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# Supporting Information

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# Suzuki Cross-Couplings of Alkyl Tosylates that Possess β Hydrogens: Synthetic and Mechanistic Studies

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## Supporting Information

## I. General

$Pd(OAc)_2$ (Johnson Matthey), $PCy_3$ (Strem), $PCy_2Cl$ (Aldrich), P*t*$Bu_2Me$ (Strem), P*t*$Bu_2Cl$ (Strem), NaOH (Aldrich, 97%), pyridine (anhydrous, Fluka), boron trifluoride etherate (Aldrich), 48 wt% aqueous $HBF_4$ (Aldrich), 30% hydrogen peroxide (Alfa-Aesar), $NaBD_4$ (Aldrich), diethyl azodicarboxylate (Aldrich), $PPh_3$ (Alfa-Aesar), 4-toluenesulfonic acid monohydrate (Fluka), dicyclohexylcarbodiimide (Avocado), 4-(dimethylamino)pyridine (Aldrich), morpholine (Aldrich), EtI (Aldrich), *i*PrLi (0.7 M in pentane, Aldrich Sure/Seal), *n*-dodecyl tosylate (Acros), 4-vinylcyclohexene (Aldrich), 1-octene (Acros), 9-BBN dimer (Aldrich), 3-cyclopentyl-1-propanol (Aldrich), 16-hydroxyhexadecanoic acid (Aldrich), 1,4-dioxane (anhydrous, Aldrich Sure/Seal), chloroform (anhydrous, EM Science DriSolv), benzene (anhydrous, EM Science DriSolv), MeLi (1.5 M in $Et_2O$, Acros), EtMgCl (3.1 M in $Et_2O$, Alfa-Aesar), MeMgBr (3.14 M in $Et_2O$, Alfa-Aesar), PhLi (1.75 M in cyclohexane/$Et_2O$ 70:30, Alfa-Aesar) and *t*BuLi (1.5 M in pentane, Acros) were used as received.  4-Toluenesulfonyl chloride (Aldrich) was purified[1] before use.

Melting points are uncorrected.

## II. Preparation of Trialkylphosphines (Figure 2)

These preparations have not been optimized.

**General procedure.** Under an atmosphere of argon, the alkyllithium or alkyl Grignard reagent (1.3-1.6 equivalents) was added to a –78 °C solution of the dialkylchlorophosphine in $Et_2O$ (~0.2 M). The reaction mixture was stirred at –78 °C for 1-2 h, and then it was warmed to room temperature. After 1-3 h at room temperature, the reaction mixture was cooled to –78 °C, quenched with degassed water, dried over $MgSO_4$, and distilled under reduced pressure. The resulting trialkylphosphine was stored under an inert atmosphere.

$PCy_2$*i*Pr [42758-13-4] (from *i*PrLi; 60% yield), bp 135-139 °C at 200 mTorr. $^{31}P$ NMR ($C_6D_6$, 121 MHz): $\delta$ 14.4.

$PCy_2Et$ [46392-44-3] (from EtMgCl; 50% yield), bp 86-89 °C at 60 mTorr. $^{31}P$ NMR ($C_6D_6$, 121 MHz): $\delta$ 0.3.

$PCy_2Me$ [50420-46-7] (from MeLi; 52% yield), bp 75-79 °C at 100 mTorr. $^{31}P$ NMR ($C_6D_6$, 121 MHz): $\delta$ –18.8.

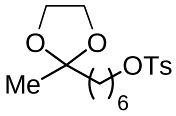
P*t*$Bu_2$*i*Pr [25032-49-9] (from *i*PrLi; 69% yield), bp 45-52 °C at 400 mTorr. $^{31}P$ NMR ($C_6D_6$, 121 MHz): $\delta$ 46.7.

P*t*$Bu_2Et$ [25032-48-8] (from EtLi;[2] 57% yield), bp 28-32 °C at 200 mTorr. $^{31}P$ NMR (THF, 121 MHz): $\delta$ 35.6.

## III. Preparation of Substrates for Table 1

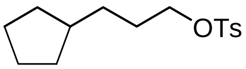
These preparations have not been optimized.

5-Benzyloxypent-1-ene[3] [81518-74-3], 9-hydroxynonanenitrile[4] [22054-08-6], and 9-phenyl-9-BBN[5] [23418-91-9] were prepared according to literature procedures.



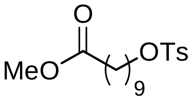
**2-Methyl-2-(6-tosyloxyhexyl)-1,3-dioxolane** [66432-71-1] was prepared according to a literature procedure.[6]

$^1$H NMR ($C_6D_6$, 400 MHz): δ 7.77 (d, *J* = 8.2 Hz, 2H), 6.72 (d, *J* = 8.2 Hz, 2H), 3.80 (t, *J* = 6.5 Hz, 2H), 3.54 (m, 4H), 1.86 (s, 3H), 1.57-1.53 (m, 2H), 1.33-1.22 (m, 7H), 1.04-0.92 (m, 4H). $^{13}$C NMR ($C_6D_6$, 100 MHz): δ 144.3, 134.7, 130.0, 128.3, 110.2, 70.5, 64.8, 39.7, 29.6, 29.2, 25.7, 24.3, 24.2, 21.3.



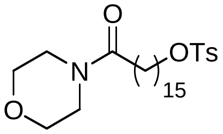
**3-Cyclopentyl-1-(tosyloxy)propane** [82195-61-7] was prepared from 3-cyclopentyl-1-propanol: Under argon, pyridine (5.02 mL, 62.4 mmol) was added to a 0 ºC solution of 3-cyclopentyl-1-propanol (4.00 g, 31.2 mmol) and tosyl chloride (7.14 g, 37.4 mmol) in chloroform (50 mL). After stirring for 6 h at 0 ºC and then 9 h at room temperature, the reaction mixture was diluted with chloroform (50 mL) and washed successively with 1 M HCl (2 x 20 mL), saturated aqueous $Na_2CO_3$ (20 mL), and brine (30 mL). It was then dried ($MgSO_4$), concentrated, and purified by column chromatography (2% EtOAc in hexanes), which afforded the title compound (5.90 g, 67%) as a colorless liquid.

$^1$H NMR ($CDCl_3$, 300 MHz): δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 4.01 (t, *J* = 6.5 Hz, 2H), 2.45 (s, 3H), 1.73-1.42 (m, 9H), 1.33-1.23 (m, 2H), 1.06-0.96 (m, 2H). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ 144.8, 133.4, 130.0, 128.1, 71.2, 39.7, 32.7, 31.8, 28.3, 25.3, 21.8.



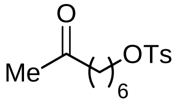
**Methyl 10-(tosyloxy)decanoate** [74120-71-1] was prepared according to a literature procedure.[7]

$^1$H NMR ($CDCl_3$, 400 MHz): δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 4.00 (t, *J* = 6.5 Hz, 2H), 3.65 (s, 3H), 2.44 (s, 3H), 2.28 (t, *J* = 7.4 Hz, 2H), 1.65-1.56 (m, 4H), 1.31-1.18 (m, 10H). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 174.5, 144.8, 133.3, 130.0, 128.1, 70.9, 51.7, 34.2, 29.33, 29.26, 29.22, 29.02, 28.95, 25.5, 25.1, 21.8.



**16-(Tosyloxy)hexadecanoic acid, morpholine amide** was prepared from 16-hydroxyhexadecanoic acid: Under argon, a solution of DCC (2.79 g, 13.5 mmol) in $CH_2Cl_2$ (15 mL) was added to a 0 °C solution of 16-hydroxyhexadecanoic acid (2.87 g, 10.5 mmol), morpholine (3.48 mL, 40.0 mmol), and DMAP (50 mg, 0.41 mmol) in $CH_2Cl_2$ (70 mL). After stirring for 3 h, the reaction was warmed to room temperature and stirred for an additional 16 h. The solvent was evaporated, and the residue was suspended in acetone and filtered through Celite to remove the precipitated dicyclohexylurea. The filtrate was diluted with $CH_2Cl_2$ (150 mL) and then washed with 1 M HCl (2 x 50 mL), saturated aqueous $Na_2CO_3$ (50 mL), and brine (50 mL). It was then dried ($MgSO_4$), concentrated, and purified by column chromatography ($CH_2Cl_2$/EtOAc 2:1), which furnished 16-hydroxyhexadecanoic acid, morpholine amide (1.71 g) as a white solid that was tosylated without further purification: Under argon, pyridine (1.0 mL, 12 mmol) was added to a 0 ºC solution of the 16-hydroxyhexadecanoic acid, morpholine amide (1.5 g, 4.4 mmol) and tosyl chloride (1.2 g, 6.1 mmol) in chloroform (15 mL). After stirring for 4 h at 0 ºC and a further 20 h at room temperature, the reaction mixture was diluted with chloroform (50 mL) and washed successively with 1 M HCl (2 x 50 mL) and saturated aqueous $Na_2CO_3$ (30 mL). It was then dried ($MgSO_4$), concentrated, and purified by column chromatography ($CH_2Cl_2$ to $CH_2Cl_2$/EtOAc 1:1), which afforded the title compound (1.46 g, 67%) as a white solid (mp 55-56 ºC).

$^1$H NMR ($CDCl_3$, 400 MHz): δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 3.98 (t, *J* = 6.5 Hz, 2H), 3.65-3.57 (m, 6H), 3.45-3.41 (m, 2H), 2.42 (s, 3H), 2.28 (t, *J* = 7.9 Hz, 2H), 1.63-1.55 (m, 4H), 1.33-1.15 (m, 22H). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 172.1, 144.8, 133.4, 130.0, 128.1, 70.9, 67.2, 66.9, 46.2, 42.0, 33.3, 29.82, 29.80, 29.77, 29.69, 29.67, 29.63, 29.57, 29.1, 29.0, 25.50, 25.45, 21.8. IR (thin film, cm$^{-1}$): 2923, 2852, 1648, 1430, 1359, 1188, 1177, 1116, 814, 663. HRMS (ESI) Calcd for $C_{27}H_{45}NO_5S$ $(M+H)^+$: 496.3091. Found 496.3085.



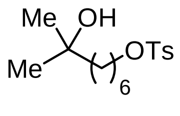
**1-(Tosyloxy)octan-7-one** was prepared from 2-methyl-2-(6-tosyloxyhexyl)-1,3-dioxolane: 4-Toluenesulfonic acid monohydrate (15 mg, 0.079 mmol) was added to a solution of 2-methyl-2-(6-tosyloxyhexyl)-1,3-dioxolane (1.31 g, 3.83 mmol) in acetone (10 mL). After stirring at room temperature for 3 h, the reaction was quenched with solid anhydrous $K_2CO_3$, and the solvent was removed. The residue was taken up in $Et_2O$ (100 mL), washed successively with water (20 mL) and brine (2 x 20 mL), and dried over $MgSO_4$. Removal of the solvent provided the title compound (1.12 g, 98%) as a colorless liquid that was used without further purification.

$^1$H NMR ($CDCl_3$, 400 MHz): δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 3.98 (t, *J* = 6.5 Hz, 2H), 2.43 (s, 3H), 2.37 (t, *J* = 7.4 Hz, 2H), 2.10 (s, 3H), 1.61 (quint, *J* = 6.5 Hz, 2H), 1.49 (quint, *J* = 7.4 Hz, 2H), 1.34-1.18 (m, 4H). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 209.1, 144.9, 133.2, 130.0, 128.0, 70.7, 45.6, 30.1, 28.8, 28.5, 25.3, 23.6, 21.8. IR (thin film, cm$^{-1}$): 2938, 2862, 1715, 1598, 1359, 1177, 1189, 1098, 944, 908, 817, 664, 555. HRMS (ESI) Calcd for $C_{15}H_{22}O_4SNa$ $(M+Na)^+$: 321.1131. Found 321.1131.

$NC(CH_2)_8–OTs$

**9-(Tosyloxy)nonanenitrile** was prepared from 9-hydroxynonanenitrile: Under argon, pyridine (2.45 mL, 30.4 mmol) was added to a 0 °C solution of 9-hydroxynonanenitrile (2.36 g, 15.2 mmol) and tosyl chloride (3.48 g, 18.2 mmol) in chloroform (30 mL). After 6 h, the reaction mixture was diluted with chloroform (50 mL) and washed successively with 1 M HCl (3 x 50 mL), saturated aqueous $Na_2CO_3$ (2 x 50 ml), and brine (50 mL). It was then dried ($MgSO_4$), concentrated, and purified by column chromatography (10% EtOAc to 25% EtOAc in hexanes), which afforded the title compound (2.88 g, 62%) as a colorless oil.

$^1$H NMR ($CDCl_3$, 300 MHz): δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 4.01 (t, *J* = 6.6 Hz, 2H), 2.45 (s, 3H), 2.32 (t, *J* = 7.1 Hz, 2H), 1.68-1.57 (m, 4H), 1.45-1.23 (m, 8H). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ 144.9, 133.3, 130.0, 128.1, 120.0, 70.7, 28.9, 28.8, 28.72, 28.66, 25.44, 25.40, 21.8, 17.3. IR (thin film, cm$^{-1}$): 2933, 2859, 2245, 1598, 1466, 1358, 1189, 1176, 1098, 939, 817, 664, 555. HRMS (ESI) Calcd for $C_{16}H_{23}NO_3SNa$ $(M+Na)^+$: 332.1291. Found 332.1284.



**2-Methyl-8-(tosyloxy)octan-2-ol** was prepared from 1-(tosyloxy)octan-7-one: MeMgBr (5.63 mmol; 1.79 mL of a 3.14 M solution in $Et_2O$) was added to a solution of 1-

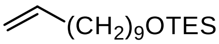
(tosyloxy)octan-7-one (1.40 g, 4.69 mmol) in $Et_2O$ (50 mL) at –78 ºC. After stirring for 1 h, the solution was warmed to room temperature and stirred for an additional 30 min. The reaction was quenched with 1M HCl (5 mL), and the resulting solution was washed successively with water (2 x 10 mL) and brine (10 mL), and then dried over $MgSO_4$. Removal of the solvent, followed by column chromatography (100% $CH_2Cl_2$ to 10% EtOAc in $CH_2Cl_2$), provided the title compound as a colorless liquid (1.41 g, 96%).

$^1$H NMR ($CDCl_3$, 400 MHz): δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 3.99 (t, *J* = 6.3 Hz, 2H), 2.43 (s, 3H), 1.62 (quint, *J* = 6.3 Hz, 2H), 1.42-1.20 (m, 9H), 1.17 (s, 6H). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 144.7, 133.1, 129.9, 127.9, 71.1, 70.8, 43.9, 29.7, 29.5, 29.0, 25.6, 24.4, 21.9. IR (thin film, cm$^{-1}$): 3553 (br), 3428 (br), 2967, 2935, 2861, 1713, 1599, 1467, 1359, 1177, 1098, 943, 816, 664. HRMS (ESI) Calcd for $C_{16}H_{26}O_4SNa$ $(M+Na)^+$: 337.1444. Found 337.1444.

$TsO{-}(CH_2)_{12}{-}OTs$

**1,12-Bis(tosyloxy)dodecane** [36247-34-4] was prepared according to a literature procedure.[8]

$^1$H NMR ($CDCl_3$, 300 MHz): δ 7.78 (d, *J* = 8.2 Hz, 4H), 7.34 (d, *J* = 8.3 Hz, 4H), 4.02 (t, *J* = 6.5 Hz, 4H), 2.46 (s, 6H), 1.64 (quint, *J* = 6.5 Hz, 4H), 1.33-1.19 (m, 16H). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ 144.7, 133.2, 129.9, 128.0, 70.9, 29.7, 29.6, 29.2, 29.1, 25.6, 22.0.



**11-(Triethylsiloxy)undec-1-ene** was prepared according to a procedure used to synthesize the *tert*-butyldimethylsiloxy analogue.[9]

$^1$H NMR ($C_6D_6$, 400 MHz): δ 5.84-5.76 (m, 1H), 5.07-4.97 (m, 2H), 3.60 (t, *J* = 6.4 Hz, 2H), 2.00 (q, *J* = 6.8 Hz, 2H), 1.58 (quint, *J* = 6.8 Hz, 2H), 1.41-1.18 (m, 12H), 1.04 (t, *J* = 7.9 Hz, 9H), 0.63 (q. *J* = 7.9 Hz, 6H). $^{13}$C NMR ($C_6D_6$, 100 MHz): δ 139.6, 114.9, 63.4, 34.6, 33.8, 30.4, 30.26, 30.24, 29.9, 29.7, 26.7, 7.5, 5.3.

## IV. Suzuki Cross-Couplings (Table 1)

**Preparation of (9-BBN)–$R^1$.** Under an inert atmosphere, the olefin (3.40 mmol) was added to a suspension of 9-BBN dimer (417 mg, 3.40 mmol) in ~18 mL of dioxane. The reaction mixture was stirred at room temperature for at least 3 h, and then dioxane was added to the resulting homogeneous solution to produce a total volume of 20 mL (0.17 M in (9-BBN)–$R^1$).

Each of the yields reported in Table 1 reflects the average of two runs, one following Procedure A and one following Procedure B.

**Cross-coupling Procedure A (without glove box).** In air, $Pd(OAc)_2$ (9.0 mg, 0.040 mmol) and NaOH (48 mg, 1.2 mmol) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). The alkyl tosylate (1.0 mmol), $Pt\mathit{Bu}_2Me$ (32 μL, 0.16 mmol), and the organoborane (1.2 mmol; 0.17 M solution in dioxane) were added in turn by syringe (if the alkyl tosylate is a solid, it was added along with the $Pd(OAc)_2$ and NaOH). The resulting reaction mixture (pale-brown to colorless) was stirred vigorously at 50 °C for the indicated amount of time, during which a fine white precipitate formed. The reaction mixture (thick / heterogeneous) was then diluted with $Et_2O$, filtered through silica gel with copious washings ($Et_2O$ or EtOAc), concentrated, and purified by column chromatography.

**Cross-coupling Procedure B (with a glove box).** In a glove box, $Pd(OAc)_2$ (9.0 mg, 0.040 mmol), NaOH (48 mg, 1.2 mmol), $Pt\mathit{Bu}_2Me$ (32 μL, 0.16 mmol), and the alkyl tosylate were placed in a screw-cap vial equipped with a stir bar. The organoborane solution was then added, and the resulting reaction mixture (pale-brown to colorless) was stirred vigorously at 50 °C for the indicated amount of time, during which a fine white precipitate formed. The reaction mixture (thick / heterogeneous) was then diluted with $Et_2O$, filtered through silica gel with copious washings ($Et_2O$ or EtOAc), concentrated, and purified by column chromatography.

**Eicosane [112-95-8] (Table 1, entry 1).** Procedure B: *n*-Dodecyl tosylate (340 mg, 1.00 mmol) and the organoborane (7.0 mL of a 0.17 M solution in dioxane; 1.2 mmol) prepared from hydroboration of 1-octene with 9-BBN. After 48 h at 50 ºC, workup followed by column chromatography (hexanes) afforded the title compound as a white, waxy solid (228 mg, 81%) that was identical to authentic material (Alfa-Aesar) by $^{1}$H NMR, $^{13}$C NMR, and GC.

**2-Methyl-2-(17-(triethylsiloxy)heptadecyl)-1,3-dioxolane (Table 1, entry 2).** Procedure B: 2-Methyl-2-(6-tosyloxyhexyl)-1,3-dioxolane (343 mg, 1.00 mmol) and the organoborane (7.0 mL of a 0.17 M solution in dioxane; 1.2 mmol) prepared by hydroboration of 11-(triethylsiloxy)undec-1-ene with 9-BBN. After 46 h at 50 ºC, workup and column chromatography (5% EtOAc in hexanes) yielded the title compound as a colorless liquid (311 mg, 68%).

$^{1}$H NMR ($C_6D_6$, 400 MHz): δ 3.60 (t, *J* = 6.4 Hz, 2H), 3.56 (s, 4H), 1.75-1.71 (m, 2H), 1.61-1.52 (m, 4H), 1.45-1.38 (m, 2H), 1.34 (s, 3H), 1.33-1.29 (m, 24H), 1.04 (t, *J* = 8.0 Hz, 9H), 0.63 (q, *J* = 8.0 Hz, 6H). $^{13}$C NMR ($C_6D_6$, 75 MHz): δ 110.6, 65.2, 63.5, 40.4, 34.0, 31.0, 30.78-30.75 (eight coincident resonances), 30.72, 30.70, 30.5, 27.0, 25.2, 24.7, 7.8, 5.6. IR (thin film, cm$^{-1}$): 2925, 2854, 2876, 1465, 1415, 1376, 1099, 744. HRMS (ESI) Calcd for $C_{27}H_{57}O_3Si$ $(M+H)^+$: 457.4071. Found 457.4075.

**8-Cyclopentyl-octan-1-ol [22565-50-0] (Table 1, entry 3).** Procedure B: 3-Cyclopentyl-1-(tosyloxy)propane (283 mg, 1.00 mmol) and the organoborane (7.0 mL of a 0.17 M solution in dioxane; 1.2 mmol) prepared by hydroboration of 5-benzyloxypent-1-ene with 9-BBN. After 72 h at 50 ºC, workup and column chromatography (1% EtOAc in hexanes) provided the crude coupled product as a colorless liquid. Treatment of this residue with 10% Pd / C (50 mg) in EtOH (25 ml) under $H_2$ (1 atm.) for 16 h, followed by column chromatography (4% EtOAc to 10% EtOAc in hexanes), furnished the title compound as a colorless liquid (125 mg, 63%).

$^1$H NMR (CDCl$_3$, 300 MHz): δ 3.58 (t, *J* = 6.7 Hz, 2H), 2.00 (s, 1H), 1.74-1.62 (m, 3H), 1.58-1.40 (m, 6H), 1.36-1.20 (m, 12H), 1.18-0.98 (m, 2H). $^{13}$C NMR (CDCl$_3$, 75 MHz): δ 63.1, 40.4, 36.4, 32.93, 32.90, 30.1, 29.8, 29.6, 29.0, 25.9, 25.4. IR (thin film, cm$^{-1}$): 3335 (br), 2925, 2855, 1454, 1057, 722. HRMS (EI) Calcd for $C_{13}H_{24}$ $(M-H_2O)^+$: 180.1878. Found 180.1880.

**Methyl 15-benzyloxypentadecanoate (Table 1, entry 4).** Procedure B: Methyl 10-(tosyloxy)decanoate (357 mg, 1.00 mmol) and the organoborane (7.0 mL of a 0.17 M solution in dioxane; 1.2 mmol) prepared by hydroboration of 5-benzyloxypent-1-ene with 9-BBN. After 48 h at 50 ºC, workup and column chromatography (4% EtOAc in hexanes) provided the title compound as a white solid (213 mg, 59%; mp 29-30 ºC).

$^1$H NMR (CDCl$_3$, 400 MHz): δ 7.35-7.33 (m, 4H), 7.30-7.25 (m, 1H), 4.50 (s, 2H), 3.66 (s, 3H), 3.46 (t, *J* = 6.6 Hz, 2H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.65-1.58 (m, 4H), 1.37-1.22 (m, 20H). $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 174.5, 138.9, 128.5, 127.8, 127.6, 73.0, 70.7, 51.6, 34.3, 30.0, 29.82 (two coincident resonances), 29.79 (two coincident resonances), 29.78, 29.68, 29.64, 29.4, 29.3, 26.4, 25.1. IR (thin film, cm$^{-1}$): 3020, 2926, 2860, 1734, 1607, 1495, 1452, 1106, 1050, 876, 825. HRMS (ESI) Calcd for $C_{23}H_{38}O_3Na$ $(M+Na)^+$: 385.2713. Found 385.2700.

**Tetracosanoic acid, morpholine amide (Table 1, entry 5).** Procedure A: 16-(Tosyloxy)hexadecanoic acid, morpholine amide (495 mg, 1.00 mmol) and the organoborane (7.0 mL of a 0.17 M solution in dioxane; 1.2 mmol) prepared by hydroboration of 1-octene with 9-BBN. After 48 h at 50 ºC, workup and column chromatography (25% EtOAc in hexanes) provided the coupled product as a white solid (339 mg, 78%; mp 67-68 ºC).

$^1$H NMR (CDCl$_3$, 400 MHz): δ 3.70-3.60 (m, 6H), 3.49-3.45 (m, 2H), 2.32 (t, *J* = 8.0 Hz, 2H), 1.68-1.58 (m, 2H), 1.39-1.18 (m, 40H), 0.89 (t, *J* = 6.6 Hz, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 172.1, 67.2, 66.9, 46.3, 42.1, 33.4, 32.1, 29.92 (nine coincident resonances), 29.90, 29.88, 29.84, 29.73, 29.70, 29.65, 29.58, 25.5, 22.9, 14.3. IR (thin film, cm$^{-1}$): 2917, 2849, 1651, 1472, 1111, 716. HRMS (ESI) Calcd for $C_{28}H_{55}NO_2$ $(M+H)^+$: 438.4306. Found 438.4293.

**19-(Triethylsiloxy)nonadecan-2-one (Table 1, entry 6).** Procedure A: 1-(Tosyloxy)octan-7-one (299 mg, 1.00 mmol) and the organoborane (7.0 mL of a 0.17 M solution in dioxane; 1.2 mmol) prepared by hydroboration of 11-(triethylsiloxy)undec-1-ene with 9-BBN. After 48 h at 50 °C, workup and column chromatography (3% EtOAc in hexanes) provided the title compound as a colorless liquid (219 mg, 53%).

$^1H$ NMR ($C_6D_6$, 300 MHz): δ 3.69 (t, *J* = 6.3 Hz, 2H), 2.04 (t, *J* = 7.4 Hz, 2H), 1.76 (s, 3H), 1.74-1.21 (m, 30H), 1.14 (t, *J* = 7.7 Hz, 9H), 0.73 (q, *J* = 7.7 Hz, 6H). $^{13}C$ NMR ($C_6D_6$, 75 MHz): δ 206.4, 63.5, 43.9, 34.0, 30.78 (three coincident resonances), 30.76 (three coincident resonances), 30.72, 30.71, 30.58, 30.54, 30.51, 30.2, 29.9, 27.0, 24.7, 7.8, 5.6. IR (thin film, $cm^{-1}$): 2926, 2854, 2876, 1721, 1465, 1414, 1359, 1237, 1100, 1016, 744, 727. HRMS (ESI) Calcd for $C_{25}H_{53}O_2Si$ $(M+H)^+$: 413.3809. Found 413.3810.

**4-(10-Cyanodecyl)cyclohexene (Table 1, entry 7).** Procedure A: 9-(Tosyloxy)nonanenitrile (311 mg, 1.00 mmol) and the organoborane (7.0 mL of a 0.17 M solution in dioxane; 1.2 mmol) derived from hydroboration of 4-vinylcyclohexene with 9-BBN. After 48 h at 50 °C, workup and column chromatography (2% EtOAc in hexanes) yielded the title compound as a colorless liquid (161 mg, 65%).

$^1H$ NMR ($CDCl_3$, 300 MHz): δ 5.67-5.64 (m, 2H), 2.35 (t, *J* = 6.9 Hz, 2H), 2.18-2.00 (m, 3H), 1.78-1.60 (m, 5H), 1.58-1.40 (m, 4H), 1.38-1.18 (m, 13H). $^{13}C$ NMR ($CDCl_3$, 75 MHz): δ 127.1, 126.8, 120.0, 37.0, 33.8, 32.3, 30.2, 29.9, 29.8, 29.6. 29.3, 29.1, 29.0, 27.2, 25.7, 25.6, 17.5. IR (thin film, $cm^{-1}$): 2926, 2855, 2245, 1677, 1464, 1390, 723. HRMS (ESI) Calcd for $C_{17}H_{29}NNa$ $(M+Na)^+$: 270.2192. Found 270.2196.

**2-Methyl-8-phenyloctan-2-ol (Table 1, entry 8).** Procedure B: 2-Methyl-8-(tosyloxy)octan-2-ol (314 mg, 1.00 mmol) and 9-phenyl-9-BBN (238 mg, 1.2 mmol in 7.0 mL of dioxane). After 48 h at 50 °C, workup and column chromatography ($CH_2Cl_2$) provided the coupled product as a pale-yellow liquid (133 mg, 60%).

$^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.33-7.28 (m, 2H), 7.23-7.20 (m, 3H), 2.64 (t, *J* = 7.6 Hz, 2H), 1.69-1.63 (m, 2H), 1.50-1.45 (m, 2H), 1.42-1.34 (m, 7H), 1.23 (s, 6H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 143.0, 128.6, 128.4, 125.8, 71.2, 44.1, 36.1, 31.7, 30.2, 29.5, 29.4, 24.5. IR (thin film, cm$^{-1}$): 3374 (br), 3027, 2968, 2931, 2856, 1604, 1496, 1453, 1376, 1177, 1149, 906, 748, 698. HRMS (CI, $NH_3$ + $CH_4$) Calcd for $C_{15}H_{28}NO$ $(M+NH_4)^+$: 238.2171. Found 238.2170.

**Octacosane [630-02-4] (Table 1 entry 9).** Procedure A: 1,12-Bis(tosyloxy)dodecane (256 mg, 0.500 mmol) and the organoborane (7.0 mL of a 0.17 M solution in dioxane; 1.2 mmol) prepared by hydroboration of 1-octene with 9-BBN. After 48 h at 50 ºC, workup and column chromatography (hexanes) provided the title compound as a white, waxy solid (141 mg, 71%) that was identical to authentic material (Alfa-Aesar) by $^1$H NMR, $^{13}$C NMR, and GC.

## V. Suzuki Cross-Coupling with [HP*t*Bu$_2$Me]BF$_4$ (eq 2)

**Preparation of [HP*t*Bu$_2$Me]BF$_4$:** Under an atmosphere of argon, HBF$_4$ (48 wt% aqueous solution; 2.0 mL, 15 mmol) was added to a solution of P*t*Bu$_2$Me (860 mg, 5.37 mmol) in CH$_2$Cl$_2$ (10 mL), and the resulting mixture was stirred vigorously for 5 min. The organic layer was then separated from the aqueous layer, dried over MgSO$_4$, and filtered. Removal of the solvent provided a white solid, which was dissolved in hot acetone (2 mL) and precipitated with *n*-pentane (20 mL). Filtration provided the title compound (926 mg, 70%) as a white powder (mp 275-279 ºC (dec.)).

$^1$H NMR (CD$_2$Cl$_2$, 300 MHz): δ 5.78 (dq, $^1J_{PH}$ = 471 Hz, $^3J_{HH}$ = 5.8 Hz, 1H), 1.85 (dd, $^2J_{PH}$ = 13.2 Hz, $^3J_{HH}$ = 5.8 Hz, 3H), 1.48 (d, $^3J_{PH}$ = 16.8 Hz, 18H). $^{13}$C NMR (CD$_2$Cl$_2$, 75 MHz): δ 32.1 (d, $^1J_{PC}$ = 38 Hz), 27.3 (d, $^2J_{PC}$ = 1.3 Hz), –1.7 (d, $^1J_{PC}$ = 47 Hz). $^{31}$P{$^1$H} NMR (CD$_2$Cl$_2$, 121 MHz): δ 40.0. IR (thin film, cm$^{-1}$): 2976, 2943, 1476, 1382, 1313, 1194, 1097, 1054, 942, 925, 815.

**Suzuki cross-coupling with [HP*t*Bu$_2$Me]BF$_4$ (eq 2):** In air, Pd(OAc)$_2$ (9.0 mg, 0.040 mmol), NaOH (48 mg, 1.2 mmol), [HP*t*Bu$_2$Me]BF$_4$ (40 mg, 0.16 mmol), and *n*dodecyl tosylate (340 mg, 1.00 mmol) were added to a vial equipped with a stir bar. The vial was closed with a septum cap, and then evacuated and filled with argon (three cycles). A solution of 9-*n*-octyl-9-BBN (1.2 mmol; 7.0 mL of a 0.17 M solution in dioxane) was added by syringe. The resulting reaction mixture was stirred vigorously at 50 ºC for 48 h, and then it was diluted with Et$_2$O, filtered through silica gel with copious washings (Et$_2$O), concentrated, and purified by column chromatography (hexanes), which provided eicosane (229 mg, 81%) as a white solid.

A second run furnished 233 mg (82%) of eicosane as a white solid.

## VI. Mechanistic Studies

**Preparation of *erythro*-3,3-dimethylbutan-1-ol-*1,2-$d_2$* [2390-47-4]:**[10] A hydroboration / oxidation protocol, reported for the preparation of a related compound, was followed:[11] Boron trifluoride etherate (11.3 mL, 89.1 mmol) was added over 1 h to a room-temperature suspension of $NaBD_4$ (2.74 g, 65.3 mmol) and (*E*)-3,3-dimethylbutene-*1*-$d_1$[12] (5.05 g, 59.4 mmol) in THF (40 mL). The resulting suspension was heated to 40 ºC and stirred for 3 h. The reaction mixture was then cooled in an ice bath, and water (28 mL) was added dropwise (**CAUTION:** vigorous evolution of hydrogen gas), followed by 3 M NaOH (23 mL), and then 30% hydrogen peroxide (23 mL; dropwise). The resulting reaction mixture heated to 50 ºC for 2 h. NaCl was then added to the reaction mixture until no more solid dissolved, and the organic layer was separated, washed with brine (3 x 50 mL), and dried over $MgSO_4$. The solvent was removed, and the product was purified by distillation (bp 140-145 ºC), which furnished the title compound (4.78 g, 77%) as a colorless liquid.

**Preparation of *erythro*-3,3-dimethylbutyl-*1,2-$d_2$* tosylate (1):** The procedure used to prepare the corresponding 4-bromophenylsulfonate ester was adapted:[13] A solution of *erythro*-3,3-dimethylbutan-1-ol-*1,2*-$d_2$ (1.00 g, 9.62 mmol) was dissolved in THF (20 mL) and cooled to –78 ºC. *n*-BuLi (10.6 mmol; 6.63 mL of a 1.60 M solution in hexane) was added dropwise, and the reaction mixture was stirred for 30 min. A solution of tosyl chloride (2.02 g, 10.6 mmol) in THF (5 mL) was added over 1 min. After stirring at –78 ºC for 2 h, the reaction was warmed to room temperature and stirred for an additional 3 h. Water (5 mL) and $Et_2O$ (100 mL) were then added, and the organic layer was washed successively with saturated $Na_2CO_3$ (10 mL) and brine (3 x 40 mL) before being dried over $MgSO_4$. Removal of the solvent provided the title compound (2.06 g, 83%) as a straw-colored liquid.

$^1H\{^2H\}$ NMR ($C_6D_6$, 500 MHz): δ 7.80 (d, $J$ = 8.4 Hz, 2H), 6.72 (d, $J$ = 8.4 Hz, 2H), 3.98

(d, $J$ = 8.2 Hz, 1H), 1.84 (s, 3H), 1.31 (d, $J$ = 8.2 Hz, 1H), 0.63 (s, 9H). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ 144.7, 133.3, 129.9, 127.9, 68.2 (t, $^1J_{CD}$ = 23 Hz), 41.6 (t, $^1J_{CD}$ = 19 Hz), 29.9, 29.7, 22.0. IR (thin film, cm-1): 2959, 2870, 1599, 1477, 1367, 1189, 1177, 1098, 944, 816, 661. HRMS (ESI) Calcd for $C_{13}H_{18}D_2SO_3Na$ $(M+Na)^+$: 281.1161. Found 281.1155.

**Preparation of *threo*-3,3-dimethylbutyl-*1,2-d*$_2$ tosylate:** A Mitsunobu reaction was employed:[14] Diethyl azodicarboxylate (4.18 g, 24.0 mmol) was added dropwise to a suspension of *erythro*-3,3-dimethylbutan-1-ol-*1,2-d*$_2$ (500 mg, 4.81 mmol), $Zn(OTs)_2$ (1.18 g, 2.89 mmol), and $PPh_3$ (6.29 g, 24.0 mmol) in dry benzene (100 mL) at room temperature. The resulting pale-yellow suspension was stirred at room temperature for 2.5 hours, then concentrated. Column chromatography (5% EtOAc in hexanes) provided the title compound (704 mg, 57%) as a pale-pink liquid.

$^1H\{^2H\}$ NMR ($C_6D_6$, 500 MHz): δ 7.80 (d, $J$ = 8.4 Hz, 2H), 6.72 (d, $J$ = 8.4 Hz, 2H), 3.98 (d, $J$ = 6.3 Hz, 1H), 1.81 (s, 3H), 1.31 (d, $J$ = 6.3 Hz, 1H), 0.63 (s, 9H). $^{13}$C NMR ($C_6D_6$, 75 MHz): δ 144.5, 134.9, 130.2, 128.5, 68.2 (t, $^1J_{CD}$ = 23 Hz), 42.1 (t, $^1J_{CD}$ = 19 Hz), 29.95, 29.85, 21.7. IR (thin film, cm-1): 2959, 2870, 1599, 1477, 1367, 1189, 1177, 1098, 949, 816, 662. HRMS (ESI) Calcd for $C_{13}H_{18}D_2SO_3Na$ $(M+Na)^+$: 281.1161. Found 281.1161.

**Preparation of Pd(P*t*Bu$_2$Me)$_2$:** The procedure of Yoshida and Otsuka,[15] which has been used to prepare bis(phosphine)palladium(0) complexes with other bulky trialkylphosphines, was employed: P*t*Bu$_2$Me (570 mg, 3.54 mmol) was added to a stirred solution of (π-allyl)PdCp[16] (340 mg, 1.60 mmol) in toluene (15 mL) in a Schlenk tube under nitrogen. The vessel was closed and heated to 75 ºC for 3 h. After cooling to room temperature, the solvent was removed under reduced pressure, and the dark residue was dried under high vacuum for 1 h. Attempts to triturate or recystallize the resulting solid were unsuccessful due to its high solubility in a wide range of organic solvents, including MeOH. Because the palladium complex was pure by $^1$H, $^{13}$C, and $^{31}$P NMR spectroscopy, it was used without additional purification.

$^1$H NMR ($C_6D_6$, 300 MHz): δ 1.28 (br s, 36H), 1.07 (s, 6H). $^{13}$C NMR ($C_6D_6$, 75 MHz):

δ 33.4, 30.6, 7.7. $^{31}$P NMR ($C_6D_6$, 121 MHz): δ 41.0.

**Suzuki cross-coupling with 1:2 Pd(P*t*Bu$_2$Me)$_2$/P*t*Bu$_2$Me as the catalyst:** Pd(P*t*Bu$_2$Me)$_2$ (0.040 mmol) was prepared as described above from (π-allyl)PdCp (8.4 mg, 0.040 mmol) and P*t*Bu$_2$Me (16 μL, 0.080 mmol) in toluene (1 mL). The resulting Pd(P*t*Bu$_2$Me)$_2$ was combined with NaOH (48 mg, 1.2 mmol), *n*-dodecyl tosylate (340 mg, 1.00 mmol), P*t*Bu$_2$Me (16 μL, 0.080 mmol), and *9-n*-octyl-9-BBN (1.2 mmol; 7.0 mL of a 0.17 M solution in dioxane) under an atmosphere of nitrogen. The vessel was closed, and the mixture was stirred at 50 °C for 48 h. At the conclusion of the reaction, the mixture (thick / heterogeneous) was diluted with $Et_2O$, filtered through silica gel with copious washings ($Et_2O$), concentrated, and then purified by column chromatography (hexanes), which furnished eicosane (236 mg, 84%) as a white solid.

**Control reaction: 3,3-dimethylbutyl tosylate with P*t*Bu$_2$Me:** A solution of 3,3-dimethylbutyl tosylate ([68880-56-8];[17] 204 mg, 0.800 mmol) and P*t*Bu$_2$Me (171 mg, 1.05 mmol) in dioxane-$d_8$ was sealed in a Schlenk tube under nitrogen and heated to 70 °C for 47 hours. $^1$H NMR spectroscopic analysis of the reaction mixture revealed that no elimination to 3,3-dimethyl-1-butene had occurred.

**Reaction of *erythro*-3,3-dimethylbutyl-*1,2-d$_2$* tosylate (1) with 1:2 Pd(P*t*Bu$_2$Me)$_2$ / P*t*Bu$_2$Me:** Pd(P*t*Bu$_2$Me)$_2$ (0.48 mmol) was prepared as described above from (π-allyl)PdCp (102 mg, 0.480 mmol) and P*t*Bu$_2$Me (171 mg, 1.05 mmol) in toluene (5 mL). The complex was dissolved in degassed dioxane-$d_8$ (1 mL) and combined with P*t*Bu$_2$Me (156 mg, 0.960 mmol) and *erythro*-3,3-dimethylbutyl-*1,2-d$_2$* tosylate (**1**; 207 mg, 0.800 mmol). The vessel was closed under an atmosphere of nitrogen and heated to 70 °C for 47 hours. At the conclusion of the reaction, the bulk of the liquid was transferred via trap-to-trap distillation and analyzed by $^1$H NMR spectroscopy. Inspection of the vinylic region revealed the presence of (*E*)-3,3-dimethyl-1-butene-*1,2-d$_2$* [84784-40-7] and (*Z*)-3,3-dimethyl-1-butene-*1-d* [6833-43-8] in a 3:1 ratio.

Vinylic $^1$H NMR signal (500 MHz, dioxane-$d_8$) for (*E*)-3,3-dimethyl-1-butene-*1,2-d$_2$*:

δ 4.89 (t, $^3J_{\mathrm{HD}}$ = 2.6 Hz). Vinylic $^1$H NMR signals (500 MHz, dioxane-$d_8$) for (*Z*)-3,3-dimethyl-1-butene-*1*-*d*: δ 5.83 (dt, $^3J_{\mathrm{HH}}$ = 10.7 Hz, $^3J_{\mathrm{HD}}$ = 2.7 Hz), 4.80 (d, $^3J_{\mathrm{HH}}$ = 10.7 Hz).

The palladium-containing residue was washed with pentane under nitrogen to afford XPd(P*t*Bu$_2$Me)$_2$OTs (X = H, D; 236 mg, 82%) as a light-brown solid.

$^1$H NMR ($C_6D_6$, 500 MHz): δ 8.24 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 2.00 (s, 3H), 1.54 (apparent t, *J* = 2.8 Hz, 6H), 1.09 (apparent t, *J* = 6.7 Hz, 36H), –18.04 (t, $^2J_{\mathrm{PH}}$ = 2.2 Hz, 1H). $^{13}$C NMR ($C_6D_6$, 125 MHz): δ 145.4, 139.3, 129.0, 127.4, 33.4 (t, *J* = 9.8 Hz), 29.5 (t, *J* = 3.5 Hz), 21.5, 4.6 (t, *J* = 9.2 Hz). $^{31}$P NMR ($C_6D_6$, 121 MHz): δ 55.3. $^2$H NMR ($C_6D_6$, 76 MHz): δ –18.01.

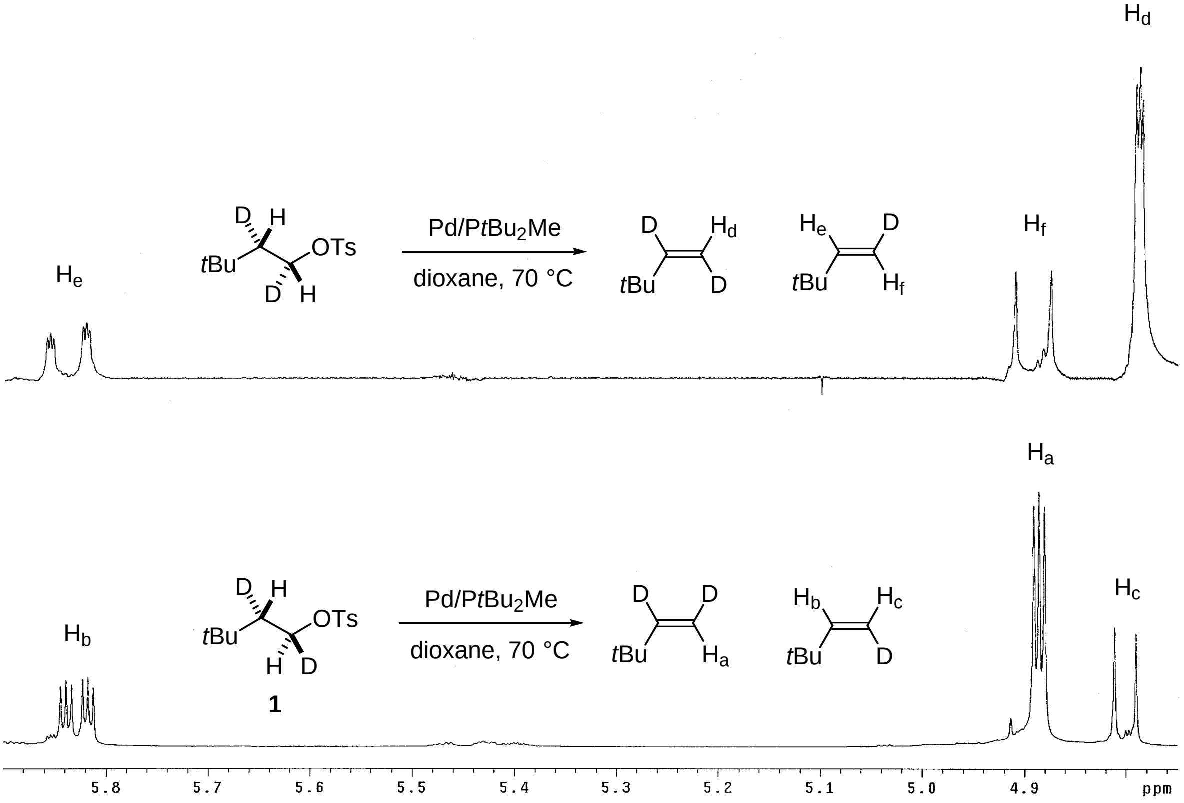


**Figure A.** $^1$H NMR spectra of the products from the reaction of the threo (top) and the erythro (bottom) tosylates with 1:2 Pd(P*t*Bu$_2$Me)$_2$ / P*t*Bu$_2$Me.

**Reaction of *threo*-3,3-dimethylbutyl-*1,2-d*$_2$ tosylate with 1:2 Pd(P*t*Bu$_2$Me)$_2$/P*t*Bu$_2$Me:** The *threo* diastereomer was treated in the manner described above for the *erythro* isomer to give a 3:1 mixture of (*Z*)-3,3-dimethyl-1-butene-*1,2-d*$_2$ [102369-35-7] and (*E*)-3,3-dimethyl-1-butene-1-*d* [57002-05-8].

Vinylic $^1$H NMR signal (500 MHz, dioxane-$d_8$) for (*Z*)-3,3-dimethyl-1-butene-*1,2-d*$_2$: δ 4.80 (t, $^3J_{HD}$ = 1.4 Hz). Vinylic $^1$H NMR signals (500 MHz, dioxane-$d_8$) for (*E*)-3,3-dimethyl-1-butene-*1-d*: δ 5.84 (dt, $^3J_{HH}$ = 17.5 Hz, $^3J_{HD}$ = 1.4 Hz), 4.90 (d, $^3J_{HH}$ = 17.5 Hz).

**Suzuki cross-coupling of 9-phenyl-9-BBN with *erythro*-3,3-dimethylbutyl-*1,2-d*$_2$ tosylate (1):** In a glove box, a vial was charged with Pd(OAc)$_2$ (22.4 mg, 0.100 mmol), NaOH (48 mg, 1.2 mmol), *erythro*-3,3-dimethylbutyl-*1,2-d*$_2$ tosylate (**1**; 230 mg, 1.00 mmol), P*t*Bu$_2$Me (64 mg, 0.40 mmol), and a solution of 9-phenyl-9-BBN (238 mg, 1.20 mmol in 7.0 mL of dioxane). The vial was closed under nitrogen and heated to 70 ºC for 109 h. The reaction mixture was diluted with pentane (10 mL) and purified by column chromatography (pentane), which furnished 3,3-dimethyl-1-phenylbutane-*1,2-d*$_2$[18] as an ~6:1 mixture of *threo:erythro* diastereomers (colorless liquid, 88 mg, 54%).

**Suzuki cross-coupling of 9-phenyl-9-BBN with *threo*-3,3-dimethylbutyl-*1,2-d*$_2$ tosylate:** The *threo* diastereomer was coupled with 9-phenyl-9-BBN as described above for the *erythro* isomer to give an ~6:1 *erythro*:*threo* mixture of 3,3-dimethyl-1-phenylbutane-*1,2-d*$_2$ (75 mg, 46%) as a colorless liquid.

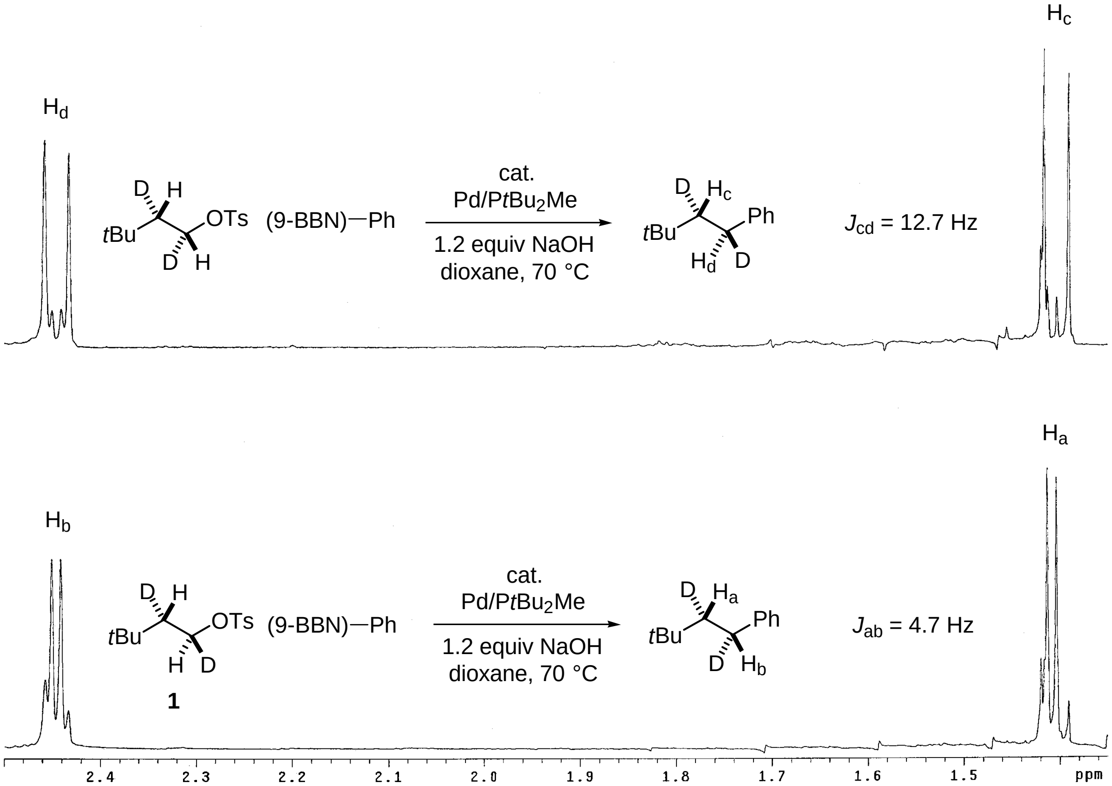


**Figure B.** $^1H\{^2H\}$ NMR spectra of the products from Suzuki cross-coupling of the threo (top) and the erythro (bottom) tosylates.

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