A Carbene Catalysis Strategy for the Synthesis Protoilludane Natural Products:
Total Synthesis of Armillaridin and Isovelleral

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Step 7: Please name the reaction
Michaelis–Arbuzov reaction

Step 10: Please come up with a mechanism see below

Step 11: How do you prepare the reagent? What is the difference to LAH?
LiAlH$_4$ + 3 i-BuOH → LiAl(Ot-Bu)$_3$H + H$_2$

Compared to LAH this reagent is less reactive, sterically more hindered and stoichiometry can be better controlled.

Relative reactivity can be ranked as follows:
(J. Am. Chem. Soc. 1964, 86, 1079)
LiAlH$_4$ > LiAl(OMe)$_3$H > LiAl(Ot-Bu)$_3$H > NaBH$_4$
15) TBDPSCl, imH
16) Li₂CO₃, LiBr, DMF
17) LDA, 4
18) K₂CO₃, Mel
19) Pd₂dba₃, DPPE
20) OsO₄, NMO
21) NaO₄
22) VCl₃, Zn, HMPA

23) DMS, NCS, NEt₃
24) NaHB(OAc)₃
25) EDCI, DMAP, 5
26) TBAF
27) 4-NHAc-TEMPO, p-TsOH

28) DIAD, PPh₃, ArCOOH
29) TBAF
30) 4-NHAc-TEMPO, p-TsOH

Step 19: Please name the reaction. What is DPPE? What could be the drawbacks of direct allylation?
Tsüji–Trost–Stoltz decarboxylative allylation
DPPE = 1,2-Bis(diphenylphosphino)ethane
Direct allylation might be plagued by O-alkylation (in this case also oxidation to the phenol).

Step 20: Please name the reaction. What is the active Vanadium species?
Pinacol reaction

Step 23 and 28: Please name the reaction
23: Corey–Kim oxidation
28: Pinacol rearrangement

Step 27 and 30: What is the active species in this reaction? What is the advantage of 4-NHAc-TEMPO over TEMPO?

The reaction is colorometric (yellow to colorless) and the hydroxyl ammonium salt is insoluble in CH₂Cl₂ and can be easily removed by filtration.
Step 10 mechanism

\[ \text{R}_1 \text{N}=\text{N} \xrightarrow{i\text{-Pr}_2\text{NEt}} \text{R}_1 \text{N}=\text{N} \]  
\[ \text{addition} \quad \text{H} \quad \text{O} \]  
\[ \text{NHC} \quad \text{O} \]  
\[ \text{Michael addition} \quad \text{acylation} \]