**Table S2**: Optimized geometrical parameters (bond length (Å), bond angles (deg.) and dihedral angle (deg.)) of aryldimesitylborane (DMB (1)).

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Bond Length | Theoretical (Å) | Exp.  (Å) | Bond and Dihedral Angles | Theoretical (degrees) | Exp. (degrees) |
| B-C18 | 1.570 | 1.582 | C18BC10 | 118.82 | 118.40 |
| C18-C19 | 1.407 | 1.401 | C2BC10 | 122.37 | 122.61 |
| C19-C21 | 1.389 | 1.383 | C18BC2 | 118.82 | 119.91 |
| C21-C25 | 1.393 | 1.393 | C33C11C10B | 5.54 | 5.65 |
| C25-C23 | 1.393 | 1.396 | C29C12C10B | 0.80 | 0.78 |
| C23-C20 | 1.389 | 1.385 | C2C4C45B | 0.97 | 0.88 |
| C20-C18 | 1.407 | 1.398 | C41C2C3B | 1.51 | 1.89 |
| B-C10 | 1.581 | 1.578 | C11C10BC18 | 56.68 | 56.65 |
| C33-C11 | 1.510 | 1.509 | C4C2BC18 | 121.58 | 121.58 |
| C12-C29 | 1.508 | 1.610 | C12C10BC18 | 121.56 | 121.57 |
| C15-C37 | 1.504 | 1.509 | C3C2BC18 | 56.67 | 56.67 |
| B-C2 | 1.581 | 1.584 | C12C10BC2 | 58.43 | 58.41 |
| C3-C41 | 1.510 | 1.507 | C4C2BC10 | 58.43 | 58.43 |
| C4-C45 | 1.508 | 1.508 | C20C18BC2 | 22.15 | 22.16 |
| C7-C49 | 1.504 | 1.509 | C19C18BC10 | 22.15 | 22.15 |