TableS1- The calculated activation enthalpies ($\Delta H^{\#}$/kcalmol^{-1}), reaction enthalpies (ΔHr/kcalmol^{-1}) and entropy (ΔS/calmol$^{-1}k^{-1}$) of the HDA reactions between 1,2-diaza-1,3-butadiene and 1,2-oxaza-1,3-butadienes derivatives (**3** and **4**) with some olefins (**5**, **10** and **15**) at the B3LYP/cc-pVDZ level of theory.

Species	TSs	$\Delta H^{\#}$	$\Delta S^{\#}$	ΔHr	ΔSr
3a+5a→6aa	**TS1aa**	10.60	-49.81	-37.65	-57.21
3a+5a→7aa	**TS2aa**	18.95	-50.09	-42.48	-56.01
3a+5a→8aa	**TS3aa**	15.75	-47.96	-42.98	-58.62
3a+5a→9aa	**TS4aa**	16.82	-50.78	-42.35	-55.20
3b+5a→6ba	**TS1ba**	10.29	-40.98	-44.54	-45.01
3b+5a→7ba	**TS2ba**	11.29	-43.87	-44.50	-47.02
3b+5a→8ba	**TS3ba**	13.62	-45.42	-44.99	-48.91
3b+5a→9ba	**TS4ba**	12.61	-49.55	-44.49	-46.35
3a+5b→6ab	**TS1ab**	12.29	-51.76	-32.63	-58.97
3a+5b→7ab	**TS2ab**	16.94	-53.25	-37.96	-57.24
3a+5b→8ab	**TS3ab**	10.85	-53.05	-32.86	-59.34
3a+5b→9ab	**TS4ab**	15.93	-53.51	-37.45	-57.40
3b+5b→6bb	**TS1bb**	12.12	-44.13	-40.32	-46.37
3b+5b→7bb	**TS2bb**	13.93	-45.77	-40.31	-48.98
3b+5b→8bb	**TS3bb**	10.52	-43.42	-40.18	-49.56
3b+5b→9bb	**TS4bb**	13.04	-44.87	-39.74	-49.89
3a+10→11a	**TS5a**	19.84	-54.10	-36.77	-58.19
3a+10→12a	**TS6a**	14.67	-53.52	-38.40	-59.25
3a+10→13a	**TS7a**	19.57	-54.78	-34.64	-63.58
3a+10→14a	**TS8a**	23.84	-55.52	-38.59	-59.84
3b+10→11b	**TS5b**	11.88	-46.30	-43.79	-50.61
3b+10→12b	**TS6b**	12.72	-49.94	-40.47	-50.88
3b+10→13b	**TS7b**	13.48	-44.61	-40.85	-52.36
3b+10→14b	**TS8b**	16.50	-48.37	-43.99	-50.06
4a+15→16a	**TS9a**	6.83	-58.77	-41.32	-61.82
4a+15→17a	**TS10a**	7.73	-57.69	-42.78	-62.46
4a+15→18a	**TS11a**	17.14	-59.82	-36.07	-62.17
4a+15→19a	**TS12a**	22.18	-61.38	-32.03	-61.71
4b+15→16b	**TS9b**	7.04	-56.30	-42.74	-58.70
4b+15→17b	**TS10b**	5.27	-53.07	-46.52	-57.35
4b+15→18b	**TS11b**	21.09	-56.53	-38.09	-58.19
4b+15→19b	**TS12b**	19.86	-58.52	-37.69	-60.88
4c+15→16c	**TS9c**	10.40	-53.58	-43.88	-56.27
4c+15→17c	**TS10c**	5.95	-52.42	-45.28	-58.86
4c+15→18c	**TS11c**	18.62	-52.36	-34.65	-56.18
4c+15→19c	**TS12c**	21.74	-52.77	-36.61	-58.43

Table S2- Calculated activation energies ($\Delta E^{\#}$/kcalmol^{-1}) and reaction energies (ΔEr/kcalmol^{-1}) of *ortho* pathways of the HDA reactions between 1,2-diaza-1,3-butadiene and 1,2-oxaza-1,3-butadienes derivatives **(3** and **4**) with some olefins (**5, 10** and **15**) at the MPWB1K level of theory.

Species	TSs	$\Delta E^{\#}$	ΔEr
3a+5a→6aa	**TS1aa**	6.67	-60.27
3a+5a→7aa	**TS2aa**	10.82	-64.44
3b+5a→8ba	**TS1ba**	6.13	-67.01
3b+5a→9ba	**TS2ba**	7.85	-67.18
3a+5b→6ab	**TS1ab**	7.66	-53.61
3a+5b→7ab	**TS2ab**	9.68	-58.78
3b+5b→8bb	**TS1bb**	7.21	-61.68
3b+5b→9bb	**TS2bb**	10.46	-61.80
3a+10→11a	**TS5a**	12.34	-57.73
3a+10→12a	**TS6a**	7.29	-61.36
3b+10→11b	**TS5b**	7.27	-62.11
3b+10→12b	**TS6b**	7.05	-66.66
4a+15→16a	**TS9a**	2.98	-59.38
4a+15→17a	**TS10a**	5.52	-60.89
4b+15→16b	**TS9b**	4.52	-59.66
4b+15→17b	**TS10b**	0.97	-63.94
4c+15→16c	**TS9c**	7.62	-60.63
4c+15→17c	**TS10c**	6.21	-63.09

Table S3- Calculated activation energies ($\Delta E^{\#}$/kcalmol^{-1}) and reaction energies (ΔEr/kcalmol^{-1}) of *meta* pathways of the HDA reactions 1,2-diaza-1,3-butadiene **(3)** and 1,2-oxaza-1,3-butadienes derivatives (**4**) with some olefins (**5, 10** and **15**) at the MPWB1K level of theory.

Species	TS	$\Delta E^{\#}$	ΔEr
3a+5a→8aa	**TS3aa**	12.42	-64.62
3a+5a→9aa	**TS4aa**	13.56	-63.90
3b+5a→8ba	**TS3ba**	9.61	-66.92
3b+5a→9ba	**TS4ba**	9.58	-66.35
3a+5b→8ab	**TS3ab**	10.05	-54.25
3a+5b→9ab	**TS4ab**	11.58	-57.53
3b+5b→8bb	**TS3bb**	9.69	-61.72
3b+5b→9bb	**TS4bb**	12.92	-61.53
3a+10→13a	**TS7a**	15.65	-59.09
3a+10→14a	**TS8a**	17.85	-62.02
3b+10→13b	**TS7b**	8.58	-64.75
3b+10→14b	**TS8b**	10.35	-66.95
4a+15→18a	**TS11a**	13.99	-53.61
4a+15→19a	**TS12a**	19.58	-50.46
4b+15→18b	**TS11b**	19.69	-54.67
4b+15→19b	**TS12b**	17.39	-54.88
4c+15→18c	**TS11c**	17.41	-51.24
4c+15→19c	**TS12c**	23.16	-53.61

Figure S1- The geometrical optimized of transition states for *meta* pathways of the HDA reactions between 1,2-diaza-1,3-butadiene derivatives (**3a** and **3**) and some olefines (**5a** and **5**) 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 also given.

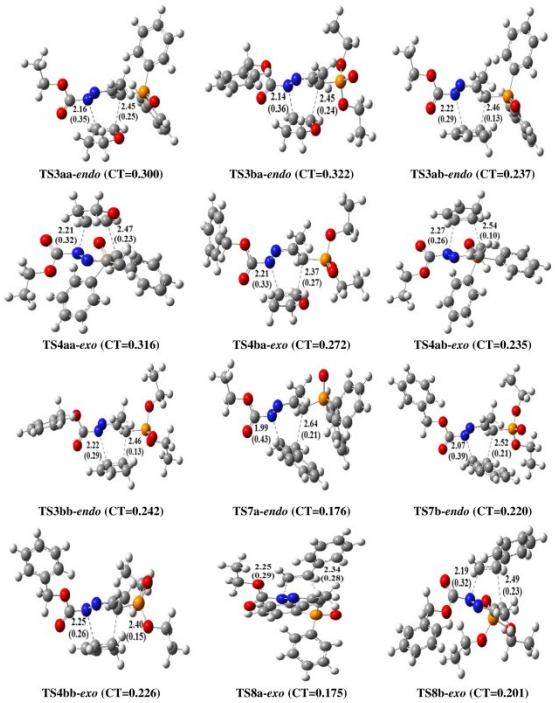

Figure S2- The geometrical optimized of transition states for *meta* pathways of the HDA reactions between 1,2-oxaza-1,3-butadiene derivatives (**4a** and **4**) and ethoxyethen (**15**) at the B3LYP/cc-pVDZ level of theory. Bond distances are given in Å, wiberg bond indices are given in parenthesis and the natural charges (*CT*) of TSs are also given.