Supplementary Material (ESI) for Dalton Transactions

Palladium complexes of new bulky fluorinated diphosphines give particularly active and regioselective catalysts for hydroxycarbonylation of styrene.

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Supplementary Information:

General Experimental procedures and instrumentation.

Routine NMR data was recorded either on a Bruker Avance 300 (^{1}H at 300 MHz, ^{13}C at 75 MHz, ^{19}F at 282 MHz, ^{31}P at 121 MHz) or a Bruker Avance II 400 (^{1}H at 400 MHz, ^{13}C at 100 MHz, ^{19}F at 376 MHz, ^{31}P at 161 MHz). ^{1}H and ^{13}C spectra were referenced to external tetramethylsilane, ^{19}F spectra were referenced to external trichlorofluoromethane, and ^{31}P spectra were referenced to external phosphoric acid. Chemical shifts are expressed in parts per million. Chemical ionisation mass spectroscopy and electron ionisation mass spectroscopy were performed on a Micromass GCT spectrometer. Electrospray mass spectroscopy was performed on a Micromass LCT spectrometer. All were operated by Mrs Caroline Horsburgh. Microanalysis was carried out for C and H using an EA 1110 CHNS CE Instruments elemental analyser by Mrs. S. Williamson. Infra-red absorbsion spectra were recorded on a Perkin Elmer GX-FTIR System spectrometer. Thin layer chromatography was performed using 0.20mm layers of silica gel supported on plastic sheets (Macherey-Nagel, Polygram Sil G/UV_{254}) or using 0.20mm layers of aluminium oxide supported on plastic sheets (Merck Aluminium oxide F_{254}). Preparative chromatography was performed using Davasil silica gel 35-70u. Dry degassed diethyl ether, petroleum ether, THF and toluene were obtained from an Innovative Technologies Puresolve 400 solvent still. Other solvents were bought and used as received without further purification other than degassing by either purging with nitrogen or repeated freeze/thaw cycles under vacuum. Organic solutions were dried by standing over anhydrous sodium sulphate and evaporated either under reduced pressure on a rotary evaporator or under reduced pressure whilst agitating manually. *Tert*-butyldichlorophosphine was obtained from the Aldrich Chemical Company and used as received. All manipulations were carried out under an atmosphere of nitrogen unless otherwise stated

Selected Experimental Procedures and spectroscopic Data

(*Ortho*-trifluoromethylphenyl)(*tert*-butyl)chlorophosphine.

Ortho-bromobenzotrifluoride (9.17g, 6.23 cm^3, 40.75 mmol) was dissolved in 20ml of diethyl ether in a dry schlenk tube and cooled to -78 °C. N-butyllithium (16.30 cm^3, 40.75 mmol as a 2.5M solution in hexanes) was added to this dropwise whilst stirring and the solution was then allowed to warm to room temperature. *Tert*-butyldichlorophosphine (6.480 g, 40.75 mmol) was dissolved in diethyl ether, and the stirred solution was cooled to -78 °C. The aryl-lithium solution was then added dropwise to the phosphine solution and after this, the reaction was allowed to gradually warm to room temperature. The solvent was then removed under vacuum and the 30 ml of hexane was added to precipitate the lithium chloride. The solution was then filtered as it was transferred by cannula to a schlenk tube and the solvent removed under vacuum to give a brown oil which was distilled under vacuum (85-105 °C) to give the title compound (7.64 g, 28.5 mmol) in 70% yield as a colourless air and moisture sensitive liquid. In the syntheses described here, a one-pot method to prepare the borane was devised, which is also reproduced below.

^{1}H-NMR (300 MHz; C_6D_6): δ_H 1.45 (9 H, d, $^{3}J_{H-P}$ = 13.7 Hz, 3(C**H**$_3$), 6.95 (1 H, t, $^{3}J_{H-H}$ = 8 Hz, Ar**H**), 7.1 (1 H, t, $^{3}J_{H-H}$ = 8 Hz, Ar**H**), 7.45 (1 H, dd, $^{3}J_{H-H}$ = 10.5 Hz, $^{3}J_{H-P}$ = 3.8 Hz Ar**H** *o*-P), 8.05 (1 H, dm, $^{3}J_{H-H}$ = 8.8 Hz, Ar**H** *o*-CF_3). ^{19}F-NMR (282 MHz; C_6D_6): δ_F 71.9 (d, J_{F-P} = 72.9 Hz). ^{31}P{^{1}H}-NMR (121.5 MHz; C_6D_6): δ_P 100.6 (q, J_{P-F} = 72.5 Hz).

(*Ortho*-trifluoromethylphenyl)(*tert*-butyl)phosphinoborane (from (*ortho*-trifluoromethylphenyl)(*tert*-butyl)chlorophosphine)

(*Ortho*-trifluoromethylphenyl)(*tert*-butyl)chlorophosphine (1.171 g, 4.37 mmol) was dissolved in THF (20ml) and the solution was cooled to 0 °C prior to the addition of $NaBH_4$ (0.495 g, 13.08 mmol). The reaction mixture was allowed to warm to room temperature gradually and was stirred until the chloride was completely converted to the secondary borane as judged by ^{31}P NMR. The solvent was removed under vacuum and (under atmospheric conditions) the residue redissolved in dichloromethane and transferred to a separating funnel for work up (water/dichloromethane). The organic layer was retained, dried over Na_2SO_4 and the solvent removed under vacuum to give 1.002 g of crude product. Flash chromatography (1-10 % diethyl ether in hexane,) gave two fractions. (*Ortho*-trifluoromethylphenyl)(*t*-butyl)phosphinoborane (0.6025 g, 2.42 mmol, 55.6% yield) was obtained in the second fraction, as a colourless white solid after the removal of the solvent. An analytical sample was prepared by recrystallisation from hexane at low temperature (-78 °C).

Anal. Calc'd for $C_{11}H_{17}F_3PB$: C, 53.27; H, 6.91% found: C, 53.05; H, 6.95%. ^{1}H-NMR (300 MHz; $CDCl_3$): δ_H 0.50 (3 H, m, B**H**$_3$), 1.05 (9 H, d, $^{3}J_{H-P}$ = 15.3 Hz, C(C**H**$_3$)$_3$), 5.45 (1 H, dm, $^{1}J_{H-P}$ = 384.8 Hz, P-**H**), 7.45 (1 H, t, $^{3}J_{H-H}$ = 7.5 Hz, Ar**H**), 7.55 (1 H, t, $^{3}J_{H-H}$ = 7.5 Hz, Ar**H**,) 7.65 (1 H, dm, $^{3}J_{H-H}$ = 7.6 Hz, Ar**H** *o*-CF_3), 7.8 (1 H, dd, $^{3}J_{H-P}$ = 12.2 Hz, $^{3}J_{H-H}$ = 7.4 Hz, Ar**H** *o*-P). ^{1}H{^{31}P}-NMR (300 MHz; $CDCl_3$): δ_H 0.50 (3 H, m, B**H**$_3$), 1.05 (9 H, s, C(C**H**$_3$)$_3$), 5.45 (1 H, m, P-**H**), 7.45 (1 H, t, $^{3}J_{H-H}$ = 7.5 Hz, Ar**H**), 7.55 (1 H, t, $^{3}J_{H-H}$ = 7.5 Hz, Ar**H**) 7.65 (1 H, dm, $^{3}J_{H-H}$ = 7.6 Hz, Ar**H** *o*-CF_3), 7.8 (1 H, d, $^{3}J_{H-H}$ = 7.4 Hz, Ar**H** *o*-P). ^{13}C-NMR (75.5 MHz; $CDCl_3$): δ_C 25.8 (d, $^{3}J_{C-P}$ = 3 Hz, **C**H$_3$), 28.4 (d, $^{1}J_{C-P}$ = 31.1 Hz, P-**C**(CH$_3$)), 122.5 (qd, $^{1}J_{C-F}$ = 276 Hz, $^{4}J_{C-P}$ = 2.2 Hz, **C**F$_3$), 124.5 (dq, $^{1}J_{C-P}$ = 40.5 Hz, J_{C-F} = 1.7 Hz, Ar**C**-P), 125.6 (dq, $^{2}J_{C-F}$ = 6.6 Hz, $^{2}J_{C-P}$ = 4.3 Hz, Ar**C** *o*-CF_3), 130.3 (d, $^{4}J_{C-P}$ = 2.2 Hz, Ar**C** *p*-P), 130.7 (dq, $^{2}J_{C-P}$ = 11.5 Hz, $^{4}J_{C-F}$ = 0.9 Hz Ar**C** *o*-P), 131.2 (qd, $^{2}J_{C-F}$ = 28.8 Hz, $^{2}J_{C-P}$ = 2.1 Hz, Ar**C**-CF_3), 134.1 (d, $^{3}J_{C-P}$ = 13.4 Hz, Ar**C** *m*-P). ^{19}F{^{1}H}-NMR (282 MHz; $CDCl_3$): δ_F 57.1 (d, $^{4}J_{F-P}$ = 2 Hz). ^{31}P-NMR (121.5 MHz; $CDCl_3$): δ_P 17.3 (br,m). ^{31}P{^{1}H}-NMR (121.5 MHz; $CDCl_3$): δ_P 17.3 (dm br, $^{1}J_{P-H}$ = 390 Hz). M.S. ES-: *m/z* 247.12 ([M- H]$^-$ requires 247.10). M.S. ES+: *m/z* 271.04 ([M + Na]$^+$ requires 271.10).

(*Ortho*-trifluoromethylphenyl)(*tert*-butyl)phosphinoborane

(direct from (*tert*-butyl) dichlorophosphine without isolation of chlorophosphine)

Bromobenzotrifluoride (1.03 cm^3, 7.58 mmol) was dissolved in 20 cm^3 of diethyl ether in a dry schlenk tube and cooled to -78 °C. N-butyllithium (3.1 cm^3, 7.75 mmol as a 2.5 M solution in hexanes) was added to this dropwise whilst stirring and then the solution allowed to warm to room temperature. *Tert*-butyldichlorophosphine (1.198 g, 7.58 mmol) was dissolved in diethyl ether, and the stirred solution was cooled to -78 °C. The solution of the lithated compound was then added dropwise and the solution allowed to warm to room temperature. The solvent was then removed under vacuum to give an oil. This was redissolved in 100 cm^3 THF and cooled to 0 °C before $NaBH_4$ (1.2 g, 30 mmol) was added. The reaction was allowed to warm to room temperature and the reaction allowed to continue

until it was judged complete by ^{31}P NMR. The solvent was then removed and the residue re-suspended in dichloromethane. After work up (dichloromethane/water) the organic layers were combined, dried over $MgSO_4$, filtered and the solvent removed to provide a clear oil which solidified on standing. This was then recrystallised from hexane at -78 °C to yield the title compound as colourless crystals (1.720 g, 0.693 mmol, 91.5% yield). Data identical to previous preparation.

1,2-Bis[(*ortho*-trifluoromethylphenyl)*tert*-butylmethylenephosphine]benzene (*meso*)

(*Ortho*-trifluoromethylphenyl)*tert*-butylphosphineborane (0.595 g, 2.4 mmol) was dissolved in THF (15 cm^3) and was cooled to -78 ˚C. N-butyllithium (0.94 ml, 2.4 mmol as a 2.5 M solution in hexanes) was added slowly whilst stirring and the reaction allowed to gradually warm to room temperature. After 1 hour the solution was cooled to -78 ˚C, *ortho*-dichloroxylene (0.175 g, 1 mmol) was added and the reaction allowed to warm to room temperature. ^{31}P NMR showed a mixture of products which gradually converted to the product apon hextended heating over 5 days. The solvent was then removed under vacuum and the residue redissolved in dichloromethane (20 cm^3) followed by workup with water (10 cm^3). The organic layer was retained and dried with $MgSO_4$, which was removed by filtration and washed with further dichloromethane yielding a light yellow solution. The solvent was then removed under vacuum yielding 0.659 g of the crude product. Recrystallisation from dichloromethane/ethanol (4 cm^3, 1/2) yielded the product (120 mgs, 0.21 mmol, 21% yield) as clear needles suitable for X-ray analysis which confirmed these to be the *rac* isomer.
Anal. Calc'd for $C_{30}H_{34}F_6P_2$: C, 63.16; H, 6.01% found: C, 63.97; H, 6.53%
^1H-NMR (300 MHz; C_6D_6): δ_H1.15 (18 H, d, $^3J_{H-P}$ = 15 Hz, 2(C(C**H**$_3$)$_3$), 3.4 (2 H, d, $^2J_{H-H}$ = 14 Hz, P-C**H**H), 3.85 (2 H, ddd, $^2J_{H-H}$ = 14 Hz, $^2J_{H-P}$ = 7.5 Hz, $^5J_{H-P}$ = 4 Hz, P-C**H**H), 6.7 (2 H, m, Ar**H** xylyl), 6.8 (2 H, m, Ar**H** xylyl), 6.9 (2 H, t, $^3J_{H-H}$ = 8 Hz, Ar**H**), 7.15 (2 H, t, $^3J_{H-H}$ = 8 Hz, Ar**H**), 7.45 (2 H, dd, $^3J_{H-H}$ = 8 Hz, $^3J_{H-P}$ = 3 Hz, Ar**H** *o*-P), 7.8 (2 H, dm, $^3J_{H-H}$ = 8 Hz, Ar**H** *o*-CF_3). $^1H\{^{31}P\}$-NMR (300 MHz; C_6D_6): δ_H1.15 (18 H, 2(C(C**H**$_3$)$_3$), 3.4 (2 H, d, $^2J_{H-H}$ = 14 Hz, P-C**H**H), 3.85 (2 H, d, $^2J_{H-H}$ = 14 Hz), 6.7 (2 H, m, Ar**H** xylyl), 6.8 (2 H, m, Ar**H** xylyl), 6.9 (2 H, t, $^3J_{H-H}$ = 8 Hz, Ar**H**), 7.15 (2 H, t, $^3J_{H-H}$ = 8 Hz, Ar**H**), 7.45 (2 H, d, $^3J_{H-H}$ = 8 Hz, Ar**H** *o*-P), 7.8 (2 H, dm, $^3J_{H-H}$ = 8 Hz, Ar**H** *o*-CF_3). ^{13}C-NMR (75 MHz; C_6D_6): δ_C 28.5 (d, $^2J_{C-P}$ = 15 Hz, C(**C**H$_3$)$_3$), 29.4 (dd, $^1J_{C-P}$ = 24 Hz, $^4J_{C-P}$ = 12 Hz, P-**C**H$_2$), 31.0 (d, $^1J_{C-P}$ = 18.5 Hz, **C**(CH$_3$)$_3$), 125.2 (q, $^1J_{C-F}$= 275 Hz, **C**F$_3$), 126.6 (s, Ar**C**),126.7 (dq, $^3J_{C-F}$ = 6 Hz, $^3J_{C-P}$ = 6 Hz, Ar**C** *o*-CF_3), 130.1 (s, Ar**C**), 130.5 (s, Ar**C**), 131.2 (d, $^2J_{C-P}$ = 6 Hz, Ar**C** *o*-P), 135.4 (d, $^3J_{C-P}$ = 3 Hz, Ar**C** *m*-P), 136.25 (d, $^1J_{C-P}$ = 40.5 Hz, Ar**C**-P), 136.8 (dd, $^2J_{C-P}$ = 6 Hz, $^3J_{C-P}$ = 3 Hz, Ar**C**-CH_2). 137.5 (m, Ar**C**-CF_3). ^{19}F-NMR (282 MHz; C_6D_6): δ_F -54.95 (d, $^4J_{F-P}$ = 58 Hz). $^{31}P\{^1H\}$-NMR (121.5 MHz; C_6D_6): δ_P -7.6 (q, $^4J_{P-F}$ = 58 Hz). MS ES+: *m/z* 593.13 ([M+ Na]$^+$ requires 593.19), 571.15 ([M+ H]$^+$ requires 571.21).

1,3-bis(*tert*-butyl(*ortho*-(trifluoromethyl)phenyl)phosphino)propane.

(*Ortho*-trifluoromethylphenyl)*tert*-butylphosphineborane (0.542 g, 2.2 mmol) was dissolved in THF (15 cm^3) and was cooled to -78˚C. N-butyllithium (0.88 ml, 2.2 mmol as a 2.5M solution in hexanes) was diluted in diethyl ether (10 cm^3) and added drop-wise over an hour and the reaction allowed to gradually warm to room temperature. Then the solution was again cooled to -78˚C and 1,3-diidopropane (0.296g, 1mmol) was added and the reaction allowed to warm to room temperature. After 24 hours $^{31}P\{H\}$NMR showed that the reaction of the anion was complete. Addition of 2 ml pyrolidine led to complete decomplexation of boranes after 24 hours at room temperature, yielding deprotected products. The solvent was then reduced under vacuum and the residue extracted with hexane, filtered and the solvent removed. Flash chromatography (gradient elution from 0.5-10% diethyl ether/hexane) of this mixture was

performed using degassed solvents under nitrogen pressure and fractions were collected in round bottomed flasks under a stream of argon and the solvent quickly removed by rotary evacuation and the resulting oil stored under argon. Fractions containing the product were identified by $^{31}P\{H\}$NMR and combined and a further short column (20% diethyl ether/hexane) was performed to remove any oxide formed during fraction collection, and the solvent removed under vacuum to give the title compound as a mixture of *rac* and meso *isomers* (0.460g, 90% yield).

^{1}H-NMR (300 MHz; C_6D_6): δ_H 0.98 (18 H of one diastereomer, d, J_{H-p} = 12.1 Hz, C(C**H$_3$**)$_3$, 1.03 (18 H of one diastereomer, d, J_{H-p} = 12.1 Hz, C(C**H$_3$**)$_3$), 1.40 (2 H, m, C**H$_2$**), 1.70 (2 H, m, C**H$_2$**) 1.90 (1H, m, CH**H**), 2.08 (1 H, m, CH**H**). $^{1}H\{^{31}P\}$-NMR (300 MHz; C_6D_6): δ_H 0.98 (18 H of one diastereomer, s, C(C**H$_3$**)$_3$, 1.03 (18 H of one diastereomer, s, C(C**H$_3$**)$_3$, 1.40 (2 H, m, C**H$_2$**), 1.70 (2H, m, C**H$_2$**) 1.90 (1 H, m, CH**H**), 2.08 (1 H, m, CH**H**) 7.0 (3 H, m, Ar**H**), 7.15 (1H, t, Ar**H**) 7.38 (1H, m, Ar**H**) 7.60 (3H, m, Ar**H**). ^{13}C-NMR (75 MHz; C_6D_6): δ_c 23.2 (t, $^{2}J_{C-P}$ = 15.7 Hz, C-**C**H$_2$C), 23.9 (dd, $^{1}J_{C-P}$ = 18.3 Hz, $^{3}J_{C-P}$ = 11.6 Hz,P-**C**H$_2$), 24.6 (m, **C**H$_2$), 28.3 (d, $^{2}J_{C-P}$ = 14.7 Hz, **C**H$_3$), 30.1 (d, $^{1}J_{C-P}$ = 16.2 Hz, **C**(CH)$_3$), 125.4 (q, J_{C-F} = 275.3 Hz, $^{3}J_{C-P}$ = 1.5 Hz, **C**F$_3$), 126.7 (dq, $^{3}J_{C-F}$ = 5.8 Hz, J_{C-P} = 9.4 Hz, Ar**C** *o*-P), 129.5 (d, J_{C-P}= 14.9 Hz, Ar**C**), 130.8 (d, J_{C-P}= 12.1 Hz, Ar**C**), 134.6 (dm, J_{C-P} = 26.9 Hz, Ar**C**), 134.9 (d, J_{C-P}= 43.1 Hz, Ar**C**) 137.5 (m, Ar**C**-CF$_3$). $^{19}F\{^{1}H\}$-NMR (282 MHz; C_6D_6): δ_F -54.8 (d, $^{4}J_{F-P}$ = 57.1 Hz), -54.7 (d, $^{4}J_{F-P}$ = 56.9 Hz); δ_P(121 MHz; C_6D_6) -10.2 (q, $^{4}J_{P-F}$ = 57.0 Hz), -8.6 (q, $^{4}J_{P-F}$ = 57.3 Hz). Single Mass Analysis MS ES+: *m/z* 509.1953 ($[M + H]^+$ ($C_{25}H_{33}F_6P_2$) requires 509.1962)

[(1,3-Bis(*tert*-butyl(*ortho*-(trifluoromethyl)phenyl)phosphino)propane)palladium]dichloride.

1,3-Bis(*tert*-butyl(*ortho*-(trifluoromethyl)phenyl)phosphino)propane (220 mg, 0.433 mmol) was dissolved in dichloromethane (10 ml), stirred at room temperature and [palladium(benzonitrile)$_2$dichloride] (166 mg, 0.433 mmol) was added before the reaction allowed to stir overnight. The reaction was reduced to near dryness by removal of solvent under vacuum, (under atmospheric conditions) hexane was then slowly added to form a precipitate which was isolated by filtration and washed with further hexane. The precipitate was then redissolved and precipitated several times to yield the product as a orange powder (70 mgs 0.102 mmol, 23.5% yield). A sample suitable for X-ray analysis was prepared by slow diffusion of hexane into a dichloromethane solution of the product. This confirmed the product to be present as the rac isomer.

Anal. Calcd for $C_{25}H_{32}Cl_2F_6P_2Pd$: C, 43.78; H, 4.70% found: C, 43.86; H, 4.42%. ^{1}H-NMR (300 MHz; $CDCl_3$): δ_H 1.4 (18 H, d, $^{3}J_{H-P}$ = 16 Hz, 6(CH_3)), 1.95, 2.15, 2.4 (6 H, m, 6C**H**H), 7.55 (4 H, m, 4Ar**H**), 7.8 (2 H, m, 2Ar**H** *o*-CF_3), 9.05 (2 H, m br, 2Ar**H** *o*-P). $^{1}H\{^{31}P\}$-NMR (300 MHz; $CDCl_3$): δ_H 1.4 (18 H, s, 6(CH_3)), 1.95, 2.15, 2.4 (6 H, m, 6C**H**H), 7.55 (4 H, m, 4Ar**H**), 7.8 (2 H, m, 2Ar**H** *o*-CF_3), 9.05 (2 H, m br, 2Ar**H** *o*-P). ^{19}F-NMR (282 MHz; $CDCl_3$): δ_F -53.2 (s). $^{31}P\{^{1}H\}$-NMR (121 MHz; CD_2Cl_2): δ_P(121 MHz; $CDCl_3$): δ_P 33.7 (s). MS ES+: *m/z* 651.08 (100%), ($[M - Cl]^+$ requires 651.06).

[(1,3-bis(*tert*-butyl(*ortho*-(trifluoromethyl)phenyl)phosphino)propane)palladium]dichloride from $Pd_2(dba)_3$

$Pd_2(dba)_3$ (50 mgs, 0.055 mmol), was added to a stirred solution of 1,3-bis(*tert*-butyl(*ortho*-(trifluoromethyl)phenyl)phosphino)propane (57 mgs, 0.11 mmols) in THF (10ml). After 1hour, the dark orange solution was filtered and the solvent removed under vacuum yielding

orange oil. This was dissolved in diethyl ether and HCl (0.6 cm^3, 1.2 mmol as 2M solution in diethyl ether) was added to form the product as a yellow precipitate. The product was purified under atmospheric conditions by filtration to isolate the precipitate followed by re-dissolving in 5 cm^3 dichloromethane and precipitation by the slow addition of hexane (42 mgs, 0.61 mmol, 55% yield). Further recrystallisation allowed the isolation of the rac isomer. Data identical to previous preparation.

Tert-butyl(_para_-(trifluoromethyl)phenyl)phosphinoborane

Magnesium cuttings (0.5 g, 20.5 mmol) were activated by being stirred dry with a catalytic amount of iodine in an inert atmosphere, to this was added a diethyl ether solution of 1-bromo-4-(trifluoromethyl)benzene (2.5 cm^3, 18.0 mmol) which reacted vigorously to form the Gringard. This solution was added dropwise to a cooled (-78 °C) solution of *tert*-butylphosphinodichloride (2.85 g, 17.9 mmol). The solution was maintained at low temperature until the dry-ice was exhausted to allow a very gradual warming to room temperature (approximately 6 hours) at which point the reaction progress was monitored by ^{31}P NMR and additional Gringard added (as above) as necessary for satisfactory conversion of the dichloride. The resulting mixture of *tert*-butyl(4-(trifluoromethyl)phenyl)phosphinochloride/bromide was then cooled to 0 °C, $NaBH_4$ (2.0 g, 60 mmol) added, and the reaction mixture stirred for several days until satisfactory conversion to the secondary phosphinoborane had been achieved as judged by ^{31}P NMR. At this point, the solvent was removed under vacuum and (under atmospheric conditions) the residue partitioned between dichloromethane/water and organic layer washed twice. The organic layer was retained, dried over $MgSO_4$ and filtered before the solvent was removed. Flash chromatography (20% diethyl ether in hexane) yielded the product in the second fraction as a clear viscous oil (2.78 g, 11.2 mmol, 62.5% yield). The material obtained in this way always contained a small amount (~2 % by ^{31}P-NMR) of impurity (thought to be the phosphine oxide, ^{31}P-NMR: δ 47.57 (d, $^1J_{P-H}$ = 453 Hz), ^{31}P{H}-NMR: δ 47.57 (s)), it was however pure enough for further synthesis.

^{1}H-NMR (300 MHz; C_6D_6): δ_H 0.6 (3 H, m br w, B**H$_3$**), 1.1 (9 H, d, $^3J_{H-P}$ = 11 Hz, 3(C**H$_3$**)), 5.1 (1 H, dq, $^1J_{H-P}$ = 387 Hz, $^3J_{H-H}$ = 7 Hz, P-**H**), 7.7 (4 H, m, 4Ar**H**). ^{1}H{^{31}P}-NMR (300 MHz; C_6D_6): δ_H 0.6 (3 H, m br w, B**H$_3$**), 1.1 (9 H, s, 3(C**H$_3$**)), 5.1 (1 H, m, P-**H**), 7.7 (4 H, m, 4Ar**H**). ^{13}C-NMR (75 MHz; $CDCl_3$): δ_c 25.5 (d, $^3J_{C-P}$ = 3 Hz, **C**H$_3$), 27.6 (d, $^1J_{C-P}$ = 32 Hz, P-**C**(CH$_3$)$_3$), 122.6 (q, $^1J_{C-F}$ = 272 Hz, **C**F$_3$), 124.4 (d q, $^3J_{C-P}$ = 9.5 Hz, $^3J_{C-F}$ = 4 Hz, Ar**C** *o*-CF$_3$), 128.9 (dq, $^1J_{C-P}$ = 50 Hz, $^5J_{C-F}$ = 1 Hz, Ar**C**-P), 132.5 (qd, $^2J_{C-F}$ = 33 Hz, $^4J_{C-P}$ = 2.5 Hz, Ar**C**-CF$_3$), 133.4 (M, $^2J_{C-P}$ = 8 Hz, Ar**C** *o*-P). ^{19}F-NMR (282 MHz; $CDCl_3$): δ_F 63.7 (s). ^{31}P-NMR (121 MHz; $CDCl_3$): δ_P 32.0 (dm, $^1J_{P-H}$ = 368 Hz). ^{31}P{^{1}H}-NMR (121 MHz; $CDCl_3$): δ_P 32.0 (m). Single Mass Analysis MS ES-: *m/z* 247.1027 ($[M - H]^+$ $C_{11}H_{16}BF_3$ requires 247.1030).

1,3-bis(_tert_-butyl(_para_-(trifluoromethyl)phenyl)phosphino)propanediborane _(rac/meso)_. (*para*-trifluoromethylphenyl)*tert*-butylphosphineborane (1.05 g, 4.2 mmol) was dissolved in THF (20 ml) and was cooled to -100 ˚C. N-butyllithium (1.8 cm^3, 4.5 mmol as a 2.5 M solution in hexanes) was diluted in THF (10ml) and added drop-wise over two hours and the reaction vessel transferred to a cold bath cooled to -40 °C and the temperature maintained for 30 minutes. Then the solution was again cooled to -78 ˚C and 1,3-diidopropane (0.230 cm^3, 2.0 mmol) was added and the reaction allowed to gradually warm to room temperature. After 16 hours ^{31}P{H}NMR showed that the reaction was complete. The solvent was then reduced

under vacuum and the residue extracted with dichloromethane, filtered and the solvent removed. Flash chromatography (1-5% diethyl ether in hexane) allowed partial separation of the *rac* and *meso* diastereomers, which were further purified by recrystallisation from hexane. Samples suitable for X-ray crystallography were prepared by diffusion of hexane into saturated dichloromethane solutions of the products. The yields were as follows; *rac* 355 mgs, *meso* 145 mgs, mixed *rac*/*meso* 275 mgs, (total, 775 mgs, 1.44 mmol, 72% yield).

Meso
^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.66 (dd, 4 H, $^{3}J_{H-H}$ = 8.5 Hz, $^{3}J_{H-P}$ = 8.5 Hz, Ar**H** *o*-P), 7.52 (dq, 4 H, $^{3}J_{H-P}$ = 7.6 Hz, $^{3}J_{H-P}$ = 1.2 Hz, Ar**H** *o*-CF_3), 1.94 (m, 2 H, 2CH**H**), 1.78 (m, 1 H, CH**H**), 1.64 (m, 2 H, 2CH**H**), 1.47 (m, 1 H, CH**H**), 0.77 (d, 18 H, $^{3}J_{H-P}$ = 14.0 Hz, C**H**$_3$), -0.1 – 0.8 (m br, 6H, B**H**$_3$). ^{1}H{P}-NMR (300 MHz, $CDCl_3$): δ 7.66 (d, 4 H, $^{3}J_{H-H}$ = 8.5 Hz, Ar**H** *o*-P), 7.52 (d, 4 H, $^{3}J_{H-H}$ = 7.6 Hz, Ar**H** *o*-CF_3), 1.94 (m, 2 H, 2CH**H**), 1.78 (m, 1 H, CH**H**), 1.64 (m, 2 H, 2CH**H**), 1.47 (m, 1 H, CH**H**), 0.77 (s, 18 H, C**H**$_3$), -0.1 – 0.8 (m br, 6H, B**H**$_3$). ^{13}C-NMR (75 MHz; $CDCl_3$): δ 134.07 (d, $^{2}J_{C-P}$ = 8.1 Hz, Ar**C** *o*-P), 133.32 (dq, $^{2}J_{C-F}$ = 33.1 Hz, $^{4}J_{C-P}$ = 2.5 Hz, Ar**C**-CF_3), 130.72 (d, $^{1}J_{C-P}$ = 44.8 Hz, Ar**C**-P), 125.15 (dq, $^{2}J_{C-P}$ = 12.9 Hz, $^{4}J_{C-F}$ = 3.6 Hz, Ar**C** *o*-P), 123.63 (qd, $^{1}J_{C-F}$ = 273.3 Hz, $^{5}J_{C-P}$ = 0.8 Hz, **C**F_3), 29.28 (d, $^{1}J_{C-P}$ = 32.2 Hz, P-**C**$(CH_3)_3$), 25.22 (d, $^{2}J_{C-P}$ = 2.2 Hz, **C**H_3), 20.24 (dd, $^{1}J_{C-P}$ = 36.8 Hz, $^{3}J_{C-P}$ = 9.5 Hz P-**C**H_2), 17.73 (s, C-**C**H_2-C).

Rac
Single Mass Analysis MS ES-: *m/z* 247.1027 ($[M - H]^+$ $C_{11}H_{16}BF_3$ requires 247.103). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.66 (dd, 4 H, $^{3}J_{H-H}$ = 8.5 Hz, $^{3}J_{H-P}$ = 8.5 Hz, Ar**H** *o*-P), 7.52 (dd, 4 H, $^{3}J_{H-P}$ = 7.6 Hz, $^{3}J_{H-P}$ = 1.2 Hz, Ar**H** *o*-CF_3), 2.50 (m, 2 H, CH**H**), 1.83 (m, 2 H, CH**H**), 1.59 (m, 2 H, CH**H**), 1.01 (d, 18 H, $^{3}J_{H-P}$ = 14.0 Hz, C**H**$_3$), -0.1 – 0.8 (m br, 6H, B**H**$_3$). ^{1}H{P}-NMR (300 MHz, $CDCl_3$): δ 7.66 (d, 4 H, $^{3}J_{H-H}$ = 8.5 Hz, Ar**H** *o*-P), 7.52 (d, 4 H, $^{3}J_{H-P}$ = 7.6 Hz, Ar**H** *o*-CF_3), 2.50 (m, 2 H, CH**H**), 1.83 (m, 2 H, CH**H**), 1.59 (m, 2 H, CH**H**), 1.01 (s, 18 H, C**H**$_3$), -0.1 – 0.8 (m br, 6H, B**H**$_3$). ^{13}C-NMR (75 MHz; $CDCl_3$): δ 134.35 (d, $^{2}J_{C-P}$ = 8.1 Hz, Ar**C** *o*-P), 133.32 (dq, $^{2}J_{C-F}$ = 33.1 Hz, $^{4}J_{C-P}$ = 2.5 Hz, Ar**C**-CF_3), 130.72 (d, $^{1}J_{C-P}$ = 44.8 Hz, Ar**C**-P), 125.38 (m, Ar**C** *o*-P), 123.86 (qd, $^{1}J_{C-F}$ = 273.3 Hz, $^{5}J_{C-P}$ = 0.8 Hz, **C**F_3), 29.72 (d, $^{1}J_{C-P}$ = 32.3 Hz, P-**C**$(CH_3)_3$), 25.64 (d, $^{2}J_{C-P}$ = 2.2 Hz, **C**H_3), 20.24 (dd, $^{1}J_{C-P}$ = 33.8 Hz, $^{3}J_{C-P}$ = 9.9 Hz P-**C**H_2), 17.69 (s, C-**C**H_2-C).
^{19}F-NMR (376 MHz; $CDCl_3$): δ -63.25 (s, *meso*) -63.79 (s, *rac*). ^{31}P-NMR (162 MHz; $CDCl_3$): δ 33.40 (m br, *meso/rac*). MS ES+: *m/z* 559.30 ($[M + Na]^+$ requires 559.24).

1,3-Bis(*tert*-butyl(*para*-(trifluoromethyl)phenyl)phosphino)propane (rac).

1,3-Bis(*tert*-butyl(*para*-(trifluoromethyl)phenyl)phosphino)propanediborane (rac) (400 mgs, 0.74 mmol) was dissolved in dichloromethane (10ml) and cooled to -20 °C before $HBF_4.OMe_2$ (0.9 ml, 7.4 mmol) was added dropwise. Once addition was complete, the reaction was allowed to warm to room temperature and stirred overnight before being cooled to 0 °C. Hydrolysis was then achieved by the addition of a saturated solution of $NaHCO_3$ (10 ml). After vigorous stirring of the biphasic mixture for 10 minutes the organic layer was removed, the aqueous layer extracted with dichloromethane two further times and the combined extracts dried over $MgSO_4$. The solution was then filtered off and the solvent removed under vacuum to yield the title compound as a clear oil (358 mgs, 95.2% yield).

^{1}H-NMR (300 MHz; C_6D_6): δ_H 0.88 (18 H, d, $^{3}J_{H-P}$ = 12 Hz, 6(C**H**$_3$)), 1.43 (2 H, m, 2C**H**H), 1.65 (2 H, m, 2C**H**H), 2.15 (2 H, m, 2C**H**H), 7.4 (8 H, m, 8 Ar**H**). ^{1}H{^{31}P}-NMR (300 MHz; $CDCl_3$): δ_H 0.88 (18 H, s, 6(C**H**$_3$)), 1.43 (2 H, m, 2C**H**H), 1.65 (2 H, m, 2C**H**H), 2.15 (2 H, m,

2C**H**H), 7.4 (8 H, m, 8 Ar**H**). ^{13}C-NMR (100 MHz; $CDCl_3$): δ_C 21.7 (dd, $^1J_{C-P}$ = 16 Hz, $^3J_{C-P}$ = 12 Hz, P-**C**H_2), 22.8 (t, $^2J_{C-P}$ = 16 Hz, **C**H_2 centre), 27.3 (d, $^2J_{C-P}$ = 13 Hz, **C**H_3), 29.1 (d, $^1J_{C-P}$ = 11.5 Hz, **C**(CH_3)), 124.0 (q, $^1J_{C-F}$ = 272 Hz, **C**F_3), 124.4 (m, Ar**C** *o*-CF_3), 130.9 (q, $^2J_{C-F}$ = 32.5 Hz, Ar**C**-CF_3), 134.3 (d, $^2J_{C-P}$ = 19 Hz, Ar**C** *o*-P), 139.9 (d, $^1J_{C-P}$ = 23 Hz, Ar**C**-P). ^{19}F-NMR (376 MHz; $CDCl_3$): δ_F -62.9 (s). ^{31}P{H}-NMR (162 MHz; $CDCl_3$): δ_P 2.03 (s). Single Mass Analysis MS ES+ 509.1962 ($[M + H]^+$ $C_{25}H_{33}F_6P_2$ requires 509.1962).

[1,3-bis(*tert*-butyl(*para*-(trifluoromethyl)phenyl)phosphino)propanepalladium]dichloride-(*rac).*

1,3-Bis(*tert*-butyl(*para*-(trifluoromethyl)phenyl)phosphino)propane-(*rac*) (248 mg, 0.49 mmol) was dissolved in CH_2Cl_2 (10 ml) and [palladium(benzonitrile)$_2$dichloride] (188 mgs, 0.49 mmol) added. There followed an almost instant colour change from deep red to yellow. Hexane was added and a precipitate formed which was filtered, washed with further hexane and dried under vacuum to yield the title compound as bright yellow crystalline powder (325 mgs, 0.475 mmol 97% yield).

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Anal. Calcd for $C_{25}H_{32}Cl_2F_6P_2Pd$: C, 43.78; H, 4.70 % found: C, 43.82; H, 4.45%. ^{1}H-NMR (400 MHz; CD_2Cl_2): δ_H 1.28(18 H, d, $^3J_{H-P}$ = 18 Hz, 6(C**H**$_3$)), 1.85 (4 H, 4 m, C**H**H), 2.05 (2 H, 2 m, C**H**H), 7.71 (4 H, d, $^3J_{H-H}$ = 8 Hz, Ar**H** *o*-CF_3), 8.22 (4 H, dd, $^3J_{H-H}$ = 8 Hz, $^3J_{H-P}$ = 9 Hz, Ar**H** *o*-P). ^{1}H{^{31}P}-NMR (400 MHz; CD_2Cl_2): δ_H 1.28 (18 H, s, 6(C**H**$_3$)), 1.85 (4 H, 4 m, C**H**H), 2.05 (2 H, 2 m, C**H**H), 7.70 (4 H, d, $^3J_{H-H}$ = 8 Hz, Ar**H** *o*-CF_3), 8.21 (4 H, d, $^3J_{H-H}$ = 8 Hz, Ar**H** *o*-P). ^{13}C-NMR (100 MHz; CD_2Cl_2): δ_C 19.15 (s, CH_2-**C**H_2-CH_2), 20.32 (m, P-**C**H_2), 29.5 (m, **C**H_3), 37.30 (d d, $^1J_{C-P}$ = 32 Hz, $^3J_{C-P}$ = 3 Hz, **C**$(CH_3)_3$), 124.20 (q, $^1J_{C-F}$ = 275 Hz, **C**F_3), 125.60 (d q, $^2J_{C-P}$ = 10 Hz, $^4J_{C-F}$ = 4 Hz, Ar**C** *o*-P), 133.45 (q, $^2J_{C-F}$ = 33 Hz, Ar**C**-CF_3), 134.40 (d, $^1J_{C-P}$ = 43 Hz, Ar**C**-P), 135.42 (d q, $^3J_{C-P}$ = 5 Hz, $^3J_{C-F}$ = 4 Hz Ar**C** *o*-CF_3). ^{19}F-NMR (376 MHz; CD_2Cl_2): δ_F 63.18 (s), ^{31}P{H}-NMR (161 MHz; CD_2Cl_2): δ_P 28.10 (s), MS ES+: *m/z* 649.15 ($[M - Cl]^+$ requires 649.06).

Typical Hydroxycarbonylation Procedure.

Lithium chloride (8.4mgs, 0.20mmol), p-toluenesulphonic acid (34.4mgs, 0.20mmol), [Pd1,3-bis[(*ortho*-trifluoromethylphenyl)t-butylphosphine]propane]Cl_2 (6.8mgs, 0.01mmol) and 1,3-bis[(*ortho*-trifluoromethylphenyl)t-butylphosphine]propane (15mgs, 0.03mmol) were weighed into a Biotage 0.5-2ml microwave vial, along with a stirring bar which was sealed with a crimp cap and put under an inert atmosphere. Styrene (114µl, 1mmol), water (45µl, 2.5mmol) and degassed butan-2-one (1.5ml) were added before the cap was pierced with a capillary tube. The reaction tube was then placed in an autoclave which was purged with CO three times then pressurized to 50 bar then placed in a heating jacket and heated to 110 °C. After 16hrs the autoclave was cooled to room temperature and the pressure released slowly. The solvent was then removed from the reaction mixture and the residue dissolved in toluene and filtered to remove precipitate. The filtrate was then extracted with 3x saturated $NaHCO_3$ and the combined extracts acidified with conc. HCl until it remained decidedly acidic by litmus paper. This was then extracted using 3x dichloromethane and the combined extracts dried over $MgSO_4$, filtered and the solvent removed to give the viscous product, a mixture containing only 2-phenylpropanoic and 3-phenylpropanoic acids.

2-Phenylpropionic acid H^1 NMR δ: 1.45 (3H, d, C**H**$_3$), 3.7 (1H, q, C**H**), 7.2 (5H, m, Ar**H**).

3-Phenylpropanoic acid H^1 NMR δ: 2.6 (2H, t, CO-C**H**$_2$), 2.9 (2H, t, Ar-C**H**$_2$) 7.2 (5H, m, Ar**H**).