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Samarium triiodide-catalyzed conjugate addition of indoles with electron-deficient olefins

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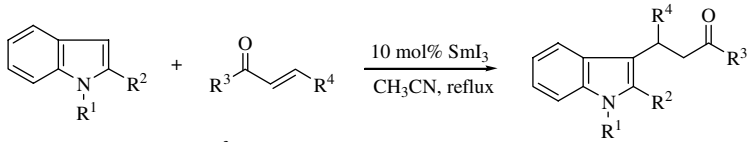
Abstract—The SmI_3-catalyzed reaction of indoles with electron-deficient olefins generated the corresponding Michael adducts in high yields. The substitution on the indole nucleus occurred exclusively at the 3-position and *N*-alkylation products have not been observed.

The development of new efficient synthetic methods leading to indole derivatives continues to receive much attention in organic synthesis because of their biological activities.[1] Various indole derivatives occur in many pharmacologically and biologically active compounds.[2] Among them 3-substituted indoles are important building blocks for the synthesis of biologically active compounds and natural products.[3] Therefore, a variety of methods have been reported for the preparations of this class of compounds.[4,5] The simple and direct method for the synthesis of 3-alkylated indoles involves the conjugate addition of indoles to α,β-unsaturated compounds in the presence of either protic[4] or Lewis acid.[5] However, the acid-catalyzed conjugate addition of indoles requires careful control of acidity to prevent side reactions such as dimerization or polymerization. Furthermore, many of these procedures involve strong acidic conditions, expensive reagents, low yields of products, and complex handling. Thus, a new efficient Lewis acid catalyst is desirable for conjugate addition of indoles to electron-deficient olefins.

Lanthanide ions are considered "hard" Lewis acids and form complexes with substantial ionic character because of poor overlap of the contracted 4f orbitals. Consequently, lanthanides preferentially coordinate to hard bases such as oxygen donor ligands and fluoride ion. Many lanthanides salts have been proved to be extraordinarily effective Lewis acids in various chemical transformations.[6,7b] Though samarium diiodide as a single electron reducing agent has played an important role in organic synthesis,[7] little work has been carried out on lanthanide salt, samarium triiodide used as a Lewis acid catalyst. This promoted us to investigate the use



R^1=H, $PhCH_2$ R^2=H, CH_3, Ph R^3=Ph, CH_3, Ph−CH=CH R^4=Ph, H R^3=R^4= $-(CH_2)_3-$

Scheme 1.

Keywords: Samarium triiodide; Indole; α,β-Unsaturated compounds; Michael reaction.
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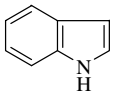
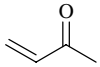
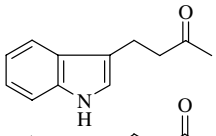
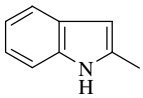
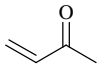
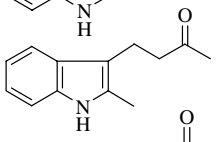
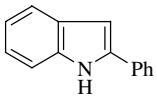
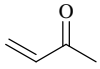
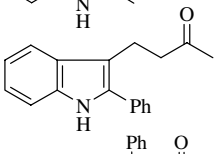
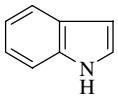
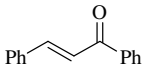
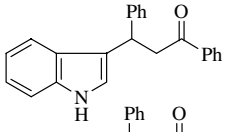
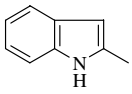
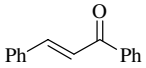
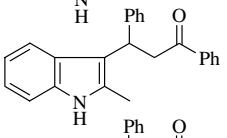
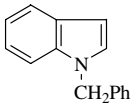
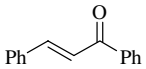
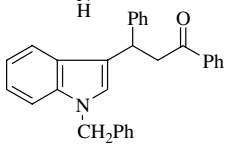
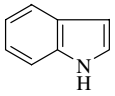
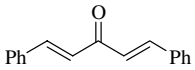
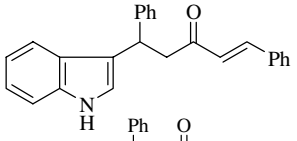
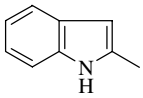
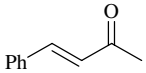
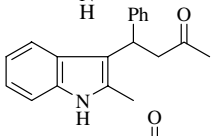
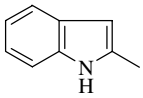
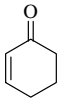
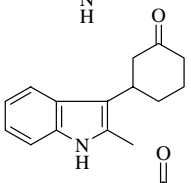
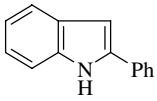
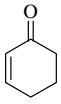
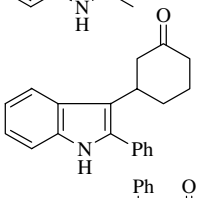
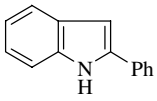
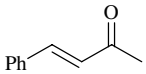
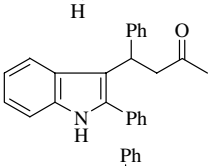
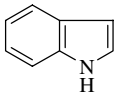
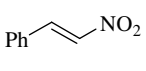
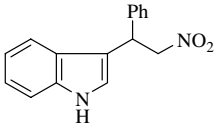
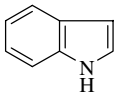
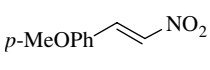
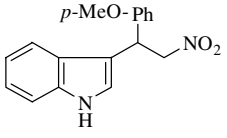
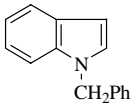
Table 1. Conjugate addition of indoles with electron-deficient olefins

Entry	Nucleophile	Electrophile	Product	Time (h)	Isolated yield (%)
1			**a** 	1	95
2			**b** 	1	95
3			**c** 	1	90
4			**d** 	6	85
5			**e** 	6	83
6			**f** 	6	75
7			**g** 	6	76
8			**h** 	6	75
9			**i** 	6	85
10			**j** 	6	90
11			**k** 	12	70
12			**l** 	1	95
13			**m** 	1	92
14			**n**	1	95