In doping control analysis, athletes’ urine samples are examined for the presence of banned substances or their metabolites. Almost half of all adverse analytical findings reported by the World Anti-Doping Agency (WADA) originate from abuse of anabolic androgenic steroids (AAS)\(^1\). Since 2006 a number of long-term metabolites (detection window > 2 weeks), including 1-6, with a 17-hydroxymethyl-17-methyl-18-nor fragment have been identified. A synthesis of the compounds 1-6 depicted in Figure 1 was carried out in our laboratories\(^{2,3}\) in order to corroborate the proposed structure and, if possible, secure the identities of the target Phase I metabolites.

The uncommon residues on the D-ring were introduced by a Wagner-Meerwein rearrangement, initiated by opening of a spiroepoxide (Scheme 1). Generally, the elaboration of the A-ring (starting from DHEA acetate 7) was carried out first with an appropriate handle on the 17-position (olefin, epoxide, ketone) to allow for rearrangement at the end of the synthesis.

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