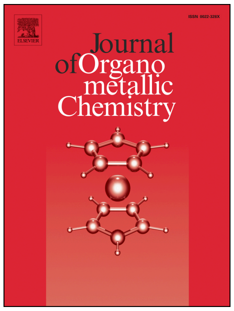

Phosphine-Free $NiBr_2$-Catalyzed Synthesis of Unsymmetrical Diaryl Ketones *via* Carbonylative Cross-Coupling of Aryl Iodides with Ph_3SnX (X = Cl, OEt)

Nasser Iranpoor, Habib Firouzabadi, Elham Etemadi-Davan

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Graphical Abstract Synopsis

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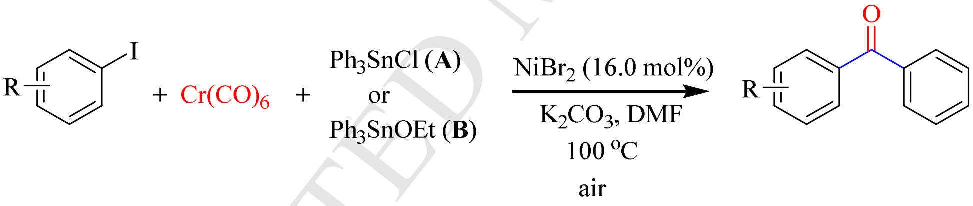
The convenient nickel-catalyzed carbonylative coupling of aryl iodides with organostannanes for synthesis of unsymmetrical diaryl ketones under phosphine-free condition is reported. The reaction occurs efficiently applying $Cr(CO)_6$ as an easy handling solid source of carbon monoxide at atmospheric pressure in DMF to deliver the desired ketones in high yield.



Phosphine-Free $NiBr_2$-Catalyzed Synthesis of Unsymmetrical Diaryl Ketones *via* Carbonylative Cross-Coupling of Aryl Iodides with Ph_3SnX (X = Cl, OEt)

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Abstract: The convenient nickel-catalyzed carbonylative coupling of aryl iodides with Ph_3SnCl or Ph_3SnOEt for synthesis of unsymmetrical diaryl ketones under phosphine-free condition is reported. The reaction occurs efficiently in the presence of $Cr(CO)_6$ as an easy handling solid source of carbon monoxide at atmospheric pressure and 100 ^oC in DMF under air to deliver the desired ketones in high yield.

Keywords:

$Cr(CO)_6$

$NiBr_2$

Ph_3SnCl or Ph_3SnOEt

Unsymmetrical Ketone

Aryl halide

1. Introduction:

The catalytic cross-coupling reaction between aryl electrophiles and organometallic nucleophiles accompanied by insertion of carbon monoxide offers symmetrical or unsymmetrical diaryl ketones [1]. Typical strategies for synthesizing diaryl ketones includes the reaction of activated carboxylic acid derivatives with organostannanes and Grignard reagents[2]; cross-coupling of aromatic aldehydes with aryl halides [3]; and the Friedel-Crafts acylation [4]. The Friedel-Crafts acylation gives isomeric mixtures, and also requires more than stoichiometric amount of a Lewis acid to perform the reaction. In this regard, the reactions in which several bonds could be formed in one operation without the need for several steps of protection/deprotection or isolating the intermediates is of great importance [5]. Therefore, carbonylative cross-coupling is a cascade process and has the advantage of high chemoselectivity and high efficiency which eliminates the application of carboxylic acid derivatives as carbon electrophiles, thus delivers polyfunctionalized ketones [6].

Carbonylative Stille reaction is the three-component reaction of diverse organostannanes with aryl or vinyl electrophiles which have been applied in the presence of carbon monoxide to give unsymmetrical diaryl ketones [7]. Pd-catalyzed cross-coupling of various aryl, and vinyl electrophiles with organostannanes in the presence of carbon monoxide have been reported [8]. In this reaction, the stoichiometric amount of organnostanes with the molecular formula of $RSnR'_3$ (R : 2-naphthyl, Ph, pyrazinyl, alkenyl, alkynyl; R' : ^{n}Bu, Me) is needed for the reaction to be completed [9], therefore it is valuable to substitute the organostannanes with a compound that has the stoichiometric economy as a carbon nucleophile source. In addition, due to the difficulty of handling of gaseous CO, a suitable substituent for CO is of great interest [10]. In this regard, the application of metal carbonyls [11] and organic compounds [12] having carbonyl in their structure have been developed. Recently, Nilsson have applied a Pd-catalyzed procedure applying $Mo(CO)_6$ as the solid source of carbonyl in carbonylative Stille cross-coupling reaction for synthesizing unsymmetrical ketones [13]. They used more than equimolar amount of the Bu_3SnR as a carbon nucleophile for the cross-coupling with long reaction times (16 h). In addition, all of the mentioned reactions are Pd-catalyzed transformation except the $Ni(acac)_2$-catalyzed carbonylative Stille reaction of aryl tri-*n*-buthylstannates with aryliodonium tetraflouroborate as hypervalent iodine substrates[14].

Lately, we reported Ph_3SnCl as a new source of stoichiometric-economy carbon nucleophile group for coupling with phenols, amines, and thiols and also for the Stille coupling of aryl halides [15]. In continuation of our research on carbonylation reactions [16], we introduce a Ni-catalyzed Stille carbonylative coupling of aryl halides with metal carbonyls as solid source of CO. In these reactions, Ph_3SnX (X= Cl, OEt) are used as stoichiometric-economy tin reagents.

2. Experimental:

Typical procedure for Ni-catalyzed Stille carbonylation of iodotoluene with Ph_3SnCl using $Cr(CO)_6$ in DMF at 100 ˚C:

4-Iodotoluene (1.0 mmol, 0.21 g) was added to a flask equipped with Ph_3SnCl (0.4 mmol, 0.15 g), $NiBr_2$ (16.0 mol%, 0.034g), K_2CO_3 (3.0 mmol, 0.29 g), and $Cr(CO)_6$ (1.0 mmol, 0.22g) in DMF (3.0 mL) and the resulting mixture was heated in an oil bath at 100 ˚C and stirred for 2.7 h. Progress of the reaction was monitored by TLC. After completion, the reaction mixture was cooled to room temperature, then H_2O (10 mL) was added and the mixture was transferred to a separatory funnel. The aqueous phase was further washed with EtOAc (3×10 mL) and the combined organic phases were dried over anhydrous Na_2SO_4 and then filtered. Column chromatography of the obtained residue on silica gel (*n*-hexane/EtOAc = 20:1) gave the desired ketone in 89% yield (0.11 g) (Table 4, entry 2).^{1}H-NMR (250 MHz, $CDCl_3$) δ(ppm):7.70-7.61 (4H, m), 7.47-7.44 (m, 1H), 7.40-7.34 (m, 2H), 7.24-7.16 (m, 2H), 2.33 (s, 3H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ 196.4, 143.2, 137.9, 133.6, 132.5, 129.9, 129.7, 128.9, 127.2, 21.0

3. Results and discussion:

To optimize the reaction condition, we run the reaction of 4-iodotoluene, $NiCl_2$, $Cr(CO)_6$, K_2CO_3, and Ph_3SnCl in PEG400 at 100 °C without inert gas protection under the conditions shown in entry 1, Table 1. The corresponding diaryl ketone (**1a**) was obtained in low yield along with the formation of the Stille coupling product (**2a**) as the major product (Table 1, entry 1). Applying different bases in PEG400 did not have significant effect on the yield of **1a** (Table 1, entries 2-4). Changing the solvent to DMF led to an increase in the yield of **1a** (Table 1, entry5). Screening other solvents showed that the reaction is performed well in DMF (Table 1, entries 6-

8). Changing the catalyst to $NiBr_2$ increased the isolated yield of **1a** to 89% (Table 1, entry 9). When we performed the reaction in the presence of Ph_3P as ligand or pre-prepared $NiCl_2(Ph_3P)_2$, the result is almost the same as when we conducted the reaction under ligand-free conditions (Table 1, entry 16, 17). Consequently, the ligand is not essential for the reaction as the ligand-free conditions gave good yield of the product. Therefore, $NiBr_2$ was applied as the catalyst for this transformation. Applying different bases in DMF showed that the reaction worked well in the presence of K_2CO_3 (Table 1, entries 10-12). The efficient amount of Ph_3SnCl was found to be 0.4 equiv for 1.0 mmol of 4-iodotoluene. Decreasing the temperature to 70 ˚C showed the low conversion of 4-iodotoluene to **1a** which is due to the inefficient liberation of the carbon monoxide from $Cr(CO)_6$ (Table 1, entry 13). Decreasing the amount of $NiBr_2$ to 6.0 mol% required longer reaction time and decreased in the yield of the product (Table 1, entry14).

Table1

We also investigated on the application of other suitable organotin compounds such as Ph_3SnOH, Ph_3SnOEt, and Ph_4Sn for this transformation. As the results of Table 2 show, we surmised Ph_3SnCl or Ph_3SnOEt as the promising organtin candidates for the reaction. We set up the reactions with 0.4 equiv of Bh_3SnCl or Ph_3SnOEt. This point revealed the stoichiometric-economy of these reagents with regard to the reported organotin reagents in literature for Stille and carbonylative Stille cross-coupling. In order to check the applicability of other carbon nucleophile instead of Ph_3SnCl (0.4 eqiuv), we performed the reaction with $PhB(OH)_2$ (1.2 equiv) and we observed that even after 5 h, the reaction did not go to completion (Table 2).

Table 2

In order to have a comparison between the efficiency of $Cr(CO)_6$ with other metal carbonyls, we replaced $Cr(CO)_6$ with other metal carbonyls such as $Mo(CO)_6$, $W(CO)_6$, $Fe(CO)_5$, and $Co_2(CO)_8$. From these reactions, it was found that the highest yield of **1a** was obtained in the presence of $Cr(CO)_6$. Therefore, $Cr(CO)_6$ was selected as the most suitable solid source of carbon monoxide for our further studies under the obtained optimized conditions (Table 3).

Table 3

When we employed the reaction for bromobenzene and phenyl triflate under the optimized reaction conditions of aryl iodides, the starting material was recovered after 24h. Performing the reaction of 4-iodotoluene in the presence of $NiCl_2$(dppf) , $NiCl_2(Ph_3P)_2$, and $NiCl_2(Ph_3P)_2/Ph_3P$ were also ineffective and 4-methylbenzophenone was obtained only in 17-20% yield.

We therefore applied our optimized conditions to various aryl iodides. It was observed that aryl iodides having electron-withdrawing or electron-donating groups give their corresponding unsymmetrical ketones in good yields (Table 4). In addition, electron-poor aryl iodides which are prone to give homo-coupling by-product reacted well under these conditions and produced their corresponding ketones in high yields. The substrate bearing -NO_2 functionality was converted to a mixture of side products due to the reduction of –NO_2 group. Sterically hindered substrates reacted efficiently under this condition and delivered the corresponding products in good yield.

Table 4

All the products were characterized with ^{1}H-NMR and ^{13}C-NMR and were compared to known samples [17].

In order to understand the plausible reaction pass way, we study the UV-Vis spectrum of the three mixtures. A solution of $NiBr_2$ in DMF; $Cr(CO)_6$ and $NiBr_2$ in DMF; and reaction mixture were stirred separately at 100 ˚C. Comparison of the UV-Vis spectrum showed that the Ni(II) peaks at 415, 571, 616 nm which exist in a solution of $NiBr_2$ in DMF were vanished in the reaction mixture and also in the solution of $NiBr_2$ and $Cr(CO)_6$ in DMF. This observation elucidates that in the reaction mixture in the presence of $Cr(CO)_6$, Ni(II) can be reduced to Ni(0).

Figure 1

For the plausible reaction mechanism, it is suggested that the Ni(II) pre-catalyst is first reduced by the generated CO to Ni(0). Oxidative addition of the carbon-iodide bond to the generated Ni(0) generates the intermediate (I) which followed by CO insertion to generate the intermediate (II). Attack of base to Ph_3SnX followed by migration of a phenyl group generates the intermediate (III) which after the reductive elimination, the corresponding unsymmetrical diaryl ketones and Ni(0) are produced. In addition, a base such as K_2CO_3 or OH^- reacts with Ph_3SnCl to migrate a Ph group (Scheme 1).

Scheme 1

4. Conclusion:

In conclusion, we have introduced the efficient Nickel-catalyzed reaction of Ph_3SnCl and Ph_3SnOEt as new sources of stoichiometric-economy phenyl nucleophile with aryl iodides for the cabonylative Stille cross-coupling to synthesize unsymmetrical diaryl ketones under mild conditions. This methodology excludes the use of any ligand. More importantly, this protocol is microwave-free and employ $Cr(CO)_6$ as a solid source of CO which makes it applicable especially for the laboratory scale. Consequently, application of Ni-catalyst over Pd-catalyst has the advantage of being cheaper, easily available and less toxic.

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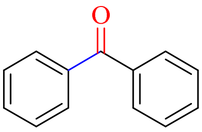
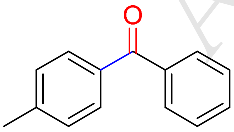
Supplementary Section:

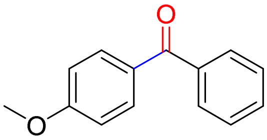
Spectral data of carbonylative Stille reaction of iodoarenes:



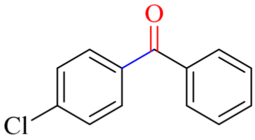
Benzophenone (Table 4, entry 1). ^{1}H-NMR ($CDCl_3$, 250 MHz): δ 7.74-7.70 (m, 4H), 7.51-7.48 (m, 2H), 7.43-7.37 (m, 4H); ^{13}C-NMR ($CDCl_3$, 62.9 MHz): δ 196.7, 137.5, 132.4, 130.0, 128.2



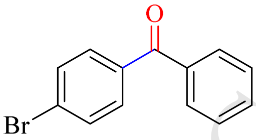
4-Methylbenzophenone (Table 4, entry 2). ^{1}H-NMR ($CDCl_3$, 250 MHz): δ 7.78 (d, J = 8.2 Hz, 2H), 7.72 (d, J = 7.1 Hz, 2H), 7.54-7.50 (m, 1H), 7.49-7.46 (m, 2H), 7.27 (d, J = 7.5 Hz, 2H), 2.43 (s, 3H); ^{13}C-NMR (CDCl$_3$, 62.9 MHz): δ 195.5, 143.2, 137.9, 134.8, 132.1, 130.3, 130.1, 128.9, 128.2, 21.6



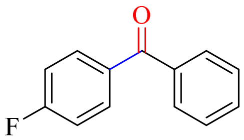
4-Methoxybenzophenone (Table 4, entry 3). ^{1}H-NMR (CDCl$_3$, 250 MHz): δ 7.87-7.85 (m, 2H), 7.77-7.74 (m, 2H), 7.53-7.51 (m, 1H), 7.45-7.42 (m, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 3.60 (s, 3H); ^{13}C-NMR (CDCl$_3$, 62.9 MHz): δ 195.1, 163.0, 137.9, 132.0, 131.3, 129.7, 129.0, 127.8, 112.8, 54.2



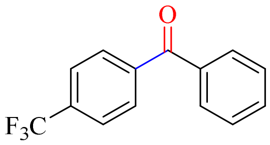
4-Cholorobenzophenone (Table 4, entry 4). ^{1}H-NMR (CDCl$_3$, 250 MHz): δ 7.72-7.70 (m, 2H), 7.60-7.55 (m, 2H), 7.45-7.41 (m, 1H), 7.38-7.33 (m, 4H); ^{13}C-NMR (CDCl$_3$, 62.9 MHz): δ 195.3, 139.2, 136.9, 135.5, 132.3, 131.0, 129.4, 128.0, 127.8



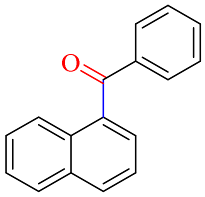
4-Bromobenzophenone (Table 4, entry 5). ^{1}H-NMR (CDCl$_3$, 250 MHz): δ7.75 (d, *J* = 8.1 Hz, 2H), 7.69-7.67 (m, 2 H), 7.63-7.59 (m, 3 H), 7.46-7.44 (m, 2 H); ^{13}C-NMR (CDCl$_3$, 62.9 MHz): δ 195.4, 137.0, 136.3, 131.9, 131.5, 130.5, 129.5, 128.7, 127.4



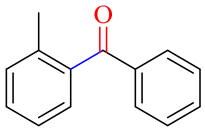
4-Fluorobenzophenone (Table 4, entry 6). ^{1}H-NMR (CDCl$_3$, 250 MHz): δ 7.85-7.77 (m, 4H), 7.58-7.50 (m, 3H), 7.26-7.16 (m, 2H); ^{13}C-NMR (CDCl$_3$, 62.9 MHz): δ 195.4, 166.0 (d, *J* = 252.0 Hz), 137.3, 133.5, 133.0 (d, *J* = 7.2 Hz), 132.7, 129.5, 128.0, 115.7 (d, *J* = 20.6 Hz)



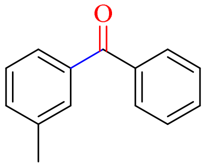
4-Trifluoromethylbenzophenone (Table 4, entry 8). ^{1}H-NMR (CDCl$_3$, 250 MHz): δ 8.10 (d, *J* = 7.8 Hz, 2H), 7.98-7.97 (m, 2H), 7.71-7.69 (m, 2H), 7.32-7.30 (m, 1H), 7.28-7.27 (m, 2H); ^{13}C-NMR (CDCl$_3$, 62.9 MHz): δ 196.0, 140.9, 137.0, 132.9 (q, *J* = 32.3 Hz), 132.3, 130.0, 129.7, 128.3, 125.1 (q, *J* = 3.6 Hz), 123.1 (q, *J* = 272.7 Hz)



1-Naphthylphenone (Table 4, entry 9). ^{1}H-NMR (CDCl$_3$, 250 MHz): δ 8.07 (d, *J* = 8.1 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.87-7.83 (m, 1H), 7.78-7.75 (m, 2H), 7.47-7.38 (m, 2 H), 7.35-7.27 (m, 5 H); ^{13}C-NMR (CDCl$_3$, 62.9 MHz): δ 195.7, 138.2, 136.3, 133.6, 133.2, 131.2, 130.7, 130.0, 128.4, 128.3, 127.8, 127.2, 126.5, 125.6, 124.3

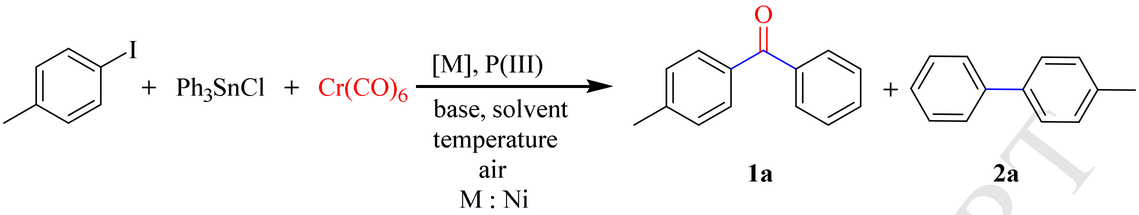


2-Methylbenzophenone (Table 4, entry 10). ^{1}H-NMR (CDCl$_3$, 250 MHz): δ 7.82-7.78 (m, 2H), 7.58-7.55 (m, 1H), 7.48-7.38 (m, 3H), 7.30-7.21 (m, 3H), 2.29 (s, 3H); ^{13}C-NMR (CDCl$_3$, 62.9 MHz): δ 198.6, 138.6, 137.7, 136.7, 133.1, 131.4, 130.9, 130.2, 130.1, 128.5, 125.1, 19.9



3-Methylbenzophenone (Table 4, entry 11). ^{1}H-NMR (CDCl$_3$, 250 MHz): δ 7.82-7.80 (m, 2H), 7.65-7.64 (m, 1H), 7.63-7.58 (m, 2H), 7.50-7.45 (m, 2H), 7.41-7.35 (m, 2H), 2.40 (s, 3H); ^{13}C-NMR (CDCl$_3$, 62.9 MHz): δ 197.1, 138.3, 137.7, 137.5, 133.3, 132.2, 130.7, 130.0, 128.3, 128.0, 127.2, 21.5

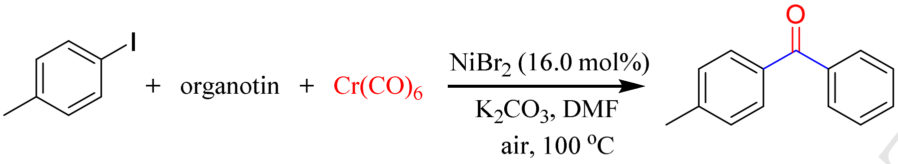
Table 1. Optimization of different parameters for the reaction of 4-iodotoluene with Ph_3SnCl.[a]



Entry	[Ni]	Solvent	Base	Temp (°C)	Time (h)	**1a**(%)	**2a**(%)
1	$NiCl_2$	PEG400	K_2CO_3	100	3.5	45	50
2	$NiCl_2$	PEG400	Et_3N	100	5	40	55
3	$NiCl_2$	PEG400	KOAc	100	4.5	40	55
4	$NiCl_2$	PEG400	K_3PO_4	100	7	33	60
5	$NiCl_2$	DMF	K_2CO_3	100	3	82	10
6	$NiCl_2$	Dioxane	K_2CO_3	100	10	-	40
7	$NiCl_2$	Diglyme	K_2CO_3	100	10	20	30
8	$NiCl_2$	CH_3CN	K_2CO_3	90	10	15	35
9	$NiBr_2$	DMF	K_2CO_3	100	2.7	89	8
10	$NiBr_2$	DMF	Et_3N	100	4	10	40
11	$NiBr_2$	DMF	KOAc	100	5	65	40
12	$NiBr_2$	DMF	DABCO	100	8	25	50
13	$NiBr_2$	DMF	K_2CO_3	70	7	70	20
14	$NiBr_2$[b]	DMF	K_2CO_3	100	8.5	60	15
15	-	DMF	K_2CO_3	100	10	0	0
16	$NiCl_2/Ph_3P$	DMF	K_2CO_3	100	3.2	85	10
17	$NiCl_2(Ph_3P)_2$	DMF	K_2CO_3	100	3.0	88	8

[a] All the reactions were performed under air. Recation condition: iodotoluene (1.0 mmol), $Cr(CO)_6$ (1.0 mmol), Ph_3SnCl (0.4 mmol), [Ni]: (16.0 mol%), base (3.0 mmol), solvent (3 mL). [b] $NiBr_2$ (6.0 mol%).

Table 2. The effect of organotin reagents on the carbonylative Stille reaction of 4-iodotoluene.[a]

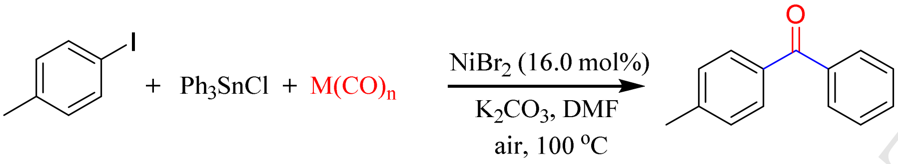


organotin : Ph_3SnCl, Ph_3SnOEt, Ph_3SnOH, Ph_4Sn

Entry	Nucleophile	Time (h)	Yield of **1a**(%)
1	Ph_3SnCl	2.7	89
2	Ph_3SnOH	5	70
3	Ph_3SnOEt	3	85
4	Ph_4Sn	5	10
5	$PhB(OH)_2$	5	60

[a] Recation condition: iodotoluene (1.0 mmol), $Cr(CO)_6$ (1.0 mmol), organotin (0.4 mmol), $NiBr_2$: (16.0 mol%), K_2CO_3 (3.0 mmol), DMF (3 mL) at 100 °C.

Table 3. The effect of metal carbonyl on the carbonylative Stille reaction of 4-iodotoluene.[a]



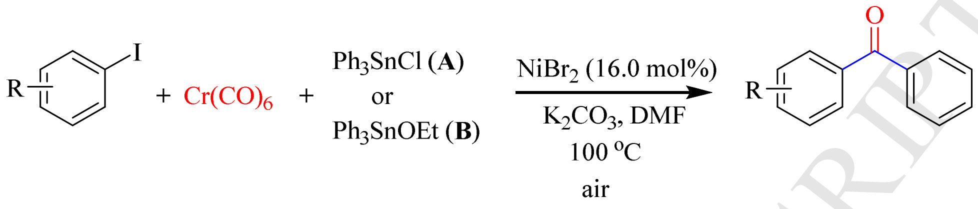
$M(CO)_n$: $Mo(CO)_6$, $Cr(CO)_6$, $W(CO)_6$, $Fe(CO)_5$, $Co_2(CO)_8$

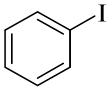
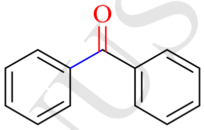
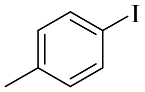
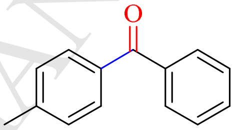
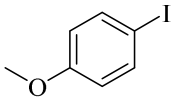
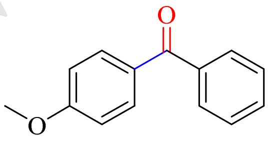
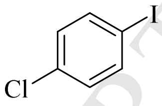
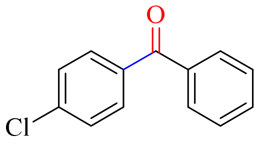
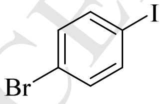
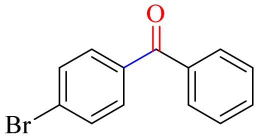
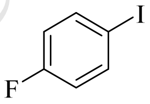
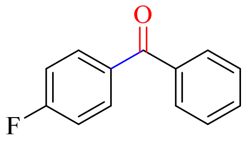
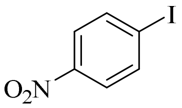
Entry	$M(CO)_n$	Time (h)	Yield of **1a**(%)
1	$Mo(CO)_6$	4	85
2	$Cr(CO)_6$	2.7	89
3	$W(CO)_6$	5	10
4	$Fe(CO)_5$	5	0
5	$Co_2(CO)_8$	6	40

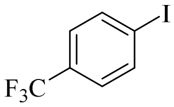
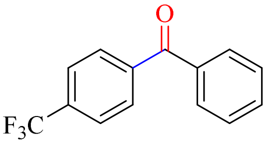
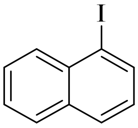
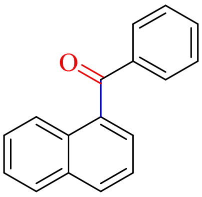
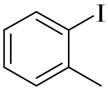
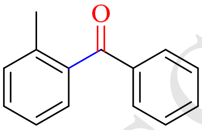
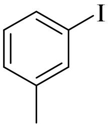
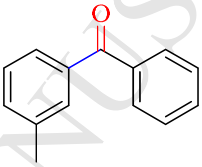
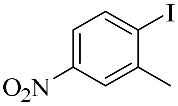
[a] Recation condition: iodotoluene (1.0 mmol), $M(CO)_n$ (1.0 mmol), Ph_3SnCl (0.4 mmol), $NiBr_2$: (16.0 mol%), K_2CO_3 (3.0 mmol), DMF (3 mL) at 100 °C.

Table 4

Ni-catalyzed stille carbonylative cross-coupling of aryl iodides with Ph_3SnCl or Ph_3SnOEt in DMF at 100 ˚C



Entry	Aryl iodide	Time (h)	Product	Yield (%)
1		A : 2.4 B : 2.4		A : 87 B :82
2		A : 2.7 B : 3.0		A : 89 B : 85
3		A : 3.5 B : 3.3		A : 80 B : 83
4		A : 2.8 B : 3		A : 85 B : 85
5		A : 2.5 B : 2.5		A : 85 B : 80
6		A : 2 B : 2		A : 80 B : 78
7		A : 3 B : 3	-	A : - B : -

8		A : 3 B : 2.7		A : 80 B : 83
9		A : 6 B : 6		A : 75 B : 70
10		A : 6.5 B : 6		A : 68 B : 70
11		A : 2 B : 2.3		A : 78 B : 70
12		A : 5 B : 6	-	A : - B :-

[a]Recation condition: aryl iodide (1.0 mmol), $Cr(CO)_6$ (1.0 mmol), Ph_3SnCl (0.4 mmol), $NiBr_2$: (16.0 mol%), K_2CO_3 (3.0 mmol), DMF (3 mL) at 100 °C under air.

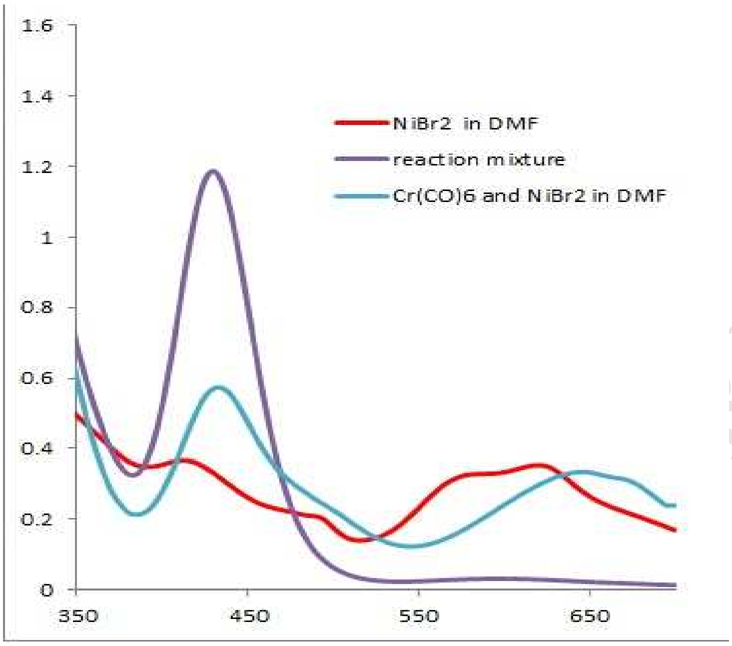
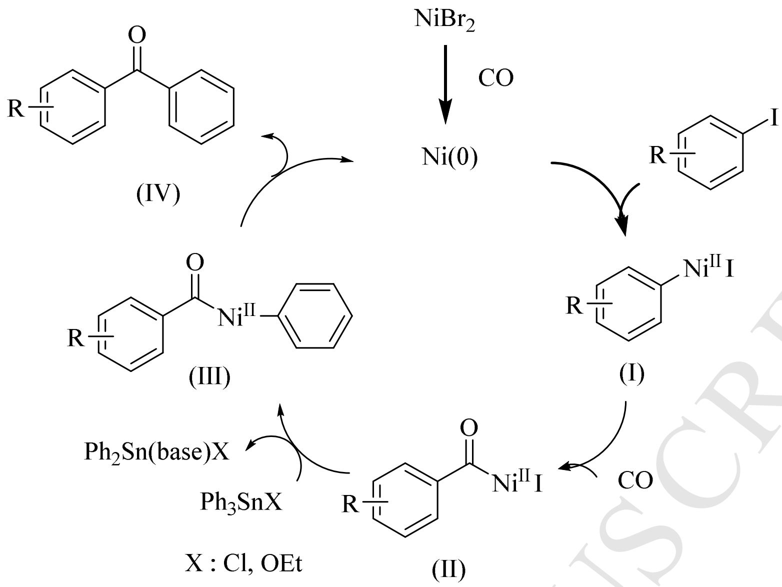


Figure 1. UV-Vis spectrum



Scheme 1. The plausible mechanism for the carbonylative Stille reaction of aryl iodides

Highlights

- Ph_3SnX (X : Cl, OEt) used for the carbonylative Stille reaction
- $NiBr_2$ as the catalyst and phosphine-free condition were applied
- $Cr(CO)_6$ employed as the solid source of CO