Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary data

Table S1. B3LYP/6-31G(d), M06-2X/6-31G(d) and MPWB1K/6-31G(d) total energies (E in a.u), in gas phase of the stationary points involved in the 32CA reaction of BF_3:nitrone **15** complex with cyclopentene **14**

System	E Gas phase		
	B3LYP	M06-2X	MPWB1K
Cyclopentene **14**	-195.326702	-195.223333	-195.212447
BF_3:nitrone **15**	-722.252589	-721.991173	-721.97764
TSn-c	-917.558343	-917.203803	-917.173422
TSx-c	-917.576172	-917.214804	-917.185413
CAn-c	-917.614919	-917.276529	-917.248971
CAx-c	-917.61191	-917.274544	-917.245451

Table S2. MPWB1K/6–31G(d) total energies (E in a.u) in gas phase and in DCM, of the stationary points for the 32CA reactions of nitrone **13** with cyclopentene **14**.

System	E (a.u) Gas phase	E (a.u) DCM
Cyclopentene **14**	-195.212446	-195.213355
Oxime **12**	-397.495984	-397.503944
Nitrone **13**	-397.487329	-397.496214
TSn	-592.6754	-592.682949
TSx	-592.68193	-592.689306
CAn	-592.76037	-592.767798
CAx	-592.76299	-592.770522

Table S3. MPWB1K/6-31G(d) enthalpies (H, in a.u), entropies (S, in cal mol^{-1} K^{-1}), and free energies (G, in a.u), for the TSs and CAs involved in the 32CA between nitrone **13** and cyclopentene **14**.

System	H	S	G
Oxime	-397.407435	85.001	-397.44753
Nitrone	-397.398908	83.499	-397.438295
penetene	-195.092936	66.598	-195.124351
TSn	-592.463785	108.123	-592.514787
TSx	-592.469919	108.349	-592.521028
CAx	-592.544326	107.971	-592.595256
CAn	-592.546739	104.531	-592.596047

Table S4. MPWB1K/6–31G(d) total energies (E in a.u) in gas phase and in DCM of the stationary points for the 32CA reactions of the BF_3:nitrone complex **15** with cyclopenetene **14**.

System	E (a.u) Gas phase	E (a.u) DCM
Cyclopentene **14**	-195.212446	-195.213355
BF_3:nitrone **15**	-721.97764	-721.994871
TSn-B	-917.173422	-917.189837
TSx-B	-917.185413	-917.19918
CAn-B	-917.248971	-917.257919
CAx-B	-917.245451	-917.256585

Table S5. MPWB1K/6-31G(d) enthalpies (H, in a.u), entropies (S, in cal mol^{-1} K^{-1}), and free energies (G, in a.u), for the TSs and CAs involved in the 32CA between nitrone **13** and cyclopentene **14** in presence of BF_3catalyst.

System	H	S	G
Nitrone-c	-721.878669	106.28	-721.928802
TSn-B	-916.951096	128.994	-917.011944
TSx-B	-916.96052	127.791	-917.0208
CAn-B	-917.015004	124.293	-917.073634
CAx-B	-917.014714	118.564	-917.070642

Table S6. MPWB1K/6–31G(d) total energies (E in a.u). in vacuum and in DCM of the stationary points for the 32CA reactions of nitrone **13** with cyclopenetene **14** in presence of LiCl and $Li(OMe_2)_3$

System	E (a.u) Gas phase	E (a.u) DCM
Nitrone:LiCl **16**	-865.3655203	-865.4036609
TSx-LiCl	-1060.5630043	-1060.5967374
18	-1060.6471804	-1060.6811125
Nitrone:$Li(OMe_2)_3$ **17**	-869.7694020	-869.8282334
TSx-$Li(OMe_2)_3$	-1064.9654953	-1065.0197319
20	-1065.0477482	-1065.1020574

Table S7. MPWB1K/6-31G(d) enthalpies (H, in a.u), entropies (S, in cal mol^{-1} K^{-1}), and free energies (G, in a.u), for the TSs and CAs involved in the 32CA between nitrone **13** and cyclopentene **14** in presence of LiCl and $Li(OMe_2)_3$ catalyst

System	H	S	G
Nitrone-LiCl	-865.300586	101.123	-865.348286
TSxLiCl	-1060.37198	118.184	-1060.42773
18	-1060.45081	126.115	-1060.51029
Nitrone-$Li(OM_2)_3$	-869,466939	167,176	-869,545797
TSx$Li(OMe_2)_3$	-1064,53481	196,428	-1064,62747
20	-1064,61267	190,405	-1064,70248