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Regio- and stereoselectivity of [3+2] cycloaddition reactions between (*Z*)-1-(anthracen-9-yl)-*N*-methyl nitrone and analogs of *trans*-β-nitrostyrene on the basis of MEDT computational study

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SUPPLEMENTARY INFORMATION

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Table S1. Kinetic and thermodynamic parameters for 32CA reaction of **1** with 4-amino-*trans*-β-nitrostyrene (**2a**) in different solvents, according to MPWB95/6-311G(d,p)(PCM) calculations (ΔH and ΔG are given in kcal/mol^{-1}; ΔS are given in cal/mol^{-1} K^{-1}).

Reaction step	Toluene (ε = 2.4)			Ethanol (ε = 24.8)		
	ΔH	**ΔG**	**ΔS**	**ΔH**	**ΔG**	**ΔS**
1 + 2a → MC$_{3a}$	-2.24	11.00	-44.40	-1.28	12.34	-45.36
1 + 2a → TS$_{3a}$	22.67	37.62	-50.14	31.90	47.12	-51.05
1 + 2a → 3a	4.27	18.26	-46.94	7.40	21.31	-46.68
1 + 2a → MC$_{4a}$	-0.59	10.78	-38.14	-0.22	11.79	-40.17
1 + 2a → TS$_{4a}$	29.21	44.70	-51.93	38.63	54.48	-53.17
1 + 2a → 4a	9.83	25.22	-51.63	13.66	29.03	-51.55
1 + 2a → MC$_{5a}$	-4.31	6.15	-35.06	-1.62	13.17	-38.72
1 + 2a → TS$_{5a}$	25.22	40.34	-50.71	34.58	49.48	-49.98
1 + 2a → 5a	9.86	25.08	-51.05	13.51	28.98	-51.87
1 + 2a → MC$_{6a}$	-2.79	7.29	-33.82	-1.13	9.52	-35.74
1 + 2a → TS$_{6a}$	23.34	37.91	-48.87	32.98	47.74	-49.51
1 + 2a → 6a	5.35	20.50	-50.82	9.38	23.95	-48.88

Table S2. Kinetic and thermodynamic parameters for 32CA reaction of **1** with 4-nitro-*trans*-β-nitrostyrene (**2c**) in different solvents, according to MPWB95/6-311G(d,p)(PCM) calculations (ΔH and ΔG are given in kcal/mol^{-1}; ΔS are given in cal/mol^{-1} K^{-1}).

Reaction step	Toluene (ε = 2.4)			Ethanol (ε = 24.8)		
	ΔH	**ΔG**	**ΔS**	**ΔH**	**ΔG**	**ΔS**
1 + 2c → MC$_{3c}$	-3.60	8.11	-39.27	-1.25	12.29	-45.40
1 + 2c → TS$_{3c}$	15.72	31.42	-52.69	24.11	39.49	-51.58
1 + 2c → 3c	-2.21	13.03	-51.09	0.44	15.14	-49.32
1 + 2c → MC$_{4c}$	-2.99	10.27	-44.46	-1.37	11.12	-41.90
1 + 2c → TS$_{4c}$	21.27	37.37	-53.98	29.48	45.94	-55.22
1 + 2c → 4c	4.37	19.74	-51.56	7.78	22.87	-50.19
1 + 2c → MC$_{5c}$	-5.52	5.89	-38.28	-2.35	9.73	-40.49
1 + 2c → TS$_{5c}$	19.49	34.78	-51.28	27.69	43.12	-51.75
1 + 2c → 5c	4.53	20.74	-54.36	7.38	23.00	-52.39
1 + 2c → MC$_{6c}$	-3.93	7.33	-37.74	-0.20	11.75	-40.10
1 + 2c → TS$_{6c}$	17.09	32.19	-50.66	25.42	40.42	-50.30
1 + 2c → 6c	-0.53	15.73	-54.55	2.51	18.72	-54.35

Table S3. Key parameters of the critical structures for 32CA reaction of **1** with 4-amino-*trans*-β-nitrostyrene (**2a**) in different solvent, according to MPWB95/6-311G(d,p)(PCM) calculations.

	Toluene (ε = 2.4)						Ethanol (ε = 24.8)					
		C3-C4		C5-O1	Δl	GEDT		C3-C4		C5-O1	Δl	GEDT
	r [Å]	l_{C3-C4}	r [Å]	l_{C5-O1}		[e]	r [Å]	l_{C3-C4}	r [Å]	l_{C5-O1}		[e]
MC_{3a}	3.658		3.007				1.825		2.052			
TS_{3a}	1.871	0.810	2.041	0.552	0.26	0.11	1.825	0.831	2.052	0.534	0.30	0.12
3a	1.572		1.410				1.561		1.400			
MC_{4a}	3.400		3.015				3.732		4.197			
TS_{4a}	1.807	0.860	2.010	0.539	0.32	0.06	1.759	0.890	1.989	0.555	0.34	0.07
4a	1.585		1.376				1.585		1.376			
MC_{5a}	5.170		3.325				2.054		1.752			
TS_{5a}	2.047	0.710	1.798	0.785	0.07	0.04	2.054	0.707	1.752	0.820	0.11	0.05
5a	1.587		1.480				1.588		1.485			
MC_{6a}	3.870		3.283				3.980		3.323			
TS_{6a}	2.087	0.660	1.825	0.755	0.10	0.08	2.109	0.649	1.750	0.808	0.16	0.12
6a	1.557		1.466				1.561		1.468			

Table S4. Key parameters of the critical structures for 32CA reaction of **1** with 4-nitro-*trans*-β-nitrostyrene (**2c**) in different solvent, according to MPWB95/6-311G(d,p)(PCM) calculations.

	Toluene (ε = 2.4)						Ethanol (ε = 24.8)					
		C3-C4		C5-O1	Δl	GEDT		C3-C4		C5-O1	Δl	GEDT
	r [Å]	l_{C3-C4}	r [Å]	l_{C5-O1}		[e]	r [Å]	l_{C3-C4}	r [Å]	l_{C5-O1}		[e]
MC_{3c}	3.181		2.681				3.143		2.743			
TS_{3c}	1.938	0.762	1.955	0.614	0.15	0.15	1.874	0.806	2.039	0.538	0.27	0.19
3c	1.566		1.411				1.569		1.395			
MC_{4c}	3.311		2.710				3.349		2.760			
TS_{4c}	2.174	0.632	1.618	0.823	0.19	0.16	2.177	0.630	1.591	0.843	0.21	0.19
4c	1.589		1.375				1.589		1.375			
MC_{5c}	5.135		3.255				5.049		3.300			
TS_{5c}	2.133	0.657	1.709	0.833	0.18	0.15	2.154	0.644	1.648	0.876	0.23	0.13
5c	1.588		1.464				1.589		1.466			
MC_{6c}	4.129		3.266				3.467		2.905			
TS_{6c}	2.054	0.682	1.850	0.733	0.05	0.15	2.120	0.641	1.737	0.811	0.17	0.15
6c	1.558		1.460				1.560		1.461			

Table S5. Thermochemistry and cartesian coordinates of **1** (MPWB95/6-311G(d,p)(PCM), toluene solution).

Zero-point correction =	0.240218 (Hartree/Particle)	**1**
Thermal correction to Energy =	0.254789 (Hartree/Particle)	
Thermal correction to Enthalpy =	0.255733 (Hartree/Particle)	
Thermal correction to Gibbs Free Energy =	0.198881 (Hartree/Particle)	
Sum of electronic and zero-point Energies =	-747.158793 (Hartree/Particle)	
Sum of electronic and thermal Energies =	-747.144222 (Hartree/Particle)	
Sum of electronic and thermal Enthalpies =	-747.143278 (Hartree/Particle)	
Sum of electronic and thermal Free Energies =	-747.200130 (Hartree/Particle)	

Center	Coordinates (Angstroms)		
	X	Y	Z
C	-0.56345	1.82796	-0.49869
C	-0.05063	0.48322	-0.24192
C	1.35985	0.31592	-0.13583
C	-0.90850	-0.64841	-0.17009
C	-0.34102	-1.95944	0.05549
C	1.91267	-1.00586	0.06440
C	1.04852	-2.10425	0.16702
C	-1.20902	-3.09326	0.12927
C	-2.32040	-0.55710	-0.36900
C	-3.12166	-1.67376	-0.30334
C	-2.56513	-2.95701	-0.04053
C	2.27010	1.41612	-0.18624
C	3.62958	1.22613	-0.08346
C	4.16967	-0.07772	0.09211
C	3.32915	-1.16204	0.17013
H	4.30087	2.08401	-0.12676
H	5.24843	-0.20983	0.17473
H	1.87717	2.42686	-0.29059
H	3.72795	-2.16679	0.31893
H	1.46871	-3.09934	0.32823
H	-3.21805	-3.82816	0.01430
H	-0.76480	-4.07300	0.31184
H	-2.76477	0.41560	-0.56755
H	-4.19671	-1.57771	-0.45800
N	-1.51466	2.42072	0.21432
H	-0.11128	2.45105	-1.26592
O	-2.12453	1.91126	1.21506
C	-1.94046	3.79925	-0.14983
H	-3.00254	3.75684	-0.41244
H	-1.35016	4.18498	-0.98551
H	-1.81155	4.42178	0.74109

Table S6. Thermochemistry and cartesian coordinates of **2b** (MPWB95/6-311G(d,p)(PCM), toluene solution).

Zero-point correction =	0.131686 (Hartree/Particle)	**2b**
Thermal correction to Energy =	0.141112 (Hartree/Particle)	
Thermal correction to Enthalpy =	0.142056 (Hartree/Particle)	
Thermal correction to Gibbs Free Energy =	0.095698 (Hartree/Particle)	
Sum of electronic and zero-point Energies =	-514.038792 (Hartree/Particle)	
Sum of electronic and thermal Energies =	-514.029366 (Hartree/Particle)	
Sum of electronic and thermal Enthalpies =	-514.028422 (Hartree/Particle)	
Sum of electronic and thermal Free Energies =	-514.074780 (Hartree/Particle)	

Center	Coordinates (Angstroms)		
	X	Y	Z
C	-1.60758	-0.47256	-0.00004
H	-1.53101	-1.55526	-0.00017
C	-0.60929	0.42949	0.00008
H	-0.91904	1.47798	0.00022
C	0.82054	0.16314	0.00004
C	1.70032	1.26542	0.00016
C	1.36939	-1.13797	-0.00012
C	3.08117	1.07854	0.00012
H	1.28483	2.27407	0.00029
C	2.74797	-1.32148	-0.00016
H	0.71072	-2.00655	-0.00021
C	3.60861	-0.21551	-0.00005
H	3.74707	1.94118	0.00021
H	3.15875	-2.33100	-0.00029
H	4.68812	-0.36635	-0.00008
O	-3.25284	1.18538	-0.00002
O	-3.85174	-0.93130	-0.00005
N	-2.99565	-0.02874	0.00006

Table S7. Thermochemistry and cartesian coordinates of $\mathbf{MC_{3b}}$ (MPWB95/6-311G(d,p)(PCM), toluene solution).

Zero-point correction =	0.398903 (Hartree/Particle)
Thermal correction to Energy =	0.399847 (Hartree/Particle)
Thermal correction to Enthalpy =	0.315137 (Hartree/Particle)
Thermal correction to Gibbs Free Energy =	-1261.202609 (Hartree/Particle)
Sum of electronic and zero-point Energies =	-1261.177047 (Hartree/Particle)
Sum of electronic and thermal Energies =	-1261.176102 (Hartree/Particle)
Sum of electronic and thermal Enthalpies =	-1261.260812 (Hartree/Particle)
Sum of electronic and thermal Free Energies =	-1261.260812 (Hartree/Particle)

MC_{3b}

Center	Coordinates (Angstroms)		
	X	Y	Z
C	-2.77431	-0.03711	0.52219
C	-3.45252	-0.65859	-0.46139
O	-1.51471	-1.03897	-2.56335
N	-0.42224	-1.17303	-1.91035
C	0.14181	-0.17082	-1.24102
C	0.19404	-2.52314	-2.01160
H	-0.45303	-3.22214	-1.47121
H	1.20642	-2.52765	-1.60043
H	0.19471	-2.76917	-3.07747
C	0.85582	-2.84919	2.12813
C	2.12066	-2.86343	2.77724
C	3.10049	-1.98796	2.37964
C	2.87913	-1.06850	1.30785
C	0.61049	-1.99295	1.07898
C	1.61307	-1.09192	0.60549
C	3.85225	-0.12975	0.94722
C	3.63495	0.79682	-0.08087
C	1.39720	-0.20249	-0.48674
C	2.39480	0.75997	-0.82389
C	4.62516	1.76704	-0.42348
C	4.42034	2.65850	-1.44806
C	3.21352	2.61063	-2.19721
C	2.23869	1.68489	-1.90143
H	0.06699	-3.52050	2.46836
H	2.30125	-3.55664	3.59887
H	4.06845	-1.96687	2.88326
H	-0.37200	-1.99790	0.60890
H	4.80101	-0.11095	1.48810
H	5.55318	1.78210	0.15043
H	5.18304	3.39578	-1.69875
H	3.06468	3.30708	-3.02272
H	1.33399	1.64418	-2.50751
H	-0.39005	0.77035	-1.38193
H	-1.21868	3.59492	2.90953
C	-1.91955	3.22900	2.15943
C	-1.92726	1.87781	1.81772
H	-1.23195	1.18823	2.29891
C	-2.82079	1.38219	0.84513
C	-3.71580	2.28481	0.23175
H	-4.42629	1.92536	-0.51271
C	-3.70955	3.63205	0.57912
H	-4.41021	4.31622	0.10054
C	-2.81120	4.11020	1.54208
N	-3.33296	-2.09151	-0.65137
O	-2.43995	-2.71660	-0.04325
O	-4.15423	-2.61908	-1.41367
H	-2.12076	-0.66114	1.13601
H	-4.15089	-0.21723	-1.16413
H	-2.81108	5.16663	1.81051

Table S8. Thermochemistry and cartesian coordinates of **MC_{4b}** (MPWB95/6-311G(d,p)(PCM), toluene solution).

	MC_{4b}
Zero-point correction =	0.399402 (Hartree/Particle)
Thermal correction to Energy =	0.400346 (Hartree/Particle)
Thermal correction to Enthalpy =	0.316805 (Hartree/Particle)
Thermal correction to Gibbs Free Energy =	-1261.200712 (Hartree/Particle)
Sum of electronic and zero-point Energies =	-1261.175268 (Hartree/Particle)
Sum of electronic and thermal Energies =	-1261.174324 (Hartree/Particle)
Sum of electronic and thermal Enthalpies =	-1261.257865 (Hartree/Particle)
Sum of electronic and thermal Free Energies =	-1261.257865 (Hartree/Particle)

Center	Coordinates (Angstroms)		
	X	Y	Z
C	-2.43689	-1.15988	-0.98485
C	-2.63586	-2.23581	-0.19991
O	-0.88909	-2.26267	1.94681
N	-0.04051	-1.31753	1.76894
C	0.60126	-1.12873	0.62044
C	0.20895	-0.48292	2.97290
H	-0.68640	0.11698	3.16863
H	1.07978	0.16237	2.83335
H	0.36218	-1.18775	3.79515
C	-0.46224	3.07821	0.88099
C	0.52084	4.08060	0.65442
C	1.79077	3.72050	0.27496
C	2.15595	2.34675	0.12672
C	-0.14320	1.74487	0.76687
C	1.17793	1.32251	0.42399
C	3.42830	1.97533	-0.32616
C	3.78366	0.63106	-0.50314
C	1.54381	-0.04953	0.32255
C	2.83459	-0.40540	-0.16468
C	5.07377	0.26042	-0.99158
C	5.42265	-1.06003	-1.13953
C	4.49896	-2.08175	-0.78877
C	3.24976	-1.76437	-0.30662
H	-1.48180	3.37032	1.13346
H	0.25550	5.13260	0.75990
H	2.54605	4.47990	0.06564
H	-0.92036	0.99417	0.90238
H	4.15852	2.75368	-0.55841
H	5.77827	1.05442	-1.24451
H	6.40927	-1.32971	-1.51643
H	4.78783	-3.12751	-0.89492
H	2.56481	-2.56243	-0.02201
H	0.40666	-1.91649	-0.10953
H	-5.26703	1.89382	1.12161
C	-4.62487	1.66194	0.27173
C	-3.97275	0.43390	0.21477
H	-4.10264	-0.28187	1.02689
C	-3.13640	0.11415	-0.87693
C	-2.96970	1.07226	-1.89719
H	-2.31736	0.84043	-2.74020
C	-3.62763	2.30008	-1.84000
H	-3.48941	3.02660	-2.64059
C	-4.45968	2.59840	-0.75720
H	-4.97482	3.55790	-0.71044
N	-1.91356	-3.47195	-0.44176
O	-0.94090	-3.47012	-1.22083
O	-2.33377	-4.47711	0.14837
H	-1.70204	-1.26675	-1.78623
H	-3.35035	-2.34064	0.60838

Table S9. Thermochemistry and cartesian coordinates of $\mathbf{MC_{5b}}$ (MPWB95/6-311G(d,p)(PCM), toluene solution).

Zero-point correction =	0.399121 (Hartree/Particle)	$\mathbf{MC_{5b}}$
Thermal correction to Energy =	0.400065 (Hartree/Particle)	
Thermal correction to Enthalpy =	0.314696 (Hartree/Particle)	
Thermal correction to Gibbs Free Energy =	-1261.206159 (Hartree/Particle)	
Sum of electronic and zero-point Energies =	-1261.180361 (Hartree/Particle)	
Sum of electronic and thermal Energies =	-1261.179417 (Hartree/Particle)	
Sum of electronic and thermal Enthalpies =	-1261.264786 (Hartree/Particle)	
Sum of electronic and thermal Free Energies =	-1261.264786 (Hartree/Particle)	

Center	Coordinates (Angstroms)		
	X	Y	Z
C	3.54551	-1.74510	-0.23530
C	3.47230	-0.47073	0.19896
O	1.09025	1.20853	1.83409
N	-0.07072	0.71628	1.58284
C	-0.79923	1.06647	0.53133
C	-0.56241	-0.24480	2.60423
H	0.03759	-1.15736	2.52904
H	-1.62273	-0.46497	2.45626
H	-0.38464	0.23509	3.57102
C	-1.21244	-3.16140	-0.31037
C	-2.47774	-3.70303	-0.66924
C	-3.56534	-2.87427	-0.80686
C	-3.45779	-1.46814	-0.57315
C	-1.07525	-1.81392	-0.06998
C	-2.18571	-0.92208	-0.15340
C	-4.54614	-0.60758	-0.76572
C	-4.43821	0.77490	-0.55997
C	-2.07299	0.47051	0.12120
C	-3.18639	1.32972	-0.09677
C	-5.54637	1.64919	-0.77866
C	-5.43975	3.00003	-0.55146
C	-4.21641	3.54546	-0.07533
C	-3.12862	2.73394	0.15421
H	-0.33584	-3.80524	-0.22667
H	-2.57545	-4.77334	-0.85127
H	-4.53532	-3.27361	-1.10800
H	-0.09261	-1.42053	0.18131
H	-5.50170	-1.02304	-1.09360
H	-6.48412	1.21619	-1.13078
H	-6.29279	3.65626	-0.72421
H	-4.14513	4.61571	0.11986
H	-2.20634	3.16297	0.54604
H	-0.35024	1.87463	-0.04725
H	7.17212	1.38847	-1.96087
C	6.26594	1.54017	-1.37450
C	5.49750	0.44565	-0.99294
H	5.81377	-0.55856	-1.27615
C	4.32574	0.62792	-0.22689
C	3.95378	1.93680	0.14902
H	3.04215	2.07178	0.73349
C	4.72615	3.03029	-0.24081
H	4.42732	4.03689	0.05170
C	5.88205	2.83574	-1.00181
H	6.48893	3.68992	-1.30289
N	2.60449	-2.74145	0.23537
O	2.62957	-3.84115	-0.34794
O	1.82431	-2.46419	1.16533
H	4.22055	-2.15150	-0.98230
H	2.68611	-0.22352	0.92101

Table S10. Thermochemistry and cartesian coordinates of $\mathbf{MC_{6b}}$ (MPWB95/6-311G(d,p)(PCM), toluene solution).

Zero-point correction =	0.400107 (Hartree/Particle)
Thermal correction to Energy =	0.315519 (Hartree/Particle)
Thermal correction to Enthalpy =	-1261.203485 (Hartree/Particle)
Thermal correction to Gibbs Free Energy =	-1261.177830 (Hartree/Particle)
Sum of electronic and zero-point Energies =	-1261.176886 (Hartree/Particle)
Sum of electronic and thermal Energies =	-1261.261474 (Hartree/Particle)
Sum of electronic and thermal Enthalpies =	-1261.261474 (Hartree/Particle)
Sum of electronic and thermal Free Energies =	-1261.261474 (Hartree/Particle)

MC_{6b}

Center	Coordinates (Angstroms)		
	X	Y	Z
C	2.13323	-2.27457	1.38619
C	2.43819	-1.61618	0.25148
O	0.98008	-1.31352	-2.65114
N	0.14010	-0.47732	-2.15094
C	-0.61462	-0.75084	-1.09366
C	0.04340	0.80835	-2.88868
H	0.96974	1.36960	-2.71949
H	-0.82252	1.38930	-2.56115
H	-0.03229	0.53965	-3.94621
C	0.65761	3.02879	0.63894
C	-0.29601	3.90975	1.21892
C	-1.61632	3.53828	1.28567
C	-2.05856	2.28322	0.76393
C	0.26609	1.82266	0.10522
C	-1.10193	1.41167	0.11573
C	-3.38973	1.86995	0.89633
C	-3.82584	0.62600	0.42090
C	-1.54084	0.17315	-0.43360
C	-2.89353	-0.23911	-0.26636
C	-5.17909	0.20054	0.58485
C	-5.60408	-1.01169	0.09797
C	-4.69476	-1.85669	-0.59491
C	-3.38474	-1.47769	-0.77983
H	1.71282	3.30406	0.62965
H	0.02847	4.86673	1.62765
H	-2.35547	4.19017	1.75419
H	1.01887	1.15329	-0.30732
H	-4.10418	2.52868	1.39498
H	-5.86947	0.86394	1.10832
H	-6.63873	-1.32708	0.23257
H	-5.04233	-2.81144	-0.98989
H	-2.70752	-2.12901	-1.33177
H	-0.50554	-1.77996	-0.74544
H	4.58383	1.56641	-2.31124
C	4.41230	1.16229	-1.31345
C	3.57498	0.05883	-1.14640
H	3.07565	-0.40046	-2.00197
C	3.34381	-0.47990	0.13824
C	3.97682	0.12035	1.24824
H	3.80806	-0.27119	2.25143
C	4.81149	1.21964	1.07579
H	5.29365	1.67393	1.94139
C	5.03277	1.74497	-0.20487
H	5.68865	2.60615	-0.33407
N	1.19881	-3.38669	1.37405
O	0.58557	-3.66750	0.32865
O	1.07086	-4.00174	2.44760
H	2.52679	-2.09605	2.38226
H	1.96317	-1.95713	-0.67627

Table S11. Thermochemistry and cartesian coordinates of $\mathbf{TS_{3b}}$ (MPWB95/6-311G(d,p)(PCM), toluene solution).

Zero-point correction =	0.398036 (Hartree/Particle)
Thermal correction to Energy =	0.398980 (Hartree/Particle)
Thermal correction to Enthalpy =	0.320634 (Hartree/Particle)
Thermal correction to Gibbs Free Energy =	-1261.169776 (Hartree/Particle)
Sum of electronic and zero-point Energies =	-1261.145775 (Hartree/Particle)
Sum of electronic and thermal Energies =	-1261.144831 (Hartree/Particle)
Sum of electronic and thermal Enthalpies =	-1261.223177 (Hartree/Particle)
Sum of electronic and thermal Free Energies =	-1261.223177 (Hartree/Particle)

TS_{3b}

Center	Coordinates (Angstroms)		
	X	Y	Z
C	-1.76059	0.39623	0.38576
C	-3.01607	0.38232	-0.30009
O	-2.34582	0.04704	-2.19305
N	-1.24119	-0.58193	-1.93751
C	-0.47891	0.06831	-0.9667
C	-1.11815	-1.98295	-2.37719
H	-1.87699	-2.61012	-1.9005
H	-0.1141	-2.34016	-2.13049
H	-1.25697	-1.99028	-3.46416
C	0.03558	-3.56482	1.44866
C	1.31311	-3.9131	1.96351
C	2.40114	-3.13423	1.65843
C	2.27098	-1.97556	0.83267
C	-0.13145	-2.45483	0.65197
C	0.97005	-1.60804	0.31087
C	3.38515	-1.18733	0.52841
C	3.28942	-0.06436	-0.30019
C	0.84364	-0.44938	-0.50584
C	2.00182	0.31233	-0.84585
C	4.44941	0.70622	-0.61807
C	4.37298	1.79016	-1.45587
C	3.12237	2.14504	-2.02741
C	1.98165	1.43252	-1.73643
H	-0.82829	-4.18719	1.68361
H	1.42318	-4.79598	2.59305
H	3.3927	-3.38505	2.03871
H	-1.12612	-2.23406	0.26943
H	4.35886	-1.46133	0.94068
H	5.40246	0.40329	-0.1815
H	5.26403	2.37073	-1.69398
H	3.06605	2.98965	-2.71438
H	1.05464	1.72242	-2.22638
H	-0.44273	1.12751	-1.22657
H	0.23482	2.933	3.75424
C	-0.25773	2.93046	2.78156
C	-0.68697	1.72245	2.22729
H	-0.52815	0.78645	2.76519
C	-1.3284	1.69736	0.97975
C	-1.51058	2.90858	0.28925
H	-1.98977	2.90362	-0.69276
C	-1.08368	4.11552	0.84406
H	-1.23782	5.04653	0.29803
C	-0.45701	4.1306	2.09407
H	-0.12187	5.07288	2.52762
N	-3.84023	-0.78809	-0.23945
O	-3.28814	-1.89109	0.00644
O	-5.05808	-0.65616	-0.45246
H	-1.62204	-0.45656	1.05312
H	-3.59225	1.27543	-0.51727

Table S12. Thermochemistry and cartesian coordinates of **TS_{4b}** (MPWB95/6-311G(d,p)(PCM), toluene solution).

Zero-point correction =	0.398274 (Hartree/Particle)
Thermal correction to Energy =	0.399218 (Hartree/Particle)
Thermal correction to Enthalpy =	0.320930 (Hartree/Particle)
Thermal correction to Gibbs Free Energy =	-1261.158930 (Hartree/Particle)
Sum of electronic and zero-point Energies =	-1261.135000 (Hartree/Particle)
Sum of electronic and thermal Energies =	-1261.134055 (Hartree/Particle)
Sum of electronic and thermal Enthalpies =	-1261.212343 (Hartree/Particle)
Sum of electronic and thermal Free Energies =	-1261.212343 (Hartree/Particle)

TS_{4b}

Center	Coordinates (Angstroms)		
	X	Y	Z
C	-1.66900	-0.90573	-0.61567
C	-2.38536	-1.93864	0.07468
O	-1.47934	-2.27951	1.61448
N	-0.57319	-1.31119	1.73306
C	0.01019	-1.03128	0.50961
C	-0.82886	-0.35680	2.80962
H	-1.74977	0.21796	2.62750
H	0.02471	0.32346	2.89755
H	-0.94317	-0.93246	3.73391
C	-0.15009	3.38734	0.92307
C	0.99674	4.17408	0.63559
C	2.16071	3.55529	0.25582
C	2.24252	2.13300	0.14660
C	-0.10604	2.01653	0.82542
C	1.07860	1.31924	0.43897
C	3.43103	1.51820	-0.25488
C	3.54481	0.12805	-0.35531
C	1.15861	-0.09786	0.32200
C	2.40099	-0.70614	-0.04993
C	4.78169	-0.47071	-0.74409
C	4.91943	-1.83363	-0.81431
C	3.81677	-2.66251	-0.48098
C	2.60720	-2.12190	-0.10918
H	-1.08292	3.87160	1.21285
H	0.94702	5.26016	0.71440
H	3.05465	4.13820	0.02746
H	-1.00843	1.45366	1.02829
H	4.29773	2.14017	-0.49092
H	5.61936	0.18884	-0.97702
H	5.86798	-2.28147	-1.11033
H	3.92971	-3.74642	-0.51076
H	1.80792	-2.80623	0.16477
H	0.17173	-1.98814	0.01148
H	-4.59269	2.55765	0.58572
C	-3.82834	2.19271	-0.10142
C	-3.28864	0.92028	0.08172
H	-3.63650	0.31397	0.92038
C	-2.29920	0.41996	-0.78898
C	-1.89489	1.23430	-1.86351
H	-1.13682	0.86023	-2.55378
C	-2.43611	2.50558	-2.04806
H	-2.10165	3.11754	-2.88620
C	-3.39976	2.99666	-1.16304
H	-3.82239	3.99130	-1.30496
N	-2.23732	-3.30215	-0.46832
O	-1.16021	-3.59002	-1.01900
O	-3.18527	-4.07747	-0.30588
H	-1.15620	-1.26653	-1.51008
H	-3.39625	-1.80029	0.44720

Table S13. Thermochemistry and cartesian coordinates of **TS_{5b}** (MPWB95/6-311G(d,p)(PCM), toluene solution).

Zero-point correction =	0.398253 (Hartree/Particle)
Thermal correction to Energy =	0.399197 (Hartree/Particle)
Thermal correction to Enthalpy =	0.319402 (Hartree/Particle)
Thermal correction to Gibbs Free Energy =	-1261.164554 (Hartree/Particle)
Sum of electronic and zero-point Energies =	-1261.140410 (Hartree/Particle)
Sum of electronic and thermal Energies =	-1261.139466 (Hartree/Particle)
Sum of electronic and thermal Enthalpies =	-1261.219261 (Hartree/Particle)
Sum of electronic and thermal Free Energies =	-1261.219261 (Hartree/Particle)

TS_{5b}

Center	Coordinates (Angstroms)		
	X	Y	Z
C	1.35277	-1.02369	-0.72311
C	2.49442	-1.00542	0.16874
O	1.95254	-0.32660	1.66849
N	0.60559	-0.35411	1.69607
C	0.07559	0.10279	0.52618
C	0.01940	-1.33328	2.61141
H	0.28461	-2.35306	2.30359
H	-1.06809	-1.20533	2.62125
H	0.42153	-1.13092	3.60973
C	-3.01088	-3.06006	-0.00566
C	-4.33743	-2.70253	-0.36472
C	-4.66338	-1.37796	-0.51159
C	-3.69145	-0.35161	-0.30403
C	-2.04782	-2.09971	0.19864
C	-2.33545	-0.70794	0.06600
C	-4.03391	0.99305	-0.47436
C	-3.11512	2.02272	-0.24578
C	-1.37266	0.32102	0.26446
C	-1.76559	1.69273	0.15682
C	-3.50181	3.39031	-0.38758
C	-2.62261	4.40853	-0.11465
C	-1.31366	4.09675	0.33749
C	-0.90183	2.78991	0.47321
H	-2.74426	-4.11143	0.10108
H	-5.08539	-3.47864	-0.52617
H	-5.67466	-1.07805	-0.79076
H	-1.04951	-2.42495	0.47077
H	-5.05042	1.24687	-0.78314
H	-4.52307	3.60421	-0.70690
H	-2.92817	5.44905	-0.22192
H	-0.62792	4.90366	0.59674
H	0.09237	2.60476	0.87494
H	0.68161	0.93558	0.17278
H	4.47542	2.88707	-1.52191
C	4.61013	1.92078	-1.03537
C	3.50122	1.11712	-0.77288
H	2.50886	1.46735	-1.06209
C	3.65386	-0.13407	-0.15050
C	4.94451	-0.55341	0.20919
H	5.07219	-1.52024	0.69839
C	6.05590	0.24890	-0.05465
H	7.05161	-0.09451	0.22660
C	5.89179	1.48853	-0.67821
H	6.75830	2.11626	-0.88675
N	0.79091	-2.31906	-0.99321
O	0.16049	-2.46765	-2.05514
O	0.91240	-3.22378	-0.12796
H	1.33820	-0.41792	-1.62603
H	2.77192	-2.00406	0.51227

Table S14. Thermochemistry and cartesian coordinates of $\mathbf{TS_{6b}}$ (MPWB95/6-311G(d,p)(PCM), toluene solution).

Zero-point correction =	0.398395 (Hartree/Particle)
Thermal correction to Energy =	0.399339 (Hartree/Particle)
Thermal correction to Enthalpy =	0.320455 (Hartree/Particle)
Thermal correction to Gibbs Free Energy =	-1261.167475 (Hartree/Particle)
Sum of electronic and zero-point Energies =	-1261.143480 (Hartree/Particle)
Sum of electronic and thermal Energies =	-1261.142536 (Hartree/Particle)
Sum of electronic and thermal Enthalpies =	-1261.221420 (Hartree/Particle)
Sum of electronic and thermal Free Energies =	-1261.221420 (Hartree/Particle)

TS_{6b}

Center	Coordinates (Angstroms)		
	X	Y	Z
C	1.15554	-0.92555	1.17719
C	2.26531	-1.42221	0.41138
O	1.60570	-1.80784	-1.19556
N	0.61392	-0.93441	-1.40850
C	-0.29042	-0.93817	-0.39313
C	0.90694	0.15557	-2.33972
H	1.74045	0.77341	-1.97842
H	0.00863	0.76789	-2.46864
H	1.18841	-0.29805	-3.29649
C	0.13052	3.36856	0.34223
C	-1.02233	4.18171	0.51132
C	-2.26989	3.61625	0.41853
C	-2.43205	2.22277	0.14904
C	0.01271	2.02185	0.08456
C	-1.26279	1.38852	-0.03192
C	-3.70769	1.65218	0.06977
C	-3.89354	0.29208	-0.20287
C	-1.42931	0.00047	-0.29310
C	-2.73854	-0.55609	-0.39897
C	-5.20491	-0.26539	-0.30199
C	-5.38826	-1.59305	-0.59879
C	-4.25931	-2.42562	-0.82240
C	-2.98075	-1.92537	-0.73026
H	1.12169	3.81633	0.41956
H	-0.91051	5.24586	0.71766
H	-3.16754	4.22200	0.55151
H	0.91667	1.43172	-0.04240
H	-4.58277	2.28809	0.22065
H	-6.05883	0.39453	-0.14140
H	-6.39257	-2.00953	-0.67349
H	-4.40799	-3.47505	-1.07697
H	-2.14439	-2.58952	-0.93824
H	-0.48514	-1.96297	-0.06847
H	6.24076	-0.64720	-1.85302
C	5.51489	-0.26268	-1.13600
C	4.39475	-1.02313	-0.81099
H	4.23299	-1.99085	-1.28567
C	3.43950	-0.55069	0.10969
C	3.65578	0.70082	0.71123
H	2.96335	1.07896	1.46339
C	4.77990	1.46528	0.38244
H	4.93204	2.43124	0.86474
C	5.71009	0.99066	-0.54362
H	6.58776	1.58642	-0.79473
N	0.50761	-1.85628	2.06757
O	0.48729	-3.06583	1.74325
O	-0.06668	-1.39516	3.07175
H	1.12727	0.07322	1.59933
H	2.51167	-2.46365	0.63041

Table S15. Thermochemistry and cartesian coordinates of **3b** (MPWB95/6-311G(d,p)(PCM), toluene solution).

Zero-point correction =	0.400452 (Hartree/Particle)
Thermal correction to Energy =	0.401396 (Hartree/Particle)
Thermal correction to Enthalpy =	0.321801 (Hartree/Particle)
Thermal correction to Gibbs Free Energy =	-1261.197259 (Hartree/Particle)
Sum of electronic and zero-point Energies =	-1261.173398 (Hartree/Particle)
Sum of electronic and thermal Energies =	-1261.172454 (Hartree/Particle)
Sum of electronic and thermal Enthalpies =	-1261.252049 (Hartree/Particle)
Sum of electronic and thermal Free Energies =	-1261.252049 (Hartree/Particle)

3b

Center	Coordinates (Angstroms)		
	X	Y	Z
C	-1.62804	0.12733	-0.04213
C	-2.67744	1.05961	-0.65851
O	-2.07422	1.82357	-1.68058
N	-0.68041	1.37666	-1.89745
C	-0.33290	0.82519	-0.57380
C	-0.66898	0.43246	-3.01921
H	-1.33668	-0.42984	-2.87987
H	0.36774	0.09371	-3.14499
H	-0.97237	0.97720	-3.92027
C	0.56562	-3.55904	-1.06044
C	1.80348	-4.06733	-0.58578
C	2.76942	-3.19031	-0.16169
C	2.54546	-1.77916	-0.16429
C	0.30104	-2.20837	-1.04742
C	1.25213	-1.25140	-0.56438
C	3.57384	-0.90485	0.20132
C	3.41470	0.48208	0.12898
C	1.02919	0.15082	-0.49340
C	2.12618	1.02418	-0.24057
C	4.49818	1.36655	0.41958
C	4.34736	2.72695	0.31802
C	3.09873	3.26693	-0.09408
C	2.02490	2.44816	-0.35850
H	-0.18135	-4.24586	-1.45929
H	1.98985	-5.14103	-0.58883
H	3.74460	-3.55176	0.16892
H	-0.63286	-1.87197	-1.48514
H	4.53321	-1.31743	0.52127
H	5.45479	0.93038	0.71171
H	5.18199	3.39391	0.53378
H	2.99473	4.34541	-0.21603
H	1.10261	2.88887	-0.73417
H	-0.25488	1.71337	0.07390
H	-1.60388	-2.37362	3.91332
C	-1.62847	-1.38276	3.45935
C	-1.63317	-1.25850	2.06817
H	-1.60934	-2.15226	1.44287
C	-1.66632	0.00591	1.46326
C	-1.69210	1.14586	2.28308
H	-1.71704	2.14134	1.83388
C	-1.68878	1.02339	3.67310
H	-1.71259	1.91837	4.29516
C	-1.65681	-0.24258	4.26580
H	-1.65509	-0.33851	5.35164
N	-3.86538	0.21848	-1.26030
O	-3.59985	-0.69454	-2.04752
O	-4.99620	0.56366	-0.91756
H	-1.77577	-0.86109	-0.48503
H	-3.19827	1.72658	0.03795

Table S16. Thermochemistry and cartesian coordinates of **4b** (MPWB95/6-311G(d,p)(PCM), toluene solution).

Zero-point correction =	0.400957 (Hartree/Particle)
Thermal correction to Energy =	0.401902 (Hartree/Particle)
Thermal correction to Enthalpy =	0.325153 (Hartree/Particle)
Thermal correction to Gibbs Free Energy =	-1261.186272 (Hartree/Particle)
Sum of electronic and zero-point Energies =	-1261.162785 (Hartree/Particle)
Sum of electronic and thermal Energies =	-1261.161841 (Hartree/Particle)
Sum of electronic and thermal Enthalpies =	-1261.238590 (Hartree/Particle)
Sum of electronic and thermal Free Energies =	-1261.238590 (Hartree/Particle)

4b

Center	Coordinates (Angstroms)		
	X	Y	Z
C	-1.27052	-1.10832	-0.53441
C	-1.75900	-2.39465	0.14690
O	-1.40924	-2.37570	1.47594
N	-0.18094	-1.52042	1.65501
C	0.07719	-0.98841	0.29034
C	-0.53139	-0.59592	2.73024
H	-1.48268	-0.06107	2.57936
H	0.28893	0.12723	2.82093
H	-0.59179	-1.17184	3.66150
C	-0.83970	3.38142	0.83488
C	0.10737	4.35360	0.41770
C	1.34466	3.94639	-0.01532
C	1.69545	2.56190	-0.06374
C	-0.54620	2.03944	0.77026
C	0.71264	1.55656	0.29907
C	2.98136	2.16846	-0.44757
C	3.37827	0.82873	-0.40464
C	1.05386	0.17893	0.20697
C	2.41333	-0.18531	-0.03459
C	4.72194	0.45115	-0.71201
C	5.13202	-0.85426	-0.61091
C	4.21292	-1.84503	-0.17128
C	2.90299	-1.52552	0.10357
H	-1.81242	3.69711	1.21311
H	-0.14349	5.41351	0.46054
H	2.09942	4.67618	-0.31309
H	-1.28907	1.32968	1.11027
H	3.70275	2.92968	-0.75299
H	5.41909	1.23458	-1.01388
H	6.16092	-1.13081	-0.84086
H	4.55352	-2.87151	-0.03466
H	2.25111	-2.30269	0.50153
H	0.63170	-1.80924	-0.18255
H	-5.09074	1.20721	0.98123
C	-4.30283	1.11685	0.23289
C	-3.35749	0.09461	0.34586
H	-3.40851	-0.59797	1.18893
C	-2.33355	-0.03759	-0.60681
C	-2.30410	0.85227	-1.69122
H	-1.52499	0.74441	-2.44773
C	-3.24463	1.87604	-1.80256
H	-3.20000	2.56326	-2.64757
C	-4.24346	2.01709	-0.83561
H	-4.98126	2.81508	-0.91982
N	-1.08054	-3.64006	-0.59208
O	-0.18912	-4.24597	-0.00541
O	-1.52089	-3.88580	-1.71665
H	-0.97565	-1.33612	-1.56690
H	-2.82928	-2.60425	0.04304

Table S17. Thermochemistry and cartesian coordinates of **5b** (MPWB95/6-311G(d,p)(PCM), toluene solution).

Zero-point correction =	0.400973 (Hartree/Particle)
Thermal correction to Energy =	0.401917 (Hartree/Particle)
Thermal correction to Enthalpy =	0.324443 (Hartree/Particle)
Thermal correction to Gibbs Free Energy =	-1261.186294 (Hartree/Particle)
Sum of electronic and zero-point Energies =	-1261.162895 (Hartree/Particle)
Sum of electronic and thermal Energies =	-1261.161951 (Hartree/Particle)
Sum of electronic and thermal Enthalpies =	-1261.239424 (Hartree/Particle)
Sum of electronic and thermal Free Energies =	-1261.239424 (Hartree/Particle)

5b

Center	Coordinates (Angstroms)		
	X	Y	Z
C	1.20305	-0.55015	-0.31966
C	2.39055	-0.45807	0.66536
O	1.94642	0.46089	1.72120
N	0.51151	0.32983	1.85646
C	0.09170	0.28427	0.44844
C	0.21287	-0.83960	2.68862
H	0.64089	-1.78085	2.30094
H	-0.87828	-0.93312	2.75672
H	0.61313	-0.64706	3.69007
C	-2.59854	-3.31863	0.20813
C	-3.90584	-3.18357	-0.32995
C	-4.37717	-1.93493	-0.64707
C	-3.57396	-0.76866	-0.45702
C	-1.78776	-2.22156	0.37698
C	-2.21261	-0.90188	0.03202
C	-4.09355	0.49974	-0.73051
C	-3.36339	1.66120	-0.46137
C	-1.40711	0.25993	0.17588
C	-2.00902	1.54679	0.03551
C	-3.93958	2.95265	-0.66461
C	-3.24932	4.09524	-0.34740
C	-1.94962	3.99204	0.21690
C	-1.35080	2.76676	0.39988
H	-2.23122	-4.30376	0.49568
H	-4.53086	-4.06511	-0.47119
H	-5.38786	-1.80164	-1.03621
H	-0.81248	-2.37061	0.82532
H	-5.10569	0.58572	-1.13200
H	-4.95310	3.00476	-1.06539
H	-3.70002	5.07583	-0.49956
H	-1.42569	4.89622	0.52782
H	-0.38762	2.73001	0.90665
H	0.41139	1.27060	0.08590
H	5.08086	3.01640	-0.94882
C	4.97778	1.94785	-0.75811
C	3.80539	1.45628	-0.18280
H	2.99850	2.13506	0.09381
C	3.66613	0.08437	0.07449
C	4.71772	-0.78468	-0.24503
H	4.61721	-1.85107	-0.03571
C	5.88808	-0.29225	-0.82770
H	6.70047	-0.97668	-1.07273
C	6.02055	1.07477	-1.08490
H	6.93623	1.46040	-1.53358
N	0.92251	-1.98289	-0.74926
O	0.35729	-2.10724	-1.83660
O	1.25737	-2.92364	-0.01466
H	1.39389	-0.06006	-1.27817
H	2.56020	-1.46123	1.08410

Table S18. Thermochemistry and cartesian coordinates of **6b** (MPWB95/6-311G(d,p)(PCM), toluene solution).

Zero-point correction =	0.400852 (Hartree/Particle)
Thermal correction to Energy =	0.401796 (Hartree/Particle)
Thermal correction to Enthalpy =	0.324063 (Hartree/Particle)
Thermal correction to Gibbs Free Energy =	-1261.194536 (Hartree/Particle)
Sum of electronic and zero-point Energies =	-1261.171053 (Hartree/Particle)
Sum of electronic and thermal Energies =	-1261.170109 (Hartree/Particle)
Sum of electronic and thermal Enthalpies =	-1261.247841 (Hartree/Particle)
Sum of electronic and thermal Free Energies =	-1261.247841 (Hartree/Particle)

6b

Center	Coordinates (Angstroms)		
	X	Y	Z
C	1.05163	-0.40484	0.82713
C	2.18161	-1.33080	0.32652
O	1.60976	-2.08125	-0.79439
N	0.44515	-1.36981	-1.28863
C	-0.15586	-0.88018	-0.03527
C	0.87162	-0.33719	-2.24006
H	1.62477	0.36090	-1.83371
H	-0.02001	0.22480	-2.54718
H	1.29386	-0.83933	-3.11752
C	-0.43864	3.59372	-0.36626
C	-1.69722	4.22777	-0.19324
C	-2.82635	3.45776	-0.07342
C	-2.75898	2.03095	-0.10010
C	-0.33116	2.22209	-0.37094
C	-1.47067	1.36934	-0.20905
C	-3.93052	1.27002	-0.03334
C	-3.90571	-0.12388	-0.13546
C	-1.42065	-0.05087	-0.18265
C	-2.63141	-0.80038	-0.23547
C	-5.11511	-0.88482	-0.13862
C	-5.09044	-2.25006	-0.27390
C	-3.84578	-2.91795	-0.42923
C	-2.65943	-2.22231	-0.40792
H	0.45521	4.20085	-0.51116
H	-1.76192	5.31548	-0.17885
H	-3.80893	3.92131	0.02873
H	0.64496	1.78984	-0.56484
H	-4.88959	1.78127	0.07499
H	-6.06057	-0.34873	-0.04166
H	-6.01810	-2.82217	-0.28026
H	-3.83172	-3.99765	-0.57932
H	-1.73055	-2.75991	-0.58988
H	-0.44476	-1.80065	0.49430
H	5.95426	-0.54476	-2.35558
C	5.39870	-0.28243	-1.45471
C	4.19341	-0.93120	-1.17371
H	3.80029	-1.69465	-1.84451
C	3.46670	-0.59929	-0.02331
C	3.97093	0.37699	0.84943
H	3.42374	0.63438	1.75947
C	5.17571	1.02371	0.56640
H	5.55438	1.78381	1.25001
C	5.89216	0.69693	-0.58836
H	6.83254	1.20145	-0.81069
N	0.76037	-0.64579	2.30252
O	0.45931	-1.79363	2.64484
O	0.84393	0.32847	3.05609
H	1.30740	0.65234	0.78038
H	2.38473	-2.09661	1.09082