DOI: 10.1002/ejoc.200901279

Hydrosilanes Are Not Always Reducing Agents for Carbonyl Compounds, II: Ruthenium-Catalyzed Deprotection of *tert*-Butyl Groups in Carbamates, Carbonates, Esters, and Ethers

Shiori Hanada,[a] Akihiro Yuasa,[b] Hirotaka Kuroiwa,[a] Yukihiro Motoyama,[b] and Hideo Nagashima*[b]

Keywords: Protecting groups / Hydrosilanes / Ruthenium / Cleavage reactions / Si–H activation

Hydrosilanes act as a reagent to cleave the C–O bond of O*t*Bu groups in carbamates, carbonates, esters, and ethers by catalysis of a triruthenium cluster. The reaction offers a novel deprotection method for O*t*Bu groups under neutral conditions, showing unique selectivities that have never been accomplished with conventional Brønsted or Lewis acidic promoters. Possible mechanisms for C–O cleavage are discussed on the basis of NMR spectroscopic analysis.

Introduction

Hydrosilanes are one of the most useful reducing reagents for carbonyl compounds with the aid of acids or transition metals.[1] In particular, reductions of ketones and aldehydes with hydrosilanes have actively been investigated in the last four decades by catalysis of a variety of transition-metal salts and complexes. There has been a smaller number of papers reporting successful reduction of carboxylic acid derivatives with hydrosilanes; however, recent studies using Ti, Rh, and Mo have provided effective procedures for the reduction of esters to alcohols and amides to amines.[2] A triruthenium cluster, ($\mu_3,\eta^2,\eta^3,\eta^5$-acenaphthylene)$Ru_3(CO)_7$ (**1**; Figure 1), is an interesting catalyst that realizes the reduction of ketones, aldehydes, carboxylic acids, esters, and amides with trialkylsilanes under mild conditions.[3] The high catalytic activity of **1** towards activation of the Si–H bond of trialkylsilanes is typically seen in the reduction of tertiary and secondary amides, leading to exothermic reactions giving the corresponding tertiary and secondary amines as a single product in high yields.[3c–3f]

An interesting observation found in the studies of the reduction of amides catalyzed by **1** is that hydrosilanes do not always act as reducing reagents. As reported previously, hydrosilanes induce dehydration of primary amides to nitriles with the aid of **1**.[4,5] The reaction takes place stepwise: the first step is dehydrogenative silylation towards the NH_2 moiety of primary amides to form *N*,*O*-disilyl imidates, whereas the second is elimination of siloxane from the formed *N*,*O*-disilyl imidates. In both steps, **1** behaves as a catalyst to facilitate the reaction. This observation offers a possibility of the reactions of hydrosilanes with organic compounds, which may provide new synthetic protocols other than hydrosilane reduction, dehydrogenative silylation, and elimination of siloxane with the aid of **1**. In this paper, we wish to report a new aspect of this issue, in which hydrosilanes activated by **1** effectively cleave the C–O bond of O*t*Bu groups in carbamates, carbonates, esters, and ethers, leading to a unique deprotection method of these functional groups.

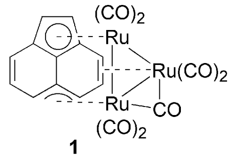

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Figure 1. ($\mu_3,\eta^2,\eta^3,\eta^5$-acenaphthylene)$Ru_3(CO)_7$ (**1**).

Results and Discussion

Table 1 summarizes the results when $PhCH_2CH_2NHCO_2R$ **2a**–**f** was treated with several hydrosilanes (2.2 equiv. to urethane **2**) in the presence of **1** (1 mol-%) in dimethoxyethane (DME) at 40 °C for 7 h followed by workup with methanol. First, the results were highly dependent on the R group; no reaction took place in the cases where R = Me, Et, Bn, and *i*Pr (Table 1, Entries 1–4), whereas the C–O bond in **2e** [R = $–CH_2CH=CMe_2$ (prenyl)] and **2f** (R = *t*Bu) was smoothly cleaved to form a primary amine, $PhCH_2CH_2NH_2$ (**3**), in 65 and 99% yield, respectively (Table 1, Entries 5 and 6). As shown in Entries 6–11 (Table 1), hydrosiloxanes and trialkylsilanes were effective

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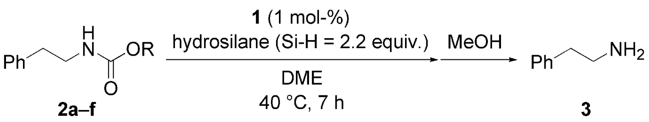
[a] Graduate School of Engineering Sciences, Kyushu University
[b] Institute for Materials Chemistry and Engineering, Kyushu University,
Kasuga, Fukuoka 816-8580, Japan
Fax: +81-92-583-7819
E-mail: nagasima@cm.kyushu-u.ac.jp

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.200901279.

for the deprotection of a Boc group of **2f**; $PhMe_2SiH$ and $HMe_2Si(CH_2)_2SiMe_2H$[6] gave the best results among them (Table 1, Entries 6 and 7).

Table 1. Deprotection of $PhCH_2CH_2NHCO_2R$ by $HSiR_3$ in the presence of a catalytic amount of **1**.[a]

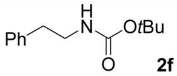
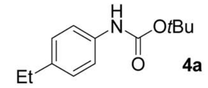
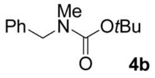
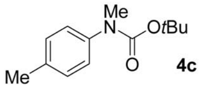
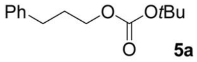
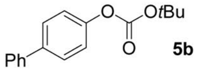
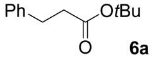
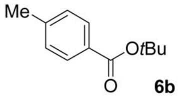
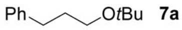
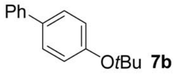


Entry	Substrate	Hydrosilane	Yield [%][b]
1	**2a**: R = Me	$PhMe_2SiH$	0
2	**2b**: R = Et	$PhMe_2SiH$	0
3	**2c**: R = Bn	$PhMe_2SiH$	0
4	**2d**: R = *i*Pr	$PhMe_2SiH$	0
5	**2e**: R = prenyl	$PhMe_2SiH$	65
6	**2f**: R = *t*Bu	$PhMe_2SiH$	99
7	**2f**	$Me_2SiHCH_2CH_2SiHMe_2$	99
8	**2f**	$EtMe_2SiH$	52
9	**2f**	$Me_3SiOSiHMe_2$	53
10	**2f**	$Me_2HSiOSiHMe_2$	52
11	**2f**	$(EtO)Me_2SiH$	52

[a] Reaction conditions: substrate **2** (0.5 mmol), ruthenium complex **1** (1 mol-% to **2**), DME (0.25 mL), hydrosilane (Si–H = 1.1 mmol), 40 °C, 7 h, under a nitrogen atmosphere. [b] Determined by ^1H NMR spectroscopic analysis with 4,4′-bipyridyl (0.125 mmol) as an internal standard.

The combination of $PhMe_2SiH$ and a catalytic amount of **1** also induced deprotection of other *N*-Boc derivatives **4** as well as several *O*-Boc derivatives **5**, *tert*-butyl esters **6**, and *tert*-butyl ethers **7** as shown in Table 2. Although deprotection of NHBoc derivatives **2f** and **4a** required 2.2 equiv. of $PhMe_2SiH$ to the substrate, that of NMeBoc compounds **4b** and **4c** needed only half that amount (Table 2, Entries 1–4). These results suggest that dehydrogenative silylation towards the N–H moiety was precedent in the former cases, leading to evolution of H_2. Conversion of carbonates **5a** and **5b** to the corresponding alcohols **10a** and **10b** and that of *tert*-butyl esters **6a** and **6b** to carboxylic acids **11a** and **11b** was accomplished with 1.2 equiv. of $PhMe_2SiH$ under similar conditions to those used for deprotection of *N*-Boc derivatives (Table 2, Entries 5–8). Deprotection of *tert*-butyl ethers **7a** and **7b** required a higher catalyst loadings (3 mol-% to **7**) and prolonged reaction time (20 h) to afford the corresponding alcohol **10a** and phenol **10b** in satisfactory yields (Table 2, Entries 9 and 10).

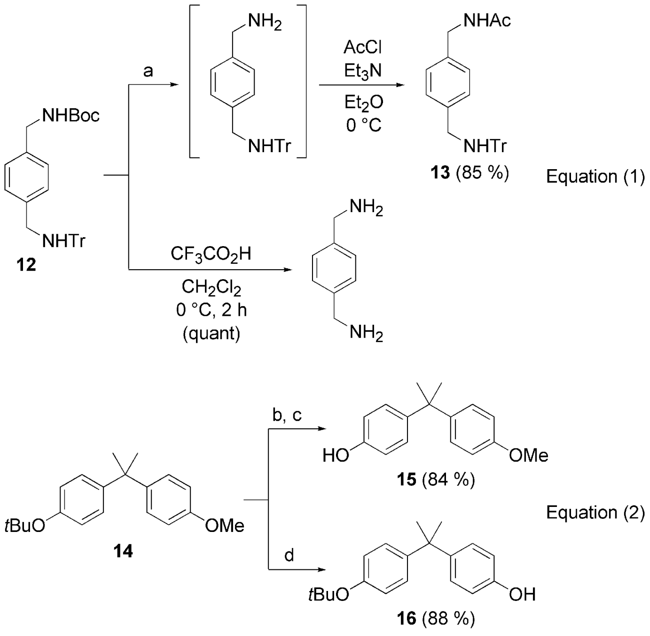
Table 2. Deprotection of *N*-Boc and *O*-Boc derivatives, *tert*-butyl esters, and *tert*-butyl ethers.[a]

Entry	Substrate	Conditions	Product	Yield [%]
1	 **2f**	**1** (1 mol-%) Si–H = 2.2 equiv. 40 °C, 7 h	**8**[b]	80
2	 **4a**	**1** (1 mol-%) Si–H = 2.2 equiv. 40 °C, 7 h	**9a**[b]	75
3	 **4b**	**1** (1 mol-%) Si–H = 1.2 equiv. 70 °C, 24 h	**9b**[b]	64
4	 **4c**	**1** (1 mol-%) Si–H = 1.2 equiv. 40 °C, 7 h	**9c**[b]	83
5	 **5a**	**1** (1 mol-%) Si–H = 1.2 equiv. 40 °C, 7 h	**10a**[c]	76
6	 **5b**	**1** (1 mol-%) Si–H = 1.2 equiv. 40 °C, 7 h	**10b**[c]	93
7	 **6a**	**1** (1 mol-%) Si–H = 1.2 equiv. 40 °C, 7 h	**11a**	95
8	 **6b**	**1** (1 mol-%) Si–H = 1.2 equiv. 40 °C, 7 h	**11b**	93
9	 **7a**	**1** (3 mol-%) Si–H = 1.2 equiv. 40 °C, 20 h	**10a**[c]	70
10	 **7b**	**1** (3 mol-%) Si–H = 1.2 equiv. 40 °C, 20 h	**10b**	95

[a] Reaction conditions: substrate (0.5 mmol), ruthenium complex **1** (0.005–0.015 mmol), DME (0.25 mL), hydrosilanes (Si–H = 0.6 or 1.1 mmol), under a nitrogen atmosphere. [b] The product was isolated as the corresponding acetamide. [c] The product was isolated as the corresponding alcohol after treatment of the crude material with TBAF.

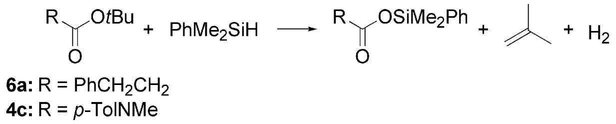
It is well known that deprotection of the *tert*-butyl group in *N*-Boc and *O*-Boc derivatives, *tert*-butyl esters, and *tert*-butyl ethers is generally accomplished by treatment with acids.[7] Strong Brønsted acids such as trifluoroacetic acid, hydrochloric acid, and sulfuric acids cleave the C–O bond of the O*t*Bu moiety at room temperature. Lewis acids such as $TiCl_4$, $SnCl_4$, BX_3, and AlX_3 (X = Cl, Br) are also effective. These have a drawback in that the reaction media is strongly acidic, and elaboration has been performed to develop the deprotection methods proceeding under neutral conditions. For instance, deprotection of Boc groups and *t*Bu ethers are reportedly accomplished with $Ce(NH_4)_2(NO_3)_6$ (CAN),[8a] Zn and In powders,[8b] and iodotrimethylsilane (TMSI).[9] The reactions with CAN or metal powders (Zn or In) are likely to proceed under neutral conditions; however, the reactions of *N*-Boc and *O*-Boc do not occur at low temperature even in the presence of a large amount of metal species (0.2 equiv. for CAN and 2 equiv. for both Zn and In). TMSI is Lewis acidic and facilely generates HI in contact with moisture. Furthermore, a stoichiometric quantity is required for the deprotection of Boc derivatives and *t*Bu ethers.

It is of interest that the combination of $PhMe_2SiH$ and a catalytic amount of **1** cleaves the C–O bond in all of the *N*-Bocs, *O*-Bocs, *tert*-butyl esters, and *tert*-butyl ethers under neutral conditions. One interesting aspect of this hydrosilane-promoted reaction is the selective deprotection of molecules having dual *t*Bu groups. A selective cleavage of an *N*-Boc group of *N*-Boc-*N*′-trityl-*p*-xylilenediamine (**12**) was realized with an *N*-trityl moiety remaining intact to afford *N*-trityl-1,4-xylilenediamine, which was isolated as acetamide **13** in 85% yield [Scheme 1, Equation (1)]. Because the *N*-trityl group is sensitive to acids, both the *N*-trityl and *N*-Boc groups are usually deprotected under usual acidic conditions.[7] Selective deprotection of the *t*Bu group of bisphenol A *tert*-butyl methyl ether (**14**) is also an example showing the uniqueness of this process: The conversion of aryl ethers into the corresponding phenols is generally performed by treatment with BBr_3 or TMSI, and the reactivity of the O–R groups is decreased in the order MeOAr > *i*PrOAr > *t*BuOAr.[7] In fact, we have found that treatment of **14** with TMSI (1.5 equiv. to **14**) in dichloromethane at –78 to 0 °C gave a demethylated product, bisphenol A mono-*tert*-butyl ether (**16**), selectively in 88% yield. In sharp contrast, selective deprotection of the O*t*Bu group occurred in the reaction of **14** with $PhMe_2SiH$ (1.2 equiv. to **14**) in the presence of **1** (3 mol-%) at 40 °C for 7 h to afford bisphenol A monomethyl ether (**15**) in 84% yield [Scheme 1, Equation (2)] as a single product.



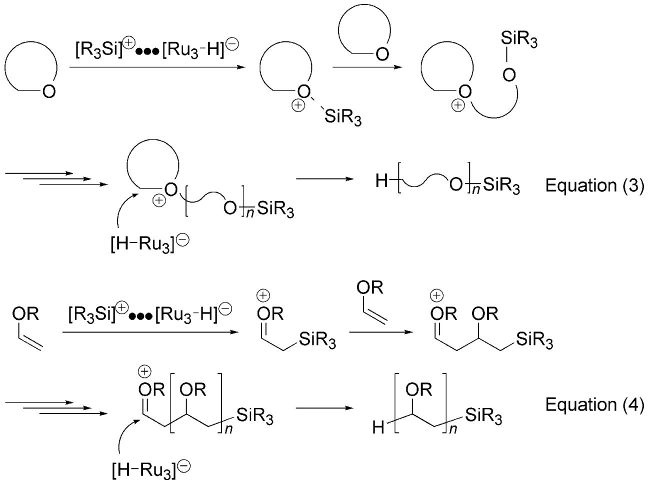
Scheme 1. Selective deprotection of *N*-Boc-*N′*-trityl-*p*-xylilenediamine [**12**; Equation (1)] and bisphenol A *tert*-butyl methyl ether [**14**; Equation (2)]. Conditions: (a) **1** (1 mol-%), $PhMe_2SiH$ (3.2 equiv.), DME, 40 °C, 7 h; (b) **1** (3 mol-%), $PhMe_2SiH$ (3.2 equiv.), DME, 40 °C, 7 h; (c) TBAF (1.2 equiv.), Et_2O, r.t., 1 h; (d) TMSI (1.2 equiv.), CH_2Cl_2, –78 to 0 °C, 1 h.

Why did deprotection that usually occurred under acidic conditions take place with the combination of hydrosilane and the ruthenium catalyst under neutral conditions? NMR analyses of the crude products showed that the *tert*-butyl group in *N*-Bocs, *O*-Bocs, *tert*-butyl esters, and *tert*-butyl ethers was replaced by the organosilyl moiety derived from the hydrosilane used. In typical examples, treatment of $PhCH_2CH_2CO_2tBu$ (**6a**) with $PhMe_2SiH$ in the presence of a catalytic amount of **1** gave the corresponding phenyldimethylsilyl ester, $PhCH_2CH_2CO_2SiMe_2Ph$, quantitatively, the structure of which was unequivocally determined by comparison of the ^1H NMR spectroscopic data with those of $PhCH_2CH_2CO_2SiMe_2Ph$ prepared from $PhCH_2CH_2CO_2H$ (**11a**) and $PhMe_2SiCl$. The fate of the *tert*-butyl group in this reaction was proved to be the formation of isobutene; the ^1H NMR spectrum of the reaction mixture in $[D_6]$benzene showed two signals at $\delta = 1.73$ (br. s, 6 H, CH_3) and 4.83 (br. s, 2 H, *vinylic proton*) ppm. A similar result for the formation of silyl carbamate and isobutene was obtained by the reaction of *p*TolN(Me)CO_2tBu (**4c**) with $PhMe_2SiH$ (see Supporting Information). Thus, the following equation explains the present transformation (Scheme 2).



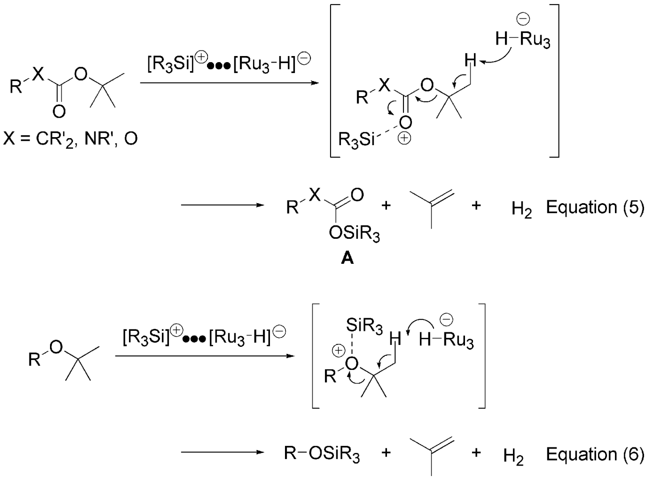
Scheme 2. The reactions of **6a** and **4c** with $PhMe_2SiH$ in the presence of **1**.

A clue to understanding the mechanism of the present deprotection reaction is in our previous findings, in which the combination of hydrosilanes with a catalytic amount of **1** initiates ring-opening polymerization of epoxides, oxetanes, and THF and addition polymerization of vinyl ethers.[3a,10] The formed polymer contains the organosilyl end group derived from the hydrosilane used. Experiments using $R_3Si–D$ revealed that the deuterium atom is located at the other end of the polymer formed. Because these monomers are usually polymerized through cationic polymerization, the mechanisms shown in Scheme 3 [Equations (3) and (4)] are proposed,[10] in which heterolytic cleavage of the $R_3Si–H$ bond is induced by the catalyst species to form an ionic intermediate, $[R_3Si]^+\cdots[Ru_3–H]^-$. The polymerization is initiated by $[R_3Si]^+$ and terminated by the hydride in $[Ru_3–H]^-$.



Scheme 3. Reaction mechanisms of silane-induced ring-opening polymerization of epoxides, oxetanes, and THF [Equation (3)] and addition polymerization of vinyl ethers [Equation (4)].

If a similar ionic species is involved in the mechanism of the present deprotection, Equations (5) and (6) shown in Scheme 4 would reasonably explain the reactions. The Lewis acidic $[R_3Si]^+$ species coordinates to the carbonyl or ether oxygen atom, leading to loosening of the C–O bond of the O*t*Bu groups. Elimination of isobutene is accompanied by generation of H_2 from a proton of the *t*Bu group and a hydride of the hydrosilane. In the reactions of *N*-Boc and *O*-Boc derivatives, subsequent elimination of CO_2 from intermediate **A** proceeds by treatment with methanol to afford the corresponding amine and alcohol.



Scheme 4. Possible reaction mechanisms.

Conclusions

As described above, cleavage of the C–O bond of O*t*Bu groups in carbamates, carbonates, esters, and ethers is facilely accomplished by $PhMe_2SiH$ activated by triruthenium cluster **1**, giving rise to a new deprotection method of O*t*Bu groups under neutral conditions. The proposed mechanism indicates in situ generation of the Lewis acidic $[R_3Si]^+$ species; however, it is noteworthy that the $[R_3Si]^+$ species is formed from a stable and neutral hydrosilane and the ruthenium catalyst. The typical Lewis acidic $[R_3Si]^+$ species is produced from Me_3SiI and Me_3SiOTf, of which the Si–I or Si–O bond is highly polarized and instantly formed acidic HI or HOTf in contact with moisture. Hydrosilanes activated by transition-metal catalysts have been utilized for the hydrosilylation of alkenes and alkynes, reduction of carbonyl compounds, dehydration of primary amides to nitriles, and polymerization of cyclic ethers and vinyl ethers. The present reaction is the first example of a transition-metal-catalyzed activation of Si–H bonds leading to deprotection of O*t*Bu groups. *It is noteworthy that platinum,*[11a,11b] *iridium,*[11c] *and iron catalysts*[11d] *are active towards reduction of tertiary amides with* $Me_2SiHOSiHMe_2$, *but do not induce deprotection of tert-butyl groups in carbamates, carbonates, esters, or ethers.* This implies that **1** exhibits the highest activity towards the generation of the Lewis acidic $[R_3Si]^+$ species from Si–H groups among the catalysts described above. Application of this unique catalytic property of **1** to other organic transformations is currently under investigation.

Experimental Section

General Remarks: ^1H and ^{13}C NMR spectra were measured with JEOL GSX-270 (270 MHz) and ECA 400 (396 MHz) spectrometers. Chemical shifts for ^1H NMR are described in parts per million downfield from tetramethylsilane as an internal standard (δ = 0 ppm) in $CDCl_3$, unless otherwise noted. Chemical shifts for ^{13}C NMR are expressed in parts per million in $CDCl_3$ as an internal standard (δ = 77.1 ppm), unless otherwise noted. IR spectra were measured with a JASCO FT/IR-4200 spectrometer. Analytical thin-layer chromatography (TLC) was performed on glass plates precoated with silica gel (Merck, Kieselgel 60 F_{254}, layer thickness 0.25 mm). Visualization was accomplished by UV light (254 nm), iodine, and phosphomolybdic acid. ($\mu_3,\eta^2,\eta^3,\eta^5$-acenaphthylene)-$Ru_3(CO)_7$ (**1**)[3c] and 1,2-bis(dimethylsilyl)ethane[12] were prepared by literature methods.

Typical Procedure for Deprotection: To a stirred solution of *tert*-butyl 4-biphenyl ether (**7b**; 113 mg, 0.5 mmol) and ($\mu_3,\eta^2,\eta^3,\eta^5$-acenaphthylene)$Ru_3(CO)_7$ (**1**; 10 mg, 3 mol-%) in dimethoxyethane (0.25 mL) was added dimethylphenylsilane (93 µL, 0.6 mmol). After the mixture was stirred at 40 °C for 7 h, the reaction mixture was quenched by the addition of methanol (100 µL). Following stirring at room temperature for an additional 30 min, the resultant mixture was concentrated under reduced pressure. Then, the residue was treated with tetrabutylammonium fluoride (0.6 mmol) in ether at room temperature for 1 h. After removal of the solvent, purification of the residue by silica gel column chromatography gave 4-phenylphenol (**10b**) in 95% yield (81 mg). White solid. IR (KBr): $\tilde{\nu}$ = 3411, 3036, 1605, 1522, 1456, 1427, 1379, 1247, 1109, 835, 752, 680 cm^{-1}. ^1H NMR (396 MHz, $CDCl_3$): δ = 4.75 (br. s, 1 H, OH), 6.91 (d, J = 8.7 Hz, 2 H, 2-H), 7.31 (t, J = 7.5 Hz, 1 H, *p*-Ph), 7.42 (dd, J = 7.5, 7.2 Hz, 2 H, *m*-Ph), 7.49 (d, J = 8.7 Hz, 2 H, 3-H), 7.55 (d, J = 7.2 Hz, 2 H, *o*-Ph) ppm. ^{13}C NMR (99.5 MHz, $CDCl_3$): δ = 115.7, 126.8 (2 C), 128.5, 128.8, 134.2, 140.8, 155.1 ppm.

Supporting Information (see footnote on the first page of this article): Detailed experimental procedures and characterization data of both the substrates and the products.

Acknowledgments

This work was partially supported by a Grant-in Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan. S.H. is grateful to the Japan Society for the Promotion of Science for Young Scientists for a Research Fellowship.

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Received: November 9, 2009