  |
| C  | -1.457339999 | 0.848540000  | 2.355409999  |
| H  | -2.037299999 | 1.012330000  | 3.256249999  |
| C  | 0.183740000  | -0.419430000 | -1.135969999 |
| C  | 0.671680000  | -1.672519999 | -0.705420000 |
| C  | -0.562410000 | -0.293220000 | -2.294469999 |
| C  | -0.548130000 | -1.425339999 | 3.163509999  |
| H  | -1.044160000 | -1.367869999 | 4.124819998  |
| C  | 0.590190000  | -4.049499998 | -0.690290000 |
| H  | 0.550960000  | -4.998409998 | -1.212199999 |
| C  | 0.671710000  | -1.672909999 | 0.704910000  |
| C  | -0.562270000 | -0.294430000 | 2.294829999  |
| C  | -1.648099999 | 1.669249999  | 1.303689999  |
| H  | -2.330709999 | 2.506749999  | 1.398289999  |
| C  | -0.021250000 | -2.633379999 | 2.757899999  |
| H  | -0.107290000 | -3.483489998 | 3.425659998  |
| C  | -0.072940000 | 0.359520000  | 0.000330000  |
| C  | 0.071690000  | 2.871709999  | 0.000210000  |
| H  | -0.586520000 | 3.735999998  | 0.000540000  |
| Cl | 1.075430000  | 2.973949999  | 1.442499999  |
| Cl | 1.074510000  | 2.974399999  | -1.442689999 |

**Table S25.** Cartesian coordinates for {CCl<sub>3</sub>-*rim*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 0.032100000  | -1.892449999 | -2.759509999 |
| C | 0.086050000  | -0.124570000 | -4.458159998 |
| H | -0.090070000 | 0.155290000  | -5.491149998 |
| C | 0.518680000  | 1.209379999  | -1.068930000 |
| C | -0.959810000 | -1.775209999 | 1.319649999  |
| H | -1.484989999 | -2.538779999 | 1.882979999  |
| C | -0.475760000 | -3.102039999 | -2.144779999 |
| H | -0.753110000 | -3.938899998 | -2.774509999 |
| C | -0.905910000 | -0.416120000 | 1.993019999  |
| H | -1.947499999 | -0.201510000 | 2.273649999  |
| C | -0.707600000 | -3.183019999 | -0.801640000 |
| H | -1.152519999 | -4.080719998 | -0.390310000 |
| C | 0.351080000  | 0.906320000  | -3.485689998 |
| C | -0.393340000 | 0.726800000  | 1.138319999  |
| C | -0.471640000 | 2.968469999  | 0.145670000  |
| H | -0.804500000 | 3.996119998  | 0.237460000  |
| C | 0.222420000  | -0.970730000 | -0.519650000 |
| C | 0.493490000  | -0.925020000 | -1.882219999 |

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | -0.459400000 | -2.046809999 | 0.073950000  |
| C  | -0.026770000 | 3.086059999  | -2.413359999 |
| H  | -0.302120000 | 4.128679998  | -2.520479999 |
| C  | -0.067630000 | -1.457199999 | -4.114989998 |
| H  | -0.359630000 | -2.159119999 | -4.886689998 |
| C  | 0.652940000  | 0.428950000  | -2.235979999 |
| C  | 0.072880000  | 2.509419999  | -1.099469999 |
| C  | -0.701580000 | 2.115329999  | 1.213319999  |
| H  | -1.198769999 | 2.514559999  | 2.087149999  |
| C  | 0.103670000  | 2.321109999  | -3.552039998 |
| H  | -0.073560000 | 2.789739999  | -4.512889998 |
| C  | 0.269160000  | 0.345370000  | 0.008590000  |
| C  | -0.174010000 | -0.554750000 | 3.369659998  |
| Cl | -0.968250000 | -1.807799999 | 4.346939998  |
| Cl | -0.255610000 | 0.966000000  | 4.263439998  |
| Cl | 1.518349999  | -0.996240000 | 3.104759999  |

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**Table S26.** Cartesian coordinates for {CCl<sub>3</sub>-spoke-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 0.395090000  | -1.429689999 | -3.240189999 |
| C  | 0.416140000  | 0.689350000  | -4.464179998 |
| H  | 0.324800000  | 1.211179999  | -5.409559998 |
| C  | 0.204790000  | 1.135200000  | -0.816880000 |
| C  | -1.372619999 | -2.350899999 | 0.531610000  |
| H  | -1.951529999 | -3.247699999 | 0.719920000  |
| C  | -0.117900000 | -2.757899999 | -3.017759999 |
| H  | -0.248020000 | -3.425949998 | -3.862019998 |
| C  | -1.516809999 | -1.303549999 | 1.365699999  |
| H  | -2.154359999 | -1.396389999 | 2.235759999  |
| C  | -0.581290000 | -3.162189999 | -1.783419999 |
| H  | -1.075750000 | -4.122299998 | -1.699089999 |
| C  | 0.395090000  | 1.429379999  | -3.240439999 |
| C  | -0.748830000 | 0.000270000  | 1.236339999  |
| C  | -1.372279999 | 2.351459999  | 0.531360000  |
| H  | -1.950939999 | 3.248419999  | 0.719660000  |
| C  | 0.204720000  | -1.135069999 | -0.816700000 |
| C  | 0.624880000  | -0.704900000 | -2.094419999 |
| C  | -0.535470000 | -2.293029999 | -0.654850000 |
| C  | -0.581170000 | 3.162179999  | -1.783919999 |
| H  | -1.075570000 | 4.122349998  | -1.699729999 |
| C  | 0.416170000  | -0.689880000 | -4.464069998 |
| H  | 0.324890000  | -1.211879999 | -5.409349998 |
| C  | 0.624850000  | 0.704770000  | -2.094539999 |
| C  | -0.535300000 | 2.293249999  | -0.655190000 |
| C  | -1.516299999 | 1.304359999  | 1.365779999  |
| H  | -2.153779999 | 1.397399999  | 2.235879999  |
| C  | -0.117910000 | 2.757619999  | -3.018219999 |
| H  | -0.248150000 | 3.425489998  | -3.862609998 |
| C  | -0.005210000 | 0.000140000  | -0.021100000 |
| C  | 0.317920000  | -0.000010000 | 2.471549999  |
| Cl | -0.572480000 | 0.000290000  | 4.001369998  |
| Cl | 1.346749999  | 1.431189999  | 2.405049999  |
| Cl | 1.345929999  | -1.431799999 | 2.405149999  |

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**Table S27.** Cartesian coordinates for {H-*rim*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (RIJCOSX-PBE0/cc-pVTZ).

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 0.097212000  | -2.201979000 | -1.458988000 |
| C | -0.169194000 | -3.378746000 | 0.707398000  |
| H | -0.468894000 | -4.280994000 | 1.226682000  |
| C | 0.422088000  | 0.194640000  | 1.094548000  |
| C | -0.521719000 | 1.895371000  | -2.470307000 |
| H | -0.912899000 | 2.273940000  | -3.407952000 |
| C | -0.278320000 | -1.885548000 | -2.810125000 |
| H | -0.594006000 | -2.678474000 | -3.477819000 |
| C | -0.579869000 | 2.721451000  | -1.360573000 |
| H | -1.011695000 | 3.708235000  | -1.476208000 |
| C | -0.359161000 | -0.582403000 | -3.254422000 |
| H | -0.735419000 | -0.400644000 | -4.254329000 |
| C | 0.100783000  | -2.188669000 | 1.449828000  |
| C | -0.190770000 | 2.256426000  | -0.070207000 |
| C | -0.511232000 | 1.851649000  | 2.441331000  |
| H | -0.913234000 | 2.239963000  | 3.372980000  |
| C | 0.478211000  | 0.192230000  | -1.177414000 |
| C | 0.561562000  | -1.139494000 | -0.724934000 |
| C | -0.076313000 | 0.530409000  | -2.388983000 |
| C | -0.313666000 | -0.572326000 | 3.260034000  |
| H | -0.631867000 | -0.375128000 | 4.276489000  |
| C | -0.170527000 | -3.382274000 | -0.676880000 |
| H | -0.470397000 | -4.294590000 | -1.180836000 |
| C | 0.553592000  | -1.129904000 | 0.683216000  |
| C | -0.089876000 | 0.544034000  | 2.354355000  |
| C | -0.532435000 | 2.802745000  | 1.284162000  |
| H | -1.516875000 | 3.290380000  | 1.282459000  |
| C | -0.229787000 | -1.864705000 | 2.822522000  |
| H | -0.494240000 | -2.663169000 | 3.505559000  |
| C | 0.404264000  | 1.028359000  | -0.051407000 |
| H | 0.140495000  | 3.639275000  | 1.547842000  |

**Table S28.** Cartesian coordinates for {H-*spoke*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (RIJCOSX-PBE0/cc-pVTZ).

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 0.155194000  | -2.206610000 | -1.433860000 |
| C | -0.117679000 | -3.402413000 | 0.689008000  |
| H | -0.427080000 | -4.302210000 | 1.207447000  |
| C | 0.529109000  | 0.187165000  | 1.143547000  |
| C | -0.595981000 | 1.894632000  | -2.393422000 |
| H | -1.042806000 | 2.237555000  | -3.319673000 |
| C | -0.266254000 | -1.866463000 | -2.769331000 |
| H | -0.588565000 | -2.654188000 | -3.441238000 |
| C | -0.607622000 | 2.726488000  | -1.324900000 |
| H | -1.006533000 | 3.727928000  | -1.432007000 |
| C | -0.400386000 | -0.558484000 | -3.185423000 |
| H | -0.829332000 | -0.362288000 | -4.160569000 |
| C | 0.150936000  | -2.210259000 | 1.436779000  |
| C | -0.005521000 | 2.362058000  | 0.007196000  |
| C | -0.602951000 | 1.888395000  | 2.404881000  |
| H | -1.052504000 | 2.228895000  | 3.330709000  |
| C | 0.532444000  | 0.190100000  | -1.133324000 |
| C | 0.639089000  | -1.148619000 | -0.701518000 |
| C | -0.103816000 | 0.533313000  | -2.312273000 |
| C | -0.409625000 | -0.566727000 | 3.191057000  |
| H | -0.841289000 | -0.372999000 | 4.165498000  |

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | -0.115604000 | -3.400687000 | -0.689893000 |
| H | -0.423442000 | -4.299185000 | -1.211491000 |
| C | 0.637015000  | -1.150428000 | 0.708568000  |
| C | -0.110574000 | 0.527284000  | 2.321533000  |
| C | -0.611509000 | 2.723022000  | 1.338471000  |
| H | -1.010793000 | 3.724168000  | 1.446995000  |
| C | -0.274342000 | -1.873611000 | 2.771935000  |
| H | -0.598555000 | -2.663073000 | 3.440885000  |
| C | 0.487478000  | 1.006262000  | 0.006106000  |
| H | 0.916712000  | 2.999387000  | 0.009369000  |

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**Table S29.** Cartesian coordinates for {CH<sub>3</sub>-*rim*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (RIJCOSX-PBE0/cc-pVTZ).

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 0.101023000  | -2.193204000 | -1.455615000 |
| C | -0.165484000 | -3.369926000 | 0.711156000  |
| H | -0.464059000 | -4.272542000 | 1.230468000  |
| C | 0.418926000  | 0.204471000  | 1.097437000  |
| C | -0.528333000 | 1.902022000  | -2.466235000 |
| H | -0.920804000 | 2.279885000  | -3.403674000 |
| C | -0.273744000 | -1.878052000 | -2.807278000 |
| H | -0.586410000 | -2.671945000 | -3.475237000 |
| C | -0.588098000 | 2.727216000  | -1.355493000 |
| H | -1.024710000 | 3.711881000  | -1.473095000 |
| C | -0.357603000 | -0.575146000 | -3.251361000 |
| H | -0.733278000 | -0.394445000 | -4.251707000 |
| C | 0.100980000  | -2.178737000 | 1.453739000  |
| C | -0.197739000 | 2.265597000  | -0.063736000 |
| C | -0.512299000 | 1.863894000  | 2.437679000  |
| H | -0.910104000 | 2.254846000  | 3.370833000  |
| C | 0.475361000  | 0.202696000  | -1.173433000 |
| C | 0.561773000  | -1.129434000 | -0.721265000 |
| C | -0.078614000 | 0.538793000  | -2.385674000 |
| C | -0.320655000 | -0.561372000 | 3.261432000  |
| H | -0.642328000 | -0.363636000 | 4.276723000  |
| C | -0.164747000 | -3.374002000 | -0.672963000 |
| H | -0.462053000 | -4.287096000 | -1.177053000 |
| C | 0.553258000  | -1.119967000 | 0.686995000  |
| C | -0.095885000 | 0.554566000  | 2.355223000  |
| C | -0.541160000 | 2.832554000  | 1.288538000  |
| H | -1.588109000 | 3.176517000  | 1.256009000  |
| C | -0.233588000 | -1.854225000 | 2.825417000  |
| H | -0.499269000 | -2.652718000 | 3.507933000  |
| C | 0.399512000  | 1.039537000  | -0.047440000 |
| C | 0.291861000  | 4.095135000  | 1.637747000  |
| H | -0.021646000 | 4.509723000  | 2.595001000  |
| H | 1.352492000  | 3.851101000  | 1.686185000  |
| H | 0.141000000  | 4.851587000  | 0.868958000  |

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**Table S30.** Cartesian coordinates for {CH<sub>3</sub>-*spoke*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (RIJCOSX-PBE0/cc-pVTZ).

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 0.158010000  | -2.211028000 | -1.431883000 |
| C | -0.116297000 | -3.407217000 | 0.688772000  |
| H | -0.427219000 | -4.305862000 | 1.208352000  |

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 0.543483000  | 0.183368000  | 1.143098000  |
| C | -0.604281000 | 1.889329000  | -2.375663000 |
| H | -1.074102000 | 2.228683000  | -3.291707000 |
| C | -0.271508000 | -1.869460000 | -2.764247000 |
| H | -0.599295000 | -2.656284000 | -3.434678000 |
| C | -0.584581000 | 2.719596000  | -1.308887000 |
| H | -0.983769000 | 3.722711000  | -1.409383000 |
| C | -0.409466000 | -0.560604000 | -3.176135000 |
| H | -0.849571000 | -0.362130000 | -4.145882000 |
| C | 0.153886000  | -2.214630000 | 1.434768000  |
| C | 0.076545000  | 2.384905000  | 0.007256000  |
| C | -0.611289000 | 1.883120000  | 2.386902000  |
| H | -1.083864000 | 2.220068000  | 3.302418000  |
| C | 0.546769000  | 0.186263000  | -1.132981000 |
| C | 0.647800000  | -1.154168000 | -0.701826000 |
| C | -0.103708000 | 0.528647000  | -2.304258000 |
| C | -0.418453000 | -0.568756000 | 3.181705000  |
| H | -0.861167000 | -0.372697000 | 4.150755000  |
| C | -0.114290000 | -3.405514000 | -0.689637000 |
| H | -0.423700000 | -4.302878000 | -1.212312000 |
| C | 0.645778000  | -1.155954000 | 0.708790000  |
| C | -0.110361000 | 0.522684000  | 2.313383000  |
| C | -0.588622000 | 2.716091000  | 1.322269000  |
| H | -0.988285000 | 3.718888000  | 1.424114000  |
| C | -0.279333000 | -1.876535000 | 2.766838000  |
| H | -0.608905000 | -2.665083000 | 3.434364000  |
| C | 0.510172000  | 1.005372000  | 0.006053000  |
| C | 1.396568000  | 3.287235000  | 0.010656000  |
| H | 1.097807000  | 4.334150000  | 0.011532000  |
| H | 1.980656000  | 3.072751000  | 0.903725000  |
| H | 1.983677000  | 3.075108000  | -0.881002000 |

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**Table S31.** Cartesian coordinates for {CH<sub>2</sub>Cl-*rim*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (RIJCOSX-PBE0/cc-pVTZ).

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 0.133254000  | -1.922683000 | -2.162356000 |
| C | 0.189536000  | -3.903594000 | -0.716097000 |
| H | 0.036238000  | -4.973806000 | -0.625658000 |
| C | 0.479714000  | -0.791235000 | 1.202279000  |
| C | -1.008114000 | 2.041045000  | -1.359239000 |
| H | -1.522921000 | 2.722982000  | -2.032008000 |
| C | -0.353876000 | -1.116706000 | -3.264000000 |
| H | -0.582500000 | -1.596111000 | -4.208403000 |
| C | -1.047823000 | 2.437369000  | 0.095207000  |
| H | -2.123273000 | 2.574898000  | 0.303313000  |
| C | -0.623712000 | 0.214784000  | -3.119948000 |
| H | -1.048560000 | 0.765023000  | -3.950415000 |
| C | 0.398126000  | -3.120643000 | 0.476088000  |
| C | -0.514535000 | 1.426770000  | 1.078689000  |
| C | -0.583076000 | 0.076225000  | 3.122032000  |
| H | -0.926754000 | -0.018732000 | 4.145855000  |
| C | 0.215610000  | 0.125706000  | -0.858885000 |
| C | 0.534655000  | -1.216934000 | -1.041871000 |
| C | -0.448556000 | 0.882042000  | -1.838519000 |
| C | -0.066490000 | -2.455213000 | 2.799555000  |
| H | -0.363083000 | -2.751770000 | 3.798603000  |
| C | 0.063387000  | -3.336211000 | -1.972882000 |
| H | -0.185393000 | -3.980337000 | -2.807666000 |
| C | 0.671966000  | -1.798320000 | 0.233778000  |

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 0.006073000  | -1.057904000 | 2.464799000  |
| C  | -0.836194000 | 1.264423000  | 2.457143000  |
| H  | -1.367018000 | 2.045136000  | 2.990581000  |
| C  | 0.117224000  | -3.438715000 | 1.850598000  |
| H  | -0.042361000 | -4.470752000 | 2.139474000  |
| C  | 0.207824000  | 0.410659000  | 0.530084000  |
| C  | -0.463921000 | 3.854891000  | 0.278470000  |
| H  | -0.973065000 | 4.563712000  | -0.371997000 |
| H  | -0.582003000 | 4.170780000  | 1.312049000  |
| Cl | 1.264831000  | 3.907840000  | -0.112487000 |

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**Table S32.** Cartesian coordinates for {CH<sub>2</sub>Cl-*spoke*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (RIJCOSX-PBE0/cc-pVTZ).

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 0.232910000  | -2.129781000 | -1.901107000 |
| C  | 0.399643000  | -3.837664000 | -0.150947000 |
| H  | 0.316358000  | -4.880418000 | 0.131862000  |
| C  | 0.396759000  | -0.410585000 | 1.182703000  |
| C  | -1.388776000 | 1.823723000  | -1.723640000 |
| H  | -1.999741000 | 2.266725000  | -2.501588000 |
| C  | -0.380878000 | -1.570538000 | -3.079396000 |
| H  | -0.614931000 | -2.220932000 | -3.915216000 |
| C  | -1.425863000 | 2.357055000  | -0.484464000 |
| H  | -2.016041000 | 3.249721000  | -0.306711000 |
| C  | -0.805203000 | -0.259043000 | -3.133028000 |
| H  | -1.366757000 | 0.072571000  | -3.998029000 |
| C  | 0.508955000  | -2.833519000 | 0.864524000  |
| C  | -0.593632000 | 1.855125000  | 0.669510000  |
| C  | -0.964193000 | 0.643090000  | 2.857971000  |
| H  | -1.421845000 | 0.631493000  | 3.840255000  |
| C  | 0.183774000  | 0.148439000  | -1.011672000 |
| C  | 0.581360000  | -1.204529000 | -0.946268000 |
| C  | -0.629929000 | 0.623173000  | -2.025552000 |
| C  | -0.204127000 | -1.821737000 | 2.997769000  |
| H  | -0.581963000 | -1.964517000 | 4.002800000  |
| C  | 0.265750000  | -3.499161000 | -1.481357000 |
| H  | 0.080631000  | -4.286271000 | -2.202620000 |
| C  | 0.717073000  | -1.550567000 | 0.414880000  |
| C  | -0.200173000 | -0.514804000 | 2.424347000  |
| C  | -1.207437000 | 1.693202000  | 2.044498000  |
| H  | -1.802657000 | 2.523072000  | 2.409992000  |
| C  | 0.148757000  | -2.929585000 | 2.255991000  |
| H  | 0.047762000  | -3.908093000 | 2.712431000  |
| C  | 0.098856000  | 0.637614000  | 0.296407000  |
| C  | 0.504552000  | 2.989161000  | 0.953511000  |
| H  | -0.022027000 | 3.893352000  | 1.250401000  |
| H  | 1.145404000  | 2.649489000  | 1.762738000  |
| Cl | 1.520306000  | 3.372849000  | -0.432097000 |

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**Table S33.** Cartesian coordinates for {CHCl<sub>2</sub>-*rim*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (RIJCOSX-PBE0/cc-pVTZ).

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 0.022204000  | -2.757021000 | -1.895084000 |
| C | 0.062603000  | -4.461629000 | -0.130101000 |
| H | -0.123146000 | -5.493755000 | 0.146724000  |



|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 0.527364000  | -1.080250000 | 1.212191000  |
| C  | -0.942176000 | 1.328130000  | -1.759865000 |
| H  | -1.458557000 | 1.900942000  | -2.526128000 |
| C  | -0.475193000 | -2.132743000 | -3.105427000 |
| H  | -0.753303000 | -2.756863000 | -3.946262000 |
| C  | -0.899834000 | 1.981584000  | -0.396300000 |
| H  | -1.947947000 | 2.242648000  | -0.183157000 |
| C  | -0.692828000 | -0.787029000 | -3.184664000 |
| H  | -1.127965000 | -0.369889000 | -4.084555000 |
| C  | 0.339158000  | -3.494809000 | 0.903235000  |
| C  | -0.380525000 | 1.130832000  | 0.739646000  |
| C  | -0.437229000 | 0.142289000  | 2.982146000  |
| H  | -0.754436000 | 0.236211000  | 4.014401000  |
| C  | 0.224723000  | -0.520982000 | -0.965421000 |
| C  | 0.487530000  | -1.886232000 | -0.924580000 |
| C  | -0.446540000 | 0.082287000  | -2.043354000 |
| C  | -0.018958000 | -2.423722000 | 3.087616000  |
| H  | -0.289373000 | -2.531542000 | 4.131350000  |
| C  | -0.089138000 | -4.113157000 | -1.462696000 |
| H  | -0.388770000 | -4.880351000 | -2.166170000 |
| C  | 0.648716000  | -2.245470000 | 0.427931000  |
| C  | 0.089529000  | -1.109268000 | 2.514386000  |
| C  | -0.668430000 | 1.212487000  | 2.132948000  |
| H  | -1.150904000 | 2.093510000  | 2.535429000  |
| C  | 0.097104000  | -3.561977000 | 2.318746000  |
| H  | -0.086126000 | -4.522464000 | 2.785823000  |
| C  | 0.277490000  | 0.000479000  | 0.351837000  |
| C  | -0.204624000 | 3.359553000  | -0.556205000 |
| H  | -0.643655000 | 3.898510000  | -1.391175000 |
| Cl | -0.449527000 | 4.369576000  | 0.869925000  |
| Cl | 1.513691000  | 3.159900000  | -0.921222000 |

**Table S34.** Cartesian coordinates for {CHCl<sub>2</sub>-*spoke*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (RIJCOSX-PBE0/cc-pVTZ).

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 0.499936000  | -2.829747000 | -1.431080000 |
| C | 0.581802000  | -4.051130000 | 0.688476000  |
| H | 0.539888000  | -5.000109000 | 1.209936000  |
| C | 0.184279000  | -0.420164000 | 1.136628000  |
| C | -1.455220000 | 0.850463000  | -2.358133000 |
| H | -2.031537000 | 1.016924000  | -3.260774000 |
| C | -0.017698000 | -2.631816000 | -2.761532000 |
| H | -0.101600000 | -3.480838000 | -3.431228000 |
| C | -1.652386000 | 1.667656000  | -1.303983000 |
| H | -2.335422000 | 2.504601000  | -1.399869000 |
| C | -0.540659000 | -1.422051000 | -3.168409000 |
| H | -1.031311000 | -1.361922000 | -4.131970000 |
| C | 0.500312000  | -2.830398000 | 1.429977000  |
| C | -0.886940000 | 1.564949000  | 0.000603000  |
| C | -1.454723000 | 0.849300000  | 2.359105000  |
| H | -2.030879000 | 1.015367000  | 3.261920000  |
| C | 0.184035000  | -0.419627000 | -1.136557000 |
| C | 0.669898000  | -1.674189000 | -0.705493000 |
| C | -0.558529000 | -0.292287000 | -2.297631000 |
| C | -0.539891000 | -1.423563000 | 3.168225000  |
| H | -1.030307000 | -1.363871000 | 4.131934000  |
| C | 0.581609000  | -4.050817000 | -0.690153000 |
| H | 0.539545000  | -4.999568000 | -1.212014000 |
| C | 0.670055000  | -1.674518000 | 0.704836000  |

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | -0.557998000 | -0.293385000 | 2.297973000  |
| C  | -1.652004000 | 1.667116000  | 1.305450000  |
| H  | -2.334999000 | 2.504031000  | 1.401883000  |
| C  | -0.016967000 | -2.633118000 | 2.760677000  |
| H  | -0.100654000 | -3.482437000 | 3.430018000  |
| C  | -0.074040000 | 0.359192000  | 0.000250000  |
| C  | 0.066081000  | 2.870954000  | 0.000583000  |
| H  | -0.591382000 | 3.735541000  | 0.000525000  |
| Cl | 1.069211000  | 2.973924000  | 1.443432000  |
| Cl | 1.069203000  | 2.973736000  | -1.442301000 |

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**Table S35.** Cartesian coordinates for {CCl<sub>3</sub>-*rim*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (RIJCOSX-PBE0/cc-pVTZ).

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 0.032253000  | -1.893275000 | -2.759178000 |
| C  | 0.083811000  | -0.124120000 | -4.458294000 |
| H  | -0.094346000 | 0.155906000  | -5.490928000 |
| C  | 0.521684000  | 1.209404000  | -1.068938000 |
| C  | -0.960018000 | -1.775377000 | 1.318852000  |
| H  | -1.486121000 | -2.539298000 | 1.881049000  |
| C  | -0.475261000 | -3.103199000 | -2.143894000 |
| H  | -0.752582000 | -3.940379000 | -2.773279000 |
| C  | -0.906919000 | -0.415401000 | 1.991709000  |
| H  | -1.948676000 | -0.200027000 | 2.270614000  |
| C  | -0.706078000 | -3.183780000 | -0.800510000 |
| H  | -1.150724000 | -4.081180000 | -0.388005000 |
| C  | 0.350724000  | 0.907007000  | -3.485699000 |
| C  | -0.391519000 | 0.726956000  | 1.137836000  |
| C  | -0.469896000 | 2.968612000  | 0.146125000  |
| H  | -0.804039000 | 3.995759000  | 0.237057000  |
| C  | 0.224783000  | -0.971073000 | -0.519419000 |
| C  | 0.494784000  | -0.925705000 | -1.882183000 |
| C  | -0.457708000 | -2.046880000 | 0.074098000  |
| C  | -0.025717000 | 3.086293000  | -2.412364000 |
| H  | -0.301074000 | 4.128916000  | -2.518473000 |
| C  | -0.069343000 | -1.457435000 | -4.114996000 |
| H  | -0.363386000 | -2.159123000 | -4.886014000 |
| C  | 0.654555000  | 0.429037000  | -2.236304000 |
| C  | 0.075403000  | 2.509103000  | -1.098920000 |
| C  | -0.700181000 | 2.115454000  | 1.213741000  |
| H  | -1.198988000 | 2.512850000  | 2.087577000  |
| C  | 0.103072000  | 2.321657000  | -3.551498000 |
| H  | -0.075012000 | 2.790073000  | -4.512312000 |
| C  | 0.271793000  | 0.345226000  | 0.008736000  |
| C  | -0.176213000 | -0.553911000 | 3.368497000  |
| Cl | -0.967867000 | -1.809762000 | 4.343811000  |
| Cl | -0.261474000 | 0.965520000  | 4.263611000  |
| Cl | 1.517019000  | -0.991236000 | 3.104007000  |

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**Table S36.** Cartesian coordinates for {CCl<sub>3</sub>-*spoke*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (RIJCOSX-PBE0/cc-pVTZ).

|   |             |              |              |
|---|-------------|--------------|--------------|
| C | 0.392985000 | -1.430264000 | -3.240936000 |
| C | 0.414654000 | 0.689305000  | -4.464421000 |
| H | 0.326489000 | 1.211067000  | -5.410034000 |

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 0.200189000  | 1.135495000  | -0.817133000 |
| C  | -1.373343000 | -2.354693000 | 0.533390000  |
| H  | -1.947278000 | -3.253966000 | 0.725112000  |
| C  | -0.115373000 | -2.760621000 | -3.017822000 |
| H  | -0.242187000 | -3.430267000 | -3.861534000 |
| C  | -1.520339000 | -1.306650000 | 1.367536000  |
| H  | -2.155423000 | -1.402327000 | 2.238820000  |
| C  | -0.578160000 | -3.166104000 | -1.783089000 |
| H  | -1.068284000 | -4.128118000 | -1.698037000 |
| C  | 0.393146000  | 1.429953000  | -3.241119000 |
| C  | -0.754839000 | 0.000196000  | 1.235891000  |
| C  | -1.373082000 | 2.355063000  | 0.533088000  |
| H  | -1.946915000 | 3.254424000  | 0.724697000  |
| C  | 0.200064000  | -1.135476000 | -0.816987000 |
| C  | 0.620061000  | -0.704936000 | -2.095086000 |
| C  | -0.536634000 | -2.295807000 | -0.654518000 |
| C  | -0.577807000 | 3.166088000  | -1.783494000 |
| H  | -1.067823000 | 4.128167000  | -1.698565000 |
| C  | 0.414576000  | -0.689775000 | -4.464333000 |
| H  | 0.326351000  | -1.211648000 | -5.409879000 |
| C  | 0.620139000  | 0.704745000  | -2.095176000 |
| C  | -0.536380000 | 2.295930000  | -0.654813000 |
| C  | -1.520186000 | 1.307147000  | 1.367374000  |
| H  | -2.155255000 | 1.403008000  | 2.238650000  |
| C  | -0.115062000 | 2.760395000  | -3.018174000 |
| H  | -0.241800000 | 3.429948000  | -3.861972000 |
| C  | -0.011026000 | 0.000073000  | -0.021679000 |
| C  | 0.316642000  | 0.000202000  | 2.467303000  |
| Cl | -0.567832000 | 0.000522000  | 4.000539000  |
| Cl | 1.345250000  | 1.431499000  | 2.396469000  |
| Cl | 1.344835000  | -1.431409000 | 2.396824000  |

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**NBO analysis for {R-rim-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> and {R-spoke-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> isomers**

**Table S37.** The full set of NBO atomic charges for {R-rim-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

| Atom        | CH <sub>3</sub> <sup>+</sup> | CH <sub>2</sub> Cl <sup>+</sup> | CHCl <sub>2</sub> <sup>+</sup> | CCl <sub>3</sub> <sup>+</sup> | C <sub>20</sub> H <sub>10</sub> |
|-------------|------------------------------|---------------------------------|--------------------------------|-------------------------------|---------------------------------|
| <b>C(1)</b> | <b>-0.560</b>                | <b>-0.328</b>                   | <b>-0.166</b>                  | <b>-0.060</b>                 | -                               |
| C(2)        | +0.153                       | +0.163                          | +0.165                         | +0.168                        | -0.015                          |
| C(3)        | -0.131                       | -0.125                          | -0.121                         | -0.125                        | -0.043                          |
| <b>C(4)</b> | <b>+0.107</b>                | <b>+0.101</b>                   | <b>+0.090</b>                  | <b>+0.094</b>                 | <b>-0.181</b>                   |
| <b>C(5)</b> | <b>-0.305</b>                | <b>-0.325</b>                   | <b>-0.342</b>                  | <b>-0.370</b>                 | <b>-0.181</b>                   |
| <b>C(6)</b> | <b>+0.093</b>                | <b>+0.086</b>                   | <b>+0.081</b>                  | <b>+0.077</b>                 | <b>-0.043</b>                   |
| C(7)        | -0.215                       | -0.215                          | -0.206                         | -0.205                        | -0.181                          |
| C(8)        | -0.106                       | -0.104                          | -0.104                         | -0.104                        | -0.181                          |
| C(9)        | -0.033                       | -0.032                          | -0.030                         | -0.030                        | -0.043                          |
| C(10)       | -0.158                       | -0.157                          | -0.156                         | -0.156                        | -0.181                          |
| C(11)       | -0.161                       | -0.161                          | -0.160                         | -0.160                        | -0.181                          |
| C(12)       | -0.040                       | -0.041                          | -0.042                         | -0.042                        | -0.043                          |
| C(13)       | -0.088                       | -0.084                          | -0.079                         | -0.078                        | -0.181                          |
| C(14)       | -0.197                       | -0.198                          | -0.199                         | -0.200                        | -0.181                          |

|       |        |        |        |        |        |
|-------|--------|--------|--------|--------|--------|
| C(15) | +0.049 | +0.053 | +0.055 | +0.058 | -0.043 |
| C(16) | -0.169 | -0.169 | -0.167 | -0.169 | -0.181 |
| C(17) | -0.142 | -0.141 | -0.142 | -0.138 | -0.181 |
| C(18) | -0.076 | -0.067 | -0.068 | -0.068 | -0.015 |
| C(19) | -0.007 | -0.008 | -0.009 | -0.009 | -0.015 |
| C(20) | +0.014 | +0.018 | +0.020 | +0.021 | -0.015 |
| C(21) | -0.069 | -0.071 | -0.072 | -0.073 | -0.015 |

**Table S38.** The full set of NBO atomic charges for {R-*spoke*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

| Atom         | CH <sub>3</sub> <sup>+</sup> | CH <sub>2</sub> Cl <sup>+</sup> | CHCl <sub>2</sub> <sup>+</sup> | CCl <sub>3</sub> <sup>+</sup> | C <sub>20</sub> H <sub>10</sub> |
|--------------|------------------------------|---------------------------------|--------------------------------|-------------------------------|---------------------------------|
| <b>C(1)</b>  | <b>-0.509</b>                | <b>-0.304</b>                   | <b>-0.156</b>                  | <b>-0.063</b>                 | -                               |
| <b>C(2)</b>  | <b>+0.239</b>                | <b>+0.238</b>                   | <b>+0.234</b>                  | <b>+0.235</b>                 | <b>-0.015</b>                   |
| <b>C(3)</b>  | <b>-0.186</b>                | <b>-0.199</b>                   | <b>-0.211</b>                  | <b>-0.226</b>                 | <b>-0.043</b>                   |
| <b>C(4)</b>  | <b>-0.071</b>                | <b>-0.086</b>                   | <b>-0.088</b>                  | <b>-0.092</b>                 | <b>-0.181</b>                   |
| C(5)         | -0.217                       | -0.207                          | -0.200                         | -0.202                        | -0.181                          |
| C(6)         | +0.075                       | +0.072                          | +0.085                         | +0.089                        | -0.043                          |
| C(7)         | -0.208                       | -0.207                          | -0.210                         | -0.211                        | -0.181                          |
| C(8)         | -0.082                       | -0.080                          | -0.072                         | -0.068                        | -0.181                          |
| C(9)         | -0.038                       | -0.036                          | -0.038                         | -0.038                        | -0.043                          |
| C(10)        | -0.158                       | -0.158                          | -0.156                         | -0.155                        | -0.181                          |
| C(11)        | -0.158                       | -0.156                          | -0.156                         | -0.155                        | -0.181                          |
| C(12)        | -0.038                       | -0.038                          | -0.038                         | -0.038                        | -0.043                          |
| C(13)        | -0.082                       | -0.074                          | -0.072                         | -0.068                        | -0.181                          |
| C(14)        | -0.208                       | -0.209                          | -0.210                         | -0.211                        | -0.181                          |
| C(15)        | +0.075                       | +0.086                          | +0.085                         | +0.089                        | -0.043                          |
| C(16)        | -0.217                       | -0.204                          | -0.200                         | -0.202                        | -0.181                          |
| <b>C(17)</b> | <b>-0.071</b>                | <b>-0.080</b>                   | <b>-0.088</b>                  | <b>-0.092</b>                 | <b>-0.181</b>                   |
| C(18)        | -0.092                       | -0.090                          | -0.084                         | -0.087                        | -0.015                          |
| C(19)        | +0.003                       | +0.002                          | +0.003                         | +0.002                        | -0.015                          |
| C(20)        | +0.003                       | +0.005                          | +0.003                         | +0.002                        | -0.015                          |
| C(21)        | -0.092                       | -0.085                          | -0.084                         | -0.087                        | -0.015                          |

**Table S39.** The full set of Wiberg bond indexes for {R-*rim*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

| Bond               | Order                        |                                 |                                |                               |                                 |
|--------------------|------------------------------|---------------------------------|--------------------------------|-------------------------------|---------------------------------|
|                    | CH <sub>3</sub> <sup>+</sup> | CH <sub>2</sub> Cl <sup>+</sup> | CHCl <sub>2</sub> <sup>+</sup> | CCl <sub>3</sub> <sup>+</sup> | C <sub>20</sub> H <sub>10</sub> |
| <b>C(1) – C(5)</b> | <b>0.957</b>                 | <b>0.957</b>                    | <b>0.946</b>                   | <b>0.934</b>                  | -                               |
| C(2) – C(3)        | 1.189                        | 1.181                           | 1.173                          | 1.172                         | 1.340                           |
| C(3) – C(4)        | 1.521                        | 1.537                           | 1.550                          | 1.551                         | 1.216                           |
| <b>C(4) – C(5)</b> | <b>1.070</b>                 | <b>1.059</b>                    | <b>1.045</b>                   | <b>1.036</b>                  | <b>1.633</b>                    |
| <b>C(5) – C(6)</b> | <b>1.019</b>                 | <b>1.014</b>                    | <b>1.012</b>                   | <b>1.000</b>                  | <b>1.216</b>                    |
| C(6) – C(7)        | 1.276                        | 1.280                           | 1.285                          | 1.289                         | 1.216                           |
| C(7) – C(8)        | 1.588                        | 1.584                           | 1.575                          | 1.570                         | 1.633                           |
| C(8) – C(9)        | 1.219                        | 1.221                           | 1.222                          | 1.227                         | 1.216                           |
| C(9) – C(10)       | 1.216                        | 1.215                           | 1.214                          | 1.213                         | 1.216                           |
| C(10) – C(11)      | 1.631                        | 1.633                           | 1.633                          | 1.634                         | 1.633                           |

|               |       |       |       |       |       |
|---------------|-------|-------|-------|-------|-------|
| C(11) – C(12) | 1.216 | 1.215 | 1.214 | 1.214 | 1.216 |
| C(12) – C(13) | 1.206 | 1.205 | 1.205 | 1.202 | 1.216 |
| C(13) – C(14) | 1.593 | 1.590 | 1.586 | 1.587 | 1.633 |
| C(14) – C(15) | 1.257 | 1.260 | 1.264 | 1.263 | 1.216 |
| C(15) – C(16) | 1.176 | 1.173 | 1.170 | 1.172 | 1.216 |
| C(16) – C(17) | 1.699 | 1.703 | 1.707 | 1.705 | 1.633 |
| C(17) – C(3)  | 1.133 | 1.129 | 1.126 | 1.125 | 1.216 |
| C(2) – C(18)  | 1.152 | 1.148 | 1.149 | 1.142 | 1.185 |
| C(18) – C(19) | 1.188 | 1.190 | 1.191 | 1.193 | 1.185 |
| C(19) – C(20) | 1.171 | 1.169 | 1.168 | 1.166 | 1.185 |
| C(20) – C(21) | 1.172 | 1.169 | 1.169 | 1.167 | 1.185 |
| C(21) – C(2)  | 1.257 | 1.262 | 1.265 | 1.271 | 1.185 |
| C(18) – C(6)  | 1.395 | 1.398 | 1.395 | 1.398 | 1.340 |
| C(19) – C(9)  | 1.343 | 1.342 | 1.342 | 1.340 | 1.340 |
| C(20) – C(12) | 1.353 | 1.356 | 1.357 | 1.359 | 1.340 |
| C(21) – C(15) | 1.290 | 1.286 | 1.284 | 1.280 | 1.340 |

**Table S40.** The full set of Wiberg bond indexes for {R-*spoke*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

| Bond                | Order                        |                                 |                                |                               |                                 |
|---------------------|------------------------------|---------------------------------|--------------------------------|-------------------------------|---------------------------------|
|                     | CH <sub>3</sub> <sup>+</sup> | CH <sub>2</sub> Cl <sup>+</sup> | CHCl <sub>2</sub> <sup>+</sup> | CCl <sub>3</sub> <sup>+</sup> | C <sub>20</sub> H <sub>10</sub> |
| <b>C(1) – C(3)</b>  | <b>0.860</b>                 | <b>0.852</b>                    | <b>0.847</b>                   | <b>0.839</b>                  | -                               |
| <b>C(2) – C(3)</b>  | <b>1.047</b>                 | <b>1.041</b>                    | <b>1.034</b>                   | <b>1.022</b>                  | <b>1.340</b>                    |
| <b>C(3) – C(4)</b>  | <b>0.993</b>                 | <b>0.981</b>                    | <b>0.981</b>                   | <b>0.977</b>                  | <b>1.216</b>                    |
| C(4) – C(5)         | 1.784                        | 1.793                           | 1.800                          | 1.805                         | 1.633                           |
| C(5) – C(6)         | 1.147                        | 1.138                           | 1.134                          | 1.130                         | 1.216                           |
| C(6) – C(7)         | 1.251                        | 1.254                           | 1.258                          | 1.261                         | 1.216                           |
| C(7) – C(8)         | 1.604                        | 1.600                           | 1.597                          | 1.594                         | 1.633                           |
| C(8) – C(9)         | 1.195                        | 1.195                           | 1.191                          | 1.189                         | 1.216                           |
| C(9) – C(10)        | 1.230                        | 1.231                           | 1.234                          | 1.236                         | 1.216                           |
| C(10) – C(11)       | 1.612                        | 1.610                           | 1.606                          | 1.602                         | 1.633                           |
| C(11) – C(12)       | 1.230                        | 1.231                           | 1.234                          | 1.236                         | 1.216                           |
| C(12) – C(13)       | 1.195                        | 1.192                           | 1.191                          | 1.189                         | 1.216                           |
| C(13) – C(14)       | 1.604                        | 1.600                           | 1.597                          | 1.594                         | 1.633                           |
| C(14) – C(15)       | 1.251                        | 1.256                           | 1.258                          | 1.261                         | 1.216                           |
| C(15) – C(16)       | 1.147                        | 1.142                           | 1.134                          | 1.130                         | 1.216                           |
| C(16) – C(17)       | 1.784                        | 1.792                           | 1.800                          | 1.805                         | 1.633                           |
| <b>C(17) – C(3)</b> | <b>0.993</b>                 | <b>0.911</b>                    | <b>0.910</b>                   | <b>0.977</b>                  | <b>1.216</b>                    |
| C(2) – C(18)        | 1.241                        | 1.235                           | 1.249                          | 1.251                         | 1.185                           |
| C(18) – C(19)       | 1.172                        | 1.173                           | 1.170                          | 1.169                         | 1.185                           |
| C(19) – C(20)       | 1.175                        | 1.174                           | 1.175                          | 1.176                         | 1.185                           |
| C(20) – C(21)       | 1.172                        | 1.168                           | 1.170                          | 1.169                         | 1.185                           |
| C(21) – C(2)        | 1.241                        | 1.255                           | 1.249                          | 1.251                         | 1.185                           |
| C(18) – C(6)        | 1.308                        | 1.311                           | 1.301                          | 1.298                         | 1.340                           |
| C(19) – C(9)        | 1.350                        | 1.353                           | 1.351                          | 1.350                         | 1.340                           |
| C(20) – C(12)       | 1.351                        | 1.298                           | 1.351                          | 1.350                         | 1.340                           |
| C(21) – C(15)       | 1.308                        | 1.255                           | 1.301                          | 1.298                         | 1.340                           |

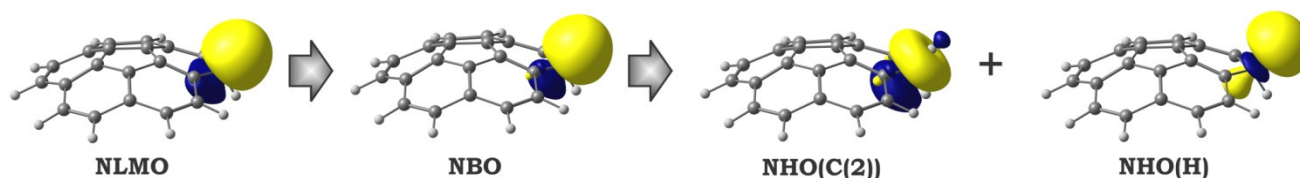
**Composition of NBO for the target bond, C(1) – C(2), as sum of corresponding NHOs:**

rim-isomers

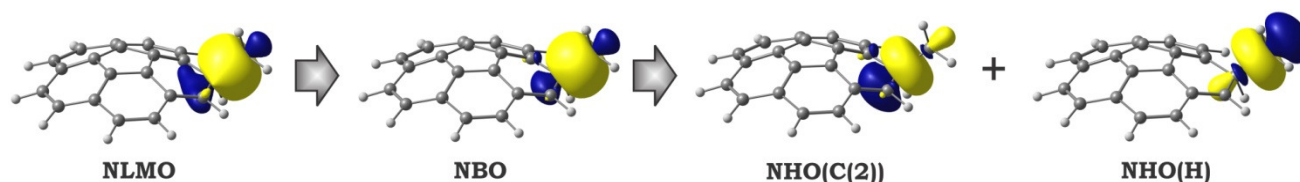
$$\begin{aligned} \text{NBO}(\text{C}(4) - \text{H}) &= 0.80 \cdot h(\text{C}(4)) + 0.60 \cdot h(\text{H}) = 0.80 \cdot (\text{sp}^{4.12}) + 0.60 \cdot (\text{s}^{1.00}) && \text{for R=H} \\ \text{NBO}(\text{C}(1) - \text{C}(4)) &= 0.73 \cdot h(\text{C}(1)) + 0.68 \cdot h(\text{C}(4)) = 0.73 \cdot (\text{sp}^{2.97}) + 0.68 \cdot (\text{sp}^{2.57}) && \text{for R=CH}_3 \\ \text{NBO}(\text{C}(1) - \text{C}(4)) &= 0.72 \cdot h(\text{C}(1)) + 0.69 \cdot h(\text{C}(4)) = 0.72 \cdot (\text{sp}^{2.97}) + 0.69 \cdot (\text{sp}^{2.37}) && \text{for R=CH}_2\text{Cl} \\ \text{NBO}(\text{C}(1) - \text{C}(4)) &= 0.72 \cdot h(\text{C}(1)) + 0.69 \cdot h(\text{C}(4)) = 0.72 \cdot (\text{sp}^{2.98}) + 0.69 \cdot (\text{sp}^{2.22}) && \text{for R=CHCl}_2 \\ \text{NBO}(\text{C}(1) - \text{C}(4)) &= 0.72 \cdot h(\text{C}(1)) + 0.70 \cdot h(\text{C}(4)) = 0.72 \cdot (\text{sp}^{2.88}) + 0.70 \cdot (\text{sp}^{2.09}) && \text{for R=CCl}_3 \end{aligned}$$

spoke-isomers

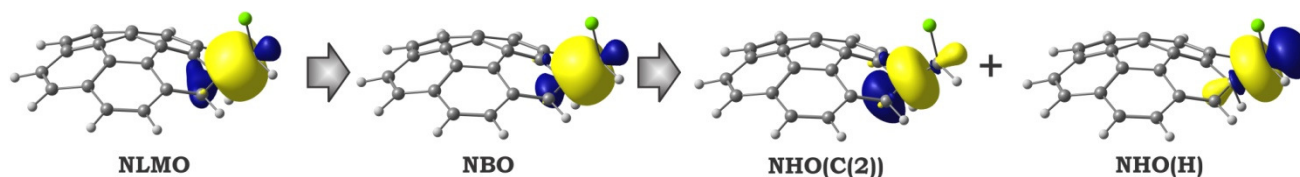
$$\begin{aligned} \text{NBO}(\text{C}(3) - \text{H}) &= 0.81 \cdot h(\text{C}(3)) + 0.58 \cdot h(\text{H}) = 0.81 \cdot (\text{sp}^{5.96}) + 0.59 \cdot (\text{s}^{1.00}) && \text{for R=H} \\ \text{NBO}(\text{C}(1) - \text{C}(3)) &= 0.74 \cdot h(\text{C}(1)) + 0.67 \cdot h(\text{C}(3)) = 0.74 \cdot (\text{sp}^{4.27}) + 0.67 \cdot (\text{sp}^{2.67}) && \text{for R=CH}_3 \\ \text{NBO}(\text{C}(1) - \text{C}(3)) &= 0.73 \cdot h(\text{C}(1)) + 0.68 \cdot h(\text{C}(3)) = 0.73 \cdot (\text{sp}^{4.26}) + 0.68 \cdot (\text{sp}^{2.50}) && \text{for R=CH}_2\text{Cl} \\ \text{NBO}(\text{C}(1) - \text{C}(3)) &= 0.73 \cdot h(\text{C}(1)) + 0.69 \cdot h(\text{C}(3)) = 0.73 \cdot (\text{sp}^{4.09}) + 0.69 \cdot (\text{sp}^{2.32}) && \text{for R=CHCl}_2 \\ \text{NBO}(\text{C}(1) - \text{C}(3)) &= 0.72 \cdot h(\text{C}(1)) + 0.70 \cdot h(\text{C}(3)) = 0.72 \cdot (\text{sp}^{3.93}) + 0.70 \cdot (\text{sp}^{2.19}) && \text{for R=CCl}_3 \end{aligned}$$



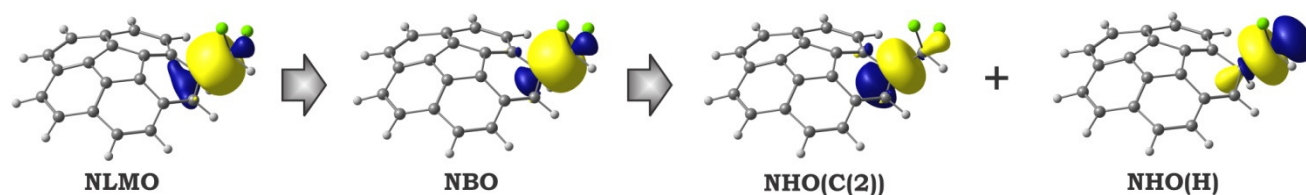
**Figure S6.** NLMO, NBO and two NHOs taking part in the formation of a given NBO corresponding to the C(1)–C(2) bond in {H-rim-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup>.



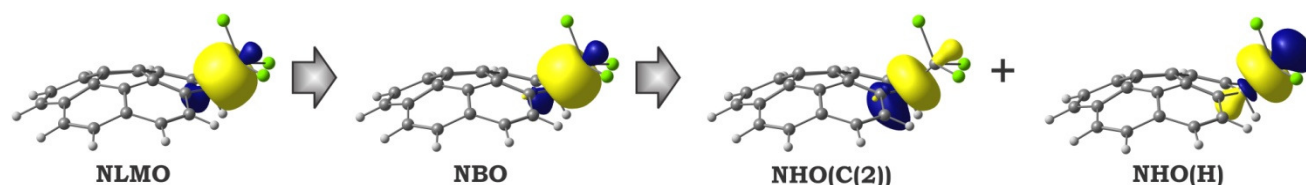
**Figure S7.** NLMO, NBO and two NHOs taking part in the formation of a given NBO corresponding to the C(1)–C(2) bond in {CH<sub>3</sub>-rim-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup>.



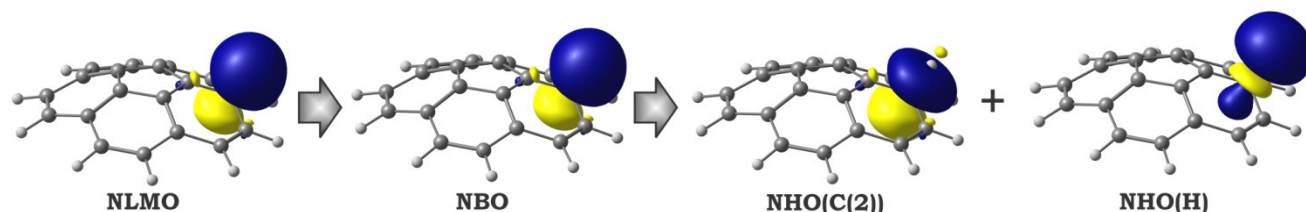
**Figure S8.** NLMO, NBO and two NHOs taking part in the formation of a given NBO corresponding to the C(1)–C(2) bond in {CH<sub>2</sub>Cl-rim-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup>.



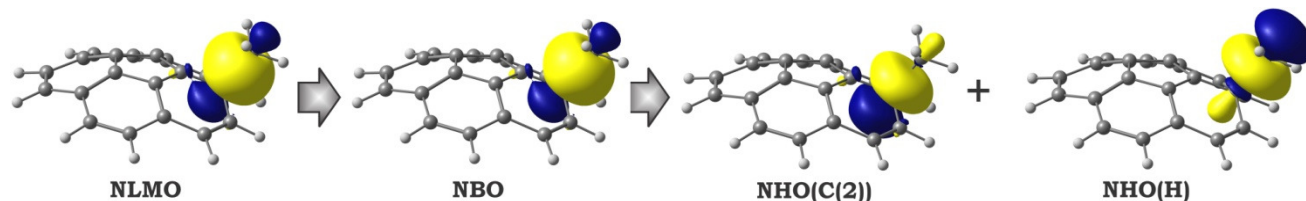
**Figure S9.** NLMO, NBO and two NHOs taking part in the formation of a given NBO corresponding to the C(1)–C(2) bond in  $\{\text{CHCl}_2\text{-rim-C}_{20}\text{H}_{10}\}^+$ .



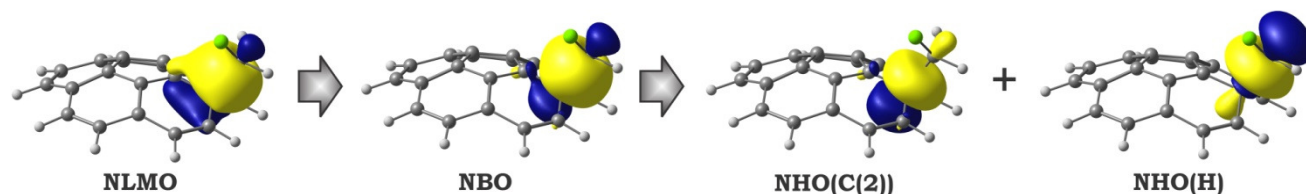
**Figure S10.** NLMO, NBO and two NHOs taking part in the formation of a given NBO corresponding to the C(1)–C(2) bond in  $\{\text{CCl}_3\text{-rim-C}_{20}\text{H}_{10}\}^+$ .



**Figure S11.** NLMO, NBO and two NHOs taking part in the formation of a given NBO corresponding to the C(1)–C(2) bond in  $\{\text{H-spoke-C}_{20}\text{H}_{10}\}^+$ .

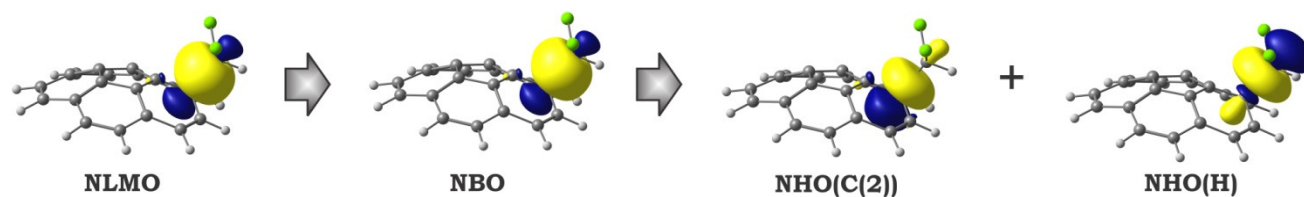


**Figure S12.** NLMO, NBO and two NHOs taking part in the formation of a given NBO corresponding to the C(1)–C(2) bond in  $\{\text{CH}_3\text{-spoke-C}_{20}\text{H}_{10}\}^+$ .

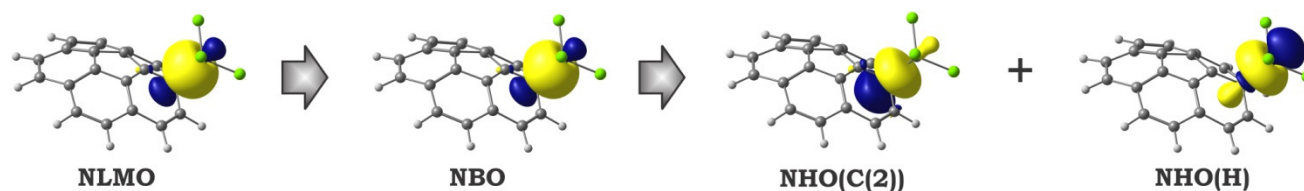


**Figure S13.** NLMO, NBO and two NHOs taking part in the formation of a given NBO corresponding to the C(1)–C(2) bond in  $\{\text{CH}_2\text{Cl-spoke-C}_{20}\text{H}_{10}\}^+$ .





**Figure S14.** NLMO, NBO and two NHOs taking part in the formation of a given NBO corresponding to the C(1)–C(2) bond in  $\{\text{CHCl}_2\text{-spoke-C}_{20}\text{H}_{10}\}^+$ .



**Figure S15.** NLMO, NBO and two NHOs taking part in the formation of a given NBO corresponding to the C(1)–C(2) bond in  $\{\text{CCl}_3\text{-spoke-C}_{20}\text{H}_{10}\}^+$ .



Transformation between isomers: 1,2-migration of the R-group

Table S41. Absolute energies for transition states at different levels of theory.

| Compound                        | RIJCOSX-PBE0/cc-pVTZ | MP2/cc-pVTZ      |
|---------------------------------|----------------------|------------------|
| H-hub-hub-TS                    | -767.795409004       | -766.8154852415  |
| H-hub-spoke-TS                  | -767.792539728       | -766.8066295781  |
| H-spoke-rim-TS                  | -767.787982560       | -766.8059686091  |
| H-rim-rim-TS                    | -767.801365806       | -766.8162206151  |
| CH <sub>3</sub> -hub-hub-TS     | -807.060404585       | -806.0337921423  |
| CH <sub>3</sub> -hub-spoke-TS   | -807.062535143       | -806.0307730894  |
| CH <sub>3</sub> -spoke-rim-TS   | -807.050817704       | -806.0206132267  |
| CH <sub>3</sub> -rim-rim-TS     | -807.075135372       | -806.0408568984  |
| CH <sub>2</sub> Cl-hub-hub-TS   | -1266.524968582      | -1265.1476133076 |
| CH <sub>2</sub> Cl-hub-spoke-TS | -1266.524328325      | -1265.1414926322 |
| CH <sub>2</sub> Cl-spoke-rim-TS | -1266.510398758      | -1265.1268309143 |
| CH <sub>2</sub> Cl-rim-rim-TS   | -1266.533892652      | -1265.1486281427 |
| CHCl <sub>2</sub> -hub-hub-TS   | -1725.985347661      | -1724.2497952137 |
| CHCl <sub>2</sub> -hub-spoke-TS | -1725.986072741      | -1724.2513952299 |
| CHCl <sub>2</sub> -spoke-rim-TS | -1725.979991812      | -1724.2393507341 |
| CHCl <sub>2</sub> -rim-rim-TS   | -1725.990930210      | -1724.2525078038 |
| CCl <sub>3</sub> -hub-hub-TS    | -2185.448725162      | -2183.3599991760 |
| CCl <sub>3</sub> -hub-spoke-TS  | -2185.445379625      | -2183.3515683347 |
| CCl <sub>3</sub> -spoke-rim-TS  | -2185.443805437      | -2183.3470453173 |
| CCl <sub>3</sub> -rim-rim-TS    | -2185.444656432      | -2183.3512528456 |

\* Energy at the MP2/cc-pVTZ level of theory was obtained as result of single-point calculations for RIJCOSX-PBE0/cc-pVTZ optimized geometries of transition states.

Table S42. Cartesian coordinates for {H-hub-hub-TS-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 0.794433000  | -2.239264000 | -1.484793000 |
| C | 0.802491000  | -3.449654000 | 0.663367000  |
| H | 0.689668000  | -4.396504000 | 1.178100000  |
| C | 0.657415000  | 0.172027000  | 1.129829000  |
| C | -0.732599000 | 1.648485000  | -2.431317000 |
| H | -1.212205000 | 1.933095000  | -3.360916000 |
| C | 0.338426000  | -1.987644000 | -2.819447000 |
| H | 0.183315000  | -2.820915000 | -3.495036000 |
| C | -0.968491000 | 2.437258000  | -1.318180000 |
| H | -1.615401000 | 3.299636000  | -1.423257000 |
| C | -0.043118000 | -0.726147000 | -3.243178000 |
| H | -0.482764000 | -0.627161000 | -4.228421000 |
| C | 0.827265000  | -2.234009000 | 1.421704000  |
| C | -0.485890000 | 2.073368000  | -0.021547000 |
| C | -0.679078000 | 1.647993000  | 2.409945000  |
| H | -1.146816000 | 1.947564000  | 3.340654000  |
| C | 0.639358000  | 0.178589000  | -1.174986000 |
| C | 1.009410000  | -1.095375000 | -0.734146000 |
| C | 0.004223000  | 0.413356000  | -2.374857000 |
| C | 0.015618000  | -0.725066000 | 3.216141000  |
| H | -0.394937000 | -0.632980000 | 4.214139000  |
| C | 0.792130000  | -3.450762000 | -0.720400000 |

|   |              |              |              |
|---|--------------|--------------|--------------|
| H | 0.674965000  | -4.400698000 | -1.228857000 |
| C | 1.038069000  | -1.103231000 | 0.663419000  |
| C | 0.030785000  | 0.416588000  | 2.354333000  |
| C | -0.924240000 | 2.434169000  | 1.282702000  |
| H | -1.566759000 | 3.298446000  | 1.405076000  |
| C | 0.395788000  | -1.979359000 | 2.770553000  |
| H | 0.262776000  | -2.815892000 | 3.447367000  |
| C | 0.401746000  | 0.993926000  | -0.048769000 |
| H | 1.446689000  | 1.125157000  | 0.717429000  |

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**Table S43.** Cartesian coordinates for {H-*hub-spoke-TS*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 0.145317000  | -2.178343000 | -1.446481000 |
| C | -0.108849000 | -3.374204000 | 0.689292000  |
| H | -0.402895000 | -4.281882000 | 1.203103000  |
| C | 0.480953000  | 0.208513000  | 1.160298000  |
| C | -0.572460000 | 1.928727000  | -2.414030000 |
| H | -0.970967000 | 2.300412000  | -3.351436000 |
| C | -0.247259000 | -1.845198000 | -2.787910000 |
| H | -0.554041000 | -2.636148000 | -3.462853000 |
| C | -0.635976000 | 2.753784000  | -1.323548000 |
| H | -1.059857000 | 3.743954000  | -1.428505000 |
| C | -0.369907000 | -0.538619000 | -3.219660000 |
| H | -0.765177000 | -0.353617000 | -4.211161000 |
| C | 0.141041000  | -2.182035000 | 1.449456000  |
| C | -0.214039000 | 2.309733000  | 0.006813000  |
| C | -0.579485000 | 1.922436000  | 2.425633000  |
| H | -0.980732000 | 2.291701000  | 3.362830000  |
| C | 0.484320000  | 0.211495000  | -1.150130000 |
| C | 0.600238000  | -1.110450000 | -0.703652000 |
| C | -0.102904000 | 0.562140000  | -2.343505000 |
| C | -0.379267000 | -0.546966000 | 3.225435000  |
| H | -0.777318000 | -0.364475000 | 4.216288000  |
| C | -0.106785000 | -3.372470000 | -0.690082000 |
| H | -0.399295000 | -4.278857000 | -1.207028000 |
| C | 0.598167000  | -1.112265000 | 0.710699000  |
| C | -0.109762000 | 0.556020000  | 2.352856000  |
| C | -0.639825000 | 2.750327000  | 1.337089000  |
| H | -1.064039000 | 3.740217000  | 1.443366000  |
| C | -0.255398000 | -1.852405000 | 2.790627000  |
| H | -0.564090000 | -2.645107000 | 3.462643000  |
| C | 0.389219000  | 1.020828000  | 0.006001000  |
| H | 1.026285000  | 2.291164000  | 0.008619000  |

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**Table S44.** Cartesian coordinates for {H-*spoke-rim-TS*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 0.112978000  | -2.215430000 | -1.455050000 |
| C | -0.147612000 | -3.390660000 | 0.694920000  |
| H | -0.451941000 | -4.288446000 | 1.219735000  |
| C | 0.482777000  | 0.190861000  | 1.108754000  |
| C | -0.507277000 | 1.907016000  | -2.463644000 |
| H | -0.882660000 | 2.282901000  | -3.408642000 |
| C | -0.285580000 | -1.884614000 | -2.796654000 |
| H | -0.613699000 | -2.673092000 | -3.464291000 |

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | -0.544625000 | 2.744740000  | -1.382754000 |
| H | -0.925450000 | 3.751264000  | -1.498641000 |
| C | -0.379817000 | -0.577769000 | -3.235748000 |
| H | -0.775570000 | -0.391694000 | -4.227035000 |
| C | 0.135847000  | -2.197152000 | 1.438052000  |
| C | -0.167487000 | 2.261815000  | -0.062379000 |
| C | -0.534517000 | 1.883572000  | 2.407583000  |
| H | -0.962807000 | 2.262106000  | 3.328696000  |
| C | 0.489527000  | 0.175440000  | -1.169258000 |
| C | 0.591785000  | -1.154186000 | -0.723477000 |
| C | -0.084179000 | 0.524446000  | -2.370369000 |
| C | -0.316893000 | -0.554882000 | 3.227685000  |
| H | -0.669334000 | -0.358161000 | 4.232863000  |
| C | -0.158288000 | -3.398658000 | -0.685742000 |
| H | -0.469789000 | -4.304909000 | -1.192240000 |
| C | 0.600084000  | -1.145766000 | 0.683977000  |
| C | -0.070710000 | 0.548004000  | 2.329686000  |
| C | -0.614241000 | 2.722252000  | 1.288221000  |
| H | -1.089784000 | 3.691486000  | 1.368676000  |
| C | -0.223448000 | -1.855450000 | 2.796944000  |
| H | -0.513713000 | -2.644112000 | 3.481681000  |
| C | 0.428708000  | 0.999385000  | -0.033142000 |
| H | 0.552933000  | 3.008105000  | 0.672658000  |

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**Table S45.** Cartesian coordinates for {H-*rim-rim*-TS-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 0.122393000  | -2.199940000 | -1.449804000 |
| C | -0.108278000 | -3.373950000 | 0.709779000  |
| H | -0.381306000 | -4.280173000 | 1.237204000  |
| C | 0.417077000  | 0.223673000  | 1.096348000  |
| C | -0.580675000 | 1.893386000  | -2.496638000 |
| H | -0.967503000 | 2.255581000  | -3.442147000 |
| C | -0.266324000 | -1.889152000 | -2.801062000 |
| H | -0.565478000 | -2.691013000 | -3.466320000 |
| C | -0.646093000 | 2.732575000  | -1.404365000 |
| H | -1.071910000 | 3.720578000  | -1.527825000 |
| C | -0.381237000 | -0.590827000 | -3.253718000 |
| H | -0.763681000 | -0.423811000 | -4.253699000 |
| C | 0.136422000  | -2.167241000 | 1.450241000  |
| C | -0.265082000 | 2.270624000  | -0.099865000 |
| C | -0.586702000 | 1.922505000  | 2.380867000  |
| H | -1.024154000 | 2.334496000  | 3.283916000  |
| C | 0.442240000  | 0.202451000  | -1.182680000 |
| C | 0.567024000  | -1.122692000 | -0.724228000 |
| C | -0.123090000 | 0.531768000  | -2.394939000 |
| C | -0.340607000 | -0.519643000 | 3.226630000  |
| H | -0.696101000 | -0.324793000 | 4.231182000  |
| C | -0.117329000 | -3.386405000 | -0.669630000 |
| H | -0.399367000 | -4.304886000 | -1.171544000 |
| C | 0.567191000  | -1.107060000 | 0.683733000  |
| C | -0.105559000 | 0.570144000  | 2.322390000  |
| C | -0.664328000 | 2.757651000  | 1.191898000  |
| H | -1.153509000 | 3.717917000  | 1.313359000  |
| C | -0.227595000 | -1.826333000 | 2.801021000  |
| H | -0.507021000 | -2.613368000 | 3.491811000  |
| C | 0.340731000  | 1.034924000  | -0.059672000 |
| H | 0.335660000  | 2.803074000  | 2.045781000  |

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**Table S46.** Cartesian coordinates for {CH<sub>3</sub>-*hub-hub*-TS-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 0.745738000  | -2.211542000 | -1.539490000 |
| C | 0.867004000  | -3.371974000 | 0.626482000  |
| H | 0.784239000  | -4.306224000 | 1.169352000  |
| C | 0.747576000  | 0.282675000  | 1.017109000  |
| C | -0.848229000 | 1.638788000  | -2.514073000 |
| H | -1.360404000 | 1.897299000  | -3.433635000 |
| C | 0.229916000  | -1.995987000 | -2.855783000 |
| H | 0.048194000  | -2.845914000 | -3.503464000 |
| C | -1.063490000 | 2.428537000  | -1.405253000 |
| H | -1.740763000 | 3.269936000  | -1.490394000 |
| C | -0.175967000 | -0.745556000 | -3.288117000 |
| H | -0.661698000 | -0.667975000 | -4.253484000 |
| C | 0.921659000  | -2.139855000 | 1.353308000  |
| C | -0.526774000 | 2.089672000  | -0.118662000 |
| C | -0.675942000 | 1.667625000  | 2.310184000  |
| H | -1.174190000 | 1.930143000  | 3.236547000  |
| C | 0.599369000  | 0.216882000  | -1.276662000 |
| C | 0.987750000  | -1.047628000 | -0.823246000 |
| C | -0.092460000 | 0.411572000  | -2.448672000 |
| C | 0.151477000  | -0.625585000 | 3.144851000  |
| H | -0.238188000 | -0.517062000 | 4.149832000  |
| C | 0.789528000  | -3.405877000 | -0.754260000 |
| H | 0.654003000  | -4.366951000 | -1.236654000 |
| C | 1.092720000  | -1.022736000 | 0.570674000  |
| C | 0.108211000  | 0.497561000  | 2.253804000  |
| C | -0.980528000 | 2.432002000  | 1.171573000  |
| H | -1.694897000 | 3.239425000  | 1.287697000  |
| C | 0.548434000  | -1.875217000 | 2.721099000  |
| H | 0.465006000  | -2.702077000 | 3.417135000  |
| C | 0.436369000  | 1.061484000  | -0.144393000 |
| C | 2.100230000  | 1.626759000  | 0.672838000  |
| H | 1.797628000  | 2.441203000  | 1.319350000  |
| H | 2.831576000  | 0.961774000  | 1.119338000  |
| H | 2.430264000  | 1.949016000  | -0.308593000 |

**Table S47.** Cartesian coordinates for {CH<sub>3</sub>-*hub-spoke*-TS-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 0.196378000  | -2.098612000 | -1.445275000 |
| C | -0.011020000 | -3.304391000 | 0.688252000  |
| H | -0.269049000 | -4.222238000 | 1.203398000  |
| C | 0.474206000  | 0.299865000  | 1.160458000  |
| C | -0.673652000 | 1.972895000  | -2.397538000 |
| H | -1.116319000 | 2.317734000  | -3.325482000 |
| C | -0.216840000 | -1.782490000 | -2.780234000 |
| H | -0.507443000 | -2.582506000 | -3.451524000 |
| C | -0.751403000 | 2.791662000  | -1.307968000 |
| H | -1.237198000 | 3.755086000  | -1.400213000 |
| C | -0.387385000 | -0.478982000 | -3.205080000 |
| H | -0.807546000 | -0.303390000 | -4.188132000 |
| C | 0.192147000  | -2.102406000 | 1.448468000  |
| C | -0.258337000 | 2.378953000  | 0.006939000  |
| C | -0.680572000 | 1.966496000  | 2.409120000  |
| H | -1.125940000 | 2.308874000  | 3.336684000  |
| C | 0.477513000  | 0.302915000  | -1.150033000 |
| C | 0.619998000  | -1.014403000 | -0.704498000 |

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | -0.137358000 | 0.627282000  | -2.333767000 |
| C | -0.396644000 | -0.487507000 | 3.210939000  |
| H | -0.819559000 | -0.314463000 | 4.193260000  |
| C | -0.008982000 | -3.302610000 | -0.688803000 |
| H | -0.265490000 | -4.219122000 | -1.207066000 |
| C | 0.617947000  | -1.016268000 | 0.711781000  |
| C | -0.144122000 | 0.621040000  | 2.343249000  |
| C | -0.755161000 | 2.788177000  | 1.321503000  |
| H | -1.241232000 | 3.751357000  | 1.414878000  |
| C | -0.224905000 | -1.789871000 | 2.783089000  |
| H | -0.517410000 | -2.591670000 | 3.451420000  |
| C | 0.410396000  | 1.140052000  | 0.006236000  |
| C | 1.597092000  | 2.678940000  | 0.009886000  |
| H | 1.407080000  | 3.747955000  | 0.010977000  |
| H | 2.093687000  | 2.374732000  | 0.924778000  |
| H | 2.096202000  | 2.377085000  | -0.904430000 |

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**Table S48.** Cartesian coordinates for {CH<sub>3</sub>-*spoke-rim-TS*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 0.077983000  | -2.273275000 | -1.471478000 |
| C | -0.169755000 | -3.382178000 | 0.712078000  |
| H | -0.485998000 | -4.257192000 | 1.267494000  |
| C | 0.546544000  | 0.200647000  | 1.018798000  |
| C | -0.525822000 | 1.826027000  | -2.550462000 |
| H | -0.944829000 | 2.176361000  | -3.487235000 |
| C | -0.352220000 | -1.972284000 | -2.807083000 |
| H | -0.714305000 | -2.770933000 | -3.444251000 |
| C | -0.513675000 | 2.688538000  | -1.494369000 |
| H | -0.904538000 | 3.690485000  | -1.623337000 |
| C | -0.441342000 | -0.672750000 | -3.271277000 |
| H | -0.870723000 | -0.501165000 | -4.251229000 |
| C | 0.149386000  | -2.175499000 | 1.414305000  |
| C | -0.055636000 | 2.266417000  | -0.171266000 |
| C | -0.459532000 | 1.924395000  | 2.288353000  |
| H | -0.932903000 | 2.310540000  | 3.183304000  |
| C | 0.508543000  | 0.118938000  | -1.253135000 |
| C | 0.593106000  | -1.200989000 | -0.776782000 |
| C | -0.098468000 | 0.440717000  | -2.443201000 |
| C | -0.255526000 | -0.483849000 | 3.168489000  |
| H | -0.592605000 | -0.254509000 | 4.172098000  |
| C | -0.202862000 | -3.429007000 | -0.668149000 |
| H | -0.542712000 | -4.341396000 | -1.144585000 |
| C | 0.624682000  | -1.154638000 | 0.628182000  |
| C | -0.000505000 | 0.598652000  | 2.240366000  |
| C | -0.478502000 | 2.751344000  | 1.141661000  |
| H | -1.042300000 | 3.673209000  | 1.194617000  |
| C | -0.186641000 | -1.792553000 | 2.772675000  |
| H | -0.476645000 | -2.560296000 | 3.480923000  |
| C | 0.499326000  | 0.978723000  | -0.134751000 |
| C | 1.274161000  | 3.422092000  | 0.598946000  |
| H | 1.022853000  | 4.376191000  | 1.049707000  |
| H | 1.914223000  | 2.796422000  | 1.207628000  |
| H | 1.666319000  | 3.572987000  | -0.401768000 |

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**Table S49.** Cartesian coordinates for {CH<sub>3</sub>-*rim-rim*-TS-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 0.186892000  | -2.137461000 | -1.414146000 |
| C | 0.004669000  | -3.241457000 | 0.784481000  |
| H | -0.226188000 | -4.139459000 | 1.345139000  |
| C | 0.377886000  | 0.392912000  | 1.042719000  |
| C | -0.730936000 | 1.859599000  | -2.611624000 |
| H | -1.153378000 | 2.160313000  | -3.563333000 |
| C | -0.209080000 | -1.899401000 | -2.778414000 |
| H | -0.462614000 | -2.741085000 | -3.412763000 |
| C | -0.840309000 | 2.732678000  | -1.544858000 |
| H | -1.336835000 | 3.683128000  | -1.699746000 |
| C | -0.387583000 | -0.628437000 | -3.279531000 |
| H | -0.773515000 | -0.518120000 | -4.285957000 |
| C | 0.185551000  | -1.996276000 | 1.481750000  |
| C | -0.407563000 | 2.353068000  | -0.235839000 |
| C | -0.711018000 | 2.105916000  | 2.254278000  |
| H | -1.296762000 | 2.437151000  | 3.103822000  |
| C | 0.392901000  | 0.287029000  | -1.238972000 |
| C | 0.577703000  | -1.013842000 | -0.729615000 |
| C | -0.190784000 | 0.539445000  | -2.463100000 |
| C | -0.396190000 | -0.303962000 | 3.176262000  |
| H | -0.789192000 | -0.089202000 | 4.163062000  |
| C | 0.003484000  | -3.305688000 | -0.591529000 |
| H | -0.229141000 | -4.254818000 | -1.060639000 |
| C | 0.574645000  | -0.944823000 | 0.678125000  |
| C | -0.174328000 | 0.757906000  | 2.244736000  |
| C | -0.824397000 | 2.880187000  | 1.050228000  |
| H | -1.485657000 | 3.737823000  | 1.082959000  |
| C | -0.217695000 | -1.624387000 | 2.806450000  |
| H | -0.483393000 | -2.395027000 | 3.520684000  |
| C | 0.265377000  | 1.160280000  | -0.151094000 |
| C | 0.615332000  | 3.390904000  | 2.101037000  |
| H | 0.641852000  | 3.475602000  | 3.186538000  |
| H | 1.468198000  | 2.862734000  | 1.695727000  |
| H | 0.517535000  | 4.402343000  | 1.709379000  |

**Table S50.** Cartesian coordinates for {CH<sub>2</sub>Cl-*hub-hub*-TS-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | -0.000344000 | -2.172505000 | -1.502992000 |
| C | 0.036326000  | -3.315968000 | 0.678712000  |
| H | -0.091482000 | -4.243404000 | 1.224671000  |
| C | 0.025952000  | 0.332702000  | 1.026121000  |
| C | -1.425201000 | 1.731795000  | -2.545176000 |
| H | -1.908483000 | 2.004740000  | -3.476150000 |
| C | -0.480654000 | -1.948061000 | -2.830946000 |
| H | -0.682506000 | -2.795978000 | -3.475389000 |
| C | -1.620002000 | 2.545627000  | -1.447332000 |
| H | -2.249545000 | 3.420642000  | -1.556091000 |
| C | -0.831545000 | -0.686220000 | -3.283932000 |
| H | -1.294552000 | -0.603514000 | -4.260106000 |
| C | 0.119049000  | -2.081982000 | 1.398415000  |
| C | -1.122384000 | 2.192720000  | -0.149425000 |
| C | -1.302676000 | 1.821587000  | 2.289803000  |
| H | -1.780757000 | 2.135257000  | 3.211040000  |
| C | -0.071471000 | 0.263721000  | -1.261757000 |
| C | 0.267465000  | -1.010731000 | -0.790863000 |

|       |              |              |              |
|-------|--------------|--------------|--------------|
| C     | -0.725048000 | 0.475873000  | -2.455382000 |
| C     | -0.610982000 | -0.513832000 | 3.160833000  |
| H     | -1.001367000 | -0.377370000 | 4.162204000  |
| C     | -0.015123000 | -3.358838000 | -0.704910000 |
| H     | -0.177113000 | -4.319386000 | -1.180299000 |
| C     | 0.337924000  | -0.976439000 | 0.606952000  |
| C     | -0.595093000 | 0.597077000  | 2.254548000  |
| C     | -1.554853000 | 2.585484000  | 1.139284000  |
| H     | -2.211122000 | 3.442280000  | 1.244010000  |
| C     | -0.264764000 | -1.786765000 | 2.754810000  |
| H     | -0.392251000 | -2.600493000 | 3.459588000  |
| C     | -0.231622000 | 1.110324000  | -0.146360000 |
| C     | 1.698331000  | 1.664896000  | 0.672579000  |
| H     | 1.470953000  | 2.626879000  | 0.236833000  |
| H     | 1.793693000  | 1.641655000  | 1.748847000  |
| Cl    | 2.882647000  | 0.796605000  | -0.146897000 |
| ----- |              |              |              |

**Table S51.** Cartesian coordinates for {CH<sub>2</sub>Cl-*hub-spoke*-TS-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|       |              |              |              |
|-------|--------------|--------------|--------------|
| C     | 0.256868000  | -2.026013000 | -1.881157000 |
| C     | 0.473598000  | -3.735602000 | -0.123157000 |
| H     | 0.441810000  | -4.785023000 | 0.145848000  |
| C     | 0.278223000  | -0.338960000 | 1.237756000  |
| C     | -1.461592000 | 1.885090000  | -1.724862000 |
| H     | -2.031613000 | 2.351987000  | -2.520414000 |
| C     | -0.323408000 | -1.481591000 | -3.075527000 |
| H     | -0.509880000 | -2.134144000 | -3.921130000 |
| C     | -1.619028000 | 2.364950000  | -0.453399000 |
| H     | -2.294077000 | 3.194437000  | -0.280167000 |
| C     | -0.775345000 | -0.177626000 | -3.146261000 |
| H     | -1.299135000 | 0.142293000  | -4.039113000 |
| C     | 0.510111000  | -2.740750000 | 0.913630000  |
| C     | -0.956947000 | 1.746553000  | 0.681520000  |
| C     | -1.052607000 | 0.697781000  | 2.915826000  |
| H     | -1.466365000 | 0.707361000  | 3.917964000  |
| C     | 0.083725000  | 0.231746000  | -0.983112000 |
| C     | 0.526391000  | -1.094599000 | -0.901966000 |
| C     | -0.674573000 | 0.706185000  | -2.026390000 |
| C     | -0.220941000 | -1.762524000 | 3.054676000  |
| H     | -0.572852000 | -1.927211000 | 4.065979000  |
| C     | 0.351662000  | -3.395482000 | -1.453163000 |
| H     | 0.227639000  | -4.190218000 | -2.179364000 |
| C     | 0.648800000  | -1.444487000 | 0.464965000  |
| C     | -0.274702000 | -0.450370000 | 2.488454000  |
| C     | -1.389589000 | 1.720236000  | 2.073402000  |
| H     | -2.047302000 | 2.504457000  | 2.429880000  |
| C     | 0.161456000  | -2.855473000 | 2.300014000  |
| H     | 0.096692000  | -3.838428000 | 2.752740000  |
| C     | -0.065598000 | 0.712276000  | 0.341166000  |
| C     | 0.912003000  | 2.578713000  | 0.761532000  |
| H     | 0.451041000  | 3.391585000  | 1.305969000  |
| H     | 1.574098000  | 1.961099000  | 1.355184000  |
| Cl    | 1.564113000  | 3.089859000  | -0.718418000 |
| ----- |              |              |              |

**Table S52.** Cartesian coordinates for {CH<sub>2</sub>Cl-*spoke-rim*-TS-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 0.174184000  | -2.200089000 | -1.952552000 |
| C  | 0.347429000  | -3.832779000 | -0.114663000 |
| H  | 0.264678000  | -4.863818000 | 0.208372000  |
| C  | 0.339634000  | -0.366543000 | 1.070455000  |
| C  | -1.338395000 | 1.805367000  | -1.923261000 |
| H  | -1.894334000 | 2.278502000  | -2.725183000 |
| C  | -0.421533000 | -1.684108000 | -3.152408000 |
| H  | -0.669093000 | -2.363362000 | -3.960231000 |
| C  | -1.425538000 | 2.352678000  | -0.671616000 |
| H  | -2.035099000 | 3.236635000  | -0.526771000 |
| C  | -0.809971000 | -0.361066000 | -3.267929000 |
| H  | -1.346707000 | -0.056238000 | -4.158682000 |
| C  | 0.477096000  | -2.791341000 | 0.862387000  |
| C  | -0.798344000 | 1.721498000  | 0.469917000  |
| C  | -0.862612000 | 0.757954000  | 2.775183000  |
| H  | -1.282196000 | 0.819200000  | 3.772243000  |
| C  | 0.124034000  | 0.100585000  | -1.144974000 |
| C  | 0.519158000  | -1.242921000 | -1.024720000 |
| C  | -0.631391000 | 0.565237000  | -2.193718000 |
| C  | -0.102266000 | -1.697872000 | 3.002375000  |
| H  | -0.386133000 | -1.797227000 | 4.043008000  |
| C  | 0.203312000  | -3.550160000 | -1.458922000 |
| H  | 0.013533000  | -4.372004000 | -2.139630000 |
| C  | 0.662698000  | -1.532998000 | 0.345009000  |
| C  | -0.158296000 | -0.399887000 | 2.370534000  |
| C  | -1.172411000 | 1.786399000  | 1.875584000  |
| H  | -1.854781000 | 2.564223000  | 2.197581000  |
| C  | 0.193546000  | -2.827281000 | 2.283316000  |
| H  | 0.130862000  | -3.786768000 | 2.784385000  |
| C  | 0.022013000  | 0.636864000  | 0.154812000  |
| C  | 0.615943000  | 2.983865000  | 1.544849000  |
| H  | 0.217962000  | 3.538934000  | 2.382587000  |
| H  | 1.300412000  | 2.174622000  | 1.761005000  |
| Cl | 1.105284000  | 4.012011000  | 0.290559000  |

**Table S53.** Cartesian coordinates for {CH<sub>2</sub>Cl-*rim-rim*-TS-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 0.188155000  | -1.744808000 | -2.120106000 |
| C | 0.347326000  | -3.794544000 | -0.772629000 |
| H | 0.263137000  | -4.874893000 | -0.731040000 |
| C | 0.396677000  | -0.761029000 | 1.293865000  |
| C | -1.252499000 | 2.118648000  | -1.077545000 |
| H | -1.943723000 | 2.690895000  | -1.685892000 |
| C | -0.372454000 | -0.925355000 | -3.158285000 |
| H | -0.605414000 | -1.367707000 | -4.119710000 |
| C | -1.334339000 | 2.312481000  | 0.344354000  |
| H | -2.081366000 | 3.015225000  | 0.696588000  |
| C | -0.735363000 | 0.387819000  | -2.939825000 |
| H | -1.233284000 | 0.930177000  | -3.734732000 |
| C | 0.480061000  | -3.049770000 | 0.452733000  |
| C | -0.735146000 | 1.394401000  | 1.272680000  |
| C | -0.752108000 | -0.054748000 | 3.246847000  |
| H | -1.100990000 | -0.228745000 | 4.258077000  |
| C | 0.141836000  | 0.256556000  | -0.734510000 |
| C | 0.531040000  | -1.068288000 | -0.968672000 |



|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | -0.564053000 | 0.996467000  | -1.652634000 |
| C  | -0.075874000 | -2.525719000 | 2.800380000  |
| H  | -0.372322000 | -2.890765000 | 3.776411000  |
| C  | 0.210910000  | -3.176569000 | -1.996901000 |
| H  | 0.024246000  | -3.791980000 | -2.869154000 |
| C  | 0.676170000  | -1.702123000 | 0.281843000  |
| C  | -0.089169000 | -1.112352000 | 2.536237000  |
| C  | -1.064267000 | 1.147869000  | 2.646432000  |
| H  | -1.639687000 | 1.875759000  | 3.206155000  |
| C  | 0.192616000  | -3.444494000 | 1.808207000  |
| H  | 0.095978000  | -4.497652000 | 2.046004000  |
| C  | 0.059080000  | 0.447443000  | 0.672730000  |
| C  | -0.031081000 | 3.595648000  | -0.481655000 |
| H  | -0.220173000 | 4.027890000  | -1.458830000 |
| H  | -0.328607000 | 4.277251000  | 0.308691000  |
| Cl | 1.579901000  | 3.071632000  | -0.309946000 |

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**Table S54.** Cartesian coordinates for {CHCl<sub>2</sub>-hub-hub-TS-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 0.174662000  | -1.960567000 | -2.154310000 |
| C  | 0.572601000  | -3.687559000 | -0.435460000 |
| H  | 0.664235000  | -4.743324000 | -0.207531000 |
| C  | -0.126182000 | -0.407032000 | 1.017205000  |
| C  | -1.969069000 | 1.748055000  | -1.924054000 |
| H  | -2.542457000 | 2.206601000  | -2.721440000 |
| C  | -0.416166000 | -1.431542000 | -3.348773000 |
| H  | -0.495982000 | -2.060886000 | -4.227868000 |
| C  | -2.231248000 | 2.139660000  | -0.626779000 |
| H  | -2.995941000 | 2.888892000  | -0.457268000 |
| C  | -1.006990000 | -0.179323000 | -3.388572000 |
| H  | -1.525083000 | 0.112412000  | -4.294665000 |
| C  | 0.468966000  | -2.739547000 | 0.634358000  |
| C  | -1.611945000 | 1.491459000  | 0.495178000  |
| C  | -1.553235000 | 0.392909000  | 2.712272000  |
| H  | -1.990001000 | 0.338526000  | 3.703200000  |
| C  | -0.317961000 | 0.225657000  | -1.168660000 |
| C  | 0.276255000  | -1.045944000 | -1.121801000 |
| C  | -1.062471000 | 0.671420000  | -2.236500000 |
| C  | -0.403557000 | -1.940621000 | 2.805843000  |
| H  | -0.722710000 | -2.187299000 | 3.811347000  |
| C  | 0.433570000  | -3.315437000 | -1.762857000 |
| H  | 0.425672000  | -4.097999000 | -2.512836000 |
| C  | 0.423086000  | -1.427089000 | 0.222800000  |
| C  | -0.662128000 | -0.629057000 | 2.279502000  |
| C  | -2.007060000 | 1.405804000  | 1.859719000  |
| H  | -2.769563000 | 2.076954000  | 2.239806000  |
| C  | 0.133885000  | -2.941585000 | 2.022122000  |
| H  | 0.212360000  | -3.935789000 | 2.447015000  |
| C  | -0.584655000 | 0.620557000  | 0.153587000  |
| C  | 1.364918000  | 1.568499000  | 1.388030000  |
| Cl | 1.721208000  | 2.680767000  | 0.193610000  |
| H  | 0.559830000  | 1.802054000  | 2.076479000  |
| Cl | 2.627660000  | 0.631163000  | 1.952948000  |

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**Table S55.** Cartesian coordinates for {CHCl<sub>2</sub>-*hub-spoke-TS*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 0.490905000  | -2.747734000 | -1.447654000 |
| C  | 0.641163000  | -3.960184000 | 0.688075000  |
| H  | 0.661097000  | -4.913290000 | 1.203710000  |
| C  | 0.024853000  | -0.374989000 | 1.144372000  |
| C  | -1.532341000 | 0.900255000  | -2.410082000 |
| H  | -2.036524000 | 1.118155000  | -3.344926000 |
| C  | 0.011950000  | -2.560225000 | -2.789597000 |
| H  | -0.019597000 | -3.406831000 | -3.466416000 |
| C  | -1.869123000 | 1.643477000  | -1.306416000 |
| H  | -2.622987000 | 2.415848000  | -1.407253000 |
| C  | -0.528128000 | -1.362442000 | -3.219373000 |
| H  | -0.962771000 | -1.316325000 | -4.210544000 |
| C  | 0.491308000  | -2.748391000 | 1.446658000  |
| C  | -1.319172000 | 1.354831000  | 0.000569000  |
| C  | -1.531947000 | 0.898998000  | 2.411027000  |
| H  | -2.036020000 | 1.116491000  | 3.346024000  |
| C  | 0.024609000  | -0.374442000 | -1.144189000 |
| C  | 0.572261000  | -1.590735000 | -0.707150000 |
| C  | -0.633588000 | -0.235341000 | -2.342780000 |
| C  | -0.527398000 | -1.364003000 | 3.219229000  |
| H  | -0.961799000 | -1.318300000 | 4.210524000  |
| C  | 0.640954000  | -3.959869000 | -0.689659000 |
| H  | 0.660722000  | -4.912752000 | -1.205712000 |
| C  | 0.572431000  | -1.591066000 | 0.706623000  |
| C  | -0.633115000 | -0.236505000 | 2.343171000  |
| C  | -1.868872000 | 1.642837000  | 1.307817000  |
| H  | -2.622728000 | 2.415150000  | 1.409160000  |
| C  | 0.012708000  | -2.561544000 | 2.788829000  |
| H  | -0.018561000 | -3.408430000 | 3.465301000  |
| C  | -0.315400000 | 0.378843000  | 0.000309000  |
| C  | 0.636631000  | 2.711011000  | 0.000461000  |
| H  | -0.164019000 | 3.434961000  | 0.000831000  |
| Cl | 1.462037000  | 2.565055000  | 1.448994000  |
| Cl | 1.461172000  | 2.565687000  | -1.448637000 |

**Table S56.** Cartesian coordinates for {CHCl<sub>2</sub>-*spoke-rim-TS*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 0.471398000  | -2.884358000 | -1.466768000 |
| C | 0.589495000  | -4.011845000 | 0.722068000  |
| H | 0.585120000  | -4.943461000 | 1.275752000  |
| C | 0.037906000  | -0.400731000 | 1.023297000  |
| C | -1.459221000 | 0.773042000  | -2.567456000 |
| H | -1.953990000 | 0.978025000  | -3.510374000 |
| C | -0.001861000 | -2.740611000 | -2.816853000 |
| H | -0.050778000 | -3.611835000 | -3.460269000 |
| C | -1.780912000 | 1.565711000  | -1.483508000 |
| H | -2.515362000 | 2.351363000  | -1.620751000 |
| C | -0.510246000 | -1.547907000 | -3.293081000 |
| H | -0.936771000 | -1.529333000 | -4.288884000 |
| C | 0.475359000  | -2.766882000 | 1.426582000  |
| C | -1.260215000 | 1.291657000  | -0.173344000 |
| C | -1.460230000 | 0.947095000  | 2.276732000  |
| H | -1.964955000 | 1.210561000  | 3.199033000  |
| C | 0.044674000  | -0.492934000 | -1.250722000 |
| C | 0.574588000  | -1.703655000 | -0.768553000 |

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | -0.596495000 | -0.382266000 | -2.459597000 |
| C  | -0.485470000 | -1.289841000 | 3.166371000  |
| H  | -0.891886000 | -1.192041000 | 4.165782000  |
| C  | 0.589348000  | -4.066810000 | -0.657381000 |
| H  | 0.586271000  | -5.041363000 | -1.132244000 |
| C  | 0.575198000  | -1.648295000 | 0.636903000  |
| C  | -0.600684000 | -0.194342000 | 2.240713000  |
| C  | -1.770187000 | 1.664837000  | 1.132585000  |
| H  | -2.517501000 | 2.448563000  | 1.205641000  |
| C  | 0.020423000  | -2.509448000 | 2.775819000  |
| H  | -0.007592000 | -3.325969000 | 3.488948000  |
| C  | -0.290537000 | 0.306514000  | -0.138556000 |
| C  | 0.514165000  | 3.218764000  | 0.617646000  |
| H  | -0.310649000 | 3.744173000  | 1.077106000  |
| Cl | 1.546071000  | 2.394675000  | 1.596586000  |
| Cl | 0.916236000  | 3.607146000  | -0.937921000 |

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**Table S57.** Cartesian coordinates for {CHCl<sub>2</sub>-rim-rim-TS-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 0.062785000  | -2.587550000 | -1.893199000 |
| C  | 0.212593000  | -4.387595000 | -0.223495000 |
| H  | 0.095515000  | -5.441851000 | 0.001170000  |
| C  | 0.451374000  | -1.055899000 | 1.298523000  |
| C  | -1.209789000 | 1.437551000  | -1.456882000 |
| H  | -1.866365000 | 1.967819000  | -2.139906000 |
| C  | -0.511879000 | -1.930426000 | -3.035105000 |
| H  | -0.797167000 | -2.518075000 | -3.899928000 |
| C  | -1.202292000 | 1.883467000  | -0.097925000 |
| H  | -1.862275000 | 2.705213000  | 0.147849000  |
| C  | -0.821981000 | -0.586882000 | -3.028184000 |
| H  | -1.334982000 | -0.165423000 | -3.884666000 |
| C  | 0.420908000  | -3.454522000 | 0.854988000  |
| C  | -0.611165000 | 1.110827000  | 0.950411000  |
| C  | -0.584479000 | 0.018295000  | 3.143949000  |
| H  | -0.895495000 | 0.031098000  | 4.181986000  |
| C  | 0.137787000  | -0.386645000 | -0.860537000 |
| C  | 0.476062000  | -1.742445000 | -0.883712000 |
| C  | -0.582080000 | 0.222410000  | -1.865552000 |
| C  | -0.013966000 | -2.519987000 | 3.098310000  |
| H  | -0.279116000 | -2.703973000 | 4.132725000  |
| C  | 0.044424000  | -3.978127000 | -1.530232000 |
| H  | -0.198915000 | -4.723541000 | -2.277963000 |
| C  | 0.654737000  | -2.164079000 | 0.451033000  |
| C  | 0.009469000  | -1.171917000 | 2.599400000  |
| C  | -0.881051000 | 1.114558000  | 2.360578000  |
| H  | -1.407565000 | 1.948957000  | 2.808674000  |
| C  | 0.179222000  | -3.603127000 | 2.267312000  |
| H  | 0.058192000  | -4.596589000 | 2.683812000  |
| C  | 0.124039000  | 0.041472000  | 0.495199000  |
| C  | 0.273924000  | 3.092092000  | -1.232014000 |
| H  | 0.175061000  | 3.024780000  | -2.306584000 |
| Cl | -0.216251000 | 4.630889000  | -0.658121000 |
| Cl | 1.761653000  | 2.499011000  | -0.689943000 |

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**Table S58.** Cartesian coordinates for {CCl<sub>3</sub>-*hub-hub*-TS-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 0.354177000  | -1.930364000 | -1.916887000 |
| C  | 0.533072000  | -0.292996000 | -3.768769000 |
| H  | 0.603756000  | -0.125681000 | -4.847395000 |
| C  | -0.288749000 | 1.315363000  | -0.554108000 |
| C  | -1.799740000 | -1.678634000 | 1.789904000  |
| H  | -2.302157000 | -2.494647000 | 2.317407000  |
| C  | -0.084663000 | -3.161264000 | -1.293038000 |
| H  | -0.036255000 | -4.095254000 | -1.859476000 |
| C  | -2.184154000 | -0.360948000 | 2.111277000  |
| H  | -2.962436000 | -0.232352000 | 2.869919000  |
| C  | -0.675755000 | -3.186730000 | -0.038162000 |
| H  | -1.066397000 | -4.137030000 | 0.334217000  |
| C  | 0.297654000  | 0.829164000  | -2.893228000 |
| C  | -1.698062000 | 0.778919000  | 1.393894000  |
| C  | -1.865932000 | 2.933229000  | 0.191676000  |
| H  | -2.372412000 | 3.896417000  | 0.087220000  |
| C  | -0.277777000 | -0.850130000 | 0.188959000  |
| C  | 0.338175000  | -0.829455000 | -1.076990000 |
| C  | -0.893665000 | -1.977278000 | 0.722222000  |
| C  | -0.775275000 | 2.956728000  | -2.193240000 |
| H  | -1.204628000 | 3.914136000  | -2.499508000 |
| C  | 0.559116000  | -1.605651000 | -3.305896000 |
| H  | 0.645567000  | -2.409950000 | -4.041318000 |
| C  | 0.310363000  | 0.504327000  | -1.545360000 |
| C  | -0.941535000 | 2.503401000  | -0.835832000 |
| C  | -2.225331000 | 2.116617000  | 1.253357000  |
| H  | -2.997321000 | 2.467899000  | 1.943365000  |
| C  | -0.186135000 | 2.159605000  | -3.170688000 |
| H  | -0.178520000 | 2.529488000  | -4.199651000 |
| C  | -0.666429000 | 0.477331000  | 0.511806000  |
| C  | 1.643934000  | 0.003346000  | 2.104592000  |
| Cl | 0.770322000  | -0.576095000 | 3.397106000  |
| Cl | 1.909578000  | 1.652804000  | 1.962877000  |
| Cl | 2.698717000  | -1.021567000 | 1.297820000  |

**Table S59.** Cartesian coordinates for {CCl<sub>3</sub>-*hub-spoke*-TS-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 0.191178000  | -2.119120000 | -2.095104000 |
| C | 0.405097000  | -0.498159000 | -3.938036000 |
| H | 0.416820000  | -0.320602000 | -5.007517000 |
| C | -0.058365000 | 1.122797000  | -0.681418000 |
| C | -1.708872000 | -1.729574000 | 1.724692000  |
| H | -2.241746000 | -2.509104000 | 2.258027000  |
| C | -0.342366000 | -3.298917000 | -1.468494000 |
| H | -0.440784000 | -4.210358000 | -2.047524000 |
| C | -1.965935000 | -0.416743000 | 2.065429000  |
| H | -2.692396000 | -0.220786000 | 2.846591000  |
| C | -0.847275000 | -3.287602000 | -0.181490000 |
| H | -1.320703000 | -4.187044000 | 0.194454000  |
| C | 0.340812000  | 0.620305000  | -3.035189000 |
| C | -1.392965000 | 0.680285000  | 1.335620000  |
| C | -1.463460000 | 2.839877000  | 0.157227000  |
| H | -1.899509000 | 3.829679000  | 0.081351000  |
| C | -0.176634000 | -1.033805000 | 0.056668000  |
| C | 0.348754000  | -1.048743000 | -1.245955000 |

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | -0.868673000 | -2.088463000 | 0.603556000  |
| C  | -0.517336000 | 2.808801000  | -2.271819000 |
| H  | -0.889660000 | 3.789950000  | -2.541932000 |
| C  | 0.333724000  | -1.800853000 | -3.491152000 |
| H  | 0.291256000  | -2.595476000 | -4.227003000 |
| C  | 0.421294000  | 0.285283000  | -1.703212000 |
| C  | -0.628339000 | 2.351645000  | -0.918699000 |
| C  | -1.830350000 | 2.047437000  | 1.222200000  |
| H  | -2.544358000 | 2.442061000  | 1.936677000  |
| C  | -0.055114000 | 1.980883000  | -3.279414000 |
| H  | -0.083755000 | 2.351808000  | -4.297750000 |
| C  | -0.436528000 | 0.307390000  | 0.402604000  |
| C  | 1.080620000  | 0.977107000  | 2.916953000  |
| Cl | 1.407661000  | -0.643893000 | 3.024576000  |
| Cl | 0.164635000  | 1.688023000  | 4.116428000  |
| Cl | 1.984366000  | 1.958665000  | 1.926730000  |

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**Table S60.** Cartesian coordinates for {CCl<sub>3</sub>-spoke-rim-TS-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 0.387591000  | -1.448668000 | -3.138731000 |
| C  | 0.537523000  | 0.644984000  | -4.424318000 |
| H  | 0.547832000  | 1.125174000  | -5.396204000 |
| C  | -0.020449000 | 1.222767000  | -0.848252000 |
| C  | -1.553301000 | -2.284804000 | 0.593538000  |
| H  | -2.058535000 | -3.204900000 | 0.864139000  |
| C  | -0.088963000 | -2.786099000 | -2.886854000 |
| H  | -0.136892000 | -3.495175000 | -3.706091000 |
| C  | -1.856454000 | -1.139009000 | 1.301918000  |
| H  | -2.588830000 | -1.209583000 | 2.099108000  |
| C  | -0.601590000 | -3.175216000 | -1.662342000 |
| H  | -1.029720000 | -4.166840000 | -1.575778000 |
| C  | 0.422328000  | 1.449094000  | -3.238425000 |
| C  | -1.335692000 | 0.155477000  | 0.929491000  |
| C  | -1.480866000 | 2.564006000  | 0.434572000  |
| H  | -1.956321000 | 3.514108000  | 0.651635000  |
| C  | -0.051130000 | -1.051560000 | -0.768466000 |
| C  | 0.486444000  | -0.664105000 | -2.015178000 |
| C  | -0.696983000 | -2.261043000 | -0.562632000 |
| C  | -0.520906000 | 3.286455000  | -1.887519000 |
| H  | -0.922237000 | 4.292711000  | -1.862048000 |
| C  | 0.519300000  | -0.735034000 | -4.378139000 |
| H  | 0.514598000  | -1.281530000 | -5.314114000 |
| C  | 0.504075000  | 0.740189000  | -2.062669000 |
| C  | -0.631126000 | 2.446879000  | -0.724549000 |
| C  | -1.819974000 | 1.475658000  | 1.220251000  |
| H  | -2.548817000 | 1.622083000  | 2.009730000  |
| C  | -0.022450000 | 2.809045000  | -3.082370000 |
| H  | -0.054002000 | 3.461708000  | -3.947527000 |
| C  | -0.369608000 | 0.113067000  | -0.053583000 |
| C  | 1.204071000  | -0.503029000 | 2.859030000  |
| Cl | 0.410262000  | -1.105092000 | 4.189131000  |
| Cl | 1.502239000  | 1.122905000  | 2.764996000  |
| Cl | 1.818935000  | -1.533456000 | 1.735141000  |

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**Table S61.** Cartesian coordinates for {CCl<sub>3</sub>-*rim-rim-TS*-C<sub>20</sub>H<sub>10</sub>}<sup>+</sup> (PBE0/cc-pVTZ).

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 0.144733000  | -1.853566999 | -2.627599999 |
| C  | 0.286691000  | -0.156350000 | -4.403553998 |
| H  | 0.190452000  | 0.078833000  | -5.457590998 |
| C  | 0.390179000  | 1.329740999  | -1.046776000 |
| C  | -1.231451999 | -1.502491999 | 1.381268999  |
| H  | -1.820145999 | -2.236366999 | 1.920891999  |
| C  | -0.413968000 | -3.016838999 | -1.998660999 |
| H  | -0.662772000 | -3.881492998 | -2.603067999 |
| C  | -1.301789999 | -0.162815000 | 1.820771999  |
| H  | -1.938163999 | 0.049766000  | 2.673210999  |
| C  | -0.760099000 | -3.032055999 | -0.661988000 |
| H  | -1.265667999 | -3.905399998 | -0.266388000 |
| C  | 0.436307000  | 0.916258000  | -3.450825998 |
| C  | -0.723704000 | 0.913946000  | 1.083569000  |
| C  | -0.737049000 | 3.125749999  | 0.018853000  |
| H  | -1.086393000 | 4.151447998  | 0.034878000  |
| C  | 0.135026000  | -0.847168000 | -0.412735000 |
| C  | 0.504953000  | -0.842370000 | -1.759612999 |
| C  | -0.577482000 | -1.873911999 | 0.167388000  |
| C  | -0.095829000 | 3.133412999  | -2.501226999 |
| H  | -0.389785000 | 4.160996998  | -2.679875999 |
| C  | 0.150197000  | -1.472064999 | -4.014519998 |
| H  | -0.049853000 | -2.217186999 | -4.775420998 |
| C  | 0.652468000  | 0.503792000  | -2.161276999 |
| C  | -0.091630000 | 2.618410999  | -1.159045999 |
| C  | -1.039695000 | 2.315276999  | 1.094717000  |
| H  | -1.612489999 | 2.732773999  | 1.914859999  |
| C  | 0.152876000  | 2.323367999  | -3.588276998 |
| H  | 0.045816000  | 2.748664999  | -4.579686998 |
| C  | 0.064062000  | 0.502065000  | 0.030338000  |
| C  | 0.411160000  | -1.351397999 | 3.413638998  |
| Cl | -0.718225000 | -1.804012999 | 4.591042998  |
| Cl | 1.196756999  | 0.125052000  | 3.623926998  |
| Cl | 1.340630999  | -2.577452999 | 2.724887999  |

### Tests of influence of dispersion corrections on electronic structure

In order to evaluate the potential influence of dispersion corrections on electronic structure of selected systems, we have performed test calculations at the level of so-called DFT-D approach (introduced by S. Grimme<sup>2</sup>). Species of general formulae  $\{R-C_{20}H_{10}\}^+$  with  $R=CCl_3$  were selected as representative models (again, as suggested by this reviewer). Since there is no parameterization of dispersion correction for PBE0 hybrid functional, test calculations for model systems were carried out with help of B3LYP and BP86 functionals with and without empirical dispersion corrections (B3LYP *vs.* B3LYP-D and BP86 *vs.* BP86-D, respectively) and using the same basis sets as before (cc-pVTZ). All geometries were optimized at the level of theory selected. Parameters of electronic structure we were looking at are taken from NBO analysis, namely, charge distribution (NBO charges) and bond orders (in its Wiberg formulation). Results are collected in Tables S62-S64. As it follows from data obtained, there is no any notable influence of empirical dispersion corrections on parameters of electronic structure of target molecules.

**Table S62.** Selected parameters of electronic structure of  $\{CCl_3-hub-C_{20}H_{10}\}^+$  calculated at the level of B3LYP and BP86 with and without empirical dispersion corrections (method and method-D, respectively).

| Parameter             | $\{CCl_3-hub-C_{20}H_{10}\}^+$ |         |       |        |
|-----------------------|--------------------------------|---------|-------|--------|
|                       | B3LYP                          | B3LYP-D | BP86  | BP86-D |
| q(C(1))               | -0.04                          | -0.04   | -0.07 | -0.07  |
| q(C(2))               | -0.16                          | -0.16   | -0.16 | -0.16  |
| q(C(3))               | +0.09                          | +0.09   | +0.07 | +0.07  |
| q(C(18))              | +0.09                          | +0.09   | +0.08 | +0.08  |
| q(C(21))              | +0.09                          | +0.09   | +0.08 | +0.08  |
| bond order C(1)–C(2)  | 0.86                           | 0.86    | 0.84  | 0.85   |
| bond order C(2)–C(3)  | 0.98                           | 0.98    | 0.98  | 0.98   |
| bond order C(2)–C(18) | 0.97                           | 0.97    | 0.97  | 0.97   |
| bond order C(2)–C(21) | 0.97                           | 0.97    | 0.97  | 0.97   |

<sup>2</sup> (a) S. Grimme, *J. Comput. Chem.*, **2004**, 25, 1463-1473. (b) S. Grimme, *J. Comput. Chem.*, **2006**, 27, 1787-1799.

**Table S63.** *Rim-isomers.*

| Parameter            | {CCl <sub>3</sub> - <i>rim</i> -C <sub>20</sub> H <sub>10</sub> } <sup>+</sup> |         |       |        |
|----------------------|--------------------------------------------------------------------------------|---------|-------|--------|
|                      | B3LYP                                                                          | B3LYP-D | BP86  | BP86-D |
| q(C(1))              | -0.04                                                                          | -0.04   | -0.07 | -0.06  |
| q(C(3))              | +0.08                                                                          | +0.08   | +0.07 | +0.07  |
| q(C(4))              | -0.35                                                                          | -0.35   | -0.36 | -0.36  |
| q(C(5))              | +0.09                                                                          | +0.09   | +0.06 | +0.06  |
| bond order C(1)–C(4) | 0.94                                                                           | 0.94    | 0.93  | 0.92   |
| bond order C(3)–C(4) | 1.00                                                                           | 1.00    | 1.04  | 1.04   |
| bond order C(4)–C(5) | 1.03                                                                           | 1.03    | 1.00  | 1.00   |

**Table S64.** *Spoke-isomers.*

| Parameter            | {CCl <sub>3</sub> - <i>spoke</i> -C <sub>20</sub> H <sub>10</sub> } <sup>+</sup> |         |       |        |
|----------------------|----------------------------------------------------------------------------------|---------|-------|--------|
|                      | B3LYP                                                                            | B3LYP-D | BP86  | BP86-D |
| q(C(1))              | -0.05                                                                            | -0.05   | -0.08 | -0.07  |
| q(C(2))              | +0.22                                                                            | +0.22   | +0.18 | +0.18  |
| q(C(3))              | -0.21                                                                            | -0.21   | -0.20 | -0.20  |
| q(C(4))              | -0.09                                                                            | -0.09   | -0.10 | -0.10  |
| bond order C(1)–C(2) | 0.84                                                                             | 0.84    | 0.81  | 0.81   |
| bond order C(2)–C(3) | 1.02                                                                             | 1.02    | 1.03  | 1.03   |
| bond order C(3)–C(4) | 0.99                                                                             | 0.98    | 0.98  | 0.99   |