Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary:

Table S1. Main geometrical parameters in angstrom and degree at the B3LYP/6-31G (d) level in the gas phase.

			Step 1						**Step 2**		
	H65–H66	C50–C54	C50–H65	C54–H66	H66C54C50H65		H65–H66	C49–C55	C49–H65	C55–H66	H65C49C55H66
R	0.74279	1.43964	25.49375	25.76662	0.25467	R	0.74279	1.44351	25.38136	25.48872	-1.16085
TS 1	1.48172	1.52634	1.26153	1.60926	3.14320	TS 2	1.57000	1.42000	1.45042	1.47036	2.14345
IM 1	2.29311	1.60819	1.09801	1.09697	0.05832	IM 2	2.28590	1.62380	1.09760	1.09700	3.47794
			Step 3						**Step 4**		
	H67–H68	C49–C55	C49–H67	C55–H68	H67C49C55H68		H67–H68	C50–C54	C50–H67	C54–H68	H67C50C54H68
IM 1	0.74280	1.37880	20.02462	20.72177	1.05596	IM 2	0.74279	1.38157	10.09701	10.01646	1.17080
TS 3	0.96856	1.57883	1.41007	1.96570	2.03237	TS 4	1.26289	1.52563	1.22591	2.46714	-0.07264
IM 3	2.27847	1.59807	1.09503	1.09894	9.73668	IM 3	2.27957	1.58871	1.09497	1.09894	-7.10548
			Step 5						**Step 6**		
	H69–H70	C46–C53	C46–H70	C53–H69	H69C53C46H70		H67–H68	C45–C52	C45–H67	C52–H68	H68C52C45H67
IM 3	0.74279	1.42439	12.04381	12.44833	1.27364	IM 4	0.74279	1.38043	19.71290	20.69387	2.96779
TS 5	0.84267	1.38862	1.90000	1.57323	0.78645	TS 6	1.10425	1.53704	1.34009	2.14189	-0.49322
IM 4	2.29768	1.60884	1.09811	1.09733	2.09042	IM 5	2.27904	1.59616	1.09517	1.09908	-9.82709
			Step 7						**Step 8**		
	H74–H73	C57–C58	C57–H73	C58–H74	H74C58C57H73		H72–H71	C56–C59	C56–H72	C59–H71	H71C59C56H72
IM 5	0.74279	1.36926	11.49898	12.14062	-3.47135	IM 6	0.74279	1.33625	12.55806	12.85920	2.80621
TS 7	2.06409	1.51082	1.13449	1.93176	-13.25617	TS 8	0.97000	1.36676	1.74435	1.94324	-4.20058
IM 6	2.17851	1.59148	1.09807	1.09392	-2.64271	P	2.16428	1.56457	1.09276	1.10704	-20.17012

Table S2. Main geometrical parameters in angstrom and degree at the B3LYP/6-31G (d) level in decalin.

	Step 1						Step 2				
	H65–H66	C50–C54	C50–H65	C54–H66	H66C54C50H65		H65–H66	C49–C55	C49–H65	C55–H66	H65C49C55H66
R	0.74293	1.43947	12.26726	12.47615	-1.62325	R	0.74293	1.44339	13.52460	14.83953	-2.25048
TS 1	1.57582	1.52501	1.16324	2.17197	3.00972	TS 2	0.98813	1.59153	1.58848	1.32030	-5.99214
IM 1	2.29160	1.60759	1.09761	1.09656	0.10524	IM 2	2.28590	1.62293	1.09707	1.09633	3.59291
	Step 3						**Step 4**				
	H67–H68	C49–C55	C49–H67	C55–H68	H67C49C55H68		H67–H68	C50–C54	C50–H67	C54–H68	H67C50C54H68
IM 1	0.74294	1.37877	12.00212	12.59872	1.60553	IM 2	0.74293	1.38195	10.10112	10.01716	1.19221
TS 3	1.12009	1.55326	1.28325	2.34962	2.68129	TS 4	1.41386	1.51789	1.18228	2.71785	-0.87758
IM 3	2.27868	1.59769	1.09442	1.09832	9.69548	IM 3	2.27810	1.58796	1.09439	1.09837	-7.07234
	Step 5						**Step 6**				
	H69–H70	C46–C53	C46–H70	C53–H69	H69C53C46H70		H67–H68	C45–C52	C45–H67	C52–H68	H68C52C45H67
IM 3	0.74293	1.42457	12.04385	12.44836	1.27315	IM 4	0.74293	1.38073	15.25130	15.05599	2.60435
TS 5	2.00458	1.51298	2.94785	1.13627	-31.70700	TS 6	1.32986	1.51933	1.21934	2.56764	-1.48768
IM 4	2.29659	1.60971	1.09786	1.09654	2.11869	IM 5	2.27917	1.59583	1.09469	1.09854	-9.79607
	Step 7						**Step 8**				
	H74–H73	C57–C58	C57–H73	C58–H74	H74C58C57H73		H72–H71	C56–C59	C56–H72	C59–H71	H71C59C56H72
IM 5	0.74293	1.36950	11.50045	12.14342	-3.47394	IM 6	0.74293	1.33630	12.56147	12.86253	-2.80722
TS 7	1.93675	1.48190	1.13117	2.49851	-1.96193	TS 8	0.97000	1.36676	1.74435	1.94324	-4.20058
IM 6	2.17896	1.59103	1.09750	1.09326	-2.64720	P	2.16461	1.56440	1.09215	1.10612	-20.24844

Table S3. Significant natural bond orbital interactions of the reactant, intermediates and TSs in gas phase and decalin within their second-order perturbation stabilization energies E(2) (kcal. mol^{-1})

Step 1

		E(2) in the gas phase		E(2) in decalin	
Donor	Acceptor	R	TS1	R	TS1
$\pi_{C50\text{-}C54}$	$\pi^*_{C26\text{-}C35}$	3.10	3.07	3.11	2.90
	$\sigma^*_{C50\text{-}H65}$	-------	0.82	-------	2.08
	$\pi^*_{C48\text{-}C54}$	1.64	1.43	1.64	1.01
	$\pi^*_{C49\text{-}C50}$	2.85	1.90	2.89	1.55
	$\pi^*_{C54\text{-}C57}$	2.89	2.66	2.90	1.77
$\sigma_{C50\text{-}H65}$	$\pi^*_{C26\text{-}C35}$	-------	5.46	-------	4.71
	$\sigma^*_{C50\text{-}H65}$	-------	0.63	-------	0.89
	$\pi^*_{C54\text{-}C57}$	-------	1.18	-------	0.71
	$\pi^*_{C49\text{-}C55}$	-------	6.99	-------	6.10
$\pi_{C54\text{-}C57}$	$\pi^*_{C50\text{-}C54}$	1.65	2.16	2.60	-------
$\pi_{C35\text{-}C50}$	$\pi^*_{C50\text{-}C54}$	1.64	1.21	1.65	1.09
	$\sigma^*_{C50\text{-}H65}$	-----	0.74	-------	0.71
$\pi_{C48\text{-}C54}$	$\pi^*_{C50\text{-}C54}$	1.59	1.27	1.59	1.17
$\pi_{C49\text{-}C50}$	$\sigma^*_{C50\text{-}H65}$	----	0.88	-------	1.89
$\sigma_{C54\text{-}H66}$	$\sigma^*_{C50\text{-}H65}$	------	2.06	-------	-------

Step 3

		E(2) in the gas phase		E(2) in decalin	
Donor	Acceptor	IM 1	TS3	IM 1	TS3
$\pi_{C34\text{-}C49}$	$\pi^*_{C49\text{-}C55}$	2.31	0.81	2.30	0.99
	$\sigma^*_{C50\text{-}H67}$	------	2.75	-------	-------
$\pi_{C42\text{-}C55}$	$\pi^*_{C49\text{-}C55}$	2.70	0.93	2.69	1.13
$\pi_{C49\text{-}C50}$	$\pi^*_{C49\text{-}C55}$	2.74	0.62	2.76	0.82
	$\sigma^*_{C50\text{-}H67}$	------	0.73	-------	0.77
$\pi_{C49\text{-}C55}$	$\pi^*_{C55\text{-}C58}$	3.45	1.84	3.45	2.23

Step 2

		E(2) in the gas phase		E(2) in decalin	
Donor	Acceptor	R	TS2	R	TS2
$\pi_{C34\text{-}C49}$	$\pi^*_{C49\text{-}C55}$	1.50	1.40	1.51	1.00
$\pi_{C42\text{-}C55}$	$\pi^*_{C49\text{-}C55}$	1.54	1.63	1.54	1.35
$\pi_{C49\text{-}C55}$	$\pi^*_{C49\text{-}C50}$	2.96	2.14	2.97	1.16
$\sigma_{C49\text{-}H65}$	$\pi^*_{C55\text{-}C58}$	-------	4.06	-------	-------
$\pi_{C55\text{-}C58}$	$\pi^*_{C49\text{-}C55}$	2.64	1.57	2.63	1.60
$\sigma_{C55\text{-}H66}$	$\pi^*_{C34\text{-}C49}$	-------	2.08	-------	0.58
	$\pi^*_{C49\text{-}C50}$	-------	2.77	-------	-------
	$\pi^*_{C57\text{-}C58}$	--------	4.44	-------	4.01

Step 4

		E(2) in the gas phase		E(2) in decalin	
Donor	Acceptor	IM 2	TS4	IM 2	TS4
$\pi_{C48\text{-}C54}$	$\pi^*_{C50\text{-}C54}$	2.46	1.37	2.45	1.35
	$\sigma^*_{C50\text{-}H65}$	-------	2.01	-------	1.80
$\pi_{C50\text{-}C54}$	$\pi^*_{C54\text{-}C57}$	3.25	2.11	3.26	2.26
	$\pi^*_{C35\text{-}C50}$	2.24	1.61	1.21	1.07
	$\pi^*_{C49\text{-}C50}$	2.08	0.64	2.08	0.60
$\pi_{C54\text{-}C57}$	$\pi^*_{C50\text{-}C54}$	3.34	1.99	3.37	2.05
$\sigma_{C50\text{-}H67}$	$\pi^*_{C26\text{-}C35}$	------	7.61	------	6.10
$\sigma^*_{C50\text{-}H67}$	RY^*_{H67}	-----	18.89	-----	19.38
$\sigma_{C50\text{-}H68}$	LP_{H68}	-----	11.69	-----	4.97
LP_{H68}	$\sigma^*_{C50\text{-}H67}$	------	66.81	------	44.26

Step 6

		E(2) in the gas phase		E(2) in decalin	
Donor	Acceptor	IM 4	TS 6	IM	TS 6

	$\pi^*_{C42-C55}$	2.23	0.75	2.22	1.07
$\sigma_{C50-H67}$	$\pi^*_{C49-C55}$	------	1.49	------	1.77
$\sigma_{C54-H68}$	$\pi^*_{C49-C50}$	-----	0.88	-----	0.85
$\pi_{C55-C58}$	$\pi^*_{C49-C55}$	3.25	1.40	3.25	1.76

Step5

		E(2) in the gas phase		E(2) in decalin	
Donor	Acceptor	IM 3	TS5	IM 3	TS5
$\pi_{C37-C46}$	$\pi^*_{C46-C53}$	1.75	0.67	1.76	1.33
$\pi_{C45-C46}$	$\pi^*_{C46-C53}$	2.74	1.50	2.74	2.13
$\pi_{C53-C56}$	$\pi^*_{C46-C53}$	2.86	2.07	2.86	1.35
CR_{C53}	RY^*_{C46}	1.24	2.47	------	0.80
CR_{C46}	$\pi^*_{C46-C53}$	0.77	1.21	------	------
$\pi_{C46-C53}$	$\sigma^*_{H69-H70}$	------	11.24	------	------
$\pi^*_{C46-C53}$	$\sigma^*_{H69-H70}$	------	17.26	------	------

Step 7

		E(2) in the gas phase		E(2) in decalin	
Donor	Acceptor	IM 5	TS 7	IM 5	TS 7
$\pi_{C54-C57}$	$\pi^*_{C57-C58}$	3.89	1.33	1.27	1.47
	$\sigma^*_{C57-H73}$	-----	0.64	------	1.65
$\pi_{C55-C58}$	$\pi^*_{C57-C58}$	4.02	0.99	4.02	1.84
	$\sigma^*_{C58-H74}$	-----	0.53	------	------
$\pi_{C56-C57}$	$\pi^*_{C57-C58}$	3.59	1.16	3.58	1.08
	$\sigma^*_{C57-H73}$	----	0.69	------	1.30
	$\sigma^*_{C58-H74}$	----	0.68	------	------
$\pi_{C57-C58}$	$\sigma^*_{C57-H73}$	----	1.04	------	1.19
$\sigma_{C58-H73}$	$\sigma^*_{C58-H74}$	-----	3.35	------	1.34
$\sigma_{C58-H74}$	$\sigma^*_{C58-H74}$	-----	2.89	------	------
$\pi^*_{C45-C52}$	3.39	2.02	3.40	4	2.14
$\pi_{C45-C46}$	$\pi^*_{C45-C52}$	2.68	0.95	2.69	0.97
	$\sigma^*_{H67-H68}$	-----	6.02	------	------
$\pi_{C43-C52}$	$\pi^*_{C45-C52}$	2.61	1.45	2.59	1.43
$\pi_{C45-C52}$	$\pi^*_{C43-C52}$	2.14	1.18	2.13	1.30
	$\pi^*_{C40-C45}$	1.98	1.24	1.97	1.04
	$\sigma^*_{H67-H68}$	-----	9.42	------	------
CR_{C52}	RY^*_{C45}	2.02	0.83	2.05	0.75
$\sigma_{H67-H68}$	LP_{C52}	-----	93.18	------	------
	$\pi^*_{C52-C59}$	-----	13.80	------	------

Step 8

		E(2) in the gas phase		E(2) in decalin	
Donor	Acceptor	IM 6	TS 8	IM 6	TS 8
$\pi_{C52-C59}$	$\pi^*_{C56-C59}$	4.61	3.73	4.59	3.72
$\pi_{C53-C56}$	$\pi^*_{C56-C59}$	4.91	2.36	4.88	2.36
$\pi_{C56-C57}$	$\pi^*_{C56-C59}$	3.29	1.62	3.30	1.63
CR_{C56}	$\pi^*_{C56-C59}$	1.58	1.16	1.58	1.15
CR_{C59}	RY^*_{C56}	2.52	1.60	2.52	1.57
	$\pi^*_{C56-C59}$	1.91	1.65	1.91	1.66
$\pi_{C56-C59}$	$\sigma^*_{H71-H72}$	-----	9.13	------	------
$\sigma_{H71-H72}$	$\pi^*_{C56-C59}$	-----	0.29	------	0.28
$\pi^*_{C56-C59}$	$\sigma^*_{H71-H72}$	-----	19.82	------	20.73

Table S5. Natural Electron Configuration of the reactant, intermediates and TSs in gas phase and decalin

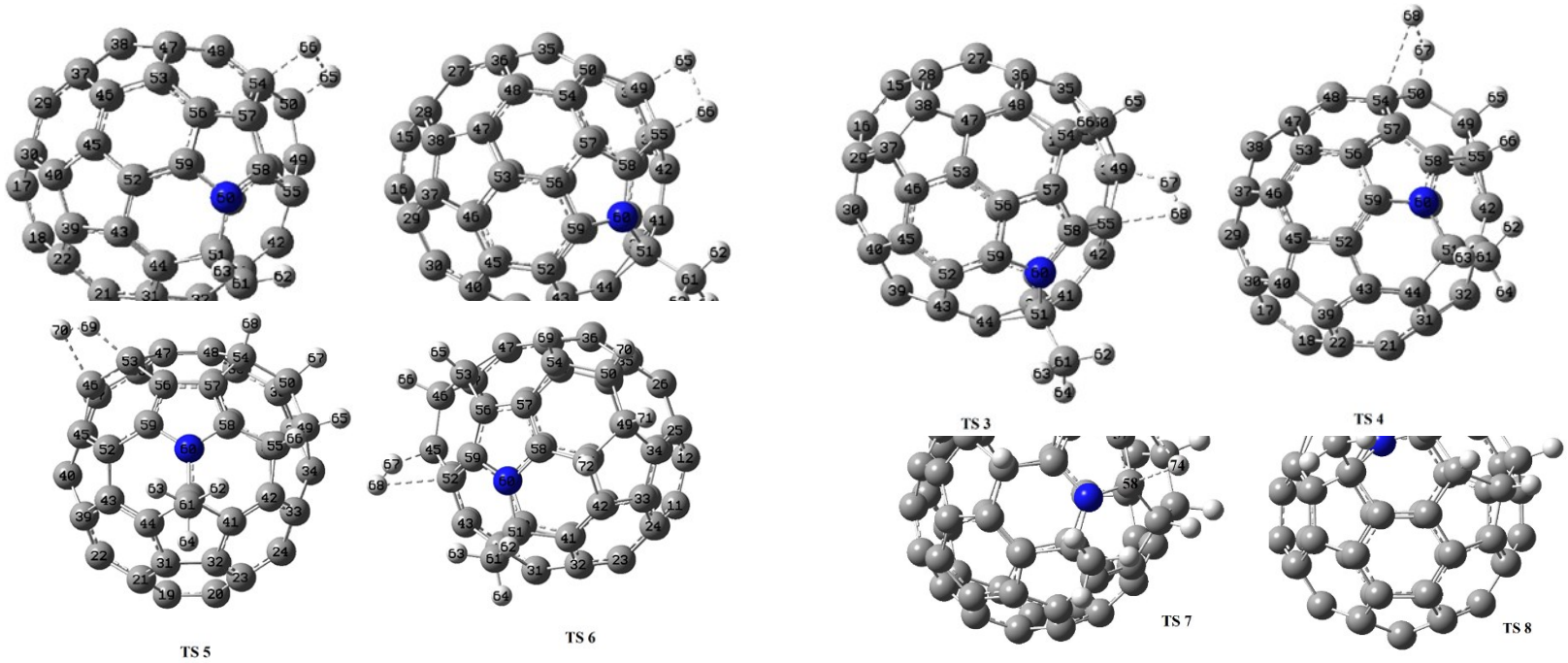
	GAS		DECALIN		GAS		DECALIN	
	R/ IM	TS	R/ IM	TS	R/ IM	TS	R/ IM	TS
Step 1	C50 [core]2s(0.86) 2p(3.15) 3p(0.01)	[core]2s(0.95) 2p(3.35) 3p(0.02)	[core]2s(0.86) 2p(3.15) 3p(0.01)	[core]2s(0.95) 2p(3.37) 3p(0.01)	Step 2 C49 [core]2s(0.87) 2p(3.11) 3p (0.01)	[core] 2s(0.95) 2p(3.26) 3p(0.02)	[core] 2s(0.87) 2p(3.11) 3p(0.01)	[core]2S(0.88) 2p(3.28) 3p(0.01)

TABLE S4. SELECTED PARTIAL CHARGES FROM THE NPA ANALYSIS OF THE REACTANTS AND TSS IN THE GAS PHASE AND DECALIN, RESPECTIVELY.

STEP 1									STEP 2								
	Gas				Decalin					Gas				Decalin			
	C50	C54	H65	H66	C50	C54	H65	H66		C49	C55	H65	H66	C49	C55	H65	H66
R	-0.027	0.011	0.000	-0.000	-0.029	0.010	0.000	-0.000	R	0.009	-0.066	0.000	-0.000	0.008	-0.066	0.0003	0.00
TS 1	-0.312	-0.096	0.330	-0.007	-0.331	0.110	0.326	-0.329	TS 2	-0.236	-0.248	0.202	0.215	-0.179	-0.245	0.436	0.261
Step 3									**Step 4**								
	Gas				Decalin					Gas				Decalin			
	C49	C55	H67	H68	C49	C55	H67	H68		C50	C54	H67	H68	C50	C54	H67	H68
IM 1	0.032	-0.049	0.000	0.000	0.034	-0.049	0.000	0.000	IM 2	-0.031	0.004	0.000	0.000	-0.032	0.004	-0.000	0.000
TS 3	-0.165	0.007	0.279	0.284	-0.260	0.114	0.193	-0.196	TS 4	-0.305	0.164	0.236	0.254	-0.318	0.172	0.275	-0.414
Step 5									**Step 6**								
	Gas				Decalin					Gas				Decalin			
	C46	C53	H69	H70	C46	C53	H69	H70		C52	C45	H67	H68	C52	C45	H67	H68
IM 3	-0.029	0.004	0.000	0.000	-0.031	0.002	0.000	-0.000	IM4	-0.023	-0.006	-0.000	0.000	-0.022	-0.008	0.000	0.000
TS 5	0.019	-0.134	0.053	-0.042	0.082	-0.301	0.297	-0.378	TS 6	0.153	-0.293	0.205	-0.195	0.188	-0.317	0.263	-0.416
Step 7									**Step 8**								
	Gas				Decalin					Gas				Decalin			
	C57	C58	H73	H74	C57	C58	H73	H74		C56	C59	H71	H72	C56	C59	H71	H72
IM 5	-0.087	0.168	0.000	0.000	-0.089	0.167	0.000	0.000	IM 6	-0.104	0.208	0.001	-0.001	-0.104	0.206	0.000	0.000
TS 7	-0.311	0.222	0.326	-0.204	-0.349	0.496	0.374	-0.753	TS 8	-0.231	0.298	0.172	0.098	-0.234	0.298	-0.176	0.098

	C54	[core]2s(0.87) 2p(3.11) 3p(0.01)	[core]2s(0.88) 2p(3.19) 3p(0.02)	[core]2s(0.87) 2p(3.11) 3p(0.01)	[core] 2s(0.88) 2p(3.00) 3p(0.01)
	H65	1s(1.00)	1S(0.67)	1s(1.00)	1S(0.67)2S(1.01)
	H66	1s(1.00)	1S(1.01)	1s(1.00)	1S(1.33)
Step 3	C49	[core]2s(0.87) 2p(3.08) 3p(0.01)	[core]2s(0.95) 2p(3.19) 3p(0.02)	[core]2s(0.87) 2p(3.08) 3p(0.01)	[core]2s(0.96) 2p(3.28) 3p(0.02)
	C55	[core]2s(0.87) 2p(3.17) 3p(0.01)	[core]2s(0.90) 2p(3.07) 3p(0.01)	[core]2s(0.87) 2p(3.17) 3p(0.01)	[core]2s(0.89) 2p(2.98) 3p(0.01)
	H67	1s(1.00)	1s(0.72)	1s(1.00)	1s(0.81)
	H68	1s(1.00)	1s(0.71)	1s(1.00)	1s(1.14)
Step 5	C53	[core]2s(0.86) 2p(3.11) 3p(0.01)	[core]2s(0.95) 2p(3.17) 3p(0.01)	[core]2s(0.87) 2p(3.15) 3p(0.01)	[core]2s(0.86) 2p(3.04) 3p(0.01)
	C46	[core]2s(0.87) 2p(3.15) 3p(0.01)	[core]2s(0.95) 2p(3.02) 3p(0.01)	[core]2s(0.87) 2p(3.12) 3p(0.01)	[core]2s(0.96) 2p(3.33) 3p(0.01)
	H69	1s(1.00)	1s(0.95)	1s(1.00)	1s(0.70)2s(0.01)
	H70	1s(1.00)	1s(1.04)	1s(1.00)	1s(1.38)
Step 7	C57	[core]2s(0.84) 2p(3.23) 3p(0.01)	[core]2s(0.95) 2p(3.35) 3p(0.01)	[core]2s(0.84) 2p(3.23) 3p(0.01)	[core]2s(0.95) 2p(3.38) 3p(0.01)
	C58	[core]2s(0.81) 2p(3.23)	[core]2s(0.89) 2p(2.86)	[core]2s(0.81) 2p(3.01) 3p(0.01)	[core]2s(0.83) 2p(2.65) 3p(0.02)
	C55	[core]2s(0.87) 2p(3.18) 3p (0.01)	[core]2s(0.96) 2p(3.27) 3p(0.02)	[core]2s(0.87) 2p(3.18) 3p(0.01)	[core]2S(0.95) 2p(3.27)3p (0.01) 3d(0.01)
	H65	1s(1.00)	1s(0.80)	1s(1.00)	1S(0.56)
	H66	1s(1.00)	1s(0.78)	1s(1.00)	1S(0.73) 2S(0.01)
Step 4	C50	[core]2s(0.86) 2p(3.15) 3p(0.01)	[core]2s(0.96) 2p(3.33) 3p(0.02)	[core]2s(0.86) 2p(3.15) 3p(0.01)	[core]2s(0.96) 2p(3.34) 3p(0.01)
	C54	[core]2s(0.87) 2p(3.11) 3p(0.01)	[core]2s(0.88) 2p(2.94) 3p(0.01)	[core]2s(0.87) 2p(3.11) 3p(0.01)	[core]2s(0.87) 2p(3.18) 3p(0.01)
	H67	1s(1.00)	1s(0.76)2s(0.01)	1s(1.00)	1s(0.72)2s(0.01)
	H68	1s(1.00)	1s(1.25)	1s(1.00)	1s(1.41)
Step 6	C45	[core]2s(0.87) 2p(3.12) 3p(0.01)	[core]2s(0.95) 2p(3.32) 3p(0.02)	[core]2s(0.87) 2p(3.13) 3p(0.01)	[core]2s(0.96) 2p(3.33) 3p(0.02)
	C52	[core]2s(0.87) 2p(3.14) 3p(0.01)	[core]2s(0.89) 2p(2.942) 3p(0.01)	[core]2s(0.87) 2p(3.14) 3p(0.01)	[core]2s(0.88) 2p(2.91) 3p(0.01)
	H67	1s(1.00)	1s(0.79)	1s(1.00)	1s(0.73)2s(0.01)
	H68	1s(1.00)	1s(1.19)	1s(1.00)	1s(1.42)
Step 8	C56	[core]2s(0.84) 2p(3.25) 3p(0.01)	[core]2s(0.94) 2p(3.27) 3p(0.02)	[core]2s(0.84) 2p(3.25) 3p(0.01)	[core]2s(0.94) 2p(3.28) 3p(0.02)
	C59	[core]2s(0.81) 2p(2.96)	[core]2s(0.81) 2p(2.87) 3p(0.01)	[core]2s(0.81) 2p(2.97) 3p(0.01)	[core]2s(0.81) 2p(2.87) 3p(0.01)

		3p(0.01)	3p(0.02) 3d(0.01)		3d(0.01)			3p(0.01) 3d(0.01)	3d(0.01)	3d(0.01)	3d(0.01)
	H69	1s(1.00)	1s(0.95)	1s(1.00)	1s(0.62)2s(0.01)		H71	1s(1.00)	1s(1.17)	1s(1.00)	1s(1.71)
	H70	1s(1.00)	1s(1.04)	1s(1.00)	1s(1.75)		H72	1s(1.00)	1s(0.90)	1s(1.00)	1s(0.90)



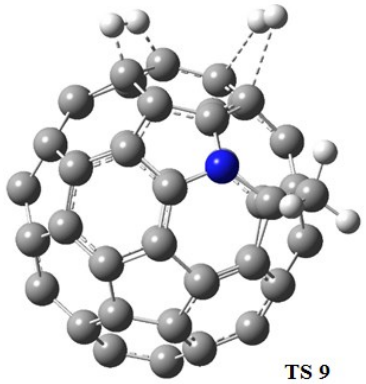


Figure S1. Optimized structures of the TSs in the hydrogen storage pathways in Scheme 1 for NEC doped fullerene in the gas phase.

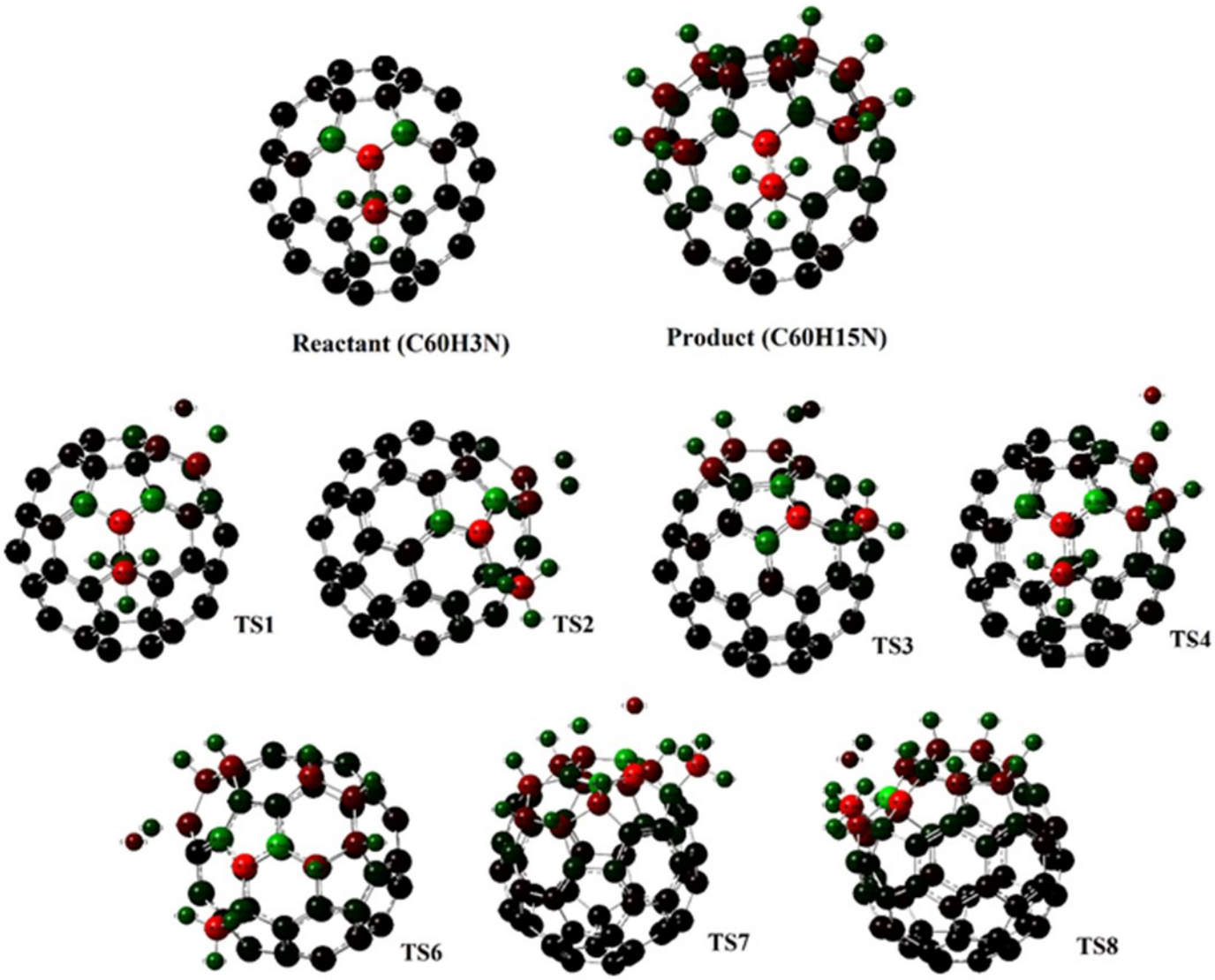


Figure S2. Mulliken analysis of the reactant, product and transition states in the gas phase (acceptor in red and donor in green color).

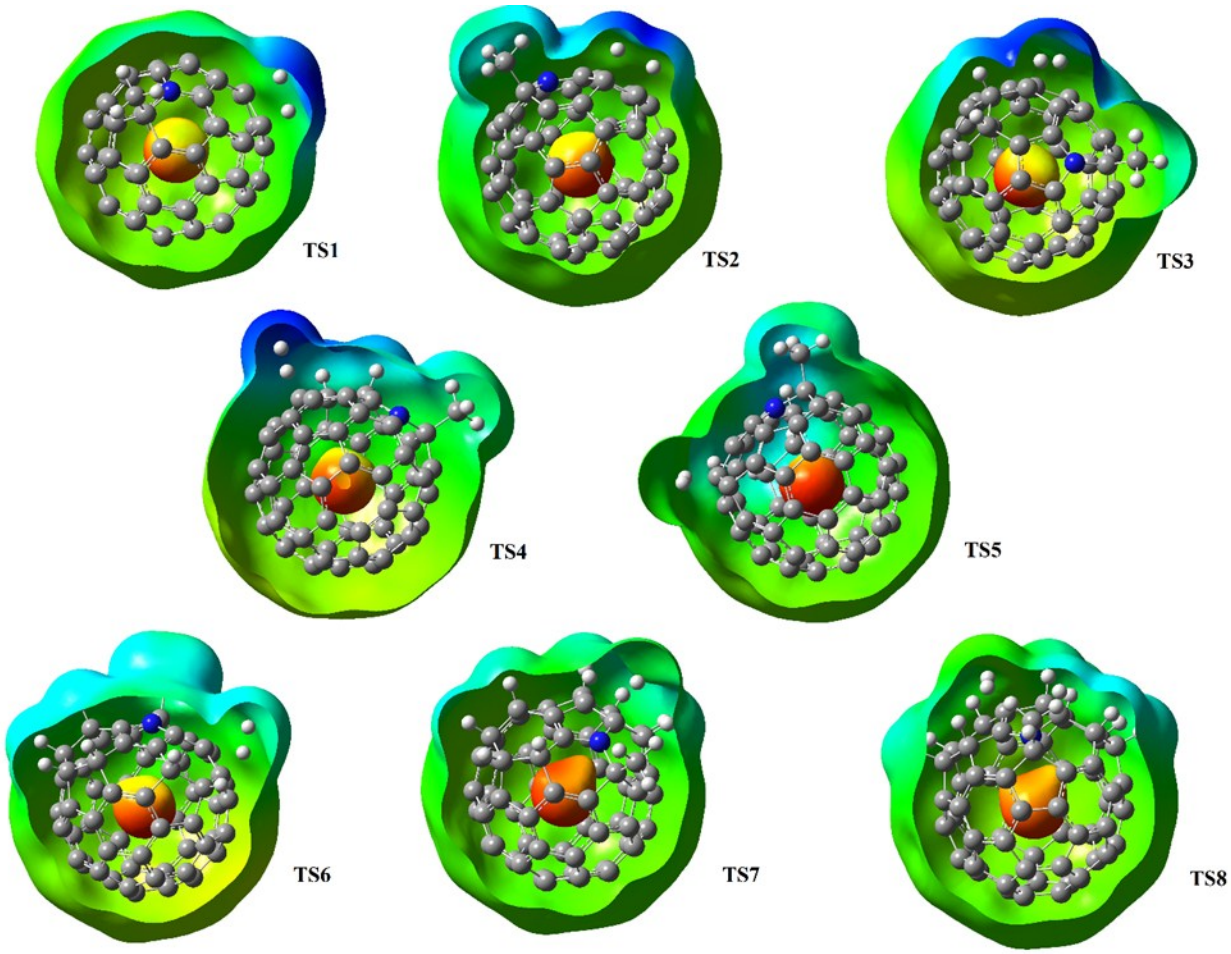


Figure S3. Electron density from total SCF density mapped with ESP of the reactant, product and transition states in the gas phase.