Supporting Information


Ehsan Ullah, James McNulty, Christine Kennedy, Al Robertson

a Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1
Tel: (+1)-905-525-9140 Ext. 27393; Fax: (+1)-905-522 2509; e-mail: jmcnult@mcmaster.ca

b Cytec Canada, Inc., P.O. Box 240, Niagara Falls, Ontario, Canada L2E 6T4

Table of Contents

<table>
<thead>
<tr>
<th>Contents</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. General Information</td>
<td>1</td>
</tr>
<tr>
<td>2. Typical Procedure for Ligands Synthesis</td>
<td>1 - 2</td>
</tr>
<tr>
<td>3. General Procedures for Suzuki-Miyaura Cross Coupling Reactions</td>
<td>4 - 6</td>
</tr>
<tr>
<td>4. New Ligands Spectroscopic Data</td>
<td>7 - 14</td>
</tr>
<tr>
<td>5. NMR and Mass Spectra of New Compounds</td>
<td>15 - 26</td>
</tr>
<tr>
<td>6. References</td>
<td>27</td>
</tr>
</tbody>
</table>
1. General Information

Reactions were carried out under nitrogen in oven-dried glassware. Diisobutylphosphine was obtained from Cytec industries, all other fine chemicals were obtained from Aldrich. CIMS were run on a Micromass Quattro Ultima spectrometer fitted with a direct injection probe (DIP) with ionization energy set at 70 eV and HRMS (EI) were performed with a Micromass Q-Tof Ultima spectrometer. $^1$H, $^{13}$C and $^{31}$P spectra were recorded on a Bruker 200 and AV 600 spectrometer in CDCl$_3$ with TMS as internal standard. Chemical shifts ($\delta$) are reported in ppm downfield of TMS and coupling constants ($J$) are expressed in Hz. All $^{31}$P NMR experiments were measured relative to an external standard (H$_3$PO$_4$, 0 ppm).

Caution: All phosphines should be considered to be pyrophoric. Contact with atmospheric oxygen must be avoided, particularly during the thermal addition reactions.


Synthesis of Ligand 3.

Into an oven dried flask was introduced dry toluene (5.0 mL) under argon, and diisobutylphosphine (1.35 ml, 7.40 mmol) added. The solution was heated to 85-90 °C (oil bath) and a solution of AIBN (0.054 g, 2.0 %) dissolved in 2,3-dihydrofuran (1.00 g, 14.22 mmol) was added to the reaction mixture through a pressure-equalizing dropping funnel over a period of 2-3 hours. The reaction mixture was maintained for one hour at the same temperature after the olefin addition. Upon removal of toluene, the product (0.96 g, 60 %) was isolated as a colourless oil by short-path vacuum distillation. $^1$H NMR (200 MHz, CDCl$_3$): $\delta$ = 4.00-3.64 (m, 3H), 3.53-3.40 (m, 1H), 2.09-2.00 (m, 2H), 1.72-1.53 (m, 4H), 1.33-1.24 (m, 3H), 0.98-0.94 (m, 12H); $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$ = 71.4 (d, $J_{p,c}$ = 21 Hz), 68.3 (d, $J_{p,c}$ = 6.5 Hz), 38.3-37.8 (m, 2C), 36.2 (d, $J_{p,c}$ = 6.5 Hz), 30.3 (d, $J_{p,c}$ = 13.5 Hz), 26.5 (d, $J_{p,c}$ = 14 Hz), 24.9 (d, $J_{p,c}$ = 8 Hz), 24.6-24.0 (m, 4C); $^{31}$P NMR (CDCl$_3$, 81.01 MHz): $\delta$ = -31.1; HRMS (CI$^+$-TOF), Calculated for C$_{12}$H$_{26}$OP (MH$^+$): 217.1368, Found: 217.1357.

Synthesis of Ligand 4.
An oven dry three neck flask equipped with a condenser, two addition funnels and stirring bar was purged with N₂. Diisobutylphosphine (2.51g, 17.12 mmol) was added under nitrogen and heated to 90°C. 2-vinylpyridine (1.0 g, 9.51 mmol) was added through additional funnel over a period of approx 4 hours. VAZO 67 (0.032 g, 0.19 mmol) dissolved in 3.0 mL toluene charged to second addition funnel. Both solutions were added in a way that initiator solution addition ran half an hour longer then the 2-vinylpyridine solution. The reaction mixture was stirred at 90-91°C for extra half an hour. The solvent was removed at high vacuum and the product (2.28 g 95%) was distilled at 177°C as colorless oil.

Scale up: A 3.0 L glass double-walled jacketed reactor, attached to a circulating bath, was fitted with a condenser, mechanical stirrer and two addition funnels. Diisobutylphosphine (610.3g, 96% purity) was charged to the reactor which was then heated to 90 °C under nitrogen. 2-Vinylpyridine (338.0g) was charged to one addition funnel and a solution of Vazo-67 (7.10g) dissolved in toluene (331g) charged to second addition funnel. Both additions were began concurrently. The 2-vinylpyridine was added slowly over 4 hours while the initiator solution in toluene was added over a period of 4.5 hours. After the initiator solution was added, the reaction was maintained at 90-91°C for a further 30 min. The solvent was removed and volatile impurities removed from the the residue which was heated under nitrogen to 177°C in the pot, (102 °C vapour temp) yielding the product as a colorless oil (775g). The spectra shown below are that of the scale-up product 4.

\begin{align*}
\text{1H NMR (200 MHz, CDCl}_3\):} & \quad \delta = 8.52 (d, J = 3.6 Hz, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.18-7.07 (m, 2H), 2.94-2.82 (m, 2H), 1.81-1.63 (m, 4H), 1.43-1.23 (m, 4H), 1.00 (br s, 6H), 0.97 (br s, 6H); \\
\text{13C NMR (50 MHz, CDCl}_3\):} & \quad \delta = 162.4 (d, J_{p,c} = 11 Hz), 149.2, 136.3, 122.4, 121.0, 39.4 (d, J_{p,c} = 13 Hz), 34.7 (d, J_{p,c} = 14.5 Hz), 28.7 (d, J_{p,c} = 14 Hz), 26.3 (d, J_{p,c} = 13 Hz), 24.3 (dd (app.), J_{p,c} = 6.0, 9.1 Hz); \\
\text{31P NMR (CDCl}_3, 81.01 MHz):} & \quad \delta = -37.88; \quad \text{HRMS (Cl}^+\text{-TOF),} \\
\text{Calculated for C}_{13}\text{H}_{25}\text{NP:} & \quad 250.1725 (M-H\text{})'; \quad \text{Found: 250.1721.}
\end{align*}

3. General Procedures for Suzuki-Miyaura Cross Coupling Reactions
Procedure A (Table 1)

Into an oven dried Schlenk flask, equipped with a magnetic stirring bar, was weighed Pd(OAc)$_2$ (7.13 mg, 0.0318 mmol), and ligand 3 (20.71 mg, 0.0954 mmol) under nitrogen. The flask was evacuated and flushed with nitrogen several times. Precomplexation$^5$ was applied by adding freshly distilled Et$_3$N and dichloromethane. The solution was heated to reflux and volatiles then removed under vacuum. Bromobenzene (0.500 g, 3.18 mmol), phenylboronic acid (0.775 g, 6.36 mmol), and K$_3$PO$_4$·H$_2$O (2.20 g, 9.54 mmol) were added into the flask and the system was further evacuated and flushed with nitrogen thrice. The solvent tert-butanol (10.0 mL) was introduced and the reaction mixture was stirred at room temperature for half an hour and then placed into preheated oil bath (110 °C) for 12 hr. After completion, the reaction mixture was quenched with water and diluted with ethyl acetate. The organic layer was separated and aqueous layer was washed with EtOAc. The combined organic phase was dried over MgSO$_4$, filtered and the solvent was removed at reduced pressure. The crude product was then purified by silica gel flash chromatography giving biphenyl in 96 % yield. The physical and spectral data of all biphenyl compounds (Table 1, entry 1-10) were identical to those previously described.$^{1a-d, 2}$

Procedure B (Table 2)

An oven dried Schlenk flask, equipped with a magnetic stirring bar was charged with phenylboronic acid (0.171 g, 1.40 mmol), Cs$_2$CO$_3$ (0.684 g, 2.10 mmol) and ligand 4 (5.27 mg, 0.021 mmol). After evacuation and refilling with nitrogen, 4-chloroanisole (0.10 g, 0.70 mmol), Pd(OAc)$_2$ (1.57 mg, 0.007 mmol), and freshly distilled toluene (3.0 ml) were injected sequentially. The system was further evacuated and flushed with nitrogen thrice and then placed into preheated oil bath (110 °C) for 12 hr. After completion of reaction, the reaction mixture was quenched with water and diluted with ethyl acetate. Organic layer was separated and aqueous layer was washed with EtOAc. The combined organics were dried over MgSO$_4$, filtered and the solvent was removed at reduced pressure. The crude product was then purified by column chromatography to give 4-Methoxybiphenyl in 74 % yield. The physical and spectral data of all biphenyl compounds (Table 2, entry 1-10) were identical to those previously described.$^{1a-c, 2}$
Procedure C (Table 3)

An oven dried Schlenk flask, equipped with a magnetic stirring bar was charged with \textit{o}-tolylboronic acid (0.190 g, 1.40 mmol), Cs$_2$CO$_3$ (0.680 g, 2.10 mmol) and ligand 4 (10.54 mg, 0.042 mmol). After evacuation and refilling with nitrogen, 2-chloroanisole (0.10 g, 0.70 mmol), Pd(OAc)$_2$ (3.14 mg, 0.014 mmol), and freshly distilled toluene (3.0 ml) were injected sequentially. The system was further evacuated and flushed with nitrogen thrice and then placed into preheated oil bath (110 °C) for 24 hr. After completion of reaction, the reaction mixture was quenched with water and diluted with ethyl acetate. Organic layer was separated and aqueous layer was washed with EtOAc. The combined organics were dried over MgSO$_4$, filtered and the solvent was removed at reduced pressure. The crude product was then purified by column chromatography to give 2-Methoxy-2-methylbiphenyl in 55 % yield. The physical and spectral data of all biphenyl compounds (Table 3, entry 5-7) were identical to those previously described.$^{1c, 3a-3b}$

\textbf{3,2',3',4', Tetramethoxybiphenyl-4-ol (Table 3, entry 1)}

$$\begin{align*}
\text{MeO} & \quad \text{OMe} \\
\text{OMe} & \quad \text{OMe} \\
\text{OH} & \\
\end{align*}$$

$^1$H NMR (200 MHz, CDCl$_3$): $\delta = 7.08-6.97$ (m,4H), 6.73 (d, $J = 8.4$ Hz, 1H), 5.62 (s, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 3.90 (s, 3H), 3.67 (s, 3H) ppm; $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta = 152.9, 151.4, 145.6, 145.2, 142.5, 131.6, 128.3, 124.7, 121.0, 115.5, 110.4, 107.4, 61.1, 60.7, 56.1, 56.0$ ppm; HRMS: (ES$^+$-TOF), calcd for C$_{16}$H$_{19}$O$_5$: 291.1232, found 291.1207.

\textbf{4,2',3',4', Tetramethoxybiphenyl-4-ol (Table 3, entry 2)}

$$\begin{align*}
\text{MeO} & \quad \text{OMe} \\
\text{OMe} & \quad \text{OMe} \\
\end{align*}$$

$^1$H NMR (200 MHz, CDCl$_3$): $\delta = 7.11$ (s, 1H), 7.01 (d, $J = 8.6$ Hz, 2H), 6.89 (d, $J = 8.2$ Hz, 1H), 6.72 (d, $J = 8.2$ Hz, 1H), 5.62 (s, 1H), 3.93 (s, 3H), 3.93 (s, 3H), 3.90 (s,
3H), 3.69 (s, 3H) ppm; $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$ = 152.9, 151.4, 145.6, 145.2, 142.5, 131.6, 128.3, 124.7, 120.9, 115.5, 110.4, 107.4, 61.1, 61.0, 56.1, 56.0 ppm; HRMS: (ES$^+$-TOF), calcd for C$_{16}$H$_{17}$O$_5$: 289.1076, found 289.1082.

3,3',4',5', Tetramethoxybiphenyl-4-ol (Table 3, entry 3)

\[
\begin{align*}
\text{MeO} & \quad \text{OH} \\
\text{MeO} & \quad \text{OMe} \\
\text{MeO} & \quad \text{OMe}
\end{align*}
\]

$^1$H NMR (200 MHz, CDCl$_3$): $\delta$ = 7.03 – 7.01 (m, 3H), 6.72 (s, 2H), 5.66 (s, 1H), 3.97 (s, 3H), 3.93 (s, 6H), 3.89 (s, 3H) ppm; $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$ = 153.0, 152.5, 145.7, 145.3, 142.6, 131.7, 128.4, 124.8, 121.0, 115.6, 110.5, 107.5, 61.2, 61.0, 56.2, 56.1 ppm; HRMS: (ES$^+$-TOF), calcd for C$_{16}$H$_{17}$O$_5$: 289.1076, found 289.1090.

4,3',4',5', Tetramethoxybiphenyl-4-ol (Table 3, entry 4)

\[
\begin{align*}
\text{MeO} & \quad \text{OH} \\
\text{MeO} & \quad \text{OMe} \\
\text{MeO} & \quad \text{OMe}
\end{align*}
\]

$^1$H NMR (200 MHz, CDCl$_3$): $\delta$ = 7.16 (s, 1H), $J$ = 8.6 Hz, 1H), 7.03 (d, 6.92 (d, $J$ = 8.4 Hz, 1H), 5.70 (s, 1H), 3.95 (s, 3H), 3.93 (s, 6H), 3.89 (s, 3H) ppm; $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$ = 153.0, 151.4, 145.7, 145.2, 142.5, 131.6, 128.3, 124.7, 120.9, 115.5, 110.4, 107.4, 61.1, 61.0, 56.1, 56.0 ppm; HRMS: (ES$^+$-TOF), calcd for C$_{16}$H$_{19}$O$_5$: 291.1232, found 291.1210.

4. New Ligands Spectroscopic Data
(tetrahydrofuran-3-yl)phosphane ligand 3 ($^1$H-NMR)
(tetrahydrofuran-3-yl)phosphane ligand 3 (\[^{31}\text{P}\text{-NMR}]\)
(tetrahydrofuran-3-yl)phosphane ligand 3 ($^{13}\text{C}\text{-NMR}$)
Elemental Composition Report

Single Mass Analysis
Tolerance = 10.0 PPM  /  DBE, min = -1.5, max = 50.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
27 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used
C 0-80  H 0-80  O 0-2  P 0-2

EUK54108
11-Mar-2008

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(tetrahydrofuran-3-yl)phosphane ligand 3 (HRMS)
2-[(diisobutylphosphinyl-ethyl)-pyridine ligand 4 (°H-NMR)
2-\([(\text{diisobutylphosphinyl-ethyl})\)-pyridine ligand 4 ($^{31}$P-NMR)\]
2-[(diisobutylphosphinyl-ethyl)-pyridine ligand 4 (\(^{13}\)C-NMR)
2-[(diisobutylphosphinyl-ethyl)-pyridine ligand 4 (HRMS)
5. NMR and Mass Spectra of New Compounds

3,2',3',4', Tetramethoxybiphenyl-4-ol (1H-NMR)

(Table 3, entry 1)
3,2',3',4', Tetramethoxybiphenyl-4-ol (13C-NMR)

(Table 3, entry 1)
3,2',3',4', Tetramethoxybiphenyl-4-ol (HR-MS)

(Table 3, entry 1)
4,2',3',4', Tetramethoxybiphenyl-4-ol (¹H-NMR)

(Table 3, entry 2)
4,2',3',4', Tetramethoxybiphenyl-4-ol ($^{13}$C-NMR)

(Table 3, entry 2)
**4,2',3',4', Tetramethoxybiphenyl-4-ol (HR-MS)**

(Table 3, entry 2)
3,3',4',5', Tetramethoxybiphenyl-4-ol (¹H-NMR)

(Table 3, entry 3)
3,3',4',5', Tetramethoxybiphenyl-4-ol (\(^{13}\text{C}\)-NMR) (Table 3, entry 3)
### Elemental Composition Report

**Single Mass Analysis**
- Tolerance = 100.0 PPM
- DBE: min = -1.5, max = 200.0
- Isotope cluster parameters: Separation = 1.0, Abundance = 1.0%

**Monoisotopic Mass, Odd and Even Electron lone**
- 6 formula(e) evaluated with 2 results within limits (up to 5 closest results for each mass)

#### Table 3, entry 3

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**3,3',4',5', Tetramethoxybiphenyl-4-ol (HR-MS)**

(Table 3, entry 3)
4,3',4',5', Tetramethoxybiphenyl-3-ol (^1H-NMR)

(Table 3, entry 4)
4,3',4',5', Tetramethoxybiphenyl-3-ol ($^{13}$C-NMR)

(Table 3, entry 4)
4,3',4',5', Tetramethoxybiphenyl-3-ol (HR-MS) 

(Table 3, entry 4)
6. References


