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Palladium-Catalyzed Direct Arylation of Selenophene

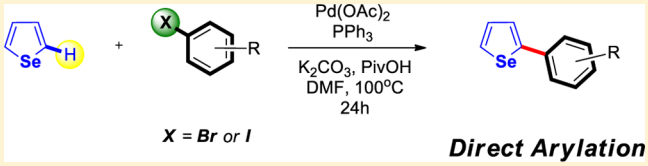
Daniel S. Rampon,[†,‡] Ludger A. Wessjohann,[‡] and Paulo H. Schneider*[,†]

[†]Instituto de Química, Departamento de Química Orgânica, Universidade Federal do Rio Grande do Sul, UFRGS, 91501-970 Porto Alegre-RS, Brazil

[‡]Department of Bioorganic Chemistry, Leibniz Institute of Plant Biochemistry, Weinberg 3, 06120 Halle (Saale), Germany

Supporting Information

ABSTRACT: An efficient and convenient method was developed for the regioselective formation of 2-aryl- or 2,5-diarylselenophenes via a palladium-catalyzed direct arylation. This protocol is suitable for a wide range of aryl halides containing different functional groups. The 2-arylated substrates can undergo an additional regioselective direct arylation event furnishing symmetrical or unsymmetrical 2,5-diaryl selenophenes in good yield. Competition experiments and the role of the acid additive are in agreement with a concerted metalation deprotonation (CMD) pathway.



INTRODUCTION

The palladium-catalyzed direct arylation of several (hetero)-arenes via direct C−H bond activation using aryl halides has brought a synthesis revolution in recent years.[1] Such couplings are very attractive to replace classical Stille,[2] Suzuki,[3] or Negishi palladium-catalyzed type couplings,[4] as they do not require the preliminary synthesis of one or two organometallic derivatives. Therefore, these reactions are atom-economical and produce less waste.

Up to now, a wide range of electron-rich and electron-poor (hetero)aromatic compounds have been successfully employed in palladium-catalyzed direct arylations,[5] but despite the recent advances, such transformations with selenophenes have been accomplished only for the synthesis of analogues for dye-sensitized photovoltaic cells, and no mechanistic considerations were displayed.[5m] Since catalyst poisoning by organoselenium species is one of the limiting factors in transition-metal-catalyzed transformations,[6] it is important to understand the pathways for these reactions. On the other hand, many efforts are directed toward the synthesis and design of organoselenium compounds, particularly due to their ability to mimic natural compounds with important biological properties, like anti-oxidant, antitumor, antimicrobial, and antiviral ones.[7] In addition, chalcogen derivatives have been intensively studied in the development of organic materials with technological interest, such as electroconductive polymers, solar cells, organic semiconductors, and liquid crystals.[8]

To date, to promote a cross-coupling reaction with the selenophene ring (**1**), a previous activation either as a halide or as an organometallic (B, Mg, Sn, and Zn) is required.[9] Direct arylation would avoid the need for prefunctionalization of the selenophene, thus reducing the number of steps to prepare these 2-arylated products. This fact and our continuous interest in the synthesis of organoselenium compounds[10] prompted us to explore a new approach on the palladium-catalyzed direct arylation of selenophene.

RESULTS AND DISCUSSION

Suitable reaction conditions were developed with commercially available selenophene (**1**) and bromobenzene (**2a**). The first attempt was performed under Fagnou direct arylation conditions.[5a] The catalytic system was composed of $Pd(OAc)_2$, an alkylphosphine as its phosphoniumtetrafluoroborate salt ($PCy_3{\cdot}HBF_4$), pivalic acid as a co-catalyst, and potassium carbonate as a base in DMA (*N*,*N*-dimethylacetamide). However, only poor yields of product **3a** could be achieved. After screening several parameters,[11] we could obtain the desired direct coupling product (**3a**) with complete selectivity for the 2-arylation, albeit in only 18% yield. Increasing the catalyst and base load or applying longer reaction times in DMF (*N*,*N*-dimethylformamide) did not improve the result. This prompted us to reevaluate the process in order to determine if any benefits would result from the appropriate choice of ligand, base, or additive in the reaction between **1** and **2a** (Table 1).

First, we observed that the amount of pivalic acid is an important feature since an improvement of the yield from 18% to 30% was achieved when 60 mol % of PivOH was used (Table 1, entries 1 and 2). A further increase in the amount of pivalic acid above 60 mol % does not improve the yield beyond that observed with 60 mol %. In another set of experiments, a variety of phosphine ligands were screened. It was observed that the use of strong σ-donor phosphines or such with a wide cone angle led to a decrease in yield (entries 1−4). This is in sharp contrast to previous reports concerning direct arylations of related heterocycles.[5] Indeed, we found a correlation between the phosphine cone angle and the yield,[12] wherein reduced phosphine cone angles increase the catalyst activity (entries 2−7), and therefore, better results of product **3a** were

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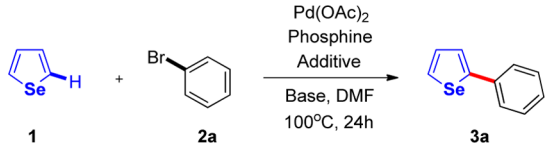
Table 1. Optimization of Direct Arylation of Selenophene[a]



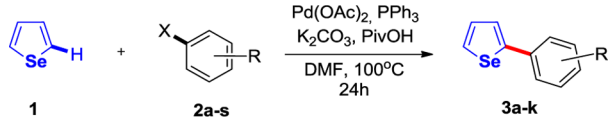
entry	phosphine (mol %)	additive (mol %)	base	yield[b] (%)
1	$PCy_3{\cdot}HBF_4$ (8)	PivOH (30)	K_2CO_3	18
2	$PCy_3{\cdot}HBF_4$ (8)	PivOH (60)	K_2CO_3	30
3	$P(t\text{-}Bu)_2Me{\cdot}HBF_4$ (8)	PivOH (60)	K_2CO_3	46
4	$P(o\text{-}tol)_3$ (8)	PivOH (60)	K_2CO_3	8
5	XPhos (8)	PivOH (60)	K_2CO_3	55
6	PPh_3 (8)	PivOH (60)	K_2CO_3	73
7	**PPh_3 (16)**	**PivOH (60)**	**K_2CO_3**	**82**
8	PPh_3 (16)	PivOH (60)	Cs_2CO_3	37
9	PPh_3 (16)	PivOH (60)	K_3PO_4	46
10	PPh_3 (16)	PivOH (60)	KOAc	68
11	PPh_3 (16)	butyric acid (60)	K_2CO_3	42
12	PPh_3 (16)	AcOH (60)	K_2CO_3	71
13	PPh_3 (16)	CF_3CO_2H (60)	K_2CO_3	29
14	PPh_3 (16)	HCO_2H (60)	K_2CO_3	0
15[c]		PivOH (60)	K_2CO_3	80
16[d]	PPh_3 (8)	PivOH (60)	K_2CO_3	60

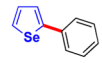
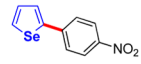
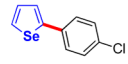
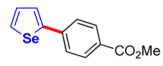
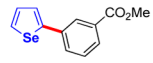
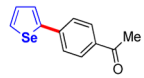
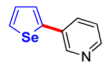
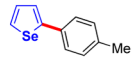
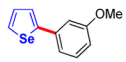
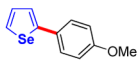
[a]Conditions: **2a** (0.1 mmol, 1 equiv), **1** (3 equiv), base (3 equiv), acid additive (mol %), $Pd(OAc)_2$ (4 mol %), phosphine (mol %), DMF (1 mL), under 24 h and 100 °C. [b]HPLC assay yield. [c]$Pd(PPh_3)_4$ (4 mol %). [d]$PdCl_2(PPh_3)_2$ (4 mol %).

reached with PPh_3 as ligand (entries 6 and 7, respectively). The observation that less bulky, electron-deficient phosphines can provide a better outcome in direct arylation has previously been noted.[13] It is plausible that the use of such ligands may facilitate the arene binding by creating a more electron-deficient palladium metal atom or by providing a vacant site for arenes undergoing an easy displacement from the metal center.[14] Additionally, by increasing the amount of PPh_3 to 16 mol %, higher yields were achieved (82%) (entry 7). Several bases and acid additives were tested (entries 7−14), and we found that the combination of PPh_3−$Pd(OAc)_2$ with PivOH−K_2CO_3 afforded the best yields of 2-phenylselenophene (**3a**). Further screening of the palladium sources showed that $Pd(PPh_3)_4$ and $PdCl_2(PPh_3)_2$ also proved to be effective for this method (entries 15 and 16). It is worth mentioning that the formation of 2,5-diarylation side reaction product was observed only in small amounts.

To explore the scope and limitation of this method, the coupling reactions between a variety of aryl halides (**2a−s**) and selenophene (**1**) were investigated under the improved conditions (Table 2). In each case, the reaction regioselectively provided the 2-arylation product in moderate to excellent yield (30−93%). The reaction is compatible with a variety of functional groups, such as oxo, nitro, ester, ether or halogen substituents. Both electron-withdrawing (entries 3−12) and electron-releasing (entries 13−19) aryl halides were found to be reactive. Direct arylation of selenophene **1** is also successful with heteroaryl bromides, such as 3-bromopyridine, to provide the desired coupling product in 70% yield (entry 12). The effect of steric hindrance at the aryl group was briefly evaluated. Arylation occurred with 1-bromo-2-methylbenzene (entry 15) in similar yield (65%) as with the *para* derivative (entry 13), but no conversion was observed with 2-bromo-1,3,5-trimethyl-

Table 2. Scope of the Direct Arylation of Selenophene (1)[a]



entry	Product **3**		Aryl Halide (**X**)	Yield (%)[b]
1		**3a**	Br	82
2			I	93
3		**3b**	Br	78
4			I	90
5		**3c**	Br	64
6		**3d**	Br	56
7			I	68
8		**3e**	Br	55
9			I	65
10		**3f**	Br	40
11			I	60
12		**3g**	Br	70
13		**3h**	Br	50
14			I	57
15		**3i**	Br	65
16		**3j**	Br	60
17			I	69
18		**3k**	Br	30
19[c]			I	47

[a]Conditions: aryl halide (**2a−s**) (0.5 mmol, 1 equiv), **1** (3 equiv), $Pd(OAc)_2$ (4 mol %), PPh_3 (16 mol %), PivOH (60 mol %), K_2CO_3 (1.5 mmol), DMF (5 mL), 100 °C for 24 h, N_2. [b]Isolated yields. [c]48 h.

benzene. Another relevant feature of this protocol is that, surprisingly, aryl iodides react with **1** furnishing the desired products in good to excellent yields (entries 2, 4, 7, 9, 11, 14, 17, and 19). These results are in contrast to earlier reports about inhibition of such reactions due to catalyst poisoning by the iodide anion in direct arylations.[1g,15] Perhaps, in this system, the selenophene ring (**1**) binds more effectivelyto Pd and overcomes the deleterious effect of iodide anion accumulation.[16]

In order to generate 2,5-diarylselenophenes, a more than 2-fold excess of aryl iodide equivalents was used relative to selenophene (**1**), and extended reaction times and increased catalyst amounts were applied (Scheme 1). However, when the reaction was performed using 3.3 equiv of aryl iodide, no improvement on the yields were observed, and only trace of direct triarylation of selenophene was found, suggesting that this methodology is highly selective for arylation of 2,5 positions. The substituted diaryl selenophene derivatives **4a**, **4b**, and **4c** were obtained by double direct arylation in suitable yields. In addition, 2-arylated substrates can also undergo a sequential regioselective direct arylation event. Thus, the second reaction of **3b** or **3k** furnishes the interesting unsymmetrical 2,5-diaryl selenophenes **4d**, **4e**, and **4f** in

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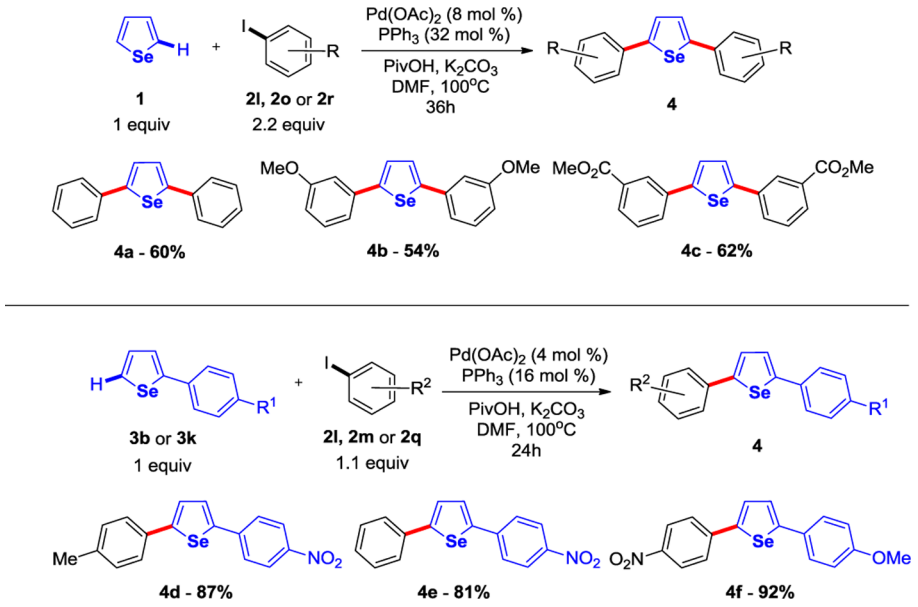
Scheme 1. Synthesis of Symmetrical and Unsymmetrical 2,5-Diarylselenophenes

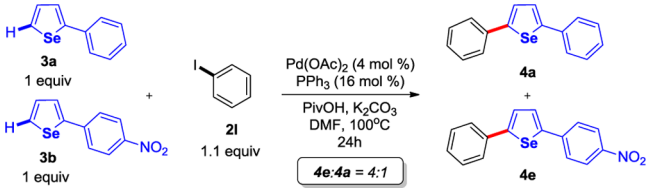


excellent yields (Scheme 1). As expected by previous studies, about distortion−interaction analysis of the C−H bond cleavage of a wide range of (hetero)aromatics through the concerted metalation−deprotonation pathway (CMD),[18a] C2-substituted aryl selenophenes were also more reactive than the parent selenophene.

Considering the importance and versatility of C−C cross-coupling reactions via direct C−H activation, it is imperative to develop a mechanistic understanding of these reactions for different substrates. Several pathways have been proposed for direct arylations.[1d,17] The S_EAr mechanism and concerted metalation deprotonation (CMD) pathways have the strongest experimental and theoretical support in reactions with π-excessive aromatics. Previous studies on the mechanism of direct arylations have highlighted the effect of a remote substituent on the reactivity of C−H bonds,[18] and since selenophenes are known to react via S_EAr in other reactions,[19] an intermolecular competition experiment was performed to determine which pathway was operative. Under the standard conditions, 1.1 equiv of iodobenzene (**2l**) was reacted in the presence of both electron-deficient 2-(4-nitrophenyl)-selenophene (**3b**) and electron-rich 2-phenylselenophene (**3a**) (Scheme 2).

Interestingly, it was seen in this intermolecular competition experiment that the aryl iodide **2l** reacted most readily with the more electron-deficient 2-(4-nitrophenyl)selenophene (**3b**) (**4e**:**4a** = 4:1), which is contrary to what would be expected if S_EAr was the acting mechanism. Furthermore, the crucial role of pivalate as proton shuttle in this regioselective direct arylation implies that the arene C−H bond functionalization would follow a CMD mechanism.

Scheme 2. Competition Experiment and Product Distribution for Direct Arylation of 2-Arylselenophenes



In an attempt to add additional insights into the reaction pathway, an experiment using selenophene (**1**) and iodobenzene (**2l**) under optimized conditions was followed by ^{31}P and ^{77}Se NMR spectroscopy.[11] For this purpose, all reagents were added in an NMR tube at room temperature, and the two peaks related to PPh_3 (δ = −5.51 ppm) and $(PPh_3)_2Pd(OAc)_2$ (δ = 25.51 ppm) (relative to 85% H_3PO_4) were quickly detected on ^{31}P NMR spectroscopy (see the Support Information). After 15 min at room temperature, the ^{31}P NMR spectrum also displayed a narrow singlet at δ = 22.43 ppm for the four-coordinate arylpalladium iodide complex $(PPh_3)_2Pd(Ar)I$,[20] indicating a fast oxidative addition of PhI on the transient 14-electron intermediate $Pd(PPh_3)_2$. The reaction was continued for more than 24 h at 100 °C, and even after this time, the ^{31}P NMR spectrum did not present any additional signal, only displaying the peak for $(PPh_3)_2Pd(OAc)_2$ (δ= 25.51 ppm), indicating that this complex is stable under these conditions. Despite the excess of PPh_3, the signal for free PPh_3 is not detected after longer reaction times, suggesting that PPh_3 is involved in at least one rapid equilibrium.[21] By following the reaction through ^{77}Se NMR, we were only able to see the peak relative to selenophene (**1**) (δ = 605.39 ppm) under the reaction conditions, and after 24 h of reaction the peak of 2-phenylselenophene (**3a**) (δ = 588.83 ppm) appeared, indicating that other possible intermediates were formed faster than the ^{77}Se NMR time scale.

On the basis of these results, a plausible reaction pathway is illustrated in Scheme 3. The oxidative addition of aryl halide (X = Br, I) to $(PPh_3)_2Pd(0)$ forms the intermediate $(PPh_3)_2Pd(Ar)X$ (**A**), which in the reaction with PivOK generates a κ^2-bound pivalate on the palladium metal (**B**). Selenophene can displace one of the carboxylate oxygens and coordinate to the metal center.[13d,22] This species can then react with selenophene through a CMD transition state (**C**) to give a biarylpalladium(II) species (**D**) that through reductive elimination gives 2-arylated selenophenes and regenerates the catalyst.

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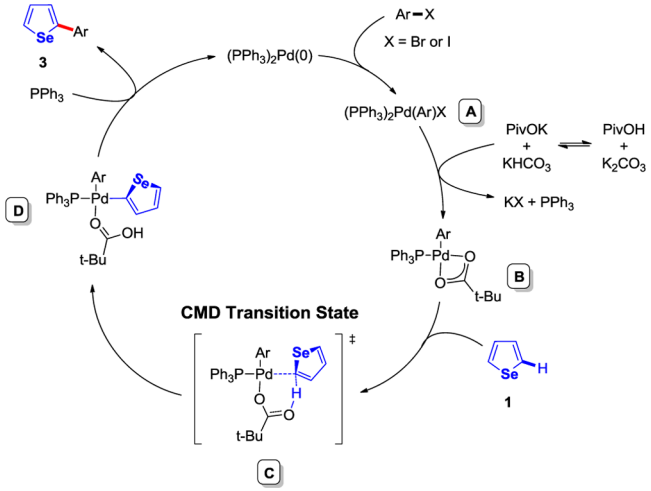
Scheme 3. Proposed Catalytic Cycle for the Direct Arylation of Selenophenes



CONCLUSION

In conclusion, an efficient palladium-catalyzed direct arylation method for selenophene regioselective at the C-2 and subsequently at the C-5-position has been developed. The versatile method allows the synthesis of a large variety of 2-aryl or symmetric 2,5-diarylselenophenes in one step in good to excellent yields. The 2-arylated substrates can undergo an additional arylation to furnish unsymmetric 2,5-diarylselenophenes in good yields. The crucial role of the acid additive, competition experiments, and ^{31}P NMR studies are also in agreement with a CMD mechanism.

EXPERIMENTAL SECTION

General Methods. All starting materials were purchased from commercial suppliers and used without further purification. All reactions were carried out under a nitrogen atmosphere in oven-dried glassware with magnetic stirring. DMF (dimethylformamide), DMA (dimethylacetamide), DMSO (dimethyl sulfoxide), and toluene were dried, purified, and degassed under classical methods.[1] Solvents used in extraction and purification were distilled prior to use. Phosphonium salts were obtained from commercial suppliers, stored in a desiccator and used without further purification. Palladium sources were stored in a desiccator and were weighed out to air unless otherwise specified. Thin-layer chromatography (TLC) was performed using silica gel 60 F254 aluminum sheets, and the visualization of the spots has been done under UV light (254 nm) or stained with iodine vapor. Products were purified by flash chromatography on silica gel 60 M, 230−400 mesh. Melting points were measured using an BX43 microscope equipped with a hot stage apparatus. HPLC analysis were performed with a LiChroCART column LiChrospher C18 100 Å 5 μm (i.d. 4 mm, length 125 mm) at 210 and 254 nm, 2−100% MeCN in water over 20 min gradient, and hold at 100% MeCN for 5 min. ^{1}H, ^{13}C, ^{31}P, and ^{77}Se NMR spectra were recorded at 300 or 400, 75 or 100, 121, and 57 MHz on a magnetic resonance spectrometer using $CDCl_3$ as solvent unless stated. The ^{1}H and ^{13}C chemical shifts were reported in parts per million (δ) referenced to residual solvent signals at $\delta_{H/C}$ 7.26/77.00 ($CDCl_3$) relative to tetramethylsilane (TMS) as internal standard. ^{31}P and ^{77}Se NMR chemical shifts were reported in parts per million (δ) referenced to 85% H_3PO_4 in D_2O and diphenyl diselenide in DMSO-d_6, respectively. Coupling constants J (Hz) were directly taken from the spectra and are not averaged. Splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). Low-resolution mass spectra were obtained with a GC−MS-QP5050 mass spectrometer interfaced with a GC-17A gas chromatograph equipped with a DB-17 MS capillary column. HRMS spectra were obtained from a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer equipped with an Infinity cell, a 7.0 T superconducting magnet, an RF-only hexapole ion guide, and an external electrospray ion source (off axis spray) and with ESI(+)-MS and tandem ESI(+)-MS/MS using a hybrid high-resolution and high accuracy MicrOTOF-Q II mass spectrometer.

General Experimental Procedure I for the Palladium-Catalyzed Direct 2-Arylation of Selenophene. A 25 mL screw-cap vial containing a magnetic stirring bar was flame-dried under vacuum and filled with nitrogen after cooling to room temperature. To this vessel were added K_2CO_3 (1.5 mmol, 3 equiv), $Pd(OAc)_2$ (4 mol %), PPh_3 (16 mol %), and PivOH (60 mol %). The aryl halide (0.5 mmol, 1 equiv) was added at this point if solid, and then DMF (0.1 M) and selenophene were added. The flask was placed in an oil bath and heated to 100 °C with constant stirring over the indicated time. After completion of the reaction, the resulting mixture was cooled to room temperature, diluted with EtOAc, washed with saturated brine (3 × 20 mL) and water (20 mL), dried over Na_2SO_4, and filtered. The residue obtained was purified by flash column chromatography over silica gel (hexane/EtOAc = 98:2, unless otherwise indicated).

*2-Phenylselenophene (**3a**).*[9b] Yield: 96 mg (93%). White solid. Mp: 56−58 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.92 (d, J = 5.6 Hz, 1H), 7.56 (d, J = 7.6 Hz, 2H), 7.45 (d, J = 3.8 Hz, 1H), 7.37−7.25 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 150.8, 136.4, 130.6, 129.9, 128.9, 127.5, 126.3, 125.2. MS (EI, 70 eV): m/z 208 [M^+].

*2-(4-Nitrophenyl)selenophene (**3b**).*[22] Yield: 113 mg (90%). Yellow solid. Mp: 142−145 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.21 (d, J = 8.8 Hz, 2H), 8.11 (d, J = 5.6 Hz, 1H), 7.67 (d, J = 8.8 Hz, 2H), 7.64 (d, J = 3.8 Hz, 1H), 7.38 (dd, J = 3.9 and 5.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 147.7, 146.2, 142.5, 133.2, 131.1, 128.0, 126.5, 124.4. MS (EI, 70 eV): m/z 253 [M^+].

*2-(4-Chlorophenyl)selenophene (**3c**).*[9b] Yield: 77 mg (64%). Pale green solid. Mp: 135−138 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.93 (d, J = 5.6 Hz, 1H), 7.46 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 3.6 Hz, 1H), 7.30 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 149.3, 134.8, 130.6, 130.4, 129.1, 129.0, 127.5, 125.7. MS (EI, 70 eV): m/z 242 [M^+].

*Methyl 4-(Selenophene-2-yl)benzoate (**3d**).*[23] Yield: 90 mg (68%). White solid. Mp: 134−135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.02 (d, J = 8.0 Hz, 2H), 8.02 (d, J = 5.2 Hz, 1H), 7.61 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 3.6 Hz, 1H), 7.34 (dd, J = 5.6 and 3.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.7, 149.3, 140.6, 131.6, 130.8, 130.2, 128.8, 126.7, 126.0, 52.1. MS (EI, 70 eV): m/z 266 [M^+]. HRMS (ESI, M^+) calcd for $C_{12}H_{10}O_2Se^+$: [M + Na]$^+$ 288.9744, found [M + Na]$^+$ 288.9739.

*Methyl 3-(Selenophene-2-yl)benzoate (**3e**).* Yield: 86 mg (65%). White solid. Mp: 42−44 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.23 (s, 1H), 7.95 (m, 2H), 7.73 (d, J = 8.0 Hz, 1H), 7.53 (d, J = 4.0 Hz, 1H), 7.42 (t, J = 8.0 Hz, 1H), 7.33 (dd, J = 5.6 and 3.8 Hz, 1H), 3.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.7, 149.4, 136.7, 130.8, 130.7, 130.6, 130.5, 128.9, 128.4, 127.2, 126.0, 52.2. MS (EI, 70 eV): m/z 266 [M^+]. HRMS (ESI, M^+) calcd for $C_{12}H_{10}O_2Se^+$: [M + Na]$^+$ 288.9744, found [M + Na]$^+$ 288.9740.

*1-(4-(Selenophene-2-yl)phenyl)ethanone (**3f**).*[9b] Yield: 75 mg (60%). White solid. Mp: 125−127 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.03 (d, J = 5.5 Hz, 1H), 7.94 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 3.8 Hz, 1H), 7.35 (dd, J = 5.6 and 3.8 Hz, 1H), 2.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 197.2, 149.2, 140.7, 135.8, 131.8, 130.8, 129.1, 126.8, 126.1, 26.5. MS (EI, 70 eV): m/z 250 [M^+]. HRMS (ESI, M^+) calcd for $C_{12}H_{10}OSe^+$: [M + Na]$^+$ 272.9795, found [M + Na]$^+$ 272.9795.

*3-(Selenophene-2-yl)pyridine (**3g**).* Yield: 73 mg (70%). Light brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.83 (s, 1H), 8.51 (s, 1H), 8.03 (d, J = 5.6 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.53 (d, J = 3.8 Hz, 1H), 7.35 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 147.4, 146.3, 145.8, 134.1, 132.8, 131.8, 130.8, 126.1, 124.0. MS (EI, 70 eV): m/z 209 [M^+]. HRMS (ESI, M^+) calcd for $C_9H_7NSe^+$ [M + H]$^+$ 209.9822, found [M + H]$^+$ 209.9820.

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*2-(p-Tolyl)selenophene (**3h**).*[9b] Yield: 63 mg (57%). White solid. Mp: 27−30 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.87 (d, J = 5.6 Hz, 1H), 7.44 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 3.7 Hz, 1H), 7.28 (m, 1H), 7.15 (d, J = 7.9 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 149.4, 137.4, 133.6, 129.6, 128.9, 127.5, 125.9, 125.6, 21.2. MS (EI, 70 eV): m/z 222 [M^+].

*2-(o-Tolyl)selenophene (**3i**).*[9b] Yield: 72 mg (65%). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.00 (d, J = 5.6 Hz, 1H), 7.38 (d, J = 6.7 Hz, 1H), 7.31 (m, 1H), 7.21 (m, 4H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 149.4, 136.2, 135.6, 130.7, 130.6, 130.5, 129.6, 128.5, 127.7, 125.8, 21.2. MS (EI, 70 eV): m/z 222 [M^+].

*2-(3-Methoxyphenyl)selenophene (**3j**).*[24] Yield: 82 mg (69%). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.92 (d, J = 5.6 Hz, 1H), 7.45 (d, J = 3.8 Hz, 1H), 7.31−7.22 (m, 2H), 7.15 (d, J = 7.8, 1H), 7.01 (s, 1H), 6.83 (dd, J = 8.2 and 2.4, 1H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 159.9, 150.6, 137.7, 130.5, 130.1, 129.8, 125.4, 119.0, 112.9. 112.0, 55.3. MS (EI, 70 eV): m/z 238 [M^+]. HRMS (ESI, M^+) calcd for $C_{11}H_{10}OSe^+$ [M + H]$^+$ 238.9975, found [M + H]$^+$ 238.9971.

*2-(4-Methoxyphenyl)selenophene (**3k**).*[24] Yield: 56 mg (47%). White solid. Mp: 107−109 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.84 (d, J = 5.6 Hz, 1H), 7.48 (d, J = 8.7 Hz, 2H), 7.33 (d, J = 3.7 Hz, 1H), 7.27 (dd, J = 5.6 and 3.8, 1H), 6.88 (d, J = 8.7 Hz, 2H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 159.2, 150.6, 130.5, 128.8, 127.7, 127.5, 124.1, 114.2, 55.3. MS (EI, 70 eV): m/z 238 [M^+].

General Experimental Procedure II for the Palladium-Catalyzed Direct 2,5-Arylation of Selenophene. A 50 mL screw-cap vial containing a magnetic stirring bar was flame-dried under vacuum and filled with nitrogen after cooling to room temperature. To this vessel were added K_2CO_3 (2.2 equiv), $Pd(OAc)_2$ (8 mol %), PPh_3 (32 mol %), and PivOH (60 mol %). The aryl halide (2.2 equiv) was added at this point if solid. After, DMF (0.1 M) and selenophene (1 equiv) were added. The flask was placed in an oil bath and heated to 100 °C with constant stirring over the indicated time. After completion of the reaction, the resulting mixture was cooled to room temperature, diluted with EtOAc, washed with saturated brine (3 × 30 mL) and water (30 mL), dried over Na_2SO_4, and filtered. The residue obtained was purified by flash column chromatography over silica gel (hexane/EtOAc = 95:5, unless otherwise indicated).

*2-Diphenylselenophene (**4a**).*[9b] Yield: 511 mg (60%). White solid. Mp: 172−173 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.56 (d, J = 7.3 Hz, 4H), 7.44 (s, 2H), 7.36 (t, J = 7.5 Hz, 4H), 7.27 (t, J = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 149.8, 136.3, 128.9, 127.6, 126.2, 126.0. MS (EI, 70 eV): m/z 284 [M^+].

*2,5-Bis(3-methoxyphenyl)selenophene (**4b**).* Yield: 556 mg (54%). Pale orange solid. Mp: 73−74 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.44 (s, 2H), 7.29 (t, J = 7.9 Hz, 2H), 7.16 (d, J = 7.8 Hz, 2H), 7.10 (m, 2H), 6.84 (dd, J = 8.2 and 2.0 Hz, 2H), 3.86 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 160.0, 149.7, 137.6, 129.9, 126.3, 118.7, 113.1, 111.7, 55.3.MS (EI, 70 eV): m/z 344 [M^+]. HRMS (ESI, M^+) calcd for $C_{18}H_{16}O_2Se^+$ [M + H]$^+$ 345.0394, found [M + H]$^+$ 345.0383.

*Dimethyl 3,3′-(Selenophene-2,5-diyl)dibenzoate (**4c**).* Yield: 743 mg (62%). Green solid. Mp: 119−120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.23 (s, 2H), 7.95 (d, J = 7.7 Hz, 2H), 7.73 (d, J = 7.8 Hz, 2H), 7.53 (s, 2H), 7.44 (t, J = 7.8 Hz, 2H), 3.95 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.6, 149.1, 136.4, 130.9, 130.2, 129.0, 128.6, 127.0, 126.9, 52.2. MS (EI, 70 eV): m/z 400 [M^+]. HRMS (ESI, M^+) calcd for $C_{20}H_{16}O_4Se^+$ [M + Na]$^+$ 423.0112, found [M + Na]$^+$ 423.0112.

General Experimental Procedure III for the Synthesis of Unsymmetrical 2,5-Diarylselenophenes. A 25 mL screw-cap vial containing a magnetic stirring bar was flame-dried under vacuum and filled with nitrogen after cooling to room temperature. To this vessel were added K_2CO_3 (1.1 equiv), $Pd(OAc)_2$ (4 mol %), PPh_3 (16 mol %), and PivOH (60 mol %). The aryl halide (1.1 equiv) was added at this point. After, DMF (0.1 M) and 2-(4-nitrophenyl)selenophene (**3b**) (1 equiv) were added. The flask was placed in an oil bath and heated to 100 °C with constant stirring over the indicated time. After completion of the reaction, the resulting mixture was cooled to room temperature, diluted with EtOAc, washed with saturated brine (3 × 20 mL) and water (20 mL), dried over Na_2SO_4, and filtered. The residue obtained was purified by flash column chromatography over silica gel (hexane/EtOAc = 96:4).

*2-(4-Nitrophenyl)-5-(p-tolyl)selenophene (**4d**).*[25] Yield: 298 mg (87%). Yellow solid. Mp: Cr 180.6 °C, N 193.7 °C I. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.25 (d, J = 8.9 Hz, 2H), 7.71−7.63 (m, 4H), 7.50 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 7.9 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 153.6, 145.7, 142.5, 138.5, 132.9, 129.8, 129.2, 129.1, 126.2, 126.1, 124.5, 21.3. MS (EI, 70 eV): m/z 343 [M^+]. HRMS (ESI, M^+) calcd for $C_{17}H_{13}NO_2Se^+$: [M + H]$^+$ 344.0190, found [M + H]$^+$ 344.0189.

*2-(4-Nitrophenyl)-5-phenylselenophene (**4e**).*[6] Mp: 208−210 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.22 (d, J = 8.9, 2H), 7.69−7.57 (m, 5H), 7.50 (d, J = 4.1 Hz, 1H), 7.24−7.33 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 165.0, 153.4, 146.7, 146.4, 142.5, 135.7, 129.1, 128.4, 126.6, 126.2, 126.1, 124.4. MS (EI, 70 eV): m/z 329 [M^+]. HRMS (ESI, M^+) calcd for $C_{16}H_{11}NO_2Se^+$: [M + H]$^+$ 330.0033, found [M + H]$^+$ 330.0031.

*2-(4-Methoxyphenyl)-5−4-(nitrophenyl)selenophene (**4f**).*[25] Mp: Cr 170.2 °C, N 220.0 °C I. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.15 (d, J = 8.9, 2H), 7.58 (d, J = 8.9, 2H), 7.53 (d, J = 4.1 Hz, 1H), 7.45 (d, J = 8.8, 2H), 7.31 (d, J = 4.1, 1H), 6.86 (d, J = 8.8, 2H), 3.78 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 159.9, 153.4, 145.2, 142.6, 129.2, 128.6, 127.6, 127.5, 125.9, 125.5, 124.5, 114.5, 55.4. MS (EI, 70 eV): m/z 359 [M^+]. HRMS (ESI, M^+) calcd for $C_{17}H_{13}NO_3Se^+$: 359.0061, found 359.0094.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Complete set of conditions for the reaction optimization, competition experiment, and ^{1}H, ^{13}C, and ^{31}P NMR spectra of compounds **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: paulos@iq.ufrgs.br.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147. (b) Ackermann, L.; Vicente, R.; Kapdi, A. R. *Angew. Chem., Int. Ed.* **2009**, *48*, 9792. (c) Chen, X.; Engle, K. M.; Wang, D.-H.; Yu, J.-Q. *Angew. Chem., Int. Ed.* **2009**, *48*, 5094. (d) Ackermann, L. *Chem. Rev.* **2011**, *111*, 1315. (e) Campeau, L.-C.; Stuart, D. R.; Fagnou, K. *Aldrichimica Acta* **2007**, *40*, 35. (f) Seregina, I. V.; Gevorgyan, V. *Chem. Soc. Rev.* **2007**, *36*, 1173. (g) Campeau, L.-C.; Fagnou, K. *Chem. Commun.* **2006**, 1253. (h) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174.

(2) Espinet, P.; Echavarren, E. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 4704.

(3) Suzuki, A. *Angew. Chem., Int. Ed.* **2011**, *50*, 6722.

(4) Negishi, E.-I. *Angew. Chem., Int. Ed.* **2011**, *50*, 6738.

(5) (a) Liégault, B.; Lapointe, D.; Caron, L.; Vlassova, A.; Fagnou, K. *J. Org. Chem.* **2009**, *74*, 1826. (b) Guchhait, S. K.; Kandekar, S.; Kashyap, M.; Taxak, N.; Bharatam, P. V. *J. Org. Chem.* **2012**, *77*, 8321. (c) Ueda, K.; Yanagisawa, S.; Yamaguchi, J.; Itami, K. *Angew. Chem., Int. Ed.* **2010**, *49*, 8946. (d) Reddy, V. P.; Qiu, R.; Iwasaki, T.; Kambe, N. *Org. Lett.* **2013**, *15*, 1290. (e) Bensaid, S.; Roger, J.; Beydoun, K.; Roy, D.; Doucet, H. *Synth. Commun.* **2011**, *41*, 3524. (f) Campeau, L.-

C.; Rousseaux, S.; Fagnou, K. *J. Am. Chem. Soc.* **2005**, *127*, 18020. (g) Campeau, L.-C.; Stuart, D. R.; Leclerc, J.-P.; Bertrand-Laperle, M.; Villemure, E.; Sun, H.-Y.; Lasserre, S.; Guimond, N.; Lecavallier, M.; Fagnou, K. *J. Am. Chem. Soc.* **2009**, *131*, 3291. (h) Carrër, A.; Brinet, D.; Florent, J.-C.; Rousselle, P.; Bertounesque, E. *J. Org. Chem.* **2012**, *77*, 1316. (i) Chen, L.; Bruneau, C.; Dixneuf, P. H.; Doucet, H. *Green Chem.* **2012**, *14*, 1111. (j) Fu, H. Y.; Chen, L.; Doucet, H. *J. Org. Chem.* **2012**, *77*, 4473. (k) Yokooji, A.; Satoh, T.; Miura, M.; Nomura, M. *Tetrahedron.* **2004**, *60*, 6757. (l) Tamba, S.; Okubo, Y.; Tanaka, S.; Monguchi, D.; Mori, A. *J. Org. Chem.* **2010**, *75*, 6998. (m) Tamba, S.; Fuji, R.; Mori, A.; Hara, K.; Koumura, N. *Chem. Lett.* **2011**, *40*, 922. (n) Do, H.-Q.; Khan, R. M. K.; Daugulis, O. *J. Am. Chem. Soc.* **2008**, *130*, 15185.

(6) (a) Rhoden, C. R. B.; Zeni, G. *Org. Biomol. Chem.* **2011**, *9*, 1301. (b) Beletskaya, I. P.; Ananikov, V. P. *Chem. Rev.* **2011**, *111*, 1596.

(7) (a) Nogueira, C. W.; Zeni, G.; Rocha, J. B. T. *Chem. Rev.* **2004**, *104*, 6255. (b) Mugesh, G.; du Mont, W.-W.; Sies, H. *Chem. Rev.* **2001**, *101*, 2125. (c) Nascimento, V.; Alberto, E. E.; Tondo, D. W.; Dambrowski, D.; Detty, M. R.; Nome, F.; Braga, A. L. *J. Am. Chem. Soc.* **2012**, *134*, 138. (d) Shabaan, S.; Ba, L. A.; Abbas, M.; Burkholz, T.; Denkert, A.; Gohr, A.; Wessjohann, L. A.; Sasse, F.; Weber, W.; Jacob, C. *Chem. Commun.* **2009**, 4702. (e) Doering, M.; Ba, L. A.; Lilienthal, N.; Nicco, C.; Scherer, C.; Abbas, M.; Zada, A. L. P.; Coriat, R.; Burkholz, T.; Wessjohann, L. A.; Diederich, M.; Batteux, F.; Herling, M.; Jacob, C. *J. Med. Chem.* **2010**, *53*, 6954.

(8) (a) Kim, B.; Yeom, H. R.; Yun, M. H.; Kim, J. Y.; Yang, C. *Macromolecules* **2012**, *45*, 8658. (b) Gao, D.; Hollinger, J.; Seferos, D. S. *ACS Nano* **2012**, *6*, 7114. (c) Edmund, F.; McNeil, P.; McNeil, A. J. *Macromolecules* **2012**, *45*, 5948. (d) Haid, S.; Mishra, A.; Uhrich, C.; Pfeiffer, M.; Bäuerle, P. *Chem. Mater.* **2011**, *23*, 4435. (e) Okamoto, T.; Kudoh, K.; Wakamiya, A.; Yamaguchi, S. *Org. Lett.* **2005**, *7*, 5301. (f) Takimiya, K.; Kunugi, Y.; Konda, Y.; Ebata, H.; Toyotakimia, Y.; Otsubo, T. *J. Am. Chem. Soc.* **2006**, *128*, 3044. (g) Patra, A.; Wijsboom, Y. H.; Leitus, G.; Bendikov, M. *Chem. Mater.* **2011**, *23*, 896. (h) *Handbook of Thiophene-based Materials*; Perepichka, I. F., Perepichka, D. F., Eds.; Wiley-VCH: Weinheim, 2009. (i) Rampon, D. S.; Rodembusch, F. S.; Schneider, J. M. F. M.; Bechtold, I. H.; Gonçalves, P. F. B.; Merlo, A. A.; Schneider, P. H. *J. Mater. Chem.* **2010**, *20*, 715. (j) Mei, J.; Diao, Y.; Appleton, A. L.; Fang, L.; Bao, Z. *J. Am. Chem. Soc.* **2013**, *135*, 6724.

(9) (a) Prediger, P.; Brandão, R.; Nogueira, C. W.; Zeni, G. *Eur. J. Org. Chem.* **2007**, 5422. (b) Prediger, P.; Moro, A. V.; Nogueira, C. W.; Savegnago, L.; Menezes, P. H.; Rocha, J. B. T.; Zeni, G. *J. Org. Chem.* **2006**, *71*, 3786. (c) Barros, O. S. R.; Nogueira, C. W.; Stangherlin, E. C.; Menezes, P. H.; Zeni, G. *J. Org. Chem.* **2006**, *71*, 1552. (d) Barros, O. S. R.; Favero, A.; Nogueira, C. W.; Menezes, P. H.; Zeni, G. *Tetrahedron Lett.* **2006**, *47*, 2179. (e) Schumacher, R. F.; Alves, D.; Brandão, R.; Nogueira, C. W.; Zeni, G. *Tetrahedron Lett.* **2005**, *46*, 2647. (f) Schumacher, R. F.; Alves, D.; Brandão, R.; Nogueira, C. W.; Zeni, G. *Tetrahedron Lett.* **2008**, *49*, 538. (g) Alghamdi, A. A. B.; Watters, D. C.; Yi, H.; Al-Faifi, S.; Almeataq, M. S.; Coles, D.; Kingsley, J.; Lidzey, D. G.; Iraqi, A. *J. Mater. Chem. A* **2013**, *1*, 5165. (h) Stedt, T.; Frejd, T. *Organometallics* **1983**, *5*, 598. (i) Takahashi, K.; Gunji, A. *Heterocycles* **1996**, *43*, 941. (j) Shabana, R.; Galal, A.; Mark, H. B., Jr.; Zimmer, H.; Gronowitz, S.; Hörnfeldt, A.-B. *Phosphorus, Sulfur Silicon Relat. Elem.* **1990**, 239.

(10) (a) Rampon, D. S.; Rodembusch, F. S.; Lourega, R.; Gonçalves, P. F. B.; Merlo, A. A.; Schneider, P. H. *J. Braz. Chem. Soc.* **2010**, *21*, 2100. (b) Rampon, D. S.; Giovenardi, R.; Silva, T. L.; Rambo, R. S.; Merlo, A. A.; Schneider, P. H. *Eur. J. Org. Chem.* **2011**, 7066. (c) Radatz, C. S.; Alves, D.; Schneider, P. H. *Tetrahedron* **2013**, *28*, 1316. (d) Schwab, R. S.; Schneider, P. H. *Tetrahedron* **2012**, *23*, 10499. (e) Abbas, M.; Wessjohann, L. A. *Org. Biomol. Chem.* **2012**, *10*, 9330.

(11) See the Supporting Information for details.

(12) (a) Bilbrey, J. A.; Kazez, A. H.; Locklin, J.; Allen, W. D. *J. Comput. Chem.* **2013**, *34*, 1189. (b) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(13) (a) Yanagisawa, S.; Sudo, T.; Noyori, R.; Itami, K. *J. Am. Chem. Soc.* **2006**, *128*, 11748. (b) Hitce, J.; Retailleau, P.; Baudoin, O. *Chem.—Eur. J.* **2007**, *13*, 792. (c) Campeau, L.-C.; Parisien, M.; Leblanc, M.; Fagnou, K. *J. Am. Chem. Soc.* **2004**, *126*, 9186. (d) Lafrance, M.; Lapointe, D.; Fagnou, K. *Tetrahedron.* **2008**, *64*, 6015. (e) Engle, K. M.; Wang, D.-H.; Yu, J.-Q. *J. Am. Chem. Soc.* **2010**, *132*, 14137. (f) Zhuravlev, F. A. *Tetrahedron Lett.* **2006**, *47*, 2929.

(14) (a) Biswas, B.; Sugimoto, M.; Sakaki, S. *Organometallics* **2000**, *19*, 3895. (b) René, O.; Fagnou, K. *Adv. Synth. Catal.* **2010**, *352*, 2116.

(15) (a) Campeau, L.-C.; Parisien, M.; Jean, A.; Fagnou, K. *J. Am. Chem. Soc.* **2006**, *128*, 581. (b) Leclerc, J.-P.; Fagnou, K. *Angew. Chem., Int. Ed.* **2006**, *46*, 7781. (c) Wang, J.-X.; McCubbin, J. A.; Jin, M.; Laufer, R. S.; Mao, Y.; Crew, A. P.; Mulvihill, M. J.; Snieckus, V. *Org. Lett.* **2008**, *10*, 2923.

(16) Amatore, C.; Jutand, A. *Acc. Chem. Res.* **2000**, *33*, 314.

(17) Gallego, G. M.; Sierra, M. A. *Chem. Rev.* **2011**, *111*, 4857.

(18) (a) Gorelsky, S. I.; Lapointe, D.; Fagnou, K. *J. Org. Chem.* **2012**, *77*, 658. (b) Lane, B. S.; Brown, M. A.; Sames, D. *J. Am. Chem. Soc.* **2005**, *127*, 8050.

(19) (a) Lebedev, M. V.; Nenajdenko, V. G.; Balenkova, E. S. *Synthesis* **1998**, 89. (b) Cyranski, M. K.; Krygowski, T. M. *Topics in Heterocyclic Chemistry: Aromaticity in Heterocyclic Compounds*; Springer: Heidelberg, 2009. (c) Umezawa, S. *Bull. Chem. Soc. Jpn.* **1936**, *11*, 775. (d) Yur'ev, Yu. K.; Zaitseva, E. L.; Rozantsev, G. G. *Zh. Obshch. Khim.* **1960**, *30*, 2207. (e) Kim, K.; Jo, C.; Easwaramoorthi, S.; Sung, J.; Kim, D. H.; Churchill, D. G. *Inorg. Chem.* **2010**, *49*, 4881. (f) Arena, G.; Cali, R.; Maccarone, E.; Passerini, A. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1941.

(20) (a) Amatore, C.; Pflüger, F. *Organometallics* **1990**, *9*, 2276. (b) Fauvarque, J.-F.; Pflüger, F. *J. Organomet. Chem.* **1981**, *208*, 419. (c) Amatore, C.; Azzabi, M.; Jutand, A. *J. Am. Chem. Soc.* **1991**, *113*, 8375. (d) Negishi, E.-I.; Takahashi, T.; Akiyoshi, K. *J. Chem. Soc., Chem. Commun.* **1986**, 1338.

(21) Amatore, C.; Carré, E.; Jutand, A.; M'Barki, M. R. *Organometallics* **1995**, *14*, 1818.

(22) (a) Gronowitz, S.; Johnson, I.; Hornfeldt, A. B. *Chem. Scr.* **1975**, *7*, 111. (b) Ng, S.-C.; Xu, L. *Adv. Mater.* **1998**, *18*, 1525.

(23) Matyushecheva, G. I.; Tolmachev, A. I.; Shulezhko, A. A.; Shulezhko, L. M.; Yagupolskii, L. M. *Zh. Obshch. Khim.* **1976**, *46*, 162.

(24) Fringuelli, F.; Serena, B.; Taticchi, A. *J. Am. Chem. Soc., Perkin Trans. 2* **1980**, *7*, 971.

(25) Prim, D.; Joseph, D.; Kirsch, G. *Phosphorus, Sulfur Silicon Relat. Elem.* **1994**, *1*−*4*, 137.