

Supporting Information

The purpose of the supporting information is to show addition TPD and HREELS data as described in the text.

Furan TPD results. Figure S1 shows the furan desorption signal detected after various exposures of furan on Pd(111). Exposures were conducted in a similar manner as that described for 2,5-DHF and 2,3-DHF in the main text.

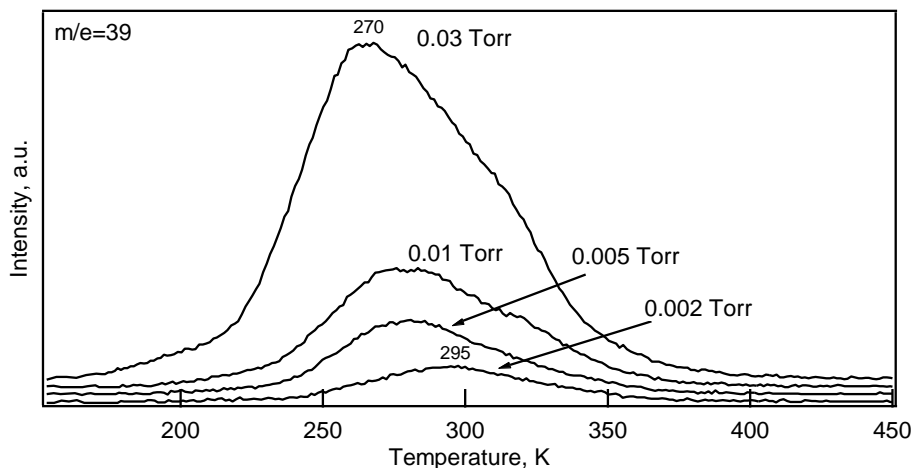


Figure S1. Furan (m/e=39) TPD traces following a series of increasing exposures of furan on Pd(111).

TPD exposure trends. Figures S2-S5 show the exposure-dependent TPD signals for CO and benzene from 2,3-DHF and 2,5-DHF.

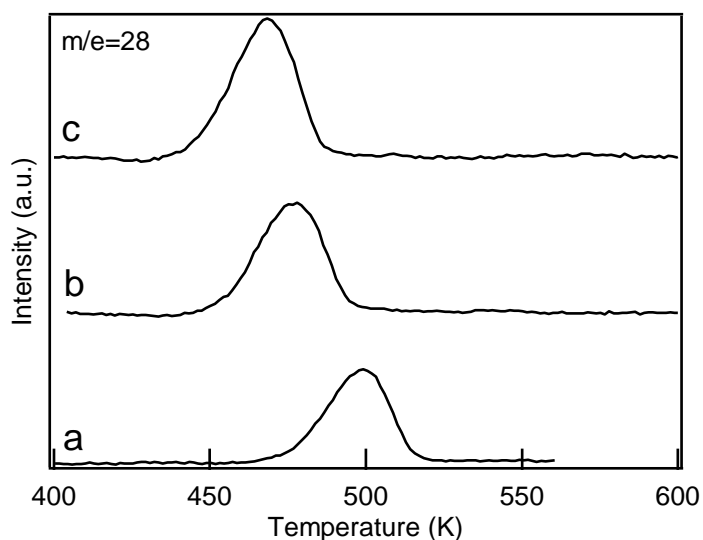


Figure S2. CO (m/e=28) TPD traces following a series of increasing exposures of 2,3-DHF on Pd(111). Exposures (in Torr) and yield (in ML): a) 0.005, 0.08 b) 0.04, 0.12 c) 0.10, 0.15.

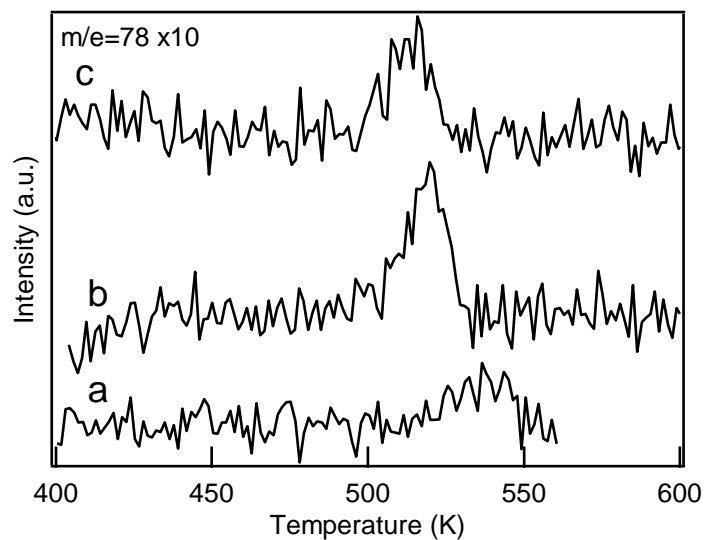


Figure S3. Benzene ($m/e=78$, $\times 10$) TPD traces following a series of increasing exposures of 2,3-DHF on Pd(111). Exposures (in Torr): a) 0.005 b) 0.04 c) 0.10

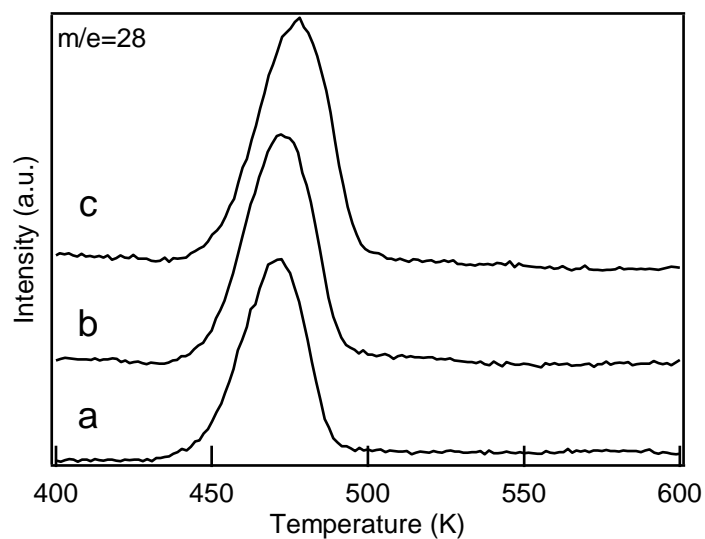


Figure S4. CO ($m/e=28$) TPD traces following a series of increasing exposures of 2,5-DHF on Pd(111). Exposures (in Torr) and yield (in ML): a) 0.002, 0.11 b) 0.04, 0.14 c) 0.15, 0.15.

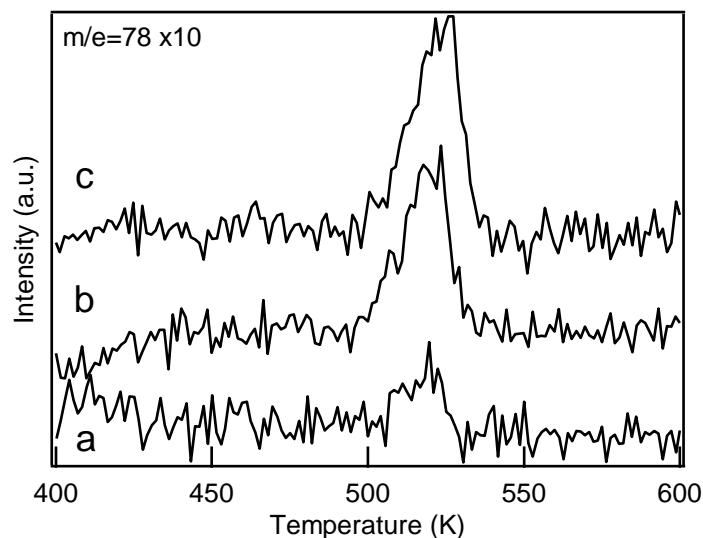


Figure S5. Benzene ($m/e=78$, $\times 10$) TPD traces following a series of increasing exposures of 2,5-DHF on Pd(111). Exposures (in Torr): a) 0.002 b) 0.04 c) 0.15

Effect of dose temperature on benzene yield. Figures S6 and S7 show the benzene desorption yield after exposures of 2,3-DHF and 2,5-DHF at low temperature versus high temperature. The high temperature exposures yield significantly higher amounts of benzene, as shown by the figures. Figures S6 and S7 are reported for cases that gave similar CO yields. Since similar CO yields should indicate similar coverages of C3 fragments that hypothetically produce benzene, it is surprising that the benzene yield varies to such a large extent in both cases. Note that the benzene yield is also significantly higher for the higher temperatures if the exposure, rather than the CO yield, is kept constant for the comparison.

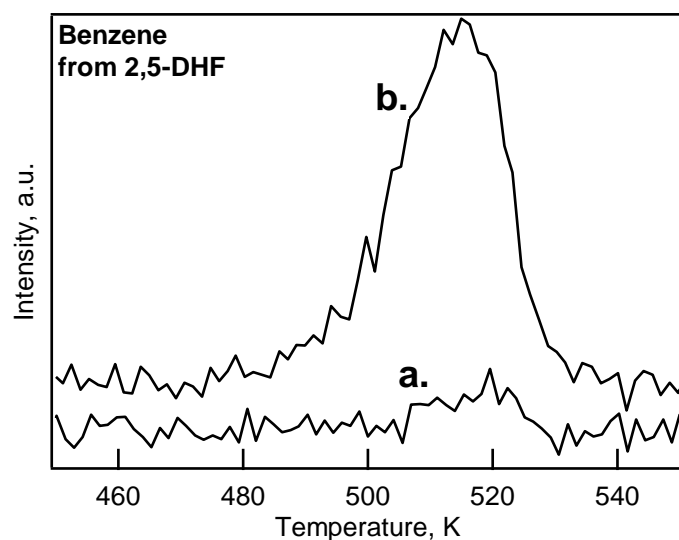


Figure S6. Benzene ($m/e=78$) TPD traces for 2,5-DHF experiments on Pd(111). Trace a) corresponds to a 2,5-DHF exposure pressure of 0.002 Torr at a temperature of 163K. Trace b) corresponds to a 2,5-DHF exposure pressure of 0.06 Torr, performed at 286K. Each experiment yielded 0.11 ML of CO desorption.

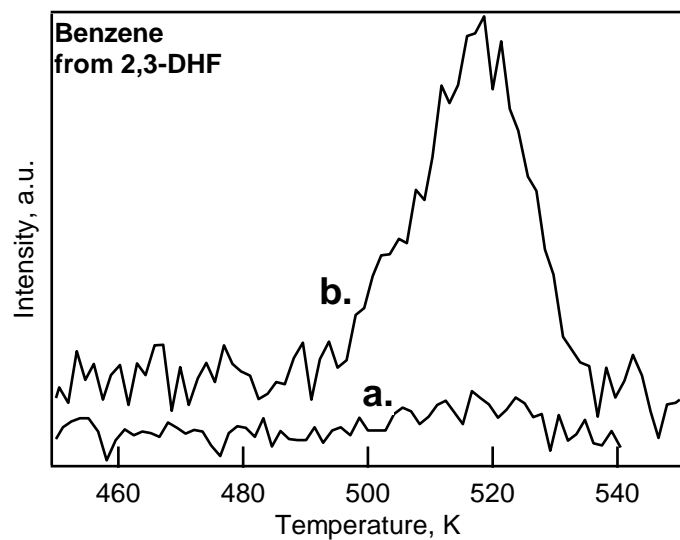


Figure S7. Benzene ($m/e=78$) TPD traces for 2,3-DHF experiments on Pd(111). Trace a) corresponds to 2,3-DHF exposure pressure of 0.005 Torr at a temperature of 153K. Trace b) corresponds to a 2,3-DHF exposure pressure of 0.06 Torr, performed at 280K. Each experiment yielded 0.08 ML of CO desorption.

Comparison of 323K and 373K HREEL spectra from 2,3-DHF and 2,5-DHF. To enable objective comparison between the vibrational spectra of intermediates from 2,3-DHF and 2,5-DHF at higher temperature, figure S8 is provided below.

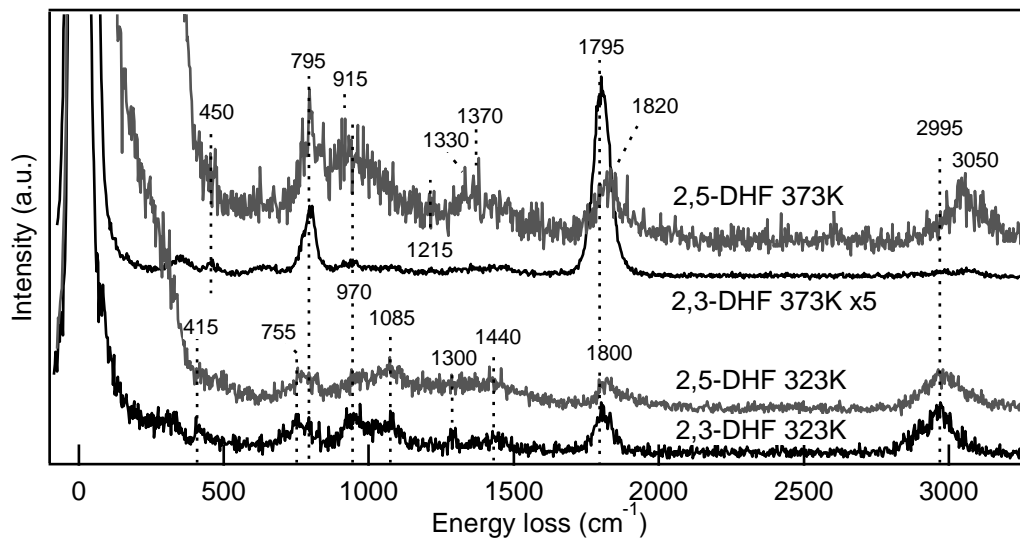


Figure S8 Comparing HREEL spectra for 2,3-DHF and 2,5-DHF at 323 and 373K.