Supporting information for:

On Ortho-Derivatization of Phenols Through C-H Nickelation: Synthesis, Characterization and Reactivities of Orthonickelated Phosphinite Complexes

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Contents:

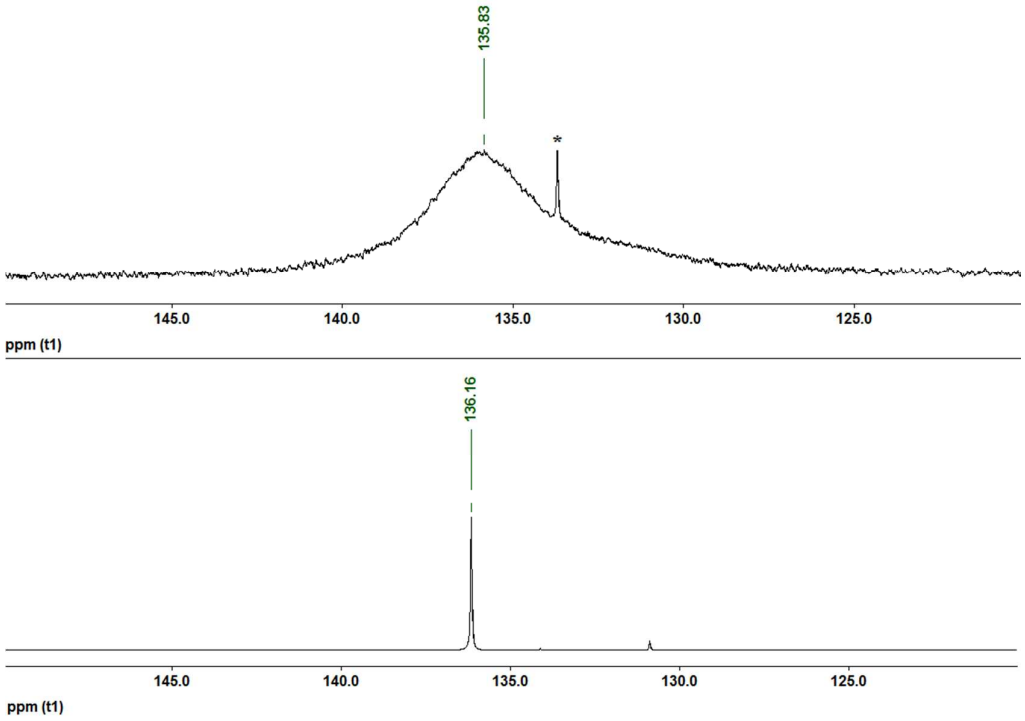

Figure S1 : $^{31}P\{^{1}H\}$ NMR (201 MHz) of **2a** at 20 °C (top) and at -68 °C (below) in CD_2Cl_2 (* = impurity).

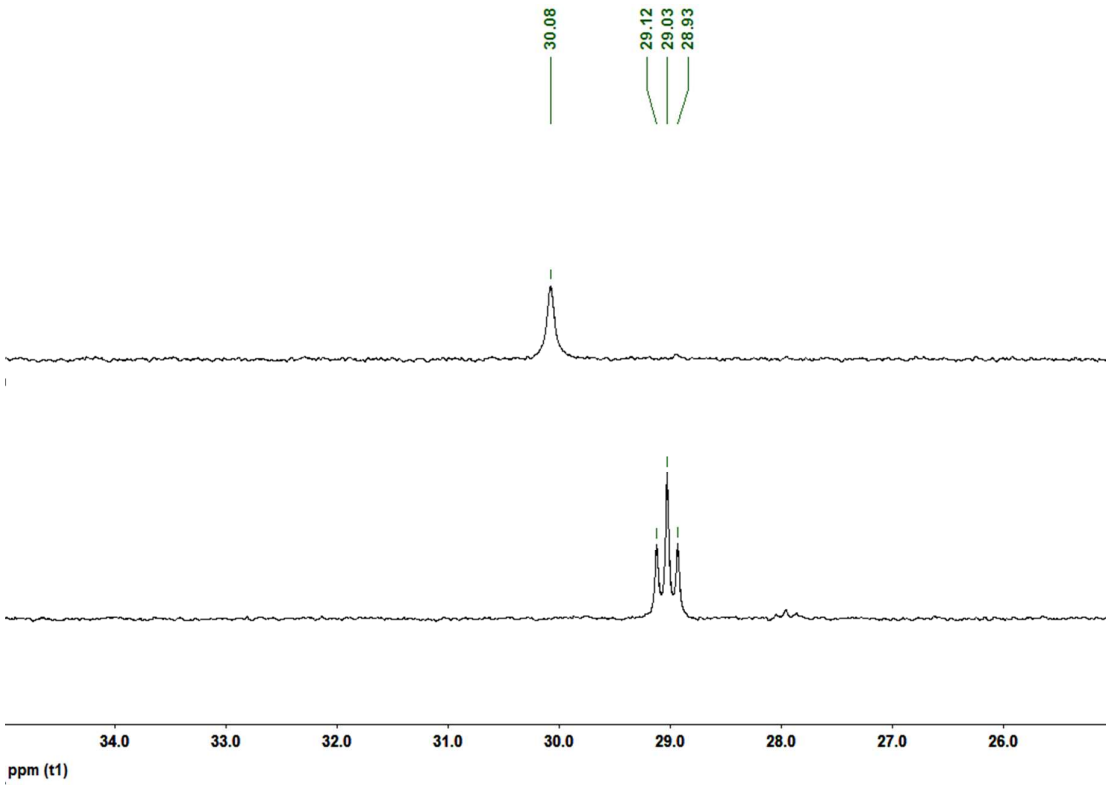

Figure S2. Upfield region of the $^{13}C\{^{1}H\}$ NMR spectrum of **2a** (125 MHz, CD_2Cl_2) showing the resonance for P*C*H$(CH_3)_2$ at 20 °C (top) and at -68 °C (below).

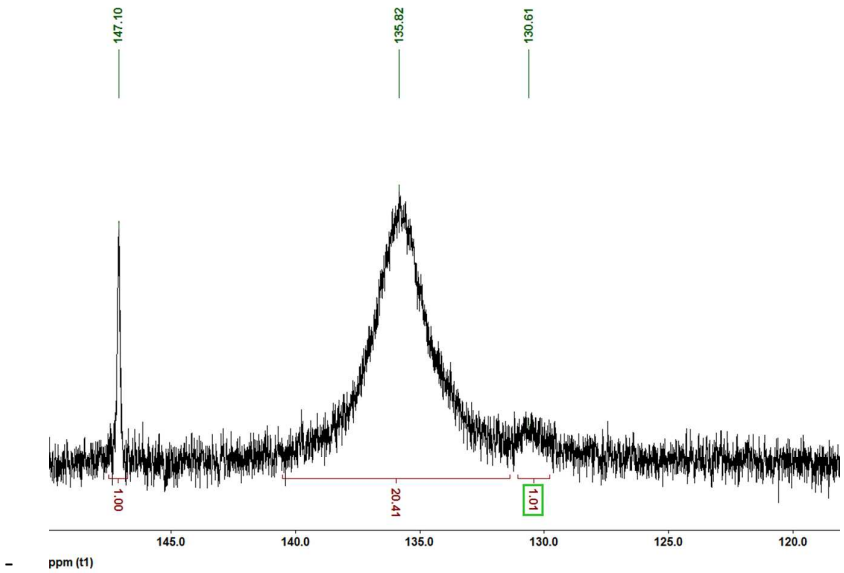

Figure S3. $^{31}P\{^{1}H\}$ NMR (162 MHz, rt) spectrum of a solution of **2a** (50mg, 78.2 µmol) in Toluene (1.2 mL) after addition of NEt_3 (13 µL, 93.8 µmol).

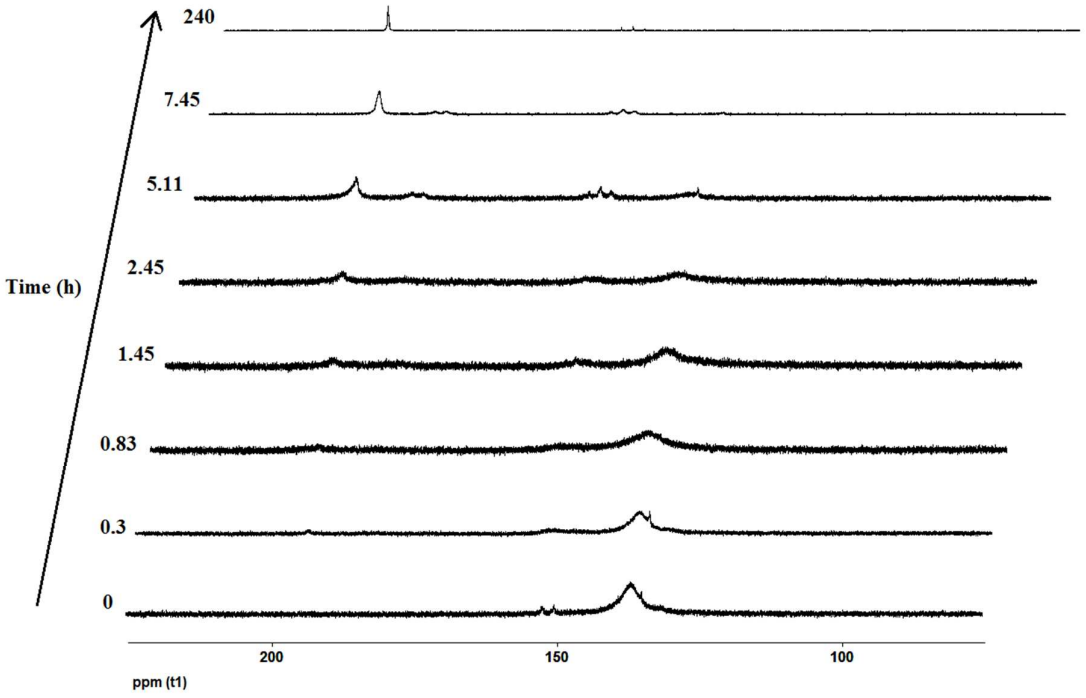

Figure S4 : $^{31}P\{^{1}H\}$ NMR monitoring of a solution of **1a** (34 mg, 0.16 mmol), $NiBr_2(NC^{i}Pr)]_n$ (46 mg, 0.16 mmol) and NEt_3 (22 µL, 0.16 mmol) in Toluene (0.6 mL) at 90°C.

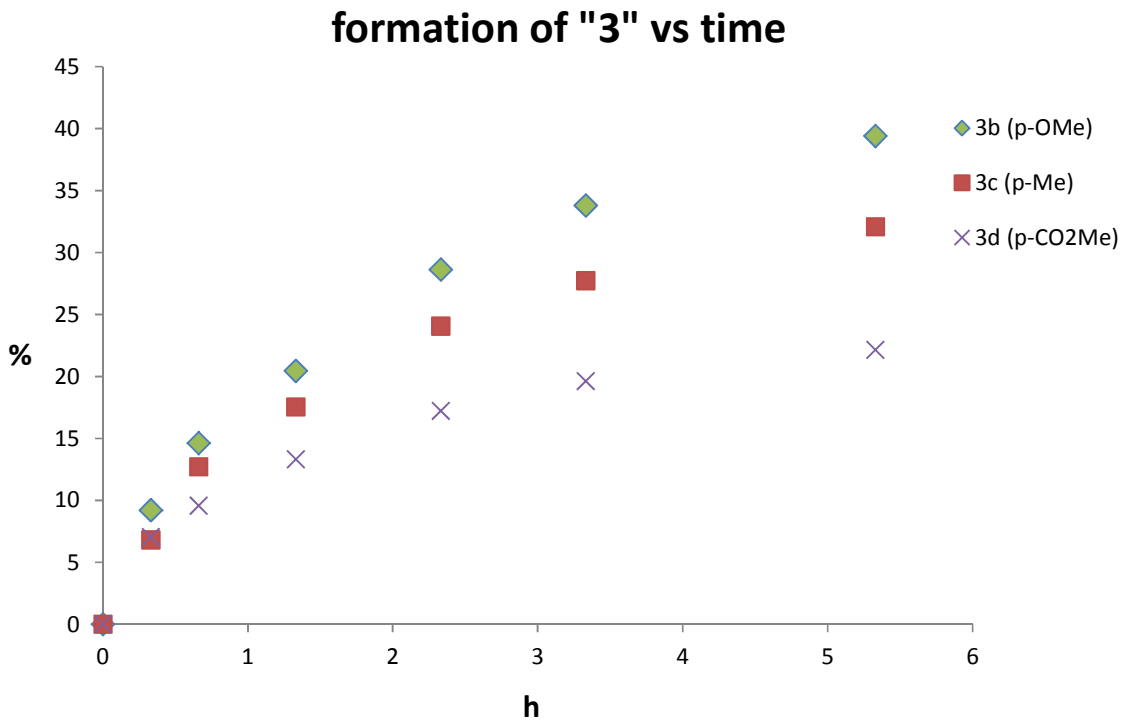

Figure S5 : Time profile for conversion of **2b**, **2c**, and **2d** to **3b**, **3c** and **3d**. Reactions were run at 100 °C in toluene solutions (382 µL) containing 0.16 mmol of **2b-d** and 218 µL of NEt_3 (1.6 mmol).

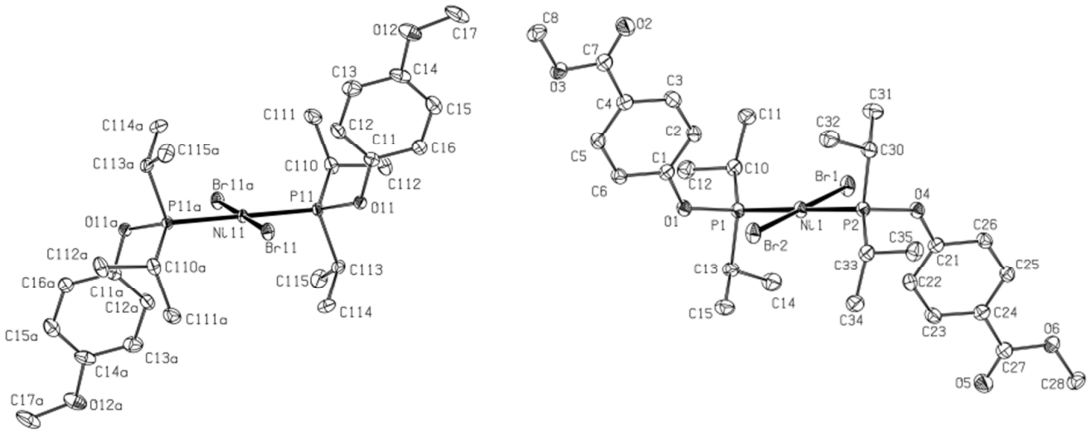

Figure S6. Structure diagrams for complexes **2b** and **2d**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

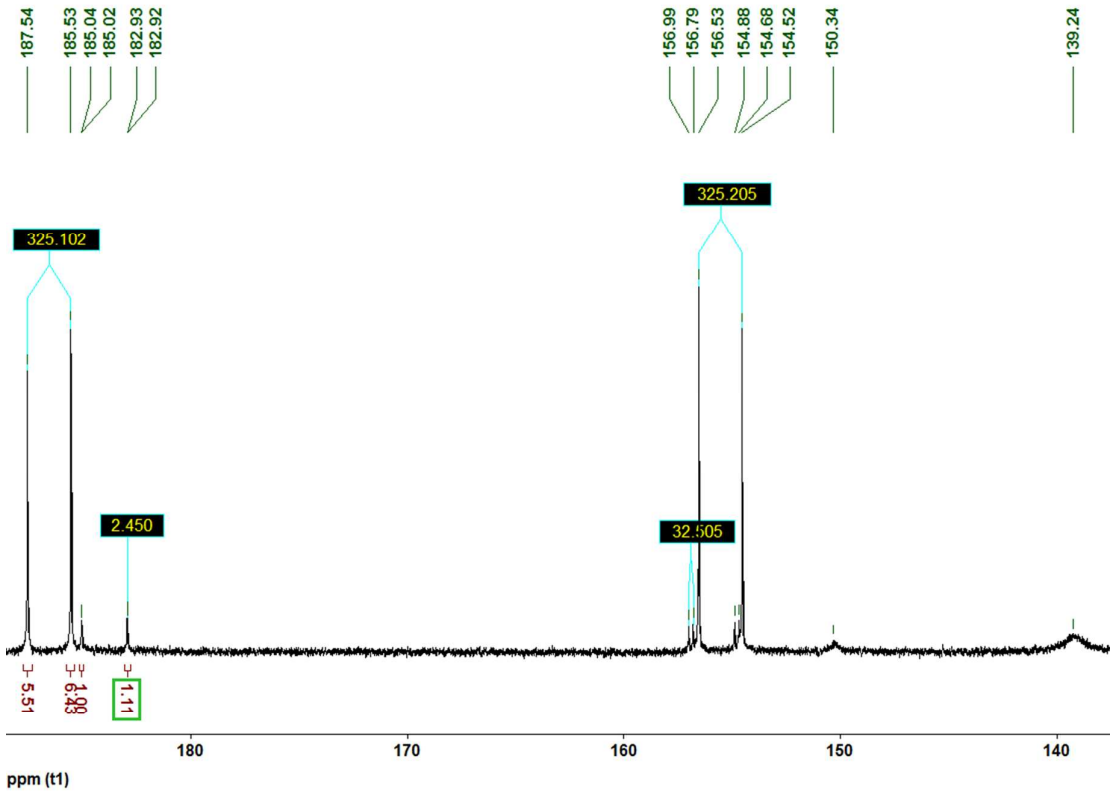

Figure S7. $^{31}P\{^{1}H\}$ NMR (162 MHz) of a mixture of *trans*-[$NiBr_2$\{3-F-(*i*-Pr_2PO)-C_6H_4\}$_2$], of ligand **1e**, and complexes **3e^{o}** and **3e^{p}** in C_6D_6.

Table S1. Crystal Data Collection and Refinement Parameters for Complex **2a**, **3a**, and **4a**.

	2a	**3a**	**4a**
chemical formula	$C_{24}H_{38}Br_2NiO_2P_2$	$C_{24}H_{37}BrNiO_2P_2$	$C_{24}H_{36}Br_2Ni_2O_2P$
crystal colour	red	yellow	yellow
***Fw*; *F*(000)**	639.01; 326	558.10; 1160	695.71; 704
***T* (K)**	150	150	100
wavelength (Å)	1.54178	1.54178	1.54178
space group	P-1	P21/n	P21/n
***a* (Å)**	8.2865(8)	10.7627(4)	9.89710(10)
***b* (Å)**	8.7999(8)	13.6755(5)	11.02090(10)
***c* (Å)**	10.9270(10)	17.913(6)	12.80450(10)
α (deg)	109.64(4)	90	90
β (deg)	93.043(4)	93.7180(16)	104.5970(10)
γ (deg)	114.612(3)	90	90
Z	1	4	2
***V* (Å^3)**	664.70(11)	2630.96(16)	1351.57(2)
ρ_{calcd} (g·cm^{-3})	1.596	1.409	1.709
μ (mm^{-1})	5.854	4.122	6.462
θ range (deg); completeness	4.41 − 69.65; 0.991	4.07 − 69.68; 0.992	6.475 – 71.018; 0.994
R1[a]; wR2[b] [I > 2σ(I)]	0.0282; 0.0748	0.0318; 0.0842	0.0408; 0.1353
R1; wR2 [all data]	0.0284; 0.0751	0.0325; 0.0849	0.0408; 0.1353
GOF	1.018	1.062	1.021
largest diff peak and hole	0.692 and -0.435	0.655 and -0.332	1.043 and -1.274

[a] $R_1=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$ [b] $wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{½}$

Table S2. Crystal data collection and refinement parameters for **2b**, **2c**, and **2d**.

	2b	**2c**	**2d**
chemical formula	$C_{26}H_{42}Br_2NiO_4P_2$	$C_{26}H_{42}Br_2NiO_2P_2$	$C_{28}H_{42}Br_2NiO_6P_2$, C_7H_8
crystal colour	red	red	yellow
***Fw*; *F*(000)**	699.06; 716	667.06; 1368	847.22; 872
***T* (K)**	100	100(2)	100(2)
wavelength (Å)	1.54178	1.54178	1.54178
space group	P-1	P 1 21/c 1	P-1
***a* (Å)**	9.0321(2)	8.48140(10)	10.4323(6)
***b* (Å)**	11.0400(3)	20.749(2)	12.5239(7)
***c* (Å)**	15.7000(4)	17.7094(2)	15.3754(9)
α (deg)	102.066(1)	90	99.459(2)
β (deg)	96.868(1)	107.9730(10)	106.577(2)
γ (deg)	96.906(1)	90	95.334(2)
Z	2	4	2
***V* (Å^3)**	1502.84(7)	2964.4(3)	1878.28(19)
ρ_{calcd} (g·cm^{-3})	1.545	1.495	1.498
μ (mm^{-1})	5.283	5.275	4.379
θ range (deg); completeness	2.911 – 71.175; 0.975	3.379 − 71.755; 0.997	3.061 − 69.828; 0.992
R1[a]; wR2[b] [I > 2σ(I)]	0.0403; 0.1067	0.0201; 0.0522	0.0326; 0.0910
R1; wR2 [all data]	0.0404; 0.1067	0.0202; 0.0522	0.0340; 0.0934
GOF	1.197	1.157	1.053
largest diff peak and hole	1.808 and -0.406	0.370 and -0.253	0.793 and -0.371

[a] $R_1=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$ [b] $wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{½}$