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Supporting Information

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**Cp*Ir(NHC) complexes as highly versatile and efficient catalysts for
the cross-coupling of alcohols and amines**

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Table 1. N-alkylation of aromatic amines with *n*-hexylamine^[a]

Entry	Aryl amine	Catalyst	Conv.(%)	Yield(%)
1	aniline	1	30	80
2	aniline	Shvo's	20	80
3	<i>o</i> -toluidine	1	45	85
4	<i>o</i> -toluidine	Shvo's	40	85
5	4-fluoroaniline	1	40	>95
6	4-fluoroaniline	Shvo's	50	>95
7	4-trifluoromethylaniline	1	35	>95
8	4-trifluoromethylaniline	Shvo's	30	>95

^[a]Reaction conditions: 0.2 mmol alkyl amine, 0.4 mmol aryl amine, 1 mol % catalyst and 0.03 mmol AgOTf, toluene-d₈, 24 h, 150°C. Conversions and yields were calculated by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene (0.02 mmol) as internal standard.

Table 2. N-alkylation of primary amines with primary and secondary alcohols^[a]

Entry	Alcohol	Amine	Catalyst	t(h)	Conv. (%)	A (%)	B (%)
1	benzyl alcohol	benzylamine	2	7	60	20	0
2	benzyl alcohol	benzylamine	3	7	>95	>95	0
3	benzyl alcohol	benzylamine	Shvo's	7	>95	>95	0
4	1-phenyl ethanol	<i>n</i> -hexylamine	3	24	>95	50	31
5	1-phenyl ethanol	<i>n</i> -hexylamine	Shvo's	24	80	30	0
6	1-phenyl ethanol	benzylamine	3	24	85	75	0

^[a]Reaction conditions: 0.2 mmol amine, 1.0 mmol alcohol, 0.01 mmol (5 mol %) catalyst, 0.03 mmol AgOTf, 110°C. Conversion and yields determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene (0.02 mmol) as standard.