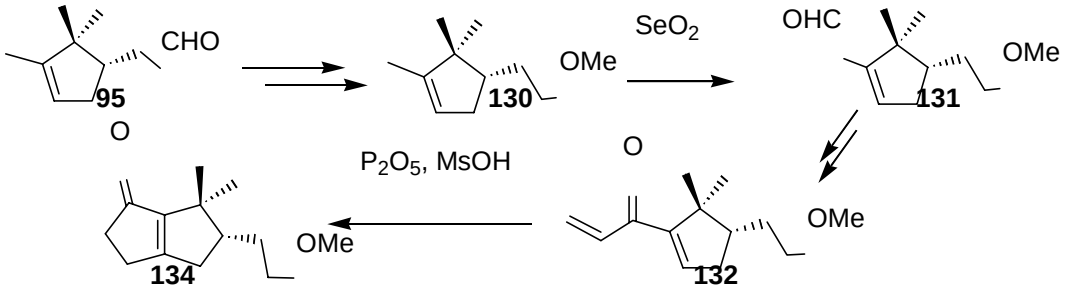
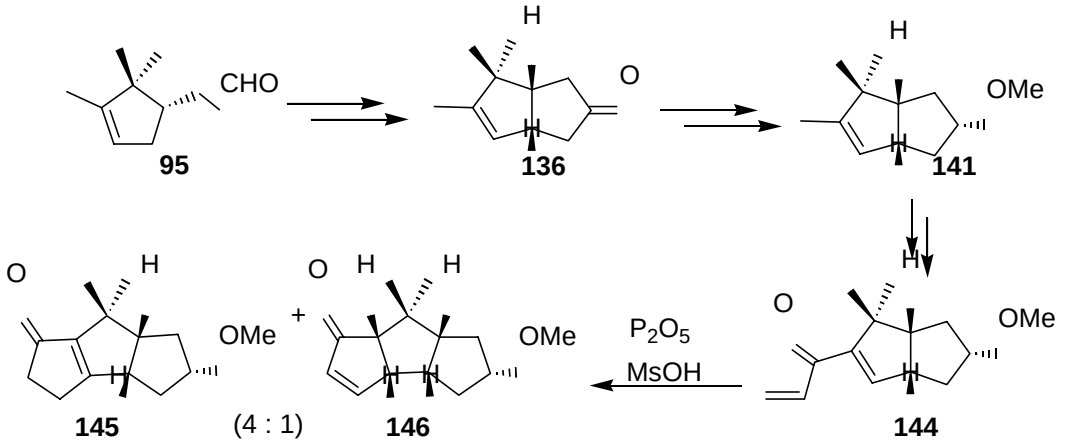
Employing a chiral pool strategy, enantiospecific syntheses of di- and triquinanes have been accomplished. α-Campholenaldehyde **95**, readily available from the abundantly available monoterpene α-pinene **94**, has been utilised as the chiral starting material.

To begin with, enantiospecific synthesis of the diquinane **134** has been developed employing Nazarov cyclisation of the cross-conjugated dienone **132** as the key reaction (Scheme 37).[71] Synthesis of the dienone **132** was accomplished by selenium dioxide mediated oxidation of the olefinic methyl group in α-campholenyl methyl ether **130**, followed by further elaboration of the resultant aldehyde **131**.



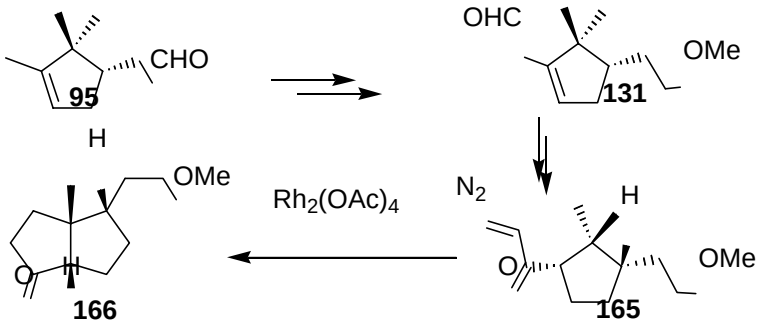

**SCHEME 37**




**SCHEME 38**

The Nazarov cyclisation strategy has been further extended, as depicted in Scheme 38, for the synthesis of the triquinane enones **145** and **146** *via* the cross conjugated enone **144**.[71] The dienone **144** was obtained from the diquinane **136**, which is readily available from campholenaldehyde **95** via an intramolecular rhodium carbenoid CH insertion reaction.

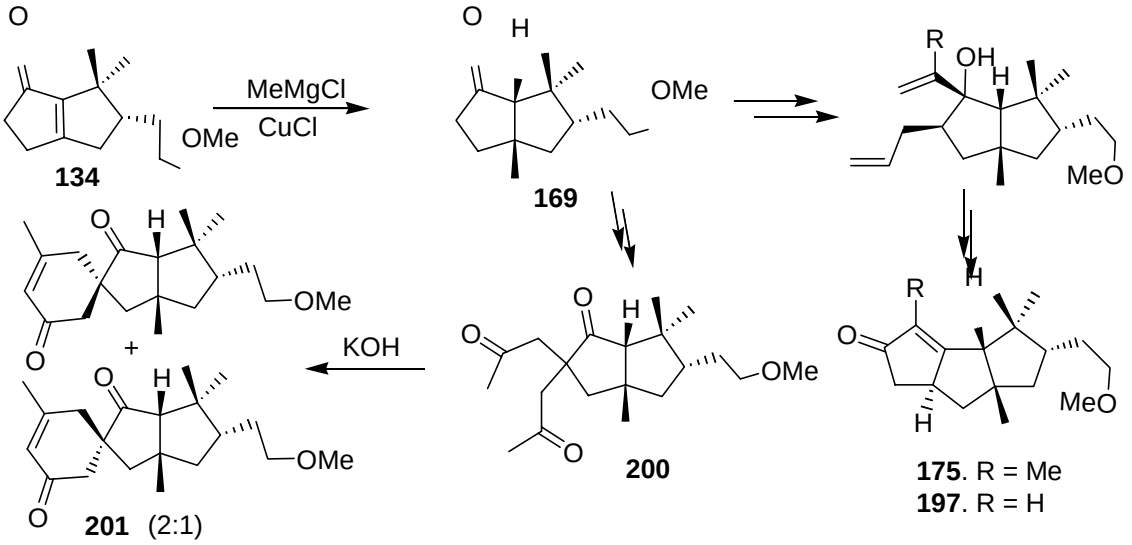
Of the three methyl groups in campholenaldehyde **95**, the olefinic methyl group can easily be functionalised, for example, *via* allylic oxidation. However, the remaining two tertiary methyl groups are difficult to functionalise, and there is no report in the literature on the utility of these two gem dimethyl groups either for functionalisation or for further elaboration, and remained only as gem dimethyl group in the products. It was conceived that it could be possible to utilise the tertiary methyl carbon for the ring construction *via* an intramolecular rhodium carbenoid γ-CH insertion reaction. To test the hypothesis, campholenaldehyde **95** was converted into the diazoketone **165**. Treatment of the diazoketone **165** with a catalytic amount of rhodium acetate furnished the diquinane **166**, via a highly regio- and stereoselective insertion of the intermediate rhodium carbenoid in the CH bond of the tertiary methyl group, which is located *cis* with respect to the diazoketone, Scheme 39.[72]




**SCHEME 39**

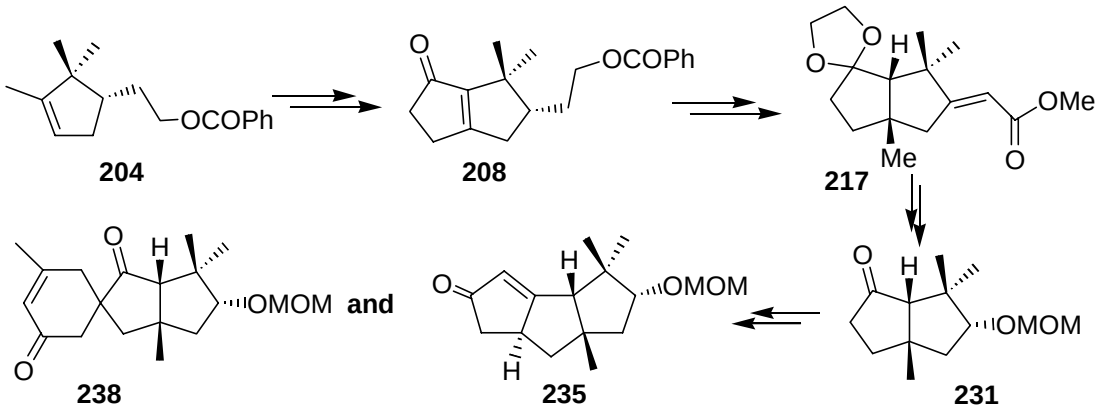
As an application of the Nazarov cyclisation mediated synthesis of the diquinane **134**, enantiospecific synthesis of the analogues of capnellenes, ABC and ABD ring systems of aberraranes have been carried out. A methyl cuprate reaction on the enone **134** generated the key intermediate, the ketone **169**. A ring-closing metathesis (RCM) based cyclo-

pentannulation has transformed the diquinane **169** into the analogue of capnellene **175**, as well as the analogue **197** of the ABC ring system of aberrarane. On the other hand, a Wacker reaction-intramolecular aldol condensation based spirocyclohexannulation transformed the diquinane **169** into an analogue **201** of the ABD ring system of aberrarane, Scheme 40.[73]




**SCHEME 40**

Finally, degradation of the two additional carbon atoms present on the A-ring furnished the ABC and ABD ring systems **235** and **238** of aberrarane, Scheme 41.




**SCHEME 41**