Electronic Supplementary Information (ESI)

Methyl substitution effects on non-adiabatic dynamics of benzene:
Lifting three-state quasi-degeneracy at conical intersections

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Figure S1. TRPES spectra of (a) benzene, (b) toluene, and (c) o-xylene. Dotted curves show ridge lines of the contours of the fast components $[I_{\text{fast}}(t; E)]$ determined from by the fitting. Bold lines indicate spectral peaks of $A_{\text{slow}}(E)$. The regions painted by grey represent rise times of the slow components $([T_0, T_0 + T_{\text{rise}}])$. 
**Figure S2.** (a) Results of least squares fitting for benzene at the eBEs of (a) 5.1 eV and (b) 6.2 eV. Symbols, experimental; solid, fitting; dotted, individual fast and slow components.
Figure S3. Comparison of ridge lines of the contours in Fig. 2.
Photoelectron signals due to ionization to the cationic excited states:

Figure S4 shows the result of least squares fitting for o-xylene at eBE = 6.0 eV (Symbols, experimental; solid, fitting; dotted, individual fast and slow components). Both fast (blue) and slow (green) components are due to ionization to the cationic ground state $D_0$; they are respectively assignable to $D_0 \leftarrow S_0$ and $D_0 \leftarrow S_1$ transitions. Meanwhile, there exists a small bump around the time origin in the experimental time profile. This may be attributed to $D_x \leftarrow S_2$ ionization.

**Figure S4.** Result of least squares fitting for o-xylene at eBE = 6.0 eV. Symbols, experimental; solid, fitting; dotted, individual fast and slow components.
TRPES spectra of toluene in the even higher eBE region:

Figure S5(a) and (b) show two different eBE regions of the same TRPES spectra of toluene. In Fig. 5(b), toluene molecules unexcited by the pump pulses give rise to a one-color background signal. The one-color signal was evaluated by averaging the photoelectron spectra over negative delays and subtracted it to obtain Fig. S5(b). Figure S5(c) shows expected band positions due to ionization from S_0 (blue) and S_1 (red). The former is a static photoelectron spectrum of toluene digitized from ref. 18. To yield the latter, the former is shifted by 4.0 eV so that expected band position via D_0 ← S_1 transition matches observed one. It is notable that the latter is only as a guide. Under the frozen-orbital approximation, the selection rules for D_x ← S_0 and D_x ← S_1 transitions are different from each other.
Figure S5. (a) and (b) Two different eBE regions of the same TRPES spectra of toluene. (c) Expected band positions due to ionization from S$_0$ (blue) and S$_1$ (red).