Supporting information for:

# Competitive Gold/Nickel Transmetalation

Mitchell J. Demchuk,<sup>a,†</sup> Joseph A. Zurakowski,<sup>a,†</sup> Brady J. H. Austen,<sup>a</sup> David J. Nelson,<sup>b,\*</sup> and

Marcus W. Drover<sup>a,\*</sup>

<sup>a</sup>Department of Chemistry and Biochemistry, The University of Windsor, 401 Sunset Avenue, Windsor, ON, N9B 3P4, Canada \*E-mail: <u>marcus.drover@uwindsor.ca</u>

<sup>b</sup>WestCHEM Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow, G1 1XL, Scotland, <u>david.nelson@strath.ac.uk</u> <sup>+</sup> These authors contributed equally.

1. Experimental Section	S2
2. Preparation of Compounds	<b>S</b> 3
3. Multinuclear NMR data	<b>S8</b>
4. Crystallography	S35
5. Computational Chemistry	S38

## **Experimental Section:**

**General Considerations.** All experiments were carried out employing standard Schlenk techniques under an atmosphere of dry nitrogen employing degassed, dried solvents in a solvent purification system supplied by PPT, LLC. Non-halogenated solvents were tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran in order to confirm effective moisture removal. *d*<sub>6</sub>-benzene was dried over molecular sieves and degassed by three freeze-pump-thaw cycles. HBCy<sub>2</sub><sup>1</sup>,  $[Ni(P_2B^{Cy}_4)_2]$ ,  $^2[Ni(P_2B^{Cy}_4)_2]$ ,  $^2$ 

**Physical methods.** <sup>1</sup>H NMR spectra are reported in parts per million (ppm) and are referenced to residual solvent e.g., <sup>1</sup>H(C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.16; <sup>13</sup>C(C<sub>6</sub>D<sub>6</sub>): 128.06; coupling constants are reported in Hz. <sup>13</sup>C, <sup>11</sup>B, and <sup>31</sup>P NMR spectra were performed as proton-decoupled experiments and are reported in ppm.

<sup>&</sup>lt;sup>1</sup> A. Abiko, Org. Synth. **2002**, 79, 103.

<sup>&</sup>lt;sup>2</sup> M. W. Drover, M. C. Dufour, L. A. Lesperance-Nantau, R. P. Noriega, K. Levin and R. W. Schurko, *Chem. –Eur. J.* **2020**, *26*, 11180;

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#### **Preparation of Compounds:**

**Representative procedure for transmetalation:** In the glovebox,  $[Ni(P_2B^{Cy_4})(4-C_6H_4F)(I)]^3$  (5 mg, 1 equiv.) and  $[(R-C_6H_4) - Au(PPh_3)]$  (R = H, CH<sub>3</sub>O, F, CF<sub>3</sub>) were combined and dissolved in *ca.* 500 µL C<sub>6</sub>D<sub>6</sub>; 1 equiv. of C<sub>6</sub>H<sub>5</sub>CF<sub>3</sub> and Ph<sub>3</sub>P=O was added as an internal standard. The mixture was transferred to a J. Young NMR tube, removed from the glovebox, and immediately analyzed by NMR spectroscopy. Alternative preparations of  $[Ni^{II}(P_2B^{Cy_4})(4-CH_3OC_6H_4)(I)]$  and  $[Ni^{II}(P_2B^{Cy_4})(4-CF_3C_6H_4)(I)]$  are provided below.

[Ni<sup>II</sup>(P<sub>2</sub>B<sup>Cy</sup><sub>4</sub>)(4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>)(I)] (2-OCH<sub>3</sub>; C<sub>69</sub>H<sub>123</sub>B<sub>4</sub>IOP<sub>2</sub>Ni,

 $M_W$  = 1259 g/mol): In the glovebox, [Ni<sup>0</sup>(P<sub>2</sub>B<sup>Cy<sub>4</sub></sup>)<sub>2</sub>] (1) (35 mg, 0.018 mmol) and 4-iodoanisole (4 mg, 0.018 mmol, ≈ 1 equiv.) were added to a 20 mL scintillation vial equipped with a stir bar and 4 mL of toluene. This mixture was stirred for 6 h and toluene removed *in-vauco*, providing crude complex **2-OCH**<sub>3</sub>, which was recrystallized from hexanes (1 mL) at -35 °C to provide



orange crystals (7 mg, 33%). <sup>1</sup>H{<sup>31</sup>P} NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = 7.71 (app. t, <sup>3</sup>*J*<sub>H,H</sub> = 8.4 Hz, 2H, Ni-Ar<sub>ortho</sub>), 7.01 (t, 2H, <sup>3</sup>*J*<sub>HH</sub> = 8.4 Hz; Ni-Ar<sub>meta</sub>), 3.43 (s, OC<u>H</u><sub>3</sub>) 2.26 (m, 4H), 2.00 – 1.15 (multiple overlapping C(*sp*<sup>3</sup>)–H resonances). <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = 157.2, 137.8, 113.8 (d, *J*<sub>P,C</sub> = 6 Hz), 54.6, 36.2, 30.5 (d, *J*<sub>P,C</sub> = 22 Hz), 29.2 (d, *J*<sub>P,C</sub> = 28 Hz), 28.0, 27.9, 27.6, 27.5, 27.4, 26.8 (m), 22.9 (m), 20.6, 20.0, (some alkyl signals are overlapping, one aryl signal not observed). <sup>31</sup>P{<sup>1</sup>H} NMR (202.5 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = + 61.0 (d, <sup>2</sup>*J*<sub>P,P</sub> = 25 Hz), 52.0 (d, <sup>2</sup>*J*<sub>P,P</sub> = 25 Hz). <sup>11</sup>B{<sup>1</sup>H} NMR (160.5 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = + 83.8 (Δ<sub>1/2</sub> = 2900 Hz; BCy<sub>2</sub>R).

**[Ni<sup>II</sup>(P<sub>2</sub>B<sup>Cy<sub>4</sub></sup>)(4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)(I)]** (2-CF<sub>3</sub>; C<sub>69</sub>H<sub>120</sub>B<sub>4</sub>IF<sub>3</sub>P<sub>2</sub>Ni, M<sub>W</sub> = 1297 g/mol): In the glovebox, [Ni<sup>0</sup>(P<sub>2</sub>B<sup>Cy<sub>4</sub></sup>)<sub>2</sub>] (1) (35 mg, 0.018 mmol) and 4-iodobenzotrifluoride ( $\approx$  5 mg, 0.018 mmol,  $\approx$  1 equiv.) were added to a 20 mL scintillation vial equipped with a stir bar and 4 mL of toluene. This mixture was stirred for 6 h and toluene removed *in-vauco*, providing crude complex **2-CF**<sub>3</sub>, which was recrystallized from hexanes (1



mL) at -35 °C to provide orange crystals, contaminated with "free" P<sub>2</sub>B<sup>Cy</sup><sub>4</sub>. Unlike previous *p*-X (X = H, F, OCH<sub>3</sub>) oxidative addition adducts, the *p*-CF<sub>3</sub> variant could not be separated from free ligand due to similar solubility. The conversion of **1** by <sup>31</sup>P NMR spectroscopy was found to be > 95%. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = 7.93 (app. t, <sup>3</sup>*J*<sub>H,H</sub> = 7.9 Hz, 2H, Ni-Ar<sub>ortho</sub>), 7.48 (d, 2H, <sup>3</sup>*J*<sub>HH</sub> = 7.8 Hz; Ni-Ar<sub>meta</sub>), 2.22 (m, 4H), 2.00 – 1.15 (multiple overlapping C(*sp*<sup>3</sup>)–H resonances). <sup>31</sup>P{<sup>1</sup>H} NMR (202.5 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = + 62.3 (d, <sup>2</sup>*J*<sub>P,P</sub> = 25 Hz), 53.5 (d, <sup>2</sup>*J*<sub>P,P</sub> = 25 Hz). <sup>19</sup>F{<sup>1</sup>H} NMR (470.8 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = - 64.3 (s). <sup>11</sup>B{<sup>1</sup>H} NMR (160.5 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = + 83.9 ( $\Delta$ <sub>1/2</sub> = 2900 Hz; BCy<sub>2</sub>R).

**[Ni<sup>o</sup>(P<sub>2</sub>B<sup>Cy<sub>4</sub></sup>)(PPh<sub>3</sub>)<sub>2</sub>] (3**; C<sub>98</sub>H<sub>146</sub>B<sub>4</sub>P<sub>4</sub>Ni, M<sub>W</sub> = 1550 g/mol): In the glovebox, [Ni<sup>o</sup>(P<sub>2</sub>B<sup>Cy<sub>4</sub></sup>)<sub>2</sub>] (**1**) (35 mg, 0.018 mmol) and PPh<sub>3</sub> (9 mg, 0.036 mmol, 2 equivs.) were added to a 20 mL scintillation vial equipped with a stir bar and 4 mL of toluene. This mixture was stirred for 2 h and toluene removed *in-vauco*, providing crude complex **3** and free P<sub>2</sub>B<sup>Cy<sub>4</sub></sup> ligand in >99% conversion by <sup>31</sup>P NMR spectroscopy. Efforts to separate **3** from "free" P<sub>2</sub>B<sup>Cy<sub>4</sub></sup> were unsuccessful. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = 7.54-7.49 (m, 12H), 7.11-7.06 (m,



18H), 2.00 – 1.08 (multiple overlapping C(*sp*<sup>3</sup>)–H resonances). \*Free PPh<sub>3</sub> also present at  $\delta$  = 7.41-7.37 (m, 6H), 7.03-7.05 (m, 9H). <sup>31</sup>P{<sup>1</sup>H} NMR (202.5 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = + 34.8 (t, <sup>2</sup>*J*<sub>P,P</sub> = 27 Hz; PPh<sub>3</sub>), 19.7 (t, <sup>2</sup>*J*<sub>P,P</sub> = 27 Hz; P<sub>2</sub>B<sup>Cy</sup><sub>4</sub>). <sup>11</sup>B{<sup>1</sup>H} NMR (160.5 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = + 84.3 ( $\Delta$ <sub>1/2</sub> = 1800 Hz; BCy<sub>2</sub>R). Compound **3** was not isolated and thus an elemental analysis was not performed.

[Ni<sup>II</sup>(*dnppe*)(4-FC<sub>6</sub>H<sub>4</sub>)(I)] (4-F; C<sub>20</sub>H<sub>36</sub>FIP<sub>2</sub>Ni, M<sub>W</sub> = 543 g/mol): In the glovebox, [Ni<sup>0</sup>(COD)<sub>2</sub>] (30 mg, 0.11 mmol) was added in one portion to a 20 mL scintillation vial equipped with a stir bar containing *dn*ppe (28 mg, 0.11 mmol, 1 equiv.) and 4fluoroiodobenzene (48 mg, 0.22 mmol, 2 equiv.) in 4 mL of



toluene. This mixture was stirred for 6 h and toluene was removed *in-vauco*, providing crude complex **4**-F, which was recrystallized from toluene (1 mL) layered with hexanes (1 mL) at -35 °C to provide orange crystals (23 mg, 40%). <sup>1</sup>H{<sup>31</sup>P} NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, **298 K)**:  $\delta$  = 7.49 (app. t, <sup>3</sup>*J*<sub>H,H</sub> = 7.1 Hz, 2H, Ni-Ar<sub>ortho</sub>), 6.99 (t, 2H, <sup>3</sup>*J*<sub>HH</sub> = 8.7 Hz; Ni-Ar<sub>meta</sub>), 2.02 (m, 2H), 1.79 (m, 2H), 1.54 (m, 4H), 1.37 (m, 2H), 1.23 (m, 2H), 1.17 (m, 2H), 1.04 (m, 2H), 0.97 (t, 6H, <sup>3</sup>*J*<sub>HH</sub> = 7.2 Hz), 0.91 (m, 2H), 0.83 (m, 2H), 0.73 (t, 6H, <sup>3</sup>*J*<sub>HH</sub> = 7.2 Hz).

<sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = 162.5 (m), 137.7, 113.8 (m), 28.9 (d, *J*<sub>P,C</sub> = 23.5 Hz), 27.5 (d, *J*<sub>P,C</sub> = 30 Hz), 26.0 (m), 22.3 (m), 18.8, 18.3, 16.4 (d, *J*<sub>P,C</sub> = 13.6 Hz), 16.1 (d, *J*<sub>P,C</sub> = 15.0 Hz); one Ar-C under C<sub>6</sub>D<sub>6</sub>. <sup>31</sup>P{<sup>1</sup>H} NMR (202.5 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = + 62.3 (d, <sup>2</sup>*J*<sub>P,P</sub> = 24 Hz), 52.3 (d, <sup>2</sup>*J*<sub>P,P</sub> = 24 Hz). <sup>19</sup>F{<sup>1</sup>H} NMR (470.8 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = -124.4 (s). Anal. Calcd. for C<sub>20</sub>H<sub>36</sub>FIP<sub>2</sub>Ni (543): C, 44.24; H, 6.68. Found: C, 45.11; H, 6.57.

[Ni<sup>II</sup>(*dn*ppe)(C<sub>6</sub>H<sub>5</sub>)(I)] (4-H; C<sub>20</sub>H<sub>37</sub>IP<sub>2</sub>Ni, M<sub>W</sub> = 524 g/mol): In the glovebox, [Ni<sup>0</sup>(COD)<sub>2</sub>] (30 mg, 0.11 mmol) was added in one portion to a 20 mL scintillation vial equipped with a stir bar containing *dn*ppe (28 mg, 0.11 mmol, 1 equiv.) and iodobenzene (44 mg, 0.22 mmol, 2 equiv.) in 4 mL of toluene. This mixture was



stirred for 6 h and toluene was removed *in-vauco*, providing crude complex 4-H as an orange powder, which was recrystallized from toluene (1 mL) layered with hexanes (1 mL) at –35 °C to provide orange crystals (26 mg, 46%). <sup>1</sup>H{<sup>31</sup>P} NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, **298 K)**:  $\delta$  = 7.49 (app. t, <sup>3</sup>J<sub>H,H</sub> = 7.1 Hz, 2H, Ni-Ph<sub>ortho</sub>), 6.99 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 8.7 Hz; Ni-Ph<sub>meta</sub>), 2.02 (m, 2H), 1.79 (m, 2H), 1.54 (m, 4H), 1.37 (m, 2H), 1.23 (m, 2H), 1.17 (m, 2H), 1.04 (m, 2H), 0.97 (t, 6H, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz), 0.91 (m, 2H), 0.83 (m, 2H), 0.73 (t, 6H, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = 161.2 (m), 137.8, 126.7 (d, *J*<sub>P,C</sub> = 6 Hz), 122.2, 28.9 (d, *J*<sub>P,C</sub> = 23.5 Hz), 27.6 (d, *J*<sub>P,C</sub> = 30 Hz), 26.1 (m), 22.3 (m), 18.8, 18.4, 16.4 (d, *J*<sub>P,C</sub> = 13.5 Hz), 16.1 (d, *J*<sub>P,C</sub> = 15.0 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (470.8 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = -124.4 (s).

[Au(PPh<sub>3</sub>)(4-Pyr)] (5; C<sub>23</sub>H<sub>19</sub>AuNP, M<sub>w</sub> = 537.1 g/mol): Prepared used a modified literature procedure.<sup>5</sup> Outside the glovebox, [Br—Au(PPh<sub>3</sub>)] (100 mg, 0.19 mmol, 1 equiv.), Cs<sub>2</sub>CO<sub>3</sub> (121 mg, 0.37 mmol, 2 equivs.), and 4-pyridylboronic acid (46 mg, 0.37 mmol, 2 equivs.) were combined in a 10 mL reaction vessel. Approximately 5 mL of isopropanol was added and the solution was heated at 50 °C for 4 days, giving a colorless solution with some white solid on the sides of



the vessel. Next, volatiles were removed *in-vacuo* and the resulting white solid was extracted into toluene; crystallization from hexane-layered toluene at –35 °C overnight gave white crystals of **5** (75 mg, 75%). **<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):**  $\delta$  = 8.88 (d, 2H, <sup>3</sup>*J*<sub>H,H</sub> = 5.4 Hz), 7.75 (d, 2H, <sup>3</sup>*J*<sub>H,H</sub> = 5.4 Hz), 7.35 (m, 6H; PPh<sub>3</sub>), 6.98 (m, 3H; PPh<sub>3</sub>), 6.93 (m, 6H; PPh<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = 149.2, 136.2, 134.5 (d, *J*<sub>C,P</sub> = 13.8 Hz),

<sup>&</sup>lt;sup>5</sup> D. V. Partyka, M. Zeller, A. D. Hunter, and T. G. Gray, Inorg. Chem. 2012, 51, 8394.

131.2, 129.2 (d,  $J_{C,P}$  = 10.5 Hz); (two aryl signals not observed). <sup>31</sup>P{<sup>1</sup>H} NMR (161.9 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = 42.9 (br). Anal. Calcd. for C<sub>23</sub>H<sub>19</sub>AuNP (537.4): C, 51.41; H, 3.56; N, 2.61. Found: C, 51.96; H, 3.85; N, 2.47.

 $[Ni(P_2B^{Cy_4}[(4-NC_5H_4)-Au(PPh_3)])_2]$ (6: C308H384Au8B8N8NiP12, Mw = 6291.1 g/mol): In the glovebox,  $[Ni(P_2B^{Cy_4})_2]$  (1) (10 mg, 0.005) mmol, 1 equiv.) and  $[(4-NC_5H_4)-Au(PPh_3)]$ (5) (22 mg, 0.04 mmol, 8 equivs.) were combined in a 20 mL scintillation vial equipped with a stir bar. Approximately 500 µL of THF was added and the solution was transferred into a J. Young NMR tube. This compound was not isolated. <sup>1</sup>H NMR (500 MHz, THF-d<sub>8</sub>, 298 K):  $\delta = 8.18$  (br, 16H; (4-NC<sub>5</sub>H<sub>4</sub>)-Au), 7.59 (m, 48H; PPh<sub>3</sub>), 7.47 (m, 88H; PPh<sub>3</sub> (72H) + (4-NC<sub>5</sub>H<sub>4</sub>)-Au (16H)), 1.7 - 0.5 (overlapping C(*sp*<sup>3</sup>)—H resonances, 232 H). <sup>31</sup>P{<sup>1</sup>H} NMR (203



MHz, THF-d<sub>8</sub>, 298 K):  $\delta$  = 41.1 ([Au]-P), 35.1 ([Ni]-P). <sup>11</sup>B{<sup>1</sup>H} NMR (160.5 MHz, THF-d<sub>8</sub>, 193 K):  $\delta$  = -4.1. Compound 6 was not isolated and thus an elemental analysis was not performed.

**Reaction of 5 with 4-iodofluorobenzene:** In the glovebox,  $[Ni(P_2B^{cy_4}){[(4-NC_5H_4)-Au(PPh_3)]_2]}$  (6) (generated *in-situ* from  $[Ni(P_2B^{cy_4})_2]$  (10 mg, 0.005 mmol, 1 equiv.) and  $[(4-NC_5H_4)-Au(PPh_3)]$  (5) (21.6 mg, 0.04 mmol, 8 equivs.)) and 4-iodofluorobenzene (1 equiv.) were combined and dissolved in *ca*. 500 µL THF-ds. The mixture was transferred to a J. Young NMR tube, removed from the glovebox, and immediately analyzed by NMR spectroscopy. Cross-coupled product was not observed by <sup>19</sup>F NMR spectroscopy. Compound **6** was found to decompose overnight.

**Catalytic Reactivity Study**: In the glovebox, ~ 10 mg of  $[Ni^0(P_2B^{Cy_4})_2]$  (1) (0.005 mmol), 4fluoroiodobenzene (10 equivs.), and trifluorotoluene (1 equiv.) and were dissolved in *ca*. 500 µL C<sub>6</sub>D<sub>6</sub> and stirred for 1 h.  $[(4-CH_3OC_6H_4)-Au(PPh_3)]$  (~10 equivs.) was added and the mixture was transferred to a J. Young NMR tube. The reaction mixture was analyzed by <sup>19</sup>F NMR spectroscopy after 18 h at room temperature indicating the formation of 4-fluoro-4'-methoxy-1,1'-biphenyl in 86% conversion.

# Multinuclear NMR data:

Figure S1. 2-OCH<sub>3</sub>, <sup>1</sup>H NMR, C<sub>6</sub>D<sub>6</sub>, 500 MHz, 298 K



Figure S2. 2-OCH<sub>3</sub>, <sup>31</sup>P{<sup>1</sup>H} NMR, C<sub>6</sub>D<sub>6</sub>, 203 MHz, 298 K



Figure S3. 2-OCH<sub>3</sub>, <sup>11</sup>B NMR, C<sub>6</sub>D<sub>6</sub>, 160.5 MHz, 298 K



Figure S4. 2-OCH<sub>3</sub>, <sup>13</sup>C{<sup>1</sup>H} NMR, C<sub>6</sub>D<sub>6</sub>, 125 MHz, 298 K



Figure S5. Mixture of 2-CF<sub>3</sub> and free  $P_2B^{Cy_4}$ , <sup>1</sup>H NMR, C<sub>6</sub>D<sub>6</sub>, 500 MHz, 298 K



**Figure S6.** Mixture of **2-CF**<sub>3</sub> and free  $P_2B^{Cy_4}$ ,  ${}^{31}P{}^{1}H$  NMR,  $C_6D_6$ , 203 MHz, 298 K (\*\*free  $P_2B^{Cy_4} \delta_P = 14.0 \text{ ppm}$ )



Figure S7. Mixture of 2-CF<sub>3</sub> and free  $P_2B^{Cy_{4, 19}}F_{1H}$  NMR, C<sub>6</sub>D<sub>6</sub>, 471 MHz, 298 K



Figure S8. 2-F + [(C<sub>6</sub>H<sub>5</sub>) – Au(PPh<sub>3</sub>)], <sup>1</sup>H NMR, C<sub>6</sub>D<sub>6</sub>, 500 MHz, 298 K



**Figure S9. 2**-F **+ [(C<sub>6</sub>H<sub>5</sub>)**—**Au(PPh<sub>3</sub>)]**, <sup>31</sup>P{<sup>1</sup>H} NMR, C<sub>6</sub>D<sub>6</sub>, 203 MHz, 298 K (# signals at δ<sub>P</sub> = 35.9 and 20.8 ppm due to [Ni<sup>0</sup>(P<sub>2</sub>B<sup>Cy<sub>4</sub></sup>)(PPh<sub>3</sub>)<sub>2</sub>])



**Figure S10. 2**-F + [(C<sub>6</sub>H<sub>5</sub>) – Au(PPh<sub>3</sub>)], <sup>19</sup>F{<sup>1</sup>H} NMR, C<sub>6</sub>D<sub>6</sub>, 471 MHz, 298 K





Figure S11. 2-F + [(4-MeOC<sub>6</sub>H<sub>4</sub>) – Au(PPh<sub>3</sub>)], <sup>1</sup>H NMR, C<sub>6</sub>D<sub>6</sub>, 500 MHz, 298 K

Figure S12. 2-F + [(4-MeOC<sub>6</sub>H<sub>4</sub>) – Au(PPh<sub>3</sub>)], <sup>31</sup>P{<sup>1</sup>H} NMR, C<sub>6</sub>D<sub>6</sub>, 203 MHz, 298 K





Figure S13. 2-F + [(4-MeOC<sub>6</sub>H<sub>4</sub>) – Au(PPh<sub>3</sub>)], <sup>19</sup>F{<sup>1</sup>H} NMR, C<sub>6</sub>D<sub>6</sub>, 471 MHz, 298 K

**Figure S14. 2**-F + [(4-FC<sub>6</sub>H<sub>4</sub>) – Au(PPh<sub>3</sub>)], <sup>1</sup>H NMR, C<sub>6</sub>D<sub>6</sub>, 500 MHz, 298 K



**Figure S15. 2**-F + **[(4-FC<sub>6</sub>H<sub>4</sub>)** – **Au(PPh<sub>3</sub>)]**, <sup>31</sup>P{<sup>1</sup>H} NMR, C<sub>6</sub>D<sub>6</sub>, 203 MHz, 298 K (# signals at  $\delta_P$  = 35.9 and 20.8 ppm due to [Ni<sup>0</sup>(P<sub>2</sub>B<sup>Cy</sup><sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub>])



Figure S16. 2-F + [(4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>) – Au(PPh<sub>3</sub>)], <sup>31</sup>P{<sup>1</sup>H} NMR, C<sub>6</sub>D<sub>6</sub>, 203 MHz, 298 K



Figure S17. 3, <sup>1</sup>H NMR, C<sub>6</sub>D<sub>6</sub>, 500 MHz, 298 K (P<sub>2</sub>B<sup>Cy<sub>4</sub></sup> and free PPh<sub>3</sub> impurities present)



**Figure S18. 3**,  ${}^{31}P{}^{1}H{}$  NMR, C<sub>6</sub>D<sub>6</sub>, 203 MHz, 298 K ( $\delta_{P} = -6.1$  (PPh<sub>3</sub>), 14.4 (P<sub>2</sub>B<sup>Cy</sup><sub>4</sub>), 38.2 ([Ni(P<sub>2</sub>B<sup>Cy</sup><sub>4</sub>)<sub>2</sub>]))





Figure S19. Stacked plot showing presence of 3 in cross-coupling reactions,  $^{31}P\{^{1}H\}$  NMR, C<sub>6</sub>D<sub>6</sub>, 203 MHz, 298 K

Figure S20. Mixture of 3 and free P<sub>2</sub>B<sup>Cy</sup><sub>4</sub>, <sup>11</sup>B NMR, C<sub>6</sub>D<sub>6</sub>, 160.5 MHz, 298 K



# Figure S21. 4-F, <sup>1</sup>H NMR, C<sub>6</sub>D<sub>6</sub>, 500 MHz, 298 K



Figure S22. 4-F, <sup>31</sup>P{<sup>1</sup>H} NMR, C<sub>6</sub>D<sub>6</sub>, 203 MHz, 298 K



**Figure S23. 4**-F, <sup>19</sup>F{<sup>1</sup>H} NMR, C<sub>6</sub>D<sub>6</sub>, 471 MHz, 298 K



Figure S24. 4-F, <sup>13</sup>C{<sup>1</sup>H} NMR, C<sub>6</sub>D<sub>6</sub>, 125 MHz, 298 K



# **Figure S25. 4-**H, <sup>1</sup>H NMR, C<sub>6</sub>D<sub>6</sub>, 500 MHz, 298 K



Figure S26. 4-H, <sup>31</sup>P{<sup>1</sup>H} NMR, C<sub>6</sub>D<sub>6</sub>, 203 MHz, 298 K



# **Figure S27. 4**-H, <sup>13</sup>C{<sup>1</sup>H} NMR, C<sub>6</sub>D<sub>6</sub>, 125 MHz, 298 K



**Figure S28.** 4-F + [(C<sub>6</sub>H<sub>5</sub>) – Au(PPh<sub>3</sub>)], <sup>1</sup>H NMR, C<sub>6</sub>D<sub>6</sub>, 500 MHz, 298 K



**Figure S29.** 4-F + **[(C<sub>6</sub>H<sub>5</sub>)** – **Au(PPh<sub>3</sub>)]**, <sup>31</sup>P{<sup>1</sup>H} NMR, C<sub>6</sub>D<sub>6</sub>, 203 MHz, 298 K (# signals at  $\delta_P = 35.3$  and 20.6 ppm due to [Ni<sup>0</sup>(d*n*ppe)(PPh<sub>3</sub>)<sub>2</sub>])



**Figure S30.** 4-F + [(C<sub>6</sub>H<sub>5</sub>) – Au(PPh<sub>3</sub>)], <sup>19</sup>F{<sup>1</sup>H} NMR, C<sub>6</sub>D<sub>6</sub>, 471 MHz, 298 K





Figure S31. 5, <sup>1</sup>H NMR, C<sub>6</sub>D<sub>6</sub>, 500 MHz, 298 K

Figure S32. 5, <sup>1</sup>H NMR (expansion), C<sub>6</sub>D<sub>6</sub>, 203 MHz, 298 K



# Figure S33. 5, <sup>31</sup>P{<sup>1</sup>H} NMR, C<sub>6</sub>D<sub>6</sub>, 203 MHz, 298 K



Figure S34. 5, <sup>13</sup>C{<sup>1</sup>H} NMR, C<sub>6</sub>D<sub>6</sub>, 125 MHz, 298 K







**Figure S36.** <sup>1</sup>H NMR, THF-d<sub>8</sub>, 500 MHz, 298 K of **a**) [(4–NC<sub>5</sub>H<sub>4</sub>)–Au(PPh<sub>3</sub>)] and **b**) [Ni(P<sub>2</sub>B<sup>Cy</sup><sub>4</sub>)<sub>2</sub>] + 8 equivs. [(4–NC<sub>5</sub>H<sub>4</sub>)–Au(PPh<sub>3</sub>)]



**Figure S37.** <sup>1</sup>H NMR, THF-d<sub>8</sub>, 500 MHz, 298 K of **a**) [(4–NC<sub>5</sub>H<sub>4</sub>)–Au(PPh<sub>3</sub>)] and **b**) [Ni(P<sub>2</sub>B<sup>Cy</sup><sub>4</sub>)<sub>2</sub>] + 8 equivs. [(4–NC<sub>5</sub>H<sub>4</sub>)–Au(PPh<sub>3</sub>)]



**Figure S38. 6**, <sup>31</sup>P{<sup>1</sup>H} NMR, THF-d<sub>8</sub>, 203 MHz, 298 K



**Figure S39.** <sup>31</sup>P{<sup>1</sup>H} NMR, THF-d<sub>8</sub>, 203 MHz, 298 K of a) [Ni(P<sub>2</sub>B<sup>Cy</sup><sub>4</sub>)<sub>2</sub>], b) [(4-NC<sub>5</sub>H<sub>4</sub>)-Au(PPh<sub>3</sub>)], and c) [Ni(P<sub>2</sub>B<sup>Cy</sup><sub>4</sub>)<sub>2</sub>] + 8 equivs. [(4-NC<sub>5</sub>H<sub>4</sub>)-Au(PPh<sub>3</sub>)]



**Figure S40. 6**, <sup>11</sup>B{<sup>1</sup>H} NMR, THF-d<sub>8</sub>, 160.5 MHz, 298 K (no signal at 298 K)





Figure S41. 6, <sup>1</sup>H NMR, THF-d<sub>8</sub>, 500 MHz

Figure S42. 6,  ${}^{31}\mathrm{P}\{{}^{1}\mathrm{H}\}$  NMR, THF-d\_8, 203 MHz





Figure S43. 6, VT  $^{\rm 31}\rm{P}\{^{1}\rm{H}\}$  NMR (baseline enhanced), THF-d\_8, 203 MHz

Figure S44. 5, VT  $^{11}B\{^{1}H\}$  NMR, THF-d\_8, 160.5 MHz





Figure S45. 2-F + [(4-NC<sub>5</sub>H<sub>4</sub>) – Au(PPh<sub>3</sub>)], <sup>1</sup>H NMR, C<sub>6</sub>D<sub>6</sub>, 500 MHz, 298 K

**Figure S46. 2**-F **+ [(4-NC**<sub>5</sub>H<sub>4</sub>) – **Au(PPh**<sub>3</sub>)], <sup>31</sup>P{<sup>1</sup>H} NMR, C<sub>6</sub>D<sub>6</sub>, 203 MHz, 298 K (# signals at δ<sub>P</sub> = 35.9 and 20.8 ppm due to [Ni<sup>0</sup>(P<sub>2</sub>B<sup>Cy</sup><sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub>])





**Figure S47. 2-F + [(4-NC<sub>5</sub>H<sub>4</sub>) – Au(PPh<sub>3</sub>)]**, <sup>19</sup>F{<sup>1</sup>H} NMR, C<sub>6</sub>D<sub>6</sub>, 471 MHz, 298 K

**Figure S48.** 2-OCH<sub>3</sub> + **[(4-NC**<sub>5</sub>H<sub>4</sub>) – Au(PPh<sub>3</sub>)], <sup>31</sup>P{<sup>1</sup>H} NMR, C<sub>6</sub>D<sub>6</sub>, 203 MHz, 298 K (# signals at  $\delta_P$  = 35.9 and 20.8 ppm due to [Ni<sup>0</sup>(P<sub>2</sub>B<sup>Cy<sub>4</sub></sup>)(PPh<sub>3</sub>)<sub>2</sub>])



### Yield Tables:

## Table S2. 2-F + [(C<sub>6</sub>H<sub>5</sub>) – Au(PPh<sub>3</sub>)]



<sup>a</sup>determined by <sup>31</sup>P NMR spectroscopy using Ph<sub>3</sub>P=O as an internal standard <sup>b</sup>determined by <sup>19</sup>F NMR spectroscopy using  $C_6H_5CF_3$  as an internal standard <sup>c</sup>NQ = not quantified

#### $(P_2B^{Cy}_4)Ni$ products OCH<sub>3</sub> C<sub>6</sub>D<sub>6</sub>, r.t. OCH<sub>3</sub> OCH<sub>3</sub> Ph₃ (P<sub>2</sub>B<sup>Cy</sup><sub>4</sub>)Ni $(P_2 B^{Cy}_4)Ni$ $(P_2B^{Cy}_4)Ni$ PPh<sub>3</sub> OCH<sub>3</sub> **2-**F 2-0CH3 3 **OCH**<sub>3</sub> time 29%<sup>b</sup> 5%<sup>b</sup> 7 min 31%<sup>a</sup> 16%<sup>a</sup> 14%<sup>a</sup> NQ 6%<sup>b</sup> 35 min 19%<sup>a</sup> 0%<sup>a</sup> 21%<sup>a</sup> 31%<sup>b</sup> NQ 60 min 0%<sup>a</sup> 0%<sup>a</sup> 21%<sup>a</sup> 37%<sup>b</sup> 9%<sup>b</sup> NQ

#### Table S3. 2-F + [(4-CH<sub>3</sub>OC<sub>5</sub>H<sub>4</sub>) – Au(PPh<sub>3</sub>)]

<sup>a</sup>determined by <sup>31</sup>P NMR spectroscopy using Ph<sub>3</sub>P=O as an internal standard

<sup>b</sup>determined by <sup>19</sup>F NMR spectroscopy using C<sub>6</sub>H<sub>5</sub>CF<sub>3</sub> as an internal standard

<sup>c</sup>NQ = not quantified

#### Table S4. 2-F + [(4-F<sub>3</sub>CC<sub>5</sub>H<sub>4</sub>) – Au(PPh<sub>3</sub>)]



<sup>a</sup>determined by <sup>31</sup>P NMR spectroscopy using Ph<sub>3</sub>P=O as an internal standard <sup>b</sup>determined by <sup>19</sup>F NMR spectroscopy using  $C_6H_5CF_3$  as an internal standard <sup>c</sup>NQ = not quantified

### Table S5. 4-F + $[(C_5H_5) - Au(PPh_3)]$



<sup>a</sup>determined by <sup>31</sup>P NMR spectroscopy using Ph<sub>3</sub>P=O as an internal standard <sup>b</sup>determined by <sup>19</sup>F NMR spectroscopy using  $C_6H_5CF_3$  as an internal standard <sup>c</sup>NQ = not quantified

#### Table S6. 2-F + [(4-NC<sub>5</sub>H<sub>4</sub>) – Au(PPh<sub>3</sub>)]



<sup>a</sup>determined by <sup>31</sup>P NMR spectroscopy using Ph<sub>3</sub>P=O as an internal standard

<sup>b</sup>determined by <sup>19</sup>F NMR spectroscopy using C<sub>6</sub>H<sub>5</sub>CF<sub>3</sub> as an internal standard

<sup>c</sup>NQ = not quantified

<sup>d</sup>These products engage with the boron-rich secondary coordination sphere

<u>A note regarding yields</u>: Yields were determined by NMR spectroscopy using the standards noted in Tables 2-6. An initial time point of 7 min was chosen for all reactions to ensure consistent measurements – this represented the time that the sample could be most quickly introduced into the NMR instrument from the laboratory. As time progressed, the concentration of all [(diphosphine)Ni<sup>II</sup>(C<sub>6</sub>H<sub>5</sub>R)(I)] species decreased, giving [(diphosphine)Ni<sup>0</sup>(PPh<sub>3</sub>)<sub>2</sub>]; only F-containing biaryls were quantified. During this period, the solution turned from orange to green (e.g., Figure S49). In all reactions, [Ni]<sub>tot</sub> and [F]<sub>tot</sub> are less than 100%, suggesting the formation of paramagnetic species; efforts to observe such species using CW X-band EPR spectroscopy were not successful.

![](_page_33_Picture_7.jpeg)

**Figure S49.** NMR tube containing  $4-F + [(C_5H_5) - Au(PPh_3)]$  after 60 mins, showing characteristic green color.

## Crystallographic details:

All crystals were mounted on a mitegen loop. All measurements were made using graphitemonochromated Cu K<sub> $\alpha$ </sub> ( $\lambda$  = 1.54178 Å) radiation on a Bruker D8 Venture diffractometer. The structures were solved by direct methods<sup>5</sup> and refined by full-matrix least-squares procedures on F2 (SHELXL-2013)<sup>6</sup> using the OLEX2 interface.<sup>7</sup> All hydrogen atoms were placed in calculated positions. Non-hydrogen atoms were refined anisotropically. The dataset obtained for **5** contains a disordered toluene molecule, which was masked from the structure using OLEX2. The dataset obtained for **4-H** suffered from poor diffraction and is shown to confirm net connectivity only (**Figure S50**).

CCDC **2102983-2102984** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data\_request/cif.

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<sup>&</sup>lt;sup>7</sup> O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard and H.J. Puschmmann, *Appl. Cryst.* 2009, 42, 339.

Compound	<b>4</b> -F	5	
Empirical formula	$C_{20}H_{36}FINiP_2$	C23H19AuNP	
Formula weight	543.04	537.33	
Temperature/K	170(2)	170(2)	
Crystal system	Triclinic	Triclinic	
Space group	P-1	<i>P</i> -1	
a/Å	8.5374(3)	11.6301(3)	
b/Å	9.2036(4)	12.1425(3)	
c/Å	17.4252(7)	24.6036(7)	
α/°	95.226(2)	82.9700(10)	
β/°	93.002(2)	86.1880(10)	
γ/°	116.8530(10)	68.0260(10)	
V/Å <sup>3</sup>	1209.70(8)	3197.05(15)	
Z	2	6	
$ ho_{calc}/g/cm^{-3}$	1.491	1.675	
μ/ mm <sup>-1</sup>	12.489	13.706	
F(000)	552.0	1548.0	
Crystal size/ mm <sup>3</sup>	$0.12\times0.11\times0.11$	$0.12\times0.1\times0.08$	
Radiation	$CuK\alpha (\lambda = 1.54178)$	$CuK\alpha$ ( $\lambda$ = 1.54178)	
$2\theta$ range for data collection/°	5.12 to 106.928	7.242 to 106.85	
	$\textbf{-8} \leq \textbf{h} \leq \textbf{8},  \textbf{-9} \leq \textbf{k} \leq \textbf{9},  \textbf{-18} \leq \textbf{l} \leq$	-11 $\leq$ h $\leq$ 12, -12 $\leq$ k $\leq$ 12, -25 $\leq$	
Index ranges	17	1≤25	
Reflections Collected	30539	82892	
	2837 [ $R_{int} = 0.0383$ , $R_{sigma} =$	7490 [ $R_{int}$ = 0.0540, $R_{sigma}$ =	
Independent reflections	0.0178]	0.0310]	
Data/restraints/parameters	2837/0/230 7490/612/703		
Goodness-of-fit on F <sup>2</sup>	1.146	1.146 1.016	
R [I>=2θ (I)] (R1, wR2)	$R_1 = 0.0241, wR_2 = 0.0564$	$R_1 = 0.0338$ , $wR_2 = 0.0678$	
R (all data) (R1, wR2)	$R_1 = 0.0255, wR_2 = 0.0569$	$R_1 = 0.0504$ , $wR_2 = 0.0748$	
Largest diff. peak/hole / (e Å-³)	0.25/-0.56	1.29/-0.97	

 Table S7. Crystallographic data for 4-F and 5

 $R1 = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|; wR2 = [\Sigma(w(F_{o}^{2} - F_{c}^{2})^{2}) / \Sigma w(F_{o}^{2})^{2}]^{1/2}$ 

Table S8. Select crystallographic data for 4-H (non-publishable).

Compound	<b>4-H</b>
Empirical formula	C20H37INiP2
Formula weight	525.04
Temperature/K	170(2)
Crystal system	Triclinic
Space group	<i>P</i> -1
a/Å	8.4462(10)
b/Å	9.2584(12)
c/Å	19.194(2)
α/°	87.871(8)
β/°	87.105(8)
γ/°	63.286(7)
V/Å <sup>3</sup>	1338.9(3)
Z	2

![](_page_36_Figure_2.jpeg)

**Figure S50.** Crystal structure of **4-H**. Hydrogens omitted for clarity, ellipsoids shown at 20% probability. This structure suffers from a high R1-value and provides a heavy-atom connectivity map only.

## **Computational details:**

- DFT calculations were carried out using Gaussian16 Rev. C.01.<sup>8</sup>
- DLPNO-CCSD(T) calculations were carried out using ORCA 5.0.0.9
- All energies are quoted in kcal mol<sup>-1</sup>.
- The B3LYP functional<sup>10</sup> was used throughout, in combination with Grimme's D3 dispersion corrections<sup>11</sup> for geometry optimizations. Single point calculations were carried out using the M06 functional without any additional empirical dispersion corrections.<sup>12</sup>
- No symmetry constraints were used.
- Solvation using the SMD model in benzene solvent was included for single point calculations only.
- For optimization, the 6-31G(d) basis set <sup>13</sup> was used for H, C, and P, the LANL2DZ(d,p) basis set<sup>14</sup> was used for I, and the LANL2TZ(f) basis set<sup>15</sup> was used for Ni and Au.
- For single point calculations, the 6-311+G(d,p) basis set<sup>16</sup> was used for all atoms except I, for which the LANL2DZ(d,p) basis set was employed, and Au, for which the LANL2TZ(f) basis set was used.
- The nature of all stationary points was confirmed using frequency calculations, with all minima having no imaginary frequencies and all transition states having one.
- DLPNO-CCSD(T) calculations were carried out with the TIGHTSCF and TIGHTPNO options; the cc-pVTZ-PP basis set and SK-MCDHF-RSC ECP were used for I and Au, and the cc-pVTZ basis set was used for all other atoms.

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# Table of Energies:

Species	B	3LYP-D3	M06	DLPNO- CCSD(T)	
	E	Hcorr	Gcorr	E	Ε
AuI(PPh <sub>3</sub> )	-1183.301179	0.298125	0.222054	-1182.840435	-1465.007618
Au(Ph)(PPh <sub>3</sub> )	-1403.497226	0.390922	0.305894	-1402.934127	-1401.272450
Au(C <sub>6</sub> H <sub>4</sub> F)(PPh <sub>3</sub> )	-1502.732241	0.383606	0.297008	-1502.176691	-1500.404828
Au(C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub> )(PPh <sub>3</sub> )	-1740.540104	0.399427	0.304704	-1739.972200	-1737.937405
Au(C <sub>6</sub> H <sub>4</sub> OMe)(PPh <sub>3</sub> )	-1518.022450	0.426389	0.335638	-1517.427106	-1515.626179
Au(C5NH4)(PPh3)	-1419.536089	0.379140	0.294408	-1418.978738	-1417.301163
NiI(Ph)(d <i>n</i> ppe)	-1648.019566	0.567941	0.469253	-2986.391899	-3267.414617
NiI(C <sub>6</sub> H <sub>4</sub> F)(d <i>n</i> ppe)	-1747.253519	0.560635	0.459808	-3085.633817	-3366.546345
NiI(C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub> )(d <i>n</i> ppe)	-1985.062790	0.576492	0.467954	-3323.430671	-3604.080115
NiI(C <sub>6</sub> H <sub>4</sub> OMe)(d <i>n</i> ppe)	-1762.543981	0.603402	0.498682	-3100.883782	-3381.767850
NiI(C5NH4)(dnppe)	-1983.489056	0.641276	0.534539	-3321.773812	-3318.840645
Ni(C <sub>6</sub> H <sub>4</sub> F)(Ph)(d <i>n</i> ppe)	-1967.448475	0.653001	0.546075	-3305.726973	-3302.809523
Ni(C <sub>6</sub> H <sub>4</sub> F)(C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub> )(dnppe)	-2304.492639	0.661556	0.544522	-3642.766576	-3639.476009
Ni(C <sub>6</sub> H <sub>4</sub> F)(C <sub>6</sub> H <sub>4</sub> OMe)(dnppe)	-2081.972495	0.688364	0.575046	-3420.218386	-3417.161967
Ni(C <sub>6</sub> H <sub>4</sub> F)(C <sub>5</sub> NH <sub>4</sub> )(dnppe)	-1983.489056	0.641276	0.534539	-3321.773812	-3318.840645

All values in the table are given in Hartrees.

# XYZ Coordinates:

These data are available:

1) *via* IOChem-BD, for which the DOI is provided in the manuscript. This allows direct download of files suitable for important into GaussView or other computational chemistry/3D molecular visualization and editing packages.

2) As a separate supporting information file, in XYZ format, which can readily be imported into software such as ChemCraft, Avogadro, etc. or into a text editor to prepare input files for ORCA, Gaussian, etc

## **Summary of Data:**

![](_page_39_Figure_1.jpeg)

**Figure S51.** Summary of thermodynamics of transmetalation (kcal mol<sup>-1</sup>).  $\Delta G^{\circ}(CC)$  was calculated using DLPNO-CCSD(T),  $\Delta G^{\circ}(DFT)$  was calculated using DFT.

#### In summary:

- Ar-for-Ar transmetalation is slightly downhill for Ar = Ph, 4-F<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>, 4- pyridyl, and a little uphill for 4-MeOC<sub>6</sub>H<sub>4</sub>;
- Ar-for-I transmetalation is always uphill;
- Ar-for-Ar is always most favourable;
- M06 and DLPNO-CCSD(T) continue to agree quite nicely all within 0.7 kcal/mol.