**Weaker Lewis Acid, Better Catalytic Activity:
Dual Mechanisms in Perfluoroarylborane Catalyzed Allylstannation Reactions.**

Darryl J. Morrison and Warren E. Piers

Supporting Information

General. All manipulations of air- and moisture-sensitive materials were undertaken using standard vacuum and Schlenk techniques or in a glovebox under an atmosphere of argon. Toluene was dried and purified using the Grubbs' method.¹ CH₂Cl₂ was distilled from CaH₂. CD₂Cl₂ and C₇D₈ were purchased from Cambridge Isotopes and rigorously dried then distilled from CaH₂ and Na/benzophenone, respectively. ¹H (300 MHz or 400 MHz) and ¹³C NMR spectra (100 MHz) were referenced externally to Me₄Si at 0 ppm by referencing the solvent peak (CD₂Cl₂, ¹H NMR: 5.32 ppm. ¹³C NMR: 154.0). ¹¹B NMR (128 MHz) spectra were referenced relative to BF₃•Et₂O (C₆D₆, 298 K) at 0 ppm. ¹⁹F NMR (282 MHz) spectra were referenced externally to C₆F₆ (C₆D₆, 298 K) at -163 ppm relative to CFCl₃ at 0 ppm. ¹¹⁹Sn NMR (149 MHz) spectra were referenced relative to Me₄Sn (CD₂Cl₂, 298 K) at 0 ppm. GC analyses were performed on a Varian 3900 GC equipped with a Varian Saturn 2000 MS detector. B(C₆F₅)₃ was purchased from Boulder Scientific and was dried with Cl₂SiMe₂, sublimed under vacuum at ~100 °C and stored in a glove box. BPh(C₆F₅)₂ was prepared by the literature method.² [Ph₃C]⁺[B(C₆F₅)₄]⁻ was received as a generous gift from NOVA Chemicals. Bu₄NBr, BPh₃, and allylSnBu₃ were purchased from Aldrich and used as received. HSnBu₃, *ortho*-anisaldehyde, and PhCHO were purchased from Aldrich and vacuum distilled before use.

General procedure for equilibrium measurements, Method 1; Scheme 2: To an NMR tube charged with *ortho*-anisaldehyde (200 μ L of a 0.367M stock solution in CD_2Cl_2 , 0.0734 mmol) was added a CD_2Cl_2 solution of either $\text{B}(\text{C}_6\text{F}_5)_3$ (306 μ L of a 0.0801 M stock solution, 0.0245 mmol) or $\text{BPh}(\text{C}_6\text{F}_5)_2$ (295 μ L of a 0.0830 M stock solution, 0.0245 mmol) at room temperature in a glovebox to make a yellow/green solution. To the septum sealed NMR tube was added allylSnBu₃ (50 μ L of a 0.490 M stock solution in CD_2Cl_2 , 0.0245 mmol) while cooling the tube to -78°C . The tube was quickly shaken to ensure mixing while not allowing for significant warming. The sample was then transferred to the NMR probe precooled to -60°C . In both cases, consumption of allylSnBu₃ occurred rapidly and was followed by equilibration of the resulting product mixture. ^1H NMR spectra (64 scans, 10 second pulse delay) and ^{19}F NMR spectra (64 scans, 5 second pulse delay) were collected at each temperature after allowing for equilibration.

Calculation of equilibrium constants, K_{eq} , for $\text{B}(\text{C}_6\text{F}_5)_3$ promoted equilibria:

Complete NMR data for **1a** has previously been reported.³ Observation of the reaction mixture at temperatures between -40°C and 10°C allowed for measurable concentrations of all 4 components of the equilibrium. Equilibration of the reaction mixture at -40°C from -80°C required approximately 330 minutes. Ratios of **1a:2a** were calculated from the ratio of ^{19}F NMR signals for **1a**(*p*-F) (δ -157.0 ppm) and **2a**(*m*-F) (δ -167.1 ppm, 243 K; -167.7 ppm, 293K). The ratios of **2a:4**:(total ArCHO) were readily calculated by integration of ArOCH_3 signals in the ^1H NMR spectra; **2a** (δ 3.55 ppm, 243 K; 3.60 ppm, 293 K), **4** (δ 3.80 ppm, 243 K; 3.81 ppm, 293 K), and total ArCHO (free, and bound in **2a**, and **1a**) ($\delta \sim 3.95$ ppm). The concentration of free ArCHO, $[\text{ArCHO}]$, was calculated by subtraction of **1a** and $2 \times [\text{2a}]$ (assuming bis-ligation of $[\text{SnBu}_3]^+$ by ArCHO) from the total ArCHO, $[\text{ArCHO}]_{\text{total}}$.

Table 2. Equilibrium concentrations and constants for $B(C_6F_5)_3$ promoted equilibria according to Scheme 2 and eq. 1.

Temp. / K	Concentration / M				K_{eq}
	1a	4	ArCHO	2a	
233.2	0.0321	0.0407	0.0336	0.0286	0.0015
243.2	0.0352	0.0435	0.0370	0.0193	0.0029
253.2	0.0397	0.0461	0.0362	0.0130	0.0051
263.2	0.0417	0.0476	0.0373	0.0084	0.0088
273.2	0.0407	0.0476	0.0416	0.0051	0.0157
283.2	0.0429	0.0481	0.0405	0.0035	0.0235

Calculation of equilibrium constants, K_{eq} , for $BPh(C_6F_5)_2$ promoted equilibria:

Ratios of **1b:2b** were calculated from the ratio of ^{19}F NMR signals for **1b**(*m*-F) (δ -163.9 ppm, 203 K; -164.2 ppm, 243 K) and the **2b**(*m*-F) signals for diastereotopic C_6F_5 groups (δ -166.3 and -166.8 ppm, 203 K; -166.8 and -167.3 ppm, 243 K). The ratios of **2b:4**:(total ArCHO) were readily calculated by integration of $ArOCH_3$ signals in the 1H NMR spectra; **2b** (δ 3.59 ppm, 203 K; 3.60 ppm, 243 K), **4** (δ 3.77 ppm, 203 K; 3.80 ppm, 243 K), and total ArCHO (free, and bound in **2b**, and **1b**) (δ 3.90 – 3.84 ppm). 1H and ^{19}F NMR chemical shifts for **2b** were confirmed by *in situ* preparation of the corresponding salt $[NBu_4]^+[(o\text{-anisyl})CH(OBPh(C_6F_5)_2)allyl]^-$ (see below). The concentration of free ArCHO, $[ArCHO]$, was calculated by subtraction of $[1b]$ and $2 \times [2b]$ (assuming bis-ligation of $[SnBu_3]^+$ by ArCHO) from the total ArCHO, $[ArCHO]_{total}$.

Table 3. Equilibrium concentrations and constants for $BPh(C_6F_5)_2$ promoted equilibria according to Scheme 2 and eq. 1.

Temp. / K	Concentration / M				K_{eq}
	1b	4	ArCHO	2b	
191.5	0.0392	0.0338	0.0383	0.0169	0.0030
201.5	0.0389	0.0371	0.0429	0.0091	0.0068
211.5	0.0413	0.0400	0.0414	0.0054	0.0127
221.4	0.0430	0.0406	0.0413	0.0031	0.0229
231.7	0.0443	0.0413	0.0407	0.0018	0.0417

Figure 1. Van't Hoff plots of $-\ln(K_{eq})$ versus $1000 T^{-1}$ for the equilibria in Scheme 2; o = $B(C_6F_5)_3$; Δ = $BPh(C_6F_5)_2$.

Table 4. Thermodynamic parameters from van't Hoff plots.

$B(C_6F_5)_3$		$BPh(C_6F_5)_2$	
slope ($\Delta H/R$) / K	ΔH (kcal/mol)	slope ($\Delta H/R$) / K	ΔH (kcal/mol)
3631	7.21(6)	2871	5.70(5)
intercept ($-\Delta S/R$)	ΔS (eu)	intercept ($-\Delta S/R$)	ΔS (eu)
-9.092	18.0(7)	-9.212	18.3(1)

Generation of equilibria by reaction of (*ortho*-anisyl)CH(allyl)OSnBu₃, **4, with adducts **1** and *ortho*-anisaldehyde; Method 2:** A 0.296 M solution of **4** was prepared as previously described³ by adding allylSnBu₃ (46 μ L, 0.147 mmol) to a CD₂Cl₂ solution (400 μ L) of *ortho*-anisaldehyde (20 mg, 0.147 mmol) and BPh(C₆F₅)₂ (50 μ L of a 0.0687 M CD₂Cl₂ solution, 0.0034 mmol, 2 mol%) at room temperature with shaking over 2 minutes. NMR analysis

confirmed quantitative clean conversion to **4**. To another tube containing a CD₂Cl₂ solution (360 μ L) of B(C₆F₅)₃ or BPh(C₆F₅)₂ (0.025 mmol) and *ortho*-anisaldehyde (113 μ L of a 0.441 M CD₂Cl₂ solution, 0.050 mmol) was added 84 μ L of 0.296 M solution of **4** (0.025 mmol) at -78°C . The reaction mixture was then transferred to the NMR probe precooled to the appropriate temperature and was allowed to reach equilibrium. ¹H and ¹⁹F NMR spectra were obtained and equilibrium constants were calculated as described for Method 1 above; tabulated below for comparison, Table 5.

Table 5. Equilibrium constants according to Scheme 2, eq 1. Comparison of Methods 1 and 2.

R = C₆F₅						
Temp. / K	Method 2					Method 1
	Concentration / M				<i>K</i> _{eq}	<i>K</i> _{eq}
	1a	4	ArCHO	2a		
253	0.0448	0.407	0.0327	0.0119	0.0050	0.0051
R = Ph						
Temp. / K	Method 2					Method 1
	Concentration / M				<i>K</i> _{eq}	<i>K</i> _{eq}
	1b	4	ArCHO	2b		
213	0.385	0.0391	0.0469	0.0054	0.0130	0.0127

General procedure for borane Lewis acid catalyzed allylstannation of benzaldehyde: In the glovebox, a 10 mL 2-neck round-bottomed flask was charged with dry CH₂Cl₂ (4 mL), the appropriate borane (250 μ L of a 0.1 M CH₂Cl₂ solution, 0.025 mmol), and PhCHO (500 μ L of a 1.0 M CH₂Cl₂ solution, 0.50 mmol). To the cooled solution (-78°C , acetone/CO₂; or -44°C , acetonitrile/CO₂) under argon atmosphere was added allylSnBu₃ (170 μ L, 0.55 mmol) in one portion. Aliquots (approx. 50 μ L) were taken from the reaction mixtures at appropriate time intervals and quickly quenched into 1N HCl, extracted into a small portion of EtOAc, and injected into the GC/MS. Percent conversions of PhCHO were calculated by comparing peak areas for PhCHO (*t*_R = 6.3 min) and the hydrolyzed homoallylic alcohol product

PhCH(OH)CH₂CH=CH₂ (t_R = 10.3 min). Retention times for the two components were verified by comparison to authentic samples.

Preparation of CH₂Cl₂ solutions of [(C₇H₈)SnBu₃]⁺[B(C₆F₅)₄]⁻ for Lewis acid catalyzed

allylstannation of benzaldehyde: In a glovebox, excess HSnBu₃ (30 μ L, 0.11 mmol) was added to a vial containing a two-phase red-orange toluene solution (approx. 400 μ L) of [Ph₃C]⁺[B(C₆F₅)₄]⁻ (23 mg, 0.025 mmol) and the vial was shaken for 30 seconds. The yellow toluene layer was removed by syringe and the bottom orange ion-pair layer was washed with small portions of toluene (2 $\times$ approx. 400 μ L). The orange bottom layer was then dissolved in CH₂Cl₂ (approx. 400 μ L total volume) for use in allylstannation reactions. NMR analysis of CD₂Cl₂ solutions of [(C₇D₈)SnBu₃]⁺[B(C₆F₅)₄]⁻ prepared analogously confirmed complete conversion of [Ph₃C]⁺[B(C₆F₅)₄]⁻ and that all excess HSnBu₃ had been removed during washing with toluene. ¹H, ¹³C, and ¹¹⁹Sn NMR data has been reported elsewhere.³

Procedure for [SnBu₃]⁺[B(C₆F₅)₄]⁻ catalyzed allylstannation of benzaldehyde: To a dry CH₂Cl₂ solution (4.5 mL) of benzaldehyde (500 μ L of a 1.0 M CH₂Cl₂ solution, 0.50 mmol) in a 10 mL 2-neck round-bottomed flask cooled to the appropriate temperature under argon atmosphere was added a CH₂Cl₂ solution (approx. 400 μ L) of [(C₇H₈)SnBu₃]⁺[B(C₆F₅)₄]⁻ (0.025 mol, prepared as described above and transferred from the glovebox using a gas-tight syringe). To the solution was added allylSnBu₃ (326 μ L, 1.05 mmol) in one portion. Aliquots (approx. 50 μ L) were taken at appropriate time intervals, quenched, and analyzed by GC/MS as described for the borane-catalyzed allylstannations of benzaldehyde.

Scheme 3

Preparation of $\text{Bu}_4\text{NBr}:\text{BPh}(\text{C}_6\text{F}_5)_2$: An NMR sample was prepared by mixing $\text{BPh}(\text{C}_6\text{F}_5)_2$ (21 mg, 0.05 mmol) with Bu_4NBr (16 mg, 0.05 mmol) in CD_2Cl_2 (approx. 500 μL). ^1H NMR (CD_2Cl_2 , -50°C): δ 7.46 (app. d, 2H, $J = 6.7$ Hz, $o\text{-ArH}$), 7.14-7.03 (m, 3H, $m\text{-ArH}$ and $p\text{-ArH}$), 2.97 (m, 8H, $\text{NCH}_2(\text{CH}_2)_2\text{CH}_3$), 1.49 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.29 (m, 8H, $\text{N}(\text{CH}_2)_2\text{CH}_2\text{CH}_3$), 0.94 (t, 12H, $J = 7.2$ Hz, $\text{N}(\text{CH}_2)_3\text{CH}_3$). ^{19}F NMR (CD_2Cl_2 , -50°C): δ -130.0 (app. dd, 4F, $J = 24.3$ Hz and $J = 7.2$ Hz, $o\text{-F}$), -161.6 (app. t, 2H, $J = 21.2$ Hz, $p\text{-F}$), -166.0 (m, 4H, $m\text{-F}$).

Preparation of $[\text{Bu}_4\text{N}]^+[\text{allylBPh}(\text{C}_6\text{F}_5)_2]^-$: Allyl SnBu_3 (15.5 μL , 0.05 mmol) was added to a CD_2Cl_2 solution (approx. 500 μL) of $\text{Bu}_4\text{NBr}:\text{BPh}(\text{C}_6\text{F}_5)_2$ (0.05 mmol) at room temperature and the NMR tube was shaken vigorously. ^1H NMR (CD_2Cl_2 , -50°C): δ 7.43 (app. d, 2H, $J = 7.2$ Hz, $o\text{-ArH}$), 7.04 (app. t, 2H, $J = 6.9$ Hz, $m\text{-ArH}$), 6.91 (tm, 1H, $J = 6.9$ Hz, $p\text{-ArH}$), 5.92 (m, 1H, $\text{BCH}_2\text{CH}=\text{CH}_2$), 4.35 (dd, 1H, $J = 10.1$ Hz and 2.4 Hz, $\text{BCH}_2\text{CH}=\text{C}(H_{\text{trans}})(H_{\text{cis}})$), 4.26 (dm, 1H, $J = 17.3$ Hz, $\text{BCH}_2\text{CH}=\text{C}(H_{\text{trans}})(H_{\text{cis}})$), 2.93 (m, 8H, $\text{NCH}_2(\text{CH}_2)_2\text{CH}_3$), 1.98 (br d, 2H, $J = 7.4$ Hz, $\text{BCH}_2\text{CH}=\text{CH}_2$), 1.66-1.19 (several multiplets, 42H, n -butyl CH_2 signals for $[\text{NBu}_4]^+$ and BrSnBu_3 by-product), 0.96 (t, 12H, $J = 7.0$ Hz, $\text{N}(\text{CH}_2)_3\text{CH}_3$), 0.87 (t, 9H, $J = 7.7$ Hz, $\text{Sn}(\text{CH}_2)_3\text{CH}_3$ of BrSnBu_3 by-product). ^{19}F NMR (CD_2Cl_2 , -50°C): δ -130.9 (app. dd, 4F, $J = 25.3$ Hz and 6.7 Hz, $o\text{-F}$), -165.0 (app. t, 2F, $J = 21.2$ Hz, $p\text{-F}$), -166.8 (m, 4F, $m\text{-F}$). ^{13}C NMR

(CD₂Cl₂, -50°C, includes signals for BrSnBu₃ by-product): δ 147.6 (dm, $^1J_{C-F}$ = 236 Hz, aryl C-F), 145.5 (vinylic CH=CH₂), 136.7 (dm, $^1J_{C-F}$ = 243 Hz, aryl C-F), 136.2 (dm, $^1J_{C-F}$ = 245 Hz), 132.0, 126.5, 123.4, 108.3 (vinylic CH=CH₂), 58.4 (NCH₂), 33.0 (br. s, BCH₂), 28.4 ($^3J_{C-Sn}$ = 24.5 Hz), 27.2 ($^2J_{C-Sn(117)}$ = 69.8 Hz, $^2J_{C-Sn(119)}$ = 66.7 Hz), 23.6 (NCH₂CH₂), 19.8 (NCH₂CH₂CH₂), 18.0 ($^1J_{C-Sn(117)}$ = 333 Hz, $^1J_{C-Sn(119)}$ = 318 Hz), 13.9, 13.7. The two *ipso* carbons bonded to B were not located. ¹¹B NMR (CD₂Cl₂, -50°C): δ -11.8.

Preparation of [NBu₄]⁺[(*o*-anisylCH(allyl)OB(C₆F₅)₃)]⁻: Preparation and ¹H, ¹³C, ¹¹B, and ¹⁹F NMR data reported previously.³

Preparation of [NBu₄]⁺[(*o*-anisylCH(allyl)OBPh(C₆F₅)₂)]⁻: To an NMR tube containing a solution of [Bu₄N]⁺[allylBPh(C₆F₅)₂]⁻ was added a CD₂Cl₂ solution (approx. 100 μ L) of *ortho*-anisaldehyde (7 mg, 0.05 mmol) and B(C₆F₅)₃ (used as a catalyst, approx. 1-2 mg). The solution was shaken and maintained at room temperature for 6 hours. ¹⁹F NMR analysis indicated that the reaction had proceeded to 35% conversion to form ion pair [NBu₄]⁺[(*o*-anisylCH(allyl)OBPh(C₆F₅)₂)]⁻ (ratio of ion pairs was 1:0.52 by ¹⁹F NMR). This is in contrast to the analogous preparation of [NBu₄]⁺[(*o*-anisylCH(allyl)OB(C₆F₅)₃)]⁻, which goes to completion in 2 hours. ¹H NMR (CD₂Cl₂, -50°C. Resonances for [NBu₄]⁺ and BrSnBu₃ are not included for simplicity. Only diagnostic signals for *ortho*-anisaldehyde and [NBu₄]⁺[(*o*-anisylCH(allyl)OBPh(C₆F₅)₂)]⁻ are listed.): δ 10.41 (s, 1H, CHO of *o*-anisaldehyde), approx. 5.90 (m, 1H, vinylic CH=CH₂ of ion pair), 4.93 (t, 1H, J = 5.3 Hz, ArCH(OBR₃)allyl of ion pair), 4.83 – 4.67 (m, 2H, vinylic CH=CH₂ of ion pair), 3.89 (s, 3H, OCH₃ of *o*-anisaldehyde), 3.58 (s, 3H, OCH₃ of ion pair), 2.44 (t, 2H, J = 5.9 Hz, CH₂CH=CH₂ of ion pair). ¹⁹F NMR (CD₂Cl₂, -50°C.

Two sets of ^{19}F resonances were observed for diastereotopic C_6F_5 groups: δ -130.0 (br. s, 2F, *o*-F), -132.1 (br. s, 2F, *o*-F), -164.57 (app. t, 1F, $J = 21.2$ Hz, *p*-F), -164.61 (app. t, 1F, $J = 21.2$ Hz, *p*-F), -166.3 (m, 2F, *m*-F), -166.9 (m, 2F, *m*-F).

Preparation of *o*-anisaldehyde:BPh(C₆F₅)₂ adduct, 2b: An NMR sample was prepared by mixing BPh(C₆F₅)₂ (21 mg, 0.05 mmol) with *o*-anisaldehyde (7 mg, 0.05 mmol) in CD₂Cl₂ at room temperature to give a yellow/green solution. ^1H NMR (CD₂Cl₂, -50°C): δ 9.53 (s, 1H, ArCHO), 8.18 (app. d, 1H, $J = 7.7$ Hz), 7.91 (app. t, 1H, $J = 7.2$ Hz), 7.27 (m, 5H, BC₆H₅), 7.16 (app. t, 1H, $J = 7.6$ Hz), 7.05 (app. d, 1H, $J = 8.6$ Hz), 3.87 (s, 3H, ArOCH₃). ^{19}F NMR (CD₂Cl₂, -50°C): δ -132.2 (app. dd, 4F, $J = 24.8$ Hz and 8.3 Hz, *o*-F), -157.6 (app. t, 2F, $J = 20.7$ Hz, *p*-F), -164.0 (app. m, 4F, *m*-F). ^{13}C NMR (CD₂Cl₂, -50°C): δ 194.4 (CHO), 166.6, 147.8 (dm, $^1J_{\text{C-F}} = 242$ Hz, aryl C-F), 144.8, 142.7 (dm, $^1J_{\text{C-F}} = 354$ Hz, aryl C-F), 137.2 (dm, $^1J_{\text{C-F}} = 257$ Hz, aryl C-F), 132.6, 132.0, 127.6, 127.2, 122.0, 119.8, 118.4 (br. tm, $^3J_{\text{C-F}} \sim 26$ Hz, *ipso* B-CAr_F), 112.8, 56.7 (OCH₃). One *ipso* carbon was not located. ^{11}B NMR (CD₂Cl₂, room temp.): δ 7.1.

Competition experiment between BPh(C₆F₅)₂ and B(C₆F₅)₃ for PhCHO: To a CH₂Cl₂ solution (approx. 500 μL) of B(C₆F₅)₃ (24 mg, 0.047 mmol) and BPh(C₆F₅)₂ (20 mg, 0.047 mmol) was added PhCHO (4.3 μL , 0.042 mmol, 0.9 equiv.). Analysis of the ^{19}F NMR spectrum obtained at room temperature or -60°C revealed only signals attributable to B(C₆F₅)₃:PhCHO adduct, free B(C₆F₅)₃, and free BPh(C₆F₅)₂. The data indicates that all of the added PhCHO was sequestered as an adduct with B(C₆F₅)₃, the stronger Lewis acid of the two boranes. Relevant spectroscopic data for all possible species in this competition experiment are listed below.

BPh(C₆F₅)₂: Complete NMR data has previously been reported.¹ ¹⁹F NMR (CD₂Cl₂, room temp.): δ -128.4 (m, 4F, *o*-F), -148.1 (app. t, 2F, *J* = 20.2 Hz, *p*-F), -161.0 (m, 4F, *m*-F).

BPh(C₆F₅)₂:PhCHO adduct: To a CD₂Cl₂ solution (500 μL) of BPh(C₆F₅)₂ (15 mg, 0.036 mmol) was added PhCHO (3.6 μL, 0.036 mmol). ¹H NMR (CD₂Cl₂, room temp.): δ 9.39 (s, 1H, PhCHO), 8.13 (dm, 2H, *J* = 7.05 Hz, PhCHO *o*-ArH), 7.94 (tm, 1H, *J* = 7.94 Hz, PhCHO *p*-ArH), 7.69 (app. t, 2H, *J* = 7.69, PhCHO, *m*-ArH), 7.38 (m, 5H, BPh(C₆F₅)₂). ¹⁹F NMR (CD₂Cl₂, room temp.): δ -131.6 (app. dd, 4F, *J* = 24.3 and 8.3 Hz, *o*-F), -156.3 (app. t, 2F, *J* = 20.2 Hz, *p*-F), -164.9 (m, 4F, *m*-F).

B(C₆F₅)₃: ¹⁹F NMR (CD₂Cl₂, room temp.): δ -127.4 (m, 6F, *o*-F), -143.0 (tt, 3F, *J* = 21.2 Hz and 6.2 Hz, *p*-F), -160.4 (m, 6F, *m*-F).

B(C₆F₅)₃:PhCHO adduct: To a CD₂Cl₂ solution (500 μL) of B(C₆F₅)₃ (15 mg, 0.029 mmol) was added PhCHO (3.0 μL, 0.029 mmol). ¹H NMR (CD₂Cl₂, room temp.): δ 9.39 (s, 1H, PhCHO), 8.22 (app. d, 2H, *J* = 7.31 Hz, PhCHO *o*-ArH), 8.02 (app. t, 1H, *J* = 7.44 Hz, PhCHO *p*-ArH), 7.74 (app. t, 2H, *J* = 7.69 Hz, PhCHO *m*-ArH). ¹⁹F NMR (CD₂Cl₂, room temp.): δ -134.2 (app. dd, 6F, *J* = 22.8 and 7.2 Hz, *o*-F), -156.3 (app. t, 3F, *J* = 20.2 Hz, *p*-F), -163.8 (m, 6F, *m*-F).

¹ Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics*, **1996**, *15*, 1518.

² Deck, P. A.; Beswick, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 1772.

³ Blackwell, J. M.; Piers, W. E.; McDonald, R. *J. Am. Chem. Soc.* **2002**, *124*, 1295.