

Autoxidative Annulation of the α -Cyano β -TMS-capped Alkynyl Cycloalkanone System. Discovery of A Novel Synthetic Reaction in Organic Chemistry

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During the course of our studies on α -activated cross conjugated cycloalkenone systems in organic synthesis, we have serendipitously discovered that compound **2**, obtained through 1,4-conjugate addition of 1-(trimethylsilyl)-1-butyne-4-yl magnesium chloride to α -cyano cyclohexenone **1**, could undergo autoxidative annulation upon exposure to air and light to afford cyclic products **3** and **4**, respectively (Figure 1).

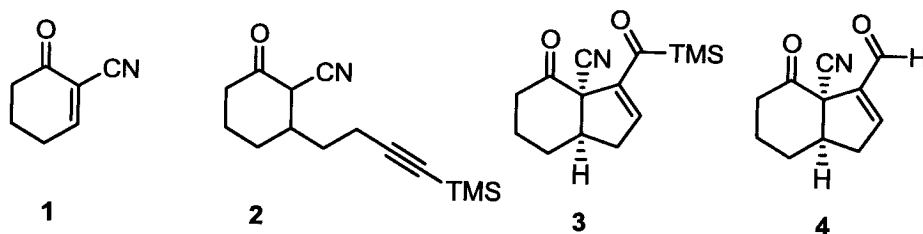
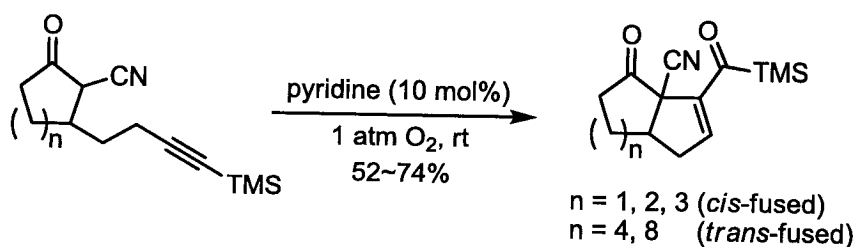


Figure 1

To optimize reaction conditions, reaction parameters, including solvents, bases and time, were systematically varied and monitored. As a result, the system (pyridine (catalyst)/O₂ (1 atm)/rt) is found to be the method of choice to effect the observed autoxidative reaction. On the basis of this newly developed protocol, a variety of highly functionalized bicyclic frameworks can be effectively constructed in moderate to good yields as illustrated in Scheme 1.



Scheme 1