Selective lithiation at the methyl group of 2-tolyl isocyanide (1) was successfully performed by treatment of 1 with 2 equiv of lithium diisopropylamide (LDA) in diglyme at -78°C. The resulting \( \text{C} \)-lithiomethylphenyl isocyanide (2) in diglyme at -78°C was allowed to warm up to room temperature to produce, after \( \text{H}_2\text{O} \) workup, indole in an almost quantitative yield. The lithiomethylphenyl isocyanide (2) at -78°C was reacted with 2 equiv of alkyl halides to give \( \alpha \)-substituted phenyl isocyanides (3) in high yields [e.g., \( \text{CH}_3 \text{I} : \alpha \)-ethylphenyl isocyanide (95%), \( \text{C}_8\text{H}_7\text{Br} : \alpha \)-(3-methylbutyl)phenyl isocyanide (78%)]. \( \alpha \)-Alkylphenyl isocyanides (3) thus obtained were cyclized to 3-substituted indoles (4) in fairly good yields via the ortho-lithiation of the alkyl group in 3 using 2 equiv of lithium 2,2,6,6-tetramethylpiperidide (LTMP) [e.g., 3-methylindole (95%), 3-\( \alpha \)-isobutylindole (78%)]. A mixture of the lithiomethylphenyl isocyanide (2) and 2 equiv of alkylene oxide which had been stirred at -78°C for 2~5 hr was subsequently treated with 2 equiv of LDA at the same temperature and allowed to warm up to room temperature to give 3-(\( \beta \)-hydroxyalkyl)-indole (6) in moderate yield [e.g., 4\( \alpha \)-butene oxide : 3-(\( \beta \)-hydroxy-\( \beta \)-methylpropyl)indole (68%), Propylene oxide : 3-(\( \beta \)-hydroxypropyl)indole (65%)]. Next, 2 generated at -78°C was allowed to warm up to above -25°C, and then reacted with alkyl halides and alkylene oxides producing 1-substituted indoles (10) in good yields [e.g., 1-\( \text{CH}_3 \)butylindole (82%), 1-(\( \beta \)-hydroxybutyl)indole (84%)]. Finally, \( \alpha \)-(\( \beta \)-hydroxyalkyl)phenyl isocyanides (8), which were prepared by the reaction of 2 in diglyme at -78°C with 2 equiv of ketones or aldehydes, were heated with a catalytic amount of \( \text{Cu}_2\text{O} \) in benzene to afford dihydrobenzoxazepine derivatives (9) in high yields. Similarly, \( \text{Cu}_2\text{O} \)-catalyzed cyclizations of \( \alpha \)-(\( \beta \)-hydroxyalkyl)phenyl isocyanides (5), which were prepared from 2 and alkylene oxides, gave tetrahydrobenzoxazocine derivatives (7) in moderate yields.