Supporting Information (5 pages)

Ultrafast dynamics of isolated phenylcarbenes: Velocity map imaging a promising technique for studying reactive intermediates.

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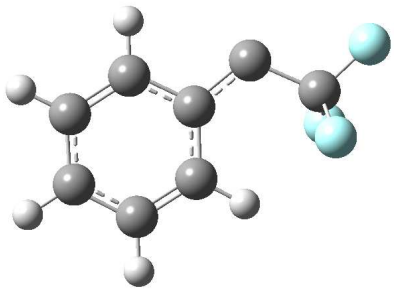
Supporting Calculations

Singlet-triplet gap of TFPC (B3LYP/6-311^{++}G**):

The calculations were performed using Gaussian 03.[1] Full optimization, tight convergence criteria, GDIIS, ultrafine grid

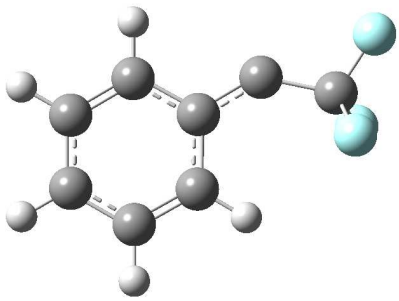
- triplet TFPC geometry (0 imaginary frequencies, no spin contamination)
(Sum of electronic and zero-point energies= -607.344393 ha, E(UB+HF-LYP) = -607.451561864 ha):

Atomic Name	Coordinates (Angstroms) X	Y	Z
C	3.337700	-0.342528	0.007417
C	2.353532	-1.336916	0.000824
C	1.010540	-1.002674	-0.009113
C	0.611066	0.368134	-0.011062
C	1.628431	1.364947	-0.004739
C	2.964433	1.006229	0.004163
C	-0.731725	0.736487	-0.019909
C	-2.033606	0.067460	0.000150
F	-2.250056	-0.625437	1.153353
F	-3.043228	0.954446	-0.121753
F	-2.172052	-0.837472	-1.010384
H	0.255227	-1.778308	-0.017232
H	1.337506	2.408318	-0.006549
H	2.641293	-2.382192	0.002707
H	3.725700	1.777897	0.009086
H	4.386075	-0.616385	0.014658



- singlet TFPC geometry (0 imaginary frequencies, negligible spin contamination)
(Sum of electronic and zero-point energies= -607.337751 ha, E(UB+HF-LYP) = -607.445458990 ha):

Atomic Name	Coordinates (Angstroms) X	Y	Z
C	0.768541	1.038773	0.000018
C	1.933445	0.091203	0.000003
C	-0.524320	0.447850	0.000004
C	-0.845749	-0.944580	0.000011
C	-1.604100	1.376113	-0.000004
C	-2.162937	-1.362606	0.000009
H	-0.051888	-1.678781	0.000012
C	-2.923157	0.951285	-0.000011
H	-1.347479	2.428283	-0.000002
C	-3.198116	-0.417423	-0.000004
H	-2.399970	-2.420102	0.000016
H	-3.734023	1.669790	-0.000021
H	-4.228501	-0.757088	-0.000007
F	3.121244	0.728960	-0.000060
F	1.944976	-0.715869	1.103823
F	1.944916	-0.715957	-1.103779

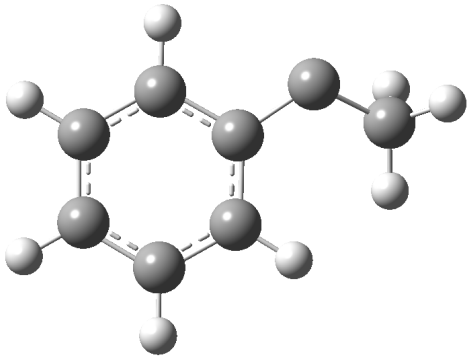


*Isomerization of MPC to Styrene (BMK/6-311G** QST3)[2,3]:*

The calculations were performed using Gaussian 03.[1] Full optimization, tight convergence criteria, GDIIS, ultrafine grid

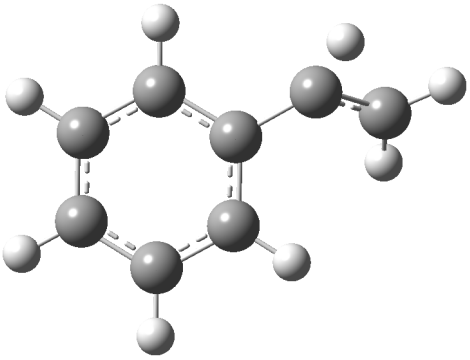
-Methylphenylcarbene (0 imaginary frequencies):
(Sum of electronic and zero-point energies= -309.253270 ha, E(RBMK+HF-BMK) = -309.383888293 ha):

Atomic Name	Coordinates (Angstroms) X	Y	Z
C	-2.237103	0.312349	0.106986
C	-1.310879	1.351289	-0.042499
C	0.046873	1.063128	-0.133061
C	0.503994	-0.279067	-0.139822
C	-0.460766	-1.310958	-0.046405
C	-1.811076	-1.019616	0.120029
C	1.890704	-0.694174	-0.298942
C	2.910543	0.254937	0.221686
H	2.619395	1.289691	0.462564
H	3.190927	-0.231998	1.175746
H	3.827659	0.231825	-0.376384
H	0.757257	1.876292	-0.239601
H	-0.105857	-2.335532	-0.097749
H	-1.653541	2.381039	-0.071961
H	-2.534883	-1.821885	0.223262
H	-3.294698	0.543244	0.196291



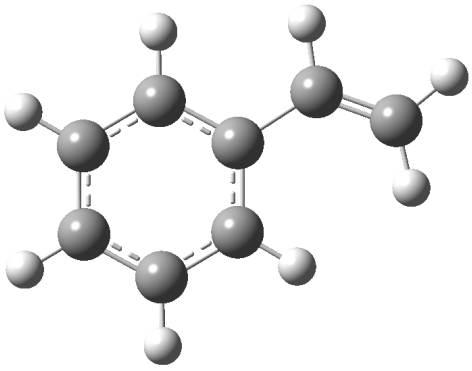
-Transition state (1 imaginary frequencies):
(Sum of electronic and zero-point energies= -309.241399 ha, E(RBMK+HF-BMK) = -309.369687 ha):

Atomic Name	Coordinates (Angstroms) X	Y	Z
C	-2.233420	0.235408	0.148098
C	-1.365710	1.313936	-0.035881
C	0.002996	1.093233	-0.191307
C	0.521792	-0.215787	-0.201688
C	-0.370483	-1.294282	-0.063064
C	-1.729898	-1.069238	0.142202
C	1.958036	-0.469633	-0.448725
C	2.834129	0.280287	0.337669
H	2.520082	1.064159	1.044456
H	2.625304	-0.964654	0.608553
H	3.910722	0.200669	0.173100
H	0.672711	1.936956	-0.334997
H	0.019916	-2.306163	-0.117054
H	-1.753626	2.328096	-0.049516
H	-2.402724	-1.911359	0.272726
H	-3.297038	0.408752	0.278914



-Styrene (0 imaginary frequencies):
(Sum of electronic and zero-point energies= -309.355705 ha, E(RBMK+HF-BMK) = -309.489581 ha):

Atomic Name	Coordinates (Angstroms) X	Y	Z
C	2.264078	0.263220	0.000007
C	1.359735	1.330573	-0.000004
C	-0.011515	1.091660	-0.000012
C	-0.512534	-0.222236	-0.000008
C	0.407117	-1.282933	0.000001
C	1.782372	-1.045397	0.000008
C	-1.960000	-0.532983	-0.000014
C	-2.972158	0.337947	0.000018
H	-2.820962	1.413012	0.000053
H	-2.195064	-1.596402	-0.000045
H	-4.000413	-0.007630	0.000011
H	-0.696907	1.932986	-0.000023
H	0.037034	-2.304705	0.000002
H	1.726930	2.352299	-0.000007
H	2.474092	-1.882146	0.000015
H	3.332711	0.453478	0.000012



Frequencies (cm^{-1}):

Methylphenylcarbene	*Transition state*	*Styrene*
3206.9, 3201.3, 3194.2, 3183.5, 3174.6, 3089.1, 3018.1, 2963.1, 1628.3, 1603.2, 1519.8, 1501.9, 1468.5, 1427.4, 1356.8, 1339.5, 1297.5, 1264.2, 1204.8, 1182.0, 1116.4, 1080.9, 1060.9, 1040.9, 1033.1, 1012.7, 1008.4, 971.6, 876.1, 817.2, 794.8, 763.1, 705.6, 626.5, 563.5, 481.3, 427.1, 416.7, 267.3, 223.7, 147.3, 74.8	3203.7, 3194.9, 3187.0, 3180.0, 3172.5, 3140.6, 3004.0, 2323.0, 1639.2, 1611.3, 1534.2, 1523.5, 1472.9, 1411.5, 1351.4, 1310.9, 1288.5, 1210.9, 1182.5, 1177.0, 1116.1, 1095.8, 1067.0, 1045.7, 1019.1, 1010.2, 1002.5, 941.6, 878.1, 801.0, 783.0, 724.7, 686.8, 630.7, 570.2, 495.1, 418.2, 386.4, 241.8, 169.9, 108.2, ***i****1087.6*	3239.7, 3205.3, 3198.6, 3188.5, 3178.7, 3171.8, 3155.4, 3143.9, 1701.4, 1650.2, 1623.4, 1536.7, 1491.1, 1469.6, 1373.2, 1340.1, 1302.5, 1229.4, 1217.3, 1182.6, 1119.0, 1063.4, 1052.2, 1042.4, 1022.2, 1014.1, 997.4, 965.8, 949.2, 868.7, 812.0, 789.5, 725.1, 667.2, 633.4, 567.9, 454.7, 453.0, 414.7, 267.3, 217.9, 68.6

Mass spectra of 3,3-methylphenyldiazirine:

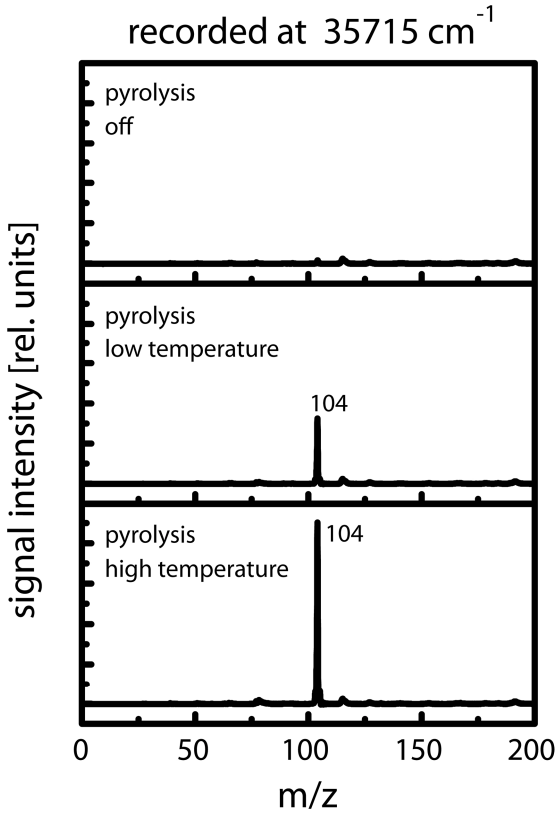


Figure 1. TOF mass spectra of 3,3-methylphenyldiazirine at different pyrolysis conditions using nanosecond lasers. By turning on the pyrolysis an intense mass peak becomes visible at m/z=104.

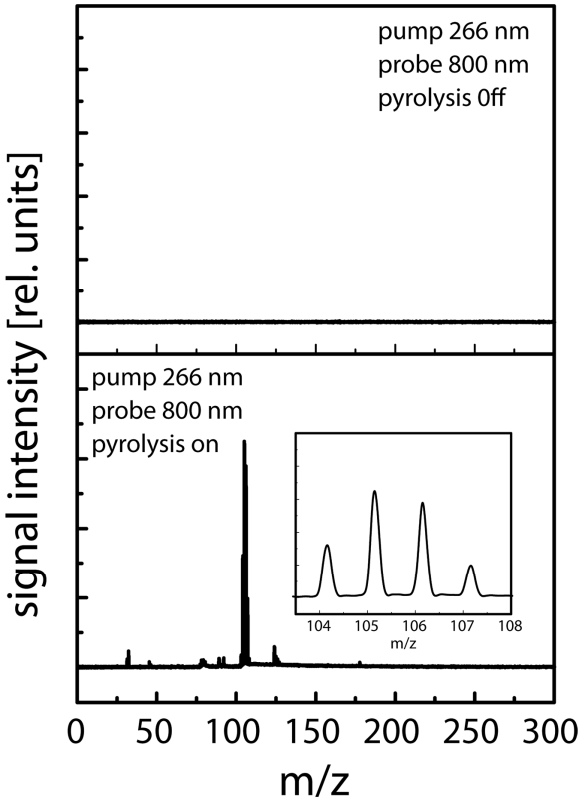


Figure 2. TOF mass spectra of partially deuterated 3,3-methylphenyldiazirine (R=CH_3,CDH_2,CD_2H,CD_3) at different pyrolysis conditions using femtosecond lasers. The synthesis yielded a mixture of all four combinations of deuteration at the methyl group. In the time-resolved pump probe experiments all four peaks showed the exact same excited state dynamics which was already known from authentic styrene (ref. 4).

(1) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Jr., J. A. M.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision C.02*, 2004.

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Full Ref. 35:

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Jr., J. A. M.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision C.02*, 2004.