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SUPPLEMENTARY MATERIAL TO

Stepwise or concerted? DFT study on the mechanism of ionic Diels–Alder reaction of chromanes

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TABLE S-I. The calculated activation energies ($\Delta E^{\#}$ / kJ mol^{-1}), activation free energies ($\Delta G^{\#}$ / kJ mol^{-1}) and reaction energies (ΔE_r / kJ mol^{-1}) of the I-DA reaction between phenyl(pyridin--2-ylmethylene)oxonium **1** and styrene derivatives **2a–c** for the *meta* pathways of the concerted mechanism at the B3LYP/cc-pVDZ level of theory

Entry	Species	TS	$\Delta E^{\#}$	$\Delta G^{\#}$	ΔE_r
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

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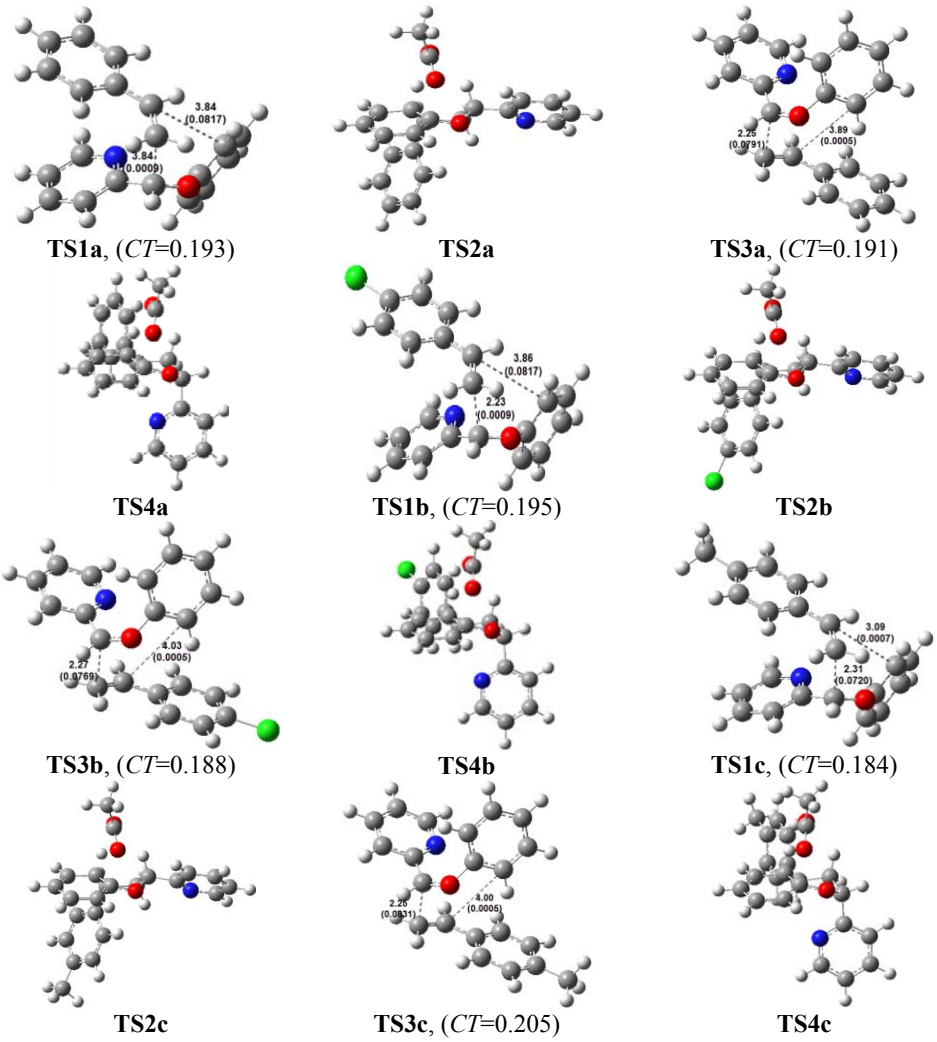

TS1a, (*CT*=0.193) **TS2a** **TS3a**, (*CT*=0.191)

TS4a **TS1b**, (*CT*=0.195) **TS2b**

TS3b, (*CT*=0.188) **TS4b** **TS1c**, (*CT*=0.184)

TS2c **TS3c**, (*CT*=0.205) **TS4c**

Fig. S-1. The geometrically optimized transition states for *ortho* pathways of the I-DA reactions between phenyl(pyridin-2-ylmethylene)oxonium (**1**) and styrene derivatives **2a**–**c** *via* concerted mechanism at the B3LYP/cc-pVDZ level of theory. Bond distances are given in Å, Wiberg bond indices are given in parenthesis and the natural charges (*CT*) of TSs are given.

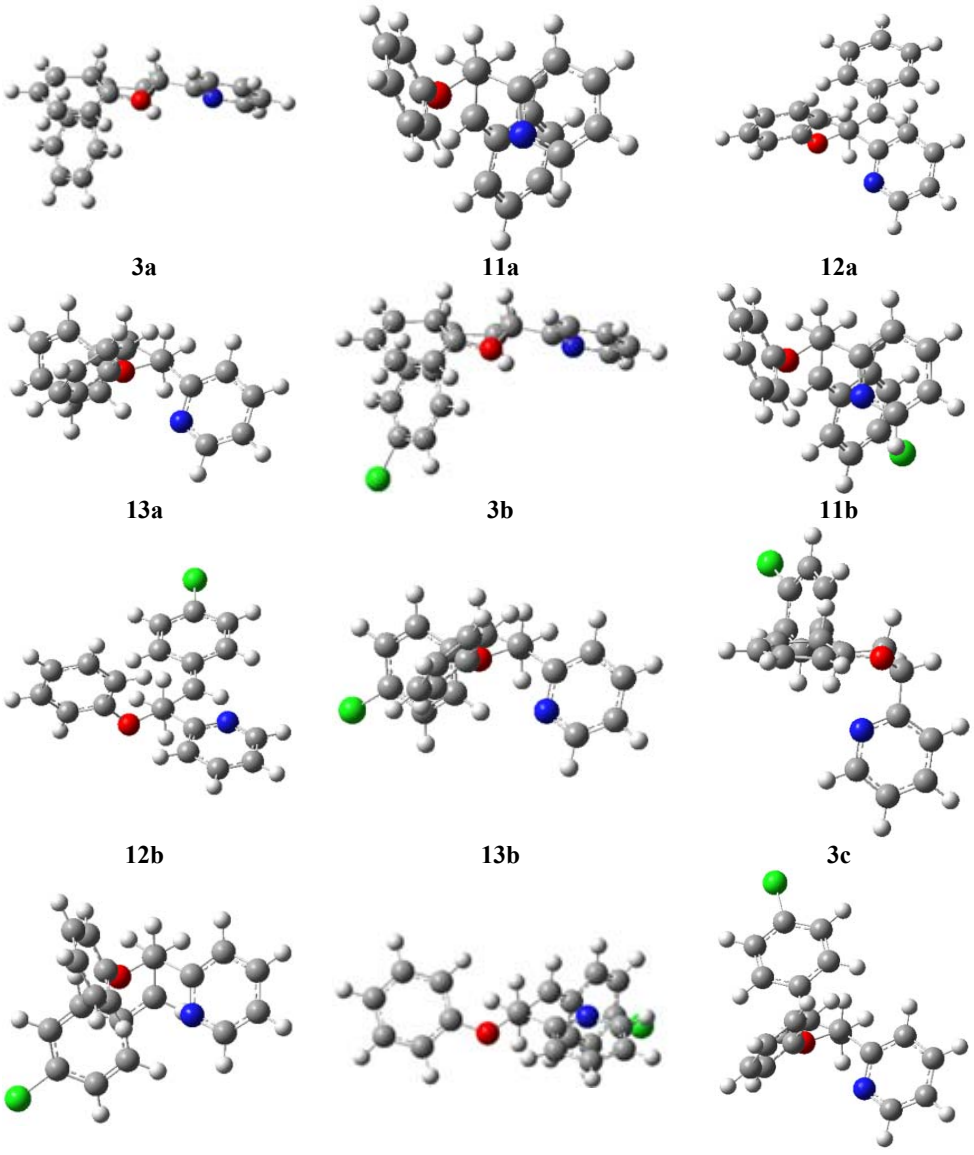

Fig. S-2. The geometrically optimized intermediates for *ortho-endo* pathways of the I-DA reactions between phenyl(pyridin-2-ylmethylene)oxonium (**1**) and styrene derivatives **2a–c** *via* concerted and stepwise mechanisms at the B3LYP/ cc-pVDZ level of theory.

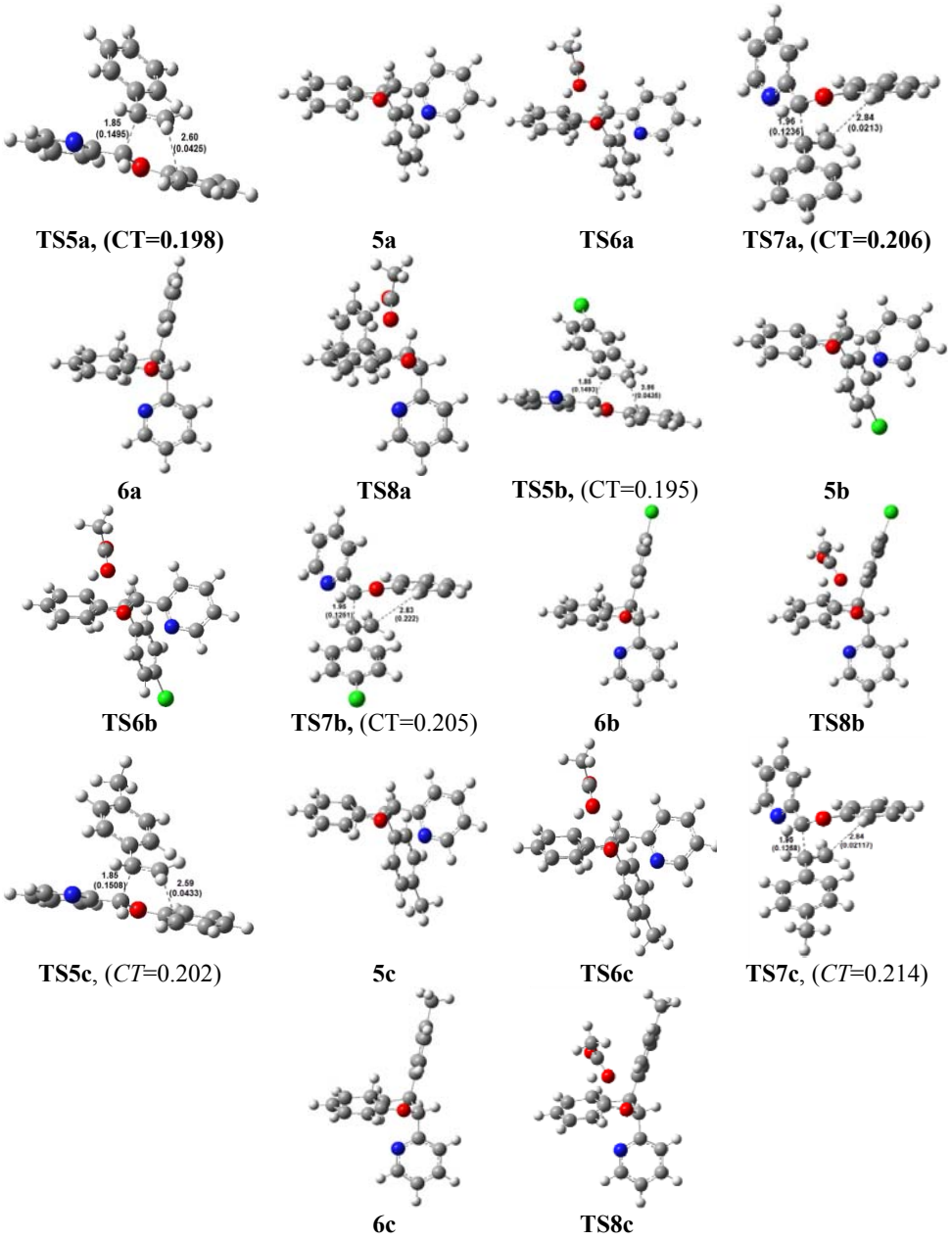

Fig. S-3. Geometrically optimized transition states and intermediates for the *meta* pathways of the I-DA reactions between phenyl(pyridin-2-ylmethylene)oxonium (**1**) and styrene derivatives **2a**–**c** *via* the concerted mechanism at the B3LYP/6-31G level of theory. Bond distances are given in Å, Wiberg bond indices are given in parenthesis and the natural charges (*CT*) of the TSs are given.

TABLE S-II. The calculated activation energies ($\Delta E^{\#}$), activation free energies ($\Delta G^{\#}$) and reaction energies (ΔE_r), all in kJ mol^{-1}, of the I-DA reaction between phenyl (pyridin-2-yl-methylene)oxonium **1** and styrene **2a** for the *meta* pathway of the stepwise mechanism at the B3LYP/cc-pVDZ level of theory

Entry	Species	TS	$\Delta E^{\#}$	$\Delta G^{\#}$	ΔE_r
1	**1+2a→17a**	**TS17a**	66.77	121.98	57.28
2	**17a→18a**	**TS18a**	81.02	148.80	31.15
3	**18a→19a**	**TS19a**	127.76	183.13	79.58
4	**19a→5a**	**TS20a**	88.24	152.18	–89.21
5	**1+2a→20a**	**TS21a**	39.94	93.37	40.62
6	**20a→21a**	**TS22a**	103.17	164.94	22.46
7	**21a→22a**	**TS23a**	105.64	167.21	39.57
8	**22a→6a**	**TS24a**	50.77	116.45	–84.87

TABLE S-III. Selected geometrical parameters, bond lengths (r / Å) and dihedral angles (φ / °) for the stationary points of I-DA reactions between phenyl(pyridin-2-ylmethylene)oxonium **1** and styrene derivatives **2b** and **2c** for the *ortho* pathway of the stepwise mechanism at the B3LYP/cc-pVDZ level of theory; for numbering of the atoms, see Scheme 2 of the native paper

Species	$\varphi_{O\text{-}C1\text{-}C5\text{-}C6}$	$r_{C1\text{-}O}$	$r_{C3\text{-}C4}$	$r_{C4\text{-}C6}$	$r_{C5\text{-}C6}$
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

TABLE S-III. Continued

Species	$\varphi_{O\text{-}C1\text{-}C5\text{-}C6}$	$r_{C1\text{-}O}$	$r_{C3\text{-}C4}$	$r_{C4\text{-}C6}$	$r_{C5\text{-}C6}$
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