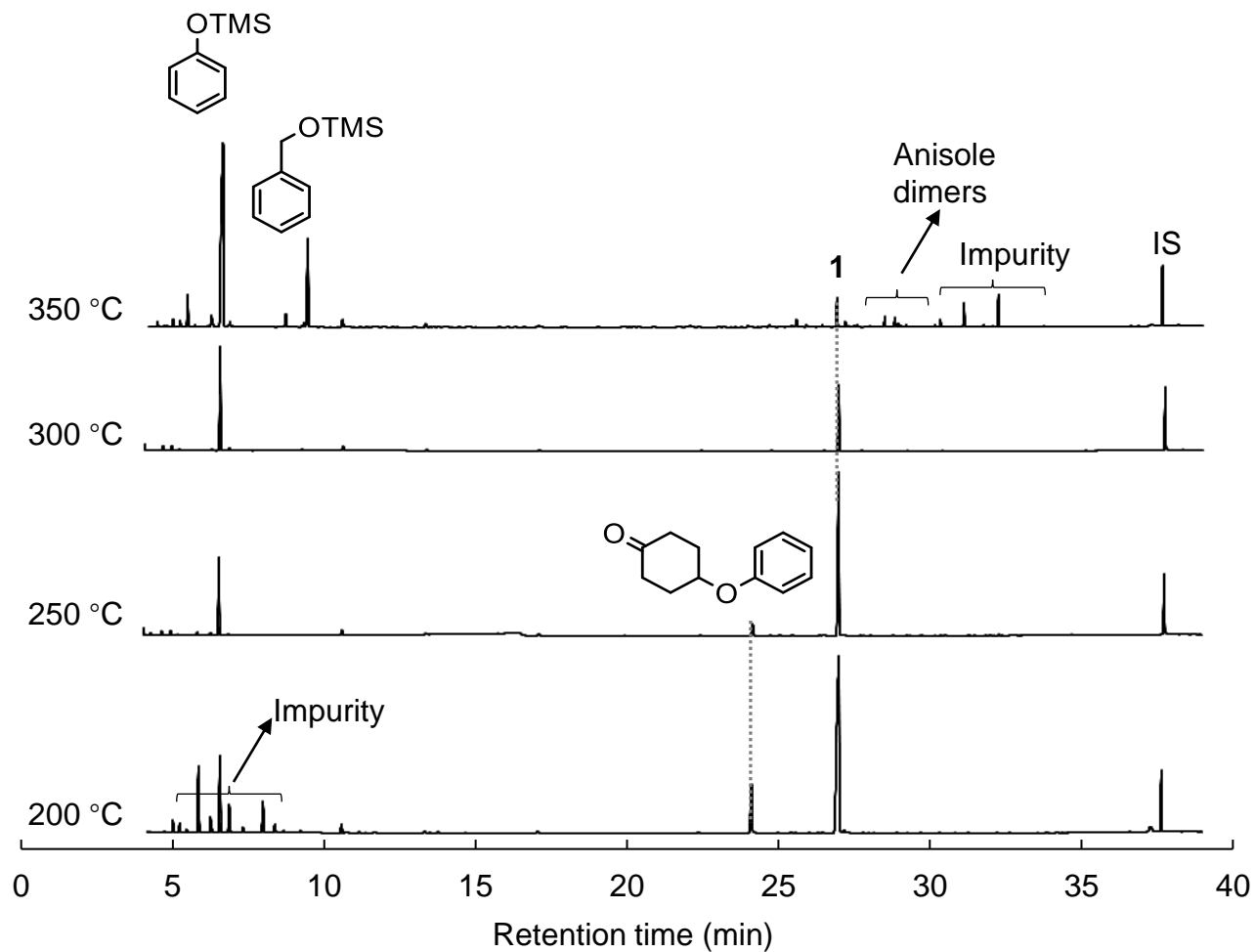
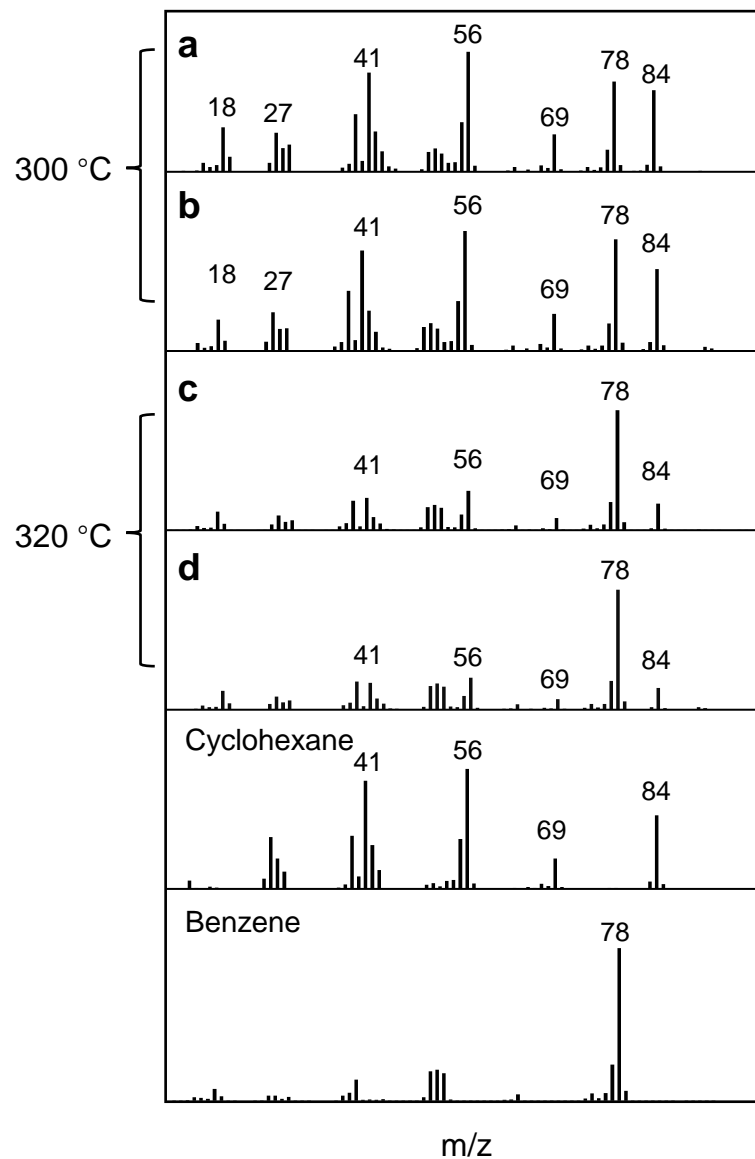


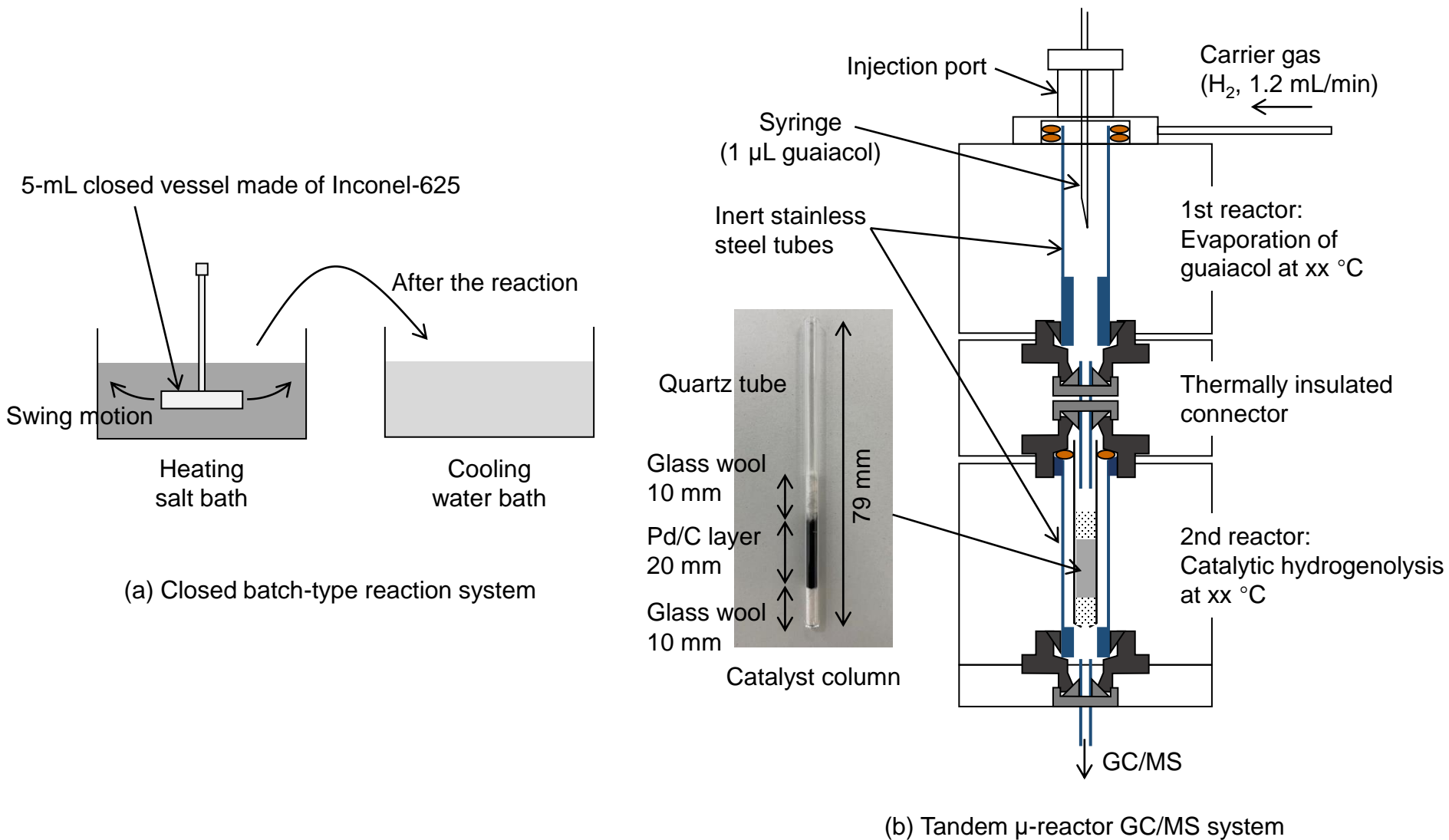
**Figure S1.** The mass spectra of various standard dimers used for identification purposes (corresponding to the compounds shown in Fig. 6).



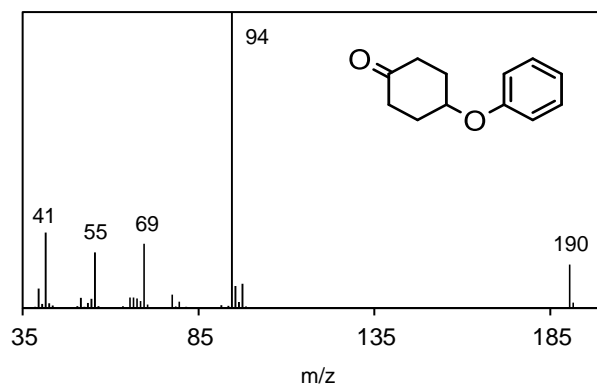
**Figure S2.** The GC/MS total ion chromatograms of the TMS-derivatives of reaction mixtures obtained from the pyrolysis-assisted catalytic hydrogenolysis of the 4-O-5 model compound (**1**) in anisole at 200–350 °C for 60 min.



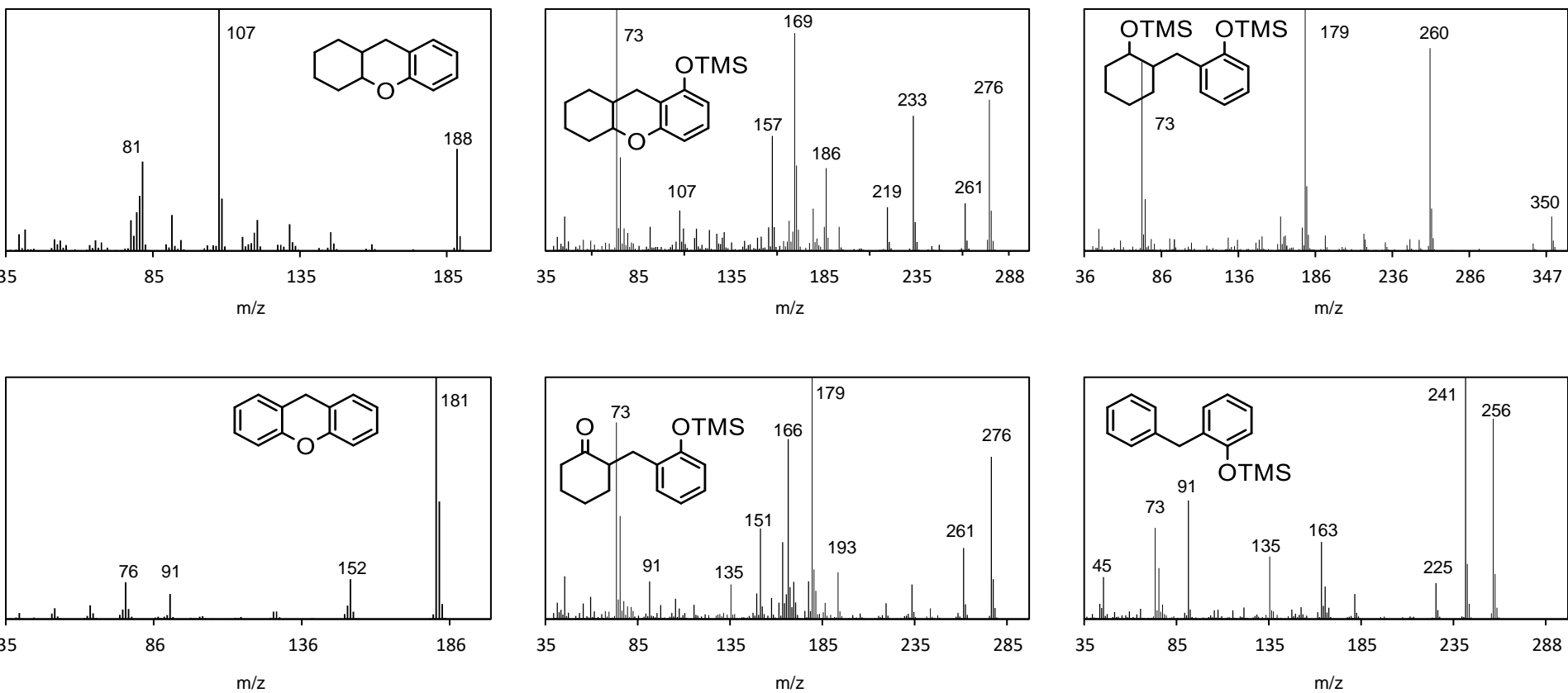
**Figure S3.** The mass spectra obtained from the reaction of guaiacol with Pd/C at 300–320 °C using a tandem micro-reactor GC/MS system with H<sub>2</sub> as the carrier gas. The spectra were obtained at retention times of a) 6.4, b) 8.0, c) 6.0 and d) 7.6 min (corresponding to the labels in Fig. 12).



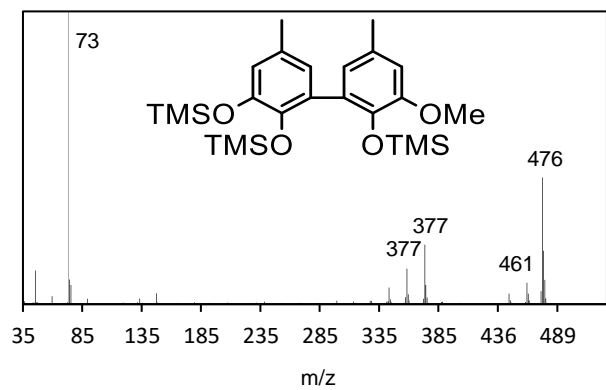
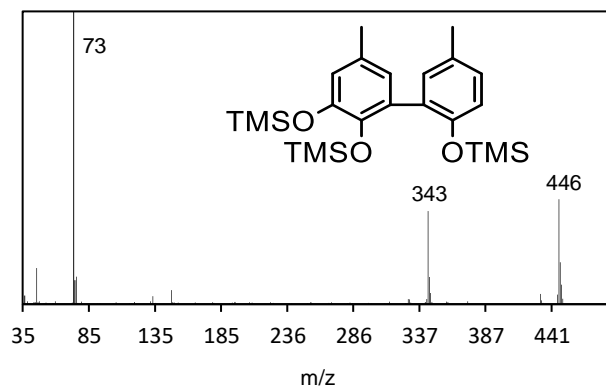
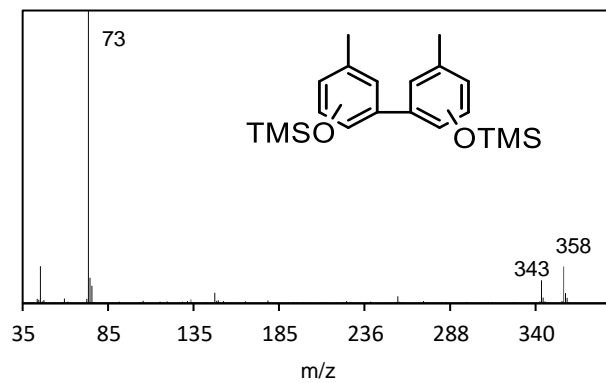
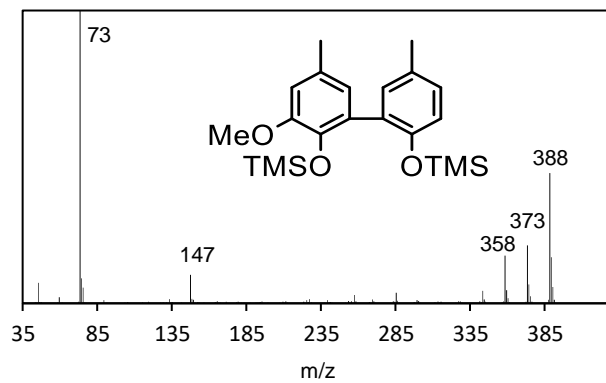
**Figure S4.** (a) A diagram of the closed batch-type reaction system and (b) a photograph and diagram of the tandem micro-reactor GC/MS system.



**Figure S5.** The mass spectrum of the saturated ring products obtained from the 4-O-5 model compound (**1**) used for identification purposes.



**Figure S6.** The mass spectra of the TMS-derivatives of products obtained from the  $\alpha$ -aryl model compound (**2**) used for identification purposes.



**Figure S7.** The mass spectra of the TMS-derivatives of products obtained from the 5-5 model compound (**3**) used for identification purposes.