Effective synthesis of methano- and pyrazolinofullerenes

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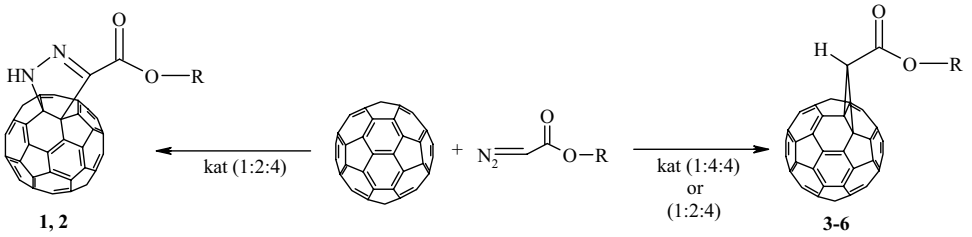
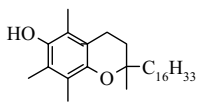
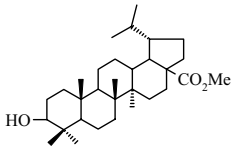
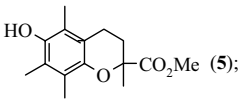
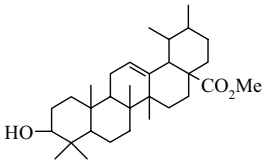
In the present report, a synthetic approach to the selective synthesis of methano- and pirazolinofullerenes with potential biological activity through cycloaddition of the synthesized on the basis of farmaco-significant compounds diazoacetates to the C_{60} carbon clusters in the presence of the three-component catalyst $Pd(acac)_2$-PPh_3-Et_3Al is discussed. In this study, α-tocopherol, trolox, 20,29-dihydro betulinic and ursolic acids were used as pharmacophores.

Thus, the reaction of diazoacetates, derived from α-tocopherol and methyl ester of 20,29-dihydro betulinic acid, with [60]fullerene (*o*-dichlorobenzene, ~ 80°C, 1.5 h) assisted by the $Pd(acac)_2$-PPh_3-Et_3Al (1:2:4) catalyst leads to the corresponding fulleropirazolines **1** and **2** in the yields of 45 and 50% respectively. A change in the Pd:P:Al catalyst component ratio from 1:2:4 to 1:4:4 favors the formation of individual methanofullerenes **3** and **4**. It is shown that the synthesized fulleropirazolines **1** and **2** are quite stable compounds and do not undergo any change even after boiling them in toluene for a day.

Metanofullerenes **5** and **6** have been exclusively obtained, when diazoacetates synthesized on the basis of the methyl esters of trolox and ursolic acid, were used in the reaction assisted by the catalytic system $Pd(acac)_2$-PPh_3-Et_3Al with a component ratio of 1:2:4.



kat = $Pd(acac)_2$-PPh_3-Et_3Al

R=  (**1**, **3**);  (**2**, **4**);  (**5**);  (**6**)

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