

# Ni(acac)<sub>2</sub>-catalyzed cross-coupling and carbonylative cross-coupling of organostannanes with hypervalent iodonium salts

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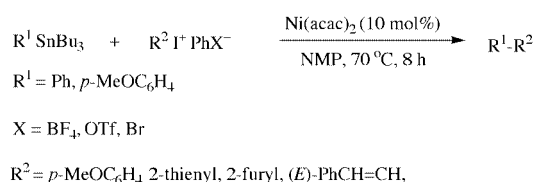
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**The Ni-catalyzed cross-coupling and carbonylative cross-coupling of organostannanes with hypervalent iodonium salts were achieved in the presence of Ni(acac)<sub>2</sub> (10 mol%) in NMP at 70 °C in moderate yields.**

The palladium-catalyzed cross-coupling and carbonylative cross-coupling of organostannanes with organic electrophiles (*i.e.*, halides and triflates) are known as the Stille reaction<sup>1</sup> and have become an extremely powerful tool for carbon–carbon bond formation. In the search for alternatives to the palladium catalyst, the copper and manganese-catalyzed cross-coupling of organostannanes with organic halides has been reported.<sup>2</sup> Hypervalent iodine compounds have received much attention as the electrophiles with organostannanes in palladium-catalyzed reactions<sup>3</sup> due to their good reactivities, ready availability and nontoxic properties. Recently we have reported<sup>4</sup> copper(i)-catalyzed cross-coupling and carbonylative cross-coupling of organostannanes with hypervalent iodine compounds. Here we wish to report nickel-catalyzed cross-coupling and carbonylative cross-coupling of iodonium salts with organostannanes.

Generally, to generate active nickel(0) species a reducing agent such as Zn, NaBH<sub>4</sub>, or DIBAL-H is needed. Thus, in the nickel-catalyzed cross-coupling of organostannanes with arylmethanesulfonates by Percec *et al.*<sup>5</sup> the presence of zinc was essential to get an active catalyst. However in the literature, Ni(dppf)Cl<sub>2</sub>-catalyzed cross-coupling of chloroarenes with arylboronic acids was realized in the absence of a reducing agent.<sup>6</sup> We have studied nickel-catalyzed cross-coupling and carbonylative cross-coupling of hypervalent iodonium salts with organostannanes and found that the catalyst Ni(acac)<sub>2</sub> is effective and surprisingly the catalyst performed much better when the reducing agent was omitted (Scheme 1).



Scheme 1

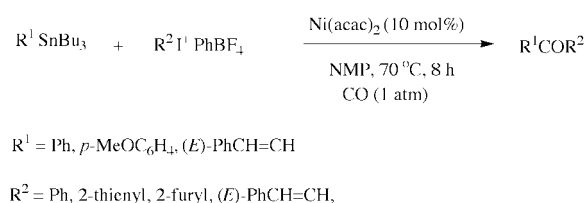
Initially, we examined the cross-coupling of *p*-methoxyphenyl(phenyl)iodonium tetrafluoroborate (**1b**) with 2-thienyltributylstannane (**2c**) to form the coupled product **3g** and to find optimum conditions. After a series of experiments, it was found that of the catalysts tested [Ni(acac)<sub>2</sub>, [Ni(acac)<sub>2</sub>-Zn, NiCl<sub>2</sub>(Ph<sub>3</sub>P)<sub>2</sub>, NiCl<sub>2</sub>(Ph<sub>3</sub>P)<sub>2</sub>-Zn, NiCl<sub>2</sub>(dppe), Ni(acac)<sub>2</sub>-Zn-Ph<sub>3</sub>P, Ni(acac)<sub>2</sub>-Et<sub>2</sub>Zn, Ni(acac)<sub>2</sub>-ZnCl<sub>2</sub>, NiCl<sub>2</sub>(dppe)-Zn, NiCl<sub>2</sub>] Ni(acac)<sub>2</sub> was the only catalyst which afforded the coupled product in a high yield. Of the solvents tested (NMP, DMF, CH<sub>3</sub>CN, CHCl<sub>3</sub>, THF, CHCl<sub>3</sub>-NMP) the solvents NMP and DMF were effective and NMP was the best choice.

The nickel-catalyzed cross-coupling of hypervalent iodonium salts with organostannanes is summarized in Table 1. The di-

phenyliodonium tetrafluoroborate (**1a**) reacted with 2-thienyltributylstannane (**2c**) in the presence of Ni(acac)<sub>2</sub> (10 mol%) in NMP at 70 °C for 8 h to afford 2-phenylthiophene (**3a**)<sup>7</sup> in 79% yield (entry 1 in Table 1). Under the same conditions, treatment of the iodonium salt **1a** with 2-furyltributylstannane (**2d**) gave 2-phenylfuran (**3b**)<sup>8</sup> in 78% yield (entry 2). This coupling was applied to alkenyl- and alkynylstannane **2e** and **2f**. The iodonium salt **1a** was readily coupled with **2e** and **2f** to provide the coupled alkene **3c** and alkyne **3d** in 82 and 80% yields, respectively (entries 3 and 4) (see Experimental section). For the *p*-methoxyphenyl(phenyl)iodonium tetrafluoroborate (**1b**), reaction with *p*-methoxyphenyltributylstannane (**2b**) gave 4,4'-dimethoxy-1,1'-biphenyl (**3e**) in 73% yield (entry 5). Coupling of **1b** with 2-furyl- and 2-thienyltributylstannane (**2d**) and (**2c**) afforded *p*-methoxyphenyl-substituted furan and thiophene **3f** and **3g**<sup>9</sup> in 71 and 77% yields, respectively (entries 6 and 7). For the *p*-methoxyphenyl(phenyl)iodonium triflate and bromide (**1c**) and (**1d**), which have different counterions from **1b**, reaction with **2c** afforded the coupled product **3g** in 75 and 78% yields (entries 8 and 9). It is notable that the yields of cross-coupling were not dependent on the counterions.

In considering a plausible mechanism for the coupling, it is presumed that the oxidative addition of highly reactive electrophilic iodonium salt **1a** with Ni(0) gives polar and reactive PhNi(II)L<sub>2</sub>, which if subjected to transmetalation with organostannanes followed by reductive elimination would give the cross-coupled product.

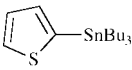
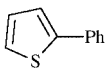
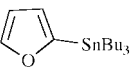
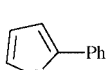
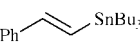
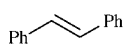
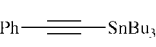
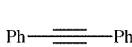
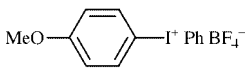
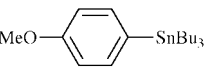
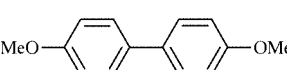
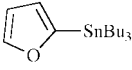
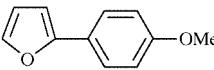
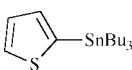
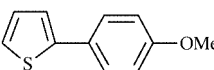
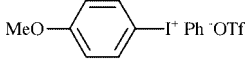
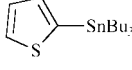
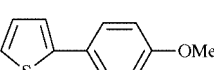
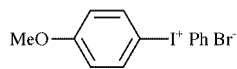


This cross-coupling was extended to carbonylation cross-coupling and the results of carbonylative cross-coupling of hypervalent iodonium salts with organostannanes under atmospheric pressure are summarized in Scheme 2 and Table 2.



Scheme 2

The iodonium salt **1a** reacted with phenyltributylstannane (**2a**) in the presence of Ni(acac)<sub>2</sub> (10 mol%) in NMP under an atmospheric pressure of carbon monoxide at 70 °C for 8 h to afford benzophenone (**4a**) in 81% yield (entry 1 in Table 2) (see Experimental section). Under the same conditions, 2-thienyltributylstannane (**2c**) was readily coupled with carbon monoxide to give the ketone **4b**<sup>10</sup> in 76% yield (entry 2). This carbonylative cross-coupling was applied to alkenyl- and alkynyl-substituted stannanes **2e** and **2f** which were smoothly coupled to afford unsaturated ketones **4c** and **4d**<sup>11</sup> in 72 and 78% yields, respectively (entries 3 and 4). For *p*-methoxyphenyl(phenyl)iodonium tetrafluoroborate (**1b**), 2-thienyltributylstannane (**2c**) was readily coupled under CO to give aryl

**Table 1** Ni(acac)<sub>2</sub>-catalyzed cross-coupling of organostannanes with hypervalent iodonium salts

Entry	Hypervalent iodonium salts	Organostannanes	Product	Isolated yield (%)
1	Ph <sub>2</sub> I <sup>+</sup> BF <sub>4</sub> <sup>-</sup> <b>1a</b>	 <b>2c</b>	 <b>3a</b>	79
2	<b>1a</b>	 <b>2d</b>	 <b>3b</b>	78
3	<b>1a</b>	 <b>2e</b>	 <b>3c</b>	82
4	<b>1a</b>	 <b>2f</b>	 <b>3d</b>	80
5	 <b>1b</b>	 <b>2b</b>	 <b>3e</b>	73
6	<b>1b</b>	 <b>2d</b>	 <b>3f</b>	71
7	<b>1b</b>	 <b>2c</b>	 <b>3g</b>	77
8	 <b>1c</b>	 <b>2c</b>	 <b>3g</b>	75
9	 <b>1d</b>	 <b>2c</b>	 <b>3g</b>	78

ketone **4e**<sup>10</sup> in 70% yield (entry 5). Treatment of **1b** with alkynyl-substituted stannane **2f** afforded ynone **4f**<sup>12</sup> in 69% yield (entry 6). Finally the alkenyl-substituted iodonium salt **1c** was reacted with 2-furyltributylstannane (**2d**) to afford the enone **4g**<sup>13</sup> in 65% yield (entry 7).

## Experimental

### Typical procedure

To a mixture of diphenyliodonium tetrafluoroborate (**1a**) (500 mg, 1.36 mmol) and nickel(II) acetylacetonate (34.9 mg, 10 mol%) was added tributyl(phenylethynyl)stannane (**2f**) (532 mg, 1.36 mmol) under N<sub>2</sub> charged at 70 °C in NMP (20 ml). The reaction mixture was stirred at 70 °C for 8 h, extracted with ether (20 mL × 3) and washed with water (20 mL × 3). The organic layer was dried over anhydrous MgSO<sub>4</sub> and evaporated *in vacuo*. The crude product was separated by SiO<sub>2</sub> column chromatography (hexanes, *R*<sub>f</sub> = 0.49) to afford diphenylacetylene (**3d**) (194 mg, 80%).

To a mixture of diphenyliodonium tetrafluoroborate (**1a**) (500 mg, 1.36 mmol) and nickel(II) acetylacetonate (34.9 mg, 10 mol%) was added tributylphenylstannane (**2a**) (499 mg, 1.36

mmol) under atmospheric CO at 70 °C in NMP (20 ml). The reaction mixture was stirred at 70 °C for 8 h, extracted with ether (20 mL × 3), and washed with water (20 mL × 3). The organic layer was dried over anhydrous MgSO<sub>4</sub> and evaporated *in vacuo*. The crude product was separated by SiO<sub>2</sub> column chromatography (EtOAc–hexanes 1:10 *R*<sub>f</sub> = 0.45) to afford benzophenone (**4a**) (200 mg, 81%).

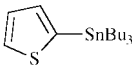
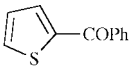
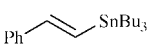
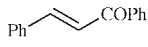
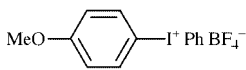
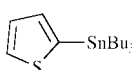
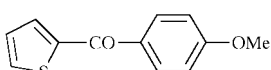
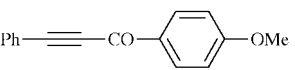
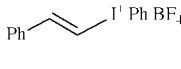
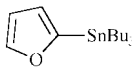
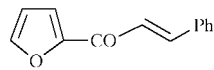
### Acknowledgements

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**Table 2** Ni(acac)<sub>2</sub>-catalyzed carbonylative cross-coupling of organostannanes with hypervalent iodonium salts

Entry	Hypervalent iodonium salts	Organostannanes	Product	Isolated yield (%)
1	$\text{Ph}_2\text{I}^+\text{BF}_4^-$ <b>1a</b>	$\text{PhSnBu}_3$ <b>2a</b>	$\text{PhCOPh}$ <b>4a</b>	81
2	<b>1a</b>	 <b>2c</b>	 <b>4b</b>	76
3	<b>1a</b>	 <b>2e</b>	 <b>4c</b>	72
4	<b>1a</b>	$\text{Ph-C}\equiv\text{C-SnBu}_3$ <b>2f</b>	$\text{Ph-C}\equiv\text{C-COPh}$ <b>4d</b>	78
5	 <b>1b</b>	 <b>2c</b>	 <b>4e</b>	70
6	<b>1b</b>	$\text{Ph-C}\equiv\text{C-SnBu}_3$ <b>2f</b>	 <b>4f</b>	69
7	 <b>1c</b>	 <b>2d</b>	 <b>4g</b>	65

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