Electronic Supplementary Information for:

Nickel-catalyzed cross-coupling of O, N-chelated diarylborinates with
aryl chlorides and mesylates

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1. General information

All reactions were carried out under nitrogen by using standard Schlenk techniques unless otherwise stated. Commercially available chemicals were used as received. trans-NiCl(Ph)(PPh3)2, trans-NiCl(1-Nath)(PPh3)2, trans-NiCl(o-Tol)(PCy3)2, trans-NiCl(o-Tol)(dppf), NiCl2(PPh3)2, 1a-1j, 4a-4g, 4a', N-heterocyclic carbene precursors of [Bmim]Br, [Omim]Br, [diOim]Br, [diBim]Br, IMes·HCl, IPr·HCl, [Iprmim]I, [Ipreim]Br, [Iprbim]Br, [Mesmim]I, were prepared according to previously reported procedures. Column chromatography was performed on 300-400 mesh silica gel. 1H and 13C NMR spectra were recorded in CDCl3 or DMSO-d6 at ambient temperature. Chemical shifts in NMR are reported in ppm (δ), relative to the internal standard of tetramethylsilane (TMS). The signals observed are described as s (singlet), d (doublet), t (triplet), q (quartet), dd (double doublet), m (multiplets). The number of protons (n) for a given resonance is indicated as nH. Coupling constants are reported as J in Hz.

2. Typical procedure for cross-coupling

Under a N2 atmosphere, to a 10 ml dry flask were added aryl chloride/mesylates (1 mmol), diarylborinates (0.65 mmol), NiCl(Ph)(PPh3)2 (3mol%), [Iprmim]I (3mol%), K3PO4·3H2O (2 mmol), and dry toluene (5 ml). The mixture was stirred at 110°C for a given time or monitored by TLC until the starting material was completely consumed. The reaction mixture was diluted with CH2Cl2 (15 ml), followed by washing with H2O (3×10 ml). The organic layer was dried over Na2SO4, filtered, and evaporated under reduced pressure to give crude product, which was purified by column chromatography on silica gel to afford biaryl compounds.

3. Characterization data of biaryl compounds

4-Acetylbiphenyl 3aa
White solid (0.1904g, 97%), mp 121-123°C; 1H NMR (400 MHz, CDCl3) δ 8.02 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 7.6 Hz, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.39 (t, J = 7.2 Hz, 1H), 2.62 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 197.8, 145.8, 139.9, 135.9, 128.99, 128.95, 128.3, 127.3, 127.2, 26.7.

2-Acetylbiphenyl 3ab
Yellow oil (0.1668g, 85%); 1H NMR (400 MHz, CDCl3) δ 7.56-7.49 (m, 2H), 7.43-7.38 (m, 5H), 7.34 (dd, J = 1.6, 7.6 Hz, 2H), 2.0 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 204.9, 140.9, 140.8, 140.5, 130.8, 130.3, 128.9, 128.7, 127.93, 12791, 127.5, 30.5.

3-Acetylbiphenyl 3ac
Yellow oil (0.1766g, 90%); 1H NMR (400 MHz, CDCl3) δ 8.18 (t, J = 1.6 Hz, 1H), 7.92 (dd, J = 1.6, 8.0 Hz, 1H), 7.80-7.78 (m, 1H), 7.61 (d, J = 7.2 Hz, 2H), 7.53 (t, J = 8.0 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.40-7.36 (m, 1H); 13C NMR (100 MHz, CDCl3) δ 198.1, 141.7, 140.2, 137.6, 131.8, 129.1, 129.0, 127.9, 127.3, 127.0, 26.8.

Biphenyl-4-carbaldehyde 3ad
Yellow solid (1a/2d (0.1676g, 92%), 1a/4b (0.1658g, 91%)), mp 57-58°C; 1H NMR
Methyl biphenyl-4-carboxylate 3ae
White solid (1a/2e (0.1974g, 93%), 1a/4c (0.2059g, 97%)), mp 114-115°C; 1H NMR (400 MHz, CDCl3) δ 8.10 (d, J = 8.4 Hz, 2H), 7.67-7.61 (m, 4H), 7.47 (t, J = 7.2 Hz, 2H), 7.31 (t, J = 7.6 Hz, 1H), 7.22 (d, J = 6.0 Hz, 2H), 2.39 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 167.0, 145.6, 140.0, 130.1, 129.0, 128.9, 128.2, 127.3, 127.1, 52.2.

4-Methylbiphenyl 3ah
White solid (1a/2h (0.1598g, 95%), 1a/4d (0.1615g, 96%)), mp 46-48°C; 1H NMR (400 MHz, CDCl3) δ 7.57 (dd, J = 1.6, 8.4 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.42 (t, J = 7.2 Hz, 2H), 7.31 (t, J = 7.6 Hz, 1H), 7.22 (d, J = 6.0 Hz, 2H), 2.39 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 141.3, 138.5, 137.1, 129.6, 128.8, 127.0, 124.1.

2-Phenylanisole 3al
White solid, (0.1474g, 80%), mp 29-30°C; 1H NMR (400 MHz, CDCl3) δ 7.54-7.52 (m, 2H); 7.42-7.38 (m, 2H), 7.33-7.30 (m, 3H), 7.05-7.00(m, 2H), 3.80 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 156.5, 138.6, 130.9, 130.7, 129.6, 128.7, 128.0, 120.9, 111.2, 55.6.

4-Methoxybiphenyl 3ak
White solid (1a/2k (0.1713g, 93%), 1a/4f (0.1732g, 94%)), mp 88-89°C; 1H NMR (400 MHz, CDCl3) δ 7.56-7.51 (m, 4H), 7.40 (t, J = 8.0 Hz, 2H), 7.30 (t, J = 7.6 Hz, 1H), 6.97 (dd, J = 2.0, 6.8 Hz, 2H), 3.84 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 159.2, 140.9, 133.8, 128.8, 128.2, 128.6, 126.7, 114.3, 55.4.

1-(2'-Methylbiphenyl-4-yl)ethenone 3ca
Colourless oil (1c/2a (0.1598g, 93%), 1c/4a (0.1619g, 97%)); 1H NMR (CDCl3, 400 MHz) δ 8.01 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.30-7.21 (m, 4H), 2.65 (s, 3H), 2.27 (s, 3H); 13C NMR (CDCl3, 100 MHz) δ 198.0, 147.0, 140.9, 133.8, 128.8, 128.2, 128.6, 126.7, 114.3, 55.4.
1-(4’-Methylbiphenyl-4-yl)ethanone 3ea
White solid (0.1914 g, 91%), mp 118-120°C; 1H NMR (400 MHz, CDCl3) δ 8.01 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 2.63 (s, 3H), 2.41 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 197.8, 145.7, 138.3, 136.9, 135.6, 129.7, 127.1, 126.9, 26.7, 21.2.

1-(4’-Methoxybiphenyl-4-yl)ethanone 3fa
White solid (0.2036 g, 90%), mp 156-158°C; 1H NMR (400 MHz, CDCl3) δ 8.00 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H), 2.62 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 196.8, 139.5, 135.4, 129.7, 128.9, 128.8, 128.3, 126.6, 114.4, 55.4, 26.6.

1-(2’-Methoxybiphenyl-4-yl)ethanone 3ga
White solid (0.1674 g, 74%), mp 105-106°C; 1H NMR (CDCl3, 400 MHz) δ 8.00 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.38-7.32 (m, 2H), 7.07-6.99 (m, 2H), 3.82 (s, 3H), 2.63 (s, 3H); 13C NMR (CDCl3, 100 MHz) δ 198.0, 156.5, 143.6, 135.5, 130.7, 129.8, 129.5, 129.4, 128.1, 121.0, 111.3, 55.6, 26.7.

1-(4’-trifluoromethyl-4-yl)ethanone 3ha
White solid (0.1797, 68%), mp 122-123°C; 1H NMR (CDCl3, 400 MHz) δ 8.06 (d, J = 7.6 Hz, 2H), 7.73-7.68 (m, 6H), 2.65 (s, 3H); 13C NMR (CDCl3, 100 MHz) δ 197.6, 144.2, 143.4, 136.6, 130.2 (q, J = 32.4 Hz), 129.1, 127.6, 127.5, 125.9 (q, J = 3.8 Hz), 122.8, 26.7.

1-(4’-Fluorobiphenyl-4-yl)ethanone 3ia
White solid (0.2014 g, 94%), mp 108-109°C; 1H NMR (400 MHz, CDCl3) δ 8.02 (d, J = 8.4 Hz, 2H), 7.64-7.56 (m, 4H), 7.15 (t, J = 8.4 Hz, 2H), 2.63 (s, 3H); 13C NMR (CDCl3, 100 MHz) δ 197.7, 163.0 (d, J = 246.5 Hz), 144.7, 136.0 (d, J = 3.4 Hz), 135.8, 129.0, 128.9, 127.1, 115.9 (d, J = 21.5 Hz), 26.7.

1-(3’-Fluorobiphenyl-4-yl)ethanone 3ja
White solid (0.1950 g, 91%), mp 90-91°C; 1H NMR (CDCl3, 400 MHz) δ 8.04 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H), 7.48-7.40 (m, 2H), 7.36-7.32 (m, 1H), 7.14-7.08 (m, 1H), 2.65 (s, 3H); 13C NMR (CDCl3, 100 MHz) δ 197.7, 164.4, 162.0, 144.4, 142.1 (d, J = 7.7 Hz), 136.3, 130.5 (d, J = 8.5 Hz), 129.0, 127.2, 122.9 (d, J = 3.0 Hz), 114.6 (dd, J = 21 Hz, J = 85.6 Hz), 26.7.

4. References
5. $^1$H and $^{13}$CNMR spectra of biaryl compounds

4-Acetylbiphenyl 3aa

$^1$H NMR
$^{13}$C NMR
1-(2'-Methylbiphenyl-4-yl)ethenone 3ca

$^1$H NMR
$^{13}$C NMR
1-(3'-Methylbiphenyl-4-yl)ethenone 3da

$^1$H NMR
1-(4'-Methylbiphenyl-4-yl)ethenone 3ea

$^1$H NMR
$^{13}$C NMR
1-(4′-Methoxybiphenyl-4-yl)ethanone 3fa

$^1$H NMR
1-(2'-Methoxybiphenyl-4-yl)ethanone 3ga

$^1$H NMR
$^{13}\text{C NMR}$
1-(4'-trifluoromethyl-4-yl)ethanone 3ha

$^1$H NMR
$^{13}$C NMR
1-(4'-Fluorobiphenyl-4-yl)ethanone 3ia

$^1$H NMR
1-(3'-Fluorobiphenyl-4-yl)ethanone 3ja

$^1$H NMR
$^{13}$C NMR
2-Acetylbiphenyl 3ab

$^1$H NMR
$^{13}$C NMR
3-Acetylbiphenyl 3ac

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

![13C NMR spectrum diagram](image-url)
Biphenyl-4-carbaldehyde 3ad

$^1$H NMR
$^{13}$C NMR
Methyl biphenyl-4-carboxylate 3ae

$^3$H NMR


$^{13}$C NMR
4-Nitrobiphenyl 3af

$^1$H NMR
2-Nitrobiphenyl 3ag

$^1$H NMR
4-Methylbiphenyl 3ah

$^1$H NMR
$^{13}$C NMR
2-Methylbiphenyl 3ai

$^1$H NMR
$^{13}$C NMR
2,6-Dimethylbiphenyl 3aj

$^1$H NMR
$^{13}$C NMR
4-Methoxybiphenyl 3ak

$^1$H NMR
$^{13}$C NMR
2-Phenylanisole 3al

$^1$H NMR
\[ ^{13}\text{C} \text{ NMR} \]