Electronic Supplementary Information

Understanding the different reactivity of (*Z*)- and (*E*)-*β*-nitrostyrenes in [3+2] cycloaddition reactions. An MEDT study

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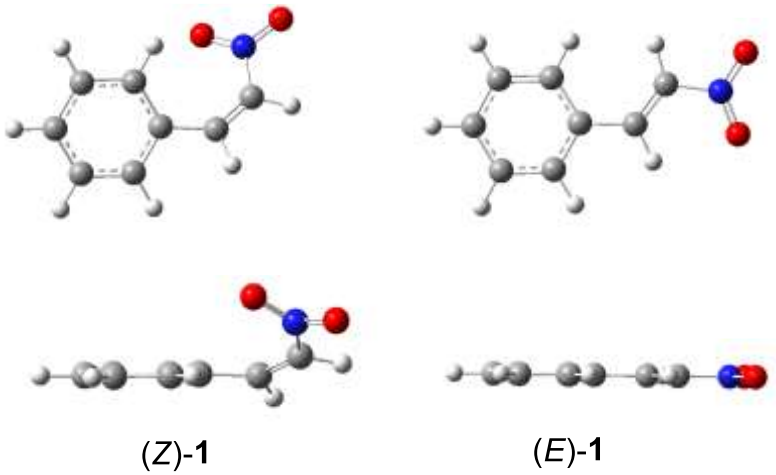

Figure S1. *ω*B97X-D/6-311G(d,p) optimised geometries of (*Z*)- and (*E*)-*β*-nitrostyrenes. (*Z*)-**1** and (*E*)-**1**. The ArC–C–C–N dihedral angle at (*Z*)-**1** is 3.5 degrees.

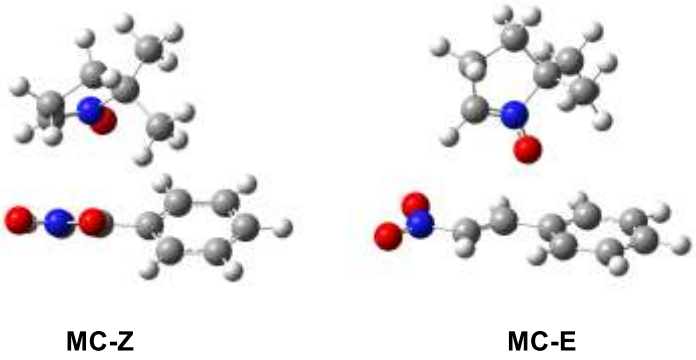

Figure S2. *ω*B97X-D/6-311G(d,p) optimised geometries of MCs **MC-Z** and **MC-E**.

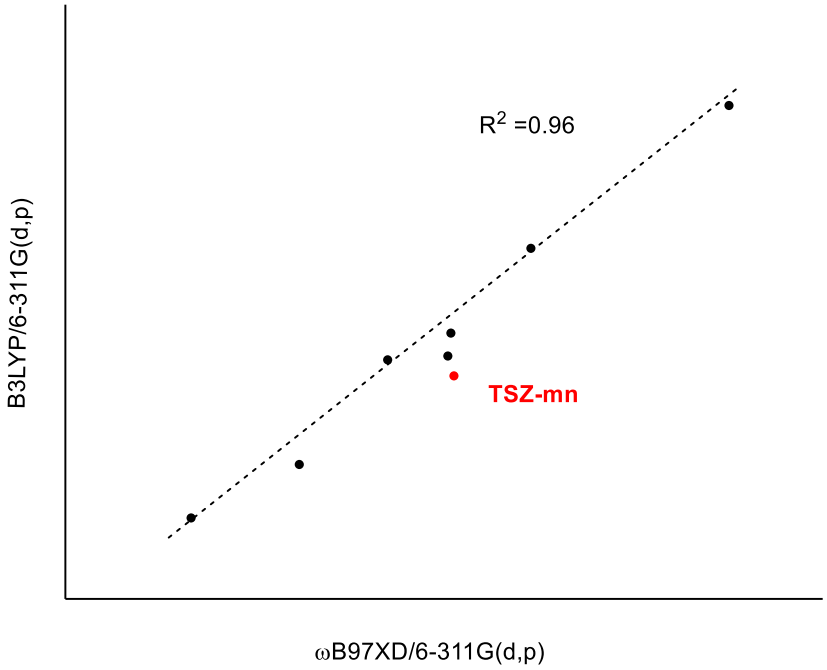

Figure S3. Plot of the B3LYP/6-311G(d,p) total energies, in a.u., vs the *ω*B97X-D/6-311G(d,p) ones, in a.u., in benzene, of the eight TSs involved in the 32CA reactions of (*Z*)- and (*E*)-*β*-nitrostyrenes (*Z*)-**1** and (*E*)-**1** with nitrone **2** (see Tables S1-S4).

Table S1. *ω*B97X-D/6-311G(d,p) total energies, E in a.u., enthalpies, H in a.u., entropies, ΔS in cal·mol^{-1}K^{-1}, and Gibbs free energies, G in a.u., computed at 25 ºC and 1 atm. in benzene, of the stationary points involved in the 32CA reaction of (*Z*)-*β*-nitrostyrene (*Z*)-**1** with nitrone **2**.

	E	H	S	G
(*Z*)-**1**	-514.095089	-513.947175	97.7	-513.993607
2	-365.162654	-364.986862	85.0	-365.027262
MC-Z	-879.276365	-878.950385	140.8	-879.017290
TS-Zon	-879.235604	-878.909949	131.1	-878.972232
TS-Zox	-879.244029	-878.918790	132.9	-878.981933
TS-Zmn	-879.251824	-878.927000	129.3	-878.988422
TS-Zmx	-879.250870	-878.926078	132.9	-878.989233
cis-**9**	-879.302746	-878.974366	127.9	-879.035140
cis-**10**	-879.309221	-878.980853	129.6	-879.042428
cis-**8**	-879.302489	-878.974077	129.2	-879.035474
cis-**4**	-879.306082	-878.977762	129.3	-879.039187

Table S2. *ω*B97X-D/6-311G(d,p) total energies, E in a.u., enthalpies, H in a.u., entropies, ΔS in cal·mol^{-1}K^{-1}, and Gibbs free energies, G in a.u., computed at 25 ºC and 1 atm. in benzene, of the stationary points involved in the 32CA reaction of (*E*)-*β*-nitrostyrene *(E)*-**1** with nitrone **2**.

	E	H	S	G
(*E*)-**1**	-514.104821	-513.956924	96.1	-514.002608
2	-365.162654	-364.986862	85.0	-365.027262
MC-E	-879.283678	-878.957663	147.8	-879.027901
TS-Eon	-879.249251	-878.924225	132.8	-878.987317
TS-Eox	-879.250681	-878.925426	131.2	-878.987770
TS-Emn	-879.260751	-878.935842	131.5	-878.998323
TS-Emx	-879.257320	-878.932355	132.3	-878.995197
trans-**6**	-879.305497	-878.976913	128.2	-879.037837
trans-**7**	-879.306691	-878.978253	129.3	-879.039711
trans-**3**	-879.305044	-878.976738	130.9	-879.038919
trans-**5**	-879.299597	-878.971429	129.9	-879.033168

Table S3. B3LYP/6-311G(d,p) total energies, E in a.u., enthalpies, H in a.u., entropies, ΔS in cal·mol^{-1}K^{-1}, and Gibbs free energies, G in a.u., computed at 25 ºC and 1 atm. in benzene, of the stationary points involved in the 32CA reaction of (*Z*)-*β*-nitrostyrene (*Z*)-**1** with nitrone **2**.

	E	H	S	G
(*Z*)-**1**	-514.280235	-514.133756	97.9	-514.180254
2	-365.280402	-365.106376	85.9	-365.147197
MC-Z	-879.568759	-879.246033	159.0	-879.321588
TS-Zon	-879.521630	-879.199731	133.6	-879.263203
TS-Zox	-879.530934	-879.209438	135.6	-879.273850
TS-Zmn	-879.534393	-879.213029	131.7	-879.275600
TS-Zmx	-879.537692	-879.216320	134.2	-879.280077
cis-**9**	-879.575272	-879.250846	130.9	-879.313045
cis-**10**	-879.581293	-879.256825	131.2	-879.319148
cis-**8**	-879.576419	-879.251870	131.2	-879.314186
cis-**4**	-879.579167	-879.254762	131.8	-879.317381

Table S4. B3LYP/6-311G(d,p) total energies, E in a.u., enthalpies, H in a.u., entropies, ΔS in cal·mol^{-1}K^{-1}, and Gibbs free energies, G in a.u., computed at 25 ºC and 1 atm. in benzene, of the stationary points involved in the 32CA reaction of (*E*)-*β*-nitrostyrene *(E)*-**1** with nitrone **2**.

	E	H	S	G
(*E*)-**1**	-514.290326	-514.144048	96.0	-514.189649
2	-365.280402	-365.106376	85.9	-365.147197
MC-E	-879.580537	-879.258091	155.2	-879.331855
TS-Eon	-879.534733	-879.213061	133.2	-879.276354
TS-Eox	-879.534733	-879.213061	133.2	-879.276354
TS-Emn	-879.546866	-879.225429	133.5	-879.288846
TS-Emx	-879.541830	-879.220246	134.7	-879.284231
trans-**6**	-879.576122	-879.251621	130.9	-879.313822
trans-**7**	-879.582934	-879.258207	133.0	-879.321408
trans-**3**	-879.578279	-879.253805	132.2	-879.316597
trans-**5**	-879.583564	-879.258835	133.3	-879.322156

Table S5. HF/6-311G(d,p) total, E in a.u., and relative, ΔE in kcal·mol^{-1}, energies of **TS-Zmx** and **TS-Emn**, computed in benzene.

	E	ΔE
(E)-**1**	-511.184701	
(Z)-**1**	-511.173066	
1	-362.937107	
TS-Zmx	-874.078897	19.6
TS-Emn	-874.084868	23.2

Table S6. M06-2X/6-311G(d,p) total, E in a.u., and relative, ΔE in kcal·mol^{-1}, energies of **TS-Zmn** and **TS-Zmx**, computed in benzene.

	E	ΔE
TS-Zmn	-879.167674	
TS-Zmx	-879.164602	1.9