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Supporting Information

Directed Gas-Phase Synthesis of Triafulvene under Single-Collision Conditions

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Table S1. Peak velocities (v_p) and speed ratios (S) of the methylidyne (CH), d_1-methylidyne (CD), allene (H_2CCCH_2), d_4-allene (D_2CCCD_2), methylacetylene (CH_3CCH), and d_4-methylacetylene (CD_3CCD), d_3-methylacetylene (CD_3CCH), and d_1-methylacetylene (CH_3CCD) beams along with the corresponding collision energies (E_C) and center-of-mass angles (Θ_{CM}).

Beam	v_p (m s^{-1})	S	E_C (kJ mol^{-1})	Θ_{CM} (degree)
CH ($X^2\Pi$)	1774 ± 14	10.5 ± 0.7	18.6 ± 0.3	54.2 ± 0.4
H_2CCCH_2 (X^1A_1)	800 ± 10	12.0 ± 0.4		
CH ($X^2\Pi$)	1779 ± 13	12.3 ± 1.2	18.7+ 0.2	54.2 ± 0.4
CH_3CCH (X^1A_1)	800 ± 10	12.0 ± 0.4		
CH ($X^2\Pi$)	1713 ± 24	9.7 ± 0.5		
CD_3CCD (X^1A_1)	790 ± 10	12.0 ± 0.4	17.8 ± 0.4	57.4 ± 0.5
D_2CCCD_2 (X^1A_1)	790 ± 10	12.0 ± 0.4	17.8 ± 0.4	57.4 ± 0.5
CD ($X^2\Pi$)	1768 ± 9	13.1 ± 1.2		
H_2CCCH_2 (X^1A_1)	800 ± 10	12.0 ± 0.4	19.3 ± 0.2	52.4 ± 0.4
CD_3CCH (X^1A_1)	790 ± 10	12.0 ± 0.4	19.4 ± 0.2	52.8 ± 0.4
CH_3CCD (X^1A_1)	800 ± 10	12.0 ± 0.4	19.5 ± 0.2	53.1 ± 0.4

Table S2. Product branching ratios of the CH + methylacetylene and CH + allene reactions calculated for single-collision conditions using RRKM theory at the collision energy of 19 kJ mol^{-1}.

CH + methylacetylene					
	vinylacetylene (**p1**) + H	butatriene (**p2**) + H	triafulvene (**p3**) + H	C_2H_2+ C_2H_3	
triple bond addition	18.39%	14.55%	66.90%	0.17%	
sp^3 CH bond insertion	97.57%	0.22%	0.00%	2.42%	
sp CH bond insertion	47.01%	52.64%	0.15%	0.20%	
CC bond insertion	99.30%	0.00%	0.00%	0.69%	
CH + allene					
	vinylacetylene (**p1**) + H	butatriene (**p2**) + H	triafulvene (**p3**) + H	C_2H_2+ C_2H_3	C_2H_4+ C_2H
double bond addition	98.58%	1.26%	0.08%	0.08%	0.00%
sp^2 CH bond insertion	16.75%	0.00%	0.00%	83.18%	0.07%

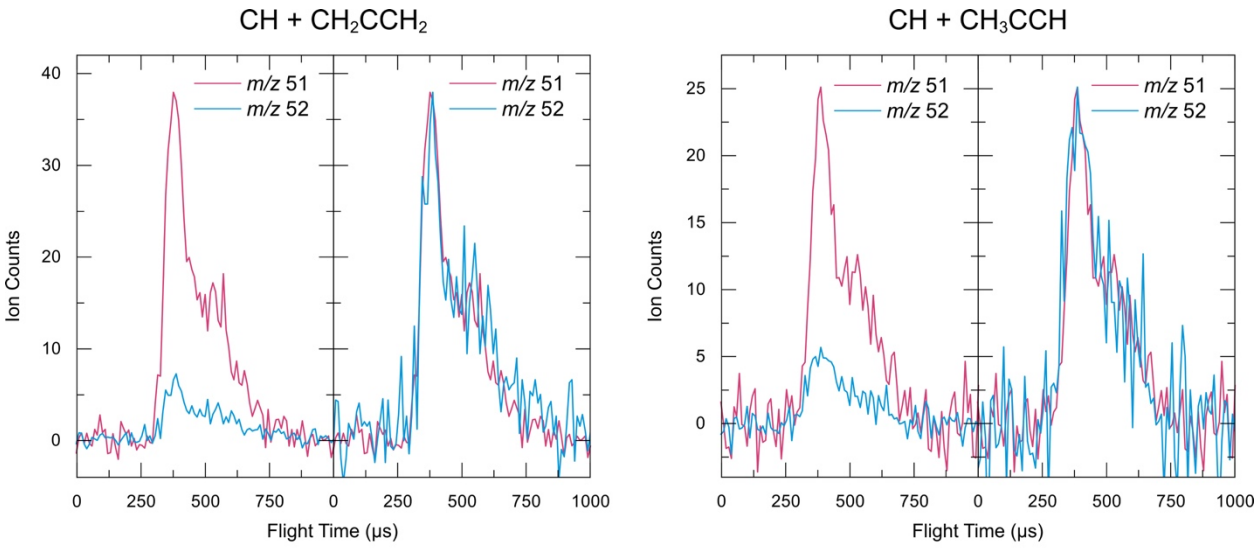

Figure S1. Time-of-flight spectra recorded at the CM angles for *m/z* = 51 ($C_4H_3^+$) and *m/z* = 52 ($C_4H_4^+$) for the reaction of the methylidyne radical (CH) with a) allene (CH_2CCH_2) and b) methylacetylene (CH_3CCH). The left and right panels depict raw and scaled TOF spectra, respectively. Since both traces overlap, signal at *m/z* = 51 represents a fragment of *m/z* = 52.

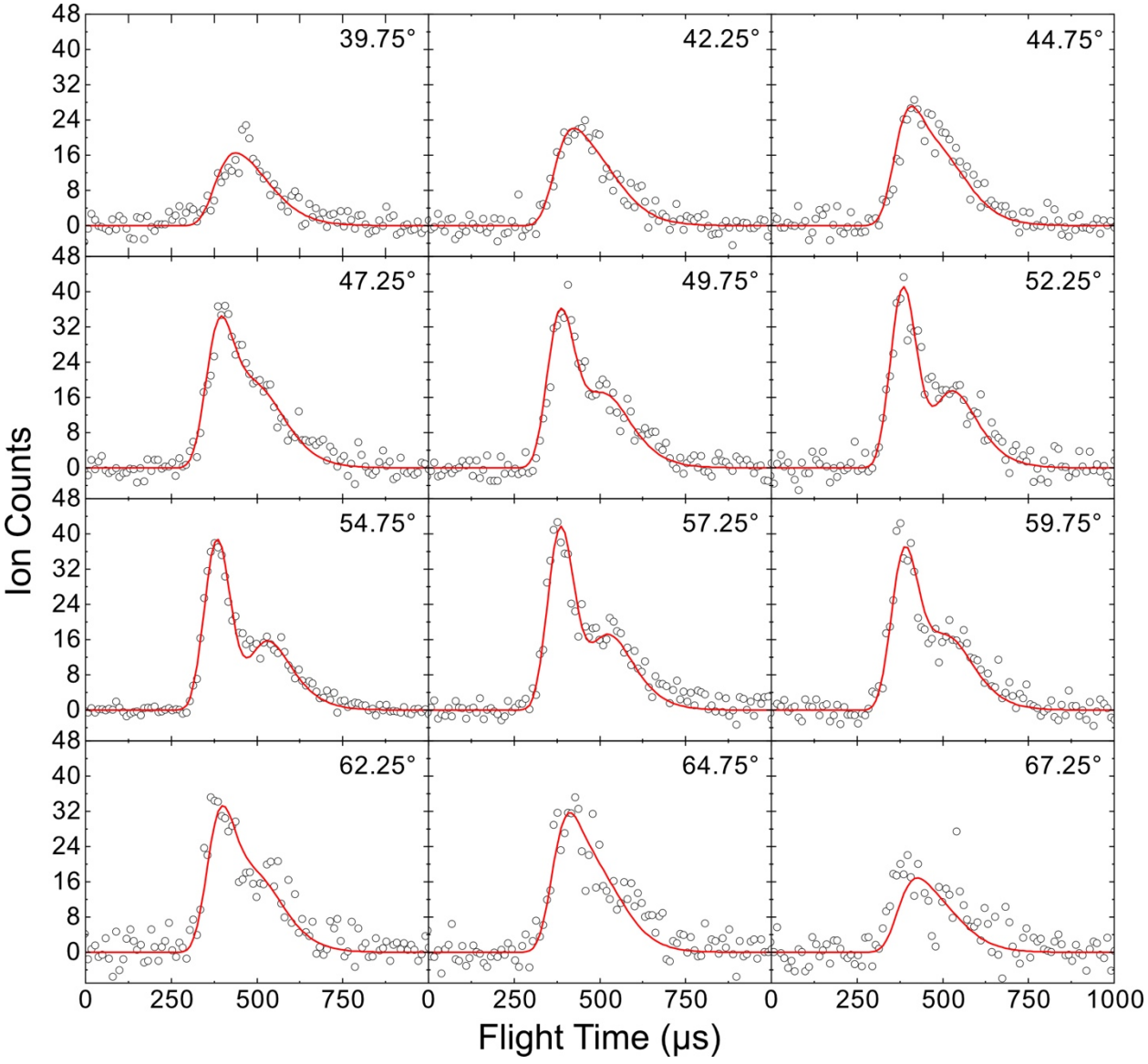

Figure S2. Time-of-flight spectra recorded at *m/z* = 51 ($C_4H_3^+$) for the reaction of the methylidyne radical (CH) with allene (CH_2CCH_2). The circles represent the experimental data and the solid lines the best fits.

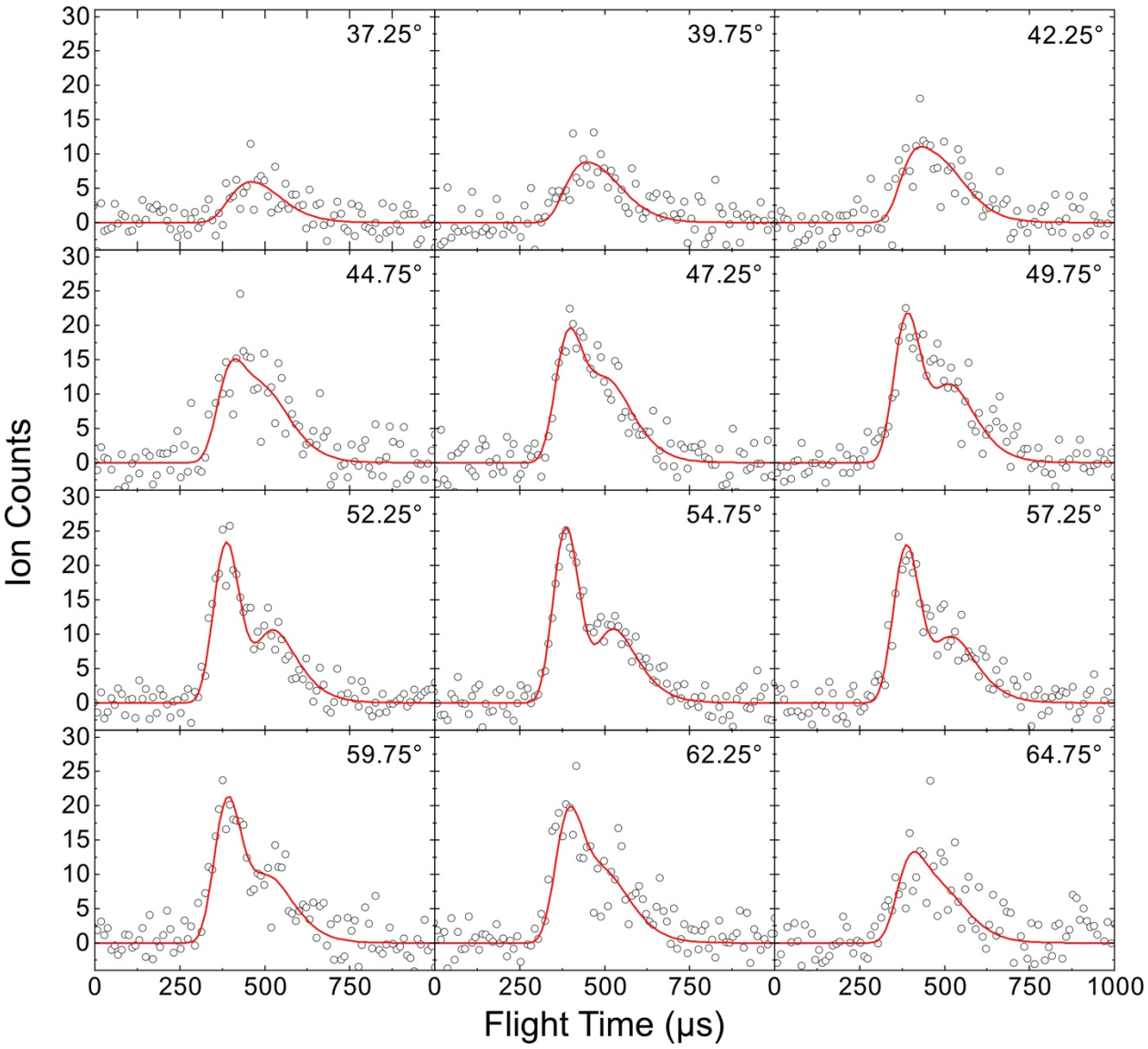

Figure S3. Time-of-flight spectra recorded at *m/z* = 51 ($C_4H_3^+$) for the reaction of the methylidyne radical (CH) with methylacetylene (CH_3CCH). The circles represent the experimental data and the solid lines the best fits.

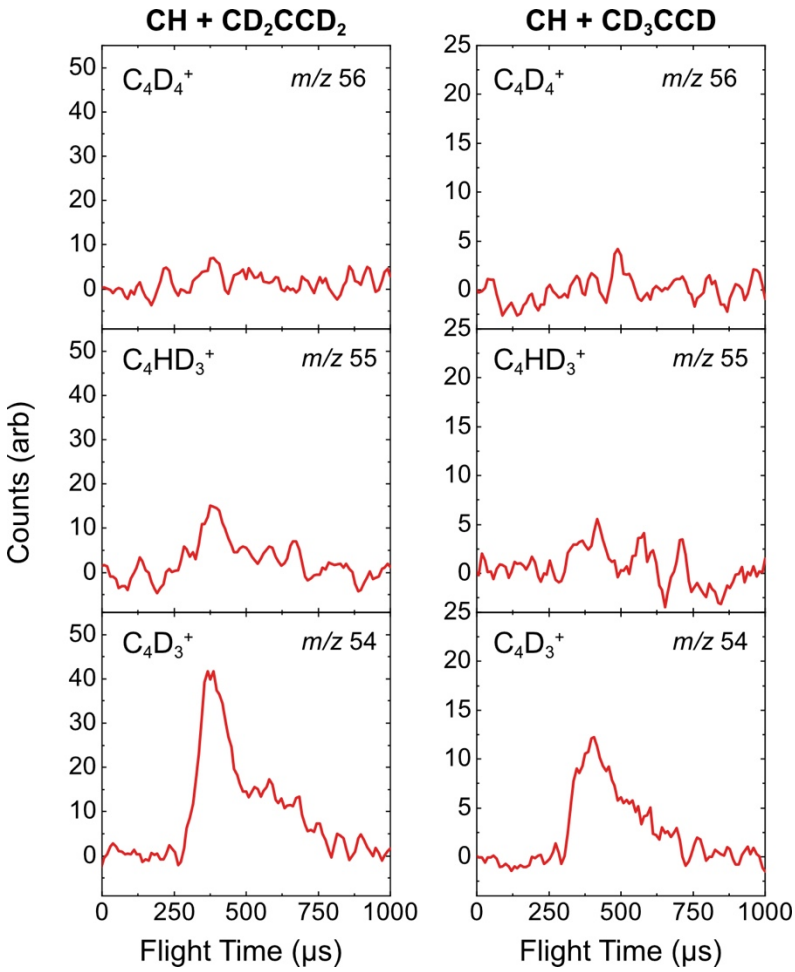

Figure S4. Time-of-flight (TOF) spectra at recorded at *m/z* 56, 55, and 54 for the reactions of the methylidyne (CH) radical with (*left*) d_4-allene (CD_2CCD_2) and (*right*) d_4-methylacetylene (CD_3CCD).

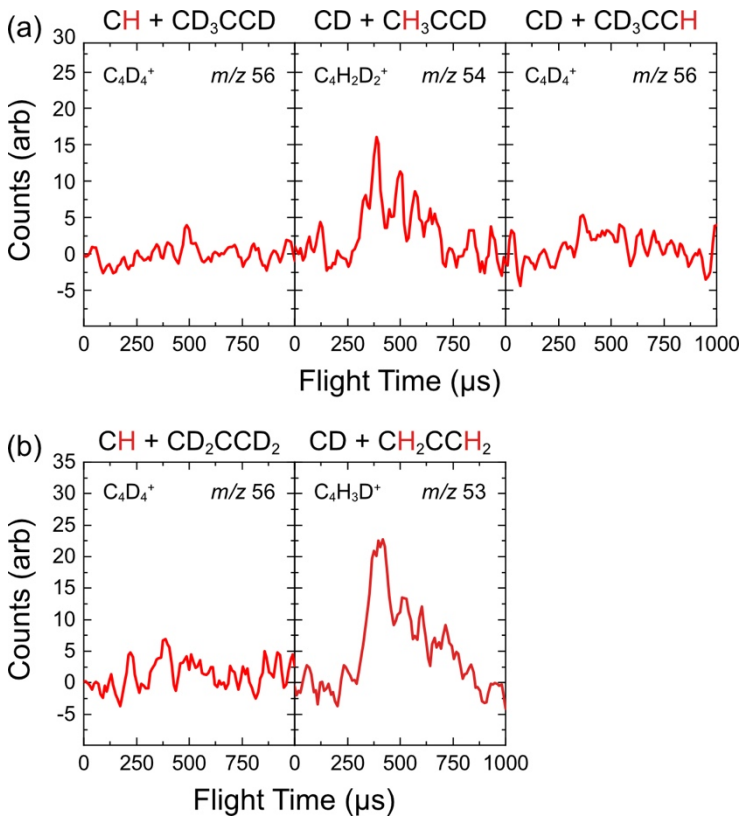

Figure S5. Time-of-flight (TOF) spectra recorded at mass-to-charge (*m/z*) ratios corresponding to the singly-ionized hydrogen-loss product formed in the partially deuterated reactions of (a) CH plus methylacetylene (CH_3CCH) and (b) CH plus allene (CH_2CCH_2) reactions. Ion counts at *m/z* = 56 for the CD/CD_3CCH system can be accounted by ^{13}C isotopes and hence $^{13}CC_3D_3H$.

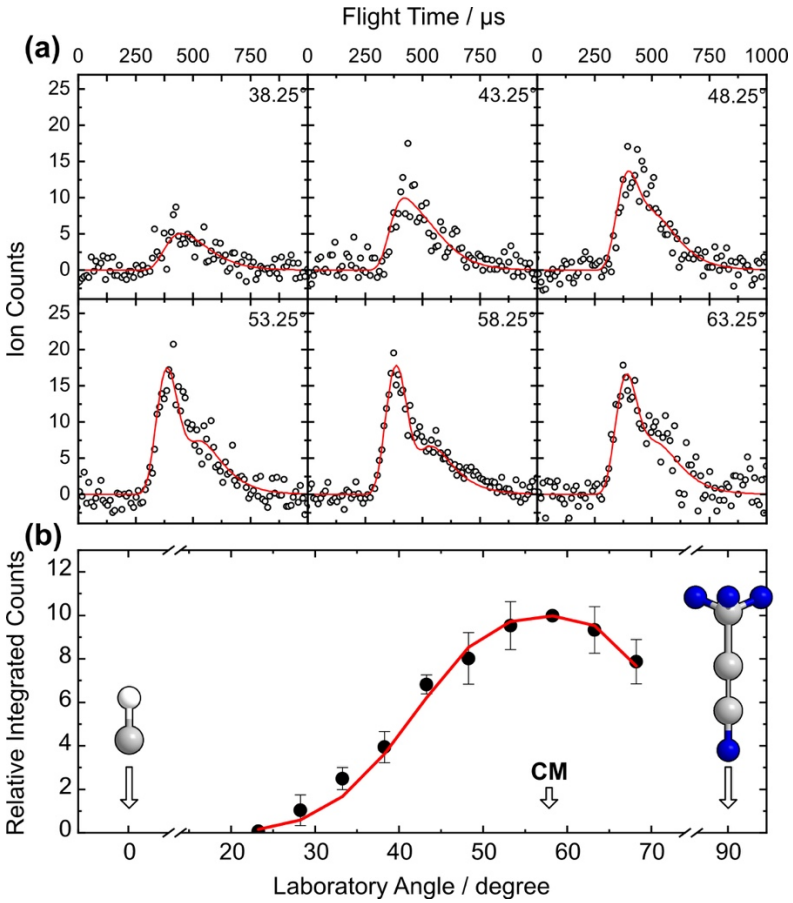

Figure S6. After establishing the source of the deuterium loss in the CH + CD_3CCD reaction, we collected time-of-flight (TOF) spectra at *m/z* 54 ($C_4D_3^+$) in 5° intervals in the laboratory frame to further constrain the deuterium-loss channel for comparison with the data obtained in the fully hydrogenated reaction. The resulting laboratory angular distribution is symmetric about the CM angle of 57.4 ± 0.5° and is otherwise similar to those obtained from the CH + H_2CCCH_2 and CH + CH_3CCH systems at *m/z* 51. a) TOF spectra and b) laboratory angular distribution recorded at *m/z* 54 ($C_4D_3^+$) for the reaction of the methylidyne radical with d_4-methylacetylene. The circles represent the experimental data and the solid lines the best fits.

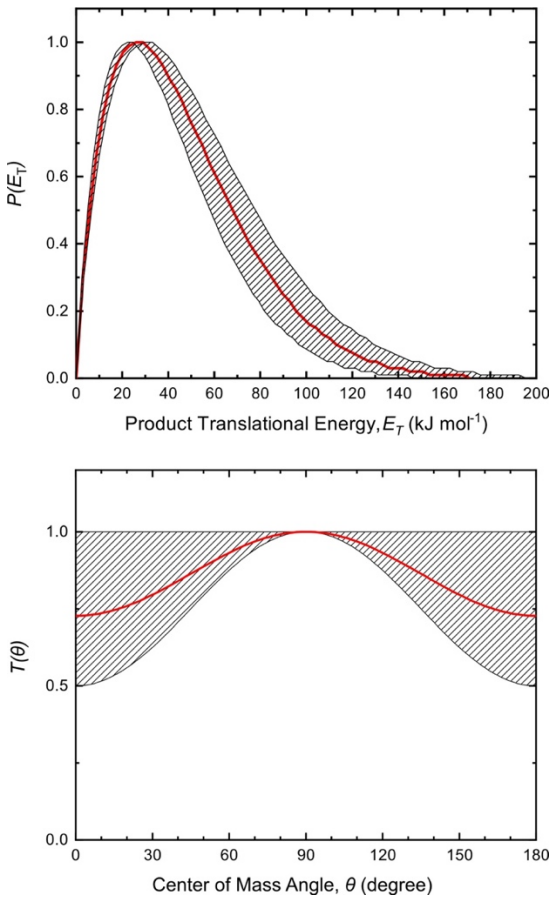

Figure S7. The CH +CD_3CCD system was fit with parameters similar to those used for the CH + CH_3CCH and CH + H_2CCCH_2 systems. The *P(E*$_T$*)* peaks at 28 ± 4 kJ mol^{-1}, extends out to 171 ± 25 kJ mol^{-1}, and has an average E_T of 46 ± 7 kJ mol^{-1}. The C_4HD_3 molecules formed in this reaction by atomic deuterium emission are therefore characterized by a reaction exoergicity of 153 ± 25 kJ mol^{-1}. The *T(θ)* portrays product flux at all angles and is forward-backward symmetric with a maximum at 90°. Hence, we draw similar conclusions regarding the CH + CD_3CCD → C_4HD_3 + D reaction coordinate, namely the involvement of relatively long-lived bound intermediates decomposing via tight exit transition states. a) center-of-mass translational energy *P*(E_T) and b) angular *T(θ)* flux distributions for the reaction of the methylidyne radical with methylacetylene-d_4 forming C_4HD_3 isomer(s) by atomic deuterium emission. Solid lines represent the best fit while shaded areas indicate the experimental error limits.