Electronic Supplementary Information

Room-temperature nickel-catalysed cross-couplings of aryl chlorides with arylzincs

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Scheme S1. Synthesis of complexes Ia-IV

Experimental Section

General

All reactions were performed under nitrogen atmosphere using standard Schlenk and vacuum line techniques. Solvents were distilled under nitrogen over sodium (toluene), sodium/benzophenone (THF, Et₂O and n-hexane) and degassed prior to use. NMP and DMA was dried over 4Å molecular sieves, fractionally distilled under reduced pressure and stored
under nitrogen atmosphere. 2-(Ph$_2$P)C$_6$H$_4$N=CHPh,\textsuperscript{1} (DME)NiCl$_2$\textsuperscript{2} Ph$_2$P(S)H,\textsuperscript{3} Ph$_2$POH\textsuperscript{4} and Ph(Et)POH\textsuperscript{4} were prepared according to the reported methods. $n$-BuLi was purchased from Acros Organics and used as received. CDCl$_3$, purchased from Cambridge Isotope Laboratories, Inc., was degassed and stored over 4Å molecular sieves. Zinc dust was purchased from Acros Organics. 2-Furyllithium was prepared from furan by direct lithiation using $n$-BuLi.\textsuperscript{5} PhLi, $p$-MeC$_6$H$_4$Li, $o$-MeC$_6$H$_4$Li and $p$-Me$_2$NC$_6$H$_4$Li were prepared from corresponding aryl bromides and Li according to literature.\textsuperscript{6} $p$-EtO$_2$CC$_6$H$_4$ZnBr, $p$-EtO$_2$CC$_6$H$_4$ZnI and $p$-MeC$_6$H$_4$ZnI was prepared according to the procedure reported in literature.\textsuperscript{7,8} NMR spectra were recorded on a Bruker av300 spectrometer at ambient temperature. The chemical shifts of the $^1$H and $^{13}$C NMR spectra were referenced to TMS or internal solvent resonances. MS data were recorded on an Agilent6890/Micromass GCT-MS spectrometer (EI) or a Thermo Finnigan LC Q Advantage Max ion trap mass spectrometer (ESI). Elemental analysis was performed by the Analytical Center of the University of Science and Technology of China.

1. Synthesis and characterization of compounds 2-5 and nickel complexes I-IV

Synthesis of 2-(Ph$_2$P)C$_6$H$_4$NHCH(Ph)PO(O)Ph$_2$ (2a)

![Chemical structure of 2-(Ph$_2$P)C$_6$H$_4$NHCH(Ph)PO(O)Ph$_2$]

A mixture of 2-(Ph$_2$P)C$_6$H$_4$N=CHPh (0.41 g, 1.12 mmol), Ph$_2$POH (0.24 g, 1.19 mmol) and toluene (15 mL) was stirred overnight at room temperature and then refluxed for 2 hours. The resulting solution was cooled to room temperature, and added hexane (10 mL) to form white precipitate. The precipitate was collected by filtration and dried in vacuo to afford white solid (0.5 g, 78%), mp 184–187 °C. $^1$H NMR (CDCl$_3$): $\delta$ 5.26 (dd, $J = 9.3$, 16.5 Hz, 1H, CH), 5.64 (q, $J = 8.7$ Hz, 1H, Ar), 6.47 (dd, $J = 5.4$, 8.1 Hz, 1H, Ar), 6.53 (t, $J = 7.5$ Hz, 1H, Ar), 6.64 (t, $J = 6.3$ Hz, 1H, Ar), 6.94–6.97 (m, 2H, Ar), 6.98–7.06 (m, 6H, Ar), 7.08–7.26 (m, 11H, Ar), 7.36–7.42 (m, 4H, Ar), 7.57–7.63 (m, 2H, Ar). $^{13}$C NMR (CDCl$_3$): $\delta$ 57.93 (d, $J = 75.2$ Hz),
111.66, 118.65, 121.33 (d, $J = 9.2$ Hz), 127.69, 128.15, 128.31, 128.46, 128.61, 128.91,
130.56, 131.79, 131.90, 132.00, 132.18, 132.30, 132.64, 133.71, 133.89, 133.96, 134.14,
134.40, 134.77, 135.17, 135.26, 148.71 (dd, $J = 12.1$, 18.7 Hz). $^{31}$P NMR (CDCl$_3$): $\delta$ –26.41,
26.37. Anal. Calcd for C$_{37}$H$_{31}$NOP$_2$: C, 78.29; H, 5.50; N, 2.47. Found: C, 77.95; H, 5.53; N,
2.17.

**Synthesis of 2-(Ph$_2$P)C$_6$H$_4$NCH(Ph)P(O)(Ph)Et (2b)**

A mixture of 2-(Ph$_2$P)C$_6$H$_4$N=CHPh (0.46 g, 1.26 mmol), Ph(Ét)POH (0.20 g, 1.30 mmol)
and toluene (15 mL) was stirred overnight at room temperature and then refluxed for 6 hours.
Solvent was removed in vacuo, and Ét$_2$O (10 mL) was added into the residue with vigorous
stirring until white precipitate generated. The precipitate was collected by filtration and dried
in vacuo to give white solid (0.52 g, 80%), mp 124–128 °C. $^1$H NMR (CDCl$_3$): $\delta$ 0.87–1.05
(m, 6H, CH$_3$), 1.68–1.87 (m, 4H, CH$_2$), 4.72 (dd, $J = 7.5$, 13.9 Hz, 1H, CH), 4.83 (dd, $J = 9.3$,
16.8 Hz, 1H, CH), 5.32 (q, $J = 7.6$ Hz, 1H, Ar), 5.76 (q, $J = 7.5$ Hz, 1H, Ar), 6.33 (dd, $J = 5.3$,
7.5 Hz, 1H, Ar), 6.41 (dd, $J = 5.3$, 7.8 Hz, 1H, Ar), 6.52 (t, $J = 7.3$ Hz, 2H, Ar), 6.60 (t, $J =
5.8$ Hz, 1H, Ar), 6.68 (t, $J = 6$ Hz, 1H, Ar), 6.86 (d, $J = 5.7$ Hz, 2H, Ar), 6.91–7.05 (m, 7H,
Ar), 7.07–7.72 (m, 31H, Ar). $^{13}$C NMR (CDCl$_3$): $\delta$ 5.21 (d, $J = 4.6$ Hz), 5.42 (d, $J = 4.5$ Hz),
18.37 (d, $J = 4.5$ Hz), 19.31, 57.66 (d, $J = 71$ Hz), 59.05 (d, $J = 72$ Hz), 111.54 (d, $J = 18.7$
Hz), 118.53 (d, $J = 8.5$ Hz), 127.54, 127.73, 128.25, 128.37, 128.43, 128.65, 129.00 (d, $J =
7.5$ Hz), 130.33 (d, $J = 14.8$ Hz), 131.39 (d, $J = 8.1$ Hz), 131.80, 132.03, 133.70, 133.96,
134.10, 134.21, 134.26, 134.35, 134.96, 135.26, 135.62, 148.90 (dd, $J = 14.9$, 29.9 Hz). $^{31}$P
NMR (CDCl$_3$): $\delta$ –24.82, 37.77, 38.26. Anal. Calcd for C$_{33}$H$_{31}$NOP$_2$: C, 76.29; H, 6.01; N,
2.70. Found: C, 75.93; H, 6.21; N, 2.77.

**Synthesis of [Ni(Cl){2-(Ph$_2$P)C$_6$H$_4$NCH(Ph)P(O)Ph$_2$}] (1a)**
To a stirred solution of 2a (0.50 g, 0.88 mmol) in THF (15 mL) was added dropwise n-BuLi (0.36 mL, a 2.5 M solution in hexanes, 0.90 mmol) at about −80 °C. The resulting mixture was warmed to room temperature and stirred for 4 h. This solution was added dropwise to a stirred suspension of (DME)NiCl₂ (0.20 g, 0.91 mmol) in THF (10 mL) at about −80 °C. The mixture was warmed to room temperature and stirred overnight. Volatiles were removed in vacuo and the residue was dissolved in toluene. The resulting solution was filtered and the filtrate was concentrated to afford brown powder (0.38 g, 65%), mp 246–248 °C. ¹H NMR (CDCl₃): δ 4.62 (d, J = 7.5 Hz, 1H, CH), 6.08 (t, J = 6.6 Hz, 1H, Ar), 6.15 (t, J = 7.2 Hz, 1H, Ar), 6.81 (t, J = 8.5 Hz, 2H, Ar), 6.99–7.23 (m, 8H, Ar), 7.26–7.31 (m, 3H, Ar), 7.35–7.44 (m, 3H, Ar), 7.54–7.69 (m, 5H, Ar), 7.79–7.91 (m, 4H, Ar), 8.19–8.25 (m, 2H, Ar). ¹³C NMR (CDCl₃): δ 64.62 (d, J = 85.2 Hz), 112.59 (d, J = 12.8 Hz), 114.05 (d, J = 7.5 Hz), 117.49, 118.22, 125.42, 126.74, 127.82, 127.96, 128.11, 128.40, 128.48, 128.68 (d, J = 6.3 Hz), 128.87, 129.25 (d, J = 11.7 Hz), 130.84, 132.27 (d, J = 9.4 Hz), 132.76, 133.23, 133.35, 133.55 (d, J = 10.6 Hz), 135.94, 163.58. ³¹P NMR (CDCl₃): δ 24.91, 58.79. Anal. Caled for C₃₇H₃₀NOP₂NiCl: C, 67.26; H, 4.58; N, 2.12. Found: C, 67.07; H, 4.55, N, 1.92.

**Synthesis of [Ni(Cl){2-(Ph₂P)C₆H₄NCH(Ph)P(O)(Ph)Et}] (IIb)**

To a stirred solution of 2b (0.60 g, 1.15 mmol) in THF (15 mL) was added dropwise n-BuLi (0.47 mL, 2.5 M solution in hexanes, 1.17 mmol) at about −80 °C. The resulting mixture was warmed to room temperature and stirred for 4 h. This solution was added dropwise to a stirred suspension of (DME)NiCl₂ (0.26 g, 1.18 mmol) in THF (10 mL) at about −80 °C. The mixture was warmed to room temperature and stirred overnight. Volatiles were removed in
vacuo and the residue was dissolved in toluene. The solution was filtered and the filtrate was concentrated. Et₂O added into the concentrated filtrate to form brown crystals of 2b (0.36 g, 51%), mp 229−232 °C. ¹H NMR (CDCl₃): δ 0.69−0.79 (m, 3H, CH₃), 1.42−1.70 (m, 2H, CH₂), 4.30 (dd, J = 1.9, 6.5 Hz, 1H, CH), 5.99 (dd, J = 5.5, 8.6 Hz, 1H, Ar), 6.14 (t, J = 6.1 Hz, 1H, Ar), 6.79 (dd, J = 7.3, 14.1 Hz, 2H, Ar), 7.23–7.55 (m, 9H, Ar), 7.64 (s, 3H, Ar), 7.83−7.99 (m, 6H, Ar), 8.29-8.44 (m, 2H, Ar). ¹³C NMR (CDCl₃): δ 4.88, 19.88 (d, J = 67 Hz), 65.64 (d, J = 80.4 Hz), 112.62 (d, J = 12.2 Hz), 113.86, 127.81, 128.49, 128.70, 128.86, 129.13, 129.75, 130.27, 130.84, 131.29, 131.42, 132.70, 132.91, 133.03, 133.24, 133.44, 133.59, 136.95, 163.91. ³¹P NMR (CDCl₃): δ 24.83, 71.33. Anal. Calcd for C₃₃H₃₀NOP₂NiCl: C, 64.69; H, 4.94; N, 2.29. Found: C, 64.76; H, 5.15, N, 2.19.

**Synthesis of 2-(Ph₂P)C₆H₄NHCH(Ph)P(S)Ph₂ (3)**

A mixture of 2-(Ph₂P)C₆H₄N=CHPh (0.40 g, 1.09 mmol), Ph₂PSH (0.24 g, 1.10 mmol) and toluene (15 mL) was stirred overnight at room temperature and then refluxed for 2 h. The resulting solution was cooled to room temperature. Hexane (10 mL) was added to the solution to form white precipitate. The precipitate was collected by filtration and dried in vacuo to afford white solid (0.52 g, 81%), mp 174−177 °C. ¹H NMR (CDCl₃): δ 2.35 (s, PhCH₃), 5.41 (dd, J = 9.4, 12.4 Hz, 1H, CH), 6.39 (q, J = 8.9 Hz, 1H, Ar), 6.50−6.61 (m, 2H, Ar), 6.75−6.79 (m, 1H, Ar), 6.84−6.88 (m, 2H, Ar), 6.97 (t, J = 7.7 Hz, 2H, Ar), 7.03−7.09 (m, 2H, Ar), 7.14−7.17 (m, 1H, Ar), 7.19−7.39 (m, 12H, Ar), 7.41−7.49 (m, 3H, Ar), 7.68−7.79 (m, 2H, Ar), 8.01−8.13 (m, 1H, Ar). ¹³C NMR (CDCl₃): δ 57.51 (d, J = 60 Hz), 111.62, 118.23, 127.61, 127.64, 127.81, 128.01, 128.48, 128.55, 128.68, 128.74, 128.83, 128.97, 130.34, 131.64, 131.70, 131.82, 132.11, 132.24, 132.47, 133.98, 134.13, 134.23, 134.48. ³¹P NMR: δ −25.69, 47.19. Anal. Calcd for C₃₇H₃₁NOP₂·0.7C₇H₈: C, 77.64; H, 5.69; N, 2.16. Found: C, 77.72; H, 5.69; N, 2.27.
Synthesis of [Ni(Cl){2-(Ph₂P)C₆H₄NCH(Ph)P(S)Ph₂}] (II)

To a stirred solution of 3·0.7C₇H₈ (0.37 g, 0.57 mmol) in THF (15 mL) was added dropwise n-BuLi (0.24 mL, 2.5 M solution in hexanes, 0.60 mmol) at about −80 °C. The resulting mixture was warmed to room temperature and stirred for 4 h. This solution was added to a stirred suspension of (DME)NiCl₂ (0.13 g, 0.59 mmol) in THF (10 mL) at about −80 °C. The mixture was warmed to room temperature and stirred overnight. Volatiles were removed in vacuo and the residue was dissolved in toluene. The solution was filtered and the filtrate was concentrated to form red crystals (0.315 g, 69%), mp 205−207 °C. ¹H NMR (CDCl₃): δ 2.35 (s, PhCH₃), 5.37 (d, J = 9.2 Hz, 1H, CH), 6.23 (s, 2H, Ar), 6.92 (d, J = 9.2 Hz, 2H, Ar), 7.00−8.18 (m, 27H, Ar). ¹³C NMR (CDCl₃): δ 70.79 (d, J = 74.4 Hz), 112.94 (d, J = 13.3 Hz), 113.95 (d, J = 6.7 Hz), 127.86 (d, J = 2.1 Hz), 128.12 (d, J = 3.1 Hz), 128.21, 128.39 (d, J = 2.7 Hz), 128.48, 128.63 (d, J = 3 Hz), 128.76, 129.23, 129.39, 130.71, 132.17 (d, J = 9.1 Hz), 132.65, 132.80, 132.94, 133.15, 133.38, 133.46, 133.52, 133.59, 134.88, 164.89 (d, J = 17.8 Hz). ³¹P NMR (CDCl₃): δ 21.72, 55.40. Anal. Calcd for C₃₇H₃₀NSP₂NiCl·1.3C₇H₈: C, 69.51; H, 5.11; N, 1.76. Found: C, 69.50; H, 5.23; N, 1.88.

Synthesis of 2-[Ph₂P(O)]C₆H₄N=CHPh (4)

A solution of 2-(Ph₂P)C₆H₄N=CHPh (0.60 g, 1.64 mmol) in THF (15 mL) was cooled to 0 °C. To the solution was added dropwise H₂O₂ (0.23 mL, 30% w/w, 2.03 mmol) and resulting mixture was stirred at 0 °C for 1.5 h. Solvents were removed in vacuo. To the residue was added Et₂O with vigorous stirring until white precipitate generated. The precipitate was collected by filtration and dried in vacuo to yield white solid (0.59 g, 94%), mp 100−101 °C.
$^1$H NMR (CDCl$_3$): δ 7.02 (dd, $J = 5.1$, 7.7 Hz, 1H, Ar), 7.26–7.42 (m, 12H, Ar), 7.58 (t, $J = 7.7$ Hz, 1H, Ar), 7.79 (dd, $J = 7.0$, 12.3 Hz, 4H, Ar), 7.96–8.03 (m, 1H, Ar), 8.09 (s, 1H, CH).

$^{13}$C NMR (CDCl$_3$): δ 118.52 (d, $J = 7.8$ Hz), 125.99 (d, $J = 11.4$ Hz), 128.26, 128.42, 128.67, 128.86, 129.38, 131.47, 131.51, 131.84, 132.12, 132.26, 132.41, 133.91, 134.60 (d, $J = 7.9$ Hz), 153.56, 160.71. $^{31}$P NMR (CDCl$_3$): δ 23.67. Anal. Calcd for C$_{25}$H$_{20}$NOP: C, 78.73; H, 5.29; N, 3.67. Found: C, 78.90; H, 5.60; N, 3.61.

**Synthesis of 2-[Ph$_2$P(S)]C$_6$H$_4$N=CHPh (5)**

![Diagram of 2-[Ph$_2$P(S)]C$_6$H$_4$N=CHPh (5)](image)

A mixture of 2-(Ph$_2$P)C$_6$H$_4$N=CHPh (0.50 g, 1.37 mmol), S$_8$ (0.044 g, 1.37 mmol) and toluene (15 mL) was refluxed for 2 h and then cooled to room temperature. Volatiles were removed in vacuo and the residue was dissolved in Et$_2$O. The solution was concentrated and added hexane to give pale yellow powder (0.48 g, 88%), mp 119–121 °C. $^1$H NMR (CDCl$_3$): δ 1.20 (t, $J = 7.0$ Hz, Et$_2$O), 3.47 (q, $J = 7.0$ Hz, Et$_2$O), 6.99 (dd, $J = 5.2$, 7.5 Hz, 1H, Ar), 7.25–7.41 (m, 12H, Ar), 7.56 (t, $J = 7.5$ Hz, 1H, Ar), 7.84-7.96 (m, 5H, Ar), 8.08 (s, 1H, CH).

$^{13}$C NMR (CDCl$_3$): δ 118.67 (d, $J = 7.4$ Hz), 125.81 (d, $J = 12.9$ Hz), 128.14, 128.31, 128.49, 129.33, 130.98 (d, $J = 2.8$ Hz), 131.69, 132.15, 132.30, 133.62 (d, $J = 2.3$ Hz), 134.72, 134.87, 153.87, 160.37. $^{31}$P NMR (CDCl$_3$): δ 38.52. Anal. Calcd for C$_{25}$H$_{20}$NSP·0.25Et$_2$O: C, 75.07; H, 5.45; N, 3.37. Found: C, 74.86; H, 5.21; N, 3.33.

**Synthesis of [Ni(Cl){2-(Ph$_2$P(O))C$_6$H$_4$NCH(Ph)PPh$_2$}] (III)**

![Diagram of [Ni(Cl){2-(Ph$_2$P(O))C$_6$H$_4$NCH(Ph)PPh$_2$}] (III)](image)

A solution of compound 4 (0.30 g, 0.78 mmol) in THF (15 mL) was cooled to about −80 °C. To the solution was added dropwise a THF solution of Ph$_2$PLi [prepared in situ from Ph$_2$PH
(0.14 g, 0.79 mmol) and Bu"Li (0.32 mL, 2.5 M solution in hexane, 0.80 mmol) in THF (5 mL)] with stirring. The mixture was warmed to room temperature and stirred for 12 h. The resulting solution was added dropwise into a stirred suspension of (DME)NiCl₂ (0.18 g, 0.81 mmol) in THF (10 mL) at about −80 °C. The mixture was warmed to room temperature and stirred overnight. Volatiles were removed in vacuo, and the residue was dissolved in toluene. The resulting solution was filtered. Et₂O was added into the filtrate to form brown powder (0.33 g, 59%), mp 166–170 °C. Anal. Calcd for C₃₇H₃₀NOP₂NiCl·0.5C₇H₈: C, 68.82; H, 4.85; N, 1.98. Found: C, 68.87; H, 5.19, N, 1.98. ESI-MS: m/z 665 [M–Cl+CH₃CN]⁺ (The sample was dissolved in CH₃CN), 624 [M–Cl]⁺.

**Synthesis of [Ni(Cl){2-(Ph₂P(S))C₆H₄NCH(Ph)PPh₂}] (IV)**

A mixture of compound 5·0.25Et₂O (0.33 g, 0.79 mmol) in THF (15 mL) was cooled to about −80 °C. To the solution was added a THF solution of Ph₂PLi [prepared in situ from Ph₂PH (0.15 g, 0.80 mmol) and n-BuLi (0.32 mL, 2.5 M solution in hexane, 0.80 mmol) in THF (5 mL)] with stirring. The mixture was warmed to room temperature and stirred for 12 h. The resulting solution was added dropwise into a stirred suspension of (DME)NiCl₂ (0.18 g, 0.81 mmol) in THF (10 mL) at about −80 °C. The mixture was warmed to room temperature and stirred overnight. Volatiles were removed in vacuo, and the residue was dissolved in toluene. The resulting solution was filtered and the filtrate was concentrated to give red crystals (0.39 g, 63%), mp 186–188 °C. Anal. Calcd for C₃₇H₃₀NSP₂NiCl·1.1C₇H₈: C, 68.99; H, 5.03; N, 1.80. Found: C, 69.15; H, 5.10; N, 1.83. ESI-MS: m/z 676 [M+1]⁺.

2. X-Ray crystallography

Single crystals of complex II were mounted in Lindemann capillaries under nitrogen. Diffraction data were collected at 295(2) K on a Oxford diffraction Gemini S Ultra diffractometer using Cu-Kα radiation (λ = 1.54184 Å). The structure was solved by direct
methods using SHELXS-97 program\textsuperscript{9} and refined against $F^2$ by full-matrix least-squares using SHELXL-97 program.\textsuperscript{10} Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determination are listed in Table S1.

Table S1. Details of the X-ray structure determination of complex II

<table>
<thead>
<tr>
<th>empirical formula</th>
<th>C$<em>{37}$H$</em>{30}$ClNNiP$_2$S</th>
<th>$D_{\text{calc}}$ (gcm$^{-3}$)</th>
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<td>fw</td>
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<td>$F(000)$</td>
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<td>$a$ (Å)</td>
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<td>no. of indep reflns ($R_{\text{int}}$)</td>
<td>5072 (0.0322)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>22.010(5)</td>
<td>restraints/params</td>
<td>12/388</td>
</tr>
<tr>
<td>$c$ (Å)</td>
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</tr>
<tr>
<td>$\beta$ (deg)</td>
<td>95.316(5)</td>
<td>final $R$ indices$^a$ [I &gt; 2$\sigma$(I)]</td>
<td>$R_1 = 0.0492$ $wR_2 = 0.1216$</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>3244(2)</td>
<td>$R$ indices (all data)</td>
<td>$R_1 = 0.0608$ $wR_2 = 0.1276$</td>
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<tr>
<td>$Z$</td>
<td>4</td>
<td>largest diff peak and hole [e.Å$^{-3}$]</td>
<td>1.823, -0.499</td>
</tr>
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</table>

$^a$ $R_1 = \sum |F_o| - |F_c|/\sum |F_o|$; $wR_2 = \left[ \sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4) \right]^{1/2}$

![Figure S1. Molecular structure of complex II (30\% thermal ellipsoids)](image)

The structure of complex Ia have been reported by us,\textsuperscript{1} but the spectral and analytical data of the complex were not provided then due to minor sample amount. In this study the complex was obtained in gram scale and was characterized by NMR spectroscopy and
3. General procedure for the Negishi cross-coupling

(1) Reaction of PhZnCl with \( p\text{-MeOC}_6\text{H}_4\text{Cl} \) catalyzed by complex \( \text{Ia} \)

A Schlenk tube was charged with \( p\text{-MeOC}_6\text{H}_4\text{Cl} \) (0.071 g, 0.5 mmol), NMP (1.5 mL) and a solution of complex \( \text{Ia} \) (0.02 mL, 0.05 M solution in THF, 0.001 mmol). To the stirred mixture PhZnCl solution (1.5 mL, 0.5 M solution in THF, 0.75 mmol) was added by syringe. The reaction mixture was stirred at room temperature for 24 h. Water (10 mL) and several drops of hydrochloric acid were successively added. The mixture was extracted with \( \text{Et}_2\text{O} \) (3 \( \times \) 10 mL). The combined organic phases were dried over anhydrous \( \text{Na}_2\text{SO}_4 \), concentrated by rotary evaporation, and purified by column chromatography (silica gel, eluted using 3% \( \text{CH}_3\text{COOEt-petroleum ether} \)) to afford \( p\text{-MeOC}_6\text{H}_4\text{Ph} \) (0.09 g, 98 %).

Other reactions of arylzinc chlorides with aryl chlorides followed the same procedure.

(2) Reaction of \( p\text{-EtOOCC}_6\text{H}_4\text{ZnBr} \) with \( p\text{-PhC(O)C}_6\text{H}_4\text{Cl} \) catalysed by complex \( \text{Ia} \)

\( p\text{-EtOOCC}_6\text{H}_4\text{ZnBr} \) was prepared according to the procedure described in literature.

After reaction completed, THF was removed \textit{in vacuo}. The residue was washed with \( \text{Et}_2\text{O} \) to remove \( \text{C}_10\text{H}_8 \). Then THF was added to prepare a about 0.5 M solution of \( p\text{-EtOOCC}_6\text{H}_4\text{ZnBr} \) in THF.

A Schlenk tube was charged \( p\text{-PhC(O)C}_6\text{H}_4\text{Cl} \) (0.108 g, 0.5 mmol), NMP (1.5 mL), and complex \( \text{Ia} \) (16.5 mg, 0.025 mmol). To the stirred mixture \( p\text{-EtOOCC}_6\text{H}_4\text{ZnBr} \) solution (1.5 mL, 0.5 M solution in THF, 0.75 mmol) was added by syringe. Then the reaction mixture was stirred at room temperature for 12 h. Water (10 mL) and several drops of hydrochloric acid were successively added. The resulting mixture was extracted with \( \text{Et}_2\text{O} \) (3 \( \times \) 10 mL), and the combined organic layers were dried over anhydrous \( \text{Na}_2\text{SO}_4 \). The \( \text{Na}_2\text{SO}_4 \) was removed by filtration and washed with \( \text{Et}_2\text{O} \). The resulting \( \text{Et}_2\text{O} \) solution was concentrated by rotary evaporation, and the residue was purified by column chromatography (silica gel, eluted using 5% \( \text{CH}_3\text{COOEt-petroleum ether} \)) to afford 4-EtOOCC \( _6\text{H}_4\text{C}_6\text{H}_4\text{C(O)Ph-4} \)\(^′\) (0.124 g, 75 %).

\( p\text{-EtOOCC}_6\text{H}_4\text{ZnI} \) and \( p\text{-MeC}_6\text{H}_4\text{ZnI} \) were prepared by reaction of corresponding aryl...
iodide with activated Zn. Their coupling reactions with aryl chlorides followed the same procedure as above.

Spectral data of the cross-coupling products

1) 4-Methoxybiphenyl

\[
\text{OMe}
\]

\(^1\)H NMR (CDCl\(_3\)): \(\delta 3.87\) (s, 3H, CH\(_3\)), 7.01 (d, \(J = 8.8\) Hz, 2H, C\(_6\)H\(_4\)), 7.33 (t, \(J = 7.5\) Hz, 1H, Ph), 7.45 (t, \(J = 7.8\) Hz, 2H, Ph), 7.54–7.61 (m, 4H, Ph+C\(_6\)H\(_4\)).

2) 4-Methylbiphenyl

\[
\text{Ph}
\]

\(^1\)H NMR (CDCl\(_3\)): \(\delta 2.35\) (s, 3H, CH\(_3\)), 7.20 (d, \(J = 8.1\) Hz, 2H, C\(_6\)H\(_4\)), 7.28 (d, \(J = 7.3\) Hz, 1H, Ph), 7.37 (t, \(J = 7.5\) Hz, 2H, Ph), 7.46 (d, \(J = 8.1\) Hz, 2H, C\(_6\)H\(_4\)), 7.54 (d, \(J = 7.7\) Hz, 2H, Ph).

3) (4'-Methylbiphenyl-4-yl)(phenyl)methanone

\[
\text{Ph}
\]

\(^1\)H NMR (CDCl\(_3\)): \(\delta 2.28\) (s, 3H, CH\(_3\)), 7.15 (d, \(J = 7.8\) Hz, 2H, Ar), 7.33–7.48 (m, 5H, Ar), 7.55 (d, \(J = 8.4\) Hz, 2H, Ar), 7.71 (d, \(J = 7.9\) Hz, 2H, Ar), 7.75 (d, \(J = 8.1\) Hz, 2H, Ar).

4) 4'-Methylbiphenyl-4-carbonitrile

\[
\text{CN}
\]

\(^1\)H NMR (CDCl\(_3\)): \(\delta 2.29\) (s, 3H, CH\(_3\)), 7.16 (d, \(J = 7.9\) Hz, 2H, C\(_6\)H\(_4\)), 7.36 (d, \(J = 8.2\) Hz, 2H, C\(_6\)H\(_4\)), 7.50–7.57 (m, 4H, C\(_6\)H\(_4\)).

5) 4-Methyl-4'-(trifluoromethyl)biphenyl

\[
\text{CF}_3
\]
\( ^1 \)H NMR (CDCl\(_3\)): \( \delta 2.40 \) (s, 3H, CH\(_3\)), 7.26 (d, \( J = 8 \) Hz, 2H, C\(_6\)H\(_4\)), 7.48 (d, \( J = 8.1 \) Hz, 2H, C\(_6\)H\(_4\)), 7.65 (s, 4H, C\(_6\)H\(_4\)).

(6) 2-\( p \)-Tolylpyridine\(^{11}\)

\[
\begin{array}{c}
\text{N} \\
\text{C} - \text{C} - \text{C} \\
\text{C} - \text{N} \\
\end{array}
\]

\( ^1 \)H NMR (CDCl\(_3\)): \( \delta 2.39 \) (s, 3H, CH\(_3\)), 7.15–7.19 (m, 1H, pyridyl), 7.27 (d, \( J = 7.9 \) Hz, 2H, C\(_6\)H\(_4\)), 7.66–7.73 (m, 2H, pyridyl), 7.88 (d, \( J = 8.2 \) Hz, 2H, C\(_6\)H\(_4\)), 8.66 (dt, \( J = 1.4, 4.8 \) Hz, 1H, pyridyl).

(7) \( N,N \)-Diethyl-4'-methylbiphenyl-4-carboxamide\(^{11}\)

\[
\begin{array}{c}
\text{C} - \text{O} \\
\text{C} - \text{C} - \text{C} \\
\text{C} - \text{N} \\
\end{array}
\]

\( ^1 \)H NMR (CDCl\(_3\)): \( \delta 1.20 \) (b, 6H, CH\(_3\)), 2.39 (s, 3H, CH\(_3\)), 3.34 (b, 2H, CH\(_2\)), 3.54 (b, 2H, CH\(_2\)), 7.25 (d, \( J = 7.9 \) Hz, 2H, C\(_6\)H\(_4\)), 7.42 (d, \( J = 8.3 \) Hz, 2H, C\(_6\)H\(_4\)), 7.49 (d, \( J = 8.1 \) Hz, 2H, C\(_6\)H\(_4\)), 7.59 (d, \( J = 8.3 \) Hz, 2H, C\(_6\)H\(_4\)).

(8) Ethyl 4'-methylbiphenyl-4-carboxylate\(^{11}\)

\[
\begin{array}{c}
\text{C} - \text{C} - \text{C} \\
\text{C} - \text{O} \\
\end{array}
\]

\( ^1 \)H NMR (CDCl\(_3\)): \( \delta 1.26 \) (t, \( J = 7.1 \) Hz, 3H, CH\(_3\)), 2.24 (s, 3H, CH\(_3\)), 4.25 (q, \( J = 7.1 \) Hz, 2H, CH\(_2\)), 7.09 (d, \( J = 8.1 \) Hz, 2H, C\(_6\)H\(_4\)), 7.35 (d, \( J = 8 \) Hz, 2H, C\(_6\)H\(_4\)), 7.47 (d, 2H, \( J = 8.2 \) Hz, C\(_6\)H\(_4\)), 7.95 (d, 2H, \( J = 8.2 \) Hz, C\(_6\)H\(_4\)).

(9) 4-Methoxy-4'-methylbiphenyl\(^{11}\)

\[
\begin{array}{c}
\text{C} - \text{O} \\
\text{C} - \text{C} - \text{C} \\
\end{array}
\]

\( ^1 \)H NMR (CDCl\(_3\)): \( \delta 2.28 \) (s, 3H, CH\(_3\)), 3.73 (s, 3H, OCH\(_3\)), 6.86 (d, \( J = 8.8 \) Hz, 2H, C\(_6\)H\(_4\)), 7.12 (d, \( J = 7.9 \) Hz, 2H, C\(_6\)H\(_4\)), 7.35 (d, \( J = 8.1 \) Hz, 2H, C\(_6\)H\(_4\)), 7.41 (d, \( J = 8.8 \) Hz, 2H, C\(_6\)H\(_4\)).

(10) (4'-Methylbiphenyl-2-yl)(phenyl)methanone\(^{11}\)
\[ \text{Ph} \overline{\text{O}} \text{Ph} \]

$^1$H NMR (CDCl$_3$): $\delta$ 2.24 (s, 3H, CH$_3$), 7.00 (d, $J = 7.5$ Hz, 2H, Ar), 7.15 (d, $J = 7.7$ Hz, 2H, Ar), 7.27 (t, $J = 7.8$ Hz, 2H, Ar), 7.36–7.59 (m, 5H, Ar), 7.66 (d, $J = 8.1$ Hz, 2H, Ar).

(11) 2-Methoxy-4'-methylbiphenyl$^{11}$

\[ \text{MeO} \overline{\text{MeO}} \text{Ar} \]

$^1$H NMR (CDCl$_3$): $\delta$ 2.29 (s, 3H, CH$_3$), 3.69 (s, 3H, CH$_3$), 6.86 (d, $J = 8.1$ Hz, 1H, C$_6$H$_4$), 6.93 (d, $J = 7.4$ Hz, 1H, C$_6$H$_4$), 7.12 (d, $J = 7.8$ Hz, 2H, C$_6$H$_4$), 7.21 (d, $J = 7.3$ Hz, 2H, C$_6$H$_4$), 7.33 (d, $J = 8$ Hz, 2H, C$_6$H$_4$).

(12) Methyl 2-methoxy-5-(p-methylphenyl)benzoate

\[ \text{MeO} \overline{\text{MeO}} \text{Ar} \]

$^1$H NMR (CDCl$_3$): $\delta$ 2.40 (s, 3H, CH$_3$), 3.93 (s, 3H, CH$_3$), 3.95 (s, 3H, CH$_3$), 7.05 (d, $J = 8.7$ Hz, 1H, Ar), 7.25 (d, $J = 8.1$ Hz, 2H, Ar), 7.47 (d, $J = 8.1$ Hz, 2H, Ar), 7.69 (dd, $J = 2.4$, 8.6 Hz, 1H, Ar), 8.03 (d, $J = 2.4$ Hz, 1H, Ar). $^{13}$C NMR (CDCl$_3$): $\delta$ 21.10, 52.11, 56.19, 112.50, 120.27, 126.57, 129.59, 130.04, 131.73, 133.28, 136.87, 136.91, 158.40, 166.76. HR-MS (EI): m/z 256.1101 [M$^+$], calcd for C$_{16}$H$_{16}$O$_3$ 256.1099.

(13) (2'-Methylbiphenyl-4-yl)(phenyl)methanone$^{11}$

\[ \text{Ph} \overline{\text{O}} \text{Ph} \]

$^1$H NMR (CDCl$_3$): $\delta$ 2.19 (s, 3H, CH$_3$), 7.11–7.18 (m, 4H, Ar), 7.28–7.50 (m, 5H, Ar), 7.73–7.77 (m, 4H, Ar).

(14) Ethyl 2'-methylbiphenyl-4-carboxylate$^{11}$
1H NMR (CDCl₃): δ 1.30 (t, J = 7.1 Hz, 3H, CH₃), 2.14 (s, 3H, CH₃), 4.29 (q, J = 7.1 Hz, 2H, CH₂), 7.09–7.16 (m, 4H, C₆H₄), 7.27 (d, J = 8.1 Hz, 2H, C₆H₄), 7.99 (d, J = 8.1 Hz, 2H, C₆H₄).

(15) N,N-Diethyl-2'-methylbiphenyl-4-carboxamide

1H NMR (CDCl₃): δ 1.20 (b, 6H, CH₃), 2.26 (s, 3H, CH₃), 3.34 (b, 2H, CH₂), 3.56 (b, 2H, CH₂), 7.21–7.26 (m, 4H, C₆H₄), 7.33 (d, J = 8.1 Hz, 2H, C₆H₄), 7.43 (d, J = 8.1 Hz, 2H, C₆H₄).

(16) 4'-Methoxy-2-methylbiphenyl

1H NMR (CDCl₃): δ 2.27 (s, 3H, CH₃), 3.83 (s, 3H, OCH₃), 6.94 (d, J = 8.7 Hz, 2H, C₆H₄), 7.21–7.26 (m, 6H, C₆H₄).

(17) 2'-Methylbiphenyl-4-carbonitrile

1H NMR (CDCl₃): δ 2.13 (s, 3H, CH₃), 7.17 (d, J = 7.5 Hz, 1H, C₆H₄), 7.25 (d, J = 7.5 Hz, 2H, C₆H₄), 7.31–7.37 (m, 3H, C₆H₄), 7.61 (d, J = 8.5 Hz, 2H, C₆H₄).

(18) 2-(4-(Trifluoromethyl)phenyl)furan
7.49 (s, 1H, furyl), 7.61 (d, J = 8.6 Hz, 2H, C₆H₄), 7.73 (d, J = 8.5 Hz, 2H, C₆H₄).

(19) Ethyl 4-(furan-2-yl)benzoate

\[
\begin{align*}
\text{O} & \quad \text{COOEt} \\
\hline
\text{O} & \quad \text{COOEt}
\end{align*}
\]

¹H NMR (CDCl₃): δ 1.29 (t, J = 7.1 Hz, 3H, CH₃), 4.27 (q, J = 7.1 Hz, 2H, CH₂), 6.38 (dd, J = 1.8, 3.4 Hz, 1H, furyl), 6.65 (d, J = 3.4 Hz, 1H, furyl), 7.39 (d, J = 1.8 Hz, 1H, furyl), 7.60 (d, J = 8.3 Hz, 2H, C₆H₄), 7.94 (d, J = 8.3 Hz, 2H, C₆H₄).

(20) 4-(Furan-2-yl)benzonitrile

\[
\begin{align*}
\text{NC} & \quad \text{O} \\
\hline
\text{O} & \quad \text{NC}
\end{align*}
\]

¹H NMR (CDCl₃): δ 6.43 (dd, J = 1.7, 3.3 Hz, 1H, furyl), 6.71 (d, J = 3.3 Hz, 1H, furyl), 7.43 (s, 1H, furyl), 7.54 (d, J = 8.6 Hz, 2H, C₆H₄), 7.63 (d, J = 8.1 Hz, 2H, C₆H₄).

(21) N,N-Dimethylbiphenyl-4-amine

\[
\begin{align*}
\text{NMe}_2 & \quad \text{NMe}_2 \\
\hline
\text{NMe}_2 & \quad \text{NMe}_2
\end{align*}
\]

¹H NMR (CDCl₃): δ 2.86 (s, 6H, CH₃), 6.69 (d, J = 8.8 Hz, 2H, Ar), 7.11-7.17 (m, 1H, Ar), 7.26-7.31 (m, 2H, Ar), 7.39–7.47 (m, 4H, Ar).

(22) 4'-Methoxy-N,N-dimethylbiphenyl-4-amine

\[
\begin{align*}
\text{MeO} & \quad \text{NMe}_2 \\
\hline
\text{NMe}_2 & \quad \text{MeO}
\end{align*}
\]

¹H NMR (CDCl₃): δ 2.97 (s, 6H, NCH₃), 3.82 (s, 3H, OCH₃), 6.79 (d, J = 8.8 Hz, 2H, C₆H₄), 6.94 (d, J = 8.8 Hz, 2H, C₆H₄), 7.46 (t, J = 8.5 Hz, 4H, C₆H₄).

(23) 1,4-Di(p-methylphenyl)benzene

\[
\begin{align*}
\text{NMe}_2 & \quad \text{NMe}_2 \\
\hline
\text{NMe}_2 & \quad \text{NMe}_2
\end{align*}
\]

¹H NMR (CDCl₃): δ 2.40 (s, 6H, CH₃), 7.26 (d, J = 7.2 Hz, 4H, C₆H₄), 7.53 (d, J = 8 Hz, 4H, C₆H₄), 7.64 (s, 4H, C₆H₄).
(24) 1,4-Di(o-methylphenyl)benzene\textsuperscript{11}

\[
\begin{array}{c}
\text{C} \quad \text{C} \\
\text{O} \quad \text{O}
\end{array}
\]

\(^1\)H NMR (CDCl\textsubscript{3}): \(\delta 2.35\) (s, 6H, CH\textsubscript{3}), 7.25–7.32 (m, 8H, C\textsubscript{6}H\textsubscript{4}), 7.37 (s, 4H, C\textsubscript{6}H\textsubscript{4}).

(25) 4-[4-(4-dimethylaminophenyl)phenyl]-N,N-dimethylaniline\textsuperscript{13}

\[
\begin{array}{c}
\text{Me}_2\text{N} \quad \text{C} \quad \text{C} \\
\text{C} \quad \text{C} \\
\text{NMe}_2
\end{array}
\]

\(^1\)H NMR (CDCl\textsubscript{3}): \(\delta 3.00\) (s, 12H, NMe), 6.82 (d, \(J = 8.8\) Hz, 4H, C\textsubscript{6}H\textsubscript{4}), 7.55 (d, \(J = 8.8\) Hz, 4H, C\textsubscript{6}H\textsubscript{4}), 7.59 (s, 4H, C\textsubscript{6}H\textsubscript{4}).

(26) 1,2-Di(p-methylphenyl)benzene\textsuperscript{11}

\[
\begin{array}{c}
\text{C} \\
\text{C} \\
\text{C} \\
\text{O}
\end{array}
\]

\(^1\)H NMR (CDCl\textsubscript{3}): \(\delta 2.32\) (s, 6H, CH\textsubscript{3}), 7.04 (s, 8H, C\textsubscript{6}H\textsubscript{4}), 7.40 (s, 4H, C\textsubscript{6}H\textsubscript{4}).

(27) 4-[2-(4-dimethylaminophenyl)phenyl]-N,N-dimethylaniline\textsuperscript{14}

\[
\begin{array}{c}
\text{NMe}_2 \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{NMe}_2
\end{array}
\]

\(^1\)H NMR (CDCl\textsubscript{3}): \(\delta 2.99\) (s, 12H, NMe), 6.69 (d, \(J = 8.0\) Hz, 4H, C\textsubscript{6}H\textsubscript{4}), 7.15 (d, \(J = 6.9\) Hz, 4H, C\textsubscript{6}H\textsubscript{4}), 7.37-7.48 (m, 4H, C\textsubscript{6}H\textsubscript{4}).

(28) 1,3,5-tris(p-tolyl)benzene\textsuperscript{15}
\(^1\)H NMR (CDCl\(_3\)): \(\delta \) 2.29 (s, 9H, \(\text{CH}_3\)), 7.16 (d, \(J = 7.8 \text{ Hz}\), 6H, \(\text{C}_6\text{H}_4\)), 7.48 (d, \(J = 7.9 \text{ Hz}\), 6H, \(\text{C}_6\text{H}_4\)), 7.63 (s, 3H, \(\text{C}_6\text{H}_3\)).

(29) Ethyl 4-(4-benzoylphenyl)benzoate\(^{16}\)

\[
\begin{array}{c}
\text{Ph} \\
\text{O} \\
\text{O} \\
\end{array}
\]

\(^1\)H NMR (CDCl\(_3\)): \(\delta \) 1.42 (t, \(J = 7.1 \text{ Hz}\), 3H, Me), 4.40 (q, \(J = 7.1 \text{ Hz}\), 2H, CH\(_2\)), 7.50 (t, \(J = 7.5 \text{ Hz}\), 2H, Ph), 7.58-7.62 (m, 1H, Ph), 7.71 (t, \(J = 7.9 \text{ Hz}\), 4H, Ph+\(\text{C}_6\text{H}_4\)), 7.82-7.84 (m, 2H, \(\text{C}_6\text{H}_4\)), 7.90 (d, \(J = 8.5 \text{ Hz}\), 2H, \(\text{C}_6\text{H}_4\)), 8.23 (d, \(J = 8.5 \text{ Hz}\), 2H, \(\text{C}_6\text{H}_4\)).

(30) Ethyl 4-(4-cyanophenyl)benzoate\(^{17}\)

\[
\begin{array}{c}
\text{NC} \\
\text{O} \\
\end{array}
\]

\(^1\)H NMR (CDCl\(_3\)): \(\delta \) 1.42 (t, \(J = 7.1 \text{ Hz}\), 3H, Me), 4.41 (q, \(J = 7.1 \text{ Hz}\), 2H, CH\(_2\)), 7.65 (d, \(J = 8.6 \text{ Hz}\), 2H, \(\text{C}_6\text{H}_4\)), 7.73 (q, \(J = 7.7 \text{ Hz}\), 4H, \(\text{C}_6\text{H}_4\)), 8.15 (d, \(J = 8.6 \text{ Hz}\), 2H, \(\text{C}_6\text{H}_4\)).

References
Scanned NMR spectra
H NMR (CDCl₃)

Ethyl 4-methyl-3-phenyl-4-carboxylate

- 7.96
- 7.94
- 7.48
- 7.45
- 7.30
- 7.33
- 7.10
- 7.07
- 4.28
- 4.26
- 4.23
- 1.28
- 1.26
- 1.23
NMR (CDCl<sub>3</sub>)
$^1$H NMR (CDCl$_3$)

- 7.47
- 7.47
- 7.45
- 7.44
- 7.47
- 7.41
- 7.40
- 7.39
- 7.31
- 7.29
- 7.26
- 7.17
- 7.17
- 7.16
- 7.14
- 7.44
- 6.91
- 6.68

-2.86