SUPPORTING INFORMATION

Catalytic Direct Cross-Coupling of Organolithium Compounds with Aryl chlorides

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General methods:

All reactions were carried out under a nitrogen atmosphere using oven-dried glassware and using standard Schlenk techniques. THF and toluene were dried and distilled over sodium. Pd$_2$(dba)$_3$, SPhos, XPhos, DavePhos, CPhos, QPhos, P'(Bu)$_3$, PCy$_3$, and Pd-PEPPSI-Ipent were purchased from Aldrich and used without further purification. BuLi (1.6 M solution in hexane) and PhLi (1.8 M solution in dibutylether) were purchased from Acros. ThiénylLi (1.0 M in THF/hexane), tert-BuLi (1.7 M in pentane) and the compounds used as precursor for the preparation of lithium reagents, namely furan, 1-bromo-2,3-dimethyl-benzene, 1-bromo-2-methoxybenzene and 1-bromo-2-(methoxymethoxy)benzene were purchased from Aldrich. All the chlorides were commercially available and were purchased from TCI Europe N.V. with the exception of 1-chloro-4-methoxybenzene (Aldrich). Organolithium reagents other than the aforementioned were prepared according to described procedures (see below).

Chromatography: Merck silica gel type 9385 230-400 mesh. TLC: Merck silica gel 60, 0.25 mm. Components were visualized by UV and cerium/molybdenum or potassium permanganate staining. Progress and conversion of the reaction were determined by GC-MS (GC, HP6890; MS HP5973) with an HP1 or HP5 column (Agilent Technologies, Palo Alto, CA). Mass spectra were recorded on an AEI-MS-902 mass spectrometer (EI+) or a LTQ Orbitrap XL (ESI+). $^1$H- and $^{13}$C-NMR were recorded on a Varian AMX400 (400 and 100.59 MHz, respectively) using CDCl$_3$ as solvent. Chemical shift values are reported in ppm with the solvent resonance as the internal standard (CHCl$_3$; $\delta$ 7.26 for $^1$H, $\delta$ 77.0 for $^{13}$C). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiple), coupling constants (Hz), and integration. Carbon assignments are based on APT $^{13}$C-NMR experiments.

Optimization Study: Additional Data

Table S1. Additional optimization data of the reaction between 1a and PhLi

<table>
<thead>
<tr>
<th>entry*</th>
<th>[Pd]</th>
<th>Ligand</th>
<th>Conv. (%)</th>
<th>2a:3:4:5$^{*}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd$_2$(dba)$_3$</td>
<td>L4,SPhos</td>
<td>55</td>
<td>51:0:0:4</td>
</tr>
<tr>
<td>2</td>
<td>Pd$_2$(dba)$_3$</td>
<td>L5,DavePhos</td>
<td>58</td>
<td>48:0:0:11</td>
</tr>
<tr>
<td>3</td>
<td>Pd$_2$(dba)$_3$</td>
<td>L6,CPhos</td>
<td>79</td>
<td>68:0:0:11</td>
</tr>
<tr>
<td>4</td>
<td>Pd$_2$(dba)$_3$</td>
<td>L7,QPhos</td>
<td>42</td>
<td>32:0:0:10</td>
</tr>
</tbody>
</table>

*Conditions: PhLi (0.45 mmol, 1.8 M solution in dibutylether diluted with THF to a final concentration of 0.6 M) was added to a solution of 2-chloronaphthalene (0.3 mmol) in toluene (2 mL, unless otherwise noted). $^*2a:3:4:5$ ratios determined by GC analysis. $^*7.5$ mol% was used. $^*In 1 mL of toluene. dba = dibenzylideneacetone.
Table S2. Additional optimization data of the reaction between 1m and PhLi

<table>
<thead>
<tr>
<th>entry</th>
<th>[Pd]</th>
<th>T°C</th>
<th>PhLi flow-rate (mL/h)</th>
<th>Conv. (%)</th>
<th>2m:6:7b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd(dba)</td>
<td>50</td>
<td>1</td>
<td>76</td>
<td>70:3:7</td>
</tr>
<tr>
<td>2</td>
<td>Pd(dba)</td>
<td>50</td>
<td>0.33</td>
<td>Full</td>
<td>88:1:1:2</td>
</tr>
<tr>
<td>3</td>
<td>Pd(dba)</td>
<td>35</td>
<td>0.33</td>
<td>64</td>
<td>61:1:1:3</td>
</tr>
<tr>
<td>4</td>
<td>Pd(dba)</td>
<td>40</td>
<td>0.33</td>
<td>82</td>
<td>77:1:5</td>
</tr>
<tr>
<td>5</td>
<td>Pd(dba)</td>
<td>45</td>
<td>0.33</td>
<td>80</td>
<td>70:4:6</td>
</tr>
<tr>
<td>6</td>
<td>Pd(dba)</td>
<td>40</td>
<td>0.33</td>
<td>96</td>
<td>86:2:8</td>
</tr>
<tr>
<td>7</td>
<td>Pd(dba)</td>
<td>40</td>
<td>0.2</td>
<td>Full</td>
<td>89:3:8</td>
</tr>
<tr>
<td>8</td>
<td>Pd-PEPSI-Ipent</td>
<td>40</td>
<td>0.2</td>
<td>Full</td>
<td>90:4:6</td>
</tr>
<tr>
<td>9</td>
<td>Pd-PEPSI-Ipent</td>
<td>30</td>
<td>0.2</td>
<td>90</td>
<td>81:3:4</td>
</tr>
</tbody>
</table>

*Conditions: Phenyllithium (1.8 M solution in diethyl ether diluted with THF to a final concentration of 0.6 M) was added to a solution of 1-buty1-4-chlorobenzene (0.3 mmol) in toluene (2 mL, unless otherwise noted). 2m:6:7 ratios determined by GC analysis. *1m in 1 mL of toluene. 4Phenyllithium was diluted with toluene (instead of THF) to reach 0.6 M concentration. dba, dibenzylideneacetone.

Scheme S1. Pd-catalyzed cross-coupling of aryl lithium reagents with deactivated aryl chlorides: Scope Limitations

The Pd-catalyzed cross-coupling with aryl lithium reagents did not proceed efficiently when very deactivated aryl chlorides were used. The reaction between 4-(4-chlorophenyl)morpholine 1t and PhLi led to low conversion and a mixture of products while the use of 6-chloroindole 1u gave no reaction. Although it was used efficiently in the Pd-catalyzed cross-coupling with activated aryl chlorides, the less reactive thienyl lithium could not be coupled with deactivated and hindered aryl chlorides.
General procedures for the cross-coupling of aryl lithium reagents with aryl chlorides

Catalytic system A:
In a dry Schlenk flask Pd-PEPPSI-IPent (5 mol%, 0.015 mmol, 11.9 mg) and the substrate (0.3 mmol) were dissolved in 1 mL of dry toluene and the solution was stirred at the indicated temperature. The corresponding lithium reagent (1.5 equiv) was diluted with THF to reach the concentration of 0.6 M; this solution was slowly added with the indicated flow rate by the use of a syringe pump. After the addition was completed a saturated aqueous solution of NH$_4$Cl was added and the mixture was extracted with ether (3 x 5 mL). The organic phases were combined and dried with anhydrous Na$_2$SO$_4$. Evaporation of the solvent under reduced pressure afforded the crude product that was then purified by column chromatography.

Note: Thiényllithium (1.5 equiv) was diluted with toluene to reach a concentration of 0.6 M and TMEDA (1.5 equiv) was added. The resulting solution was slowly added with a flow rate of 0.5 mL/h to the reaction mixture warmed at 40 °C.

Catalytic system B:
In a dry Schlenk flask Pd$_2$(dba)$_3$ (2.5 mol%, 0.0075 mmol, 6.87 mg) and XPhos (10 mol%, 0.03 mmol, 14.3 mg) were dissolved in toluene, the substrate (0.3 mmol) was added and the solution stirred at the indicated temperature. The corresponding lithium reagent (1.5 equiv) was diluted with THF to reach a concentration of 0.6 M; this solution was slowly added with the indicated flow rate by the use of a syringe pump. After the addition was completed a saturated solution of aqueous NH$_4$Cl was added and the mixture was extracted with ether (3 x 5 mL). The organic phases were combined and dried with anhydrous Na$_2$SO$_4$. Evaporation of the solvent under reduced pressure afforded the crude product that was then purified by column chromatography.

Preparation of organolithium reagents:

A. 2,3-Dimethyl-phenyllithium and 2-Methoxy-phenyllithium
In a dry Schlenk flask the corresponding aryl bromide (1.8 mmol) was dissolved in dry THF (0.9 mL) and the solution was cooled down to -78 °C. tBuLi (2 equiv) was added slowly and the solution was stirred for 1 h. Then the solution was allowed to reach room temperature.

B. Furyllithium
Furan (9.0 mmol, 612.6 mg, 654.5 µl) was dissolved in THF (4.5 mL) and the solution was cooled down to -40 °C. nBuLi (8.5 mmol) was added slowly. Then the solution was allowed to reach room temperature, stirred for 3 h and diluted with 4.4 mL of THF to reach a final concentration of 0.6M.

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C. 2-Methoxymethoxy-phenyllithium\(^2\)

In a dry Schlenk flask (methoxymethoxy)benzene (1.0 mmol, 138 mg) was dissolved in dry THF (3 mL) and the solution was cooled down to -78 °C. \(^t\)BuLi (1 equiv) was added slowly and the solution was stirred for 1 h. Then the solution was allowed to reach room temperature.

D. 2-Methoxy-1-naphthyllithium

In a dry Schlenk flask 1-bromo-2-methoxynaphthalene (1.8 mmol, 427 mg) was dissolved in dry THF (0.9 mL) and slowly added (flow rate: 8 ml/h) to a solution of \(^n\)BuLi (1.6 M in hexane, 1.05 equiv.) at -10 °C. The solution was then stirred for 30 min. and allowed to reach room temperature. The solution was diluted with 1 ml of toluene to reach a final concentration of 0.6M.

Data of Compounds 2a-2s, 10

Physical data for known compounds were identical in all respects to those previously reported (references are given).

2-Phenylnaphthalene (2a):\(^3\)

CAS Registry Number: 612-94-2.
Synthesized using catalytic systems A and B with 2-chloronaphthalene (0.3 mmol, 49 mg) and 225 µL of PhLi (1.8 M solution in dibutylether) diluted with 500 µL of THF.

**Catalytic system A:** Reaction carried out at room temperature. Flow rate of PhLi solution = 0.5 mL/h. White solid obtained after column chromatography (SiO\(_2\), n-pentane/EtOAc 100:1), 54 mg, 88% yield.

**Catalytic system B:** Reaction carried out at room temperature in 2 mL of toluene. Flow rate of PhLi solution = 1 mL/h. White solid obtained after column chromatography, 57 mg, 93% yield.

1-Phenylnaphthalene (2b):\(^4\)

CAS Registry Number: 605-02-7

Synthesized using catalytic systems A and B with 1-chloronaphthalene (0.3 mmol, 49 mg) and 225 µL of PhLi (1.8 M solution in dibutylether) diluted with 500 µL of THF.

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\(^3\) Giannerini, M.; Fañánas-Mastral, M.; Feringa, B. L. Nature Chem. 2013, doi:10.1038/nchem.1678.

**Catalytic system A:** Reaction carried out at room temperature. Flow rate of PhLi solution = 0.5 mL/h. White solid obtained after column chromatography (SiO$_2$, n-pentane/EtOAc 100:1), 56 mg, 91% yield.

**Catalytic system B:** Reaction carried out at room temperature in 2 mL of toluene. Flow rate of PhLi solution = 1 mL/h. White solid obtained after column chromatography, 60 mg, 98% yield.

The reaction performed with 10 mmol (1.63 g) of substrate in the presence of 1 mol% of Pd$_2$dba$_3$ and 4 mol% of L3 afforded product 2b in 92% yield. Toluene = 30 mL. PhLi (8.3 mL, 1.8 M solution in dibutylether) diluted with 16.6 mL of THF. Flow rate of PhLi solution = 3 mL/h.

![4-(Trifluoromethyl)-1,1'-biphenyl (2c):][5]

CAS Registry Number: 398-36-7

Synthesized using catalytic systems A and B with 1-chloro-4-(trifluoromethyl)benzene (0.3 mmol, 54 mg) and 225 µL of PhLi (1.8 M solution in dibutylether) diluted with 500 µL of THF.

**Catalytic system A:** Reaction carried out at room temperature. Flow rate of PhLi solution = 0.5 mL/h. White solid obtained after column chromatography (SiO$_2$, n-pentane/EtOAc 100:1), 59 mg, 89% yield.

**Catalytic system B:** Reaction carried out at room temperature in 2 mL of toluene. Flow rate of PhLi solution = 1 mL/h. White solid obtained after column chromatography, 63 mg, 95% yield.

![2-(Naphthalen-2-yl)thiophene (2d):][6]

CAS Registry Number: 16939-09-6

Synthesized using catalytic systems A with 2-chloronaphthalene (0.3 mmol, 49 mg) and 750 µL of thienyllithium (0.6M). White solid obtained after column chromatography (SiO$_2$, n-pentane/ EtOAc 100:1), 52 mg, 82% yield.

![2-(Naphthalen-1-yl)thiophene (2e):][7]

CAS Registry Number: 16939-09-6

Synthesized using catalytic systems A with 2-chloronaphthalene (0.3 mmol, 49 mg) and 750 µL of thienyllithium (0.6M). White solid obtained after column chromatography (SiO$_2$, n-pentane/ EtOAc 100:1), 52 mg, 82% yield.

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CAS Registry Number: 4632-51-3.
Synthesized using catalytic systems A with 1-chloronaphthalene (0.3 mmol, 49 mg) and 750 µL of thienyllithium (0.6M). Colorless oil obtained after column chromatography (SiO₂, n-pentane/ EtOAc 100:1), 55 mg, 87% yield.

![2-(4-(Trifluoromethyl)phenyl)thiophene (2f)](image)

Synthesized using catalytic systems A with 1-chloro-4-(trifluoromethyl)benzene (0.3 mmol, 54 mg) and 750 µL of thienyllithium (0.6M). White solid obtained after column chromatography (SiO₂, n-pentane/ EtOAc 100:1), 57 mg, 83% yield.

2-(2,3-Dimethylphenyl)naphthalene (2g).
CAS Registry Number: 382151-52-2.
Synthesized using catalytic systems B with 2-chloronaphthalene (0.3 mmol, 49 mg) and 725 µL of 2,3-dimethyl-phenyllithium (0.6M). Reaction carried out at room temperature in 2 mL of toluene. Flow rate of 2,3-dimethyl-phenyllithium solution = 1 mL/h. White solid obtained after column chromatography (SiO₂, n-pentane/ EtOAc 100:1), 62 mg, 89% yield.

![2-(2,3-Dimethylphenyl)naphthalene (2g)](image)

1-(2-Methoxyphenyl)naphthalene (2h).
CAS Registry Number: 93321-11-0.
Synthesized using catalytic systems A with 1-chloronaphthalene (0.3 mmol, 49 mg) and 725 µL of 2-methoxy-phenyllithium (0.6M). Reaction carried out at room temperature. Flow rate of PhLi solution = 0.5 mL/h. White solid obtained after column chromatography (SiO₂, n-pentane/ EtOAc 100:1), 59 mg, 84% yield.

![1-(2-Methoxyphenyl)naphthalene (2h)](image)

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2-Methoxy-1-(4-(trifluoromethyl)phenyl)naphthalene (2i):\(^\text{11}\)
CAS Registry Number: 922511-77-1.
Synthesized using catalytic systems A with 1-chloro-4-(trifluoromethyl)benzene (0.3 mmol, 54 mg) and 725 µL of 2-methoxy-1-naphthyllithium (0.6M). Reaction carried out at room temperature. Flow rate of PhLi solution = 0.5 mL/h. White solid obtained after column chromatography (SiO\(_2\), n-pentane/ EtOAc 100:1), 70 mg, 77% yield.

1-(2-(methoxymethoxy)phenyl)naphthalene (2j):\(^\text{12}\)
CAS Registry Number: 141362-07-4.
Synthesized using catalytic systems A with 1-chloronaphthalene (0.3 mmol, 49 mg) and 1500 µL of 2-Methoxy-phenyllithium (0.3M). Reaction carried out at room temperature. Flow rate of PhLi solution = 0.5 mL/h. Waxy solid obtained after column chromatography (SiO\(_2\), n-pentane/ EtOAc 100:2), 66 mg, 83% yield.

2-(Naphthalen-1-yl)furan (2k):\(^\text{13}\)
CAS Registry Number: 51792-32-6.
Synthesized using catalytic systems A with 1-chloronaphthalene (0.3 mmol, 49 mg) and 725 µL of furyllithium (0.6M). Pale yellow oil obtained after column chromatography (SiO\(_2\), n-pentane/ EtOAc 100:1), 56 mg, 96% yield.

2-(4-(Trifluoromethyl)phenyl)furan (2l):\(^\text{14}\)

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\(^{13}\) Molander, G. A.; Beaumard, F. *Org. Lett.* 2010, 12, 4022.
CAS Registry Number: 214463-10-2.
Synthesized using catalytic systems A with 1-chloro-4-(trifluoromethyl)benzene (0.3 mmol, 54 mg) and 725 µL of furyllithium (0.6M). White solid obtained after column chromatography (SiO₂, n-pentane/ EtOAc 100:1), 49 mg, 77% yield.

4-Butyl-1,1'-biphenyl (2m):¹⁵
CAS Registry Number: 37909-95-8.
Synthesized using catalytic systems A and B with 1-butyl-4-chlorobenzene (0.3 mmol, 51 mg) and 225 µL of PhLi (1.8 M solution in dibutylether) diluted with 500 µL of THF. Catalytic system A: Reaction carried out at 35°C. Flow rate of PhLi solution = 0.2 mL/h. White solid obtained after column chromatography (SiO₂, n-pentane/ EtOAc 100:1), 54 mg, 86% yield.
Catalytic system B: Reaction carried out at 40°C in 1 mL of toluene. Flow rate of PhLi solution = 0.2 mL/h. Colorless oil obtained after column chromatography, 53 mg, 84% yield.

2,4-Dimethyl-1,1'-biphenyl (2n):¹⁶
CAS Registry Number: 4433-10-7.
Synthesized using catalytic systems A and B with 1-chloro-2,4-dimethylbenzene (0.3 mmol, 42 mg) and 225 µL of PhLi (1.8 M solution in dibutylether) diluted with 500 µL of THF. Catalytic system A: Reaction carried out at 35°C. Flow rate of PhLi solution = 0.2 mL/h. White solid obtained after column chromatography (SiO₂, n-pentane/ EtOAc 100:1), 44 mg, 80% yield.
Catalytic system B: Reaction carried out at 40°C in 1 mL of toluene. Flow rate of PhLi solution = 0.2 mL/h. Colorless oil obtained after column chromatography, 45 mg, 82% yield.

4-Methoxybiphenyl (2o):³
CAS Registry Number: 613-37-6.
Synthesized using catalytic systems A and B with 1-chloro-4-methoxybenzene (0.3 mmol, 43 mg) and 225 µL of PhLi (1.8 M solution in dibutylether) diluted with 500 µL of THF. Catalytic system A: Reaction carried out at 40°C. Flow rate of PhLi solution =

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¹⁴ Denmark, S. E.; Baird, J. D. Org. Lett. 2006, 8, 793.
0.2 mL/h. White solid obtained after column chromatography (SiO$_2$, n-pentane/ EtOAc 100:1), 52 mg, 94% yield.

**Catalytic system B:** Reaction carried out at 40°C in 1 mL of toluene. Flow rate of PhLi solution = 0.2 mL/h. Colorless oil obtained after column chromatography, 34 mg, 62% yield.

3-Methoxy-1,1'-biphenyl (2p).\(^{17}\)  
CAS Registry Number: 2113-56-6.  
Synthesized using catalytic systems A with 1-chloro-3-methoxybenzene (0.3 mmol, 43 mg) and 225 µL of PhLi (1.8 M solution in dibutylether) diluted with 500 µL of THF. Reaction carried out at 40°C. Flow rate of PhLi solution = 0.2 mL/h. Colorless oil obtained after column chromatography (SiO$_2$, n-pentane/ EtOAc 100:1), 42 mg, 76% yield.

2',5'-Dimethyl-p-terphenyl (2q).\(^{18}\)  
CAS Registry Number: 20260-22-4.  
Synthesized using catalytic systems A with 1-chloro-4-methoxybenzene (0.3 mmol, 53 mg) and 500 µL of PhLi (1.8 M solution in dibutylether) diluted with 1.5 mL of THF. Reaction carried out at 40°C. Flow rate of PhLi solution = 0.2 mL/h. Colorless oil obtained after column chromatography (SiO$_2$, n-pentane/ EtOAc 100:1), 62 mg, 80% yield.

2'-Methoxy-2,4-dimethyl-1,1'-biphenyl (2r).  
Synthesized using catalytic systems A with 2,4-dimethylbenzene (0.3 mmol, 42 mg) and 725 µL of 2-methoxy-phenyllithium (0.6M). Reaction carried out at 35°C. Flow rate of PhLi solution = 0.2 mL/h. Colorless oil obtained after column chromatography (SiO$_2$, n-pentane/ EtOAc 100:1), 55 mg, 86% yield.  
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.38 (td, $J$ = 8.2, 1.8 Hz, 1H), 7.99 – 7.20 (m, 6H), 3.81 (s, 3H), 2.41 (s, 3H), 2.16 (s, 3H) ppm.  
$^{13}$C NMR (100 MHz, CDCl$_3$) δ 156.7, 136.9, 136.6, 135.7, 131.2, 130.8, 130.5, 130.0, 128.4, 126.3, 120.4, 110.6, 55.4, 21.2, 19.9 ppm. EI-MS m/z (%) 212 (100).

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2-(4-Methoxyphenyl)furan (2s):\textsuperscript{19}

CAS Registry Number: 17113-31-4.
Synthesized using catalytic systems A with 1-chloro-4-methoxybenzene (0.3 mmol, 43 mg) and 725 µL of furyllithium (0.6M). White solid obtained after column chromatography (SiO\textsubscript{2}, n-pentane/ EtOAc 100:2), 51 mg, 80% yield.

\begin{center}
\includegraphics{2-4-Methoxyphenylfuran.png}
\end{center}

2-((1,1'-Biphenyl)-4-yl)furan (10):\textsuperscript{20}
Synthesized using catalytic systems A with 9 (0.3 mmol, 57 mg) and 725 µL of furyllithium (0.6M). White solid obtained after column chromatography (SiO\textsubscript{2}, n-pentane), 59 mg, 90% yield.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.78 (d, \(J = 8.4\) Hz, 2H), 7.69 – 7.62 (m, 4H), 7.52 (d, \(J = 1.7\) Hz, 1H), 7.48 (t, \(J = 7.6\) Hz, 2H), 7.38 (t, \(J = 7.3\) Hz, 1H), 6.72 (d, \(J = 3.3\) Hz, 1H), 6.52 (dd, \(J = 3.3, 1.7\) Hz 1H) ppm.

\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 153.8, 142.2, 140.6, 140.0, 129.9, 128.8, 127.4, 126.9, 124.2, 111.8, 105.2 ppm.

HRMS (ESI+, \textit{m/z}): calcd for C\textsubscript{16}H\textsubscript{13}O [M+H]\textsuperscript{+}: 221.09609; found: 221.09511.


$^1$H and $^{13}$C NMR spectra

![NMR Spectra](image)

2a