Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

DFT study of propane dehydrogenation on Pt catalyst: effects of step sites

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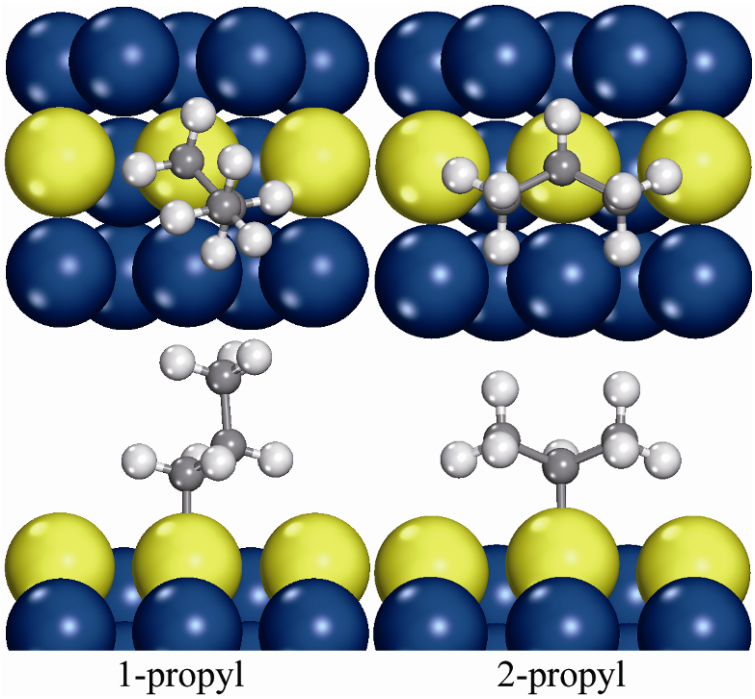

Figure S1. DFT optimized structures for the adsorbed 1-propyl and 2-propyl on Pt(211)

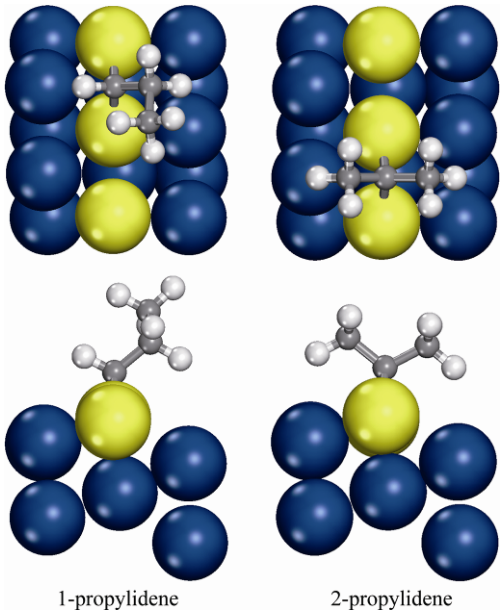

Figure S2. DFT optimized structures for the adsorbed 1-propylidene and 2-propylidene on Pt(211)

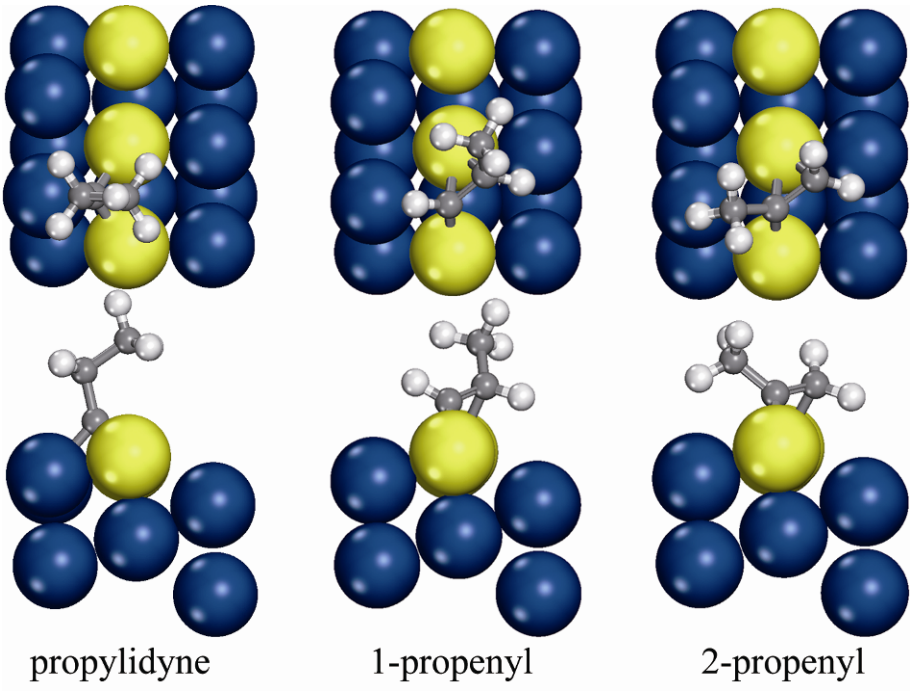

Figure S3. DFT optimized structures for the adsorbed propylidyne, 1-propenyl and 2-propenyl on Pt(211)

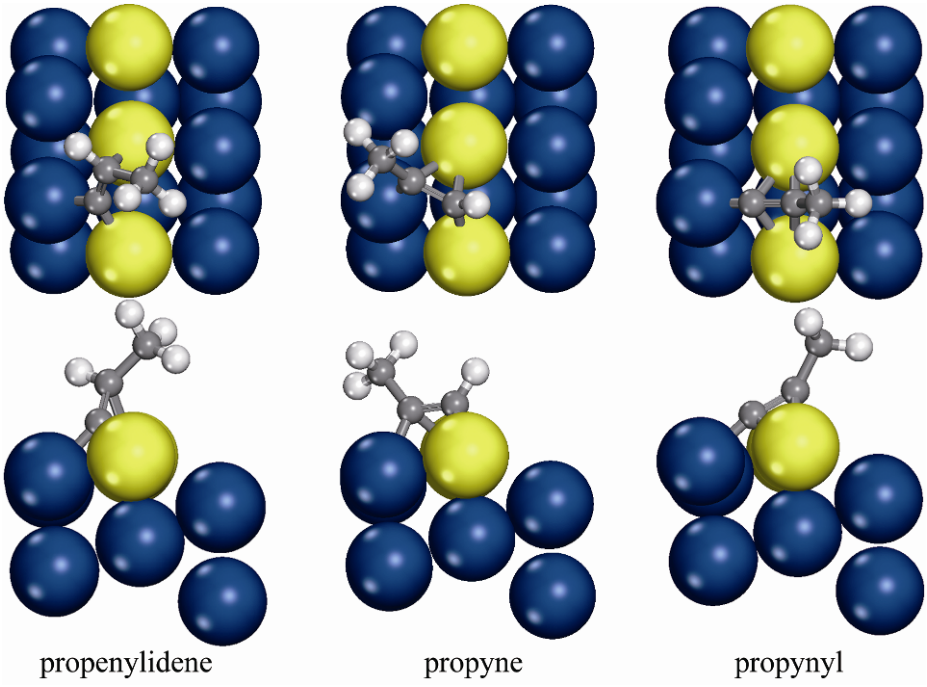

Figure S4. DFT optimized structures for the adsorbed propenylidene, propyne and propynyl on Pt(211)

Table S1: Binding energies and of C_3H_X (x=3~8) on Pt(211).

species	Favored site	ΔE_{ads} (eV)
propane	–	-0.04
1-propyl	edge-Atop	-2.11
2-propyl	edge-Atop	-1.94
Propylene	edge-Bridge	-1.43
1-propylidene	edge-Bridge	-4.50
2-propylidene	edge-Bridge	-4.23
1-propenyl	edge-Bridge	-3.46
2-propenyl	edge-Bridge	-3.24
propylidyne	near-edge-Hcp	-3.63
propenylidene	near-edge-Hcp	-2.46
propyne	near-edge-Hcp	-2.63
propynyl	near-edge-Hcp	-4.98

For some reactions on steps, it is difficult to determine whether it is the true saddle point. Hence, we searched for other TSs so as to confirm our calculated results.

$CH_3CHCH^* \rightarrow CH_3CHC^* + H^*$:

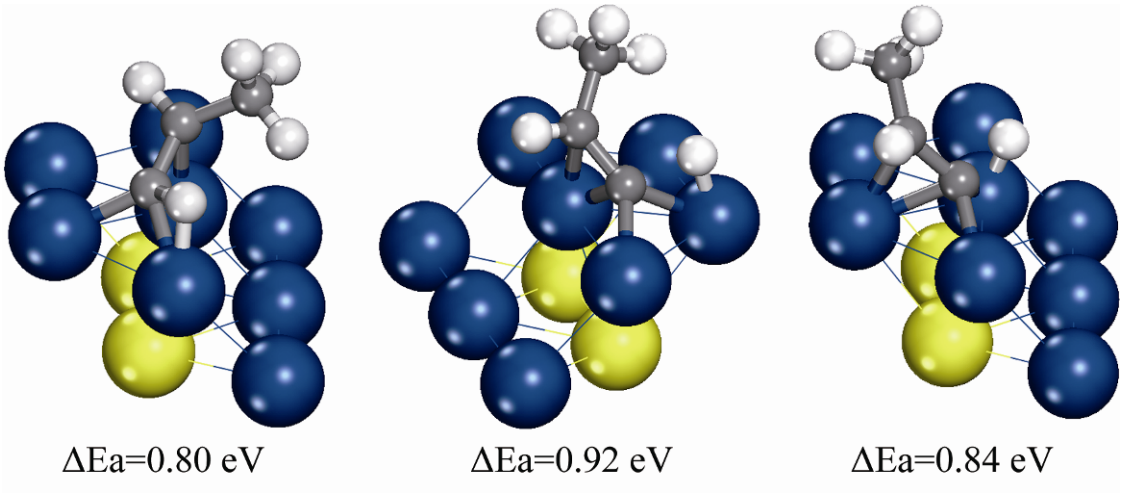

Figure S5. DFT optimized structures for the TS of 1-propenyl to propenylidene on Pt(211)

$CH_3CHCH^* \rightarrow CH_3CCH^* + H^*$:

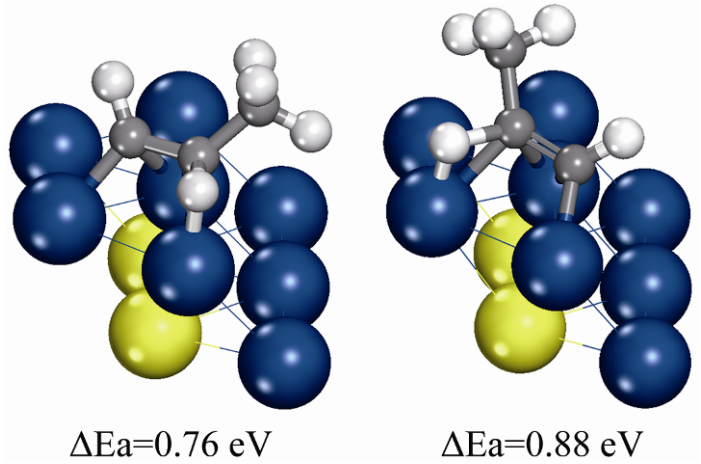

Figure S6. DFT optimized structures for the TS of 1-propenyl to propyne on Pt(211)

$CH_3CCH_2^* \rightarrow CH_3CCH^* + H^*$:

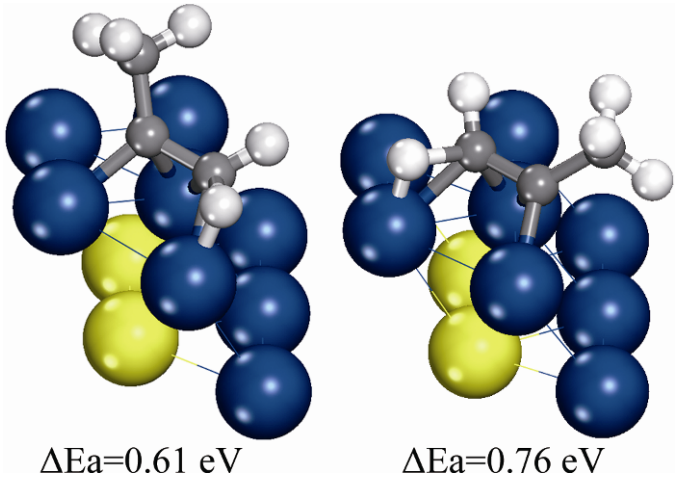

Figure S7. DFT optimized structures for the TS of 2-propenyl to propyne on Pt(211)

$CH_3CHC^* \rightarrow CH_3CC^* + H^*$:

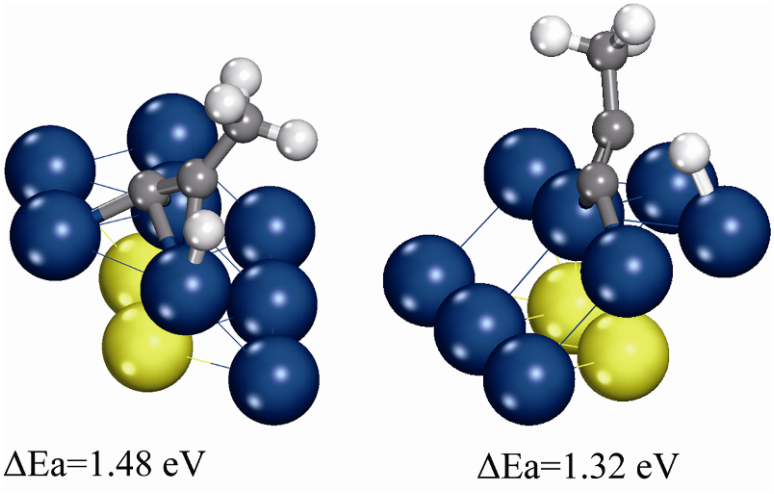

Figure S8. DFT optimized structures for the TS of propenylidene to propynyl on Pt(211)

$CH_3CHC^* \rightarrow CH_3CC^* + H^*$ on Pt(111):

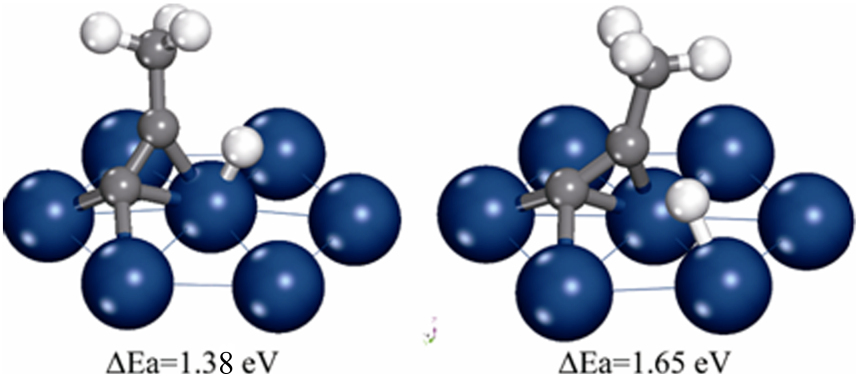

Figure S9. DFT optimized structures for the TS of propenylidene to propynyl on Pt(111)

$CH_3CCH^* \rightarrow CH_3CC^* + H^*$ on Pt(111):

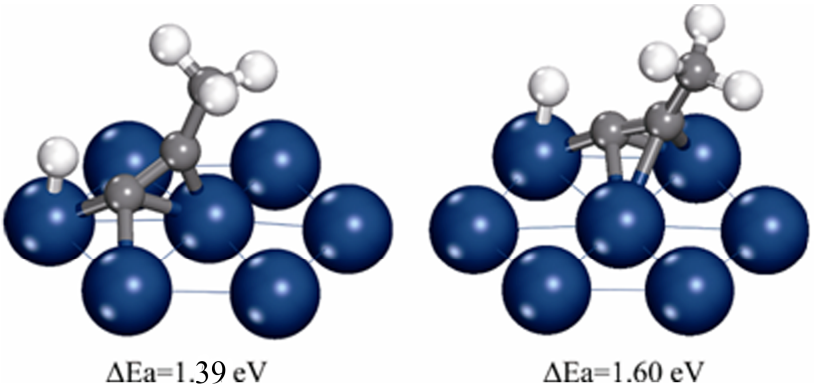

Figure S10. DFT optimized structures for the TS of propyne to propynyl on Pt(111)

Cracking reactions:

$CH_3CHCH^* \rightarrow CH^* + CH_3CH^*$

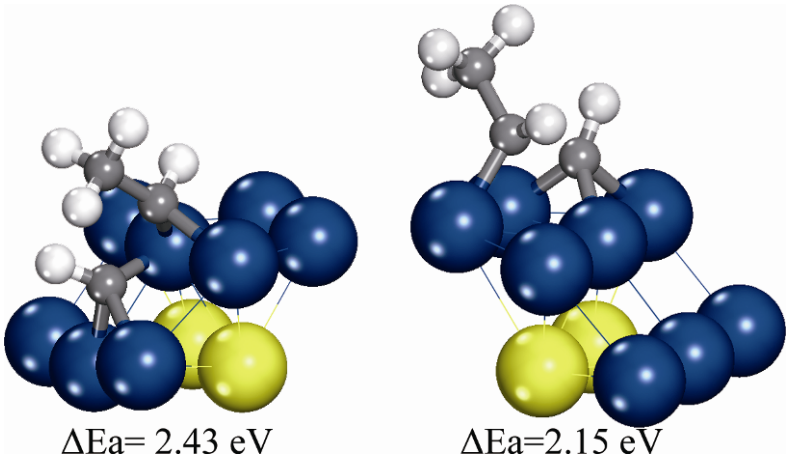

Figure S11. DFT optimized structures for the cracking TS of 1-propenyl on Pt(211)

$CH_3CHC^* \rightarrow C^* + CH_3CH^*$

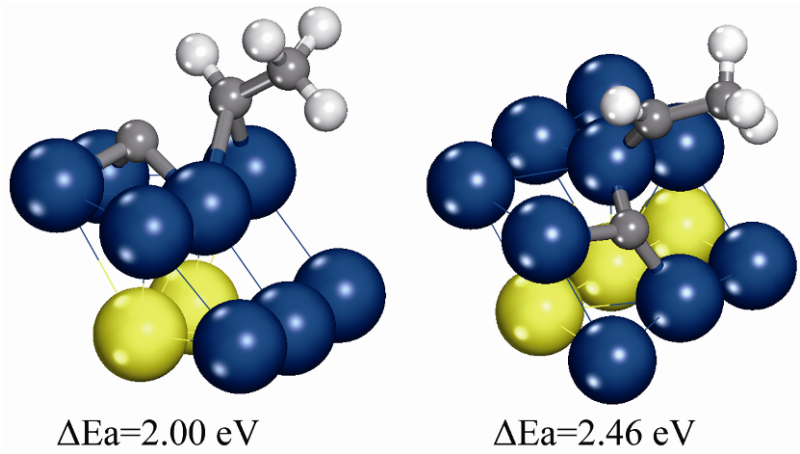

Figure S12. DFT optimized structures for the cracking TS of propenylidene on Pt(211)

$CH_3CCH^* \rightarrow CH^* + CH_3C^*$

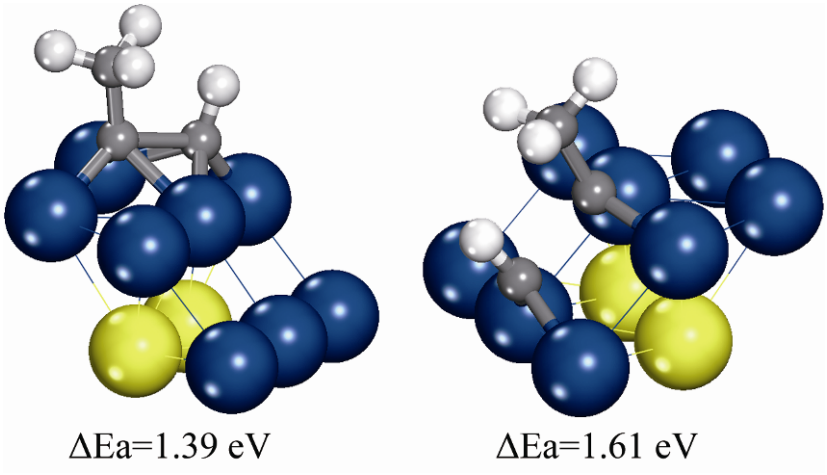

Figure S13. DFT optimized structures for the cracking TS of propyne on Pt(211)

$CH_3CC^* \rightarrow C^* + CH_3C^*$

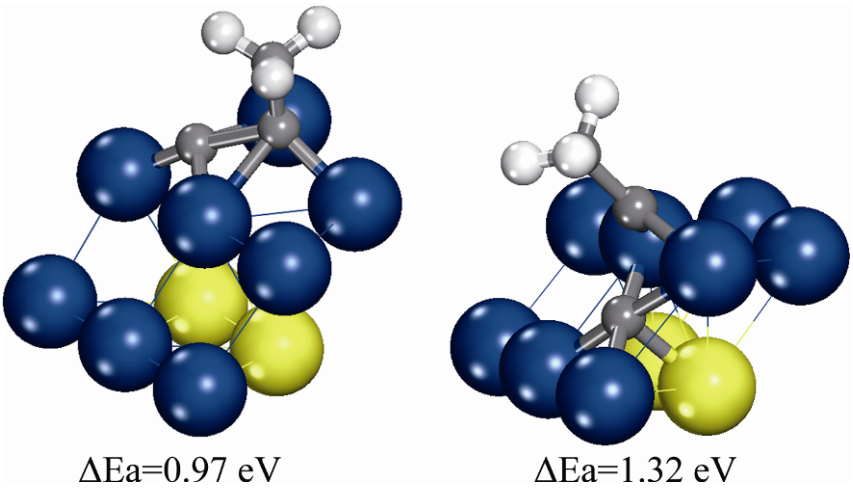

Figure S14. DFT optimized structures for the cracking TS of propynyl on Pt(211)

Table S2 Reaction heats, TS energy and FS energy of dehydrogenation of C_3 intermediates on Pt(111) and Pt(211).

	Surface reaction	ΔH (eV)		$E_{TS}-E_{IS}$ (eV)		$E_{FS}-E_{IS}$ (eV)	
		Pt(111)	Pt(211)	Pt(111)	Pt(211)	Pt(111)	Pt(211)
TS1	$CH_3CH_2CH_3^* \rightarrow CH_3CH_2CH_2^* + H^*$	-0.07	-0.48	0.65	0.28	-0.11	-0.52
TS2	$CH_3CH_2CH_3^* \rightarrow CH_3CHCH_3^* + H^*$	-0.06	-0.52	0.66	0.24	-0.10	-0.56
TS3	$CH_3CH_2CH_2^* \rightarrow CH_3CH_2CH^* + H^*$	0.03	-0.53	-1.16	-1.94	-1.86	-2.64
TS4	$CH_3CH_2CH_2^* \rightarrow CH_3CHCH_2^* + H^*$	-0.23	-0.65	-1.19	-1.77	-2.11	-2.76
TS5	$CH_3CHCH_3^* \rightarrow CH_3CHCH_2^* + H^*$	-0.24	-0.61	-0.99	-1.62	-1.91	-2.55

TS6	$CH_3CHCH_3^* \rightarrow CH_3CCH_3^* + H^*$	0.07	-0.56	-0.83	-1.72	-1.60	-2.50
TS7	$CH_3CH_2CH^* \rightarrow CH_3CH_2C^* + H^*$	-0.79	-0.34	-3.67	-3.70	-4.68	-4.84
TS8	$CH_3CH_2CH^* \rightarrow CH_3CHCH^* + H^*$	-0.19	-0.35	-3.28	-3.85	-4.09	-4.85
TS9	$CH_3CHCH_2^* \rightarrow CH_3CHCH^* + H^*$	0.06	-0.23	-0.21	-0.99	-0.90	-1.66
TS10	$CH_3CHCH_2^* \rightarrow CH_3CCH_2^* + H^*$	-0.01	-0.17	-0.20	-1.14	-0.98	-1.61
TS11	$CH_3CCH_3^* \rightarrow CH_3CCH_2^* + H^*$	-0.33	-0.22	-2.97	-3.8	-3.83	-4.46
TS12	$CH_3CH_2C^* \rightarrow CH_3CHC^* + H^*$	0.26	-0.06	-2.61	-2.79	-3.39	-3.68
TS13	$CH_3CHCH^* \rightarrow CH_3CHC^* + H^*$	-0.33	-0.04	-2.73	-2.97	-3.49	-3.94
TS14	$CH_3CHCH^* \rightarrow CH_3CCH^* + H^*$	-0.14	-0.21	-2.40	-2.93	-3.30	-3.77
TS15	$CH_3CCH_2^* \rightarrow CH_3CCH^* + H^*$	-0.07	-0.27	-2.15	-2.75	-2.99	-3.64
TS16	$CH_3CHC^* \rightarrow CH_3CC^* + H^*$	0.75	0.41	-0.97	-1.14	-1.60	-2.05
TS17	$CH_3CCH^* \rightarrow CH_3CC^* + H^*$	0.56	0.58	-0.77	-1.13	-1.60	-2.05

Table S3 Reaction heats, TS energy and FS energy of cracking of C_3 intermediates on Pt(111) and Pt(211).

	Surface reaction	ΔH (eV)		E_{TS}–E_{IS} (eV)		E_{FS}–E_{IS} (eV)	
		Pt(111)	Pt(211)	Pt(111)	Pt(211)	Pt(111)	Pt(211)
TS18	$CH_3CH_2CH_3^* \rightarrow CH_3^* + CH_3CH_2^*$	0.18	-0.30	2.40	1.60	0.12	-0.33
TS19	$CH_3CH_2CH_2^* \rightarrow CH_2^* + CH_3CH_2^*$	0.36	-0.25	-0.19	-0.99	-1.51	-2.36
TS20	$CH_3CHCH_3^* \rightarrow CH_3^* + CH_3CH^*$	0.28	-0.31	0.14	-0.72	-1.38	-2.26
TS21	$CH_3CH_2CH^* \rightarrow CH^* + CH_3CH_2^*$	-0.24	0.11	-2.72	-3.00	-4.10	-4.38
TS22	$CH_3CHCH_2^* \rightarrow CH_2^* + CH_3CH^*$	0.64	-0.14	1.04	-0.01	-0.29	-1.57
TS23	$CH_3CCH_3^* \rightarrow CH_3^* + CH_3C^*$	-0.57	-0.08	-2.20	-2.50	-4.04	-4.32
TS24	$CH_3CH_2C^* \rightarrow C^* + CH_3CH_2^*$	1.09	0.74	-1.74	-1.95	-2.47	-2.89
TS25	$CH_3CHCH^* \rightarrow CH^* + CH_3CH^*$	0.01	-0.07	-1.57	-1.58	-3.09	-3.80
TS26	$CH_3CCH_2^* \rightarrow CH_2^* + CH_3C^*$	-0.12	-0.30	-1.30	-1.87	-2.98	-3.67
TS27	$CH_3CHC^* \rightarrow C^* + CH_3CH^*$	0.90	0.26	-0.16	-0.46	-1.36	-2.20
TS28	$CH_3CCH^* \rightarrow CH^* + CH_3C^*$	-0.62	-0.19	-1.31	-1.24	-2.71	-2.82
TS29	$CH_3CC^* \rightarrow C^* + CH_3C^*$	-0.59	-0.48	-3.75	-4.01	-5.22	-5.46