Supplementary Material (ESI) for

A Pyridine-Bridged Bis-benzimidazolylidene Pincer Nickel(II) Complex: Synthesis and Practical Catalytic Application towards Suzuki-Miyaura Coupling with Less Reactive Electrophiles

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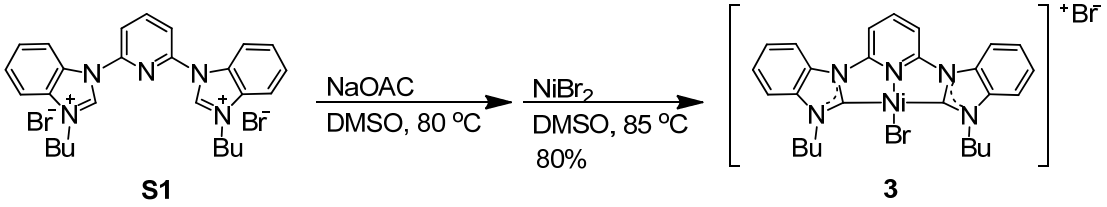
Contents :

1. General

All commercial reagents and solvents were used directly as purchased without further purification. All reactions were carried out under air unless otherwise noted. ^{1}H and ^{13}C NMR spectra were recorded on JeOL-ECA 400 and Bruker 500 DRX spectrometers. ESI-MS spectra were recorded on a micrOTOF II instrument. GC-MS spectra were recorded on Agilent Technologies 1890A GC system and 5975C inert MSD with Triple-Axis Detector. Pyridine-bridged bis-benzoimidazolium bromide **4** was synthesized according to our previous reports.[S1] Aryl tosylates and mesylates were prepared as literature procedures. [S2]

2. Synthesis of pyridine-bridged bis-benzimidazolylidene Nickel complex 3:



S1 **3**

Scheme S1. Synthesis of pyridine-bridged bis-benzimidazolylidene pincer nickel complex **3**.

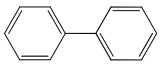
Synthesis of nickel(II)-pincer complex 3: A mixture of pyridine-bridged bis-benzoimidazolium bromide **4**[S1] (300 mg, 0.51 mmol) and sodium acetate (96 mg, 1.17 mmol) was dissolved in DMSO (5 mL) under nitrogen and stirred at room temperature for 20 minutes. After removing the solvent at 80 °C under vacuum, $NiBr_2$ (123 mg, 0.56 mmol) and DMSO (10 mL) were added. Then the reaction mixture was warmed to 85 °C for 3 days. After cooling to room temperature, the supernatant DMSO was removed under vacuum. The resulting residue was washed with little DMSO and then with water to afford a dark-violet solid **3** (252 mg, 80% yield) after drying. ^{1}H NMR (500 mHz, DMSO-d^6, 353 K): δ = 8,53 (t, *J* = 8.2 Hz, 1H), 8.38 (d, *J* = 7.6 Hz, 2H), 8.25 (d, *J* = 8.3 Hz, 2H), 7.96 (d, *J*

= 7.3 Hz, 2H), 7.63-7.69 (m, 4H), 4.96 (m, 4H), 1.94 (m, 4H), 1.51 (m, 4H), 1.00 (t, *J* = 7.4 Hz, 6H). MS (ESI) *m/z*: 562.1 $[M-Br]^+$, HR-MS(ESI) *m/z*: calcd. 562.0943 $[M-Br]^+$; found: 562.0940. Elemental analysis (%) calcd. For $C_{27}H_{29}Br_2N_5Ni$: C 50.51, H 4.55, N 10.91; found: C 50.28, H 4.67, N 10.85.

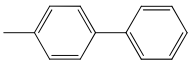
3. General Procedure for the Catalyzed Suzuki–Miyaura Reactions:

A mixture of aryl halide, tosylate or mesylate (0.5 mmol), phenyl boronic acid (122 mg, 1 mmol), nickel(II)-pincer complex **3** (6.4 mg, 0.01 mmol), base (0.6 mmol) and required catalytic amount (2 -20 mol%) of additive PPh_3 in dioxane (2 mL) was warmed to 100 °C under stirring for 24 hours. Then the reaction mixture was allowed to cool to room temperature and was diluted with water (15 mL) followed by extraction with ether three times. The combined extracts were washed with brine and dried over $MgSO_4$. The organic phase was concentrated *in vacuo* and the crude product was purified by flash column chromatography on silica gel (PE/EtOAc). Similar results were obtained when reaction were carried under nitrogen. Details please see Table S1.

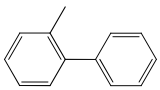
4. Analytical data of the coupling products



5a: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.60 (d, *J* = 7.2 Hz, 4H), 7.45 (t, *J* = 7.6 Hz, 4H), 7.35 (t, *J* = 7.3 Hz, 2H). GC-MS: *m/z* = 154 $[M]^+$, 76.

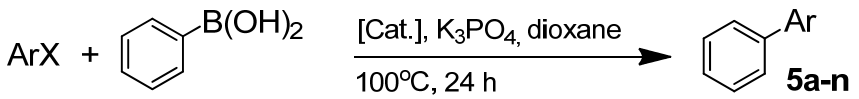


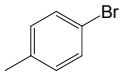
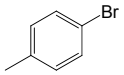
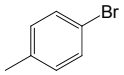
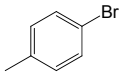
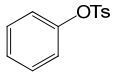
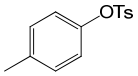
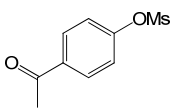
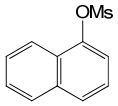
5b: ^{1}H NMR (400MHz, $CDCl_3$, 298K): δ = 7.58 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.26 (d, *J* = 7.9 Hz, 2H), 2.40 (s, 3H). GC-MS: *m/z* = 168 $[M]^+$, 152.



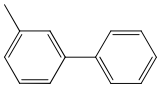
5c: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.45-7.23 (m, 9H), 2.28 (s, 3H). GC-MS: *m/z* = 168.1 $[M]^+$, 153.1, 115.1. GC-MS: *m/z* = 168 $[M]^+$.

Table S1. Suzuki-coupling of aryl halides or sulfonates with phenyl boronic acid catalyzed by pyridine-bridged palladium pincer complex **3**.[a]

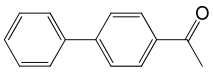


Entry	ArX	[Cat.]		Product	Yield (%)[b]
		Complex **3**	PPh_3		
1		2 mol%	/	**5a**	38
2		2 mol%	/	**5a**	55
3		2 mol%	/	**5b** **(+5a)**	35 (33)
4		2 mol%	2 mol%	**5a**	77
5		2 mol%	2 mol%	**5a**	71
6		2 mol%	2 mol%	**5b**	81
7		/	10 mol%	**5b**	0
8		10 mol% $NiBr_2$	10 mol%	**5b**	0
9		2 mol%	10 mol%	**5a**	57
10		2 mol%	10 mol%	**5b**	69
11		2 mol %	10 mol%	**5e**	82
12		2 mol%	10 mol%	**5l**	85

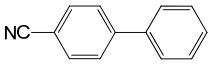
[a] Reaction conditions: 0.5 mmol aryl halide or sulfonate, 1 mmol phenyl boronic acid, 0.6 mmol base in 2 mL solvent at 100°C with catalyst. [b] Isolated yield.



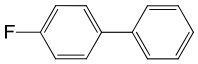
5d: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.59 (d, *J* = 7.0 Hz, 2H), 7.47-7.38 (m, 4H), 7.37-7.31 (m, 2H), 7.17 (d, *J* = 7.4 Hz, 1H), 2.43 (s, 3H). GC-MS: *m/z* = 168 $[M]^+$, 152, 115.



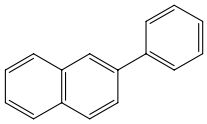
5e: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.04 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 7.0 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 2.65 (s, 3H). GC-MS: *m/z* = 196 [M^+], 181, 152.



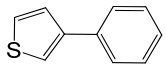
5f: ^{1}H NMR (400MHz, $CDCl_3$, 298K): δ = 7.73 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 7.0 Hz, 2H), 7.49 (t, *J* = 7.3 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 1H). GC-MS: *m/z* = 179 $[M]^+$, 151.



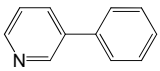
5g: ^{1}H NMR (400MHz, $CDCl_3$, 298K): δ = 7.51-7.63 (m, 4H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.13 (t, *J* = 8.6 Hz, 2H). GC-MS: *m/z* = 172 $[M]^+$



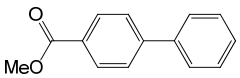
5h: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.05 (s, 1H), 7.93-7.86 (m, 3H), 7.77-7.72 (m, 3H), 7.53-7.47 (m, 4H), 7.38 (t, *J* = 7.3 Hz, 1H). GC-MS: *m/z* = 204 $[M]^+$.



5i: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.61 (d, *J* = 7.2 Hz, 2H), 7.46-7.38 (m, 5H), 7.29 (t, *J* = 7.4 Hz, 1H); GC-MS: *m/z* = 160 $[M]^+$, 128, 115.

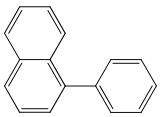


5j: ^{1}H NMR (400MHz, $CDCl_3$, 298K): δ = 8.86 (s, 1H), 8.60 (d, *J* = 4.8 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.43-7.35 (m, 2H). GC-MS: *m/z* = 155 $[M]^+$, 127, 102.

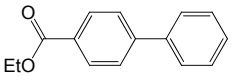


5k: ^{1}H NMR (400MHz, $CDCl_3$, 298K): *δ* = 8.10 (d, *J* = 8.4 Hz, 2H) 7.65 (d, *J* = 8.4 Hz, 2H),

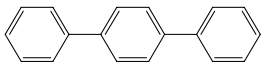
7.61 (d, *J* = 7.2 Hz, 2H) 7.47 (t, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 7.8 Hz, 3H), 3.94 (s, 3H). GC-MS: *m/z* = 212 $[M]^+$.



5l: ^{1}H NMR (400MHz, $CDCl_3$, 298K): δ = 7.70-8.20 (m, 3H), 7.29-7.65 (m, 9H). GC-MS: m/z = 204 $[M^+]$.



5m: ^{1}H NMR (400MHz, $CDCl_3$, 298K): δ = 8.12 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 4.41 (q, *J* = 7.2 Hz, 2H), 1.42 (t, *J* = 7.2 Hz, 3H). GC-MS: *m/z* = 228 $[M+2]^+$, 200, 183, 155.



5n: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.68 (s, 4H), 7.65 (d, *J* = 7.6 Hz, 4H), 7.47 (t, *J* = 7.6 Hz, 4H), 7.37 (t, *J* = 7.4 Hz, 2H); GC-MS: *m/z* = 230 $[M]^+$, 202, 152, 115.

5. References:

S1. (a) T. Tu, X. Bao, W. Assenmacher, H. Peterlik, J. Daniels, K. H. Dötz, *Chem. Eur. J.,* 2009, **15**, 1853; (b) T. Tu, W. Assenmacher, H. Peterlik, G. Schnakenburg, K. H. Dötz, *Angew. Chem. Int. Ed.,* 2008, **47**, 7127; (c) T. Tu, J. Malineni, K. H. Dötz, *Adv. Synth. Catal.,* 2008, **350**, 1791.

S2. V. Percec, J.-Y. Bae, M. Zhao, D. H. Hill, *J. Org. Chem.,* 1995, **60**, 176.