Supporting Information

Formation of 6-Methyl-1,4-Dihydronaphthalene in the Reaction of the Para-Tolyl Radical with 1,3-Butadiene under Single Collision Conditions

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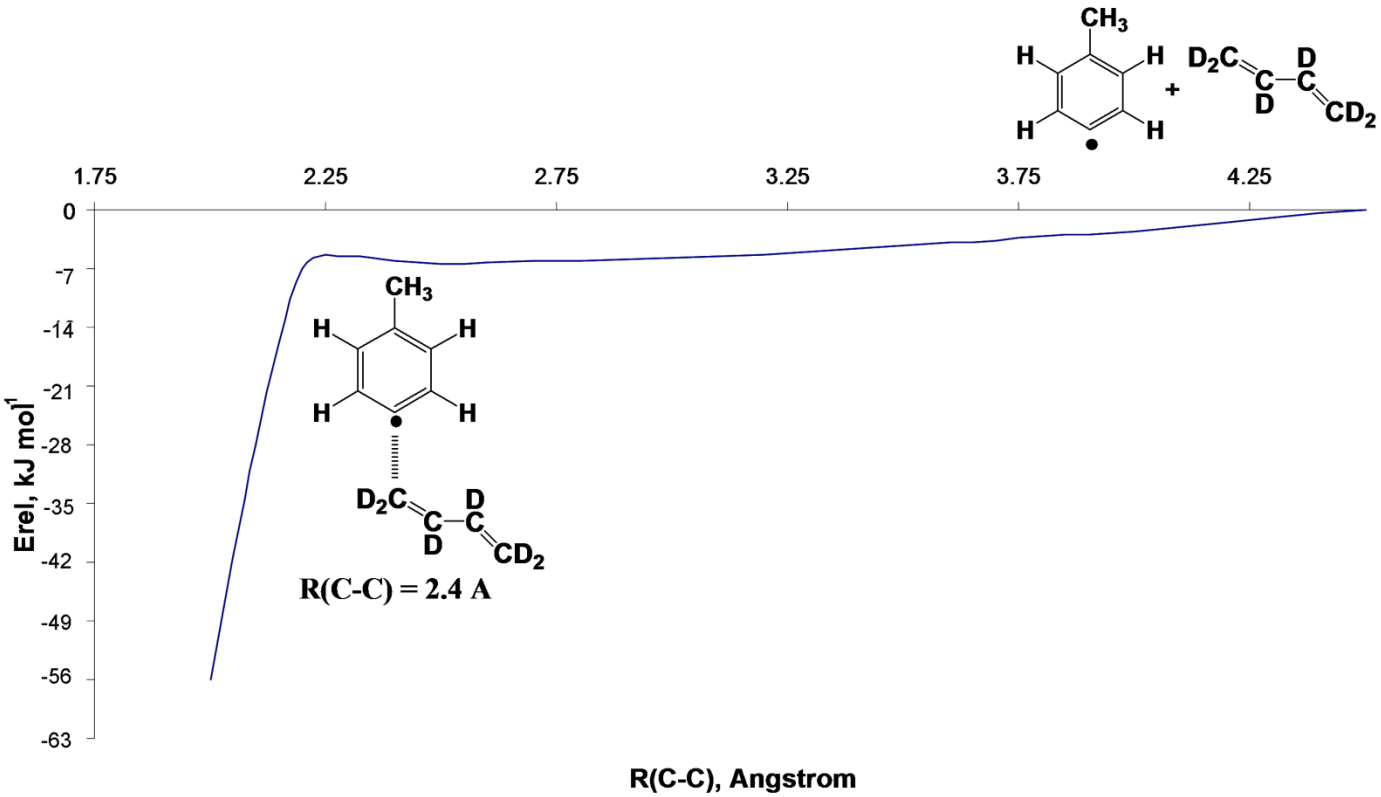

Figure S1. Potential energy scan along the minimum energy path of the para-tolyl to the terminal carbon of 1,3-butadiene. The van-der-Waals complex formed is shown at R(C-C) bond length of 2.4 Å, indicating this reaction channel has a submerged barrier.

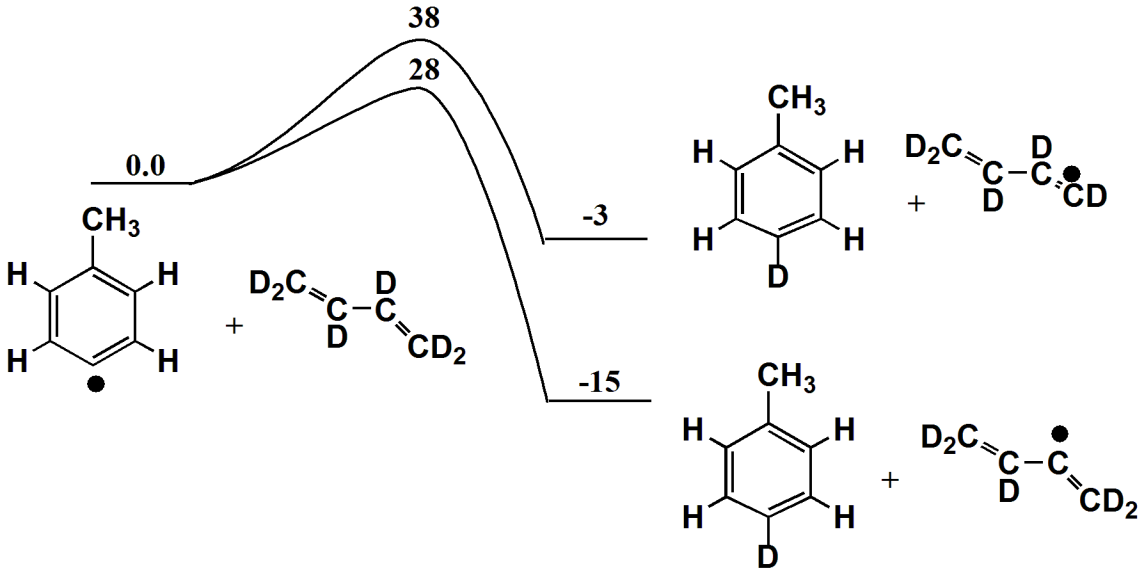

Figure S2. Potential energy diagram for the D-abstraction by p-tolyl from 1,3-butadiene. Energies for transition states and products are given relative to the reactants energy (in kJ mol^{-1}) at the E(CCSD(T)-F12/cc-pvdz//M06-2x/cc-pvtz + ZPE(M06-2x/6-cc-pvtz)) level of theory.

Table S1. Optimized Cartesian coordinates calculated at the M06-2x/cc-pvtz level of theory of the reactants, intermediates, transition states, and products of the reaction of p-tolyl with 1,3-butadiene.

Species	Optimized coordinates (x,y,z)
Para-toluene radical	C 0.009521 -0.001645 0.005201 C -0.003424 -0.013062 1.398358 C 1.209465 -0.015644 2.082573 C 2.423760 -0.002359 1.398102 C 2.364974 0.012204 0.029864 C 1.208407 0.011901 -0.704412 H -0.929915 -0.006222 -0.535169 H 1.208441 -0.031301 3.166098 H 3.363147 -0.007293 1.934624 H 1.212964 0.018011 -1.786171 C -1.307445 0.002718 2.149207 H -1.666376 1.024906 2.282202 H -2.078095 -0.548144 1.611717 H -1.197750 -0.440021 3.137960
1,3-butadiene	C -3.277225 1.621529 0.630117 H -2.778010 0.660078 0.630117 H -4.357860 1.617982 0.630117 C -2.582312 2.754258 0.630117 H -3.102368 3.707249 0.630117 C -1.125817 2.811744 0.630117 H -0.605784 1.858741 0.630117 C -0.430875 3.944454 0.630117 H -0.930047 4.905925 0.630117 H 0.649761 3.947955 0.630117
Intermediate 1	C -3.386554 0.519497 0.053880 C -2.009938 0.452364 -0.147050 C -1.242935 1.603799 -0.197536 C -1.821906 2.861745 -0.042542 C -3.195000 2.925869 0.159843 C -3.966071 1.771864 0.208989 H -1.538641 -0.516340 -0.264346 H -0.174344 1.528648 -0.360517 H -3.669751 3.892051 0.281739 H -5.035227 1.848362 0.366947 C -0.977560 4.105838 -0.066851 H -0.512689 4.277716 0.905788 H -0.177672 4.022172 -0.801852 H -1.574845 4.983469 -0.309005 C -4.220375 -0.745673 0.081099 H -5.233740 -0.481954 0.398265

	H -4.304274 -1.150237 -0.930945 C -3.657181 -1.793264 0.983456 H -3.535755 -1.529618 2.029174 C -3.262170 -3.047989 0.566055 H -3.384113 -3.281883 -0.488103 C -2.726912 -4.016907 1.385044 H -2.432625 -4.981009 1.000148 H -2.584344 -3.832575 2.441238
Intermediate 2	C -0.007901 -0.022913 -0.099104 C -0.068108 -0.105761 1.290655 C 1.088279 -0.099782 2.050939 C 2.343639 -0.001637 1.452912 C 2.399720 0.085355 0.068006 C 1.240403 0.075722 -0.697780 H -1.034551 -0.175077 1.776484 H 1.019617 -0.171863 3.130022 H 3.363099 0.162217 -0.421528 H 1.310850 0.141701 -1.776903 C 3.592210 0.032661 2.290243 H 3.736972 1.020425 2.731647 H 3.534819 -0.685146 3.108161 H 4.473568 -0.198285 1.694181 C -1.280330 -0.054672 -0.922922 H -1.020636 0.114420 -1.970230 H -1.722947 -1.050277 -0.867007 C -2.265844 0.978574 -0.481130 H -2.023929 2.006350 -0.720378 C -3.419997 0.728724 0.242209 H -4.028805 1.591259 0.490969 C -3.861820 -0.497283 0.684304 H -4.782110 -0.582470 1.241667 H -3.315234 -1.410272 0.496585
Intermediate 3	C -3.896571 -0.939231 0.396678 C -2.491188 -0.961776 0.308760 C -1.788202 0.083527 -0.200509 C -2.476986 1.339352 -0.636679 C -3.966443 1.259098 -0.563889 C -4.630658 0.191110 -0.061085 H 0.142148 -0.689655 0.289037 H -4.427642 -1.787961 0.805842 H -1.956000 -1.840714 0.650466 C -0.297531 0.090805 -0.335961 C -1.933049 2.526479 0.197269 H -4.522603 2.124124 -0.909587 C -0.433197 2.507679 0.269873 C 0.296110 1.429174 0.015902

	H -2.361581 2.477740 1.202865 H 0.063182 3.431965 0.542503 H 1.377178 1.487671 0.065510 C -6.131248 0.161965 0.027036 H -6.534903 -0.678825 -0.539301 H -6.454445 0.039869 1.062020 H -6.568278 1.079514 -0.362431 H -2.279268 3.464527 -0.242742 H -0.015035 -0.156499 -1.368450 H -2.170181 1.554242 -1.673047
Intermediate 4a	C -3.431130 0.522839 0.120181 C -2.045027 0.404013 0.160972 C -1.231093 1.521504 0.056281 C -1.770993 2.795036 -0.092893 C -3.156027 2.911050 -0.140733 C -3.972781 1.795648 -0.034269 H -1.596380 -0.575165 0.269955 H -0.154690 1.401556 0.088973 H -3.603180 3.889987 -0.265856 H -5.048445 1.914260 -0.080310 C -0.883932 4.006177 -0.175770 H -0.599946 4.347768 0.821393 H 0.033679 3.784648 -0.719567 H -1.388949 4.830814 -0.676482 C -4.331717 -0.701920 0.183073 H -4.507403 -1.047510 -0.841245 C -3.694853 -1.847153 0.935450 H -3.420467 -1.629084 1.963824 C -3.500083 -3.058650 0.437352 H -3.071728 -3.853772 1.032264 C -5.652826 -0.415752 0.821809 H -5.694682 0.202545 1.707471 H -6.504916 -1.035775 0.588601 H -3.765064 -3.293246 -0.586887
Intermediate 4b	C -4.794204 -0.788544 -0.803811 C -3.462904 -0.831711 -0.107486 C -2.908360 0.277116 0.439039 C -3.600525 1.506843 0.426701 C -4.950443 1.576925 -0.026414 C -5.541433 0.482523 -0.566483 C -5.446096 -2.105423 -0.389278 C -4.352899 -3.009745 0.120971 C -3.029198 -2.262573 0.031596 H -1.949692 0.211268 0.940498 H -3.141729 2.389764 0.850983 H -6.572509 0.532702 -0.897587

	H -4.370591 -4.067774 -0.093090 H -2.485668 -2.595895 -0.859114 H -6.257227 -2.495264 -0.986554 C -5.380120 -2.455634 1.065262 H -6.123028 -3.141938 1.442718 H -5.075893 -1.681893 1.759102 C -5.693575 2.874452 0.136442 H -6.709798 2.798150 -0.245557 H -5.741308 3.166345 1.186699 H -5.185931 3.677841 -0.399829 H -2.380017 -2.415998 0.894501 H -4.611396 -0.876238 -1.891005
Intermediate 5	C -3.735332 -0.997788 0.027205 C -2.371183 -0.850383 -0.155612 C -1.839132 0.396643 -0.418150 C -2.731372 1.574166 -0.682843 C -4.136429 1.371797 -0.226602 C -4.614695 0.143942 0.060580 H -4.150390 -1.974209 0.241330 H -1.716287 -1.703243 -0.023205 C -1.915166 2.745940 -0.108995 H -4.794809 2.233061 -0.195798 C -0.477699 2.354964 -0.485331 C -0.464018 0.840046 -0.372737 H -2.030841 2.763720 0.976379 H 0.284455 2.824996 0.133216 C -6.048760 -0.085673 0.445788 H -6.526933 -0.774573 -0.252990 H -6.117533 -0.534334 1.438199 H -6.612391 0.845202 0.448525 H -2.217517 3.713614 -0.506483 H -2.757612 1.730793 -1.778713 H -0.284932 2.640078 -1.523977 C 0.632027 0.082218 -0.233699 H 0.571034 -0.996023 -0.169728 H 1.616398 0.526749 -0.179445
Intermediate 6	C -3.538409 0.661800 0.805833 C -2.852314 0.528916 -0.403678 C -1.979789 1.511581 -0.849207 C -1.749530 2.670681 -0.111949 C -2.430730 2.825472 1.099412 C -3.279054 1.824568 1.488553 H -3.017369 -0.359353 -1.003621 H -1.465103 1.376698 -1.792349 H -2.283781 3.715042 1.700431 C -0.776549 3.716496 -0.581448

	H 0.205440 3.559750 -0.131267 H -0.654763 3.682923 -1.662917 H -1.109375 4.715689 -0.303381 C -4.521277 -0.379589 1.279512 C -5.895049 -0.193709 0.680980 C -6.282369 0.787826 -0.118117 H -7.300196 0.840385 -0.479818 C -4.624243 -0.415956 2.806631 H -3.650101 -0.607989 3.255188 H -4.990245 0.541416 3.179530 H -5.600270 1.566224 -0.435963 H -6.615648 -0.952394 0.975138 H -5.316152 -1.194675 3.127259 H -4.154842 -1.355125 0.942461
Intermediate 7	C -3.798538 -1.012903 -0.290477 C -2.451793 -0.857638 -0.590703 C -1.887699 0.406857 -0.544355 C -2.671533 1.502543 -0.198255 C -4.014243 1.343259 0.100533 C -4.593808 0.077387 0.059543 H -4.245891 -1.998592 -0.331443 H -1.854447 -1.719259 -0.863743 C -1.860696 2.776074 -0.212970 H -4.621286 2.201804 0.366513 C -0.494496 2.287422 -0.574642 C -0.455852 0.809311 -0.821717 H -1.887526 3.286701 0.756772 C -6.043850 -0.113490 0.412384 H -6.465338 -0.974680 -0.104244 H -6.163883 -0.281406 1.484472 H -6.631729 0.765015 0.149554 H -2.256952 3.496288 -0.939675 H 0.370697 2.925959 -0.667255 C 0.561189 0.070898 0.057177 H 0.335781 0.236960 1.110956 H 0.535944 -1.002259 -0.135745 H 1.571890 0.428852 -0.140387 H -0.204783 0.595135 -1.869789
Transition State 1-2	C -3.107897 0.557866 -0.086281 C -1.726771 0.684694 -0.223228 C -1.118495 1.926402 -0.171666 C -1.866745 3.086279 0.023932 C -3.242577 2.957762 0.160259 C -3.854416 1.711500 0.107097 H -1.127390 -0.206111 -0.373316 H -0.043535 2.002269 -0.286003

	H -3.846681 3.844207 0.311206 H -4.929884 1.637933 0.215426 C -1.194321 4.428676 0.107469 H -0.720791 4.565374 1.081428 H -0.417134 4.527567 -0.650067 H -1.910850 5.236653 -0.030266 C -3.755135 -0.802567 -0.150687 H -4.839433 -0.691520 -0.012625 H -3.631199 -1.228439 -1.152229 C -3.199173 -1.766204 0.848080 H -2.847825 -1.371639 1.793949 C -3.473280 -3.205327 0.733032 H -4.442450 -3.560032 1.086713 C -2.629681 -4.087147 0.214774 H -2.882248 -5.136627 0.142270 H -1.656394 -3.780416 -0.149107
Transition State 1-h	C -2.459315 0.334965 0.014524 C -1.178423 0.612018 0.497300 C -0.596418 1.847280 0.289330 C -1.267453 2.857519 -0.400977 C -2.545552 2.585409 -0.870678 C -3.134355 1.346553 -0.662766 H -0.637723 -0.140768 1.055303 H 0.397599 2.040317 0.675042 H -3.090289 3.353437 -1.405666 H -4.133762 1.157821 -1.035563 C -0.621918 4.198645 -0.608666 H 0.353501 4.092598 -1.084579 H -1.238493 4.840581 -1.235079 H -0.465136 4.705885 0.344527 C -3.110668 -0.970588 0.197806 H -3.909445 -0.514303 1.924438 H -4.149983 -1.020983 -0.112942 C -2.484792 -2.132454 0.491508 H -1.421667 -2.138426 0.706244 C -3.169538 -3.401570 0.569356 H -4.235249 -3.391309 0.362617 C -2.570031 -4.551874 0.879021 H -3.117549 -5.482101 0.926680 H -1.508923 -4.588421 1.093142
Transition State 2-3	C -3.887827 -0.812596 0.521061 C -2.501196 -0.869556 0.390824 C -1.808922 0.077991 -0.332430 C -2.534144 1.172278 -0.884518 C -3.948882 1.148132 -0.842657 C -4.626613 0.195799 -0.108523

	H 0.098681 -0.650872 0.289372 H -4.405625 -1.571852 1.093876 H -1.953337 -1.669692 0.874458 C -0.308029 0.100973 -0.392749 C -1.874123 2.519770 0.578835 H -4.503014 1.922813 -1.358352 C -0.437162 2.516313 0.321451 C 0.272032 1.456342 -0.080044 H -2.269861 1.938335 1.401609 H 0.078168 3.470581 0.389660 H 1.334304 1.573744 -0.257494 C -6.126496 0.209965 0.000316 H -6.553620 -0.715448 -0.388013 H -6.439036 0.300298 1.041542 H -6.555314 1.042153 -0.555009 H -2.395012 3.457998 0.419291 H 0.036130 -0.185897 -1.392628 H -2.050841 1.777543 -1.641616
Transition State 2-h	C -0.334431 -0.546493 0.255043 C 0.119864 -1.590324 1.052308 C 1.224622 -1.426037 1.877871 C 1.913709 -0.221049 1.918075 C 1.465218 0.818017 1.102048 C 0.363799 0.660101 0.282379 H -0.403445 -2.538470 1.036636 H 1.555489 -2.250290 2.497669 H 1.995831 1.762674 1.108641 H 0.029504 1.475881 -0.345727 C 3.126984 -0.039726 2.786800 H 3.086075 0.908042 3.323557 H 3.214624 -0.842689 3.516508 H 4.036962 -0.033828 2.184268 C -1.527549 -0.743443 -0.601700 H -0.676154 -0.043400 -2.225090 H -1.539122 -1.662283 -1.178500 C -2.667272 -0.020492 -0.580512 H -3.440201 -0.321170 -1.279655 C -2.996180 1.145687 0.237419 H -3.691201 1.845843 -0.215264 C -2.588987 1.379055 1.483022 H -2.918031 2.261388 2.014740 H -1.930414 0.699575 2.007361
Transition State 3-h	C -4.019241 -1.129776 0.402640 C -2.635840 -1.114566 0.442278 C -1.920662 0.072214 0.368502 C -2.627604 1.279878 0.198239

	C -4.039317 1.247302 0.246536 C -4.743375 0.064820 0.314814 H -0.040841 -0.485812 1.218329 H -4.550862 -2.071547 0.461828 H -2.092706 -2.048569 0.530409 C -0.416121 0.043347 0.336366 C -1.938365 2.617275 0.376721 H -4.575892 2.188419 0.192183 C -0.448206 2.535532 0.274776 C 0.223346 1.394194 0.254625 H -2.213781 3.017239 1.359074 H 0.091654 3.473553 0.225698 H 1.304244 1.413528 0.180734 C -6.246370 0.043048 0.299409 H -6.616143 -0.379138 -0.636425 H -6.637461 -0.570596 1.111171 H -6.656575 1.046156 0.400483 H -2.326322 3.329403 -0.354820 H -0.093566 -0.559755 -0.519921 H -2.374086 1.290761 -1.522553
Transition State 4-5	C -3.120001 0.387553 0.107333 C -1.973549 0.543526 -0.656833 C -1.290062 1.753658 -0.678076 C -1.733940 2.838890 0.065248 C -2.884682 2.677484 0.836347 C -3.567801 1.474668 0.855923 H -1.606750 -0.290199 -1.243579 H -0.396036 1.852033 -1.281814 H -3.246817 3.510440 1.427423 H -4.465353 1.370200 1.455302 C -1.014640 4.158918 0.031786 H -0.894642 4.566348 1.035549 H -0.027527 4.058478 -0.416165 H -1.574599 4.891208 -0.552480 C -3.871559 -0.930280 0.151679 H -3.393975 -1.587743 -0.588946 C -3.736584 -1.609640 1.503118 H -3.183168 -1.066961 2.261817 C -4.242505 -2.799588 1.783729 H -4.120708 -3.248596 2.759782 C -5.303417 -0.747746 -0.238342 H -6.093809 -1.236802 0.309078 H -5.544282 -0.192758 -1.132852 H -4.795506 -3.367811 1.043764
Transition State 4-6	C -2.927026 0.349724 0.043374 C -1.552029 0.301210 -0.142704

	C -0.837046 1.490120 -0.192512 C -1.460723 2.732245 -0.055645 C -2.844126 2.776596 0.135472 C -3.527688 1.582086 0.179806 H -1.044957 -0.651236 -0.245918 H 0.235649 1.460785 -0.341500 H -3.345087 3.730983 0.244166 H -4.829099 1.114699 0.372068 C -0.648462 3.998909 -0.084801 H -0.183421 4.182746 0.885479 H 0.149080 3.935277 -0.824357 H -1.269693 4.860352 -0.324468 C -3.912870 -0.806678 0.111663 H -3.995891 -1.266211 -0.876337 C -3.485252 -1.860391 1.088944 H -3.389493 -1.526259 2.118968 C -3.210274 -3.117245 0.775495 H -2.894671 -3.832129 1.523059 C -5.238734 -0.141585 0.491009 H -5.518339 -0.237871 1.536927 H -6.075745 -0.302880 -0.180084 H -3.295274 -3.472394 -0.244764
Transition State 4-h	C -3.432130 0.594075 0.734580 C -2.093476 0.572612 1.119156 C -1.257548 1.639202 0.828883 C -1.726407 2.757534 0.145930 C -3.065745 2.778624 -0.228278 C -3.905841 1.713935 0.059400 H -1.709577 -0.280113 1.663548 H -0.221743 1.605408 1.144534 H -3.457026 3.639800 -0.756143 H -4.944137 1.743105 -0.247609 C -0.806351 3.894677 -0.200419 H -1.352582 4.833663 -0.277777 H -0.025551 4.012469 0.549792 H -0.317302 3.717605 -1.160229 C -4.351782 -0.518477 1.128521 H -5.260315 -0.506233 -0.407260 C -3.952599 -1.927391 0.901515 H -4.585007 -2.658268 1.394371 C -2.932534 -2.341374 0.161569 H -2.723051 -3.395977 0.051082 C -5.358374 -0.254015 1.999320 H -5.983950 -1.049473 2.382293 H -5.593899 0.760560 2.287551 H -2.288845 -1.647351 -0.362774

Transition State 4-s	C -3.474703 0.427247 -0.077670 C -2.323562 0.456204 -0.858415 C -1.481267 1.557961 -0.849938 C -1.754289 2.662414 -0.052051 C -2.901330 2.626939 0.739679 C -3.745438 1.531233 0.730677 H -2.086425 -0.396802 -1.482576 H -0.595719 1.558366 -1.473604 H -3.133662 3.474080 1.374123 H -4.621061 1.529794 1.367093 C -0.832937 3.849667 -0.017036 H -1.395531 4.782976 -0.016219 H -0.217616 3.838200 0.884469 H -0.164364 3.854248 -0.876218 C -4.358965 -0.757589 -0.119859 H -3.984507 -1.586584 -0.711071 C -3.377489 -1.824789 1.613808 H -3.202219 -1.102280 2.397705 C -3.168192 -3.109917 1.510735 H -2.716186 -3.685403 2.316013 C -5.675056 -0.738565 0.192053 H -6.144881 0.123218 0.645149 H -6.290026 -1.613584 0.041041 H -3.434608 -3.662152 0.614483
Transition State 6-7	C 0.080584 -0.056934 0.023262 C 0.165202 -0.061380 1.411551 C 1.403386 0.025401 2.037067 C 2.509910 0.106449 1.215073 C 2.467707 0.103952 -0.154894 C 1.215286 0.029928 -0.777698 H -0.891706 -0.123572 -0.449273 H -0.742044 -0.133137 1.999935 C 4.007368 -0.006980 2.890353 H 3.368307 0.160133 -0.755599 C 3.052129 0.562609 3.664288 C 1.650412 0.032951 3.546110 H 4.968175 0.468933 2.743980 C 1.107238 0.072967 -2.277477 H 1.157286 1.101644 -2.639247 H 1.921426 -0.478556 -2.746679 H 0.164153 -0.352596 -2.616861 H 3.956842 -1.056854 2.627733 H 3.194368 1.553256 4.080724 C 0.627227 0.847907 4.326051 H 0.614745 1.879221 3.970551 H -0.376829 0.440833 4.215019

	H 0.870905 0.851701 5.388483 H 1.618184 -1.005256 3.895958
Transition State 7-h	C -3.719463 -0.972543 -0.349811 C -2.360189 -0.861845 -0.630865 C -1.825046 0.390119 -0.855646 C -2.642948 1.521051 -0.788353 C -3.992200 1.409741 -0.503137 C -4.544531 0.148315 -0.282419 H -4.151122 -1.951387 -0.181172 H -1.741409 -1.749848 -0.677500 C -1.803858 2.705788 -1.047476 H -4.619704 2.292066 -0.450075 C -0.548309 2.292489 -1.338801 C -0.408726 0.802980 -1.171112 H -1.681029 3.226865 0.747129 C -6.005030 0.008870 0.051343 H -6.190168 0.268324 1.095295 H -6.613753 0.671733 -0.563061 H -6.349648 -1.012131 -0.103498 H -2.190166 3.703789 -1.195385 H 0.280859 2.932662 -1.602859 C 0.584278 0.426546 -0.064761 H 0.273953 0.875188 0.879387 H 0.622949 -0.654735 0.064703 H 1.586856 0.779687 -0.304988 H -0.076801 0.348785 -2.110983
Product trans-1-para-tolyl-1,3-butadiene (p1)	C -3.097784 0.188143 -0.369545 C -2.522873 0.758147 -1.506841 C -1.847572 1.964035 -1.438759 C -1.735808 2.657043 -0.236142 C -2.338030 2.107282 0.891420 C -3.009701 0.896935 0.829622 H -2.603285 0.239925 -2.454567 H -1.405265 2.381154 -2.335318 H -2.292733 2.643841 1.831437 H -3.502525 0.510995 1.711863 C -0.981300 3.954486 -0.157812 H 0.073279 3.774954 0.060445 H -1.034093 4.497991 -1.100122 H -1.376512 4.593588 0.630463 C -3.807619 -1.094181 -0.485020 H -4.356561 -1.233073 -1.410566 C -3.830334 -2.095969 0.402075 H -4.437896 -2.963773 0.166978 C -3.072920 -2.180663 1.643213 H -2.311854 -1.428829 1.815210

	C -3.248246 -3.150632 2.537214 H -2.653336 -3.204324 3.438020 H -3.997912 -3.919175 2.391383
Product cis-1-para-tolyl-1,3-butadiene (p2)	C 1.550142 0.719623 -0.121653 C 2.889743 0.719284 -0.505235 C 3.669097 1.854646 -0.357460 C 3.143671 3.027555 0.177269 C 1.809673 3.022764 0.574486 C 1.029833 1.886821 0.437680 H 3.322150 -0.181294 -0.918887 H 4.709353 1.829467 -0.658662 H 1.379091 3.920489 1.001997 H -0.003978 1.902332 0.761089 C 3.989378 4.258675 0.347548 H 4.149808 4.477582 1.404446 H 4.964154 4.135203 -0.120920 H 3.506182 5.129958 -0.095405 C 0.691243 -0.474862 -0.229360 H 0.024163 -0.625946 0.613631 C 0.632172 -1.379880 -1.209387 H -0.027690 -2.226780 -1.049216 C 1.323357 -1.379227 -2.506880 H 1.670943 -2.346523 -2.856728 C 1.474996 -0.321697 -3.294690 H 1.965243 -0.405576 -4.254963 H 1.111496 0.655182 -3.002320
Product 6-methyl-1,4-dihydronapthalene (p3)	C -4.038560 -1.140923 0.488581 C -2.658507 -1.126794 0.493243 C -1.941794 0.067197 0.404674 C -2.645468 1.261517 0.310576 C -4.040897 1.233099 0.307596 C -4.757155 0.051613 0.393730 H -0.095585 -0.480043 1.330126 H -4.570682 -2.081865 0.560950 H -2.112569 -2.060413 0.569228 C -0.434408 0.021983 0.417809 C -1.946804 2.594492 0.212756 H -4.578530 2.173343 0.236116 C -0.453460 2.504251 0.230124 C 0.216120 1.365405 0.320600 H -2.281999 3.238530 1.032412 H 0.090856 3.438991 0.162904 H 1.299643 1.383325 0.326605 C -6.260624 0.040515 0.373119 H -6.633637 -0.384009 -0.560479 H -6.658773 -0.565014 1.187677

	H -6.664204 1.047000 0.468473 H -2.269583 3.104464 -0.700925 H -0.084455 -0.612052 -0.403525
Product para-tolyl-styrene (p5)	C -2.417191 0.393950 0.173657 C -1.073963 0.501357 -0.179404 C -0.452426 1.736909 -0.275652 C -1.154324 2.910451 -0.029307 C -2.500374 2.804569 0.320332 C -3.121997 1.574245 0.418418 H -0.507517 -0.400935 -0.375766 H 0.595153 1.789565 -0.546088 H -3.067192 3.706430 0.518315 H -4.169706 1.531641 0.684497 C -3.028878 -0.938958 0.277276 H -2.394155 -1.756731 -0.049376 C -4.244027 -1.224873 0.730099 H -4.596127 -2.245973 0.763793 H -4.925399 -0.463697 1.086905 C -0.495250 4.254245 -0.163931 H 0.581042 4.180934 -0.015588 H -0.664538 4.670476 -1.158999 H -0.894712 4.963395 0.560070
Product para-tolyl-styrene radical (p7)	C -3.621695 0.714584 -0.516969 C -3.141071 1.371779 -1.685619 C -2.219828 2.384670 -1.587613 C -1.719056 2.809335 -0.349715 C -2.189187 2.170286 0.799791 C -3.112848 1.151771 0.736521 H -3.515980 1.057829 -2.649770 H -1.869657 2.870079 -2.491029 H -1.816982 2.485770 1.766899 H -3.464735 0.670696 1.638380 C -0.698476 3.907074 -0.276032 H 0.252199 3.586386 -0.707306 H -1.024737 4.786661 -0.832776 H -0.513995 4.205895 0.754351 C -4.539579 -0.296592 -0.599787 C -5.404276 -1.255636 -0.679948 H -6.475691 -1.067271 -0.651522 H -5.100911 -2.296056 -0.779496
Product p4	C 0.519337 -0.982266 0.469361 C 1.360746 -0.566139 1.501012 C 2.104909 0.594809 1.381971 C 2.044607 1.374682 0.228688 C 1.212333 0.952853 -0.801347 C 0.459101 -0.206228 -0.684039

	H 1.418893 -1.155474 2.406981 H 2.745805 0.904514 2.198749 H 1.157538 1.535697 -1.712727 H -0.174443 -0.526505 -1.501255 C 2.840822 2.644865 0.115950 H 2.338163 3.463224 0.634855 H 3.828134 2.531444 0.562632 H 2.966904 2.939841 -0.924480 C -0.316176 -2.202671 0.605688 C -1.630031 -2.154396 0.373961 H -2.120742 -1.229163 0.104186 H -2.243069 -3.042753 0.456198 C 0.311874 -3.477897 0.982748 H -0.383922 -4.286098 1.183524 C 1.617235 -3.714992 1.058058 H 1.986434 -4.696550 1.320694 H 2.350623 -2.946383 0.852962
Product p6	C -3.676864 -1.054184 0.542652 C -2.318719 -0.883625 0.339375 C -1.813705 0.403457 0.194379 C -2.669726 1.499183 0.255693 C -4.028874 1.320773 0.459524 C -4.547494 0.038065 0.605759 H -4.082451 -2.053243 0.647405 H -1.662633 -1.742936 0.282242 C -1.901681 2.789544 0.115245 H -4.693677 2.176125 0.502547 C -0.506919 2.333250 -0.361956 C -0.430670 0.855034 -0.026027 H -1.838405 3.288961 1.084667 H 0.307852 2.898939 0.085351 C -6.015895 -0.180222 0.846008 H -6.387983 -1.021828 0.262124 H -6.207183 -0.402586 1.897470 H -6.594868 0.702973 0.581675 H -2.377091 3.485751 -0.574750 H -0.432788 2.450184 -1.445035 C 0.674883 0.125977 0.068238 H 1.651502 0.562576 -0.093357 H 0.637452 -0.926964 0.315239
Product p8	C -3.761308 -0.875538 -0.591733 C -2.409898 -0.768409 -0.908574 C -1.830191 0.483365 -0.945782 C -2.596774 1.620143 -0.664457 C -3.942161 1.508638 -0.350967 C -4.536275 0.248582 -0.310745

	H -4.226849 -1.853073 -0.563142 H -1.831999 -1.658128 -1.127777 C -1.722213 2.792408 -0.774346 H -4.534045 2.391336 -0.137840 C -0.488914 2.396653 -1.103992 C -0.411877 0.897056 -1.246626 C -5.987110 0.101157 0.060469 H -6.426180 -0.779509 -0.406098 H -6.101693 -0.006421 1.140905 H -6.562416 0.974013 -0.245469 H -2.043404 3.810645 -0.608496 H 0.367371 3.040321 -1.247746 C 0.620380 0.254728 -0.316957 H 0.388369 0.493963 0.720877 H 0.617063 -0.829342 -0.427768 H 1.623737 0.617350 -0.540282 H -0.159390 0.641188 -2.281708
C_2H_4	C 0.094577 -0.263765 -3.538297 H -0.889882 -0.273042 -3.088983 H 0.939969 -0.277834 -2.862868 C 0.256750 -0.236651 -4.849579 H 1.241209 -0.227357 -5.298893 H -0.588643 -0.222543 -5.525006
C_2H_3	C 0.018275 -0.262455 -3.595992 H -0.850881 -0.275749 -2.958353 C 0.248642 -0.235953 -4.876923 H 1.256965 -0.227819 -5.277081 H -0.562738 -0.221063 -5.603011
Transition State Terminal-central addition	C -0.85021045 -0.74074073 0.00000000 C -0.15267245 0.46701027 0.00000000 C -0.85032645 1.67551927 -0.00119900 C -2.24515145 1.67544127 -0.00167800 C -2.94275245 0.46723527 -0.00068200 H -0.30070245 -1.69325373 0.00131500 H 0.94700755 0.46709027 0.00063400 H -2.79527345 2.62772227 -0.00263100 H -4.04235645 0.46741827 -0.00086200 C -0.39483274 2.46273810 -1.24394274 H -0.84251490 3.43453540 -1.23441982 H 0.67061598 2.56074966 -1.23332466 H -0.69612007 1.93989270 -2.12754822 C -2.24537045 -0.74074073 0.00000000 C -3.54561227 -1.49088531 -0.00073501 C -2.24583964 -2.24181569 0.00200559 H -4.16394937 -1.49192470 -0.91544957 H -1.93727521 -2.77710745 0.91707900

	H -1.93483250 -2.77955045 -0.91080574 C -4.41147372 -1.48892776 1.27279556 H -4.13827465 -0.87073303 2.10231202 C -5.51826229 -2.26748739 1.34649097 H -5.79651203 -2.88777277 0.52022036 H -6.11593031 -2.26189563 2.23399403

Table S2. Forward and reverse RRKM rate constants for the terminal addition of 1,3-butadiene with para-tolyl as function of the energy E (in kJ mol^{-1}).

Channel	TS	0.0	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0	45.0	50.0	55.0	60.0
INT **1** → INT **2**	**1-2**	5.8E+08	6.8E+08	8.0E+08	9.2E+08	1.1E+09	1.2E+09	1.4E+09	1.6E+09	1.8E+09	2.0E+09	2.2E+09	2.5E+09	2.8E+09
INT **2** → INT **1**	**1-2**	1.1E+09	1.3E+09	1.5E+09	1.7E+09	2.0E+09	2.3E+09	2.6E+09	2.9E+09	3.3E+09	3.7E+09	4.1E+09	4.6E+09	5.1E+09
INT **1** → trans-1-para-tolyl-1,3-butadiene (**p1**) + D	**1-h**	8.4E-10	7.1E-08	1.2E-06	1.0E-05	5.5E-05	2.3E-04	8.2E-04	2.5E-03	7.0E-03	1.6E-02	3.9E-02	8.7E-02	1.8E-01
INT **2** → INT **3**	**2-3**	1.3E+06	1.6E+06	2.0E+06	2.5E+06	3.1E+06	3.8E+06	4.6E+06	5.5E+06	6.6E+06	7.7E+06	9.1E+06	1.1E+07	1.2E+07
INT **3** → INT **2**	**2-3**	5.1E+07	6.5E+07	8.3E+07	1.0E+08	1.3E+08	1.6E+08	1.9E+08	2.4E+08	2.8E+08	3.4E+08	4.0E+08	4.7E+08	5.6E+08
INT **2** → cis-1-para-tolyl-1,3-butadiene (**p2**) + D	**2-h**	0.0E+00	0.0E+00	0.0E+00	2.2E-09	1.5E-07	1.9E-06	1.4E-05	6.9E-05	2.8E-04	8.6E-04	2.6E-03	7.2E-03	1.8E-02
INT **3** → 6-methyl-1,4-dihydronapthalene (**p3**) + H	**3-h**	2.2E+05	3.4E+05	4.9E+05	7.1E+05	1.0E+06	1.4E+06	1.9E+06	2.6E+06	3.4E+06	4.4E+06	5.8E+06	7.5E+06	9.6E+06

Table S3. Statistical product branching ratios (%) upon the formation of intermediate **1** as function of E (in kJ mol^{-1}) of the reaction of p-tolyl with 1,3-butadiene.

Product	0.0	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0	45.0	50.0	55.0	60.0
trans-1-para-tolyl-1,3-butadiene (**p1**) + D	0.0	0.4	0.9	1.4	2.1	2.7	3.3	4.1	4.8	6.4	6.0	6.5	7.1
cis-1-para-tolyl-1,3-butadiene (**p2**) + D	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
6-methyl-1,4-dihydronapthalene (**p3**) + H	100.0	99.6	99.1	98.6	97.9	97.4	96.6	95.9	95.2	94.6	94.0	93.5	92.9