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A Novel Approach to Highly Substituted Enynes, Dienynes and Thiiranes Based on Thiophosphates

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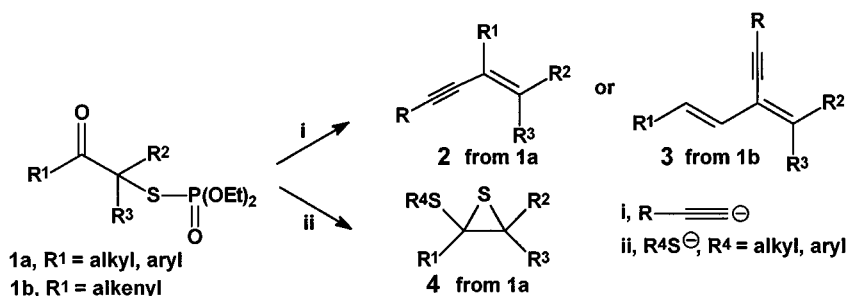
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A NOVEL APPROACH TO HIGHLY SUBSTITUTED ENYNES, DIENYNES AND THIIRANES BASED ON THIOPHOSPHATES

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Conjugated enynes and dienynes are of great interest in organic chemistry in particular as attractive precursors of conjugated dienes and trienes. As a part of our studies on the development of a novel approach to unsaturated systems and thiiranes based on thiophosphates **1a,b**, we report on the preparation of enynes **2**, dienynes **3**, and thiiranes containing thioalkyl(aryl) substituent **4**. Previously we have demonstrated the synthetic utility of thiophosphates **1a,b** as precursors of variously functionalized olefins.¹ The **1a,b** are readily available from the corresponding ketones **3**.² One-pot reactions of thiophosphates **1a** and **1b** with sodium acetylides (generated from acetylenic derivatives with NaNH_2) in THF at rt provide in one operation via single and double carbon-carbon bond formation highly substituted enynes **2** and



SCHEME 1

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dieneynes **3**, respectively. Reactions of **1a** with thiolate anions constitute the first synthesis of thiiranes **4**.

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