Table S1. Total Molecular Energies at the CCSD(T) Level Extrapolated to the Complete Basis Set (CBS) limit, Zero Point Energy Corrections (ZPE), Rotational Constants, Molecular Geometries, and Vibrational Frequencies of all Stationary Points.

Isomer Structure	Total Energy (Hartrees)	ZPE correction (Hartrees)	Rotational Constants (GHz)	Cartesian Coordinates (x,y,z in Å)	Vibrational Frequencies (cm^{-1})
si2	-230.44508	0.070250	8.15424 2.93840 2.37990	C,0,-1.4796355904,-0.3848481143,0.0328639941 C,0,-0.0207946909,-0.5287482096,0.3791831748 C,0,0.9738460429,-0.5033308133,-0.6443261566 C,0,1.8132289351,-0.5309003993,-1.5040478759 C,0,-0.907557378,0.7909462619,0.6707199769 C,0,-0.1908834137,1.6380918323,1.2962692444 H,0,-1.7193793144,-0.3022376186,-1.0224820925 H,0,-2.186498975,-0.9604470141,0.6230779036 H,0,0.2192321404,-1.0832858892,1.2780377957 H,0,2.5574227193,-0.5412928242,-2.2626077534	120.6186 166.6915 203.6193 276.3801 485.1270 522.2237 662.6969 684.3489 708.0272 779.8948 897.9912 967.7392 1050.7384 1107.1475 1111.9102 1154.8598 1357.7972 1474.4163 1934.8421 2221.7397 3105.3897 3175.7622 3191.0834 3475.3035
si3	-230.37893	0.066260	6.92648 2.57195 1.89725	C,0,-0.7799018709,-0.9951792613,-0.0378814391 C,0,0.6782996027,-1.0464214372,-0.1369009341 C,0,1.4784223564,0.0649987967,-0.0170202598 C,0,2.1364218384,1.0819479921,0.0658759901 C,0,-1.5458736929,0.1996369352,0.0100702302 C,0,-2.2650001168,1.2366957609,0.0542760665 H,0,-1.2395486546,-1.8350008309,-0.5791959947 H,0,-0.821862706,-1.368097098,1.028900636 H,0,1.1417523547,-2.024955352,-0.2200134154 H,0,2.7054503044,1.9779805622,0.1397908517	83.5552 144.6958 177.2471 205.0338 339.2549 402.1866 515.3327 642.2193 700.5114 719.3062 753.2283 816.0990 876.9665 1040.2772 1171.7806 1226.4310 1331.4299 1406.8412 1997.1665 2138.7988 2768.5212 3001.0097 3166.2151 3460.8161
si1	-230.43211	0.069248	12.65731 2.31637 1.95804	C,0,-1.7790907645,-1.4912508447,0.767504862 C,0,-0.8543067718,-1.0759032768,-0.1059706496 C,0,-0.0186791001,0.0694484238,0.124224472 C,0,0.438479496,1.0919211201,0.7762741992 C,0,1.0796119899,0.8630208837,-0.527510145 C,0,1.8943957205,1.0724147522,-1.5080574464 H,0,-2.3904014639,-2.3604553422,0.5585740363 H,0,-1.9494612922,-0.979101834,1.7076436246 H,0,-0.6977001011,-1.6002530829,-1.0411497449 H,0,0.4750994371,1.7619039095,1.6161403301	62.6353 120.0702 248.4432 286.1923 410.6736 457.6663 647.7458 691.5688 744.3804 856.8558 922.4784 969.4694 1004.6636 1017.5022 1105.4482 1323.4296 1441.8906 1642.2686 1660.1051 1914.5531 3146.3949 3186.8047 3237.6541 3297.4678
si10	-230.44869	0.071406	6.72391 5.58218 3.16440	C,0,-1.1736378993,-0.791790097,-0.195771055 C,0,0.3388061938,-1.2665611046,-0.0078651733 C,0,1.3125615859,-0.3678140764,0.0945095483 C,0,1.1437058937,0.9962611987,-0.039637631 C,0,-0.1922706077,1.2912078564,0.2397092068 C,0,-1.2525565662,0.6621260033,0.0411397648 H,0,-1.6273194518,-1.2819906183,0.6783231491 H,0,-1.7110275393,-1.1793020575,-1.0694041843 H,0,0.4557478595,-2.3300068397,0.1736214862 H,0,1.82294753,1.6507208333,-0.5750484147	248.4367 353.5183 418.7636 470.1830 553.8496 653.4294 684.0112 759.8113 856.2093 876.1089 969.9494 1099.9826 1134.0319 1171.2261 1199.2150 1273.6896 1322.3196 1403.1335 1611.1721 1903.8554 3002.6092 3043.2480 3165.8947 3168.7868
si4	-230.5243	0.069940	19.80302 1.52548 1.41638	C,0,-2.9612042714,-0.2141420281,0.2235393314 C,0,2.8139110793,-0.8811267056,-0.3401362366 C,0,1.8769788063,-0.1410334953,-0.1740850543 C,0,0.810969939,0.7707242577,0.0227304655 C,0,-0.4682414596,0.4229027858,0.0888991689 C,0,-1.6884704322,0.1151892319,0.1551296899 H,0,-3.281112169,-1.2468117279,0.1287114095 H,0,-3.7307999398,0.5355467293,0.3765719275 H,0,3.6300143761,-1.5453667275,-0.4859964218 H,0,1.078235764,1.8215474475,0.1242488957	98.0934 208.1039 263.3869 311.1678 365.1219 533.5571 563.4806 604.7958 639.2435 683.5866 851.3734 879.8090 884.3295 1029.4943 1054.5995 1313.7166 1445.5642 1671.0069 2173.4031 2214.9032 3113.3650 3122.2478 3200.4198 3475.4672

Table S1. Total Molecular Energies at the CCSD(T) Level Extrapolated to the Complete Basis Set (CBS) limit, Zero Point Energy Corrections (ZPE), Rotational Constants, Molecular Geometries, and Vibrational Frequencies of all Stationary Points.

si7	-230.54503	0.073433	8.77491 5.04292 3.20247	C,0,-1.0105572807,-1.0491073195,0.024824548 C,0,0.3784082866,-1.2873071319,-0.037106954 C,0,1.0367674321,-0.075224485,-0.0445294234 C,0,1.2143605114,1.2606849941,-0.0298308395 C,0,-0.1131831776,1.0340411433,0.0218416708 C,0,-1.2994207218,0.331160531,0.0597314246 H,0,-1.7645919999,-1.8319064371,0.043347641 H,0,0.8482149853,-2.2602636372,-0.0728263743 H,0,1.9664073949,2.0414204198,-0.0483049161 H,0,-2.2882807062,0.7652632881,0.1082011099	313.7353 396.6506 571.9497 584.7939 618.0612 776.3217 812.3044 818.2810 834.5893 907.7846 981.4983 1071.8544 1074.3169 1088.1051 1155.5330 1295.3122 1383.6354 1415.6040 1562.6302 1836.7856 3155.8477 3163.1727 3205.1690 3209.5802
si5	-230.54344	0.071029	41.69517 1.36524 1.32196	C,0,1.9611985536,0.5418597067,-0.1974149375 C,0,0.6238284337,0.3003414684,-0.1291746801 C,0,3.1489731089,0.7558879661,-0.2579390104 C,0,-0.5672177391,0.0743360672,-0.0626913323 C,0,-1.9642893481,-0.1458237507,-0.0070304984 C,0,-2.5413099026,-1.2295092459,0.5283477889 H,0,4.1927665522,0.9451935746,-0.3110252505 H,0,-2.5862687493,0.6362361446,-0.436831071 H,0,-1.9545519779,-2.0285187561,0.9652498551 H,0,-3.6190444628,-1.3354642339,0.538022485	107.6154 138.8559 256.4432 326.5300 486.2837 527.7965 549.0848 640.6146 646.1995 691.1963 696.1924 954.4413 1002.8712 1048.9655 1207.7837 1318.2015 1448.3535 1659.5750 2159.4167 2314.9589 3131.5716 3148.5610 3239.4513 3477.3641
si6	-230.56935	0.074951	7.04304 5.72893 3.15919	C,0,-0.8379614419,-0.9521560893,0.0253092476 C,0,0.5081440022,-1.3732243505,0.0290233358 C,0,1.353550922,-0.2801569006,0.0006123463 C,0,1.030471627,0.9207953939,-0.0253583923 C,0,-0.2492606476,1.4428114057,-0.0318693735 C,0,-1.2026592732,0.4037801968,-0.0040151352 H,0,-1.6180787593,-1.7064170882,0.0459235843 H,0,0.7899176194,-2.4179522223,0.0516573388 H,0,-0.5295597814,2.4879347557,-0.0544252338 H,0,-2.2559902094,0.6653366188,-0.0053678617	394.9519 427.5928 450.5705 604.0611 626.0781 750.5500 847.8291 869.3957 922.5967 971.0903 998.5968 1074.4336 1107.8311 1161.3788 1271.1234 1305.3788 1424.6503 1467.3292 1482.6076 2012.8014 3159.2409 3174.6557 3195.5322 3199.2642
1,2,3- tridehydrobenzene	-230.38324	0.061674	6.93697 6.36713 3.31992	C,0,-1.1822546167,-0.2876070956,-0.127591658 C,0,-0.2696546786,-1.3135141591,0.1911150947 C,0,1.0657235974,-0.9245225509,0.3236558211 C,0,-0.7923152488,1.0552120022,-0.3055985925 C,0,1.3352157869,0.3248113719,0.1440130765 C,0,0.5698960709,1.3223815635,-0.1471929321 H,0,-2.2311706866,-0.5427963707,-0.2407991053 H,0,-0.6061678956,-2.3348919743,0.3204323291 H,0,-1.5223268847,1.8171215527,-0.5500380821	411.0996 444.3655 471.7534 557.1136 582.3841 762.4981 842.6329 874.8171 955.5670 1024.5942 1118.1741 1119.9459 1166.1738 1296.0287 1412.0814 1419.7970 1511.1284 1557.7845 3164.1366 3187.0030 3192.7035
$H_2CCCCCCH$	-230.37507	0.055915	292.29034 1.28371 1.27810	C,0,-3.1758306894,1.4946673782,0. C,0,-1.8690396426,1.4148245842,0. C,0,-0.574658714,1.3356997055,0. C,0,0.6747624352,1.2595994362,0. C,0,2.0064360219,1.1775061467,0. C,0,3.2240758198,1.1019536028,0. H,0,-3.6899244047,2.4539792992,0. H,0,-3.8028927284,0.6050815103,0. H,0,4.2843159022,1.0371213369,0.	100.1201 111.1873 200.4019 273.8692 383.6599 462.4306 497.0958 516.4348 590.6255 634.7972 636.8241 872.1363 984.9088 1190.7705 1443.0504 1841.6338 2002.3691 2097.9838 3083.1956 3150.1960 3470.3454

Table S1. Total Molecular Energies at the CCSD(T) Level Extrapolated to the Complete Basis Set (CBS) limit, Zero Point Energy Corrections (ZPE), Rotational Constants, Molecular Geometries, and Vibrational Frequencies of all Stationary Points.

1,2,4-tridehydrobenzene	-230.3801	0.061824	7.85139 5.66044 3.28914	C,0,-0.7617922626,-1.2204209859,0.0050297849 C,0,0.6477150296,-1.1405318361,-0.0571574781 C,0,1.2410839169,0.1119705235,-0.0537520366 C,0,0.6811778286,1.3772503043,0.0026122974 C,0,-1.3190207344,0.049017013,0.0611204943 C,0,-0.6839480942,1.1366546634,0.0586726567 H,0,-1.2941918738,-2.1637736764,0.0060488537 H,0,1.2527221002,-2.0389998187,-0.1065869196 H,0,1.2101756709,2.3191354015,0.0013837551	376.0927 468.3412 482.0852 582.8521 583.0359 772.2736 794.9420 847.1616 936.1320 976.7561 1058.4213 1100.6840 1238.7304 1286.6426 1374.6209 1383.0503 1460.7517 1834.4613 3173.6661 3191.1515 3215.6922
si9	-230.43339	0.069885	11.89305 2.85240 2.49593	C,0,1.1738816764,1.4901747449,0.4055047805 C,0,0.0130810069,1.6203207324,-0.496368614 C,0,1.2888182958,0.2674982664,-0.3345777378 C,0,-0.109681366,0.2113098492,-0.2648755801 C,0,-1.153383325,-0.7076333106,0.111699123 C,0,-0.9198918935,-1.9649833027,0.5040935019 H,0,2.0524628981,-0.1891174492,-0.9507295043 H,0,-2.1659247032,-0.3224635094,0.0469583927 H,0,0.0887310843,-2.3529372365,0.5945236843 H,0,-1.7322156468,-2.6356036826,0.7563945865	117.8052 216.2410 256.3537 507.0057 543.9159 594.1080 601.7349 744.3369 794.5400 928.8906 984.2327 1023.4507 1037.8804 1094.8769 1230.0699 1261.0606 1321.5832 1434.8474 1563.0842 1672.7267 3144.1492 3168.4087 3200.2477 3234.5792
1,3,5-tridehydrobenzene	-230.36007	0.060337	6.91501 6.16045 3.25798	C,0,-0.7822122141,-0.5819162719,-0.0016199915 C,0,0.5392976458,-1.0217100896,-0.0678036985 C,0,1.306060819,0.0999613243,-0.0401487074 C,0,1.1732214531,1.4506611395,0.0291990031 C,0,-0.1980303825,1.6964943458,0.0877796226 C,0,-1.1932436247,0.7362854344,0.0756725033 H,0,0.8742252064,-2.0463369368,-0.1284155572 H,0,1.9603742873,2.1895991522,0.037782323 H,0,-2.2424511903,1.0033909019,0.1242385027	268.6831 454.2272 479.6218 529.4833 545.8605 764.7837 788.1775 813.9633 839.8612 1004.7357 1045.7083 1071.6569 1222.9233 1243.5363 1279.7806 1379.6440 1479.1909 1656.0555 3179.8867 3217.6851 3219.5145
si8	-230.51924	0.071116	6.63409 5.78872 3.09132	C,0,-0.8515664264,-0.9112263925,0.0075608169 C,0,0.6074051885,-1.1611989431,-0.0575653921 C,0,1.4141097265,-0.0896390241,-0.0727855813 C,0,1.0111044787,1.1891779586,-0.0339076697 C,0,-0.4478164249,1.4391319137,0.0311409879 C,0,-1.2545654909,0.3675735796,0.0463831162 H,0,-1.465855431,-1.8016539518,0.0170328621 H,0,0.8893417236,-2.2051717085,-0.0880355138 H,0,1.6254514873,2.0795667896,-0.0433261323 H,0,-0.7298018311,2.4830947785,0.0616175062	296.1782 456.0670 474.5720 499.9865 552.5416 701.4607 722.3837 737.1601 790.8919 849.2456 898.4142 943.1042 1075.9985 1088.1040 1162.3224 1233.9801 1301.9951 1400.5576 1477.3648 1706.5255 3201.0024 3204.4382 3220.6195 3221.2360
si2-**si3**	-230.38196	0.065779	6.83571 2.59733 1.90260	C,0,-0.6612446803,-1.0636677263,-0.1761018006 C,0,0.7967726528,-0.9744779171,-0.0594860843 C,0,1.4616038269,0.2096125449,0.1314072213 C,0,1.9816026571,1.2952368304,0.2996882319 C,0,-2.3687755236,1.0044469369,-0.051027916 C,0,-1.5426341978,0.0501040117,-0.1060956092 H,0,-0.9610564145,-1.8390288082,0.5635575386 H,0,-0.8398761106,-1.638911669,-1.1116034309 H,0,1.3645889638,-1.8974151792,-0.1292054776 H,0,2.4323951509,2.2478275739,0.4469471119	-159.8902 81.8275 132.1508 204.7801 288.6595 401.4170 511.4951 639.9952 690.1497 714.9978 758.2503 823.7421 1014.9219 1031.3822 1127.3154 1209.3420 1272.2837 1409.7042 2014.2649 2131.3902 2894.2255 2895.1162 3166.4523 3459.6847
si1-**si9**	-230.40495	0.068223	11.51191 2.75338 2.29793	C,0,0.3455036114,1.8216401447,0.5282694504 C,0,1.2635906527,1.3565922363,-0.2695401361 C,0,1.4329546439,-0.1037171938,-0.0263137356 C,0,0.1380343372,0.0378751458,0.1084280182 C,0,-1.1796407509,-0.4763163604,-0.1527249091 C,0,-1.500917316,-1.7737902497,-0.0874982658 H,0,2.229422127,-0.8156051466,-0.1548270195 H,0,-1.9345359429,0.2773481951,-0.3463593825 H,0,-2.5202359237,-2.097008455,-0.2569770591 H,0,-0.771801331,-2.5384369307,0.154440929	-458.0586 67.0479 211.4672 262.8902 344.2774 474.8325 603.0447 658.8086 763.1111 896.6051 940.9676 969.0411 1011.2983 1072.7122 1112.0374 1312.4843 1437.2408 1569.4287 1647.6025 1750.4068 3146.5315 3180.0104 3237.0600 3277.5998

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si10-si7	-230.42241	0.067988	7.05451 5.57307 3.15947	C,0,-0.8983839458,-1.0618285605,0.0486092301 C,0,0.5378585539,-1.143470659,0.3144684518 C,0,1.3488766511,-0.0568400292,0.2012300926 C,0,0.9166641495,1.2417063379,-0.1805633849 C,0,-0.4266592513,1.1485620407,-0.2833419647 C,0,-1.3997018261,0.2611059966,-0.2906292979 H,0,-1.4334721481,-0.3604879352,0.9274432095 H,0,-1.5265194943,-1.9507293341,-0.0066776583 H,0,0.9286399897,-2.10695401,0.6280630213 H,0,1.5594256653,2.0827605208,-0.4074673347	-990.9122 311.5246 484.2757 502.4984 571.2145 576.1933 751.7211 784.7694 866.4465 879.6895 926.9248 981.2203 1079.8335 1166.7614 1194.8294 1250.8696 1300.9514 1333.6404 1474.0353 1731.5326 2207.5210 3120.5526 3162.3303 3183.9337
si10-si4	-230.43441	0.069598	6.26377 5.23735 2.95031	C,0,-1.2065566034,-0.8152862331,0.6246200573 C,0,0.7197702752,-1.2685133567,0.1062459341 C,0,1.3058252605,-0.2332134331,-0.3588836931 C,0,0.9656609941,1.1099159294,-0.3767902652 C,0,-1.2778812406,0.4848707631,0.1345535602 C,0,-0.415888983,1.2355432901,-0.3759378173 H,0,-1.442203333,-1.5655476694,-0.1318159949 H,0,-1.5860902089,-1.0829761443,1.6100998039 H,0,0.836527409,-2.33797065,0.0961794322 H,0,1.6461879164,1.9065927047,-0.0973098971	-460.1435 275.0981 365.6573 415.9397 441.7946 528.9995 601.0033 700.0504 750.1370 863.2989 936.3974 993.7252 1025.4651 1067.0113 1138.0086 1279.7873 1343.3932 1447.4066 1754.2915 1955.6453 3071.0674 3140.7322 3166.5666 3288.6794
si1-si9	-230.40495	0.068223	11.5119 2.75338 2.29793	C,0,0.3455036114,1.8216401447,0.5282694504 C,0,1.2635906527,1.3565922363,-0.2695401361 C,0,1.4329546439,-0.1037171938,-0.0263137356 C,0,0.1380343372,0.0378751458,0.1084280182 C,0,-1.1796407509,-0.4763163604,-0.1527249091 C,0,-1.500917316,-1.7737902497,-0.0874982658 H,0,2.229422127,-0.8156051466,-0.1548270195 H,0,-1.9345359429,0.2773481951,-0.3463593825 H,0,-2.5202359237,-2.097008455,-0.2569770591 H,0,-0.771801331,-2.5384369307,0.154440929	-458.0586 67.0479 211.4672 262.8902 344.2774 474.8325 603.0447 658.8086 763.1111 896.6051 940.9676 969.0411 1011.2983 1072.7122 1112.0374 1312.4843 1437.2408 1569.4287 1647.6025 1750.4068 3146.5315 3180.0104 3237.0600 3277.5998
si9-si5	-230.39512	0.069851	6.56254 5.19259 3.03246	C,0,1.0120693994,1.1110563231,-0.359101788 C,0,-0.2721775847,1.0961747449,-0.7137343754 C,0,1.488516939,0.0809947506,0.2556667619 C,0,-1.3192395242,0.445714476,-0.4656106924 C,0,-1.1829890836,-0.6341482827,0.4190780643 C,0,0.0621487003,-1.2990423603,0.461880554 H,0,2.4365539603,-0.4246280103,0.3500033271 H,0,-1.8879653597,-0.7406684416,1.2398228492 H,0,0.4876707723,-1.6634963685,-0.4729353044 H,0,0.23376755,-1.9757050886,1.2940379814	-484.0800 307.8547 339.8090 431.6951 473.9791 497.7188 532.7439 681.3232 752.2432 884.0984 965.2024 1000.3398 1065.5558 1137.5930 1203.4464 1312.2253 1390.2946 1489.0184 1695.4575 1851.1104 3085.8002 3133.1680 3176.2566 3254.2883
si3-si10	-230.37314	0.066810	5.69496 4.40312 2.52015	C,0,-1.0750328425,-0.6590870262,0.0411704281 C,0,0.3398372224,-1.1191633141,-0.1645318353 C,0,1.2997449944,-0.1572034397,-0.0964779251 C,0,1.4266009946,1.0610562027,0.0903108858 C,0,-1.1358397946,1.9657724398,0.4746395164 C,0,-1.29188047,0.727236719,0.2872944181 H,0,-1.4787471309,-1.3010022005,0.8487288666 H,0,-1.6342029268,-1.0247718802,-0.8424812328 H,0,0.5261247289,-2.1699665565,-0.3531491778 H,0,1.7541252245,2.0673720558,0.224033056	-142.6119 153.6479 179.7528 244.6529 340.3176 493.0433 594.4544 634.0532 709.6462 741.6807 828.5811 846.9424 1012.6656 1061.8091 1159.3619 1185.3507 1295.0411 1379.6454 1966.8487 1988.0245 2934.4605 2940.9355 3197.0110 3438.3518
si6-C_4H_2+C_2H_2	-230.41732	0.066266	4.86009 4.81094 2.41769	6 -0.627670 1.466691 -0.000100 6 0.625200 1.467568 0.000063 6 -1.647143 -0.477346 0.000053 6 -0.669806 -1.274468 0.000032 6 0.671721 -1.273257 -0.000093 6 1.648116 -0.475150 0.000008 1 -1.566519 1.981659 -0.000343 1 1.563591 1.983631 0.000391 1 -2.704183 -0.287005 0.000239 1 2.704596 -0.282522 -0.000062	-450.5216 175.4813 232.7569 261.8817 409.9517 462.7187 468.8979 545.3606 586.7364 610.6973 649.7624 666.1025 791.5732 812.5154 888.7481 922.0288 1140.6291 1820.0586 1861.7863 2047.6056 3413.6802 3422.2875 3423.7464 3472.5624

Table S1. Total Molecular Energies at the CCSD(T) Level Extrapolated to the Complete Basis Set (CBS) limit, Zero Point Energy Corrections (ZPE), Rotational Constants, Molecular Geometries, and Vibrational Frequencies of all Stationary Points.

si7-si8	-230.44022	0.067193	7.12856 5.56315 3.15699	C,0,-0.9532915145,-1.0419341285,0.0375824569 C,0,0.4463226807,-1.2382221114,-0.0700704086 C,0,1.3281808435,-0.1758066221,-0.1042674339 C,0,1.0821282749,1.1417347919,0.0304670243 C,0,-0.3328771543,1.202865008,0.3112732013 C,0,-1.2724259583,0.2784790936,0.3923600598 H,0,-1.650143136,-1.8673124658,-0.0566915746 H,0,0.8032176349,-2.262856261,-0.1204547192 H,0,1.7122163262,2.0017699707,-0.1327562343 H,0,-1.4272490109,1.4615387304,-0.2853157022	-1484.2465 396.7583 437.3369 459.6129 528.1224 618.1336 650.4355 723.0307 804.1913 836.8594 871.2823 939.5564 1022.0747 1116.3073 1171.1630 1232.0249 1318.7630 1372.4822 1505.4190 1723.5669 2184.3024 3160.9612 3186.2369 3235.5842
ti2	-230.37101	0.065893	6.89429 2.58835 1.90386	C,0,-0.8203578415,-1.065980999,0.0170471783 C,0,0.6912186641,-1.0305938494,-0.0363722188 C,0,1.4523231538,0.1064240175,-0.0511473666 C,0,2.1407506095,1.1151075352,-0.0637165054 C,0,-1.4496988189,0.2522249271,0.0538594953 C,0,-2.2805412822,1.1671697109,0.0957880816 H,0,-1.1919438184,-1.6235719363,-0.8539683006 H,0,-1.1293990774,-1.6424451236,0.9001521598 H,0,1.1852064629,-1.9964406715,-0.0649064408 H,0,2.7339695251,1.9963496781,-0.0740294047	50.7966 85.3235 106.5710 242.9631 378.7475 415.1768 455.3365 568.5858 655.0567 669.2357 793.7469 901.8886 956.2559 1149.0680 1194.5375 1271.7399 1390.9195 1449.8204 1553.4120 2018.1977 2985.6677 3004.5516 3159.3745 3466.8322
CCCHCHCCH	-230.31834	0.057698	7.57352 2.60774 1.94173	C,0,-0.8508607797,0.9691425962,0.010251811 C,0,0.5338050158,1.0782566683,-0.0207997643 C,0,1.4220680705,0.0012309281,-0.0034385777 C,0,2.22220823,-0.9057451971,0.0065254881 C,0,-1.5404766143,-0.2173085091,0.0786468381 C,0,-2.1971535121,-1.301140881,-0.0611860595 H,0,-1.4143692944,1.899976147,-0.0159633339 H,0,0.9698819407,2.0727520368,-0.0611289912 H,0,2.9069448923,-1.7193418168,0.0170939117	104.9728 171.3231 228.2457 283.7468 422.0723 471.7661 669.9009 681.7322 724.2113 753.6589 911.7950 960.1742 1061.6368 1208.6882 1416.3837 1456.5320 1908.9760 2144.0416 3124.8667 3155.7899 3466.0556
ti3	-230.38614	0.070742	11.0969 2.70158 2.44806	C,0,-1.2615553572,-0.6125691338,0.363978291 C,0,0.3219687848,-0.2877116459,0.4253124595 C,0,0.9925642122,-0.1779288727,-0.8513350172 C,0,1.5543292381,-0.0868883787,-1.9101482421 C,0,-1.4292832189,0.6986986191,1.0882282064 C,0,-0.1308940413,0.992117192,1.1316882762 H,0,-1.522813923,-1.5114365265,0.9265807612 H,0,-1.6374387845,-0.6491172677,-0.6586559719 H,0,0.8274433811,-0.9917357564,1.091827317 H,0,2.0500316206,-0.0020171293,-2.8460959489	164.2048 187.9310 326.1979 487.9562 532.1818 674.6831 683.7456 722.5201 762.5719 860.2355 930.0878 1000.1410 1052.4260 1063.1030 1111.8673 1183.6722 1294.4010 1462.8519 1625.1039 2213.4382 3052.0758 3058.2283 3127.0299 3475.4836
ti1	-230.39538	0.067305	13.3770 1.69556 1.59029	C,0,-1.9840835423,-1.6368525131,0.5693465257 C,0,-0.6004692353,-1.5274531807,0.4558422372 C,0,0.106650225,-0.3871357543,0.4800509933 C,0,0.8243421451,0.7423370855,0.4663184581 C,0,1.1068234113,1.4244507314,-0.714011863 C,0,1.1938406627,2.1625976083,-1.751136741 H,0,-2.4571056946,-2.6082217556,0.5337421287 H,0,-2.6098709333,-0.7618390376,0.6828743654 H,0,-0.0164585506,-2.440826478,0.3342554018 H,0,1.2008131788,1.1432234092,1.4106704424	65.7117 137.3990 189.9695 230.6110 296.4315 474.0236 528.3491 572.5325 769.7100 814.9083 868.6920 903.2420 1012.0962 1069.5880 1191.3448 1313.3285 1375.8244 1488.6104 1757.5040 1895.7531 3063.3349 3100.3860 3159.7347 3264.2285
ti4	-230.4681	0.066630	19.3067 1.49649 1.40224	C,0,-2.2540956417,-1.9074597809,-0.6244345546 C,0,1.091048323,0.0128166056,0.3773246596 C,0,1.2567288855,1.3928149164,0.321030624 C,0,1.4265930019,2.5942044064,0.281244723 C,0,-1.1148549879,-1.2430936883,-0.2843320741 C,0,-0.0808713712,-0.6324754619,0.0233918799 H,0,-2.419438853,-2.2523577413,-1.6393436885 H,0,-3.0262238386,-2.1072680255,0.1106034438 H,0,1.9316028119,-0.5877482384,0.7199152535 H,0,1.5667706224,3.646532021,0.2434734449	83.7934 192.0281 258.6812 294.8824 395.7526 405.1477 483.1812 542.5425 542.8379 669.9785 677.1698 699.8302 837.8804 1003.8695 1061.5424 1262.5783 1397.9716 1464.1128 1960.5953 2097.3416 3115.6293 3122.5062 3207.2790 3469.8513
ti5	-230.43375	0.070405	7.29272	C,0,-1.2144862845,-0.87913806,0.0350451862	224.7918 372.1657 449.2276

Table S1. Total Molecular Energies at the CCSD(T) Level Extrapolated to the Complete Basis Set (CBS) limit, Zero Point Energy Corrections (ZPE), Rotational Constants, Molecular Geometries, and Vibrational Frequencies of all Stationary Points.

			5.15770 3.07792	C,0,0.2794145071,-1.2829171579,0.031387012 C,0,1.2386194851,-0.3401063108,-0.0031697026 C,0,1.1985337129,1.0730781699,-0.0406520634 C,0,-0.1834115477,1.3577661561,-0.0339538458 C,0,-1.1681886576,0.6017114696,-0.0041023814 H,0,-1.7256411827,-1.2710930259,0.9261192791 H,0,-1.7426071482,-1.317166815,-0.8241143128 H,0,0.5240757241,-2.3396085355,0.0573351046 H,0,2.0412853146,1.7455027741,-0.0666653007	467.7236 528.3858 624.0052 704.9431 719.6495 848.2770 900.5565 923.0844 994.3732 1129.0114 1129.6333 1219.6786 1239.9834 1279.3471 1435.2363 1483.2000 1865.3484 2976.3320 2986.9800 3167.3562 3234.9723
ti6	-230.51444	0.073954	6.48578 5.91733 3.09426	C,0,-1.3647058398,-0.5041081502,-0.005015519 C,0,-0.0359041762,-0.9464157376,-0.0868893092 C,0,0.9436322541,0.0218950794,-0.0877477318 C,0,0.7110907922,1.3812347585,-0.0144922295 C,0,-0.6192888953,1.7434625571,0.0637792149 C,0,-1.6770890679,0.8613647664,0.0722226462 H,0,-2.1682415371,-1.2339144776,-0.0013484364 H,0,0.1930431356,-2.0039473174,-0.1461063812 H,0,1.5149911569,2.1113622426,-0.0181675758 H,0,-2.7074748225,1.1909832787,0.1350963218	390.6758 412.3441 605.9652 615.0349 624.0423 717.0630 806.1143 874.9879 965.5203 971.3362 1022.0911 1041.7035 1073.5622 1163.9897 1248.4513 1293.8638 1392.2748 1430.6777 1557.5380 1584.8476 3151.5032 3155.7764 3178.2785 3184.4988
ti8	-230.51658	0.074072	7.02712 5.51451 3.08980	C,0,-0.7560970294,-0.5465118472,0.0005290058 C,0,0.57652699,-0.9898600107,-0.0817431327 C,0,1.549890399,-0.0160471719,-0.0824029376 C,0,1.3578268988,1.3454978303,-0.0111603536 C,0,0.0252196834,1.7888459266,0.07117913 C,0,-0.9481525794,0.8150233871,0.0718835915 H,0,-1.581466227,-1.2500455275,0.0067479738 H,0,0.8129692433,-2.0466475609,-0.1410983165 H,0,2.1832144614,2.0490078278,-0.0173096469 H,0,-0.2112338401,2.8456251463,0.1306276862	377.3563 413.8337 585.1462 621.8841 647.8835 750.4494 791.1529 921.5304 941.3774 950.0437 1024.3890 1036.8004 1076.4238 1152.0715 1287.1993 1290.7745 1377.4905 1448.9475 1526.6288 1627.8081 3158.3612 3159.4247 3171.9251 3174.9817
ti6	-230.50856	0.074156	6.51235 5.85209 3.08230	C,0,-0.7654201768,-0.5748402772,-0.002088659 C,0,0.5539601813,-1.0134691295,-0.0677076322 C,0,1.6105501432,-0.089103773,-0.0599141383 C,0,1.3133301651,1.2525505899,0.0135191516 C,0,-0.0096251581,1.6923716801,0.0792192204 C,0,-1.0545628555,0.7969223471,0.0724595055 H,0,-1.5779852355,-1.2928040169,-0.008374928 H,0,0.7720677166,-2.0740812693,-0.1251947914 H,0,2.6421391323,-0.4249886686,-0.1108504355 H,0,-2.0818979126,1.1455345175,0.1238497069	398.2256 415.8422 588.4896 601.8653 603.3659 725.1123 793.6490 923.3991 968.7976 978.3679 1015.2726 1048.2492 1105.8696 1171.0068 1216.4757 1302.5742 1430.9052 1441.5895 1554.2753 1611.6359 3148.6810 3151.6763 3169.8611 3185.4331
ti3-**ti5**	-230.35732	0.067279	10.9747 2.40434 2.16824	C,0,-1.6077324415,-0.6194270706,0.5391699535 C,0,0.5124284382,-0.197219195,0.3659916697 C,0,1.1261322145,-0.1297818112,-0.9008251558 C,0,1.6189717219,-0.0836381637,-2.0032929188 C,0,-1.3789272979,0.6086281566,1.2197172375 C,0,-0.1287433429,0.9538883594,1.014047284 H,0,-1.8901927582,-1.5272995441,1.0749858906 H,0,-1.8357593551,-0.6130957874,-0.5229300426 H,0,0.8145095439,-1.0205133326,1.0085575383 H,0,2.0586668159,-0.0337929883,-2.9694618074	-513.2593 144.0051 180.4701 330.8451 442.6213 513.1002 582.2671 633.9030 664.8436 679.7655 761.4605 944.6603 963.3349 998.8136 1063.0607 1155.6971 1310.5773 1464.0953 1691.4041 2151.3127 3073.8289 3132.7863 3177.5668 3471.8572
ti1-CCCHCHCCH	-230.31529	0.058969	6.85792 2.54925 1.92097	C,0,-0.7497817203,-0.9877272283,-0.1747884527 C,0,0.6476741119,-0.9791053205,-0.2363235043 C,0,1.4468276377,0.1376290039,-0.0040123677 C,0,2.1714732064,1.08754285,0.191131683 C,0,-1.5258396781,0.1371284209,0.0317673472 C,0,-2.2333335886,1.196203879,-0.0134111237 H,0,-1.244252992,-1.9207027788,-0.4350320155 H,0,-1.2407929719,-1.6534996756,1.7705916527 H,0,1.1545188366,-1.9119401339,-0.4665117394 H,0,2.7884073133,1.9361129577,0.3647706126	-470.7041 104.6631 161.0924 206.3925 237.2813 329.0821 360.6732 422.2451 473.3356 664.8590 671.1920 729.2234 759.3029 903.3830 953.1985 1059.5491 1205.9319 1413.3782 1445.9455 1899.1364 2129.3669 3132.5696 3157.7377 3465.0420
ti2-**ti5**	-230.36645	0.066668	5.92662	C,0,-0.9488735389,-1.1713940962,-0.0427862878	-352.7088 158.8224 235.0539

Table S1. Total Molecular Energies at the CCSD(T) Level Extrapolated to the Complete Basis Set (CBS) limit, Zero Point Energy Corrections (ZPE), Rotational Constants, Molecular Geometries, and Vibrational Frequencies of all Stationary Points.

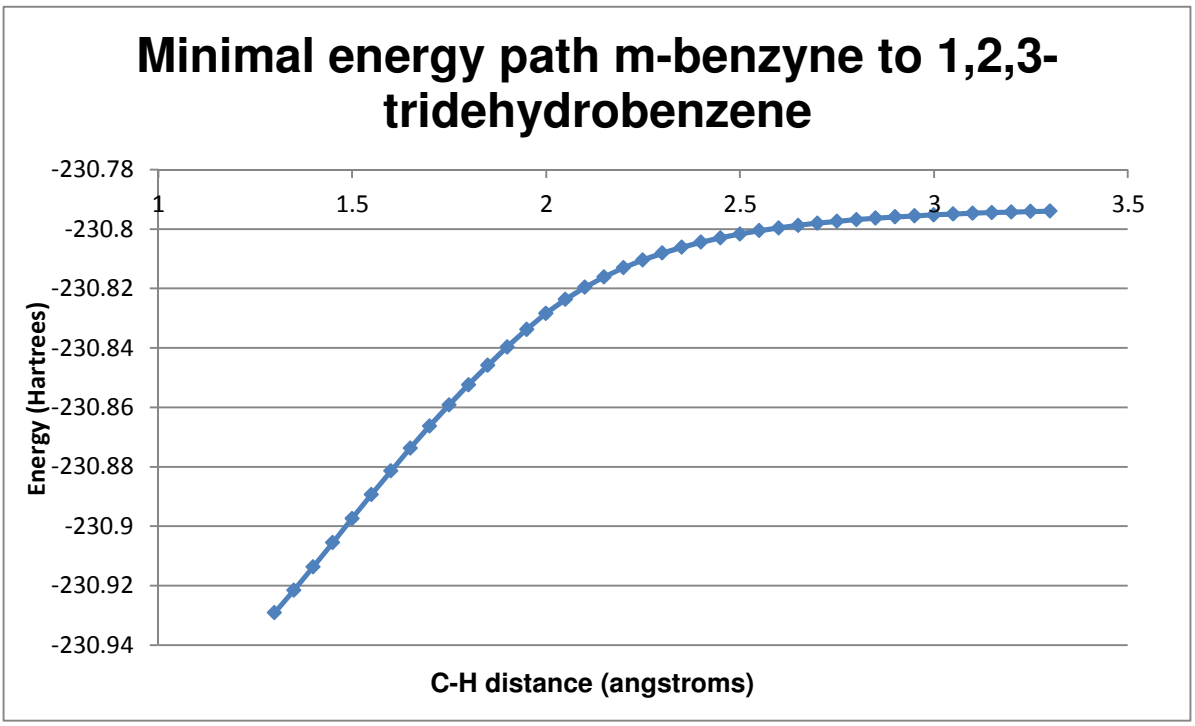
			4.86441 2.71668	C,0,0.5783208768,-1.2337942774,0.0140372958 C,0,1.2126605797,-0.0224682346,0.046873832 C,0,1.3184222918,1.2189183615,0.0592381137 C,0,-1.23536176,0.2636072286,-0.0481727098 C,0,-0.9403505421,1.5028419592,-0.0277656268 H,0,-1.3178630391,-1.6859984755,-0.9406826959 H,0,-1.3828167626,-1.6911550998,0.8225982384 H,0,1.0965946861,-2.1834196216,0.0299386442 H,0,1.6951776722,2.2143075496,0.0795981093	268.0313 397.9429 454.7334 519.4384 547.6965 650.1551 726.6961 882.8288 912.4671 952.9084 1098.2292 1151.8898 1235.4316 1337.8993 1461.4412 1785.7925 1853.4795 2985.9219 3005.7628 3202.0140 3439.1777
ti1-**ti5**	-230.37286	0.068895	5.93185 5.10869 2.84094	C,0,-1.2722260542,-0.8001571096,-0.2027904789 C,0,-0.061244064,-1.3884772715,0.1965951618 C,0,1.1293148592,-0.7137482892,0.0034523058 C,0,1.3537543909,0.6468313664,-0.0371159442 C,0,0.1640279415,1.3668410288,-0.0182131544 C,0,-1.1001868559,1.3435145995,0.1013183351 H,0,-2.2072468902,-1.1667933614,0.2069226427 H,0,-1.3523644269,-0.3491220041,-1.1850908528 H,0,-0.0691364825,-2.2905180882,0.8024701701 H,0,2.3481064949,1.0776075062,-0.0837793116	-424.5994 240.3766 275.7305 335.6713 455.6881 504.6948 672.2676 743.3827 805.9844 867.2328 952.0886 975.7666 1059.1950 1065.0793 1197.3550 1285.4040 1381.6615 1456.9090 1483.5679 1827.9101 3128.1543 3145.2337 3166.1563 3215.8714
ti4-**ti5**	-230.39809	0.066732	6.01385 5.17223 2.83301	C,0,-1.2583894935,-0.9770329524,-0.2077694684 C,0,1.4151025524,0.6288150674,0.1372999685 C,0,0.1907440034,1.305230997,0.2685810937 C,0,-1.0562501009,1.0693178104,0.2128034698 C,0,0.0868500014,-1.3442370979,-0.2747488719 C,0,1.1755896005,-0.7487829168,-0.1464496073 H,0,-1.8341129489,-0.9170499756,-1.1305328167 H,0,-1.8451955937,-1.2835284563,0.6572523613 H,0,2.3867051027,1.0902163894,0.2376231856 H,0,-2.0292759399,1.5104965963,0.2973577636	-679.6248 211.9082 319.4225 417.5960 451.7796 468.1586 562.5743 599.9061 622.6108 737.5782 762.7966 939.7873 992.1175 1018.4292 1038.1331 1169.1507 1244.9379 1448.9316 1652.5822 1858.8647 3075.4077 3146.4495 3214.8259 3338.1450
ti4-H2CCCCCCH	-230.36903	0.060638	67.3003 1.24971 1.23748	C,0,-2.0611137682,-2.551852361,-0.6260865127 C,0,-0.5579872626,0.9925981671,-0.3176589617 C,0,0.189875371,2.0961810025,-0.1701528385 C,0,0.8651745939,3.1011939861,-0.0368797259 C,0,-1.5259172893,-1.3595573435,-0.5167626122 C,0,-0.9902914718,-0.1895703768,-0.4077850352 H,0,-2.4623720284,-3.0785648376,0.2372165094 H,0,-2.1269486807,-3.062067918,-1.584771032 H,0,-2.2916935036,2.0135460716,-0.6275812425 H,0,1.4591080398,3.9740986095,0.0802474512	-836.6662 101.9962 116.3339 181.4989 272.6896 332.6601 371.5958 383.8013 450.5951 515.8122 577.6458 605.9573 661.8297 696.5027 905.4790 1055.2373 1213.2957 1570.6052 1935.2978 1996.3684 2225.0560 3327.4498 3457.3199 3661.8039
ti5-1,2,4-tridehydrobenzene	-230.37319	0.066392	7.06220 5.07805 3.09490	C,0,-1.1421157008,-0.6084758482,-0.2280668454 C,0,0.2655410679,-0.8519674928,-0.1871480762 C,0,1.114099381,0.2188048648,-0.0009963447 C,0,0.8565322145,1.5769971136,0.1221282826 C,0,-0.5265496105,1.6608590289,0.0344190384 C,0,-1.3907114536,0.7646414799,-0.1483972451 H,0,-1.6739480776,-1.17671224,1.5571284273 H,0,-1.8552127465,-1.3737970586,-0.5071946087 H,0,0.6508560306,-1.8611598402,-0.2767909973 H,0,1.583557895,2.3643699925,0.256457369	-713.5528 267.1271 328.3989 456.4790 467.7218 483.4490 573.0083 589.5213 768.2862 799.6452 846.1569 968.3952 971.9777 1042.7658 1089.4951 1230.4928 1274.1668 1352.1305 1369.8108 1447.8585 1815.7935 3177.7588 3192.2727 3218.1833
ti7-**ti8**	-230.40729	0.067496	6.89759 5.65807 3.12773	C,0,-0.7490414404,-0.5529117425,0.0144222315 C,0,0.568153519,-0.9995310082,-0.0782306255 C,0,1.5883546259,-0.0456885723,-0.0889378209 C,0,1.4660841366,1.3215761511,-0.0039426506 C,0,0.1422486383,1.6980261032,0.298528867 C,0,-0.8713090134,0.8234020323,0.2891448301 H,0,-1.5944531917,-1.2220780383,-0.0909882045 H,0,0.7979915461,-2.0570330428,-0.1666208248 H,0,2.2971718708,2.004993034,-0.1331599284 H,0,-1.0675026618,2.0627990543,-0.1144782399	-2185.2285 290.6461 399.8152 411.3339 554.5551 611.1801 662.8335 782.0556 851.3937 883.7417 948.1103 1011.7168 1020.6619 1121.2949 1196.1032 1304.6416 1339.4047 1433.4145 1501.9006 1683.5296 2107.4811 3150.7518 3176.0278 3184.8021
ti5-**ti7**	-230.37758	0.067590	6.54682	C,0,-1.348452604,-0.5551668219,-0.1141977661	-988.8558 220.3564 360.1074

Table S1. Total Molecular Energies at the CCSD(T) Level Extrapolated to the Complete Basis Set (CBS) limit, Zero Point Energy Corrections (ZPE), Rotational Constants, Molecular Geometries, and Vibrational Frequencies of all Stationary Points.

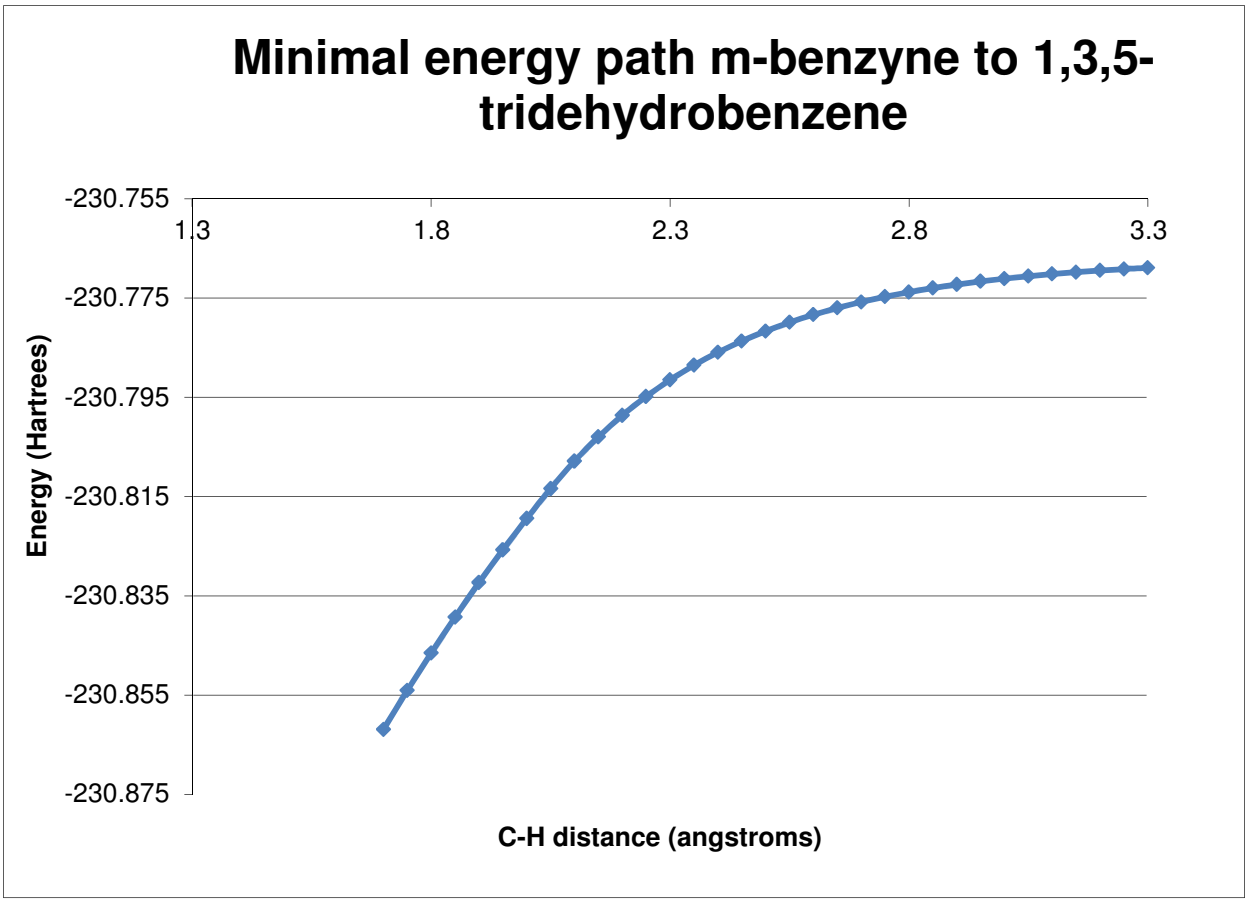
			5.79088 3.11803	C,0,0.0319954373,-0.9845061165,-0.1304376031 C,0,0.9517152619,0.0035280562,0.0078814683 C,0,0.6865433641,1.3834131471,0.0693324557 C,0,-0.6378092331,1.7361674213,-0.0049135544 C,0,-1.6887856349,0.8745195707,-0.0945777595 H,0,-1.6859678096,-0.0509797633,0.9497696476 H,0,-2.1304492474,-1.2916177192,-0.286126362 H,0,0.2959973834,-2.0290181251,-0.2570619586 H,0,1.5027520824,2.0990523508,0.1410014321	453.3996 589.2408 639.0210 710.8530 834.2676 868.7071 894.1738 962.5455 1012.4576 1074.9229 1139.2506 1162.7461 1295.6885 1355.6069 1405.6462 1460.8964 1574.7213 2233.7868 3127.1620 3129.1060 3163.8732
ti7-1,2,4-tridehydrobenzene	-230.37928	0.065714	6.65890 5.46318 3.06219	C,0,-0.2588907674,-0.9110289008,0.0983871018 C,0,0.8598371635,-0.1128367564,0.2999656257 C,0,0.8807650759,1.1369769766,0.2350538384 C,0,-0.1429139893,2.038238872,-0.0202237446 C,0,-1.2719855746,1.2542701922,-0.2018301298 C,0,-1.4033117239,-0.1255852064,-0.1728365824 H,0,-0.2970042461,-1.9924703884,0.1430476138 H,0,2.2619389648,-1.1425429955,2.0676923778 H,0,-0.1000554923,3.1169094998,-0.0743406449 H,0,-2.3631434106,-0.5975332932,-0.3499064558	-465.8137 44.2243 131.7204 376.4140 456.3265 458.1596 563.4477 586.1085 785.1212 794.6901 838.6323 936.5311 984.8466 1060.2325 1099.7747 1237.4177 1289.0764 1366.2108 1376.8788 1465.3573 1947.9317 3176.4378 3193.1893 3209.2328
ti7-**ti6**	-230.41645	0.068160	6.31747 6.13954 3.14096	C,0,-0.7359749361,-0.5674806105,0.0127628053 C,0,0.5754622233,-0.9907501397,-0.124216534 C,0,1.5239975978,0.0326758338,-0.3276413153 C,0,1.253773496,1.3601544505,-0.2536192415 C,0,-0.0422623223,1.740668387,0.0617656921 C,0,-1.0547844177,0.8178197623,0.0968059639 H,0,-1.5386071831,-1.2973967664,0.0688027402 H,0,0.8400264471,-2.040752345,-0.1088369869 H,0,2.2748740301,0.8257573072,0.3820207454 H,0,-2.0926749352,1.1183271208,0.2023621309	-1770.0707 363.4383 410.2816 465.8191 577.0144 626.6537 631.0970 763.7279 888.1541 908.9060 984.5627 1006.7611 1070.9027 1119.0993 1175.1635 1334.4739 1378.6202 1413.5959 1560.0201 1585.7801 2152.6320 3147.9320 3163.5667 3190.7638
ti6-1,2,4-tridehydrobenzene	-230.36995	0.063135	7.20481 5.36639 3.22210	C,0,-0.7246305862,-0.4033004041,-0.4530270397 C,0,0.5708664822,-0.9435942189,-0.4644952614 C,0,1.6225346372,-0.1867821489,0.0765167012 C,0,1.1576988519,1.0453702035,0.5306240933 C,0,-0.0172018207,1.4857994746,0.3705255155 C,0,-1.1410394483,0.9065284309,-0.1784588091 H,0,-1.3174541697,-1.3099318361,1.0923727469 H,0,0.7367621623,-1.9457656103,-0.8428794588 H,0,2.6444756218,-0.5438122549,0.1147663255 H,0,-2.1294557305,1.3135793641,-0.3310288133	-858.8734 318.1223 371.5160 413.5239 477.7766 486.2366 563.9599 601.4325 761.5303 792.2881 826.3479 938.7852 956.5755 1049.3402 1106.1221 1233.2109 1281.1697 1364.8748 1369.2713 1427.2796 1780.3475 3178.0063 3193.9564 3221.3510
ti6-1,2,3-tridehydrobenzene	-230.37927	0.062157	7.14493 5.50688 3.10993	C,0,-1.7053283761,-0.4499122722,0.0180135257 C,0,-0.3566030393,-0.8329427985,-0.0455944343 C,0,0.4510703353,0.272366196,-0.0204714042 C,0,0.6096305366,1.5741983179,0.0359376569 C,0,-0.7587945029,1.6859964554,0.0872582507 C,0,-1.9129456916,0.9377731069,0.0907371028 H,0,-2.5149144532,-1.1740647858,0.0110265752 H,0,-0.0027539938,-1.8509909993,-0.1057343092 H,0,-2.8952564601,1.3885287047,0.1452064217 H,0,2.550802645,-0.390869925,-0.1239443853	-591.0983 56.8617 212.0853 371.0222 377.5444 539.3029 563.5422 601.1751 763.5668 827.2228 827.8025 947.2028 955.1143 1070.0420 1083.9149 1113.9493 1300.7348 1346.2902 1427.8462 1519.9936 1787.4765 3158.0426 3199.8232 3233.0750
ti3-**ti2**	-230.26514	0.067263	8.58030 2.56959 2.17836	C,0,-1.5250996869,-0.4226440783,1.2136753216 C,0,-0.0866714594,0.0924642936,1.2736656648 C,0,0.7310789454,0.1454293954,0.1350708975 C,0,1.4290399206,0.20907602,-0.8515682967 C,0,-1.5554448371,1.0210033589,1.2525043704 C,0,-1.9463725808,2.2158086373,1.3710502953 H,0,-1.8633103402,-0.9543820404,2.1008234768 H,0,-1.8253253188,-0.8973206131,0.2823478858 H,0,0.3788052088,0.1229544392,2.2505683686 H,0,2.0433921483,0.2646515874,-1.7162789842	-581.1848 119.9720 201.7103 255.5310 349.1229 475.9751 523.6455 565.2604 680.1036 757.4582 831.7891 920.3375 993.7065 1049.1154 1109.8734 1138.8832 1338.4633 1456.6536 1749.5857 2115.2088 3081.1207 3156.4685 3182.3841 3472.6588

Supporting Information S2. Potential Energy Curves along the Minimal Energy Path for Barrierless Hydrogen Elimination Channels from Various Isomers on the Singlet and Triplet PES Calculated at the B3LYP/6-311G** Level of Theory.

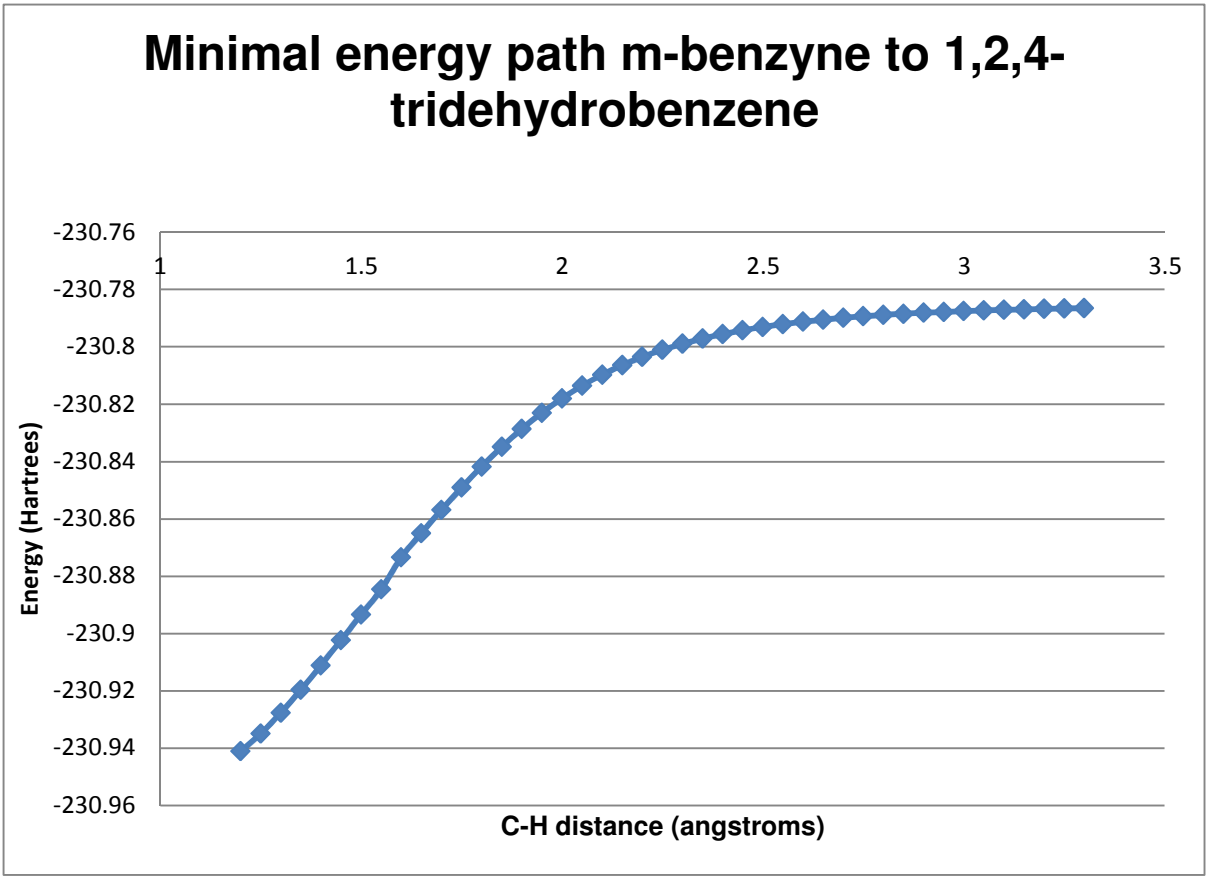
Singlet Surface:



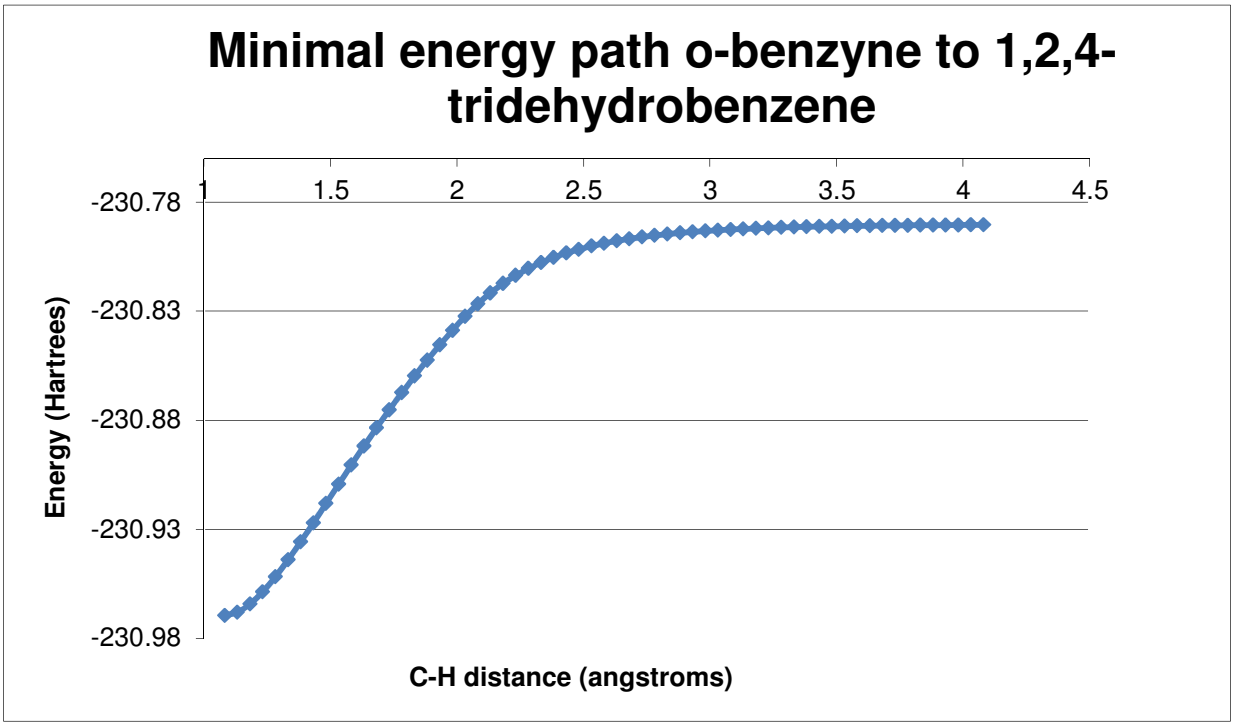
Supporting Information S2. Potential Energy Curves along the Minimal Energy Path for Barrierless Hydrogen Elimination Channels from Various Isomers on the Singlet and Triplet PES Calculated at the B3LYP/6-311G** Level of Theory.



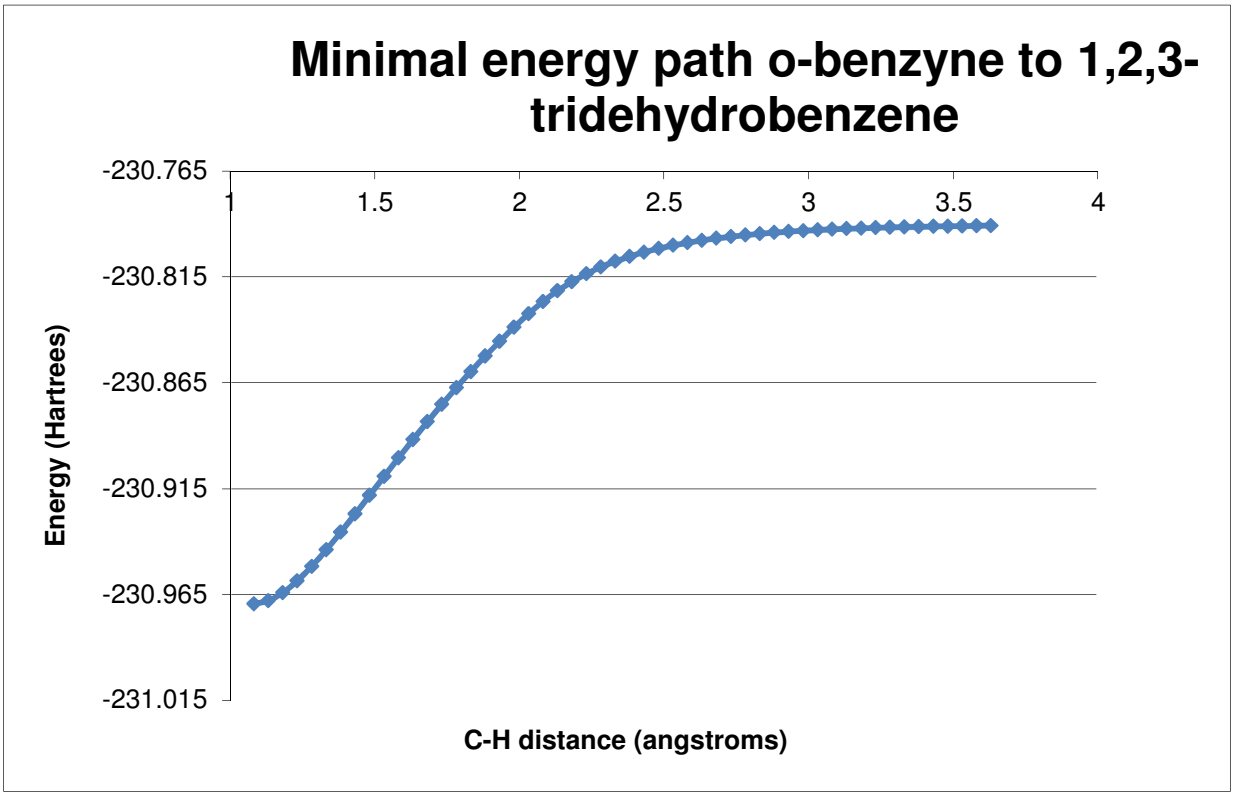
Supporting Information S2. Potential Energy Curves along the Minimal Energy Path for Barrierless Hydrogen Elimination Channels from Various Isomers on the Singlet and Triplet PES Calculated at the B3LYP/6-311G** Level of Theory.



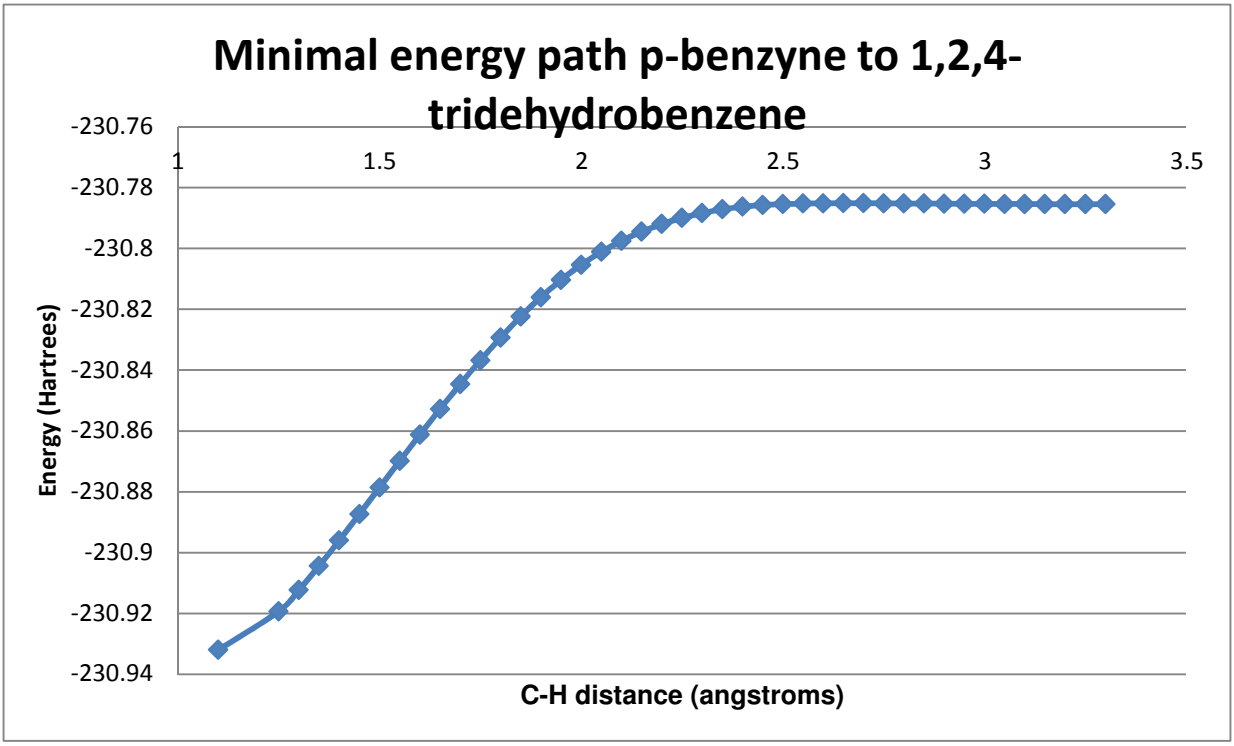
Supporting Information S2. Potential Energy Curves along the Minimal Energy Path for Barrierless Hydrogen Elimination Channels from Various Isomers on the Singlet and Triplet PES Calculated at the B3LYP/6-311G** Level of Theory.



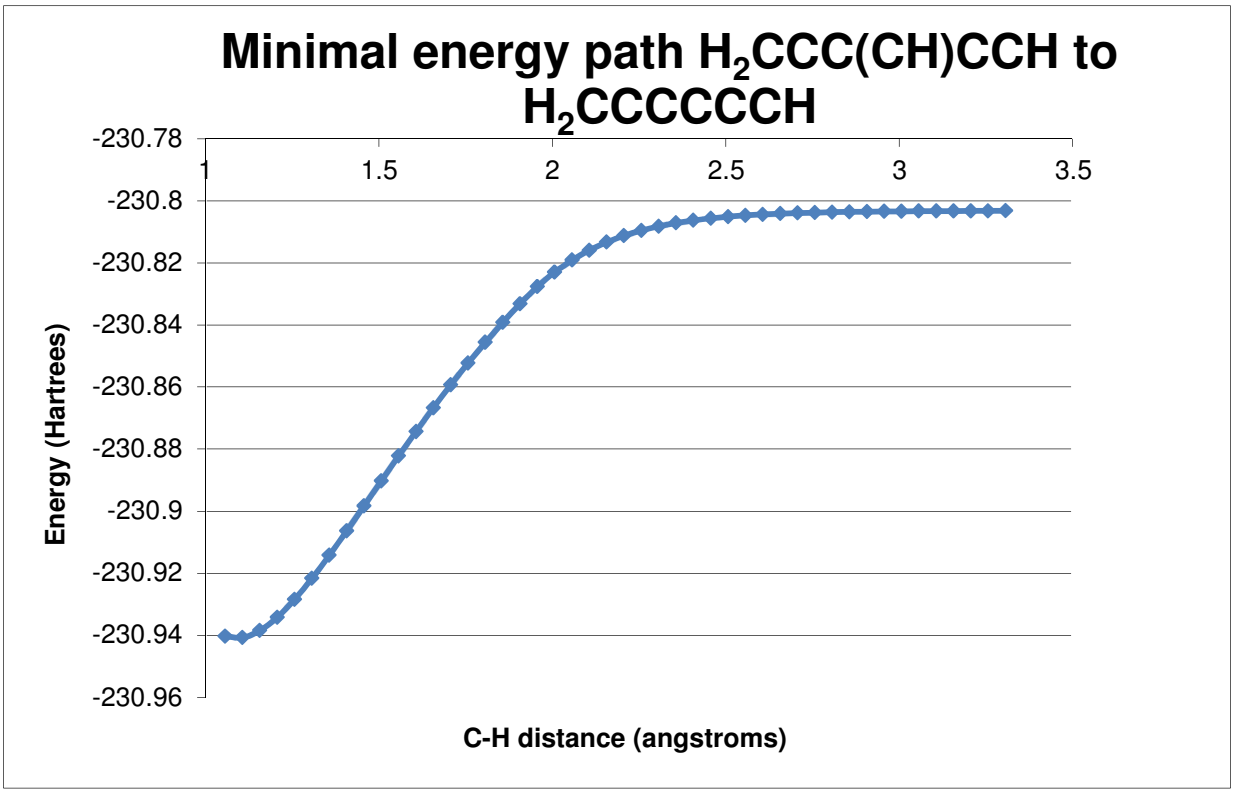
Supporting Information S2. Potential Energy Curves along the Minimal Energy Path for Barrierless Hydrogen Elimination Channels from Various Isomers on the Singlet and Triplet PES Calculated at the B3LYP/6-311G** Level of Theory.



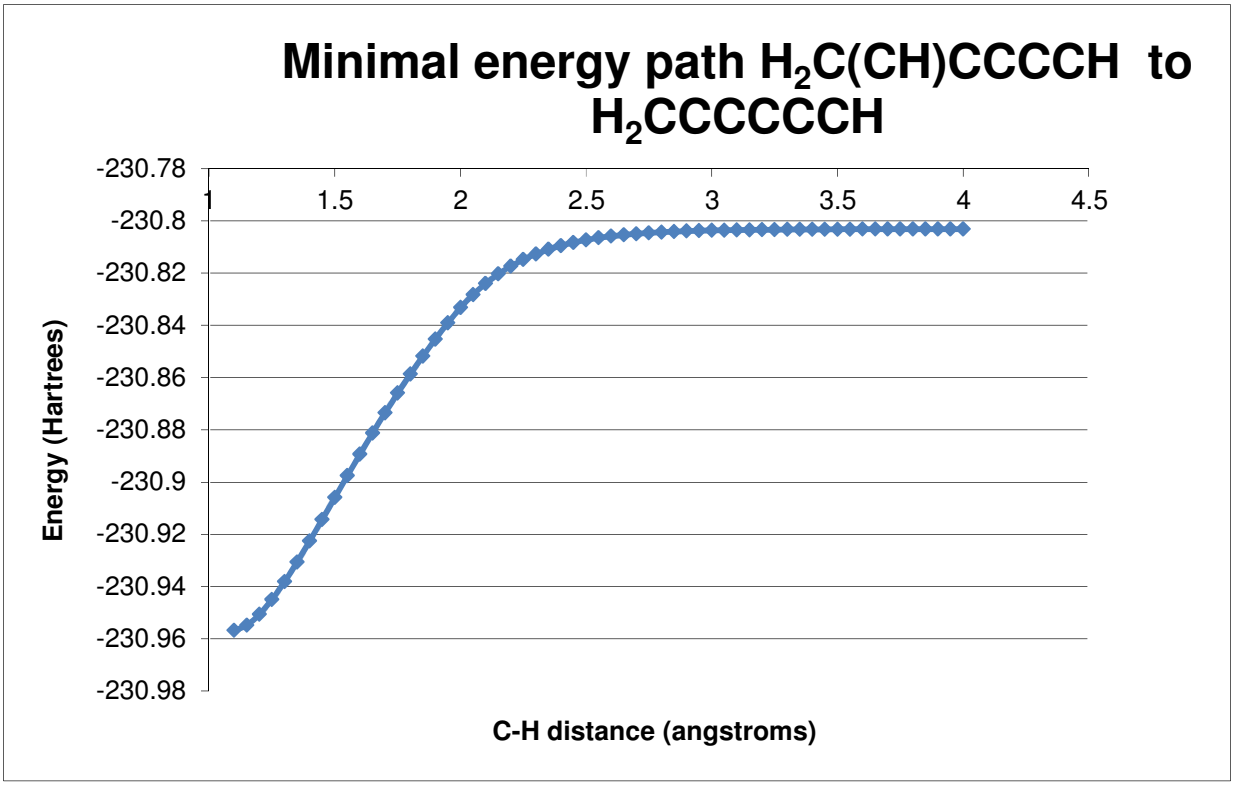
Supporting Information S2. Potential Energy Curves along the Minimal Energy Path for Barrierless Hydrogen Elimination Channels from Various Isomers on the Singlet and Triplet PES Calculated at the B3LYP/6-311G** Level of Theory.



Supporting Information S2. Potential Energy Curves along the Minimal Energy Path for Barrierless Hydrogen Elimination Channels from Various Isomers on the Singlet and Triplet PES Calculated at the B3LYP/6-311G** Level of Theory.

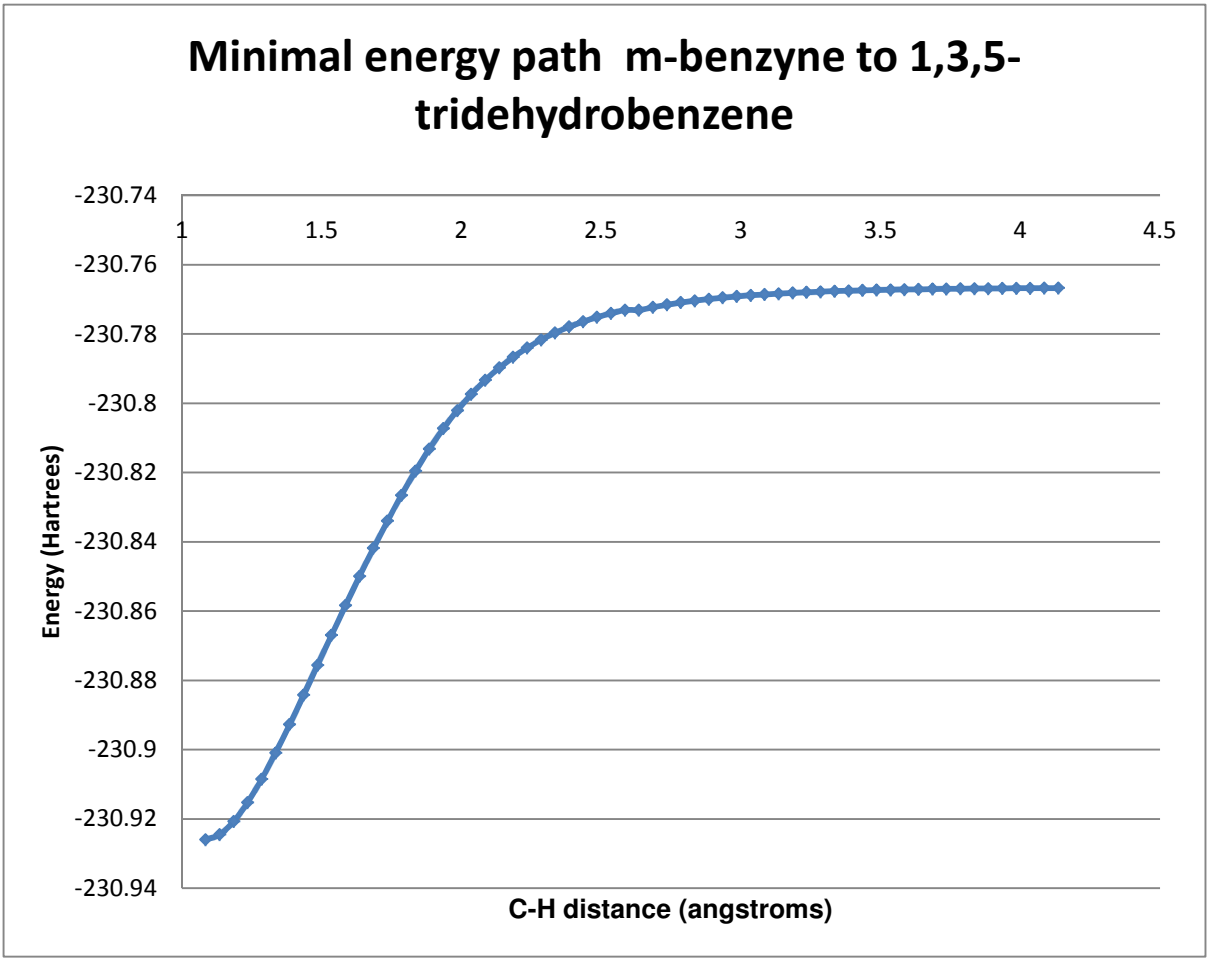


Supporting Information S2. Potential Energy Curves along the Minimal Energy Path for Barrierless Hydrogen Elimination Channels from Various Isomers on the Singlet and Triplet PES Calculated at the B3LYP/6-311G** Level of Theory.

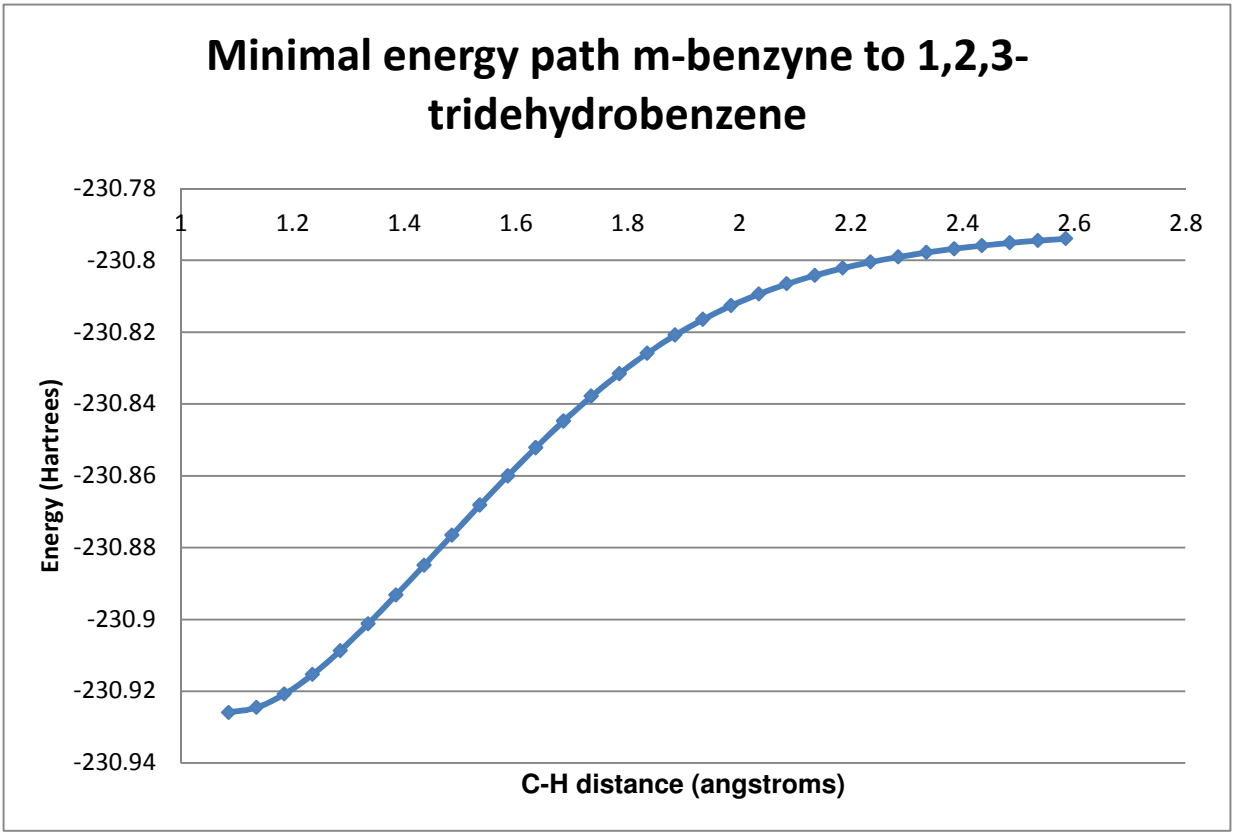


Supporting Information S2. Potential Energy Curves along the Minimal Energy Path for Barrierless Hydrogen Elimination Channels from Various Isomers on the Singlet and Triplet PES Calculated at the B3LYP/6-311G** Level of Theory.

Triplet Surface:



Supporting Information S2. Potential Energy Curves along the Minimal Energy Path for Barrierless Hydrogen Elimination Channels from Various Isomers on the Singlet and Triplet PES Calculated at the B3LYP/6-311G** Level of Theory.



Supporting Information S2. Potential Energy Curves along the Minimal Energy Path for Barrierless Hydrogen Elimination Channels from Various Isomers on the Singlet and Triplet PES Calculated at the B3LYP/6-311G** Level of Theory.

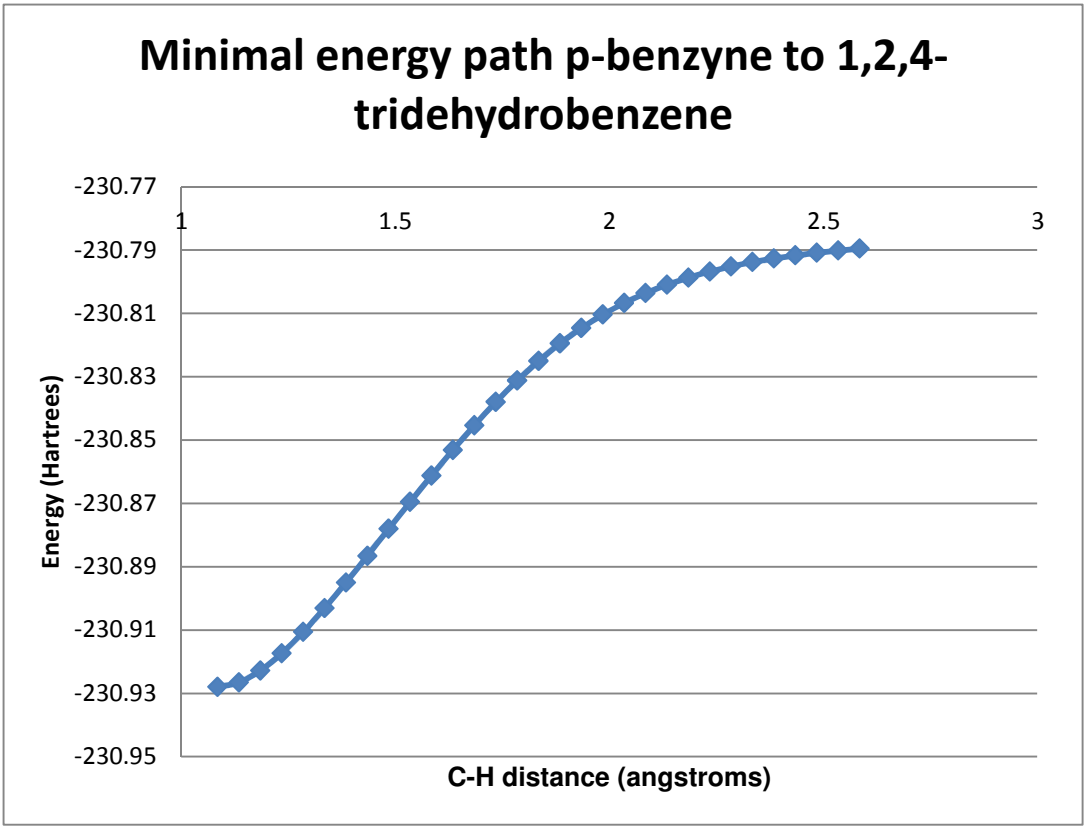


Table S3. Unimolecular Rate Constants for Various Reaction Steps on the Singlet and Triplet Surfaces Calculated Using RRKM Theory or Variational Transition State Theory (VTST, for barrierless H elimination reactions; designated with an asterisk) at Collision Energies of 0-31 kJmol^{-1} and Product Branching Ratios under Single-Collision Conditions.

Singlet Surface: [a]

	Collision Energy (kJmol^{-1})				
Rate Constants (s^{-1})	0.0	4.2	8.4	12.6	31.0
si2 → **si3**	2.40E+09	2.74E+09	3.10E+09	3.51E+09	5.84E+09
si3 → **si2**	4.80E+12	4.82E+12	4.84E+12	4.86E+12	4.99E+12
si3 → **si10**	3.24E+11	3.30E+11	3.37E+11	3.44E+11	3.72E+11
si10 → **si3**	3.02E+09	3.51E+09	4.06E+09	4.68E+09	8.40E+09
si10 → **si4**	5.07E+12	5.15E+12	5.24E+12	5.32E+12	5.62E+12
si4 → **si10**	5.07E+07	5.45E+07	5.86E+07	6.29E+07	8.44E+07
si10 → **si7**	4.88E+11	5.04E+11	5.20E+11	5.36E+11	6.08E+11
si7 → **si10**	1.61E+08	1.78E+08	1.96E+08	2.15E+08	3.25E+08
si7 → **si6**	7.52E+09	8.02E+09	8.55E+09	9.10E+09	1.18E+10
si6 → **si7**	2.32E+09	2.50E+09	2.69E+09	2.89E+09	3.89E+09
si7 → **si8**	2.83E+09	3.05E+09	3.28E+09	3.52E+09	4.89E+09
si8 → **si7**	6.97E+09	7.42E+09	7.88E+09	8.36E+09	1.12E+10
si10 → 1,2,4-tridehydrobenzene	5.82E+08	6.84E+08	8.02E+08	9.35E+08	9.80E+08
si6 → C_4H_2 + C_2H_2	2.44E+09	2.75E+09	3.09E+09	3.47E+09	5.52E+09
si6 → 1,2,3-tridehydrobenzene*	6.36E+07	7.13E+07	7.98E+07	8.91E+07	1.11E+08
si4 → $H_2CCCCCCH$*	4.32E+08	4.77E+08	5.26E+08	5.78E+08	6.97E+08
si7 → 1,2,3-tridehydrobenzene*	2.82E+08	3.13E+08	3.47E+08	3.83E+08	9.32E+08
si6 → 1,2,4-tridehydrobenzene*	6.90E+07	7.74E+07	8.65E+07	9.67E+07	1.20E+08
si7 → 1,2,4-tridehydrobenzene*	1.19E+06	1.40E+06	1.65E+06	1.93E+06	8.58E+06
si8 → 1,2,4-tridehydrobenzene*	2.07E+08	2.28E+08	2.51E+08	2.75E+08	3.03E+08

	Collision Energy (kJmol^{-1})				
Branching Ratios (%)	0.0	4.2	8.4	12.6	31.0
$H_2CCCCCCH$ + H	91.02	90.48	90.37	90.28	89.59
C_4H_2 + C_2H_2	7.54	7.69	8.07	8.02	9.19
1,2,3-tridehydrobenzene	0.98	1.39	1.06	1.15	0.82
1,2,4-tridehydrobenzene	0.46	0.45	0.49	0.54	0.40
1,3,5-tridehydrobenzene	0.00	0.00	0.00	0.00	0.00

[a]The $C_2(^1\Sigma_g^+)$ + C_4H_4 → **si1** → **si9** → **si5** → $H_2CCCCCCH$ + H path was not considered in the calculations of rate constants and branching ratios because it is expected to exclusively produce $H_2CCCCCCH$ + H.

Table S3. Unimolecular Rate Constants for Various Reaction Steps on the Singlet and Triplet Surfaces Calculated Using RRKM Theory or Variational Transition State Theory (VTST, for barrierless H elimination reactions; designated with an asterisk) at Collision Energies of 0-31 kJmol^{-1} and Product Branching Ratios under Single-Collision Conditions.

Triplet Surface:

	Collision Energy (kJmol^{-1})				
Rate Constants (s^{-1})	0.0	4.2	8.4	12.6	31.0
ti2 → **ti5**	1.44E+10	1.51E+10	1.58E+10	1.65E+10	1.96E+10
ti5 → **ti2**	3.77E+09	4.38E+09	5.06E+09	5.81E+09	1.03E+10
ti2 → CCCHCHCCH	1.90E+05	3.46E+05	6.01E+05	9.99E+05	3.21E+06
ti3 → **ti2**	1.61E+11	1.81E+11	2.03E+11	2.27E+11	3.45E+11
ti2 → **ti3**	1.32E+09	1.46E+09	1.62E+09	1.78E+09	3.87E+11
ti3 → **ti4**	1.72E+11	1.91E+11	2.11E+11	2.33E+11	3.45E+11
ti4 → **ti3**	3.26E+04	4.11E+04	5.11E+04	6.32E+04	1.51E+05
ti4 →**ti5**	5.29E+07	5.81E+07	6.35E+07	6.94E+07	1.00E+08
ti5 → **ti4**	5.97E+11	6.33E+11	6.69E+11	7.07E+11	8.88E+11
ti4 → $H_2CCCCCCH$	4.71E+08	5.54E+08	6.49E+08	7.58E+08	1.02E+09
ti5 → **ti7**	2.56E+09	2.84E+09	3.15E+09	3.47E+09	2.09E+10
ti7 → **ti5**	5.26E+06	6.23E+06	7.36E+06	8.65E+06	1.70E+07
ti5 →1,2,4-tridehydrobenzene	1.91E+10	2.15E+10	2.40E+10	2.69E+10	3.30E+10
ti7 → **ti8**	9.12E+08	1.01E+09	1.11E+09	1.23E+09	3.67E+09
ti8 → **ti7**	7.86E+08	8.71E+08	9.63E+08	1.06E+09	6.46E+09
ti7 → **ti6**	1.99E+09	2.17E+09	2.37E+09	2.58E+09	3.50E+09
ti6 → **ti7**	3.59E+09	3.90E+09	4.24E+09	4.59E+09	7.34E+09
ti7 → 1,2,4-tridehydrobenzene	2.27E+09	2.67E+09	3.13E+09	3.66E+09	7.00E+09
ti6 → 1,2,3-tridehydrobenzene	2.36E+09	2.77E+09	3.23E+09	3.76E+09	5.22E+09
ti6 → 1,2,4-tridehydrobenzene	3.18E+07	3.83E+07	4.60E+07	5.50E+07	8.00E+07
ti1 → **ti5**	2.56E+09	2.73E+09	2.90E+09	3.07E+09	5.12E+09
ti5 → **ti1**	1.73E+09	1.96E+09	2.21E+09	2.49E+09	3.06E+09
ti7 → 1,3,5-tridehydrobenzene*	4.28E+03	5.51E+03	7.08E+03	9.03E+03	1.43E+04
ti8 → 1,2,4-tridehydrobenzene*	9.56E+06	1.11E+07	1.30E+07	1.50E+07	2.00E+07
ti7 → 1,2,3-tridehydrobenzene*	9.34E+05	1.10E+06	1.29E+06	1.51E+06	4.08E+06

Branching Ratios (%)	Collision Energy (kJmol^{-1})				
starting from **ti1** or **ti2**	0.0	4.2	8.4	12.6	31.0
$H_2CCCCCCH$ + H	96.20	96.10	95.93	95.73	99.19
CCCHCHCCH + H	0.00	0.00	0.00	0.00	0.00
1,2,3-tridehydrobenzene	0.18	0.18	0.12	0.12	0.03
1,2,4-tridehydrobenzene	3.62	3.71	3.95	4.15	0.78
1,3,5-tridehydrobenzene	0.00	0.00	0.00	0.00	0.00

Table S3. Unimolecular Rate Constants for Various Reaction Steps on the Singlet and Triplet Surfaces Calculated Using RRKM Theory or Variational Transition State Theory (VTST, for barrierless H elimination reactions; designated with an asterisk) at Collision Energies of 0-31 $kJmol^{-1}$ and Product Branching Ratios under Single-Collision Conditions.

starting from **ti3**					
$H_2CCCCCCH + H$	97.96	97.90	97.81	97.71	99.42
CCCHCHCCH + H	0.00	0.00	0.00	0.00	0.00
1,2,3-tridehydrobenzene	0.10	0.10	0.06	0.06	0.02
1,2,4-tridehydrobenzene	1.94	2.00	2.23	2.23	0.56
1,3,5-tridehydrobenzene	0.00	0.00	0.00	0.00	0.00