Supplementary Material for

Hydrogen-assisted isomerizations of fulvene to benzene and of larger cyclic aromatic hydrocarbons

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The C_6H_7 potential energy surface

The energies shown in Fig. 1 of the main text are tabulated in Table S1 and compared with another dual level calculation. The calculated M06-2x/6-311++G(d,p) geometries are tabulated in Table S2.

The $C_{10}H_9$ potential energy surface

The carbon atom labeling scheme used here is shown in Fig. S1. The $C_{10}H_9$ M06-2X/6-311++G(d,p) PES for the pathways discussed in Sec. 3.2 and illustrated in Fig. 4 is shown in detail in Fig. S2. H-additions and H-shifts are grouped by their parent $C_{10}H_8$ isomer, and the adducts are labeled by "*x*-", where *x* is the location of the additional H atom. The ring opening and closing processes associated with the cyclopropylcarbinyl radicals are indicated by dotted lines. H addition/loss channels are indicated by "-H" for parent each isomer. The four cyclopropylcarbinyl radicals are labeled CPC1, CPC2, CPC3, and CPC4 and are illustrated in Fig. S3.

Table S1. Zero-point-inclusive energies on the C_6H_7 potential energy surface (kcal/mol)

Species	Label	QCISD(T)/CBS// M06-2X/6-311++G(d,p)	QCISD(T)/CBS// B3LYP/6-311++G(d,p)
H + fulvene	R	0.00	0.00
methylcyclopentadienyl	MCP	-49.9	-49.8
tert-hydrofulvenyl	*t*-HF	-27.0	-27.1
α-hydrofulvenyl	α-HF	-48.8	-48.6
β-hydrofulvenyl	β-HF	-43.8[a]	
cyclopropylcarbinyl	CPC	-34.6	-34.4
cyclohexadienyl	CHD	-53.1	-52.9
H + benzene	P	-31.4	-31.3
H-addition/loss saddle points			
[R ⇄ MCP]‡		1.04	b
[R ⇄ *t*-HF]‡		4.93	4.61
[R ⇄ *a*-HF]‡		2.05	1.00
[R ⇄ *b*-HF]‡		2.24	1.45
[CHD ⇄ P]‡		-25.8	-25.9
H-shift saddle points			
[MCP ⇄ *t*-HF]‡		4.87	-2.88
[*t*-HF ⇄ *a*-HF]‡		-9.76	-9.66
[*a*-HF ⇄ *b*-HF]‡		-14.7	-14.4
cyclopropylcarbinyl saddle points			
[*t*-HF ⇄ CPC]‡		-19.9	-19.8
[CPC ⇄ CHD]‡		-16.6	-16.6

[a]The QCISD(T) method failed for this species and the M06-2X/6-311++G(d,p) energy is reported.

[b]This species could not be located at the B3LYP/6-311++G(d,p) level of theory.

Table S2. M06-2x/6-311++G(d,p) optimized geometries on the C_6H_7 potential energy surface (Å)

Species	Label	Atom	x, Å	y, Å	z, Å
fulvene + H	R	C	0.000000	1.178260	-0.126320
		C	0.000000	0.738173	-1.399106
		C	0.000000	-0.738173	-1.399106
		C	0.000000	-1.178260	-0.126320
		C	0.000000	0.000000	0.759294
		C	0.000000	0.000000	2.095938
		H	0.000000	2.202008	0.219144
		H	0.000000	1.350632	-2.290338
		H	0.000000	-1.350632	-2.290338
		H	0.000000	-2.202008	0.219144
		H	0.000000	0.927252	2.658058
		H	0.000000	-0.927252	2.658058
		H	inf	inf	inf
methylcyclopentadienyl	MCP	C	-0.026356	0.070517	0.038743
		C	-0.015674	0.018296	1.409697
		C	1.382318	-0.032760	1.863017
		C	2.183724	-0.010512	0.764683
		C	1.328267	0.053801	-0.405262
		C	1.803296	0.079773	-1.813642
		H	-0.891528	0.115070	-0.606118
		H	-0.878288	0.015210	2.061333
		H	1.697385	-0.078252	2.895751
		H	3.263605	-0.034644	0.740517
		H	0.980564	0.222162	-2.514102
		H	2.534930	0.879869	-1.960811
		H	2.309544	-0.859430	-2.061849
tert-hydrofulvenyl	*t*-HF	C	0.118266	1.175359	0.180042
		C	1.345403	0.765352	-0.174542
		C	1.385856	-0.705507	-0.162847
		C	0.181970	-1.177017	0.195126
		C	-0.763793	-0.028486	0.449103
		C	-1.975814	-0.053527	-0.427450
		H	-0.236537	2.193936	0.255938
		H	2.182557	1.401132	-0.431319
		H	2.257567	-1.297645	-0.408587
		H	-0.112707	-2.213464	0.285942
		H	-2.923832	0.332070	-0.078541
		H	-1.850324	-0.248391	-1.484507
		H	-1.068046	-0.024685	1.504487

α-hydrofulvenyl	α-HF	C	-0.113207	-1.190408	0.000027
		C	-1.498755	-0.610460	-0.000027
		C	-1.426830	0.753169	-0.000015
		C	-0.072332	1.176175	0.000031
		C	0.783200	0.038044	0.000024
		C	2.139759	0.026971	-0.000028
		H	0.069503	-1.816068	-0.880090
		H	-2.403933	-1.201231	-0.000053
		H	-2.278315	1.421010	-0.000047
		H	0.270936	2.201605	0.000034
		H	2.697207	-0.901677	-0.000065
		H	2.704143	0.951432	-0.000047
		H	0.069448	-1.816011	0.880199
β-hydrofulvenyl	β-HF	C	-0.049338	-1.138182	-0.000050
		C	-1.478057	-0.690371	0.000035
		C	-1.353965	0.812288	-0.000034
		C	-0.066626	1.172647	-0.000009
		C	0.800290	-0.027954	-0.000011
		C	2.180400	-0.020263	0.000022
		H	0.271397	-2.170680	-0.000112
		H	-2.028372	-1.053885	-0.877505
		H	-2.204734	1.480392	-0.000050
		H	0.316768	2.185059	0.000003
		H	2.742155	-0.945258	0.000008
		H	2.734631	0.909037	0.000062
		H	-2.028070	-1.053660	0.877871
cyclopropylcarbinyl	CPC	C	0.730793	-1.142675	-0.049400
		C	1.486923	-0.000004	0.184300
		C	0.730798	1.142675	-0.049400
		C	-0.651649	0.758816	-0.414908
		C	-0.651650	-0.758811	-0.414910
		C	-1.425787	0.000000	0.648197
		H	1.071862	-2.163130	0.051394
		H	2.513786	-0.000006	0.525222
		H	1.071867	2.163128	0.051405
		H	-1.220609	1.332945	-1.134546
		H	-2.504766	-0.000003	0.562389
		H	-1.028085	-0.000002	1.655402
		H	-1.220619	-1.332940	-1.134541
cyclohexadienyl	CHD	C	-1.445222	-0.000684	0.000013
		C	-0.622091	1.250880	-0.000008
		C	0.736695	1.224212	-0.000002

		C	1.452302	0.000706	0.000009
		C	0.737924	-1.223488	-0.000002
		C	-0.620818	-1.251512	-0.000009
		H	1.288722	2.157703	-0.000014
		H	-1.147881	2.199168	-0.000027
		H	-2.126341	-0.001011	-0.866473
		H	2.533915	0.001231	0.000017
		H	1.290853	-2.156458	-0.000012
		H	-1.145703	-2.200304	-0.000028
		H	-2.126306	-0.001011	0.866528
benzene + H	P	C	0.000000	1.391353	0.000000
		C	-1.205203	0.695788	0.000000
		C	-1.205203	-0.695788	0.000000
		C	0.000000	-1.391353	0.000000
		C	1.205203	-0.695788	0.000000
		C	1.205203	0.695788	0.000000
		H	-2.143452	-1.238017	0.000000
		H	-2.143452	1.238017	0.000000
		H	0.000000	2.474972	0.000000
		H	0.000000	-2.474972	0.000000
		H	2.143452	-1.238017	0.000000
		H	2.143452	1.238017	0.000000
		H	inf	inf	inf
H-addition/loss saddle points					
[R ⇄ MCP]‡		C	-0.190110	-1.177551	-0.036954
		C	-1.461170	-0.738192	0.049602
		C	-1.461170	0.738192	0.049602
		C	-0.190110	1.177551	-0.036954
		C	0.689181	0.000000	-0.098958
		C	2.030646	0.000000	-0.181664
		H	0.156212	-2.200748	-0.058850
		H	-2.350339	-1.350696	0.108431
		H	-2.350339	1.350696	0.108431
		H	0.156212	2.200748	-0.058850
		H	2.589270	-0.926724	-0.251695
		H	2.589270	0.926724	-0.251695
		H	2.706106	0.000000	1.936178
[R ⇄ *t*-HF]‡		C	0.143080	1.179834	0.023506
		C	1.410955	0.734577	-0.078129
		C	1.410955	-0.734577	-0.078129
		C	0.143080	-1.179834	0.023505
		C	-0.750358	0.000000	0.068503

	C	-2.083176	0.000000	-0.165402
	H	-0.203214	2.202955	0.044980
	H	2.299390	1.347233	-0.144292
	H	2.299390	-1.347233	-0.144292
	H	-0.203214	-2.202955	0.044980
	H	-2.636563	0.928011	-0.246002
	H	-2.636563	-0.928011	-0.246002
	H	-0.566445	0.000000	1.927506
[R ⇄ α-HF]‡	C	-0.125894	-1.146087	-0.086333
	C	-1.407002	-0.695444	-0.123424
	C	-1.403057	0.764589	-0.001948
	C	-0.127503	1.203654	0.063861
	C	0.761989	0.036393	-0.023610
	C	2.096944	0.039399	-0.076617
	H	0.218858	-2.159626	-0.231786
	H	-2.296232	-1.304887	-0.202502
	H	-2.292951	1.378176	0.027793
	H	0.214016	2.224473	0.156431
	H	2.658367	-0.885602	-0.146325
	H	2.658007	0.966673	-0.047947
	H	0.067067	-1.434226	1.932754
[R ⇄ β-HF]‡	C	-0.109310	-1.154332	-0.101329
	C	-1.380143	-0.674859	-0.114256
	C	-1.329000	0.805614	-0.077933
	C	-0.044294	1.195891	-0.010788
	C	0.803240	-0.010454	-0.011278
	C	2.140502	-0.050836	0.056996
	H	0.202986	-2.187826	-0.139112
	H	-2.280493	-1.253183	-0.268653
	H	-2.200954	1.444714	-0.085371
	H	0.334770	2.206182	0.045375
	H	2.675869	-0.993515	0.053616
	H	2.727114	0.859102	0.115421
	H	-1.945256	-0.741617	1.830247
[CHD ⇄ P]‡	C	1.357036	-0.002007	-0.064722
	C	0.642437	-1.215536	-0.095124
	C	-0.739619	-1.207260	-0.004153
	C	-1.432301	0.002083	0.058186
	C	-0.735930	1.209387	-0.004371
	C	0.646164	1.213584	-0.095198
	H	-1.285961	-2.143074	0.006460
	H	1.182215	-2.153383	-0.147649

	H	2.420819	-0.003482	-0.271978
	H	-2.513208	0.003637	0.131306
	H	-1.279661	2.146699	0.006291
	H	1.188509	2.149982	-0.147146
	H	1.860560	-0.001883	1.655005

H-shift saddle points

[MCP ⇄ *t*-HF]‡

C	-0.021484	-0.172094	1.172216
C	-0.021484	-1.457961	0.726171
C	-0.021484	-1.457961	-0.726171
C	-0.021484	-0.172094	-1.172216
C	-0.017128	0.700411	0.000000
C	0.202964	2.154443	0.000000
H	-0.019762	0.173402	2.195868
H	-0.029870	-2.343663	1.345732
H	-0.029870	-2.343663	-1.345732
H	-0.019762	0.173402	-2.195868
H	0.256726	2.688131	0.937167
H	0.256726	2.688131	-0.937167
H	-1.013581	1.395792	0.000000

[*t*-HF ⇄ α-HF]‡

C	-0.124603	1.165305	0.038246
C	-1.428996	0.731052	-0.055438
C	-1.466920	-0.684032	-0.071846
C	-0.164971	-1.161039	-0.002640
C	0.746614	0.020410	0.079345
C	2.170061	0.008097	-0.110949
H	0.220908	2.187620	0.086676
H	-2.301059	1.370559	-0.056939
H	-2.355564	-1.297277	-0.083252
H	0.189202	-2.180845	-0.039750
H	2.715421	0.939502	-0.145597
H	2.719077	-0.921727	-0.153315
H	0.424912	-0.576592	1.131858

[*a*-HF ⇄ β-HF]‡

C	-0.073866	-1.132736	-0.049257
C	-1.471289	-0.648575	-0.033305
C	-1.407095	0.770486	-0.015798
C	-0.081569	1.154888	-0.011006
C	0.775453	0.009687	-0.021774
C	2.177782	-0.000882	0.007166
H	0.215655	-2.166184	-0.169697
H	-2.334985	-1.274942	-0.198220
H	-2.266337	1.423032	0.022589
H	0.277028	2.173485	0.054129

	H	2.729791	-0.930632	0.009259
	H	2.736364	0.924713	0.009499
	H	-0.874012	-1.066677	1.016285
cyclopropylcarbinyl saddle points				
[*t*-HF ⇄ CPC]‡	C	0.482788	-1.193412	-0.163621
	C	1.452337	-0.329177	0.222807
	C	0.980252	1.030111	0.095794
	C	-0.304695	1.003304	-0.401137
	C	-0.740084	-0.422454	-0.537194
	C	-1.617651	-0.124485	0.644128
	H	0.532930	-2.272828	-0.153928
	H	2.427355	-0.607899	0.600356
	H	1.533898	1.915593	0.373434
	H	-0.910310	1.847159	-0.694501
	H	-2.604511	0.293606	0.503619
	H	-1.218889	-0.237523	1.641320
	H	-1.278153	-0.721428	-1.434962
[CPC ⇄ CHD]‡	C	0.820817	-1.114884	-0.061803
	C	1.448979	0.052809	0.229448
	C	0.634750	1.208228	-0.072398
	C	-0.721932	0.985236	-0.223965
	C	-0.599796	-0.976585	-0.391830
	C	-1.397117	-0.155710	0.520785
	H	1.307667	-2.082886	-0.069421
	H	2.484698	0.122782	0.533133
	H	1.082588	2.154377	-0.352298
	H	-1.349500	1.661061	-0.792237
	H	-2.470693	-0.179292	0.362089
	H	-1.124093	-0.218403	1.575523
	H	-1.044874	-1.452201	-1.258216

Figure S1

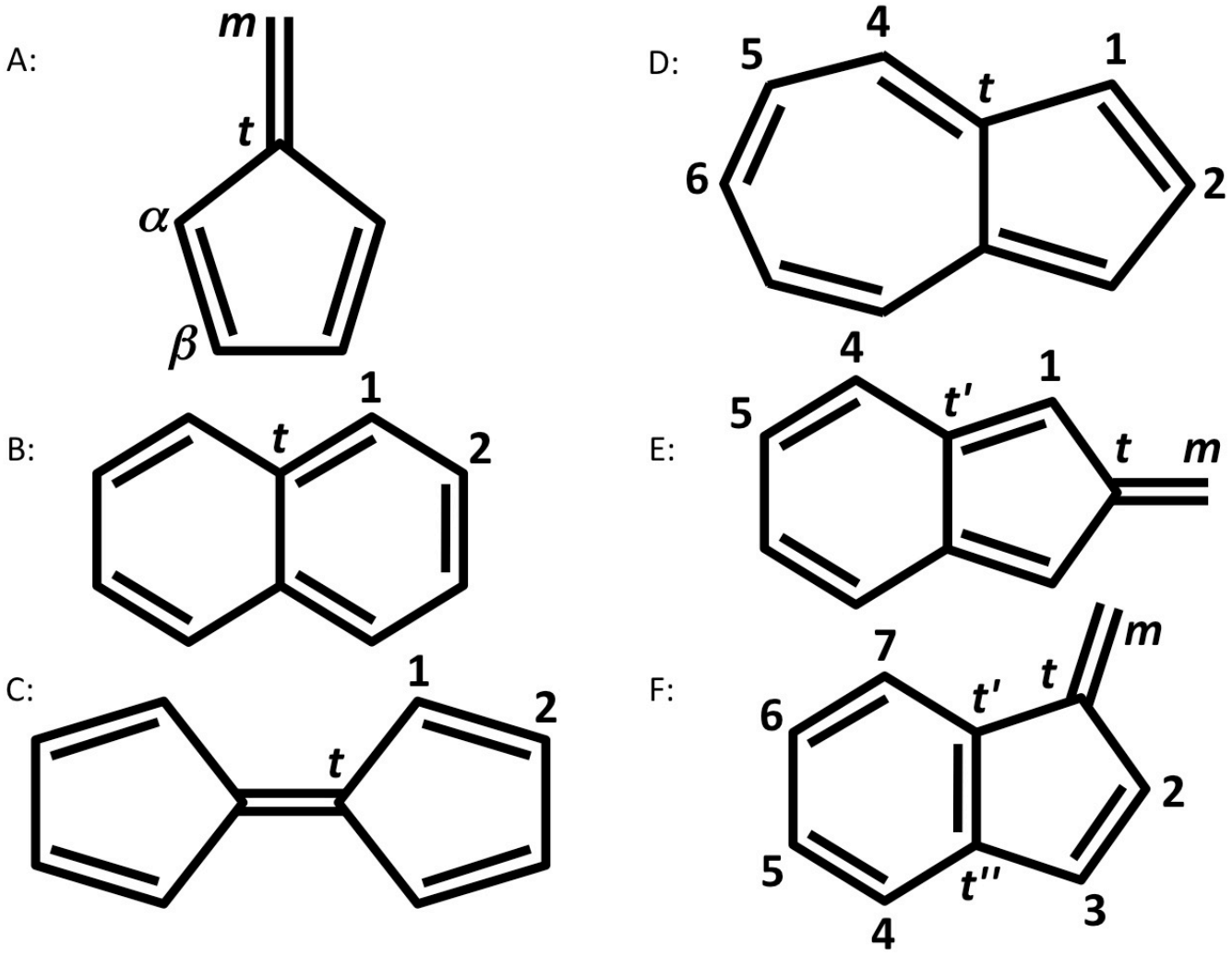

Fig. S1. Carbon atom labeling scheme for (A) fulvene, (B) naphthalene, (C) fulvalene, (D) azulene, (E) 2-methyleneindene, and (F) 1-methyleneindene.

Figure S2(a)

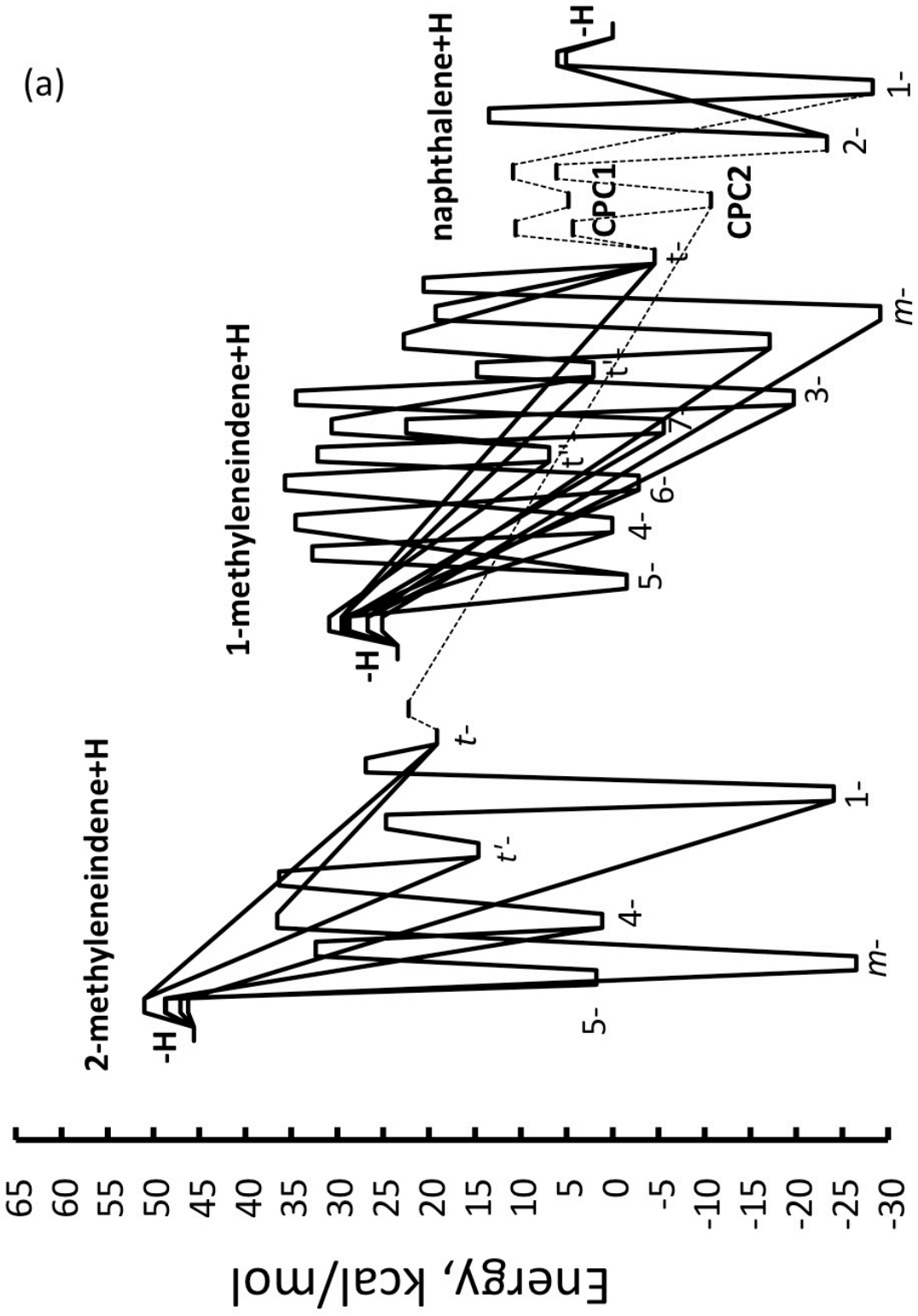
(a)
2-methylenein dene+H
1-methylenein dene+H
naphthalene+H
-H
-H
-H
CPC1
CPC2
Energy, kcal/mol
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
1-
2-
3-
4-
5-
6-
7-
m-
t-
t'-
t''-

Figure S2(b)

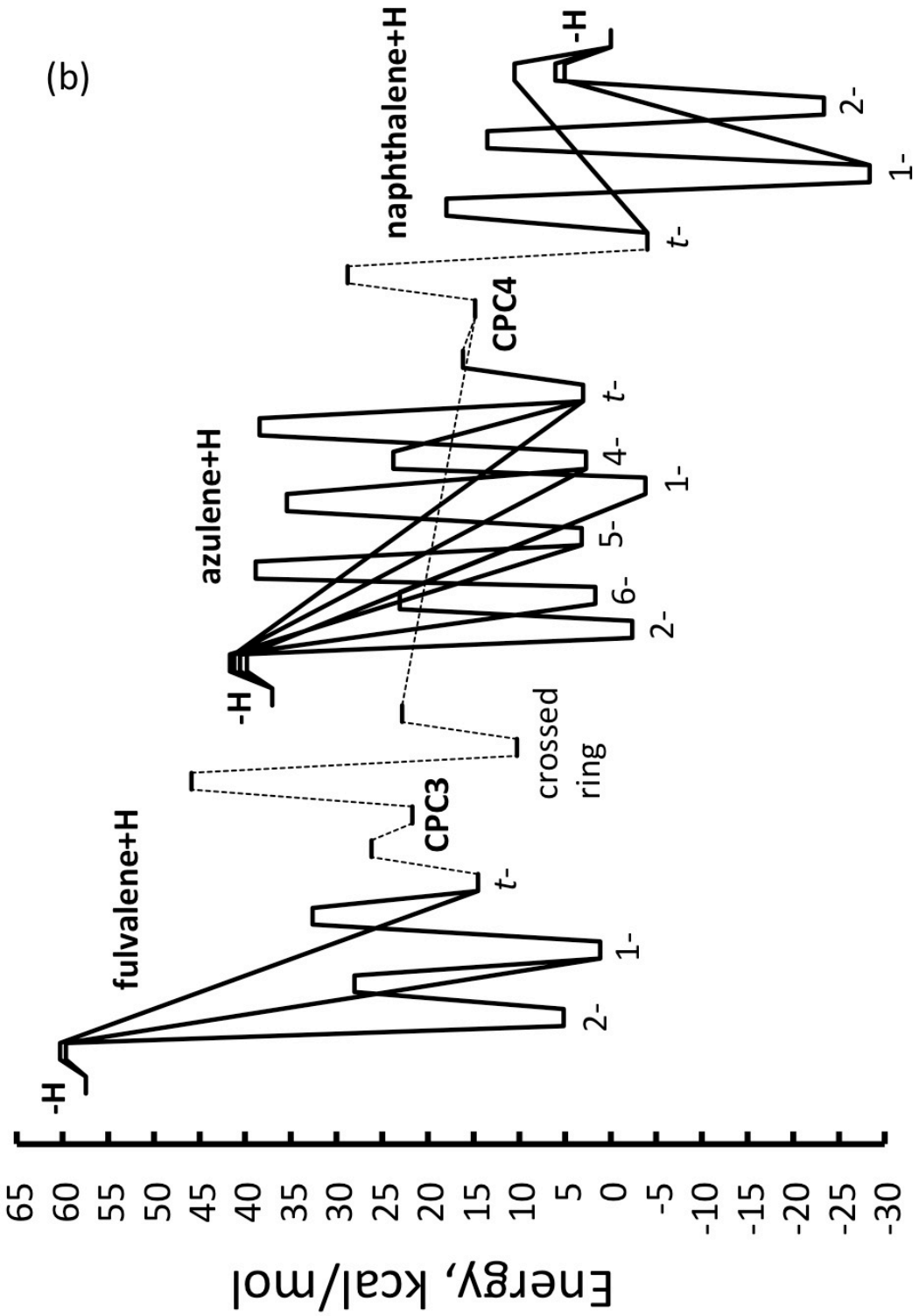

Fig. S2. Potential energy diagram for the $C_{10}H_9$ species discussed in Sec. 3.2 and for the H-assisted isomerization pathways shown schematically in Fig. 4. The figure is broken into two parts: (a) 1-methyleneindene and 2-methyleneindene + H and (b) fulvalene and azulene + H.

Figure S3

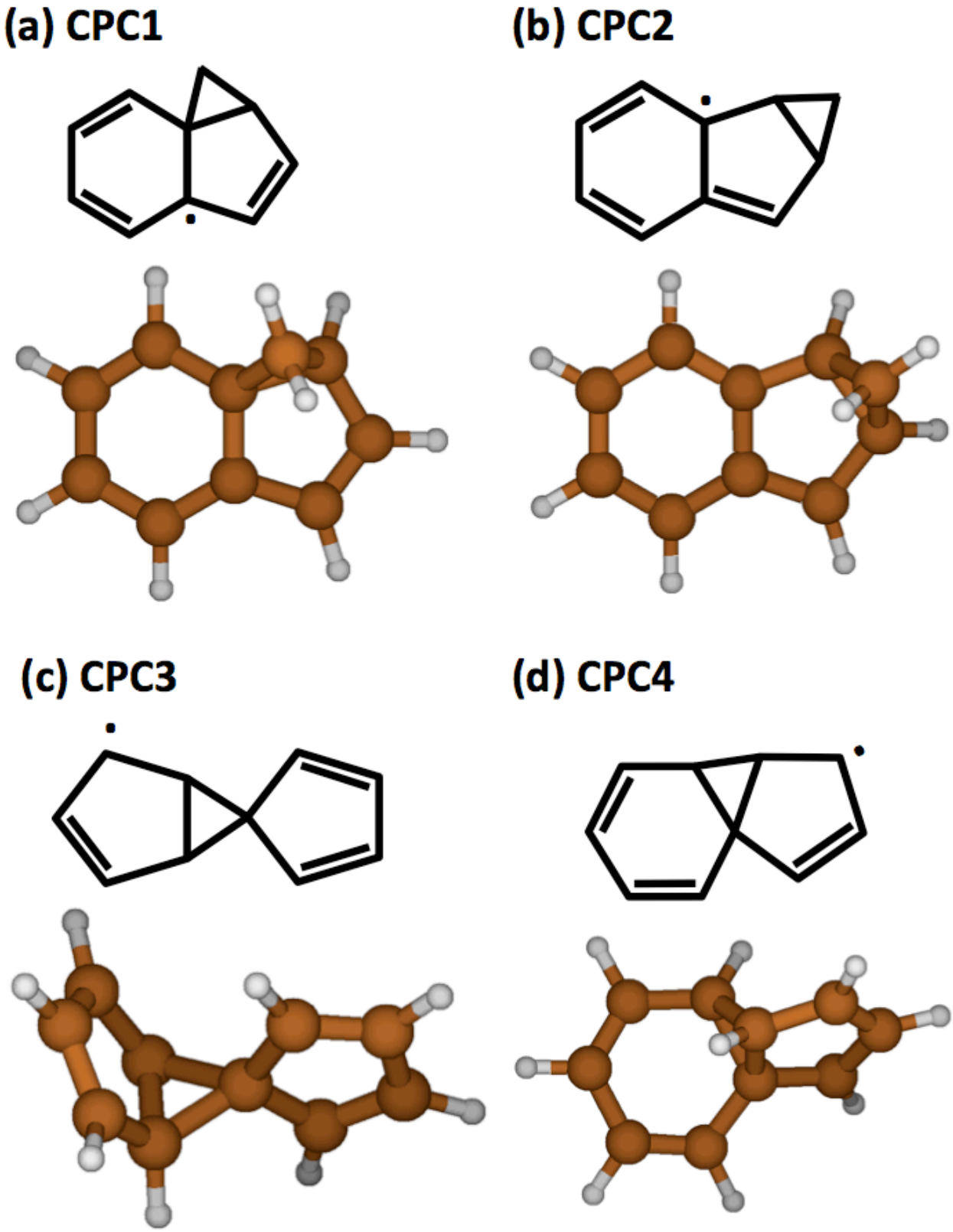

Fig S3. Line drawings and illustrations of the $C_{10}H_9$ cyclopropylcarbinyl intermediates.