TABLE CAPTIONS

Table S1**-** The calculated activation energies (Δ*E*# / kJ mol-1), activation free energies (*∆G# /* kJ mol-1) and reaction energies (*∆Er* / kJ mol-1), of I-DA reaction between phenyl (pyridin-2-yl methylene) oxonium **1** and styrene derivatives **2a-c** for the *meta* pathways of concerted mechanism at the B3LYP/cc-pVDZ level of theory

Table S2- The calculated activation energies (Δ*E*# / kJ mol-1), activation free energies (*∆G# /* kJ mol-1) and reaction energies (*∆Er* / kJ mol-1), of I-DA reaction between phenyl (pyridin-2-yl methylene) oxonium **1** and styrene **2a** for the *meta* pathway of stepwise mechanism at the B3LYP/cc-pVDZ level of theory

Table S3- The selected geometrical parameters, bond lengths (r / Ǻ) and dihedral angles (φ / °) for stationary points of I-DA reactions between phenyl (pyridin-2-yl methylene) oxonium **1** and styrene derivatives (**2b-c**) for the *ortho* pathway of stepwise mechanism at the B3LYP/cc-pVDZ level of theorya

Table S1

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Entry | | Species | TS | ∆E# | ∆G# | ∆Er |
| 1 | **1+2a**→**5a** | | **TS5a** | 42.10 | 101.98 | -89.21 |
| 2 | **5a** →**9a** | | **TS6a** | -61.92 | 2.16 | -254.62 |
| 3 | **1+2a**→**6a** | | **TS7a** | 59.85 | 117.45 | -84.87 |
| 4 | **6a** →**10a** | | **TS8a** | -43.85 | 21.62 | -241.98 |
| 5 | **1+2b**→**5b** | | **TS5b** | 50.98 | 111 | -80.93 |
| 6 | **5b** →**9b** | | **TS6b** | -62.38 | 2.31 | -256.04 |
| 7 | **1+2b**→**6d** | | **TS7b** | 68.55 | 126.43 | -75.79 |
| 8 | **6b** →**10b** | | **TS8b** | -44.90 | 20.65 | -242.68 |
| 9 | **1+2c**→**5c** | | **TS5c** | 37.97 | 96.41 | -92.27 |
| 10 | **5c** →**9c** | | **TS6c** | -48.40 | 2.39 | -254.35 |
| 11 | **1+2c**→**6c** | | **TS7c** | 54.88 | 111.55 | -88.39 |
| 12 | **6c** →**10c** | | **TS8c** | -43.47 | 22.10 | -241.43 |

Table S2

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Entry | | Species | TS | ∆E# | ∆G# | ∆Er |
| 1 | **1+2a**→**17a** | | **TS9a** | 66.77 | 121.98 | 57.28 |
| 2 | **17a** →**18a** | | **TS10a** | 81.02 | 148.80 | 31.15 |
| 3 | **18a** →**19a** | | **TS11a** | 127.76 | 183.13 | 79.58 |
| 4 | **19a** →**5a** | | **TS12a** | 88.24 | 152.18 | -89.21 |
| 5 | **1+2a**→**20a** | | **TS13a** | 39.94 | 93.37 | 40.62 |
| 6 | **20a** →**21a** | | **TS14a** | 103.17 | 164.94 | 22.46 |
| 7 | **21a** →**22a** | | **TS15a** | 105.64 | 167.21 | 39.57 |
| 8 | **22a** →**6a** | | **TS16a** | 50.77 | 116.45 | -84.87 |

Table S3

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Species | *φOC1C5C6* | *rC1O* | *rC3C4* | *rC4C6* | *rC5C6* |
| TS9b | 67.44 | 1.31 | 1.39 | 4.90 | 1.37 |
| 11b | 53.36 | 1.41 | 1.39 | 5.09 | 1.47 |
| TS10b | 116.22 | 1.43 | 1.39 | 5.74 | 1.48 |
| 12b | 172.18 | 1.41 | 1.40 | 5.22 | 1.46 |
| TS11b | 115.02 | 1.44 | 1.39 | 4.92 | 1.46 |
| 13b | 43.60 | 1.41 | 1.39 | 4.79 | 1.47 |
| TS12b | 65.23 | 1.45 | 1.44 | 2.51 | 1.48 |
| 3b | 28.65 | 1.48 | 1.47 | 1.58 | 1.55 |
| TS2b | 52.82 | 1.46 | 1.45 | 1.55 | 1.53 |
| 7b | 62.10 | 1.43 | 1.40 | 1.52 | 1.54 |
| TS13b | 65.09 | 1.30 | 1.39 | 4.53 | 1.37 |
| 14b | 60.55 | 1.41 | 1.39 | 5.14 | 1.47 |
| TS14b | 120.21 | 1.42 | 1.39 | 5.52 | 1.47 |
| 15b | 177.45 | 1.40 | 1.40 | 4.43 | 1.46 |
| TS15b | 119.65 | 1.40 | 1.40 | 4.76 | 1.46 |
| 16b | 43.12 | 1.41 | 1.39 | 4.78 | 1.47 |
| TS16b | 43.55 | 1.45 | 1.44 | 2.49 | 1.49 |
| 4b | 53.23 | 1.47 | 1.49 | 1.55 | 1.54 |
| TS4b | 51.02 | 1.45 | 1.49 | 1.55 | 1.53 |
| 8b | 53.23 | 1.43 | 1.40 | 1.52 | 1.54 |
| TS9c | 67.52 | 1.30 | 1.39 | 4.94 | 1.37 |
| 11c | 54.23 | 1.41 | 1.39 | 5.08 | 1.47 |
| TS10c | 116.64 | 1.43 | 1.39 | 5.73 | 1.48 |
| 12c | 172.95 | 1.41 | 1.40 | 5.21 | 1.46 |
| TS11c | 115.54 | 1.44 | 1.39 | 4.90 | 1.46 |
| 13c | 47.52 | 1.42 | 1.40 | 4.65 | 1.47 |
| TS12c | 64.26 | 1.45 | 1.44 | 2.51 | 1.48 |
| 3c | 26.75 | 1.48 | 1.47 | 1.58 | 1.55 |
| TS2c | 47.01 | 1.46 | 1.48 | 1.58 | 1.55 |
| 7c | 62.58 | 1.43 | 1.40 | 1.52 | 1.54 |
| TS13c | 67.44 | 1.29 | 1.39 | 4.55 | 1.37 |
| 14c | 60.21 | 1.41 | 1.39 | 5.15 | 1.47 |
| TS14c | 120.01 | 1.42 | 1.39 | 5.52 | 1.47 |
| 15c | 176.06 | 1.41 | 1.39 | 4.90 | 1.46 |
| TS15c | 119.20 | 1.40 | 1.40 | 4.76 | 1.46 |
| 16c | 46.09 | 1.43 | 1.40 | 4.59 | 1.46 |
| TS16c | 44.52 | 1.45 | 1.44 | 2.35 | 1.49 |
| 4c | 53.23 | 1.47 | 1.49 | 1.55 | 1.54 |
| TS4c | 51.86 | 1.45 | 1.49 | 1.56 | 1.53 |
| 8c | 53.25 | 1.43 | 1.40 | 1.52 | 1.54 |

aFor numbering of atoms, see Scheme 2.

FIGURE CAPTION

Figure S1- The geometrical optimized of transition states and intermediates for *meta* pathways of the I-DA reactions between phenyl (pyridin-2-yl methylene) oxonium (**1**) and styrene derivatives (**2a-c**) *via* concerted mechanism at the B3LYP/6-31G level of theory. Bond distances are given in Å, wiberg bond indices are given in parenthesis and the natural charges (CT) of TSs are also given

|  |  |  |  |
| --- | --- | --- | --- |
| G:\New folder M\axeeee\concerted\TS7a.tif | G:\New folder M\axeeee\concerted\TS6a.tif |  | G:\New folder M\axeeee\concerted\TS5a.tif |
| **TS7a, (CT=0.206)** | **TS6a** | **5a** | **TS5a, (CT=0.198)** |
|  | G:\New folder M\axeeee\concerted\TS5b.tif | G:\New folder M\axeeee\concerted\TS8a.tif |  |
| **5b** | **TS5b, (CT=0.195)** | **TS8a** | **6a** |
| G:\New folder M\axeeee\concerted\TS8b.tif |  | G:\New folder M\axeeee\concerted\TS7b.tif | G:\New folder M\axeeee\concerted\TS6b.tif |
| **TS8b** | **6b** | **TS7b, (CT=0.205)** | **TS6b** |
| G:\New folder M\axeeee\concerted\TS7c.tif | G:\New folder M\axeeee\concerted\TS6c.tif |  | G:\New folder M\axeeee\concerted\TS5c.tif |
| **TS7c, (CT=0.214)** | **TS6c** | **5c** | **TS5c, (CT=0.202)** |
|  | **G:\New folder M\axeeee\concerted\TS8c.tif** |  |  |
|  | **TS8c** | **6c**  **Figure S1** |  |