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Palladium-Catalyzed Synthesis of Biaryls from Arylzinc Compounds Using *N*-Chlorosuccinimide or Oxygen as an Oxidant

Kabir M. Hossain, Toru Kameyama, Takanori Shibata, and Kentaro Takagi*

Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama 700-8530

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In the presence of a catalytic amount of Pd^{2+} or Pd^0, oxidative homo-coupling of arylzinc compounds was achieved by the use of *N*-chlorosuccinimide (NCS) or O_2 as an oxidant. Different reaction pathways were involved in the catalytic reactions depending on the oxidants; NCS or O_2 probably oxidized I^- or Pd^0 to I^+ or Pd^{2+}, respectively. This reaction disclosed a new and facile synthetic method of biaryls from aryl halides or arenes via arylzinc intermediates.

A wide variety of transition metals (M^{n+}) achieve the oxidative cleavage of organometallic compounds (R–m) to yield homo-coupling products (R–R) efficiently; such cleavage provides a unique synthetic method of symmetrical organic compounds (Eq. 1).[1] In the reaction, transition metals act as an oxidant for R^- fragments and, accordingly, are required to be used in stoichiometric amounts.[2,3] Recently, novel catalytic reactions have been developed for such organometallic compounds as Sn, B, Si, or Bi by the use of auxiliary oxidants (Ox) like $CuCl_2$, organic dihalide, or O_2 (air), which make transition metals retain their reactive oxidation states (M^{n+}) through the reaction (Eq. 2).[4] This methodology has greatly increased the utility of the homo-coupling reaction as a

$$\text{R–m} + \text{M}^{n+} \rightarrow 1/2\ \text{R–R} + \text{m}^+ + \text{M}^{(n-1)+} \tag{1}$$

$$\text{R–m} + \text{Ox} \xrightarrow{\text{catalyst}} 1/2\ \text{R–R} + \text{m}^+ + \text{Ox}^- \tag{2}$$

synthetic procedure of R–R. During the course of our study on the synthesis and synthetic application of functionalized arylzinc compounds,[5] we were interested in the catalytic homo-coupling of the compounds: although a stoichiometric amount of Pd^{2+}, Cu^{2+}, Fe^{3+}, or V^{5+} is known to achieve the homo-coupling of organozinc compounds,[6] the catalytic process has been little explored.[7] Here, we would like to report the Pd-catalyzed method of converting arylzinc compounds into biaryls, using *N*-chlorosuccinimide (NCS) or O_2 as an oxidant.[8]

Results and Discussion

The catalytic homo-coupling of arylzinc compounds was first examined by the use of a reaction system composed of 2-methoxycarbonylphenylzinc iodide **1** and various oxidants in the presence of $[PdCl_2(PPh_3)_2]$ (2 mol%) in TMU (1,1,3,3-tetramethylurea)[9] at 45 °C for 12 h. As shown in Table 1, the desired product, dimethyl biphenyl-2,2′-dicarboxylate **2**, was obtained in a variable yield depending on the oxidant used; the reaction using O_2 or NCS gave **2** in 86% or 87% yield, respectively (Runs 1 and 2). As the catalyst, $[Pd(PPh_3)_4]$ was also effective (Runs 5 and 6). As shown in Table 2, a variety of arylzinc compounds containing such functional groups as alkoxycarbonyl, cyano, chloro, alkoxy, or acetoxy readily underwent the Pd-catalyzed homo-coupling using O_2 or NCS as an oxidant in TMU to afford the corresponding biaryls in good yields. An arylzinc compound in DMF afforded the desired homo-coupling product in a good yield, too (Run 13). Since this type of functionalized arylzinc compounds is readily prepared by the reaction between the corresponding aryl iodides and zinc powder in polar solvents[9,10] the present catalytic reaction provides a far more convenient synthetic method of functionalized biaryls from aryl halides than the reported ones using aryltin, -boron, -silicon, or -bismuth compounds,[4] whose syntheses directly from aryl halides and metallic species are generally impossible.

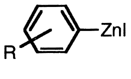
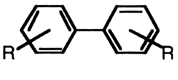
Table 1. Effect of Reaction Conditions on Pd-Catalyzed Homo-Coupling of **1**[a)]

Run	Oxidant	Pd catalyst	**2** (Yield/%)
1	O_2	$[PdCl_2(PPh_3)_2]$	86
2	NCS	$[PdCl_2(PPh_3)_2]$	87
3	$CuCl_2$	$[PdCl_2(PPh_3)_2]$	29
4	$PhCHBrCHBrCO_2Et$	$[PdCl_2(PPh_3)_2]$	27
5	O_2	$[Pd(PPh_3)_4]$	79
6	NCS	$[Pd(PPh_3)_4]$	85
7[b)]	NCS	$[Pd(PPh_3)_4]$	37
8	NCS	$Pd(OAc)_2$	< 5
9	NCS	$[PdCl_2(C_6H_5CN)_2]$	< 5
10	—	$[PdCl_2(PPh_3)_2]$	< 5

a) Molar ratio: **1**/Pd/Oxidant = 1/0.02/0.5 or 1 atm (O_2) (Runs 1, 2, 4–10), or 1/0.02/1 (Run 3). Reaction solvent: TMU. Reaction time: 12 h. Reaction temp: 45 °C.
b) Reaction time: 1 h.

Organozinc compounds, prepared from organolithium compounds and ZnI_2 in THF, were also available for the reaction. As shown in Table 3, desired products were readily produced from arene (Run 1), thiophene (Runs 2 and 3), aryl bromides (Runs 4–6), or alkyne (Runs 7 and 8) via their sequential treatment with *n*-BuLi,[11] ZnI_2, NCS or O_2, and Pd^{2+} or Pd^0. It should be noted that the reaction using phenylzinc chloride, prepared from phenyllithium and $ZnCl_2$, in place of arylzinc

Table 2. Synthesis of Functionalized Biaryls from Arylzinc Iodides[a]

Run	 R	Oxidant	Pd catalyst	 (Yield/%)[b]
1	3-CO_2CH_3	NCS	[$PdCl_2(PPh_3)_2$]	(94)
2	3-CO_2CH_3	NCS	[$Pd(PPh_3)_4$]	86 (93)
3	4-$CO_2C_2H_5$	NCS	[$Pd(PPh_3)_4$]	80
4	4-$CO_2C_2H_5$	O_2	[$PdCl_2(PPh_3)_2$]	(85)
5	4-$CO_2C_2H_5$	O_2	[$Pd(PPh_3)_4$]	(92)
6	2-Cl	NCS	[$Pd(PPh_3)_4$]	86
7	2-CN	NCS	[$Pd(PPh_3)_4$]	85
8	2-OAc, 5-CH_3	NCS	[$Pd(PPh_3)_4$]	62
9	4-OCH_3	NCS	[$Pd(PPh_3)_4$]	(81)
10	4-OCH_3	O_2	[$PdCl_2(PPh_3)_2$]	(94)
11	4-OCH_3	O_2	[$Pd(PPh_3)_4$]	(90)
12	H	NCS	[$Pd(PPh_3)_4$]	(93)
13[c]	H	NCS	[$Pd(PPh_3)_4$]	(95)
14	2-CO_2CH_3	Air	[$Pd(PPh_3)_4$]	(74)

a) Molar ratio: ArZnI/Pd/Oxidant = 1/0.02/0.5 or 1 atm (O_2). Reaction solvent: TMU. Reaction time: 2–16 h. Reaction temp: 35–45 °C.

b) Isolated yields. GLC yields are in parentheses.

c) Reaction solvent: DMF.

Table 3. Synthesis of Homo-Coupling Products from Organozinc Iodides via Corresponding Organolithium Intermediates[a]

Run	Starting Material	Organolithium	Pd catalyst	Oxidant	Product (Yield/%)[b]
1	$C_6H_5OCH_3$	2-$CH_3OC_6H_4Li$	[$Pd(PPh_3)_4$]	NCS	(84)
2	C_4H_4S[c]	2-C_4H_3SLi	[$Pd(PPh_3)_4$]	NCS	90
3	C_4H_4S[c]	2-C_4H_3SLi	[$Pd(PPh_3)_4$]	O_2	80
4	4-ClC_6H_4Br	4-ClC_6H_4Li	[$Pd(PPh_3)_4$]	NCS	85
5	4-ClC_6H_4Br	4-ClC_6H_4Li	[$PdCl_2(PPh_3)_2$]	NCS	87
6	3-$CH_3OC_6H_4Br$	3-$CH_3OC_6H_4Li$	[$PdCl_2(PPh_3)_2$]	NCS	83
7	C_6H_5CCH	C_6H_5CCLi	[$PdCl_2(PPh_3)_4$]	NCS	81
8	C_6H_5CCH	C_6H_5CCLi	[$PdCl_2(PPh_3)_2$]	O_2	95

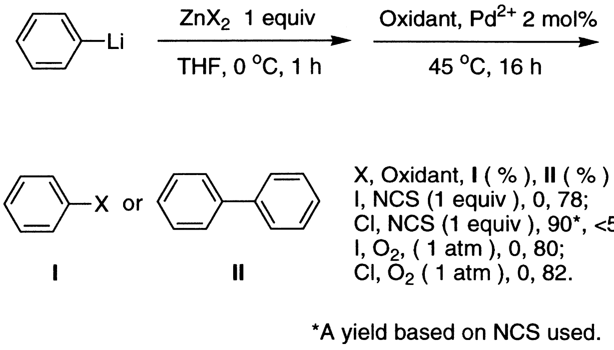
a) Lithiation was carried out at 0 °C (Runs 2 and 3) or −78 °C (Runs 1 and 4–8) to room temp using 1 equiv of *n*-BuLi in THF under N_2. The resulting organolithium intermediate was allowed to react with THF solution of ZnI_2 (1 equiv) and then with THF suspension of NCS (0.45 equiv) or O_2 (1 atm) and Pd catalyst (0.02 equiv), followed by the stirring of the resulting solution at room temp (Runs 2–6), 40 °C (Run 8), or 45 °C (Runs 1 and 7) for 10–15 h.

b) Isolated yields. GLC yield is in parenthesis.

c) C_4H_4S = thiophene.

iodides did not afford the homo-coupling product at all, when NCS was used as an oxidant. Instead, chlorobenzene was produced predominantly (Scheme 1). When O_2 was used as an oxidant, however, the desired product was obtained in a good yield from the same zinc compound (Scheme 1).

In order to elucidate the unexpected difference in reactivity between two oxidants towards phenylzinc chloride, and to see the reaction path involved in the Pd-catalyzed homo-coupling of arylzinc compounds, the progress of catalytic reaction was followed by the measurement of the amount of each component present in the solution, using the reaction systems composed of **1**, NCS or O_2, and [$Pd(PPh_3)_4$] as arylzinc compound, oxidant, and catalyst, respectively, in TMU. As shown in Fig.



Scheme 1. Effect of ZnX_2 and oxidant in the reaction.

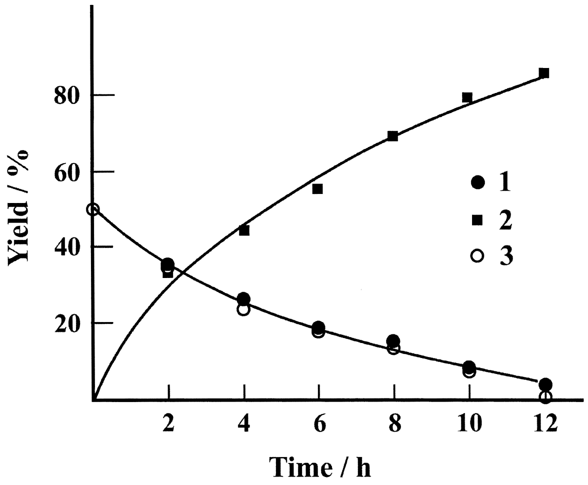


Fig. 1. The progress with time of reaction of **1** using NCS as an oxidant. The mixture composed of **1** (0.25 mmol), [Pd(PPh_3)$_4$] (0.005 mmol), NCS (0.13 mmol), and TMU was stirred at room temperature for 5 min and then at 45 °C for given periods of time.

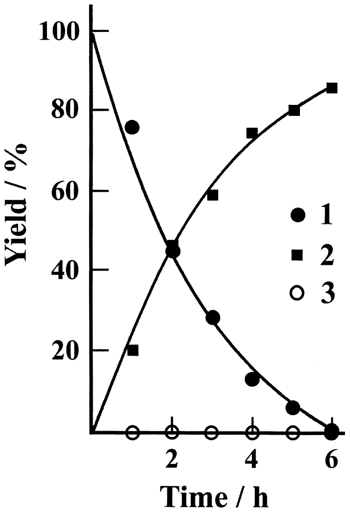
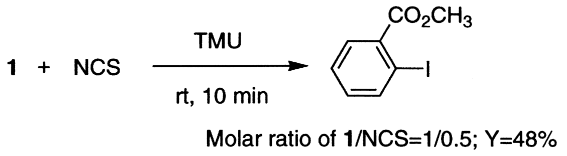
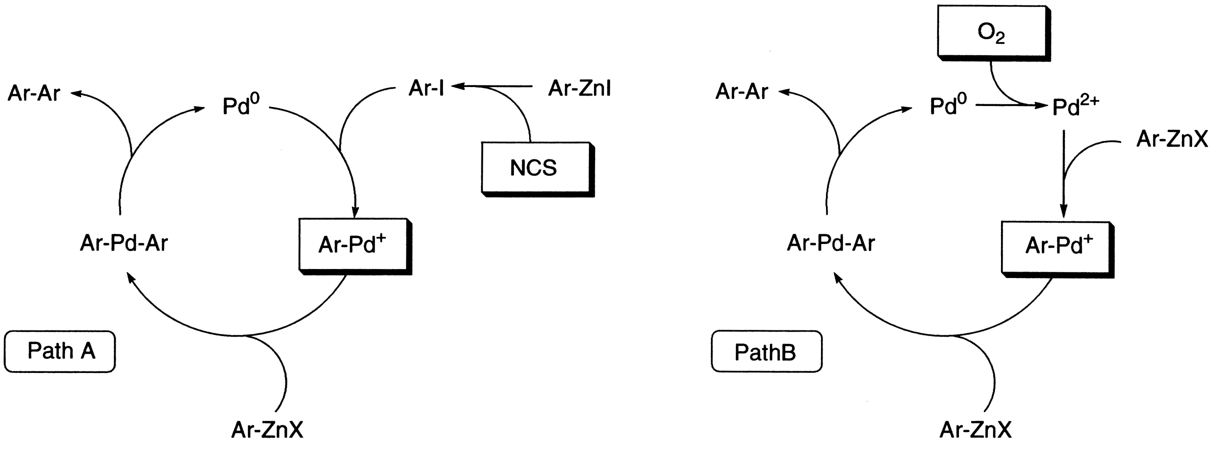


Fig. 2. The progress with time of reaction of **1** using O_2 as an oxidant. The mixture composed of **1** (0.25 mmol), [Pd(PPh_3)$_4$] (0.005 mmol), O_2 (1 atm), and TMU was stirred at 35 °C for given periods of time.



Scheme 2. Reaction of **1** with NCS.

1, in NCS reaction, methyl 2-iodobenzoate **3** was formed rapidly in a quantitative yield based on NCS, and **2** was formed gradually in compensation for the simultaneous decreases in **1** and **3** in equal amounts. The control run ascertained that the reaction between **1** and NCS takes place readily in TMU at room temperature to yield **3** in a quantitative yield (Scheme 2).[12] In O_2 reaction, however, **2** was formed gradually with the synchronous decrease in **1**, and the presence of **3** was not detected through the whole course of reaction, as shown in Fig. 2. These results clearly suggest that each of the two oxidants takes its own reaction pathway yielding the same product from the same starting material. As to the former oxidant, path A (Scheme 3, Negishi reaction[13]) might be plausible, wherein the key intermediate abbreviated as $ArPd^+$ is formed by the oxidative addition of Pd^0 to aryl iodides, generated in situ by the reaction between NCS and ArZnI, followed by the transmetallation with ArZnI to yield ArPdAr, which yields a homo-coupling product Ar–Ar to regenerate Pd^0 catalyst. In general, aryl chlorides are inert to Pd^0 under cited conditions.[14] As to the latter oxidant, path B (Scheme 3) might be plausible, which is essentially the same as that which had been proposed in Pd-



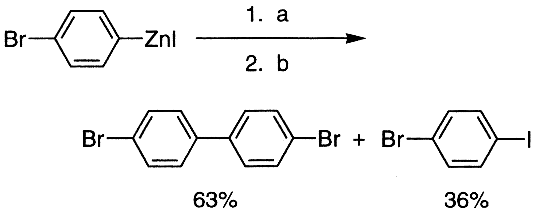
In this path, oxidant converts I^- to I^+ and products are formed through Negishi reaction.

In this path, oxidant converts Pd^0 to Pd^{2+} and products are formed through double trasmetallation.

Scheme 3. Reaction path.

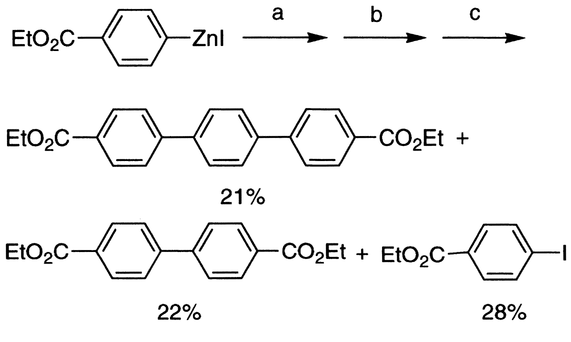
catalyzed homo-coupling of organometallic compounds (B, Sn, Si, or Bi) by the use of auxiliary oxidants including O_2.[4] That is, key intermediate $ArPd^+$ is formed by the transmetallation between ArZnX and Pd^{2+}, and the oxidant O_2 plays the role to convert Pd^0 into Pd^{2+}.[15] Here, because of the presence of Zn^{2+} between Ar^- and X^- fragments in ArZnX, the difference in reactivity of aryl fragment towards Pd^{2+} species between ArZnCl and ArZnI must be small, which probably explains the comparable reactivity of phenylzinc chloride to the corresponding iodide in O_2 reaction.

As mentioned above, both NCS and O_2 are equally available for the Pd-catalyzed homo-coupling of arylzinc compounds, albeit operating in different ways (Scheme 3). From the practical viewpoint, each possesses an advantage over the other. In the utility of O_2, one need not take care of the molar ratio of ArZnX/oxidant, since the oxidant reacts not with ArZnX but with Pd. Accordingly, the catalytic reaction may be carried out by the attachment of balloon filled with O_2 or air (Run 14, Table 2) to the reaction flask, which makes the reaction procedure simple. On the other hand, NCS has to be added, but is able to be added to the reaction solution in an accurate amount. Therefore, when one intends to stop the reaction at certain points of conversion including 100%, NCS is the oxidant of choice. Indeed, by the use of a given amount of NCS, the homo-coupling reaction not only was suspended at the expected conversion (Scheme 4 and see Experimental) but also was succeeded by the second reaction, e.g., cross-coupling, in one pot (Scheme 5 and see Experimental).



a: NCS (0.33 equiv), $Pd(PPh_3)_4$ (2 mol%), rt, 4 h
b: I_2

Scheme 4. Homo-coupling using a limited amount of NCS.



a: NCS (0.125 equiv), $Pd(PPh_3)_4$ (1 mol%), 45 °C, 5 h
b: *p*-diiodobenzene (0.125 equiv), 45 °C, 10 h
c: I_2

Scheme 5. Consecutive homo- and cross-coupling in one pot.

In conclusion, two oxidants, NCS and oxygen, are disclosed to be efficient for the homo-coupling of arylzinc compounds in the presence of a catalytic amount of Pd; such a result discloses a new synthetic method of biaryls from aryl halides or arenes via arylzinc intermediates.

Experimental

General. Melting points were determined on a Yanaco MP-3 micro melting point apparatus and are uncorrected. GLC analyses were carried out with a Hitachi G-3000 with flame ionization detectors equipped with an OV-17 column using nitrogen as carrier gas. The GLC yields were determined using appropriate aromatics as internal standards. The isolation of pure products was carried out with column chromatography on SiO_2. IR data were obtained with a Hitachi 260-10 spectrophotometer. ^1H and ^{13}C NMR were recorded with a Jeol FX90A spectrometer and a Varian VXR200 spectrometer using $CDCl_3$ as a solvent with tetramethylsilane used as an internal standard. Elemental analyses were performed on a Perkin-Elmer 2400 Series II.

Materials. TMU was distilled under N_2 and stored over Molecular Sieve 2A. Arylzinc compounds were prepared by the reaction of aryl iodides with zinc powder in TMU or DMF, following the reported procedure[9] or the reaction of aryllithium compounds[11] with ZnI_2 or $ZnCl_2$ in THF. The aliquot of the solutions were used in the homo-coupling reaction, after the concentration of arylzinc compounds was determined by quenching the aliquot of the solution with iodine, followed by the GLC analysis of the amount of aryl iodides formed. The other chemicals were commercial products and were used without purification.

Reaction of 3-Methoxycarbonylphenylzinc Iodide. A typical procedure using arylzinc compounds prepared from aryl iodides and zinc powder: To the mixture of $[Pd(PPh_3)_4]$ (0.005 mmol) and NCS (0.13 mmol), 0.89 mL of TMU-solution of 3-methoxycarbonylphenylzinc iodide (0.25 mmol) was added under nitrogen. The resulting solution was stirred at room temperature for 30 min. and then at 45 °C for 16 h. After the usual post-treatment of the resulting solution with ether/aq HCl, purification by chromatography on silica-gel column using hexane–ethyl acetate (9 : 1) as an eluent, followed by the recrystalization from EtOH, afforded 29 mg of dimethyl biphenyl-3,3′-dicarboxylate(86%): mp 104 °C (Ref. 16, mp 103–104 °C); IR ($CDCl_3$) 1732 cm^{-1}; ^1H NMR δ 3.96 (s, 6H), 7.54 (t, J = 7.8 Hz, 2H), 7.82 (dt, J = 7.8 , 1.6 Hz, 2H), 8.06 (dt, J = 7.8, 1.6 Hz, 2H), 8.31 (t, J = 1.6 Hz, 2H).

5,5′-Dimethylbiphenyl-2,2′-diyl Diacetate: mp 90.5–91 °C; IR ($CDCl_3$) 1760, 1370, 1221, 1204 cm^{-1}; ^1H NMR δ 2.0 (s, 6H), 2.4 (s, 6H), 6.9–7.2 (m, 6H); ^{13}C NMR δ 20.7, 20.8, 130.9, 137.8, 137.9, 143.6, 144.0, 156.0, 169.4. Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.5; H, 6.0%. Found: C, 72.35; H, 6.20%.

Reaction of 2-Thienylzinc Iodide. A typical procedure using arylzinc compounds prepared from aryllithium compounds and zinc salts: ZnI_2 (1.0 mmol) was dried by air-gun heating for 5 min under vacuum, then was dissolved in THF (1 mL). The solution was added by cannula into a solution of 2-thienyllithium, which was prepared by mixing a THF solution (1 mL) of thiophene (1.0 mmol) and 0.65 mL of 1.54 M hexane solution of butyllithium (1.0 mmol) at 0 °C for 3 h. The resulting solution was warmed gradually to room temperature, followed by the addition to the THF suspension (0.5 mL) of NCS (0.45 mmol) and $[PdCl_2(PPh_3)_2]$ (0.019 mmol) by the use of cannula. Then, the reaction solution was stirred at the temperature for 15 h. After the usual post-treatment of the resulting solution with ether/aq HCl, purification by chromatography on silica-gel column using hexane as an eluent afforded 67 mg of 2,2′-bithiophene (90%). mp 30 °C (Ref. 17, mp 30 °C); IR ($CDCl_3$) 830 cm^{-1}; ^1H NMR δ 6.94 (dd, $J = 5.0$, 3.6 Hz, 2H), 7.1–7.2 (m, 4H).

The Progress with Time of Reaction of 2-Methoxycarbonylphenylzinc Iodide (1). To the mixture of $[Pd(PPh_3)_4]$ (0.005 mmol) and NCS (0.13 mmol), 0.89 mL of TMU-solution of **1** (0.25 mmol) was added under nitrogen. The resulting solution was stirred at room temperature for 5 min and then at 45 °C for 0, 2, 4, 6, 8, 10, or 12 h. After 0.024 mL of octylbenzene was added to the solution, the aliquot was withdrawn and treated with aq HCl to measure the amounts of **2** and **3** or with I_2 to measure the amount of **1** in the solution by GLC analysis.

Homo-Coupling Using Limited Amount of NCS. To the mixture of $[Pd(PPh_3)_4]$ (0.006 mmol) and NCS (0.10 mmol), 0.31 mL of TMU-solution of 4-bromophenylzinc iodide (0.30 mmol) was added under nitrogen and the solution was stirred at room temperature for 4 h. The GLC analysis showed that 0.10 mmol of 4,4′-dibromobiphenyl (63% based on arylzinc compound; 95% based on NCS) and 0.11 mmol of remaining arylzinc compound (36%) was present in the resulting solution.

Consecutive Reactions Using Limited Amount of NCS. To the mixture of $[Pd(PPh_3)_4]$ (0.016 mmol) and NCS (0.10 mmol), 0.51 mL of TMU-solution of 4-ethoxycarbonylphenylzinc iodide (0.80 mmol) was added under nitrogen and the solution was stirred at 45 °C for 5 h. GLC analysis using the aliquot of the solution showed that 0.09 mmol of diethyl biphenyl-4,4′-dicarboxylate (22% based on arylzinc compound; 90% based on NCS) was present in the resulting solution, to which 0.20 mL of TMU solution of 1,4-diiodobenzene (0.10 mmol) was added; this was stirred at 45 °C for 10 h. GLC analysis showed that 0.09 mmol of diethyl 1,1′:4′,1″-terphenyl-4,4″-dicarboxylate (21% based on arylzinc compound) and 0.22 mmol of remaining arylzinc compound (28%) were present in the resulting solution along with diethyl biphenyl-4,4′-dicarboxylate.

Diethyl Biphenyl-4,4′-dicarboxylate: mp 114 °C (Ref. 18, 144°C); IR ($CDCl_3$) 1720 cm^{-1}; ^1H NMR δ 1.42 (t, $J = 7.2$ Hz, 6H), 4.41 (q, $J = 7.2$ Hz, 4H), 7.69 (d, $J = 8.4$ Hz, 4H), 8.14 (d, $J = 8.4$ Hz, 4H).

Diethyl 1,1′:4′,1″-Terphenyl-4,4″-dicarboxylate: mp 260 °C (Ref. 19, mp 259.8 °C); IR ($CDCl_3$) 1709 cm^{-1}; ^1H NMR δ 1.42 (t, $J = 7.1$ Hz, 6H), 4.42 (q, $J = 7.1$ Hz, 4H), 7.71 (d, $J = 8.2$ Hz, 8H), 7.74 (s, 4H), 8.14 (d, $J = 8.2$ Hz, 8H).

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