Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPLEMENTARY INFORMATION

for

From Benzene to Naphthalene, Direct Measurement of Reactions and Intermediates of Phenyl Radical and Acetylene

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1. Summary of molecular parameters for newly calculated stationary points on the C_8H_7 potential energy surface, G3(MP2,CC)//B3LYP/6-311G**

bicyclo[4.2.0]octa-3,5,7-trien-2-yl, C_8H_7-3

Geometry:

C	-1.8158370000	-0.7212840000	-0.0250110000
C	-1.7868480000	0.7020780000	-0.1868740000
C	-0.6279540000	-1.4589720000	0.0797550000
C	0.5377980000	-0.7484280000	0.2231210000
C	0.5739800000	0.7579140000	0.4420140000
C	-0.6484060000	1.4389790000	-0.0777380000
C	1.9145970000	-0.7316500000	-0.2079910000
C	1.9751100000	0.6275040000	-0.1950530000
H	0.6948710000	1.0147490000	1.5047510000
H	-2.7622870000	-1.2358110000	-0.1200990000
H	-0.6330610000	-2.5312660000	-0.0755710000
H	-2.7183540000	1.1993590000	-0.4297250000
H	-0.6625950000	2.5108120000	-0.2323550000
H	2.6174820000	-1.5038850000	-0.4869620000
H	2.7293190000	1.3491960000	-0.4733800000

Energy (Hartree):

ZPE(B3LYP/6-311G**) = 0.1191, E(CCSD(T)/6-311G**) = -308.1485, E(MP2/6-311G**) = -308.0055, E(MP2/G3large) = -308.1850, E(G3(MP2,CC)) = -308.2129

Frequency (cm-1): 186, 238, 385, 416, 517, 539, 603, 670, 704, 760, 774, 865, 883, 895, 925, 956, 976, 981, 1034, 1086, 1101, 1127, 1170, 1201, 1280, 1293, 1328, 1363, 1423, 1487, 1543, 1589, 2942, 3145, 3152, 3165, 3183, 3184, 3211

Rotational constant (GHz) = 1.5549, 2.2536, 4.3660; external symmetry: 1, optical isomer: 2

bicyclo[4.2.0]octa-1,3,5-trien-7-yl, C_8H_7-4

Geometry:

C	-1.8880650000	0.6408890000	0.0000000000
C	-1.8286760000	-0.7590710000	-0.0000010000
C	-0.7432890000	1.4337300000	0.0000010000
C	0.4774060000	0.7451260000	0.0000020000
C	0.5254010000	-0.6724940000	0.0000030000
C	-0.6004250000	-1.4509010000	-0.0000010000
C	1.8891530000	0.8560540000	-0.0000060000

C	2.0587340000	-0.6696190000	0.0000020000
H	-2.8605310000	1.1164490000	0.0000000000
H	-0.8100590000	2.5134180000	0.0000030000
H	-2.7535740000	-1.3205650000	-0.0000030000
H	-0.5751770000	-2.5330450000	-0.0000020000
H	2.5323160000	-1.0962370000	0.8874650000
H	2.5323190000	-1.0962430000	-0.8874580000
H	2.5932800000	1.6739290000	0.0000020000

Energy (Hartree):

ZPE(B3LYP/6-311G**) = 0.1202, E(CCSD(T)/6-311G**) = -308.1829, E(MP2/6-311G**) = -308.0473, E(MP2/G3large) = -308.2284, E(G3(MP2,CC)) = -308.2478

Frequency (cm-1): 214, 233, 391, 428, 502, 542, 550, 647, 701, 757, 796, 867, 888, 924, 936, 977, 991, 1009, 1094, 1096, 1126, 1165, 1192, 1209, 1242, 1321, 1380, 1445, 1475, 1493, 1575, 1629, 3021, 3054, 3156, 3165, 3177, 3184, 3211

Rotational constant (GHz) = 1.4895, 2.1804, 4.5655; external symmetry: 1, optical isomer: 1

benzocyclobutadiene, C_8H_6-2

Geometry:

C	-1.8395960000	-0.6863580000	-0.0000020000
C	-1.8395960000	0.6863580000	0.0000020000
C	-0.6215600000	-1.4397270000	0.0000000000
C	0.5205560000	-0.7093920000	0.0000070000
C	0.5205560000	0.7093920000	0.0000050000
C	-0.6215600000	1.4397270000	-0.0000020000
C	2.0416750000	-0.6731560000	-0.0000020000
C	2.0416750000	0.6731560000	-0.0000010000
H	-2.7823760000	-1.2171870000	-0.0000060000
H	-0.6428290000	-2.5213200000	-0.0000050000
H	-2.7823760000	1.2171870000	0.0000010000
H	-0.6428290000	2.5213200000	-0.0000060000
H	2.8187560000	-1.4218830000	-0.0000060000
H	2.8187560000	1.4218830000	-0.0000060000

Energy (Hartree):

ZPE(B3LYP/6-311G**) = 0.1099, E(CCSD(T)/6-311G**) = -307.5802, E(MP2/6-311G**) = -307.4836, E(MP2/G3large) = -307.6659, E(G3(MP2,CC)) = -307.6562

Frequency (cm-1): 228, 297, 363, 419, 549, 584, 656, 720, 754, 774, 815, 872, 888, 932, 932, 974, 988, 1050, 1071, 1093, 1098, 1190, 1261, 1310, 1441, 1459, 1487, 1567, 1642, 1691, 3159, 3171, 3178, 3187, 3204, 3233

Rotational constant (GHz) = 1.5160, 2.2023, 4.8650; external symmetry: 2, optical isomer: 1

TS_C_8H_7-1_C_8H_7-3

Geometry:

C	0.3925420000	-0.8768790000	0.4296970000
C	0.5711770000	0.5684310000	0.3319200000
C	-0.4941660000	1.4154270000	0.1003750000
C	-1.7528780000	0.8599910000	-0.1445640000
C	-1.9163400000	-0.5356800000	-0.2208910000
C	-0.8803170000	-1.4044980000	0.0563900000
C	1.9769890000	0.6497700000	-0.0130920000
C	2.1571450000	-0.5916440000	-0.4743800000
H	0.9376780000	-1.4062440000	1.2017110000
H	-2.8947730000	-0.9346890000	-0.4570380000
H	-1.0542730000	-2.4724580000	0.0732850000
H	2.6586600000	1.4899870000	0.0376490000
H	2.9623350000	-1.1736580000	-0.9046820000
H	-2.5978770000	1.5057480000	-0.3415870000
H	-0.3366690000	2.4818080000	-0.0020680000

Energy (Hartree):

ZPE(B3LYP/6-311G**) = 0.1175, E(CCSD(T)/6-311G**) = -308.1186, E(MP2/6-311G**) = -307.9612, E(MP2/G3large) = -308.1416, E(G3(MP2,CC)) = -308.1853

Frequency (cm-1): 617i, 190, 284, 414, 423, 553, 579, 607, 651, 737, 744, 793, 821, 844, 899, 935, 938, 982, 990, 1019, 1095, 1134, 1168, 1184, 1262, 1302, 1340, 1439, 1466, 1528, 1547, 1591, 3128, 3150, 3154, 3161, 3174, 3184, 3185

Rotational constant (GHz) = 1.4927, 2.0640, 4.4567; external symmetry: 1, optical isomer: 1

TS_C_8H_7-2_C_8H_7-4

Geometry:

C	1.8683070000	0.7766240000	0.0722810000
C	0.6233950000	1.3946710000	0.0644340000
C	1.9950480000	-0.6152370000	-0.0019080000
C	-0.5064110000	0.5739560000	-0.0302260000
C	-0.3479650000	-0.8130780000	-0.1196970000
C	0.8707400000	-1.4487140000	-0.0938350000
C	-1.9291040000	0.7163320000	-0.1332650000
C	-2.4454790000	-0.5548170000	0.1880380000
H	2.9834480000	-1.0581480000	0.0037400000
H	0.9802410000	-2.5233810000	-0.1524640000
H	-2.4691020000	1.4910780000	-0.6606520000
H	-2.2198370000	-1.0017640000	1.1457230000
H	-3.3491150000	-0.9392610000	-0.2789200000
H	2.7635130000	1.3809720000	0.1387020000
H	0.5396640000	2.4720820000	0.1289390000

Energy (Hartree):

ZPE(B3LYP/6-311G**) = 0.1181, E(CCSD(T)/6-311G**) = -308.1203, E(MP2/6-311G**) = -307.9602, E(MP2/G3large) = -308.1403, E(G3(MP2,CC)) = -308.1861

Frequency (cm-1): 722i, 159, 266, 399, 413, 514, 570, 609, 657, 698, 759, 770, 837, 872, 939, 951, 979, 998, 1001, 1021, 1123, 1171, 1184, 1246, 1262, 1324, 1384, 1445, 1479, 1510, 1574, 1601, 3097, 3151, 3163, 3174, 3176, 3181, 3188

Rotational constant (GHz) = 1.3789, 1.8883, 4.8251; external symmetry: 1, optical isomer: 1

TS_C_8H_7-3_C_8H_7-4

Geometry:

C	-1.8233810000	0.7150830000	0.0329660000
C	-0.6836930000	1.4708840000	0.0459600000
C	-1.8028650000	-0.7301540000	-0.0681810000
C	0.5433540000	0.7637130000	-0.0158300000
C	0.5481540000	-0.7286710000	0.1105500000
C	-0.6539260000	-1.4736790000	-0.0641560000
C	1.9161410000	0.8036110000	-0.1407670000
C	2.0001500000	-0.6716520000	-0.0162750000
H	-2.7544100000	-1.2364440000	-0.1690010000
H	-0.6730630000	-2.5515440000	-0.1523280000
H	2.6648560000	1.5782710000	-0.1042950000
H	2.7375640000	-1.4399170000	-0.1906930000
H	1.2785480000	-0.9979850000	1.1859520000
H	-0.7275910000	2.5521640000	0.0607770000
H	-2.7895030000	1.2006470000	0.0639850000

Energy (Hartree):

ZPE(B3LYP/6-311G**) = 0.1148, E(CCSD(T)/6-311G**) = -308.0693, E(MP2/6-311G**) = -307.9312, E(MP2/G3large) = -308.1156, E(G3(MP2,CC)) = -308.1427

Frequency (cm-1): 2975i, 226, 274, 406, 437, 531, 556, 616, 686, 702, 754, 789, 806, 850, 892, 948, 952, 958, 976, 1100, 1147, 1158, 1169, 1213, 1240, 1259, 1355, 1413, 1472, 1499, 1577, 1592, 1719, 3157, 3165, 3178, 3186, 3209, 3227

Rotational constant (GHz) = 1.5108, 2.2586, 4.4006; external symmetry: 1, optical isomer: 1

TS_C_8H_7-3_C_8H_6-2+H

Geometry:

C	-0.6323470000	-1.4233710000	-0.0996440000
C	0.5178290000	-0.6926390000	0.0316450000
C	0.5081740000	0.7332180000	0.0416190000
C	-0.6409960000	1.4538610000	0.0353740000
C	-1.8520250000	0.6942120000	0.0018240000
C	-1.8460500000	-0.6805110000	-0.0774840000
C	2.0361040000	-0.6311660000	-0.1021330000

C	2.0155390000	0.7147760000	-0.0764310000
H	0.6666720000	-1.1516180000	2.0351260000
H	-2.7866980000	-1.2129510000	-0.1211160000
H	-0.6438330000	-2.5018390000	-0.1792260000
H	2.7791020000	1.4752410000	-0.1287120000
H	2.8150180000	-1.3729560000	-0.1819640000
H	-2.7982010000	1.2186380000	0.0193790000
H	-0.6694350000	2.5352100000	0.0278970000

Energy (Hartree):

ZPE(B3LYP/6-311G**) = 0.1111, E(CCSD(T)/6-311G**) = -308.0742, E(MP2/6-311G**) = -307.9184, E(MP2/G3large) = -308.1005, E(G3(MP2,CC)) = -308.1489

Frequency (cm-1): 517i, 226, 274, 406, 437, 531, 556, 616, 686, 702, 754, 789, 806, 850, 892, 948, 952, 958, 976, 1100, 1147, 1158, 1169, 1213, 1240, 1259, 1355, 1413, 1472, 1499, 1577, 1592, 1719, 3157, 3165, 3178, 3186, 3209, 3227

Rotational constant (GHz) = 1.5097, 2.1592, 4.5943; external symmetry: 1, optical isomer: 1

TS_C_8H_7-4_C_8H_6-2+H

Geometry (optimized at M06-2X/cc-pVTZ):

C	-0.6070910000	-1.4383600000	-0.0757690000
C	-1.8469610000	-0.7309100000	-0.0054550000
C	-1.8968080000	0.6362250000	0.0516740000
C	-0.7126740000	1.4340100000	0.0436360000
C	0.4533970000	0.7477440000	-0.0221950000
C	0.5028210000	-0.6661940000	-0.0809970000
C	1.9624340000	0.7742850000	-0.0760710000
C	2.0212130000	-0.5733970000	-0.1194390000
H	-2.7698240000	-1.2945850000	0.0043050000
H	-0.5876010000	-2.5182620000	-0.1188530000
H	2.7072390000	1.5545900000	-0.0820910000
H	2.2010110000	-1.1987740000	1.9621340000
H	2.8216140000	-1.2843710000	-0.2486090000
H	-2.8582460000	1.1284510000	0.1046840000
H	-0.7721660000	2.5125380000	0.0861250000

Energy (Hartree):

ZPE(B3LYP/6-311G**) = 0.1113, E(CCSD(T)/6-311G**) = -308.0761, E(MP2/6-311G**) = -307.9240, E(MP2/G3large) = -308.1067, E(G3(MP2,CC)) = -308.1512

Frequency (cm-1): 693i, 218, 247, 309, 354, 381, 418, 549, 577, 658, 731, 755, 773, 819, 870, 884, 913, 933, 985, 990, 1052, 1069, 1098, 1103, 1193, 1262, 1312, 1428, 1464, 1469, 1521, 1650, 1701, 3165, 3178, 3186, 3193, 3210, 3237

Rotational constant (GHz) = 1.4959, 2.1326, 4.6139; external symmetry: 1, optical isomer: 1

2. $k_{sampling}$ fitted from NO signals

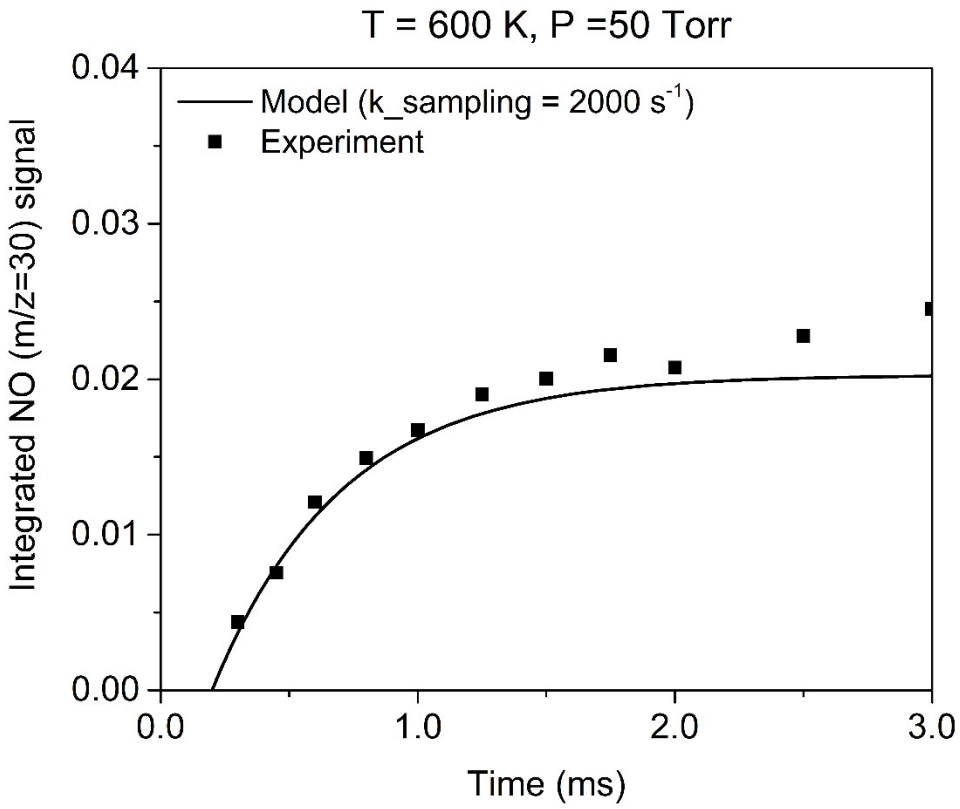

Figure S1. Time-dependent signals of NO peaks (m/z=30) measured in MBMS experiments (markers) and model predictions (line), 600 K and 50 torr (Experiment 2). By using $k_{sampling}$ = 2000 s^{-1}, the model prediction successful captures the time dependence of NO signals. t=0 is the time of the photolysis flash in the reactor; there is a short time lag between the flash and the first arrival of NO^+ at the mass spectrometer.

3. Modeling approach applied in this work

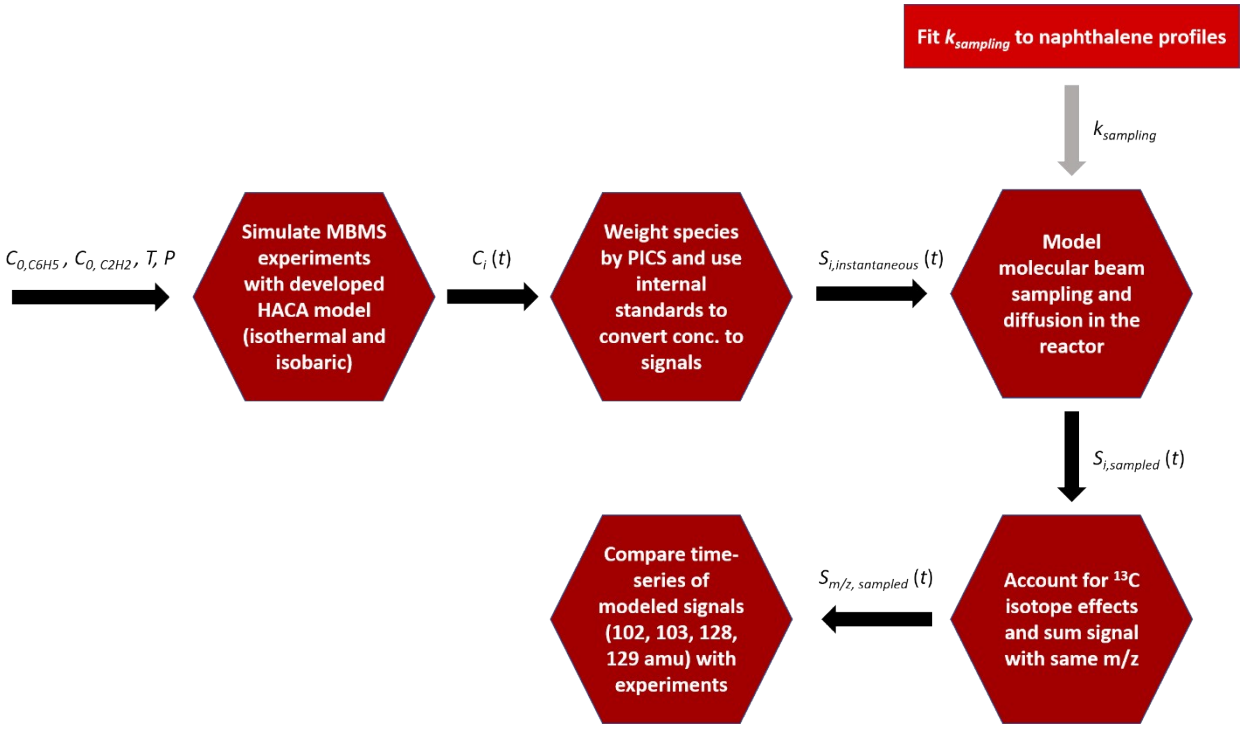

Figure S2. Overall approach to predict species concentrations and convert them into MBMS signals for comparison with experimental data.

4. Time-dependent signals of products from the vinyl + C_2H_2 reaction observed in MBMS experiments

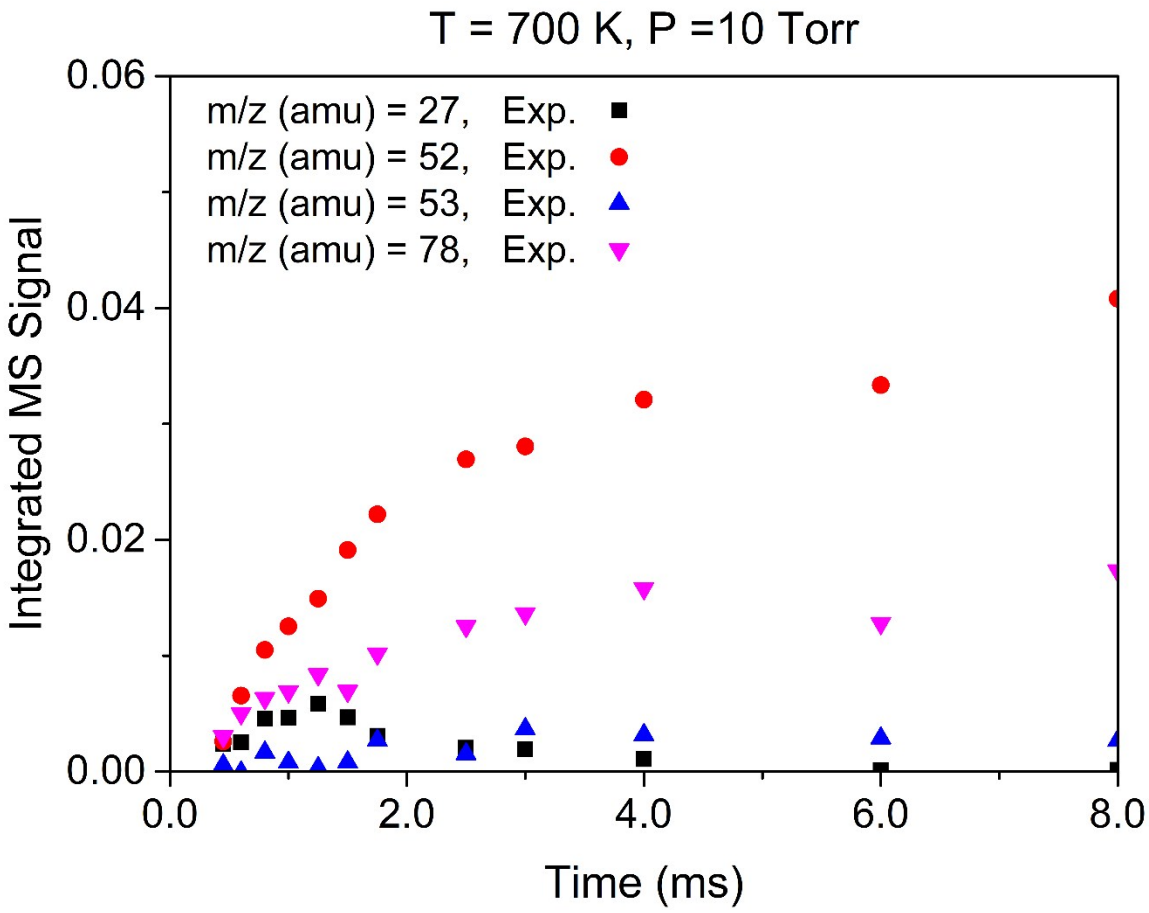

Figure S3. Time-dependent profiles of product peaks originating from the reaction of H atom with C_2H_2 in experiment 3.

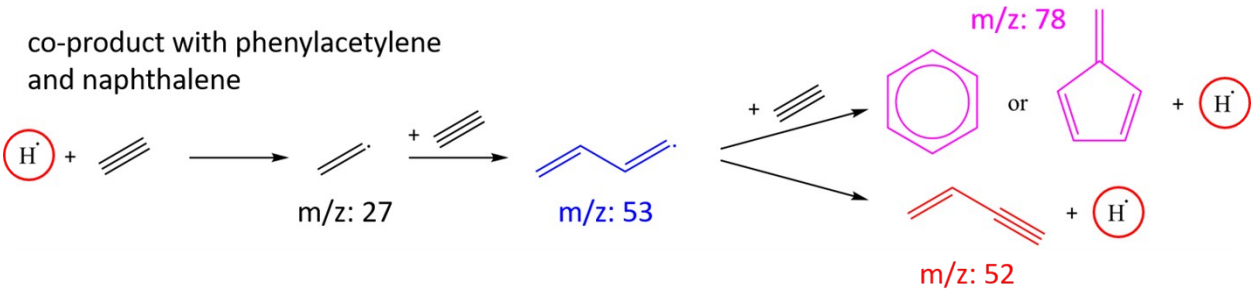

Figure S4. Leading pathways of H + C_2H_2 and vinyl + C_2H_2 reactions.

5. MBMS experiments at high C_2H_2 concentration (Exp. 5, 6, 7, 8)

Experiment 5 – 600 K, 10 Torr, C_2H_2 concentration 5.46 x 10^{16} molecule/cm^3

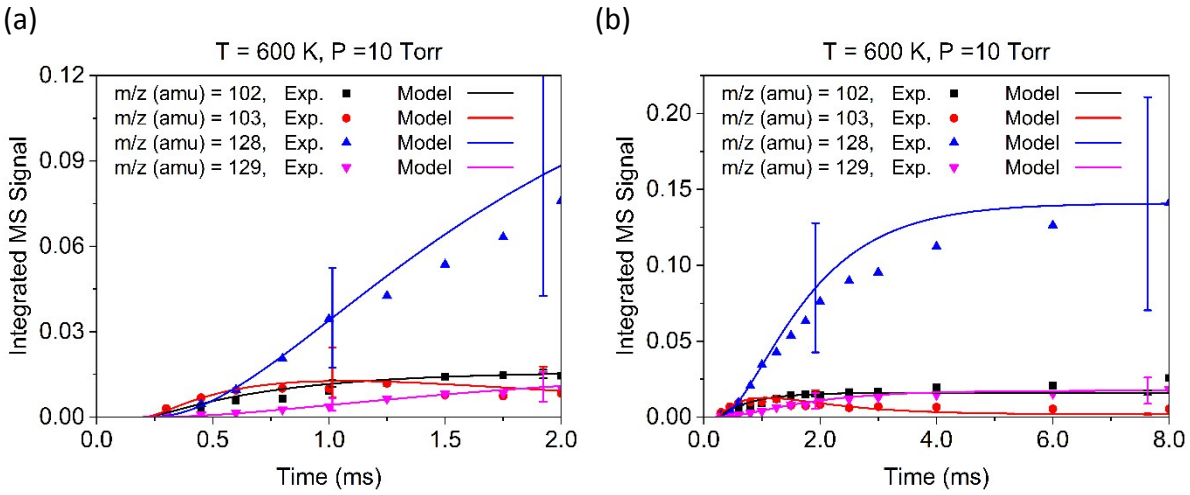

Figure S5. Experiment 5: Time-dependent signals of primary product peaks measured in MBMS experiments (markers) and model predictions (line). (a) short time scale (2.0 ms) (b) long time scale (8.0 ms)

Experiment 6 – 600 K, 50 Torr, C_2H_2 concentration 5.38 x 10^{16} molecule/cm^3

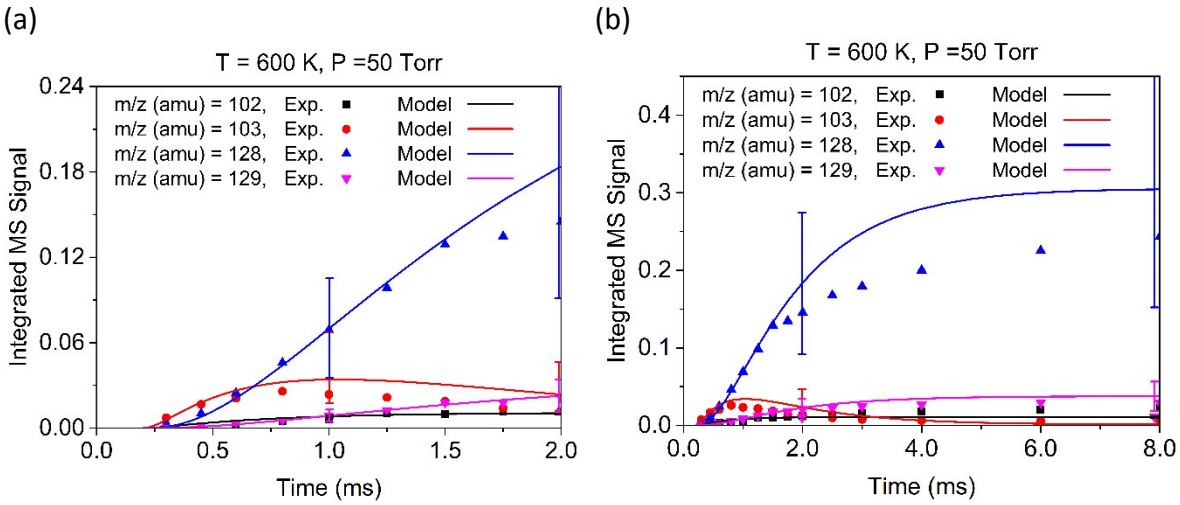

Figure S6. Experiment 6: Time-dependent signals of primary product peaks measured in MBMS experiments (markers) and model predictions (line). (a) short time scale (2.0 ms) (b) long time scale (8.0 ms)

Experiment 7 – 700 K, 10 Torr, C_2H_2 concentration 3.83 x 10^{16} molecule/cm^3

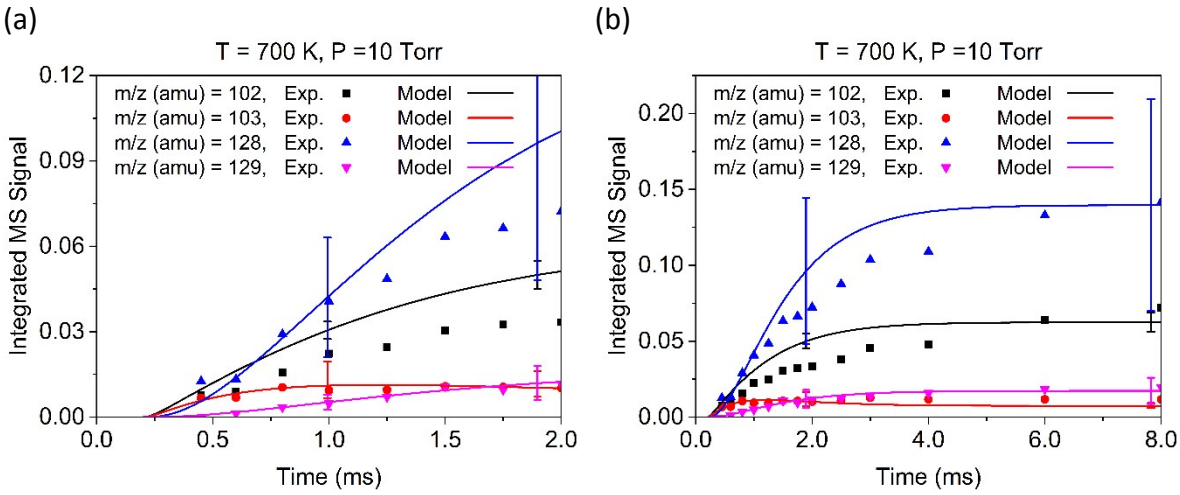

Figure S7. Experiment 7: Time-dependent signals of primary product peaks measured in MBMS experiments (markers) and model predictions (line). (a) short time scale (2.0 ms) (b) long time scale (8.0 ms)

Experiment 8 – 700 K, 50 Torr, C_2H_2 concentration 3.77 x 10^{16} molecule/cm^3

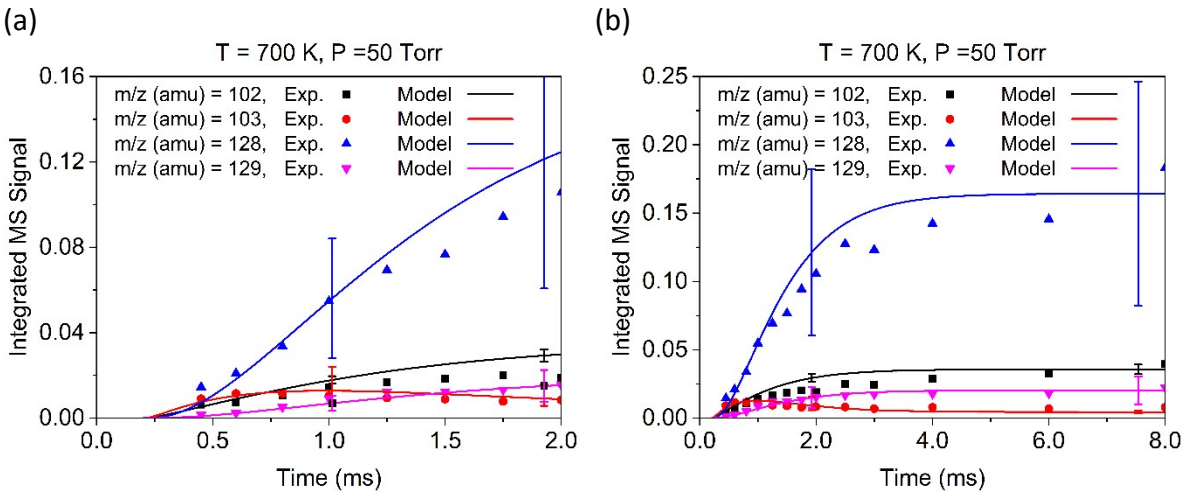

Figure S8. Experiment 8: Time-dependent signals of primary product peaks measured in MBMS experiments (markers) and model predictions (line). (a) short time scale (2.0 ms) (b) long time scale (8.0 ms)

6. Uncertainty analysis for the product branching measurement

The branching fraction for the H-loss pathway of the $C_6H_5 + C_2H_2$ reaction was determined using the following equations:

$$\text{H-loss branching} = \frac{k_3}{k_1 + k_2 + k_3}$$

$$= \frac{\frac{Signal_{102}}{\sigma_{phenylacetylene}} \times 0.92}{\frac{Signal_{128}}{\sigma_{naphthalene}} \times 0.90 + \frac{Signal_{102}}{\sigma_{phenylacetylene}} \times 0.92}$$

$$= \frac{Signal_{102} \times 0.92 \times \sigma_{naphthalene}}{\sigma_{phenylacetylene} \times Signal_{128} \times 0.90 + \sigma_{naphthalene} \times Signal_{102} \times 0.92}$$

$$= f(S_{102}, S_{128}, \sigma_{C8H6}, \sigma_{C10H8})$$

The uncertainty of the H-loss branching fraction $u_{H-loss\ branching}$, was determined using the following equations:

$$u_{H-loss\ branching} = \sqrt{\left(\frac{\partial f}{\partial S_{102}}\right)^2 u_{S_{102}}^{\ 2} + \left(\frac{\partial f}{\partial S_{128}}\right)^2 u_{S_{128}}^{\ 2} + \left(\frac{\partial f}{\partial \sigma_{C8H6}}\right)^2 u_{\sigma_{C8H6}}^{\ 2} + \left(\frac{\partial f}{\partial \sigma_{C10H8}}\right)^2 u_{\sigma_{C10H8}}^{\ 2}}$$

$$\frac{\partial f}{\partial S_{102}} = \frac{1.0222\, S_{128}\sigma_{C8H6}\sigma_{C10H8}}{(1.0222\, S_{102}\sigma_{C10H8} + S_{128}\sigma_{C8H6})^2}$$

$$\frac{\partial f}{\partial S_{128}} = \frac{-0.9783\, S_{102}\sigma_{C8H6}\sigma_{C10H8}}{(0.9783\, S_{128}\sigma_{C8H6} + S_{102}\sigma_{C10H8})^2}$$

$$\frac{\partial f}{\partial \sigma_{C8H6}} = \frac{-0.9783\, S_{102} S_{128} \sigma_{C10H8}}{\left(0.9783\, S_{128}\sigma_{C8H6} + S_{102}\sigma_{C10H8}\right)^2}$$

$$\frac{\partial f}{\partial \sigma_{C10H8}} = \frac{0.9783\, S_{102} S_{128} \sigma_{C8H6}}{\left(0.9783\, S_{128}\sigma_{C8H6} + S_{102}\sigma_{C10H8}\right)^2}$$

S_{102}, S_{128} = average product signals at m/z=102 and m/z=128 in the measure time scales

σ_{C8H6} = PICS of phenylacetylene = 63.0 Mb (measured by Zhou et al.[1])

σ_{C10H8} = PICS of naphthalene = 53.0 Mb (reported by Li et al.[2])

$u_{S_{102}}$,$u_{S_{128}}$ = uncertainty (standard deviation) in product signals at m/z=102 and m/z=128

$u_{\sigma_{C8H6}}$ = uncertainty of phenylacetylene PICS = 10%*63.0 = 6.3 Mb (estimated by Zhou et al.[1])

$u_{\sigma_{C10H8}}$ = uncertainty of naphthalene PICS = 50%*51.4 = 25.7 Mb (estimated by Li et al.[2])

1. Z. Zhou, M. Xie, Z. Wang and F. Qi, Rapid Communications in Mass Spectrometry, 2009, **23**, 3994-4002.
2. Y. Y. Li, J. Z. Yang and Z. J. Cheng, Photonionization Cross Section Database (Version 2.0), http://flame.nsrl.ustc.edu.cn/database/.