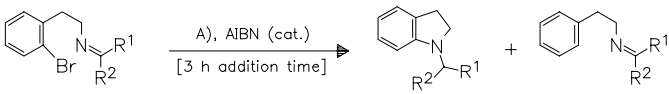
Indole derivatives

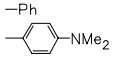
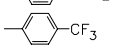
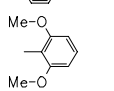
R 0140

22- 109

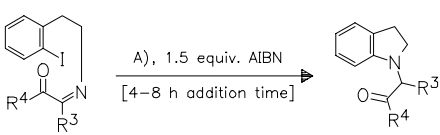
Free Radical-Mediated Aryl Amination and Its Use in a Convergent [3 + 2] Strategy for Enantioselective Indoline α-Amino Acid Synthesis. — In the presence of Bu_3SnH/AIBN ketimines of type (I) and (IV) undergo regioselective aryl-nitrogen bond formation giving indole derivatives. This is the most efficient radical-mediated aryl amination reported to date. The mild method can be applied successfully to the enantioselective synthesis of indoline α-amino acid derivatives. — (VISWANATHAN, R.; PRABHAKARAN, E. N.; PLOTKIN, M. A.; JOHNSTON*, J. N.; J. Am. Chem. Soc. 125 (2003) 1, 163-168; Dep. Chem., Indiana Univ., Bloomington, IN 47405, USA; Eng.) — Jannicke



I II III

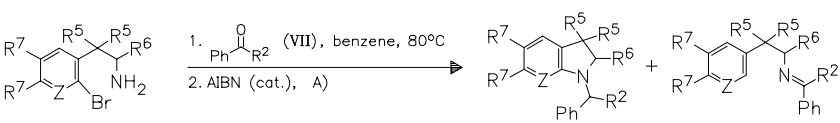
a R^1, R^2: —Me	30%	50% (GC)
b R^1: $—CF_3$; R^2: —Me	83%	6% (GC)
c R^1: —Me ; R^2: —Ph	87%	9% (GC)
d R^1: —Me ; R^2: 	90%	10% (GC)
e R^1: —Me ; R^2: 	72%	10% (GC)
f R^1: —Me ; R^2: 	27%	25% (GC)
g R^1, R^2: —Ph	86%	9% (GC)
h R^1: —H ; R^2: —Ph	8%	0%

A): Bu_3SnH, benzene, 80°C



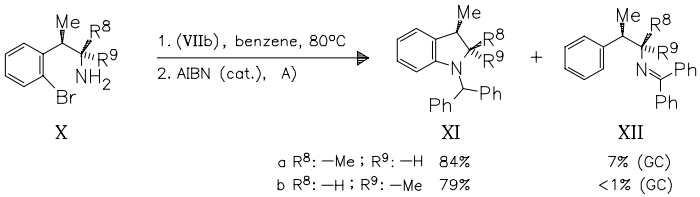
IV V

a R^3, R^4: —Me	82%
b R^3, R^4: —Ph	65%
c R^3: —Me ; R^4: —O—Me	75%
d R^3: —H ; R^4: —O—Et	<5%



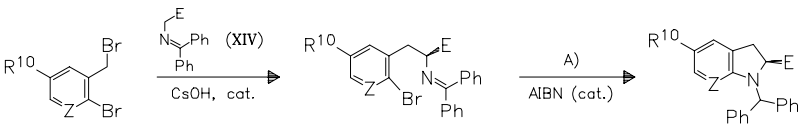
VI VIII IX

a R^2, R^5: —Me ; R^6, R^7: —H ; Z: —CH=	80%	2% (GC)
b R^2: —Ph ; R^5, R^7: —H ; R^6: —Me ; Z: —CH=	78%	<5% (GC)
c R^2: —Ph ; R^5, R^6: —H ; R^7: —O—Me ; Z: —CH=	64%	8% (GC)
d R^2: —Me ; R^5, R^6: —H ; R^7: —O—Me ; Z: —CH=	83%	10% (GC)
e R^2: —Ph ; R^5, R^6, R^7: —H ; Z: —N=	60%	20% (GC)



X XI XII

a R^8: —Me ; R^9: —H 84% 7% (GC)
b R^8: —H ; R^9: —Me 79% <1% (GC)



XIII (S)−XV (S)−XVI

a R^{10}: —H ; Z: —CH=	89% (96% e.e.)	a 69%
b R^{10}: —O—Me ; Z: —CH=	81% (94% e.e.)	b 45%
c R^{10}: —Cl ; Z: —CH=	74% (93% e.e.)	c 55%
d R^{10}: —H ; Z: —N=	77% (96% e.e.)	d 71%

E: —CO—O—tBu