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Palladium-Catalyzed Hiyama-Type Cross-Coupling Reactions of Arenesulfinates with Organosilanes

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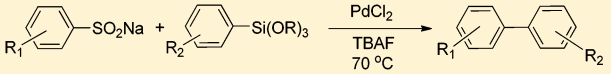
Ⓢ *Supporting Information*

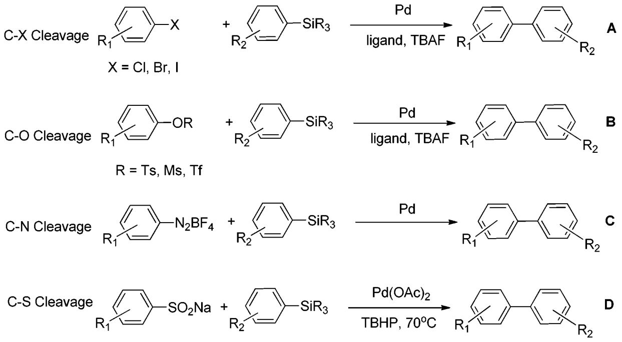
ABSTRACT: Palladium-catalyzed Hiyama-type cross-coupling reactions of various arenesulfinates with organosilanes were achieved in good to excellent yields under aerobic conditions at 70 °C. Fluoride is essential, and tetrabutylammonium fluoride (TBAF) was shown to be the most efficient additive for these cross-coupling reactions. These cross-coupling reactions of the arenesulfinates provide high yields and show wide functional group tolerance, making them attractive alternative transformations to traditional cross-coupling approaches for carbon−carbon bond construction.



Transition-metal-catalyzed cross-coupling reactions of organometallic reagents with organic halides have become routine tools for the construction of C−C bonds in synthetic organic chemistry.[1] Organoboron,[2] organozinc,[3] and organotin[4] reagents are among the most common substrates for the Pd-catalyzed cross-coupling reactions, but these coupling partners have inherent drawbacks such as high cost, high toxicity, low stability, and poor biocompatibility. In contrast, organosilicon reagents have emerged as competitive alternatives for the nucleophilic partners for cross-coupling reactions with various organic halides or pseudohalides, primarily due to their low toxicity, high chemical stability, and broad availability.[5] Tremendous progress has been made for the Hiyama cross-coupling reactions in the organic synthesis of natural products and biologically active compounds.[6] Thus, it will be valuable to develop new reagents for the Hiyama cross-coupling reactions, extending the scope and generality of their synthetic applications.

Traditionally, the Hiyama cross-coupling reactions involve aryl halides as the electrophilic reagents by the cleavage of the corresponding carbon−halogen bonds (Scheme 1, A).[7] While the carbon−oxygen bond cleavage of the electrophilic reagents such as aryl tosylates/mesylates has been reported (Scheme 1, B),[8] fairly little work has been reported concerning the carbon−nitrogen bond cleavage of the electrophilic reagents for the Hiyama cross-coupling reactions in the literature. Recently, we reported a practical carbon−nitrogen bond cleavage procedure for the Hiyama cross-coupling reactions using arenediazonium salts as the electrophilic reacgents (Scheme 1, C).[9] To the best of our knowledge, no carbon−sulfur bond cleavage of the corresponding electrophilic reagents has yet been reported in the literature for the Hiyama cross-coupling reactions even though arenesulfinates were employed as electrophilic partners for Heck cross-coupling reactions[10] and for carbon−hydrogen activation.[11] As an alternative for aromatic carboxylic acids for decarboxylative coupling reactions, arenesulfinates have been shown to be more reactive substrates for the synthesis of various aromatic compounds.[12] Arylsulfonyl chlorides have typically been used as aryl sources, however, they are not stable and moisture sensitive. Sodium arylsulfinates are stable and easy to handle, which shows great potential as aryl sources. Herein, we report our results of the Pd-catalyzed Hiyama-type cross-coupling reactions of various arenesulfinates with different organosilicon reagents in the absence of bases and ligands under mild reaction conditions (Scheme 1, D). Scheme 1 summarizes the key bond cleavages of the electrophilic reagents for several Hiyama-type cross-coupling reactions.

Scheme 1



Our initial screening experiments started with the reaction of phenyltriethoxysilane with sodium *p*-methylbenzenesulfinate in the presence of *n*-tetrabutylammonium fluoride (TBAF, dissolved in THF) and 5 mol % of $Pd(OAc)_2$ under atmospheric air for 3 h at 70 °C, resulting in the formation of

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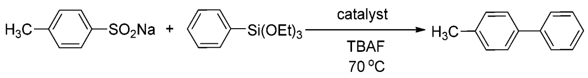
the corresponding cross-coupling product in good yield (75%) (entry 1, Table 1). This cross-coupling was then employed as a model reaction to further optimize the palladium catalytic system, and the related results are also summarized in Table 1 for comparison. Examination of entries 2–8 of Table 1 shows that the cross-coupling products were obtained in comparable yields when several palladium catalysts were used. Most interestingly, much higher cross-coupling yields were obtained when PdI_2 and $PdCl_2$ compounds were used as the catalyst (entries 9 and 10, Table 1), which are structurally less complex and less expansive than the other catalyst. Negligible cross-coupling products were formed when the ruthenium and rhodium compounds were used as the catalysts for the cross-coupling reactions (entries 11 and 12, Table 1).

Table 1. Catalyst Optimization for the Hiyama-Type Cross-Coupling[a]

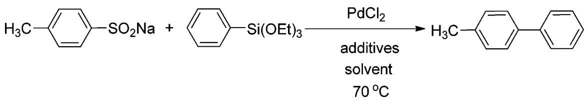


entry	catalyst	yield[b] (%)
1	$Pd(OAc)_2$	75
2	$PdCl_2(PPh_3)_2$	55
3	$Pd(PCy_3)_2Cl_2$	63
4	$Pd(dppf)Cl_2$	54
5	$Pd(PhCN)_2Cl_2$	76
6	$Pd(CH_3CN)_2Cl_2$	74
7	$Pd(PPh_3)_4$	60
8	$Pd_2(dba)_3$	57
9	PdI_2	91
10	$PdCl_2$	94
11	$RhCl(PPh_3)_3$	~0
12	$[RuCl_2(p\text{-cymene})]_2$	~0

[a]Reaction conditions: phenyltriethoxysilane (0.6 mmol), sodium *p*-methylbenzenesulfinate (0.5 mmol), catalyst (5.0 mol %), TBAF (1 M in THF, 1 mL), 3 h. [b]Isolated cross-coupling yields.

We then examined effects of solvents and additives on the $PdCl_2$-catalyzed cross-coupling of phenyltriethoxysilane with *p*-methylbenzenesulfinate, and the key results are summarized in Table 2. Examination of entries 1 and 2 of Table 2 shows that addition of TBAF (1 M in THF) and TBAF·$3H_2O$ has no major effect on the cross-coupling yield, suggesting that the corresponding transformation can tolerate a stoichiometric amount of water. Nevertheless, only about 64% of the cross-coupling yield was obtained using TBAF (75% aqueous) in DMSO solution (entry 3, Table 2). Examination of entries 4—6 of Table 2 shows that the cross-coupling yield gradually increases from 54% to 81% to 90% as the additive changes from NaF to KF to CsF, respectively, presumably due to solubility of the fluoride.[13] The yields decreasing when THF was used as solvent (entries 3–6, Table 2, in parentheses). Recently, we have shown that the BF_4^- anion may be involved with the acceleration of the Hiyama-type cross-coupling reactions of arenediazonium salts,[9] but clearly the BF_4^- anion has no effects on the Hiyama-type cross-coupling of *p*-methylbenzenesulfinate with phenyltriethoxysilane in methanol (entry 7, Table 2). Selectfluor was also tested, and no desired product was detected (entry 8, Table 2).

Table 2. Effects of the Additives on the Hiyama-Type Cross-Coupling[a]

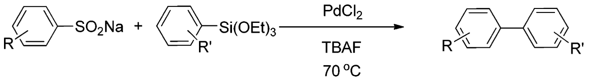


entry	additives	solvents	yield[b] (%)
1	TBAF (1 M in THF)	THF	94
2	TBAF·$3H_2O$	THF	88
3	TBAF (75% water)	DMSO (THF)	64 (47)
4	NaF	DMSO (THF)	54 (32)
5	KF	DMSO (THF)	81 (45)
6	CsF	DMSO (THF)	90 (49)
7	$NaBF_4$	CH_3OH	
8	Selectfluor	CCl_4	

[a]Reaction conditions: phenyltriethoxysilane (0.6 mmol), sodium *p*-methylbenzenesulfinate (0.5 mmol), $PdCl_2$ (5 mol %), additive (0.5 mmol), solvent (1.0 mL), 3 h. [b]Isolated cross-coupling yields. The yields of entries using THF as solvent were shown in parentheses.

The optimized $PdCl_2$-catalyzed protocol was applicable to the cross-coupling reactions of a wide variety of arenesulfinates with different organosilanes as evidenced from Table 3. Examination of entries 1—6 of Table 3 shows that essentially comparable yields (90 ± 4%) were obtained for the cross-coupling reactions of *p*-methylbenzenesulfinate regardless of the silane chemical structures (phenyltriethoxysilanes, phenyltrimethoxysilanes or dimethoxydiphenylsilane) and the aromatic ring substituents. Most intriguingly, the Hiyama-type cross-coupling reactions (entries 7–20, Table 3) also afforded good reaction yields regardless of the polarity of the aromatic ring substituents. Moreover, the Hiyama-type cross-coupling reactions were tolerant to steric hindrance of the ortho

Table 3. $PdCl_2$-Catalyzed Hiyama-Type Cross-Coupling of Arenesulfinates with Organosilanes[a]



entry	arenesulfinates	organosilanes	yield[b] (%)
1	$4\text{-MeC}_6H_4SO_2Na$	$C_6H_5Si(OEt)_3$	94
2	$4\text{-MeC}_6H_4SO_2Na$	$C_6H_5Si(OMe)_3$	91
3	$4\text{-MeC}_6H_4SO_2Na$	$(C_6H_5)_2Si(OMe)_2$	90
4	$4\text{-MeC}_6H_4SO_2Na$	$4\text{-MeC}_6H_4Si(OMe)_3$	88
5	$4\text{-MeC}_6H_4SO_2Na$	$3\text{-FC}_6H_4Si(OMe)_3$	86
6	$4\text{-MeC}_6H_4SO_2Na$	$4\text{-CF}_3C_6H_4Si(OMe)_3$	87
7	$4\text{-MeO-C}_6H_4SO_2Na$	$C_6H_5Si(OEt)_3$	92
8	$4\text{-ClC}_6H_4SO_2Na$	$C_6H_5Si(OEt)_3$	84
9	$4\text{-BrC}_6H_4SO_2Na$	$C_6H_5Si(OEt)_3$	86
10	$4\text{-FC}_6H_4SO_2Na$	$C_6H_5Si(OEt)_3$	79
11	$4\text{-NO}_2C_6H_4SO_2Na$	$C_6H_5Si(OEt)_3$	73
12	$3\text{-MeC}_6H_4SO_2Na$	$C_6H_5Si(OEt)_3$	89
13	$3\text{-NO}_2C_6H_4SO_2Na$	$C_6H_5Si(OEt)_3$	77
14	$3\text{-FC}_6H_4SO_2Na$	$C_6H_5Si(OEt)_3$	79
15	$3,5\text{-MeC}_6H_4SO_2Na$	$C_6H_5Si(OEt)_3$	84
16	$2\text{-MeC}_6H_4SO_2Na$	$C_6H_5Si(OEt)_3$	81
17	$2\text{-ClC}_6H_4SO_2Na$	$C_6H_5Si(OEt)_3$	80
18	$2,6\text{-MeC}_6H_4SO_2Na$	$C_6H_5Si(OEt)_3$	73
19	1-naphthyl-SO_2Na	$C_6H_5Si(OEt)_3$	82
20	2-naphthyl-SO_2Na	$C_6H_5Si(OEt)_3$	85

[a]Reaction conditions: silanes (0.6 mmol), arenesulfinate (0.5 mmol), $PdCl_2$ (5 mol %), TBAF (1 M in THF, 1 mL), 3 h. [b]Isolated cross-coupling yields.

substituent(s) (entries 16–19, Table 3) as well as halogen substituents (entries 8—10 and 14, Table 3). The excellent tolerance for a wide range of functional groups and the steric hindrance reveals that these straightforward transformations can be used as an effective method under very mild reaction conditions for the construction of $C(sp^2)-C(sp^2)$ bonds in the organic synthesis.

A plausible mechanism for the Hiyama-type cross-coupling reaction of arenesulfinates with aryl siloxanes is shown in Figure 1. The $PdCl_2$ catalyst may first react with arenesulfinate to form the $ArS(=O)OPdX$ reactive intermediate (Figure 1, A), followed by expulsion of SO_2 to produce the ArPdX reactive intermediate, which is similar to the palladium intermediates proposed in many other homo- and/or cross-coupling reactions.[14] The ArPdAr′ (Figure 1, B) reactive intermediate will be formed with the assistance of TBAF from the transmetalation of the ArPdX reactive intermediate with organosilane. Indeed, the formation of $Si(OEt)_3Cl$ for reactions of aryltriethoxysilanes was detected by the GC/MS analysis. Reductive elimination of the biaryl coupling products is accompanied by formation of the reduced Pd^0 species, which can be oxidized by atmospheric oxygen to furnish the catalytic cycle for the cross-coupling of arenesulfinates with organosilanes. The byproduct sulfur dioxide (SO_2) could be further neutralized using ammonia aqueous solution to produce ammonium sulfinate [$(NH_4)_2SO_3$], a common fertilizer with no environmental pollution for industrial process.[15]

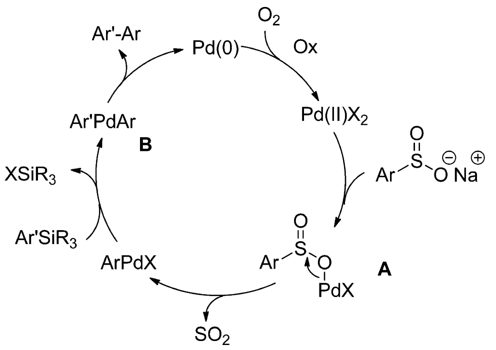


Figure 1. Mechanism proposed.

In summary, the $PdCl_2$-catalyzed Hiyama-type cross-coupling reactions of arenesulfinates with arylsiloxanes have been achieved in excellent yields under very mild reaction conditions. The widely available sodium arenesulfinates and broad functional group tolerance enable this novel transformation to be an attractive alternative to the Hiyama cross-coupling reaction for carbon–carbon bond construction in organic synthetic chemistry.

■ EXPERIMENTAL SECTION

General Procedure for the Cross-Coupling. A mixture of arylsulfinate salt (0.50 mmol), $PdCl_2$ (5 mol %), and aryltriethoxysilane (0.60 mmol) was stirred uncapped in the solvent of TBAF (1 M, in THF) (1.0 mL) at 70 °C for 3.0 h. After the mixture was cooled to room temperature, water (5 mL) was added. The insoluble was removed by filtration, and then the reaction mixture was extracted with diethyl ether (Et_2O) (2 mL) three times. The combined organic layer was washed with water and saturated brine and then dried over anhydrous sodium sulfate. Solvent was removed under reduced pressure. The cross-coupling products were purified by silica gel chromatography with a mixture of petroleum ether and ethyl acetate. The cross-coupling products were confirmed by melting points and spectroscopic (^1H NMR and HRMS-EI) analysis, which were all consistent with the literature results.

4-Methyl-1,1′-biphenyl (T3-1, CAS no. 644-08-6): white solid; mp 46–47 °C (lit.[1b] mp 47–48 °C); ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.55 (t, J = 6.8 Hz, 2 H), 7.38–7.48 (m, 4 H), 7.32 (t, J = 7.2 Hz, 1 H), 7.21 (d, J = 7.6 Hz, 2 H), 2.33 (s, 3 H). HRMS (EI) calcd for $C_{13}H_{12}$ (M^+) 168.0939, found 168.0938.

4,4′-Dimethyl-1,1′-biphenyl (T3-4, CAS no. 613-33-2): white solid; mp 120–121 °C (lit.[1c] mp 119–120 °C); ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.47 (d, J = 8.0 Hz, 4 H), 7.45 (d, J = 7.6 Hz, 4 H), 2.37 (s, 6 H); HRMS (EI) calcd for $C_{14}H_{14}$ (M^+) 182.1096, found 182.1099.

3-Fluoro-4′-methyl-1,1′-biphenyl (T3–5, CAS no. 72093-42-6): white solid; mp 39–40 °C (lit.[1c] mp 39–40 °C); ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.44 (t, J = 8.0 Hz, 2 H), 7.28–7.35 (m, 2 H), 7.19–7.23 (m, 3 H), 7.02 (t, J = 8.0 Hz, 1 H), 2.35 (s, 3 H); HRMS (EI) calcd for $C_{13}H_{11}F$ (M^+) 186.0841, found 186.0841.

4-Methyl-4′-(trifluoromethyl)-1,1′-biphenyl (T3-6, CAS no. 97067-18-0:). white solid; mp 122–124 °C (lit.[1d] mp 121 °C); ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.65–7.72 (m, 4 H), 7.46 (d, J = 7.2 Hz, 2 H), 7.21 (d, J = 7.6 Hz, 2 H), 2.37 (s, 3 H); HRMS (EI) calcd for $C_{14}H_{11}F_3$ (M^+) 236.0813, found 236.0815.

4-Methoxy-1,1′-biphenyl (T3-7, CAS no. 613–37-6): white solid; mp 88–90 °C (lit.[1b] mp 88–89 °C); ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.54 (t, J = 8.8 Hz, 4 H), 7.39 (t, J = 7.6 Hz, 2 H), 7.30 (t, J = 7.6 Hz, 1 H), 6.95 (d, J = 8.8 Hz, 2 H), 3.81 (s, 3 H); HRMS (EI) Calcd for $C_{13}H_{12}O$ (M^+) 184.0888, found 184.0884.

4-Cholro-1,1′-biphenyl (T3–8, CAS no. 644-08-6): white solid; mp 48–49 °C (lit.[1b] mp 47–48 °C); ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.56 (t, J = 6.8 Hz, 2 H), 7.40–7.48 (m, 4 H), 7.32 (t, J = 7.2 Hz, 1 H), 7.22 (d, J = 7.6 Hz, 2 H); HRMS (EI) calcd for $C_{12}H_9Cl$ (M^+) 188.0393, found 188.0396.

4-Bromo-1,1′-biphenyl (T3–9, CAS no. 92-66-0): white solid; mp 90–92 °C (lit.[1b] mp 91–92 °C); ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.58 (d, J = 7.2 Hz, 1 H), 7.51–7.54 (m, 3 H), 7.39–7.43 (m, 3 H), 7.30–7.37 (m, 2 H); HRMS (EI) calcd for $C_{12}H_9Br$ (M^+) 231.9888, found 231.9887.

4-Fluoro-1,1′-biphenyl (T3–10, CAS no. 324-74-3): white solid; mp 73–74 °C (lit.[1e] mp 73–74 °C); ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.52–7.56 (m, 4 H), 7.43 (t, J = 7.6 Hz, 2 H), 7.34 (t, J = 7.2 Hz, 1 H), 7.12 (t, J = 8.4 Hz, 2 H); HRMS (EI) calcd for $C_{12}H_9F$ (M^+) 172.0688, Found 172.0684.

4-Nitro-1,1′-biphenyl (T3–11, CAS no. 92-93-3): white solid; mp 115–117 °C (lit.[1b] mp 115–116 °C); ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 8.28 (d, J = 8.4 Hz, 2 H), 7.72 (d, J = 9.2 Hz, 2 H), 7.62 (d, J = 6.8 Hz, 2 H), 7.42–7.51 (m, 3 H); HRMS (EI) calcd for $C_{12}H_9NO_2$ (M^+) 199.0633, found 199.0634.

3-Methyl-1,1′-biphenyl (T3–12, CAS no 643-93-6): colorless oil (lit.[1e]); ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.58 (d, J = 7.2 Hz, 2 H), 7.38–7.44 (m, 4 H), 7.32 (t, J = 7.2 Hz, 2 H), 7.16 (d, J = 7.2 Hz, 1 H), 2.41 (s, 3 H); HRMS (EI) calcd for $C_{13}H_{12}$ (M^+) 168.0939, found 168.0937.

3-Nitro-1,1′-biphenyl (3–13, CAS no. 2113-58-8): white solid; mp 59–60 °C (lit.[1b] mp 59–60 °C); ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 8.45 (s, 1 H), 8.19 (d, J = 8.4 Hz, 1 H), 7.91 (t, J = 8.0 Hz, 1 H), 7.58–7.63 (m, 3 H), 7.50 (t, J = 7.2 Hz, 2 H), 7.43 (t, J = 7.6 Hz, 1 H); HRMS (EI) calcd for $C_{12}H_9NO_2$ (M^+) 199.0633, found 199.0631.

3-Fluoro-1,1′-biphenyl (T3–14, CAS no. 2367-22-8): white solid; mp 26–27 °C (lit.[1h] mp 26–27 °C); ^1H NMR (400 MHz, $CDCl_3$, TMS) δ7.56 (d, J = 7.2 Hz, 2 H), 7.44 (t, J = 7.2 Hz, 2 H), 7.34–7.39 (m, 3 H), 7.28 (d, J = 10.0 Hz, 1 H), 7.00–7.05 (m, 1 H); HRMS (EI) calcd for $C_{12}H_9F$ (M^+) 172.0688, found 172.0689.

2,6-Dimethyl-1,1′-biphenyl (T3–15, CAS no. 17057-88-4): colorless oil (lit.[1g]); ^1H NMR (400 MHz, $CDCl_3$, TMS) δ7.60 (d, J = 7.2 Hz, 3 H), 7.44 (t, J = 7.6 Hz, 3 H), 7.34 (t, J = 7.2 Hz, 1 H), 6.92 (t, J = 7.2 Hz, 1 H), 2.29 (s, 6 H); HRMS (EI) calcd for $C_{14}H_{14}$ (M^+) 182.1096, found 182.1097.

2-Methyl-1,1′-biphenyl (T 3–16, CAS no. 643-58-3): colorless oil (lit.[1h]); ^1H NMR (400 MHz, $CDCl_3$, TMS) δ7.55 (d, J = 8.4 Hz, 2

H), 7.41−7.46 (m, 3 H), 7.38 (d, J = 7.2 Hz, 1 H), 7.28−7.32 (m, 1 H), 7.20 (t, J = 7.6 Hz, 1 H), 7.16 (t, J = 9.2 Hz, 1 H), 3.46 (s, 3 H); HRMS (EI) calcd for $C_{13}H_{12}$ (M$^+$) 168.0939, found 168.0936.

2-Chloro-1,1′-biphenyl (T3−17, CAS no. 2051-60-7): white solid; mp 34−35 °C (lit.[1h] mp 34−35 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.59 (d, J = 8.4 Hz, 2 H), 7.40−7.49 (m, 4 H), 7.25−7.36 (m, 3 H). HRMS (EI) calcd for $C_{12}H_9Cl$ (M$^+$) 188.0393, Found 188.0391.

2,6-Dimethyl-1,1′-biphenyl (T 3-18, CAS no. 3976-34-9): colorless oil (lit.[1f]); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ7.60 (d, J = 7.2 Hz, 3 H), 7.44 (t, J = 7.6 Hz, 3 H), 7.34 (t, J = 7.2 Hz, 1 H), 6.92 (t, J = 7.2 Hz, 1 H), 2.29 (s, 6 H); HRMS (EI) calcd for calcd for $C_{14}H_{14}$ (M$^+$) 182.1096, found 182.1097.

1-Phenylnaphthalene (T3−19, CAS no. 643-93-6): colorless oil (lit.[1e]); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.90 (t, J = 8.0 Hz, 1 H), 7.59 (d, J = 8.4 Hz, 2 H), 7.48−7.53 (m, 3 H), 7.41−7.47 (m, 5 H), 7.33 (t, J = 7.2 Hz, 1 H); HRMS (EI) calcd for $C_{16}H_{12}$ (M$^+$) 204.0939, found 204.0937.

2-Phenylnaphthalene (T3−20, CAS no. 612-94-2): white solid; mp 96−97 °C (lit.[1e] mp 96−97 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.03 (s, 1 H), 7.84−7.93 (m, 3 H), 7.72 (t, J = 8.0 Hz, 3 H), 7.45−7.51 (m, 4 H), 7.37 (t, J = 7.2 Hz, 1 H); HRMS (EI) calcd for $C_{16}H_{12}$ (M$^+$) 204.0939, found 204.0936.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Frontiers in Transition Metal Catalyzed Reactions. *Chem. Rev.* **2011**, *111*, 1167−2486. (b) Barbero, M.; Cadamuro, S.; Dughera, S.; Giaveno, C. *Eur. J. Org. Chem.* **2006**, 4884. (c) You, E.; Li, P.; Wang, L. *Synthesis* **2006**, 1465. (d) Ackermann, L.; Althammer, A. *Org. Lett.* **2006**, *8*, 3454. (e) Zhou, W.-J.; Wang, K.-H.; Wang, J.-X. *Adv. Synth. Catal.* **2009**, *351*, 1378. (f) Ackermann, L.; Althammer, A.; Born, R.; Mayer, P. *Org. Lett.* **2010**, *12*, 1004. (g) Shi, M.; Qian, H.-X. *Tetrahedron* **2005**, *61*, 4949. (h) Beadle, J. R.; Korzeniowski, S. H.; Rosenberg, D. E.; Garcia-Slanga, B. J.; Gokel, G. W. *J. Org. Chem.* **1984**, *49*, 1594.

(2) For selected reviews, see: (a) Zeni, G.; Larock, R. C. *Chem. Rev.* **2006**, *106*, 4644. (b) Yin, L.; Liebscher, J. *Chem. Rev.* **2007**, *107*, 133. (c) *Transition Metals for Organic Synthesis: Building Blocks and Fine Chemicals*, 2nd ed.; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, Germany, 2004; (d) *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., de Meijere, A., Eds.; Wiley: New York, 2002.

(3) Negishi, E.; Liu, F. In *Metal-Catalyzed, Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, Germany, 1998; Chapter 1.

(4) (a) Stille, J. K. *Angew. Chem., Int. Ed.* **1986**, *25*, 508. (b) Mitchell, T. N. In *Metal-Catalyzed, Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, Germany, 1998; Chapter 4.

(5) (a) Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1988**, *53*, 920. (b) Gouda, K.; Hagiwara, E.; Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1996**, *61*, 7232. (c) Riggleman, S.; DeShong, P. *J. Org. Chem.* **2003**, *68*, 8106.

(6) (a) Shukla, K. H.; DeShong, P. *J. Org. Chem.* **2008**, *73*, 6283. (b) Seganish, W. M.; Handy, C. J.; DeShong, P. *J. Org. Chem.* **2005**, *70*, 8948. (c) Denmark, S. E.; Baird, J. D.; Regens, C. S. *J. Org. Chem.* **2008**, *73*, 1440.

(7) (a) Denmark, S. E.; Regens, C. S. *Acc. Chem. Res.* **2008**, *41*, 1486. (b) Seganish, W. M.; DeShong, P. *Org. Lett.* **2006**, *8*, 3951. (c) McElroy, W. T.; DeShong, P. *Org. Lett.* **2003**, *5*, 4779. (d) Denmark, S. E.; Smith, R. C. *J. Am. Chem. Soc.* **2010**, *132*, 1243. (e) Denmark, S. E.; Smith, R. C.; Chang, W.-T. T.; Muhuhi, J. M. *J. Am. Chem. Soc.* **2009**, *131*, 3104.

(8) References about C-OTs transformation: (a) Zhang, L.; Wu, J. *J. Am. Chem. Soc.* **2008**, *130*, 12250. References about C-OMs transformation: (b) Chau, M.; Lee, H. W.; Lau, C. P.; Kwong, F. Y. *Org. Lett.* **2009**, *11*, 317. (c) Zhang, L.; Qing, J.; Yang, P.; Wu, J. *Org. Lett.* **2008**, *10*, 4971. References about C-OTf transformation: (d) Seganish, W. M.; DeShong, P. *J. Org. Chem.* **2004**, *69*, 1137. (e) Riggleman, S.; DeShong, P. *J. Org. Chem.* **2003**, *68*, 8106.

(9) Cheng, K.; Wang, C.; Ding, Y.; Song, Q.; Qi, C.; Zhang, X.-M. *J. Org. Chem.* **2011**, *76*, 9261.

(10) (a) Zhou, X.; Luo, J.; Liu, J.; Peng, S.; Deng, G.-J. *Org. Lett.* **2011**, *13*, 1432. (b) Wang, G.-W.; Miao, T. *Chem.—Eur. J.* **2011**, *17*, 5787.

(11) (a) Liu, B.; Guo, Q.; Cheng, Y.; Lan, J.; You, J. *Chem.—Eur. J.* **2011**, *17*, 13415. (b) Chen, R.; Liu, S.; Liu, X.; Yang, L.; Deng, G.-J. *Org. Biomol. Chem.* **2011**, *9*, 7675. (c) Wu, M.; Luo, J.; Xiao, F.; Zhang, S.; Deng, G.-J.; Luo., H.-A. *Adv. Synth. Catal.* **2012**, *354*, 335. (d) Wang, M.; Li, D.; Zhou, W.; Wang, L. *Tetrahedron* **2012**, *68*, 1926.

(12) (a) Dubbaka, S. R.; Vogel, P. *Org. Lett.* **2004**, *6*, 95. (b) Zhang, S.; Zeng, X.; Wei, Z.; Zhao, D.; Kang, T.; Zhang, W.; Yan, M.; Luo, M. *Synlett* **2006**, 1891. (c) Behrends, M.; Sävmarker, J.; Sjöberg, P. J. R.; Larhed, M. *ACS Catal.* **2011**, *1*, 1455. (d) Liu, J.; Zhou, X.; Rao, H.; Xiao, F.; Li, C.-J.; Deng, G.-J. *Chem.—Eur. J.* **2011**, *17*, 7996. (e) Chen, W.; Zhou, X.; Xiao, F.; Luo, J.; Deng, G.-J. *Tetrahedron Lett.* **2012**, *53*, 4347. (f) Wang, H.; Li, Y.; Zhang, R.; Jin, K.; Zhao, D.; Duan, C. *J. Org. Chem.* **2012**, *77*, 4849. (g) Rao, H. H.; Yang, L.; Qi, S. A.; Li, C. J. *Adv. Synth. Catal.* **2011**, *353*, 1701. (h) Zhou, C.; Liu, Q.; Li, Y.; Zhang, R.; Fu, X.; Duan, C. *J. Org. Chem.* **2012**, *77*, 10468.

(13) Hefter, G. T. *Rev. Inorg. Chem.* **1989**, *10*, 185−224.

(14) (a) *Metal-Catalyzed Cross-Coupling Reactions*; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, 2004; Vols. *1* and *2*. (b) *Acc. Chem. Res.* **2008**, 11, Special Issue on Cross Coupling.

(15) Srivastava, R. K.; Jozewicz, W.; Singer, C. *Environ. Prog. Sustain.* **2001**, *20*, 219−228.