Supporting Information

Cobalt-Catalyzed Stereoretentive Hydrogen Isotope Exchange of C(sp^3)–H Bonds

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I. General Considerations.

All air- and moisture-sensitive manipulations were carried out using vacuum line, Schlenk and cannula techniques or in an MBraun inert atmosphere (nitrogen) dry box unless otherwise noted. All glassware was stored in a pre-heated oven prior to use. The solvents used for air- and moisture-sensitive manipulations were dried and deoxygenated using literature procedures.[1] Cyclopentylmethyl ether (CPME, Acros Organics) was dried and deoxygenated with sodium-benzophenone ketyl, distilled under reduced pressure, and stored over 4 Å molecular sieves prior to use. Heptane (Sure/Seal^{TM}, anhydrous, Sigma Aldrich) and dodecane (Sure/Seal^{TM}, anhydrous, Sigma Aldrich) were brought into the glovebox and used without further purification. Benzene-d_6 (Cambridge Isotope Laboratories) was dried over sodium metal, distilled under reduced pressure, and stored over 4 Å molecular sieves prior to use. Chloroform-*d* (Cambridge Isotope Laboratories) was used without further purification. Solid substrates or non-volatile oils were dried under reduced pressure prior to use. Volatile liquid substrates were dried over CaH_2 or $LiAlH_4$ and distilled under reduced pressure prior to use.

The following cobalt complexes were prepared according to (scaled) literature procedures: (^{Mes}PDI)CoMe,[2] (*R*)- and (*S*)-(^{iPr,NMeCy}PDI)CoMe,[3,4] (^{iPr}DI)$CoCl_2$,[5] [(^{iPr}DI)CoCl]$_2$,[6] (^{iPr}DI)Co(η^3-C_3H_5),[6] (^{Cy}ADI)Co(CH_2SiMe_3)$_2$.[7] See substrate preparation and Table S1 for structures corresponding to ligand and catalyst abbreviations. The following substrates were prepared according to (scaled) literature procedures: 3-(4'-methoxylphenyl)-1*H*-indene,[4] 4-methyl-1,2-dihydronaphthalene,[4] 2-phenyl-3-methyl-1-butene,[3] *m*-tolylboronic acid pinacol ester,[8] 4-methylbenzylboronic acid pinacol ester,[9]

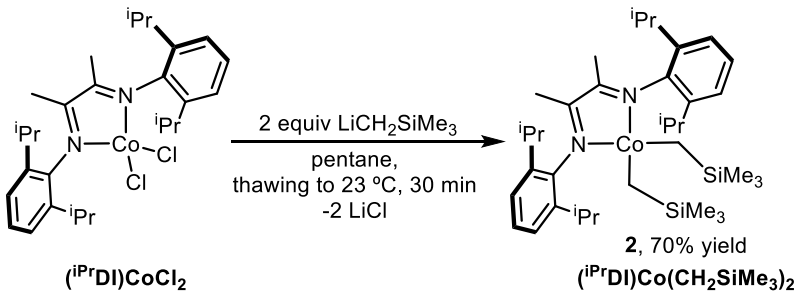
benzylboronic acid pinacol ester,[7] (3-phenylpropyl)boronic acid pinacol ester,[2] diisopropyl(3-phenylpropyl)amine,[10] (*rac*) 3-Phenylbutan-1-ol *tert*-butyldimethylsilyl ether,[7] (*rac*)-2-phenyl-3-methylbutane,[3] (*rac*) 1-indanylboronic acid pinacol ester.[11] The ^{1}H and ^{13}C NMR data of the deuterium labeled substrates reported herein are consistent with the previously reported data in the references cited for substrate preparation.

Deuterium incorporation was determined by analysis of quantitative ^{1}H and ^{13}C spectra of crude reaction mixtures following labeling procedures (see section V: General Procedures for Hydrogen Isotope Exchange for details). ^{1}H NMR spectra were recorded on either Bruker ADVANCE 300 or 500 spectrophotometers operating at 300.13 MHz, and 500.46 MHz, respectively. ^{13}C NMR spectra (proton decoupled; $\{^{1}H\}$) were recorded on either Bruker ADVANCE 300 or 500 spectrometer operating at 75.48 MHz and 125.85 MHz, respectively. The NMR spectra of all deuterated substrates were taken using chloroform-*d* as the solvent. Carbons that are directly attached to boron atoms were not observed due to quadrupolar relaxation.[12] The compositions of crude reaction mixtures and the positions and degrees of deuterium incorporation were determined by integration of characteristic peaks in the ^{1}H NMR or the quantitative ^{13}C NMR spectra. All ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to $SiMe_4$ using the ^{1}H (chloroform-*d*: 7.26 ppm; benzene-d_6: 7.16 ppm) and ^{13}C (chloroform-*d*: 77.16 ppm; benzene-d_6: 128.06 ppm) chemical shifts of the solvent as a standard. ^{1}H NMR data are reported as follows: unlabeled proton chemical shift (multiplicity, [coupling], integration, assignment); labeled proton chemical shift (multiplicity, % labeled, [coupling], integration, assignment). Quantitative ^{13}C NMR data are reported as follows: unlabeled

carbon chemical shift (multiplicity, integration, [coupling], assignment, [2° isotopic shift: degree of shift (Hz), integration, % of label on adjacent C]); labeled carbon chemical shift (multiplicity, integration, % labeled, [coupling], assignment, [2° isotopic shift: degree of shift (Hz), integration, % of label on adjacent C]). Multiplicities abbreviated as follows: s = singlet; d = doublet; t = triplet; q = quartet; br = broad, m = multiplet, app = apparent, obsc = obscured).

Chiral gas chromatography was performed on a Shimadzu GC-2010 gas chromatogram using a Supelco 30 m x 0.25 mm BETA DEX 120 capillary column as noted for each product. Enantiospecificity (es) of the HIE reactions reported herein is defined as: es = (% ee of starting material) / (% ee of product) * 100.

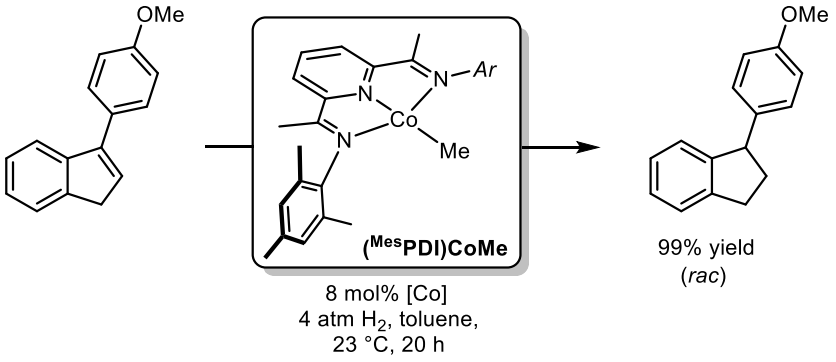
II. Preparation of Cobalt Complexes.

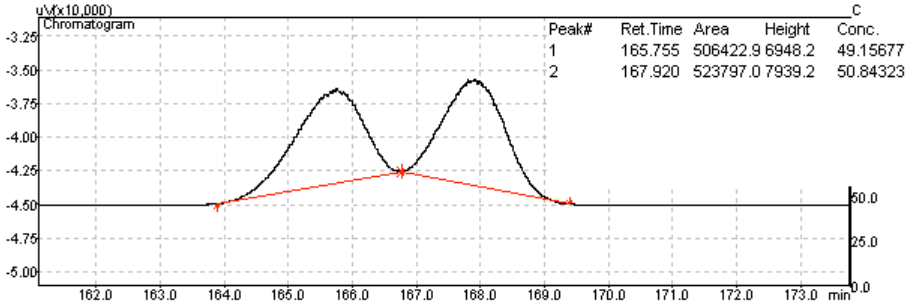


Modified preparation of (^{iPr}DI)Co(CH_2SiMe_3)$_2$ (2). In the glovebox, a 100 mL round bottom flask was charged with 1.013 g (1.90 mmol) of **(^{iPr}DI)CoCl$_2$**, 35 mL of pentane, and a magnetic stir bar. The resulting green solid suspension was chilled in a liquid N_2-cooled cold well (10 minutes). In a separate 20 mL scintillation vial, 0.357 g (3.79 mmol) of solid trimethylsilylmethyllithium was dissolved in approximately 5 mL of pentane and also chilled in the cold well (10 minutes). Both vessels were removed from the cold well and, while stirring the suspension, the $LiCH_2SiMe_3$ solution was added dropwise,

resulting in a color change to violet. The solution was allowed to warm to 23 °C and stirred for 30 minutes, then filtered through celite and concentrated in vacuo. Recrystallization of the resulting violet solid from concentrated pentane solution at -35 °C yielded 0.848 g (70%) of **2**. ^{1}H NMR and other analytical data agree with previously reported data.[7]

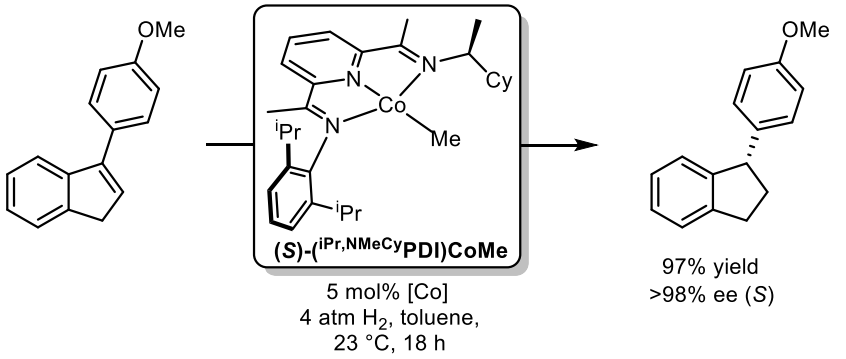
III. Preparation of Substrates.

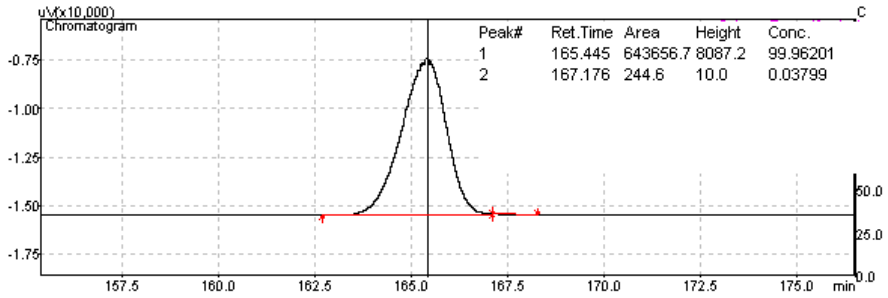




Preparation of (*rac*) 1-(4′-methoxyphenyl)indan. In a nitrogen-filled glovebox, a sealable thick-walled glass vessel was charged with 0.045 g (0.095 mmol, 8 mol%) of **(MesPDI)CoMe**, 0.254 g (1.14 mmol) of 3-(4'-methoxylphenyl)-1*H*-indene, and 2.2 mL of toluene. The vessel was sealed, brought out of the glovebox, and attached to a high-vacuum line. The entire vessel (including reaction solution) was frozen by submersion in liquid nitrogen (77 K). Following evacuation of the N_2 atmosphere in the headspace, 1 atm of H_2 gas was admitted into the vessel. The vessel was then sealed and warmed to

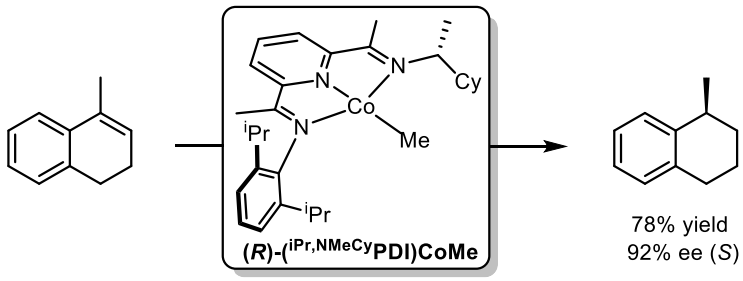
room temperature (at which point the internal pressure was ~4 atm at ~298 K). The reaction mixture was stirred at 23 °C for 20 hours. The vessel was then vented and diluted with ~15 mL hexanes. The reaction mixture was concentrated in vacuo, then redissolved in ~5 mL of hexanes and passed through two consecutive plugs of silica (in Pasteur pipettes), eluting with hexane. Following solvent evaporation, 0.253 g (99%) of (*rac*) 1-(4′-methoxyphenyl)indan was isolated. *syn*- and *anti*-to-*Ar* proton resonances assigned in analogy to the previously assigned (by 2D NMR spectroscopy) resonances in 1-phenylindan.[4] ^{1}H NMR (500 MHz, chloroform-*d*, 23 °C) δ 7.30 (d, $^3J_{HH}$ = 7.3 Hz, 1H, 8-indanyl C*H*), 7.20 (app t, $^3J_{HH}$ = 7.1 Hz, 1H, 7-indanyl C*H*), 7.17-7.10 (m, 3H, 6-indanyl C*H* and 2 x *Ar* C*H*), 6.98 (d, $^3J_{HH}$ = 7.4 Hz, 1H, 5-indanyl C*H*), 6.90-6.84 (app d, $^3J_{HH}$ = 8.1 Hz, 2H, 2 x *Ar* C*H*), 4.31 (t, $^3J_{HH}$ = 8.3 Hz, 1H, 1-indanyl benzylic C*H*), 3.80 (s, 3H, OCH_3), 3.03 (m, 1H, *syn*-to-*Ar* 3-indanyl benzylic C*H*), 2.95 (m, 1H, *anti*-to-*Ar* 3-indanyl benzylic C*H*), 2.64-2.46 (m, 1H, *anti*-to-*Ar* 2-indanyl homobenzylic C*H*), 2.03 (m, 1H, *syn*-to-*Ar* 2-indanyl homobenzylic C*H*) ppm. ^{1}H NMR data were consistent with previously reported data.[4] The product was analyzed by chiral GC according to the reported[4] isothermal method to verify racemate: hold at 160 ºC for 180 minutes; ramp 20 ºC per minute, hold at 200 ºC for 6 minutes.

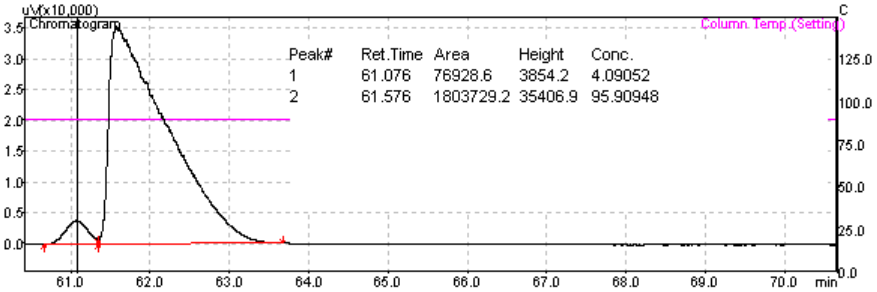




Preparation of (*S*) 1-(4′-methoxyphenyl)indan. Prepared using a modified and scaled version of the published asymmetric hydrogenation procedure.[4] In a nitrogen-filled glovebox, a sealable thick-walled glass vessel was charged with 0.051 g (0.10 mmol, 5 mol%) of **(*S*)-(^iPr,NMeCy^PDI)CoMe**, 0.445 g (2.00 mmol) of 3-(4'-methoxylphenyl)-1*H*-indene, and 8.0 mL of toluene. The vessel was sealed, brought out of the glovebox, and attached to a high-vacuum line. The entire vessel (including reaction solution) was frozen by submersion in liquid nitrogen (77 K). Following evacuation of the N_2 atmosphere in the headspace, 1 atm of H_2 gas was admitted into the vessel. The vessel was then sealed and warmed to room temperature (at which point the internal pressure was ~4 atm at ~298 K). The reaction mixture was stirred at 23 °C for 18 hours. The vessel was then vented and diluted with ~15 mL hexanes. The reaction mixture was concentrated in vacuo, then redissolved in ~5 mL of hexanes and passed through two consecutive plugs of silica (in Pasteur pipettes), eluting with hexane. Following solvent evaporation, 0.433 g (97%) of (*S*) 1-(4′-methoxyphenyl)indan was isolated. ^{1}H NMR

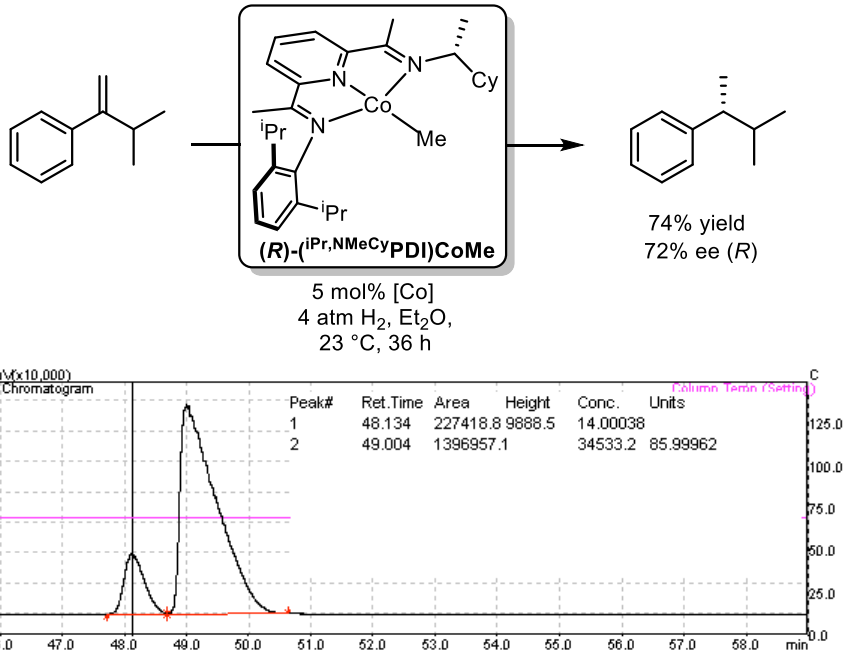
data were identical to those reported for the (*rac*) arylindan above.[4] Chiral separation and enantiomer assignment was achieved using chiral GC according to the reported[4] isothermal method: hold at 160 ºC for 180 minutes; ramp 20 ºC per minute, hold at 200 ºC for 6 minutes. Product ee: >98% (*S*).





Preparation of (*S*)-1-methyltetralin. Prepared using a modified and scaled version of the published asymmetric hydrogenation procedure[4] with the opposite enantiomer catalyst.[3] In a nitrogen-filled glovebox, a sealable thick-walled glass vessel was charged with 0.051 g (0.10 mmol, 5 mol%) of **(*R*)-(iPr,NMeCyPDI)CoMe**, 0.289 g (2.00 mmol) of 4-methyl-1,2-dihydronaphthalene, and 8.0 mL of diethyl ether. The vessel was sealed, brought out of the glovebox, and attached to a high-vacuum line. The entire vessel (including reaction solution) was frozen by submersion in liquid nitrogen (77 K). Following evacuation of the N_2 atmosphere in the headspace, 1 atm of H_2 gas was admitted into the vessel. The vessel was then sealed and warmed to room temperature (at which point the internal pressure was ~4 atm at ~298 K). The reaction mixture was

stirred at 23 °C for 36 hours. The entire vessel (including reaction solution) was again frozen by submersion in liquid nitrogen, reattached to the high-vacuum line, and the H_2 atmosphere was removed by evacuating the headspace. The vessel was again sealed, thawed, and then brought back into the glovebox. The reaction mixture was concentrated in vacuo, then the resulting crude residue was dissolved in pentane (~5 mL) and passed through a plug of silica (in a Pasteur pipette), eluting with pentane. Following solvent evaporation, 0.228 g (78%) of (*S*)-1-methyltetralin was isolated. ^{1}H NMR (500 MHz, chloroform-*d*, 23 °C) δ 7.27-7.21 (m, 1H, 9-C*H*), 7.21-7.06 (m, 3H, 6-8 tetralin positions C*H*), 3.01-2.88 (m, 1H, 1-tetralin benzylic C*H*), 2.87-2.70 (m, overlapping diastereotopic 4-tetralin benzylic CH_2), 2.02-1.83 (m, 2H, two of homobenzylic methylene protons), 1.82-1.70 (m, 1H, one of homobenzylic methylene protons), 1.63-1.52 (m, 1H, one of homobenzylic methylene protons), 1.33 (d, $^3J_{HH}$ = 7.0 Hz, 3H, chiral CHCH_3) ppm. ^{1}H NMR data were consistent with previously reported data.[4] Chiral separation and enantiomer assignment was achieved using chiral GC according to the reported[4] isothermal method: hold at 90 ºC for 75 minutes; ramp 20 ºC per minute, hold at 200 ºC for 6 minutes. Product ee: 92% (*S*).

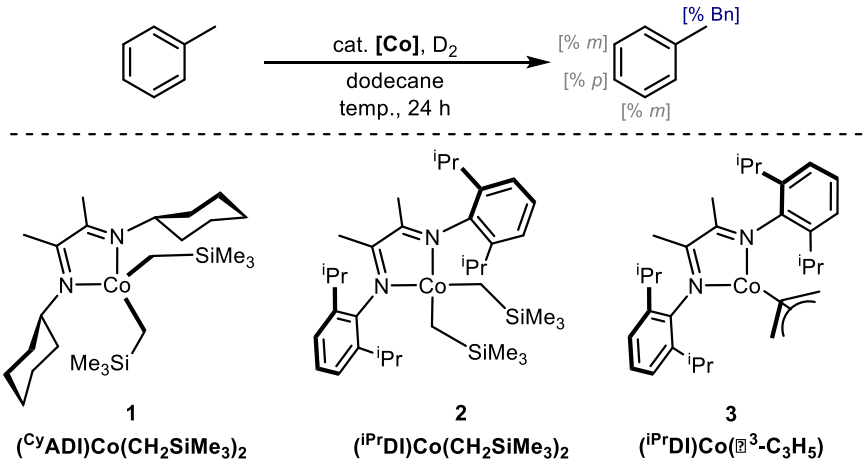


Preparation of (*R*)-2-phenyl-3-methylbutane. Prepared using a modified and scaled version of the published asymmetric hydrogenation procedure.[3] In a nitrogen-filled glovebox, a sealable thick-walled glass vessel was charged with 0.055 g (0.10 mmol, 5 mol%) of **(*R*)-(iPr,NMeCyPDI)CoMe**, 0.303 g (2.07 mmol) of 2-phenyl-3-methyl-1-butene, and 8.0 mL of diethyl ether. The vessel was sealed, brought out of the glovebox, and attached to a high-vacuum line. The entire vessel (including reaction solution) was frozen by submersion in liquid nitrogen (77 K). Following evacuation of the N_2 atmosphere in the headspace, 1 atm of H_2 gas was admitted into the vessel. The vessel was then sealed and warmed to room temperature (at which point the internal pressure was ~4 atm at ~298 K). The reaction mixture was stirred at 23 °C for 36 hours. The entire vessel (including reaction solution) was again frozen by submersion in liquid nitrogen, reattached to the high-vacuum line, and the H_2 atmosphere was removed by evacuating the headspace. The vessel was again sealed, thawed, and then brought back into the glovebox. The reaction mixture was concentrated in vacuo, then the

resulting crude residue was dissolved in pentane (~5 mL) and passed through a plug of silica (in a Pasteur pipette), eluting with pentane. Following solvent evaporation, 0.227 g (74%) of (*R*)-2-phenyl-3-methylbutane was isolated. ^{1}H NMR (500 MHz, chloroform-*d*, 23 °C) δ 7.28 (app t, $^{3}J_{HH}$ = 7.6 Hz, 2H, *m*-C*H*), 7.21-7.13 (m, 3H, *o*- and *p*-C*H*), 2.43 (app pentet, $^{3}J_{HH}$ = 7.0 Hz, benzylic C*H*), 1.77 (septet, $^{3}J_{HH}$ = 6.8 Hz, 1H, homobenzylic C*H*), 1.25 (d, $^{3}J_{HH}$ = 7.0 Hz, 3H, homobenzylic CH_3), 0.93 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, one of diastereotopic CH_3), 0.75 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, one of diastereotopic CH_3) ppm. ^{1}H NMR data were consistent with previously reported data.[3,4] Chiral separation and enantiomer assignment was achieved using chiral GC according to the reported[4] isothermal method: hold at 70 ºC for 60 minutes; ramp 20 ºC per minute, hold at 200 ºC for 6 minutes. Starting material ee: 72% (*R*).

IV. Optimization Data for Toluene Hydrogen Isotope Exchange.

Table S1. Detailed screening data for α-diimine cobalt complexes for hydrogen isotope exchange of toluene.



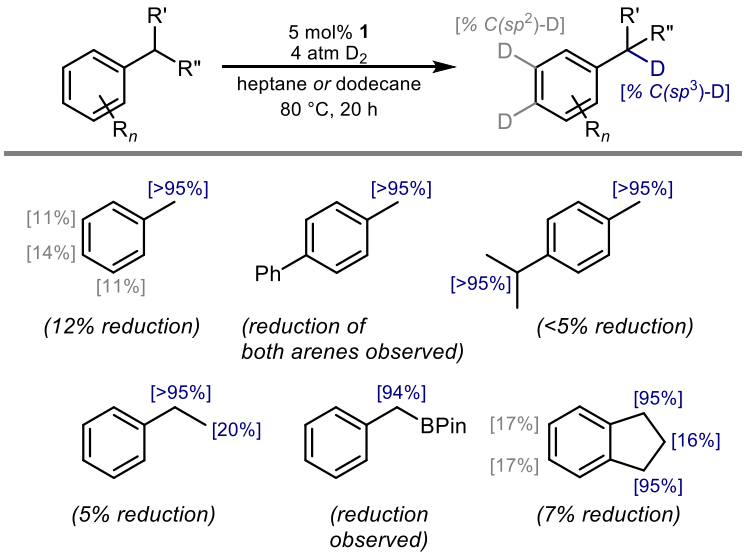
[Co]	% loading	Temp. (°C)	atm D_2	% Bn	% *m*	% *p*	% reduced arene
1	5	80	4	>95	11	14	12
2	5	80	4	>95	35	37	20
3	5	80	4	5	0	0	0
3[a]	5	80	4	6	0	0	0
2	5	80	1	92	52	60	20
2	5	50	1	70	<5	<5	<5
1	5	50	1	0	0	0	0
2	10	50	1	>95	11	15	8

[a]Repeat experiment under identical conditions to verify low catalyst activity using **3**.

Procedure for Optimization of Hydrogen Isotope Exchange Using Different α-Diimine Cobalt Precursors at Different Conditions. In a nitrogen-filled glovebox, an oven-dried, sealable thick-walled glass vessel was charged with a magnetic stir bar, the desired amount of cobalt precatalyst (5 or 10 mol%), 0.55 mmol of toluene, and 0.55 mL of dodecane. The vessel was sealed, brought out of the glovebox, and attached to a high-vacuum line. The reaction solution was frozen by submersion of the vessel containing the solution in liquid nitrogen (77 K). For 1 atm D_2 gas, only the bottom

portion of the vessel containing the solution was submerged (upon thawing sealed vessel, internal pressure ~1 atm D_2). For 4 atm D_2 gas, the whole vessel was submerged (upon thawing of sealed vessel 298K, reaches ~4 atm). Following evacuation of the N_2 atmosphere in the headspace, 1 atm of D_2 gas was admitted into the vessel. The vessel was then sealed, and the reaction mixture was thawed and stirred in a silicone oil bath at the desired temperature (50 or 80 °C) for 24 hours, during which time the solution color changed from purple to red. The vessel was removed from the oil bath, cooled to room temperature and reattached to a high-vacuum line. The reaction mixture was again frozen and the D_2 atmosphere was evacuated. The volatiles of the reaction mixture were then collected by vacuum distillation into a separate flask, dissolved in chloroform-*d*, and analyzed by ^{1}H and ^{13}C NMR spectroscopy to determine the location and extent of deuterium incorporation. For a representative example of the analysis of these data, see section VI, labeled product **4**.

Scheme S1. Hydrogen isotope exchange of a representative set of alkylarenes using **1** as a precatalyst.



Procedure for Hydrogen Isotope Exchange Using Precatalyst 1 at 4 atm D_2 and 80 °C. In a nitrogen-filled glovebox, an oven-dried, sealable thick-walled glass vessel was charged with a magnetic stir bar, 0.013 g (0.028 mmol, 5 mol%) of **1**, 0.55 mmol of the desired alkylarene substrate, and 0.55 mL of dodecane (volatile substrates, b.p. <180 °C) or heptane (non-volatile substrates, b.p. >180 °C). The vessel was sealed, brought out of the glovebox, and attached to a high-vacuum line. The entire vessel (including reaction solution) was frozen by submersion in liquid nitrogen (77 K). Following evacuation of the N_2 atmosphere in the headspace, 1 atm of D_2 gas was admitted into the vessel. The vessel was then sealed and warmed to room temperature (at which point the internal pressure was ~4 atm at ~298 K). The reaction mixture was stirred in an 80 ± 2 °C silicone oil bath for 20 hours by submerging only the portion of the vessel containing the solution in oil. The vessel was removed from the oil bath, cooled to room temperature. For reactions in dodecane (volatile substrates), the vessel was reattached to a high-vacuum line, the reaction mixture was again frozen, and the D_2 atmosphere was evacuated. The volatiles of the reaction mixture were then collected by vacuum distillation into a separate flask, dissolved in chloroform-*d*, and analyzed by ^{1}H and ^{13}C NMR spectroscopy to determine the location and extent of deuterium incorporation. For reactions in heptane (non-volatile substrates), the reaction was quenched by venting the vessel and exposing the reaction mixture to air. The reaction mixture was loaded directly onto the plug of silica gel, and the substrate was eluted with either hexanes. Following solvent evaporation, the substrate was dissolved in chloroform-*d*, and analyzed by ^{1}H and ^{13}C NMR spectroscopy to determine the location and extent of

deuterium incorporation. For a representative examples of the analyses of these data, see section VI.

Ineffective substrates for hydrogen isotope exchange with cobalt:

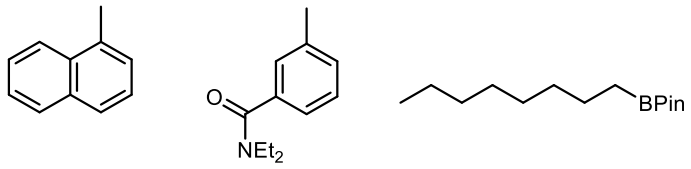


Figure S1. Representative substrates for which no hydrogen isotope exchange was observed using precatalysts **1** or **2**.

V. General Procedures Hydrogen Isotope Exchange.

General Note: Analysis of labeled substrates was carried out by quantitative ^{1}H and ^{13}C NMR of crude reaction mixtures following the workups described for each General Procedure. Because the focus of this work is on the regioselectivity and degree of labeling of known compositions of matter, purification and re-isolation of labeled substrates was not carried out. Common impurities in the NMR spectra include tetramethylsilane (from catalyst activation), free ^{iPr}DI ligand, residual solvent from reaction or workup, and reduced substrate. Where applicable, these impurities are identified and quantified (see section VI: Characterization of Deuterated Substrates). For non-volatiles substrates labeled using General Procedures B and C, percent recovery of the labeled substrate is estimated based on mass and composition of the crude reaction mixture.

General Procedure A: Hydrogen Isotope Exchange of Volatile Substrates in Dodecane under 1 atm D_2 at 50 °C. In a nitrogen-filled glovebox, an oven-dried, sealable thick-walled glass vessel was charged with a magnetic stir bar, 0.035 g (0.055 mmol, 10 mol%) of **2**, 0.55 mmol of the desired substrate, and 0.55 mL of dodecane. The vessel was sealed, brought out of the glovebox, and attached to a high-vacuum line. The reaction solution was frozen by submersion of the bottom portion of the vessel containing the solution in liquid nitrogen. Following evacuation of the N_2 atmosphere in the headspace, 1 atm of D_2 gas was admitted into the vessel. The vessel was then sealed, and the reaction mixture was thawed and stirred in a 50 ± 2 °C silicone oil bath for 24 hours, during which time the solution color changed from purple to red. The vessel was removed from the oil bath, cooled to room temperature and reattached to a high-vacuum line. The reaction mixture was again frozen and the D_2 atmosphere was evacuated. The volatiles of the reaction mixture were then collected by vacuum distillation into a separate flask, dissolved in chloroform-*d*, and analyzed by ^{1}H and ^{13}C NMR spectroscopy to determine the location and extent of deuterium incorporation. Due to volatility of the substrates, percent recovery was not determined with this method.

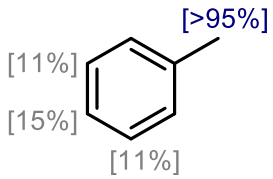
General Procedure B: Hydrogen Isotope Exchange of Non-Volatile Substrates in heptane under 1 atm D_2 at 50 °C. In a nitrogen-filled glovebox, an oven-dried, sealable thick-walled glass vessel was charged with a magnetic stir bar, 0.035 g (0.055 mmol, 10 mol%) of **2**, 0.55 mmol of the desired substrate, and 0.55 mL of heptane. The vessel was sealed, brought out of the glovebox, and attached to a high-vacuum line. The reaction solution was frozen by submersion of the bottom portion of the vessel

containing the solution in liquid nitrogen. Following evacuation of the N_2 atmosphere in the headspace, 1 atm of D_2 gas was admitted into the vessel. The vessel was then sealed, and the reaction mixture was thawed and stirred in a 50 ± 2 °C silicone oil bath for 24 hours, during which time the solution color changed from purple to red. The reaction was quenched by venting the vessel and exposing the reaction mixture to air, resulting in immediate color change from red to dark blue. The reaction mixture was loaded directly onto plug of silica gel in a Pasteur pipette and eluted with either hexanes or ethyl acetate into a 20 mL scintillation vial. Following solvent evaporation, the mass of the recovered material (sometimes containing free ^{iPr}DI ligand) was recorded to determine percent recovery. The material was then dissolved in chloroform-*d* and analyzed by ^{1}H and ^{13}C NMR spectroscopy to determine the location and extent of deuterium incorporation in the substrate.

General Procedure C: Hydrogen Isotope Exchange of Non-Volatile Substrates under 4 atm D_2 at 80 °C. In a nitrogen-filled glovebox, an oven-dried, sealable thick-walled glass vessel was charged with a magnetic stir bar, 0.018 g (0.028 mmol, 5 mol%) or 0.035 g (0.055 mmol, 10 mol%) of **2**, 0.55 mmol of the desired substrate, and 0.55 mL of heptane or CPME. The vessel was sealed, brought out of the glovebox, and attached to a high-vacuum line. The entire vessel (including reaction solution) was frozen by submersion in liquid nitrogen (77 K). Following evacuation of the N_2 atmosphere in the headspace, 1 atm of D_2 gas was admitted into the vessel. The vessel was then sealed and warmed to room temperature (at which point the internal pressure was ~4 atm at ~298 K). The reaction mixture was stirred in an 80 ± 2 °C silicone oil bath

for 24 hours by submerging only the portion of the vessel containing the solution in oil, during which time the solution color changed from purple to red. The reaction was quenched by venting the vessel and exposing the reaction mixture to air, resulting in immediate color change from red to dark blue. When using CPME, the solvent was evacuated, then the crude residue was dissolved in hexanes (~3 mL) and loaded onto a plug of silica gel in a Pasteur pipette. When using heptane, the reaction mixture was loaded directly onto the plug of silica gel. The substrate was eluted with either hexanes or ethyl acetate into a tared 20 mL scintillation vial. Following solvent evaporation, the mass of the recovered material (sometimes containing free ^{iPr}DI ligand) was recorded to determine percent recovery. The material was then dissolved in chloroform-*d* and analyzed by ^{1}H and ^{13}C NMR spectroscopy to determine the location and extent of deuterium incorporation.

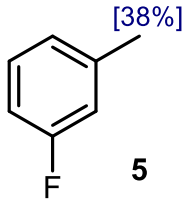
VI. Characterization of Deuterated Substrates.



4

Toluene 4. Labeled with deuterium according to General Procedure A using 0.051 g (0.55 mmol) of toluene. Dodecane, tetramethylsilane-d_1 (from precatalyst activation with D_2), and approximately 8% of deuterated methylcyclohexane were also observed by NMR spectroscopy. Percent reduction to deuterated methylcyclohexane was determined by integration of a diagnostic carbon resonance (34.83 ppm, t, $^{1}J_{CD}$ = 19 Hz, integrates to 0.16 with respect to toluene, 2 of *C*HD methylene) in the quantitative ^{13}C

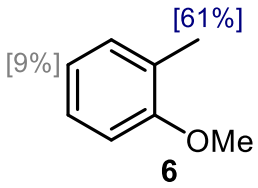
NMR spectrum. ^{1}H NMR (500 MHz, chloroform-*d*, 23 °C) δ 7.33-7.27 (m, 11% labeled, 1.78H, *m*-C*H*), 7.25-7.17 (m, 15% labeled, 2.85H, *o*- and *p*-C*H*), 2.41-2.34 (m, >95% labeled, $^{2}J_{HD}$ = 2.0 Hz, 0.14H, benzylic C*H*) ppm. Quantitative ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, 23 °C) δ 137.90 (m, 1C, ipso *C*), 129.18 (m, 2C, *o*-*C*, 2° isotopic shift: 14 Hz, 0.22C, ca. 11% D at *m*-*C*), 128.37 (m, 2C, 11% labeled, $^{1}J_{CD}$ = 24 Hz, *m*-*C*, 2° isotopic shift: 14 Hz, 0.30C, ca. 15% D at *p*-C), 125.46 (m, 1C, 15% labeled, $^{1}J_{CD}$ = 24 Hz, *p*-C), 21.43-20.23 (m, 1C, >95% labeled, $^{1}J_{CD}$ = 19 Hz, benzylic *C*) ppm.



5

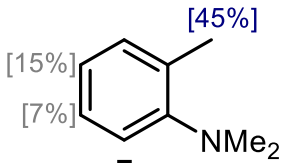
3-Fluorotoluene 5. Labeled with deuterium according to General Procedure A using 0.061 g (0.55 mmol) of 3-fluorotoluene. Reaction mixture became colorless after 3 hours, likely indicating decomposition of the catalyst. Dodecane, tetramethylsilane-d_1 (from precatalyst activation with D_2), and approximately 8% of reduced arene were observed by NMR spectroscopy. Percent arene reduction was determined by integration of a diagnostic carbon resonance (34.71 ppm, overlapping t, $^{1}J_{CD}$ = 18 Hz, integrates to 0.16 with respect to 3-fluorotoluene, 2 of *C*HD methylene) in the quantitative ^{13}C NMR spectrum in analogy to deuterated methylcyclohexane observed in the toluene labeling reaction, but this product was not further characterized. ^{1}H NMR (500 MHz, chloroform-*d*, 23 °C) δ 7.22 (app td, *J* = 7.8, 6.1 Hz, 1H, 5-C*H*), 6.96 (app d, *J* = 7.7 Hz, 1 H, 6-C*H*), 6.92-6.83 (m, 2H, 2- and 4-C*H*), 2.40-2.30 (m, 38% labeled, $^{2}J_{HD}$ = 2.0 Hz, 1.85H, benzylic C*H*) ppm. Quantitative ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, 23 °C) δ 162.87 (d, 1C, $^{1}J_{CF}$ = 245 Hz, *C*-F), 140.37 (m, 1C, ipso *C*), 129.58 (d, 1C, $^{3}J_{CF}$

= 8.5 Hz, 5-*C*), 124.71 (d, 1C, $^{4}J_{CF}$ = 2.7 Hz, 6-*C*), 115.93 (d, 1C, $^{2}J_{CF}$ = 21 Hz, 2-*C*), 112.23 (d, 1C, $^{2}J_{CF}$ = 21 Hz, 4-*C*), 21.44-20.13 (m, 1C, $^{1}J_{CD}$ = 19 Hz, $^{5}J_{CF}$ = 1.9 Hz, benzylic *C*) ppm.



6

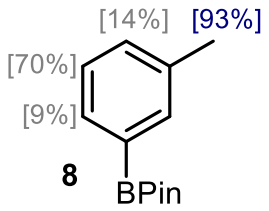
2-methylanisole 6. Labeled with deuterium according to General Procedure A using 0.067 g (0.55 mmol) of 2-methylanisole. Dodecane tetramethylsilane-*d*$_1$ (from precatalyst activation with D_2) were also observed by NMR spectroscopy. ^{1}H NMR (500 MHz, chloroform-*d*, 23 °C) δ 7.23-7.13 (m, 2H, 5- and 6-C*H*), 6.89 (app t, $^{3}J_{HH}$ = 7.4 Hz, 9% labeled, 0.91H, 4-C*H*), 6.86 (app d, $^{3}J_{HH}$ = 8.1 Hz, 1H, 3-C*H*), 2.27-2.20 (m, 61% labeled, $^{2}J_{HD}$ = 2.0 Hz, 1.16H, benzylic C*H*) ppm. Quantitative ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, 23 °C) δ 157.86 (s, 1C, *C*OCH$_3$), 130.73 (m, 1C, 3-*C*, 2° isotopic shift: 13 Hz, 0.09C, ca. 9% D at 4-*C*), 126.92 (m, 1C, 5-*C*, 2° isotopic shift: 14 Hz, 0.09C, ca. 9% D at 4-*C*), 126.70 (m, 1C, ipso *C*CH$_3$), 120.38 (m, 1C, 9% labeled, $^{1}J_{CD}$ = 25 Hz, 4-*C*), 109.98 (s, 1C, 6-*C*), 55.33 (s, 1C, O*C*H$_3$), 21.43-20.23 (m, 1C, 61% labeled, $^{1}J_{CD}$ = 19 Hz, benzylic *C*) ppm.



7

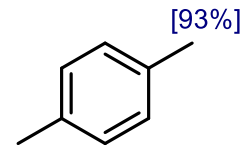
***N,N*-dimethyl-*o*-toluidine 7.** Labeled with deuterium according to General Procedure B using 0.074 g (0.55 mmol) of *N,N*-dimethyl-*o*-toluidine. Eluted with ethyl acetate, yielding 0.069 g of recovered material following evaporation of solvent. An

approximately 15% impurity in the recovered substrate was identified as free ^{iPr}DI ligand by NMR spectroscopy. From these data, the recovery of labeled **7** was determined to be 64%. ^{1}H NMR (500 MHz, chloroform-*d*, 23 °C) δ 7.25-7.18 (obsc m, 7% labeled, 1.93H, 3- and 5-C*H*), 7.09 (app d, J_{HH} = 8.2 Hz, 1H, 6-C*H*), 7.01 (app t, $^{3}J_{HH}$ = 7.4,1.2 Hz, 15% labeled, 0.85H, 4-C*H*), 2.76 (s, 6H, N(CH_3)$_2$), 2.41-2.32 (m, 45% labeled, $^{2}J_{HD}$ = 2.1 Hz, 1.66H, benzylic C*H*) ppm. Quantitative ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, 23 °C) δ 152.84 (s, 1C, *C*N(CH$_3$)$_2$), 132.20 (m, 1C, ipso *C*CH$_3$), 130.25 (m, 1C, 3-*C*, 2° isotopic shift: 14 Hz, 0.15C, ca. 15% D at 4-*C*), 126.54 (m, 1C, 7% labeled, $^{1}J_{CD}$ = 25 Hz, 5-*C*, 2° isotopic shift: 14 Hz, 0.15C, ca. 15% D at 4-*C*), 122.65 (m, 1C, 15% labeled, $^{1}J_{CD}$ = 24 Hz, 4-*C*), 118.44 (m, 1C, 6-*C*, 2° isotopic shift: 14 Hz, 0.07C, ca. 7% D at 5-*C*), 55.33 (s, 1C, O*C*H$_3$), 18.60-17.33 (m, 1C, 45% labeled, $^{1}J_{CD}$ = 19 Hz, benzylic *C*) ppm.



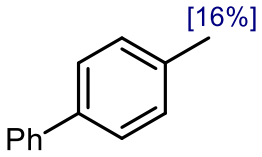
***m*-tolylboronic acid pinacol ester 8.** Labeled with deuterium according to General Procedure C using 5 mol% of **2** (0.018 g, 0.028 mmol), 0.12 g (0.55 mmol) of *m*-tolylboronic acid pinacol ester in heptane. Eluted with ethyl acetate, yielding 0.141 g of recovered material following evaporation of solvent. Trace Ethyl acetate, 11% free iPrDI ligand (by mol), and approximately 53% of reduced arene (by mol; 2 isomers) were also observed by NMR spectroscopy. Percent arene reduction was determined by integration of a diagnostic carbon resonance (24.87, 24.82, 24.81 ppm, overlapping s, integrates to 5.54 with respect to **8**, four of reduced arene BPin *C*H$_3$) in the quantitative ^{13}C NMR spectrum in analogy to deuterated methylcyclohexane observed in the toluene

labeling reaction, but these products was not further characterized. ^{1}H NMR (500 MHz, chloroform-*d*, 23 °C) δ 7.69-7.57 (m, 9% labeled at 4-position and 14% labeled at 6-position, 1.77H, arene 4- and 6-C*H*), 7.31-7.24 (m, 70% labeled at 5-position, 1.30H, arene 2- and 6-C*H*), 2.38-2.30 (m, 93% labeled, $^{2}J_{HD}$ = 2.0 Hz, 0.20H, benzylic C*H*), 1.35 (s, 12H, 4 x BPin CH_3) ppm. Quantitative ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, 23 °C) δ 137.37-136.77 (m, 1C, ipso CCH_3, 2° isotopic shift: 11 Hz, 0.14C, ca. 14% D at 6-*C*), 135.42 (s, 1C, 2-*C*), 132.16-131.92 (m, 1C, 9% labeled, 4-*C*, 2° isotopic shift: 13 Hz, 0.30C at non-shifted signals, 70% labeled at 5-*C*), 131.92-131.22 (m, 1C, 4% labeled, $^{1}J_{CD}$ = 24 Hz, 6-*C*, 2° isotopic shift: 14 Hz, 0.31C at non-shifted signals, 70% labeled at 5-*C*), 127.86-127.02 (m, 1C, 70% labeled, $^{1}J_{CD}$ = 24 Hz, 5-*C*, 2° isotopic shift: 13 Hz), 83.72 (s, 2C, 2 x BPin *C*O), 24.93 (s, 4C, 4 x BPin *C*H$_3$), 21.02-19.93 (m, 1C, 93% labeled, $^{1}J_{CD}$ = 19 Hz, benzylic *C*) ppm; one arene carbon resonance (attached to boron) was not observed.



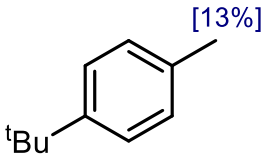
9

***p*-Xylene 9.** Labeled with deuterium according to General Procedure A using 0.058 g (0.55 mmol) of *p*-xylene. Dodecane and tetramethylsilane-d_1 (from precatalyst activation with D_2) were also observed by NMR spectroscopy. ^{1}H NMR (500 MHz, chloroform-*d*, 23 °C) δ 7.09 (s, 4H, *Ar*-C*H*), 2.33-2.25 (m, 93% labeled, $^{2}J_{HD}$ = 2.2 Hz, 0.40H, benzylic C*H*) ppm. Quantitative ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, 23 °C) δ 134.72 (m, 2C, ipso *C*CH$_3$), 129.05 (s, 4C, *Ar C*H), 21.26-19.44 (m, 2C, 93% labeled, $^{1}J_{CD}$ = 19 Hz, benzylic *C*) ppm.



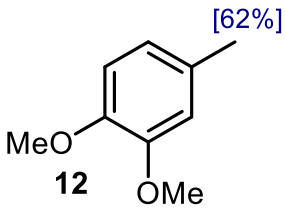
10

4-phenyltoluene 10. Labeled with deuterium according to General Procedure B using 0.093 g (0.55 mmol) of 4-phenyltoluene. Eluted with hexanes, yielding 0.098 g of recovered material following evaporation of solvent. Hexanes and approximately 10% of reduced arene were also observed by NMR spectroscopy. Percent arene reduction was determined by integration of a diagnostic carbon resonances (two species attributed to arene reduction at each ring, each 5%: 34.05, 31.42, 28.07, 26.41 ppm, all t, all $^{1}J_{CD}$ = 19 Hz, each integrates to 0.10 with respect to 4-phenyltoluene, each corresponds to 2 of *C*HD methylene) in the quantitative ^{13}C NMR spectrum in analogy to deuterated methylcyclohexane observed in the toluene labeling reaction, but these products were not further characterized. ^{1}H NMR (500 MHz, chloroform-*d*, 23 °C) δ 7.58 (dd, $^{3}J_{HH}$ = 8.3, 1.2 Hz, 2H, *Ar* C–H), 7.50 (d, $^{3}J_{HH}$ = 8.1 Hz, 2H, *Ar* C–H), 7.41 (t, $^{3}J_{HH}$ = 7.7 Hz, 2H, *Ar* C–H), 7.31 (t, $^{3}J_{HH}$ = 8.0 Hz, 1H, *Ar* C–H), 7.24 (d, $^{3}J_{HH}$ = 8.0 Hz, 2H, *Ar* C–H), 2.42-2.34 (m, 16% labeled, $^{2}J_{HD}$ = 2.2 Hz, 2.51H, benzylic C*H*) ppm. Quantitative ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, 23 °C) δ 141.26 (s, 1C, *Ar C*H_0), 138.46 (s, 1C, *Ar C*H_0), 137.09 (m, 1C, ipso *C*CH_3), 129.60 (s, 2C, *Ar C*H), 128.83 (s, 2C, *Ar C*H), 127.15-127.03 (overlapping s, 5C, *Ar C*H), 21.41-20.01 (m, 1C, 16% labeled, $^{1}J_{CD}$ = 19 Hz, benzylic *C*) ppm.



11

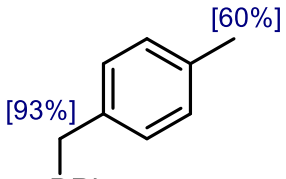
4-*tert*-butyltoluene 11. Labeled with deuterium according to General Procedure B using 0.082 g (0.55 mmol) of 4-*tert*-butyltoluene. Eluted with hexanes, yielding 0.054 g (66%) of recovered material following evaporation of solvent. ^{1}H NMR (500 MHz, chloroform-*d*, 23 °C) δ 7.38 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H, *Ar* C–H), 7.20 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H, *Ar* C–H), 2.43-2.36 (m, 13% labeled, $^{2}J_{HD}$ = 2.1 Hz, 2.62H, benzylic C*H*), 1.40 (s, 9H, C(CH_3)$_3$) ppm. Quantitative ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, 23 °C) δ 148.21 (s, 1C, *C*C(CH$_3$)$_3$), 133.94 (m, 1C, ipso *C*CH$_3$), 128.89 (s, 2C, *Ar C*H), 125.28 (s, 2C, *Ar C*H), 34.45 (s, 1C, *C*(CH$_3$)$_3$), 31.58 (s, 1C, C(*C*H$_3$)$_3$), 21.13-19.76 (m, 1C, 13% labeled, $^{1}J_{CD}$ = 19 Hz, benzylic *C*) ppm.



12

3,4-dimethoxytoluene 12. Labeled with deuterium according to General Procedure B using 0.084 g (0.55 mmol) of 3,4-dimethoxytoluene. Eluted with ethyl acetate, yielding 0.103 g of recovered material following evaporation of solvent. An approximately 11% impurity in the recovered substrate was identified as free ^{iPr}DI ligand by NMR spectroscopy. From these data, the recovery of labeled **12** was determined to be 96%. ^{1}H NMR (500 MHz, chloroform-*d*, 23 °C) δ 6.80-6.74 (m, 1H, 2-C*H*), 6.74-6.68 (m, 2H, 5- and 6-C*H*), 3.87 (s, 3H, one of OCH_3), 3.85 (s, 3H, one of OCH_3), 2.33-2.25 (m, 62% labeled, $^{2}J_{HD}$ = 2.1 Hz, 1.15H, benzylic C*H*) ppm. Quantitative ^{13}C{^{1}H} NMR (126 MHz,

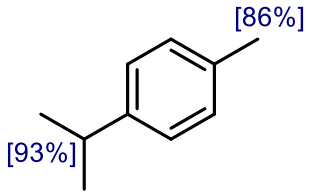
chloroform-*d*, 23 °C) δ 148.68 (s, 1C, one of *C*OCH$_3$), 146.82 (s, 1C, one of *C*OCH$_3$), 130.33 (m, 1C, ipso *C*CH$_3$), 120.74 (s, 1C, *Ar C*H), 112.38 (s, 1C, *Ar C*H), 111.19 (s, 1C, *Ar C*H), 55.89 (s, 1C, one of O*C*H$_3$), 55.71 (s, 1C, one of O*C*H$_3$), 21.12-19.50 (m, 1C, 62% labeled, $^1J_{CD}$ = 19 Hz, benzylic *C*) ppm.



13

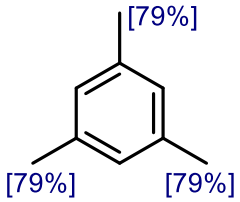
4-methylbenzylboronic acid pinacol ester 13. Labeled with deuterium according to General Procedure C using 5 mol% of **2** (0.018 g, 0.028 mmol), 0.128 g (0.55 mmol) of 4-methylbenzylboronic acid pinacol ester in heptane. Eluted with ethyl acetate, yielding 0.135 g of recovered material following evaporation of solvent. An approximately 4% impurity in the recovered substrate was identified as free ^{iPr}DI ligand by NMR spectroscopy. From these data, the recovery of labeled **13** was determined to be 99%. Relative deuterium incorporation on the benzylic positions was determined by a combination of integration of benzylic proton signals in the ^{1}H NMR spectrum and analysis of the arene ipso carbon signals in the quantitative ^{13}C NMR spectrum, which indicated high incorporation of deuterium on the benzylic methylene (one 13C singlet signal, mostly CD$_2$BPin) and a mixture of isotopic incorporation in the benzylic methyl (four 13C singlet signals, indicating CH$_3$, CH$_2$D, CHD$_2$, CD$_3$ all present). ^{1}H NMR (500 MHz, chloroform-*d*, 23 °C) δ 7.02 (ABq, J_{AB} = 7.8 Hz, 4H, *Ar*-C*H*), 2.28-2.21 (m, 60% labeled, $^2J_{HD}$ = 2.0 Hz, 1.21H, benzylic C*H*$_3$), 2.21-2.18 (br m, 93% labeled, 0.14H, benzylic C*H*$_2$BPin), 1.19 (s, 12H, 4 x BPin C*H*$_3$) ppm. Quantitative ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, 23 °C) δ 135.34 (s, 1C, ipso C-CH$_2$BPin), 134.19-133.84 (m (4 x s),

1C, ipso *C*CH_3), 129.01 (s, 2C, *Ar C*H), 128.85 (s, 2C, *Ar C*H), 83.35 (s, 2H, 2 x BPin *C*O), 24.77 (s, 4C, 4 x BPin *C*H_3), 21.39-19.33 (m, 1C, 60% labeled, $^1J_{CD}$ = 19 Hz, 1° benzylic *C*) ppm; one benzylic carbon resonance (attached to boron) was not observed.



14

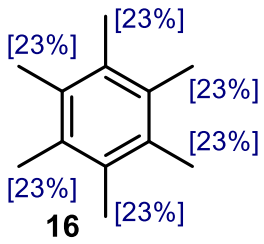
***p*-Cymene 14.** Labeled with deuterium according to General Procedure A using 0.074 g (0.55 mmol) of *p*-cymene. Dodecane and tetramethylsilane-d_1 (from precatalyst activation with D_2) were also observed by NMR spectroscopy. ^{1}H NMR (500 MHz, chloroform-*d*, 23 °C) δ 7.15 (ABq, J_{AB} = 8.0 Hz, 4H, *Ar*-C*H*), 2.90 (septet, 93% labeled, $^3J_{HH}$ = 6.8 Hz, 0.07H, benzylic C*H*$(CH_3)_2$), 2.39-2.26 (m, 86% labeled, $^2J_{HD}$ = 2.1 Hz, 0.43H, benzylic C*H*$_3$), 1.26 (app s, 6H, C(D)(*C*$H_3)_2$) ppm. Quantitative ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, 23 °C) δ 145.86 (m, 1C, ipso C-^{i}Pr), 135.06 (m, 1C, ipso *C*CH_3), 128.99 (s, 2C, *Ar C*H), 126.27 (s, 2C, *Ar C*H), 33.28 (t, 93% labeled, $^1J_{CD}$ = 19 Hz, benzylic *C*$(CH_3)_2$), 24.02 (s, 2C, C(*C*$H_3)_2$), 21.11-19.61 (m, 1C, 86% labeled, $^1J_{CD}$ = 19 Hz, 1° benzylic *C*) ppm.



15

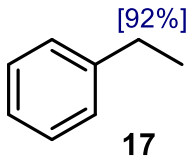
Mesitylene 15. Labeled with deuterium according to General Procedure A using 0.066 g (0.55 mmol) of mesitylene. Dodecane and tetramethylsilane-d_1 (from precatalyst activation with D_2) were also observed by NMR spectroscopy. ^{1}H NMR (500 MHz,

chloroform-*d*, 23 °C) δ 6.83 (s, 3H, *Ar*-C*H*), 2.35-2.20 (m, 79% labeled, $^{2}J_{HD}$ = 2.0 Hz, 1.93H, benzylic C*H*) ppm. Quantitative $^{13}C\{^{1}H\}$ NMR (126 MHz, chloroform-*d*, 23 °C) δ 137.75 (m, 3C, ipso *C*CH_3), 127.05 (s, 3C, *Ar C*H), 21.46-19.97 (m, 3C, 79% labeled, $^{1}J_{CD}$ = 19 Hz, benzylic *C*) ppm.



16

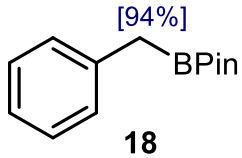
Hexamethylbenzene 16. Labeled with deuterium according to General Procedure C using 10 mol% (0.035 g, 0.055 mmol) of **2**, 0.089 g (0.55 mmol) of hexamethylbenzene in CPME. Reaction mixture became colorless after 3 hours, likely indicating decomposition of the catalyst. Eluted with hexanes following quench, yielding 0.087 g (97%) of recovered material following evaporation of solvent. A naphthalene internal standard (0.071 g, 0.55 mmol, 1.0 equiv) was added to the NMR sample for quantification of deuterium incorporation. ^{1}H NMR (500 MHz, chloroform-*d*, 23 °C) δ 2.55-2.44 (m, 23% labeled, $^{2}J_{HD}$ = 2.0 Hz, 13.80H, benzylic C*H*) ppm. Quantitative $^{13}C\{^{1}H\}$ NMR (126 MHz, chloroform-*d*, 23 °C) δ 132.08 (m, 6C, *C*CH_3), 17.08-15.60 (m, 6C, 23% labeled, $^{1}J_{CD}$ = 19 Hz, benzylic *C*) ppm.



17

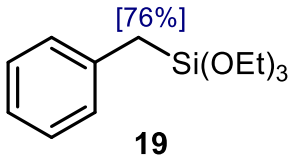
Ethylbenzene 17. Labeled with deuterium according to General Procedure A using 0.058 g (0.55 mmol) of ethylbenzene. Dodecane and tetramethylsilane-d_1 (from precatalyst activation with D_2) were also observed by NMR spectroscopy. ^{1}H NMR (500

MHz, chloroform-*d*, 23 °C) δ 7.31 (app t, $^{3}J_{HH}$ = 7.5 Hz, 2H, *m*-C*H*), 7.25-7.17 (m, 3H, *o*- and *p*-C*H*), 2.72-2.60 (m, 92% labeled, $^{3}J_{HH}$ = 7.6 Hz, $^{2}J_{HD}$ = 2.0 Hz, 0.17H, benzylic C*H*), 1.25 (s, 3H, C(D)$_2$C*H*$_3$) ppm. Quantitative ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, 23 °C) δ 144.19 (m, 1C, ipso *C*), 128.31 (s, 2C, *Ar C*H), 127.86 (s, 2C, *Ar C*H), 125.59 (s, 1C, *p*-*C*H), 28.94-27.76 (m, 1C, 92% labeled, $^{1}J_{CD}$ = 19 Hz, benzylic *C*),15.49 (s, 1C, CH_2CH_3) ppm.



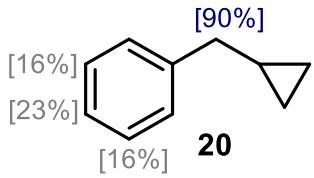
18

Benzylboronic acid pinacol ester 18. Labeled with deuterium according to General Procedure B using 0.074 g (0.55 mmol) of benzylboronic acid pinacol ester. Eluted with ethyl acetate, yielding 0.135 g of recovered material following evaporation of solvent. An approximately 10% impurity in the recovered substrate was identified as free ^{iPr}DI ligand by NMR spectroscopy. From these data, the recovery of labeled **18** was determined to be 95%. ^{1}H NMR (500 MHz, chloroform-*d*, 23 °C) δ 7.23-7.10 (m, 4H, *o*- and *m*-C*H*), 7.08 (t, $^{3}J_{HH}$ = 7.0 Hz, 1H, *p*-C*H*), 2.28-2.21 (br m, 94% labeled, 0.13H, benzylic C*H*), 1.19 (s, 12H, 4 x BPin C*H*$_3$) ppm. Quantitative ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, 23 °C) δ 138.60 (m, 1C, ipso *C*), 128.99 (s, 2C, *Ar C*H), 128.29 (s, 2C, *Ar C*H), 124.86 (s, 1C, *p*-*C*H), 83.41 (s, 2H, 2 x BPin *C*O), 24.77 (s, 4C, 4 x BPin *C*H$_3$) ppm; benzylic carbon resonance (attached to boron) was not observed.



19

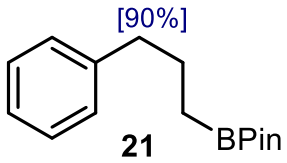
Benzyltriethoxysilane 19. Labeled with deuterium according to General Procedure B using 0.140 g (0.55 mmol) of benzyltriethoxysilane. Eluted with ethyl acetate, yielding 0.087 g of recovered material following evaporation of solvent. An approximately 28% impurity in the recovered substrate was identified as free ^{iPr}DI ligand by NMR spectroscopy. From these data, the recovery of labeled **19** was determined to be 43%. ^{1}H NMR (500 MHz, chloroform-*d*, 23 °C) δ 7.28-7.16 (m, 4H, *o*- and *m*-C*H*), 7.15-7.08 (m, 1H, *p*-C*H*), 3.79 (q, $^{3}J_{HH}$ = 7.1 Hz, 6H, 3 x CH_2CH$_3$), 2.26-2.19 (br m, 76% labeled, 0.48H, benzylic C*H*), 1.20 (t, $^{3}J_{HH}$ = 7.0 Hz, 3 x CH$_2$CH_3) ppm. Quantitative ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, 23 °C) δ 137.60 (m, 1C, ipso *C*), 128.94 (s, 2C, *Ar C*H), 128.28 (s, 2C, *Ar C*H), 124.66 (s, 1C, *p*-*C*H), 58.77 (s, 3C, 3 x *C*H$_2$CH$_3$), 20.38-19.40 (m, 1C, 76% labeled, $^{1}J_{CD}$ = 18 Hz, benzylic *C*),18.30 (s, 3C, 3 x CH$_2$*C*H$_3$) ppm.



20

Benzylcyclopropane 20. Labeled with deuterium according to General Procedure B using 0.073 g (0.55 mmol) of benzylcyclopropane. Eluted with hexanes, yielding 0.054 g of recovered material following evaporation of solvent. Two impurities were observed in the recovered substrate and were identified as free ^{iPr}DI ligand (approximately 3%) and reduced arene (approximately 10%; diagnostic ^{1}H signals for cyclopropyl: 0.71 (m, 1H), 0.42 (m, 2H), 0.02 (m, 2H) ppm; diagnostic ^{13}C signal: 32.91 (t, 1C, $^{1}J_{CD}$ = 21 Hz, *C*HD)) by NMR spectroscopy. Products from ring-opening of the cyclopropane, such as *n*-

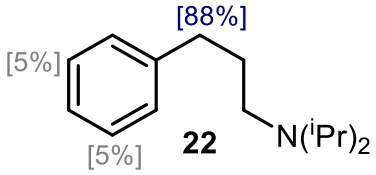
butylbenzene or isobutylbenzene, were not observed. ^{1}H NMR (500 MHz, chloroform-*d*, 23 °C) δ 7.36-7.27 (m, 16% labeled at *m*-C*H*, 3.68H, *o*- and *m*-C*H*), 7.27-7.19 (obsc m, 23% labeled, 0.77H + free ligand integration, *p*-C*H*), 2.61-2.54 (m, 90% labeled, $^{3}J_{HH}$ = 7.2 Hz, $^{2}J_{HD}$ = 1.9 Hz, 0.20H, benzylic C*H*), 1.02 (m, 1H, cyclopropyl methine), 0.59-0.54 (m, 2H, 2 of cyclopropyl methylene C*H*), 0.28-0.21 (m, 2H, 2 of cyclopropyl methylene C*H*) ppm. Quantitative ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, 23 °C) δ 142.21 (m, 1C, ipso *C*), 128.48 (obsc m, 2C, *o*-*C*), 128.36 (m, 2C, 16% labeled, $^{1}J_{CD}$ = 24 Hz, *m*-*C*, 2° isotopic shift: 14 Hz, 0.46C, ca. 23% D at *p*-*C*), 125.96 (m, 1C, 23% labeled, $^{1}J_{CD}$ = 24 Hz, *p*-*C*, 2° isotopic shift: 14 Hz, 0.16C, ca. 26% D at *m*-*C*), 40.88-38.80 (m, 1C, 90% labeled, $^{1}J_{CD}$ = 19 Hz, benzylic *C*), 11.89 (m, 1C, cyclopropyl methine *C*H), 4.73 (m, 2C, cyclopropyl *C*H$_2$) ppm.



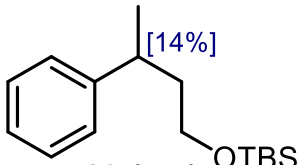
21

(3-Phenylpropyl)boronic acid pinacol ester 21. Labeled with deuterium according to General Procedure B using 0.135 g (0.55 mmol) of (3-phenylpropyl)boronic acid pinacol ester. Eluted with ethyl acetate, yielding 0.154 g of recovered material following evaporation of solvent. An approximately 10% impurity in the recovered substrate was identified as free ^{iPr}DI ligand by NMR spectroscopy. From these data, the recovery of labeled **21** was determined to be 98%.^{1}H NMR (500 MHz, chloroform-*d*, 23 °C) δ 7.27 (app t, $^{3}J_{HH}$ = 7.4 Hz, 2H, *m*-C*H*), 7.22-7.14 (m, 3H, *o*- and *p*-C*H*), 2.67-2.52 (br m, 90% labeled, $^{3}J_{HH}$ = 7.8 Hz, 0.20H, benzylic C*H*), 1.75 (t, $^{3}J_{HH}$ = 8.1 Hz, 2H, C(D)$_2$C*H*$_2$), 1.26 (s, 12H, 4 x BPin C*H*$_3$), 0.85 (t, $^{3}J_{HH}$ = 8.1 Hz, C*H*$_2$BPin) ppm. Quantitative ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, 23 °C) δ 142.66 (m, 1C, ipso *C*), 128.60 (s, 2C, *Ar C*H), 128.23

(s, 2C, *Ar C*H), 125.63 (s, 1C, *p*-*C*H), 82.96 (s, 2C, 2 x BPin *C*O), 38.55-37.38 (m, 1C, 90% labeled, $^{1}J_{CD}$ = 19 Hz, benzylic *C*), 26.05 (s, 1C, PhC(D)$_2$*C*H$_2$), 24.91 (s, 4C, 4 x BPin *C*H$_3$) ppm; one carbon resonance (attached to boron) was not observed.

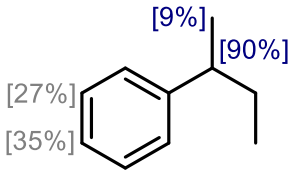


Diisopropyl(3-phenylpropyl)amine 22. Labeled with deuterium according to General Procedure B using 0.121 g (0.55 mmol) of diisopropyl(3-phenylpropyl)amine. Eluted with ethyl acetate, yielding 0.130 g of recovered material following evaporation of solvent. An approximately 8% impurity in the recovered substrate was identified as free ^{iPr}DI ligand by NMR spectroscopy. From these data, the recovery of labeled **22** was determined to be 94%. ^{1}H NMR (500 MHz, chloroform-*d*, 23 °C) δ 7.27 (app t, $^{3}J_{HH}$ = 7.4 Hz, 5% labeled, 1.90H, *m*-C*H*), 7.20-7.13 (m, 3H, *o*- and *p*-C*H*), 2.99 (septet, $^{3}J_{HH}$ = 6.5 Hz, 2 x N(C*H*(CH$_3$)$_2$)), 2.62-2.52 (br m, 88% labeled, $^{3}J_{HH}$ = 7.9 Hz, 0.24H, benzylic C*H*), 2.42 (app t, $^{3}J_{HH}$ = 7.6 Hz, 2H, CH$_2$C*H*$_2$N), 1.71 (app t, $^{3}J_{HH}$ = 7.4 Hz, 2H, CH$_2$C*H*$_2$N), 0.98 (d, $^{3}J_{HH}$ = 6.5 Hz, 2 x N(CH(C*H*$_3$)$_2$)) ppm. Quantitative ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, 23 °C) δ 142.77 (m, 1C, ipso *C*), 128.42 (m, 2C, 5% labeled, *m*-*C*H), 128.28 (m, 2C, *o*-*C*, 2° isotopic shift: 14 Hz, 0.10C, ca. 5% D at *m*-*C*), 125.59 (m, 1C, *p*-*C*, 2° isotopic shift: 14 Hz, 0.05C, ca. 5% D at *m*-C), 48.50 (s, 2C, 2 x N(*C*H(CH$_3$)$_2$), 44.93 (s, 1C, CH$_2$*C*H$_2$N), 33.65-32.66 (m, 1C, 88% labeled, $^{1}J_{CD}$ = 19 Hz, benzylic *C*), 32.88 (m, 1C, *C*H$_2$CH$_2$N), 20.81 (s, 4C, 2 x N(*C*H(CH$_3$)$_2$) ppm.



23-(*rac*)

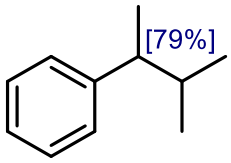
(*rac*) 3-Phenylbutan-1-ol *tert*-butyldimethylsilyl ether 23-(*rac*). Labeled with deuterium according to General Procedure B using 0.145 g (0.55 mmol) of (*rac*) 3-Phenylbutan-1-ol *tert*-butyldimethylsilyl ether. Eluted with hexanes, yielding 0.140 g (96%) of recovered material following evaporation of solvent. ^{1}H NMR (500 MHz, chloroform-*d*, 23 °C) δ 7.24 (app t, $^{3}J_{HH}$ = 7.4 Hz, 2H, *m*-C*H*), 7.18-7.10 (m, 3H, *o*- and *p*-C*H*), 3.56-3.40 (m, 2H, CH_2OTBS), 2.86 (app hextet, 14% labeled $^{3}J_{HH}$ = 7.2 Hz, 0.86H, benzylic C*H*), 1.77 (app q, $^{3}J_{HH}$ = 7.0 Hz, 2H, homobenzylic CH_2), 1.22 (d, $^{3}J_{HH}$ = 7.0 Hz, 3H, homobenzylic CH_3), 0.86 (s, 9H, SiC(CH_3)$_3$), -0.03 (s, 6H, 2 x SiCH_3) ppm. Quantitative ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, 23 °C) δ 147.36 (m, 1C, ipso *C*), 128.44 (s, 2C, *Ar*-*C*H), 127.18 (s, 2C, *Ar*-*C*H), 126.03 (s, 1C, *p*-*C*), 61.33 (s, 1C, *C*OTBS), 41.32 (m, 1C, homobenzylic *C*H_2, 2° isotopic shift: 14 Hz, 0.14C, ca. 14% D at benzylic *C*), 36.51-35.54 (m, 1C, 14% labeled, $^{1}J_{CD}$ = 20 Hz, benzylic *C*), 26.11 (s, 3C, C(*C*H_3)$_3$), 22.49 (m, 1C, homobenzylic *C*H_3, 2° isotopic shift: 14 Hz, 0.14C, ca. 14% D at benzylic *C*), 18.44 (s, 1C, Si*C*(CH$_3$)$_3$), -5.17 (s, 2C, 2 x Si*C*H$_3$) ppm.



24-(*rac*)

(*rac*) *sec*-Butylbenzene 24-(*rac*). Labeled with deuterium according to General Procedure B using 0.074 g (0.55 mmol) of (*rac*) *sec*-butylbenzene. Eluted with hexanes, yielding 0.045 g (58%) of recovered material following evaporation of solvent.

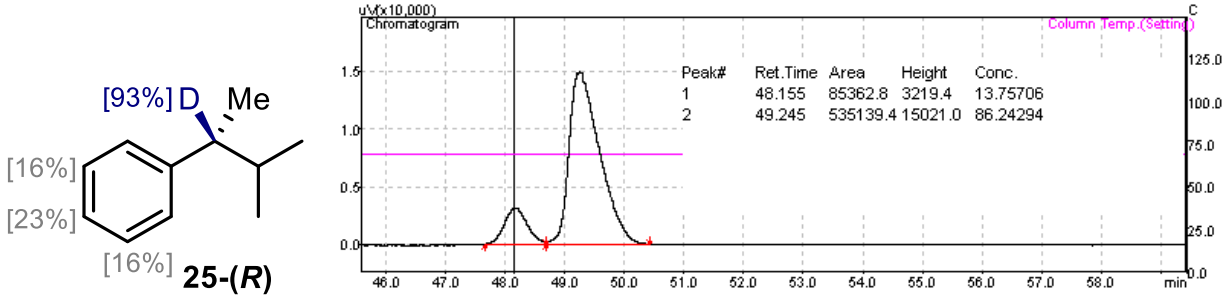
^{1}H NMR (500 MHz, chloroform-*d*, 23 °C) δ 7.34-7.27 (m, 27% labeled, 1.47H, *m*-C*H*), 7.24-7.16 (m, 35% *p*-labeled, 2.65H, *o*- and *p*-C*H*), 2.62 (app hextet, 90% labeled $^{3}J_{HH}$ = 6.9 Hz, 0.10H, benzylic C*H*), 1.62 (q, $^{3}J_{HH}$ = 7.5 Hz, 2H, homobenzylic CH_2), 1.26 (m, 9% labeled, 2.72H, homobenzylic CH_3), 0.85 (t, $^{3}J_{HH}$ = 7.4 Hz, 3H, terminal CH_3) ppm. Quantitative ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, 23 °C) δ 147.75 (m, 1C, ipso *C*), 128.37 (m, 2C, 27% labeled, $^{1}J_{CD}$ = 24 Hz, *m*-*C*, 2° isotopic shift: 14 Hz, 0.70C, ca. 35% D at *p*-C), 127.17 (m, 2C, *o*-*C*, 2° isotopic shift: 14 Hz, 0.54C, ca. 27% D at *m*-*C*), 125.89 (m, 1C, 35% labeled, $^{1}J_{CD}$ = 24 Hz, *p*-*C*), 41.98-40.93 (m, 1C, 90% labeled, $^{1}J_{CD}$ = 19 Hz, benzylic *C*), 41.32 (m, 1C, homobenzylic *C*H_2), 21.89 (m, 1C, homobenzylic *C*H_3), 12.38 (m, 1C, terminal CH_3) ppm.



25-(*rac*)

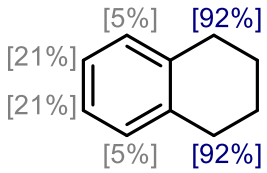
(*rac*) 2-Phenyl-3-methylbutane 25-(*rac*). Labeled with deuterium according to General Procedure B using 0.082 g (0.55 mmol) of (*rac*) 2-phenyl-3-methylbutane. Eluted with hexanes, yielding 0.063 g (77%) of recovered material following evaporation of solvent. ^{1}H NMR (500 MHz, chloroform-*d*, 23 °C) δ 7.26 (app t, $^{3}J_{HH}$ = 7.6 Hz, 2H, *m*-C*H*), 7.18-7.11 (m, 3H, *o*- and *p*-C*H*), 2.41 (app pentet, 79% labeled, $^{3}J_{HH}$ = 7.2 Hz, 0.21H, benzylic C*H*), 1.75 (septet, $^{3}J_{HH}$ = 6.8 Hz, 1H, homobenzylic C*H*), 1.22 (m, 3H, homobenzylic CH_3), 0.93 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, one of diastereotopic CH_3), 0.75 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, one of diastereotopic CH_3) ppm. Quantitative ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, 23 °C) δ 147.17 (m, 1C, ipso *C*), 128.16 (s, 2C, *m*-*C*), 127.77 (s, 2C, *o*-*C*),

(s, 1C, *p*-*C*), 47.18-46.20 (m, 1C, 79% labeled, $^{1}J_{CD}$ = 19 Hz, benzylic *C*), 34.60 (m, 1C, homobenzylic *C*H), 21.34 (m, 1C, one of *C*H$_3$), 20.34 (m, 1C, one of *C*H$_3$), 18.93 (m, 1C, one of *C*H$_3$) ppm.



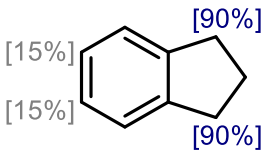
(*R*) 2-Phenyl-3-methylbutane 25-(*R*). Labeled with deuterium according to General Procedure B using 0.082 g (0.55 mmol) of (*R*) 2-phenyl-3-methylbutane (72% ee). Eluted with hexanes, yielding 0.069 g (82%) of recovered material following evaporation of solvent. ^{1}H NMR (500 MHz, chloroform-*d*, 23 °C) δ 7.26 (app t, 16% labeled, $^{3}J_{HH}$ = 7.6 Hz, 1.69H, *m*-C*H*), 7.18-7.11 (m, 23% *p*-labeled, 2.77H, *o*- and *p*-C*H*), 2.41 (app pentet, 93% labeled, $^{3}J_{HH}$ = 7.2 Hz, 0.21H, benzylic C*H*), 1.75 (septet, $^{3}J_{HH}$ = 6.8 Hz, 1H, homobenzylic C*H*), 1.22 (m, 3H, homobenzylic C*H*$_3$), 0.93 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, one of diastereotopic C*H*$_3$), 0.75 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, one of diastereotopic C*H*$_3$) ppm. Quantitative ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, 23 °C) δ 147.17 (m, 1C, ipso *C*), 128.16 (obsc m, 2C, 16% labeled, *m*-*C*, 2° isotopic shift: 14 Hz), 127.77 (m, 2C, *o*-C, 2° isotopic shift: 14 Hz, 0.30C, ca. 16% D at *m*-*C*), 125.82, m, 1C, 23% labeled, $^{1}J_{CD}$ = 24 Hz, *p*-*C*, 2° isotopic shift: 14 Hz), 47.18-46.20 (m, 1C, 93% labeled, $^{1}J_{CD}$ = 19 Hz, benzylic *C*), 34.60 (m, 1C, homobenzylic *C*H), 21.30 (m, 1C, one of *C*H$_3$), 20.32 (m, 1C, one of *C*H$_3$), 18.80 (m, 1C, one of *C*H$_3$) ppm. Chiral separation and enantiomer assignment was achieved using chiral GC according to the reported[4] isothermal method: hold at 70 ºC for 60 minutes; ramp 20 ºC per minute, hold at 200 ºC for 6

minutes. Starting material ee: 72% (*R*); ee of recovered material: 72% (*R*). Enantiospecificity: >98% es.



26

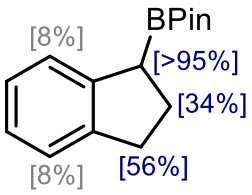
Tetralin 26. Labeled with deuterium according to General Procedure B using 0.073 g (0.55 mmol) of tetralin. Eluted with hexanes, yielding 0.060 g (78%) of recovered material following evaporation of solvent. ^{1}H NMR (500 MHz, chloroform-*d*, 23 °C) δ 7.20-7.11 (m, 52% labeled, 3.48H, *Ar*-C*H*), 2.91-2.77 (m, 92% labeled, $^{2}J_{HD}$ = 1.9 Hz, 0.34H, benzylic C*H*), 1.88 (s, 4H, homobenzylic methylene $C(D)_2CH_2$) ppm. Quantitative $^{13}C\{^{1}H\}$ NMR (126 MHz, chloroform-*d*, 23 °C) δ 137.17 (m, 1C, ipso *C*), 129.23 (m, 2C, 5% labeled, $^{1}J_{CD}$ = 21 Hz, 2-*Ar*-*C*, 2° isotopic shift: 14 Hz, 0.50C, ca. 25% D at 3-*C*), 125.53 (m, 2C, 25% labeled, $^{1}J_{CD}$ = 24 Hz, 3-*Ar*-*C*, 2° isotopic shift: 14 Hz), 29.62-28.25 (m, 2C, 92% labeled, $^{1}J_{CD}$ = 19 Hz, benzylic *C*), 23.31-22.81 (m, 2C, homobenzylic *C*) ppm.



27

Indan 27. Labeled with deuterium according to General Procedure B using 0.065 g (0.55 mmol) of indan. Eluted with hexanes, yielding 0.048 g (70%) of recovered material following evaporation of solvent. ^{1}H NMR (500 MHz, chloroform-*d*, 23 °C) δ 7.24-7.18 (m, 2H, 2-C*H*), 7.14-7.09 (m, 15% labeled, 1.70H, 3-C*H*), 2.95-2.81 (m, 90% labeled, $^{3}J_{HH}$ = 7.6 Hz, $^{2}J_{HD}$ = 1.2 Hz, 0.40Hz, benzylic C*H*), 2.02 (m, 2H, homobenzylic

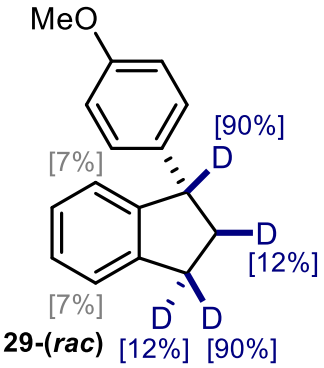
methylene) ppm. Quantitative $^{13}C\{^{1}H\}$ NMR (126 MHz, chloroform-*d*, 23 °C) δ 144.22 (m, 1C, ipso *C*), 126.11 (m, 2C, 15% labeled, $^{1}J_{CD}$ = 24 Hz, 3-*Ar*-*C*, 2° isotopic shift: 14 Hz, 0.30C, ca. 15% D at 3'-*C*), 124.52 (m, 2C, 2-*Ar*-*C*, 2° isotopic shift: 14 Hz, 0.31C, ca. 15% D at 3-*C*), 33.29-31.43 (m, 2C, 90% labeled, $^{1}J_{CD}$ = 20 Hz, benzylic *C*), 25.52-24.47 (m, 1C, homobenzylic *C*) ppm.



28-(*rac*)

(*rac*) 1-indanylboronic acid pinacol ester 28-(*rac*). Labeled with deuterium according to a modified General Procedure C using 5 mol% of **2** (0.011 g, 0.017 mmol), 0.084 g (0.34 mmol) of (*rac*) 1-indanylboronic acid pinacol ester in heptane. Eluted with ethyl acetate, yielding 0.091 g of recovered material following evaporation of solvent. An approximately 6% impurity in the recovered substrate was identified as free ^{iPr}DI ligand by NMR spectroscopy in addition to a 10% impurity of ethyl acetate. From these data, the recovery of labeled **28-(*rac*)** was determined to be 97%. ^{1}H NMR (500 MHz, chloroform-*d*, 23 °C) δ 7.22 (m, 8% labeled, 0.92H, 8-indanyl C*H*), 7.15 (m, 8% labeled, 0.92H, 5-indanyl C*H*), 7.07-6.99 (m, 2H, 6- and 7-indanyl C*H*), 2.94-2.77 (m, 56% labeled, 0.88H, 3-indanyl benzylic CH_2; diastereotopic protons not distinguished), 2.72-2.58 (m; obsc by free ligand, >95% labeled, <0.05H, 1-indanyl benzylic C*H* α-to-B), 2.18-1.98 (m, obsc by free ligand, 34% labeled, 1.32H, 2-indanyl CH_2; diastereotopic protons not distinguished), 1.18 (s, 6H, 2 x BPin CH_3), 1.17 (s, 6H, 2 x BPin CH_3) ppm. Quantitative $^{13}C\{^{1}H\}$ NMR (126 MHz, chloroform-*d*, 23 °C) δ 145.14 (m, 1C, one of ipso *C*), 144.27 (m, 1C, one of ipso *C*), 137.56 (m, 1C, one of ipso *C*),

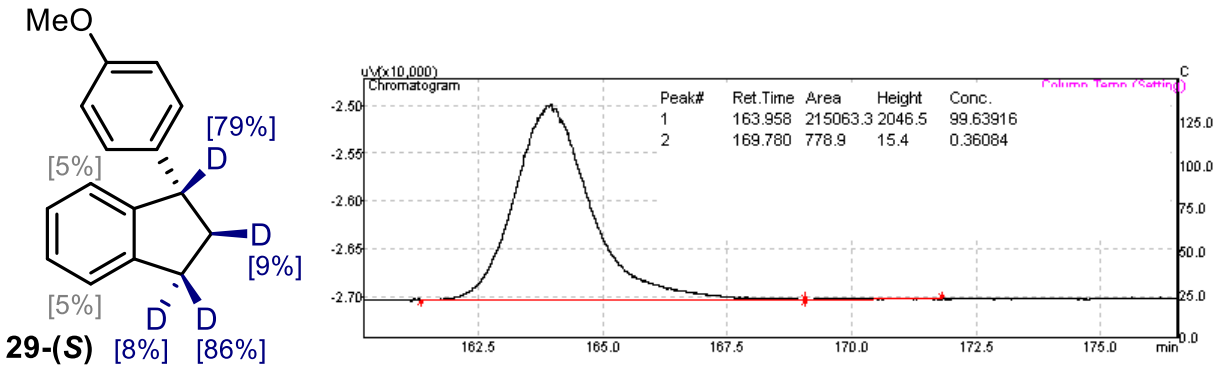
126.04 (m, 1C, 8% labeled, 8-indanyl *C*), 126.43 (m, 1C, 8% labeled, 5-indanyl *C*), 124.43 (obsc m, 1C, 7-indanyl *C*), 124.32 (m, 1C, 6-indanyl *C*, 2° isotopic shift: 14 Hz, 0.08C, ca. 8% D at 5-*C*), 83.36 (s, 2C, 2 x BPin *C*O), 33.32-32.49 (m, 1C, 56% labeled, $^{1}J_{CD}$ = 20 Hz, 3-indanyl benzylic *C*, 2° isotopic shift: 12 Hz), 27.85-26.95 (m, 1C, 34% labeled, $^{1}J_{CD}$ = 20 Hz, homobenzylic *C*), 24.94 (s, 2C, 2 x BPin *C*H_3), 24.78 (s, 2C, 2 x BPin *C*H_3) ppm; one benzylic carbon resonance (attached to boron) was not observed.



29-(*rac*)

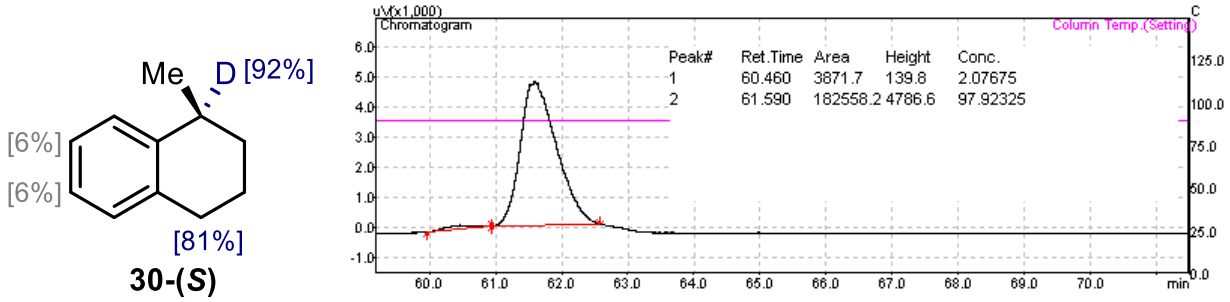
(*rac*) 1-(4′-methoxyphenyl)indan 29-(*rac*). Labeled with deuterium according to General Procedure B using 0.123 g (0.55 mmol) of racemic arylindan substrate. Eluted with hexanes, yielding 0.110 g of recovered material following evaporation of solvent. An approximately 7% impurity in the recovered substrate was identified as free ^{iPr}DI ligand by NMR spectroscopy. From these data, the recovery of labeled **22** was determined to be 79%. *syn*- and *anti*-to-*Ar* proton resonances assigned in analogy to the previously assigned (by 2D NMR spectroscopy) resonances in 1-phenylindan.[4] ^{1}H NMR (500 MHz, chloroform-*d*, 23 °C) δ 7.30 (d, 7% labeled, $^{3}J_{HH}$ = 7.3 Hz, 0.93H, 8-indanyl C*H*), 7.20 (app t, $^{3}J_{HH}$ = 7.1 Hz, 7-indanyl C*H*), 7.17-7.10 (m, 3H, 6-indanyl C*H* and 2 x *Ar* C*H*), 6.98 (d, 7% labeled, $^{3}J_{HH}$ = 7.4 Hz, 0.93H, 5-indanyl C*H*), 6.90-6.84 (app d, $^{3}J_{HH}$ = 8.1 Hz, 2H, 2 x *Ar* C*H*), 4.31 (t, 90% labeled, $^{3}J_{HH}$ = 8.3 Hz, 0.10H, 1-indanyl benzylic C*H*), 3.80 (s, 3H, OCH_3), 3.03 (app d, 12% labeled, $^{3}J_{HH}$ = 7.7 Hz,

0.88H, *syn*-to-*Ar* 3-indanyl benzylic C*H*), 2.95 (dt, 90% labeled, $^{3}J_{HH}$ = 15.9, 8.4 Hz, 0.10H, *anti*-to-*Ar* 3-indanyl benzylic C*H*), 2.61-2.50 (m, 12% labeled, 0.88H, *anti*-to-*Ar* 2-indanyl homobenzylic C*H*), 2.03 (app dd, $^{3}J_{HH}$ = 12.2, 8.7 Hz, 1H, *syn*-to-*Ar* 2-indanyl homobenzylic C*H*) ppm. Quantitative $^{13}C\{^{1}H\}$ NMR (126 MHz, chloroform-*d*, 23 °C) δ 158.20 (s, 1C, *C*OCH_3), 147.23 (m, 1C, one of ipso *C*), 144.28 (m, 1C, one of ipso *C*), 137.56 (m, 1C, one of ipso *C*), 129.09 (s, 2C, 2 x *Ar C*H), 126.57 (obsc m, 1C, 7% labeled, 8-indanyl *C*), 126.43 (m, 1C, 7% labeled, 5-indanyl *C*), 124.96 (m, 1C, 7-indanyl *C*, 2° isotopic shift: 14 Hz, 0.07C, ca. 7% D at 8-*C*), 124.44 (m, 1C, 6-indanyl *C*, 2° isotopic shift: 14 Hz, 0.07C, ca. 7% D at 5-*C*), 113.93 (s, 2C, 2 x *Ar C*H), 55.31 (s, 1C, OCH_3), 51.28-49.76 (m, 1C, labeled, $^{1}J_{CD}$ = 20 Hz, 1-indanyl benzylic *C*, 2° isotopic shift: 11 Hz), 37.04-35.85 (m, 1C, labeled, homobenzylic *C*), 32.09-31.05 (m, 1C, labeled $^{1}J_{CD}$ = 20 Hz, 3-indanyl benzylic *C*, 2° isotopic shift: 12 Hz) ppm.



(*S*) 1-(4′-methoxyphenyl)indan 29-(*S*). Labeled with deuterium according to General Procedure B using 0.123 g (0.55 mmol) of (*S*) arylindan substrate (>98% ee). Eluted with hexanes, yielding 0.141 g of recovered material following evaporation of solvent. An approximately 7% impurity in the recovered substrate was identified as free ^{iPr}DI ligand by NMR spectroscopy. From these data, the recovery of labeled **22** was determined to be quantitative. *syn*- and *anti*-to-*Ar* proton resonances assigned in

analogy to the previously assigned (by 2D NMR spectroscopy) resonances in 1-phenylindan.[4] ^{1}H NMR (500 MHz, chloroform-*d*, 23 °C) δ 7.30 (d, 5% labeled, $^{3}J_{HH}$ = 7.3 Hz, 0.95H, 8-indanyl C*H*), 7.20 (app t, $^{3}J_{HH}$ = 7.1 Hz, 7-indanyl C*H*), 7.17-7.10 (m, 3H, 6-indanyl C*H* and 2 x *Ar* C*H*), 6.98 (d, 5% labeled, $^{3}J_{HH}$ = 7.4 Hz, 0.95H, 5-indanyl C*H*), 6.90-6.84 (app d, $^{3}J_{HH}$ = 8.1 Hz, 2H, 2 x *Ar* C*H*), 4.31 (t, 79% labeled, $^{3}J_{HH}$ = 8.3 Hz, 0.21H, 1-indanyl benzylic C*H*), 3.80 (s, 3H, OCH_3), 3.03 (app d, 8% labeled, $^{3}J_{HH}$ = 7.7 Hz, 0.92H, *syn*-to-*Ar* 3-indanyl benzylic C*H*), 2.95 (dt, 86% labeled, $^{3}J_{HH}$ = 15.9, 8.4 Hz, 0.14H, *anti*-to-*Ar* 3-indanyl benzylic C*H*), 2.61-2.50 (m, 9% labeled, 0.91H, *anti*-to-*Ar* 2-indanyl homobenzylic C*H*), 2.03 (app dd, $^{3}J_{HH}$ = 12.2, 8.7 Hz, 1H, *syn*-to-*Ar* 2-indanyl homobenzylic C*H*) ppm. Quantitative ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, 23 °C) δ 158.18 (s, 1C, *C*OCH_3), 147.22 (m, 1C, one of ipso *C*), 144.25 (m, 1C, one of ipso *C*), 137.54 (m, 1C, one of ipso *C*), 129.07 (s, 2C, 2 x *Ar C*H), 126.55 (obsc m, 1C, 5% labeled, 8-indanyl *C*), 126.43 (m, 1C, 5% labeled, 5-indanyl *C*), 124.94 (m, 1C, 7-indanyl *C*, 2° isotopic shift: 14 Hz, 0.05C, ca. 5% D at 8-*C*), 124.43 (m, 1C, 6-indanyl *C*, 2° isotopic shift: 14 Hz, 0.05C, ca. 5% D at 5-*C*), 113.92 (s, 2C, 2 x *Ar C*H), 55.27 (s, 1C, O*C*H_3), 51.28-49.76 (m, 1C, labeled, $^{1}J_{CD}$ = 20 Hz, 1-indanyl benzylic *C*, 2° isotopic shift: 11 Hz), 37.04-35.85 (m, 1C, labeled, homobenzylic *C*), 32.09-31.05 (m, 1C, labeled, $^{1}J_{CD}$ = 20 Hz, 3-indanyl benzylic *C*, 2° isotopic shift: 12 Hz) ppm. Chiral separation and enantiomer assignment was achieved using chiral GC according to the reported[4] isothermal method: hold at 160 ºC for 180 minutes; ramp 20 ºC per minute, hold at 200 ºC for 6 minutes. Starting material ee: >98% (*S*); ee of recovered material: >98% (*S*). Enantiospecificity: >98% es.



(*S*)-1-methyltetralin 30-(*S*). Labeled with deuterium according to General Procedure B using 0.080 g (0.55 mmol) of (*S*)-1-methyltetralin (92% ee). Eluted with hexanes, yielding 0.069 g (84%) of recovered material following evaporation of solvent. ^{1}H NMR (500 MHz, chloroform-*d*, 23 °C) δ 7.27-7.21 (m, 1H, 9-C*H*), 7.21-7.06 (m, 6% labeled at 7-tetralin C*H* and 6% at 8-tetralin C*H,* 2.88H, 6-8 tetralin positions C*H*), 3.01-2.88 (m, 92% labeled, 0.08H, 1-tetralin benzylic C*H*), 2.87-2.70 (m, 81% labeled, 0.38H, 4-tetralin benzylic CH_2; diastereotopic protons not distinguished), 2.02-1.83 (m, 2H, two of homobenzylic methylene protons), 1.82-1.70 (m, 1H, one of homobenzylic methylene protons), 1.63-1.52 (m, 1H, one of homobenzylic methylene protons), 1.33 (s, 3H, chiral C(D)CH_3) ppm. Quantitative ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, 23 °C) δ 142.25 (m, 1C, one of ipso *C*), 136.87 (m, 1C, one of ipso *C*), 129.12 (m, 1C, 9-tetralin *C*, 2° isotopic shift: 14 Hz, 0.06C, ca. 6% D at 8-tetralin *C*), 128.20 (m, 1C, 6-tetralin *C*, 2° isotopic shift: 14 Hz, 0.06C, ca. 6% D at 7-tetralin *C*), 125.73 (m, 1C, one of 7- or 8-tetralin *C*), 32.70-31.82 (m, 1C, 92% labeled, $^{1}J_{CD}$ = 20 Hz, 1-tetralin benzylic *C*), 31.56-31.32 (m, 1C, 2-tetralin *C*, 2° isotopic shift (3-bond): 6.0 Hz), 30.19-28.94 (m, 1C, 81% labeled, $^{1}J_{CD}$ = 19 Hz, 4-tetralin benzylic *C*), 22.91 (m, 1C, homobenzylic chiral *C*), 20.59-20.01 (m, 1C, 3-tetralin *C*, 2° isotopic shift: 18 Hz) ppm. Chiral separation and enantiomer assignment was achieved using chiral GC according to the reported[4]

isothermal method: hold at 90 ºC for 75 minutes; ramp 20 ºC per minute, hold at 200 ºC for 6 minutes. Starting material ee: 92% (*S*); ee of recovered material: ~92% (*S*); chiral separation deteriorated following deuteration reaction, but ee did not appear to erode. Enantiospecificity: >98% es.

VII. Additional Spectroscopic Data.

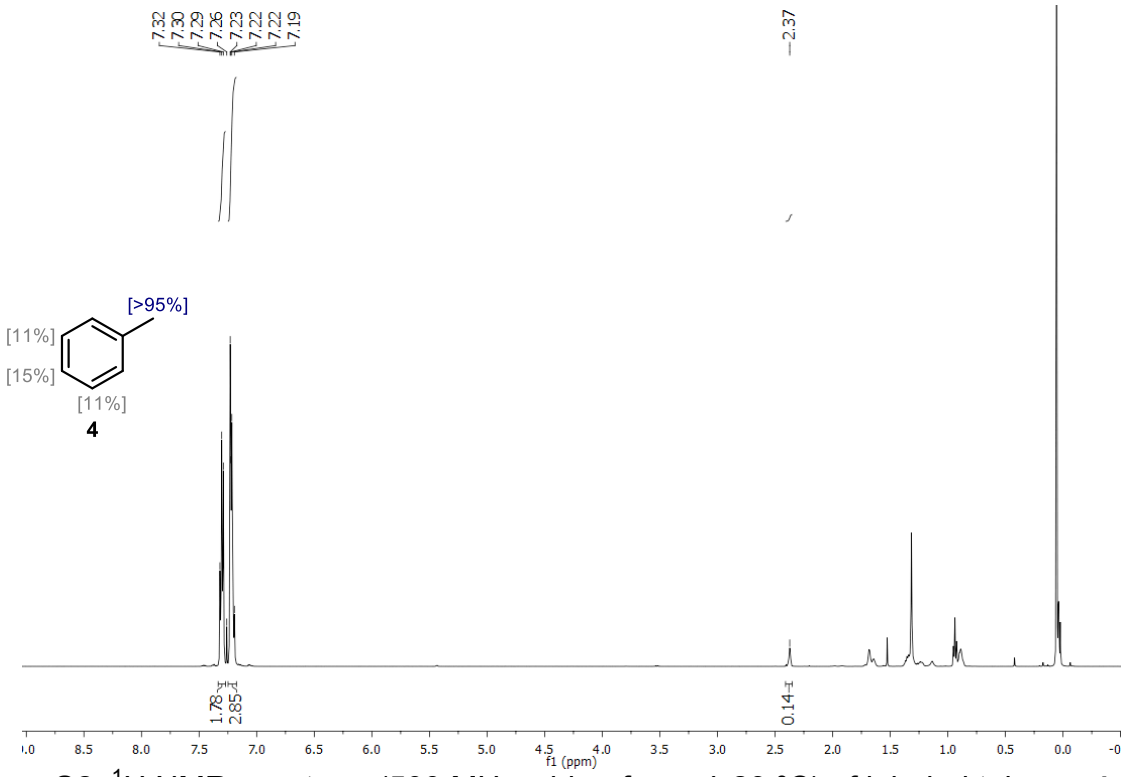


Figure S2. ^{1}H NMR spectrum (500 MHz, chloroform-*d*, 23 ºC) of labeled toluene **4**. Dodecane, TMS-d_1, and reduced arene also present.

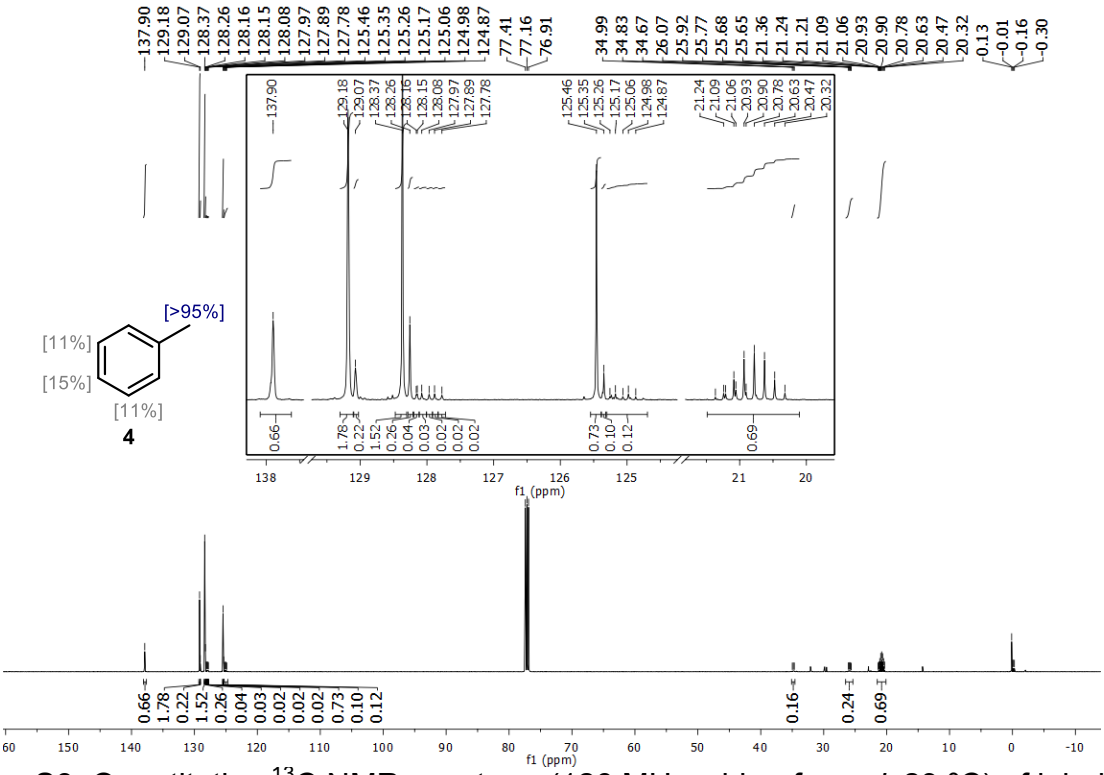


Figure S3. Quantitative ^{13}C NMR spectrum (126 MHz, chloroform-*d*, 23 ºC) of labeled toluene **4**. Dodecane, TMS-d_1, and reduced arene also present. Inset spectrum highlights signals of **4**.

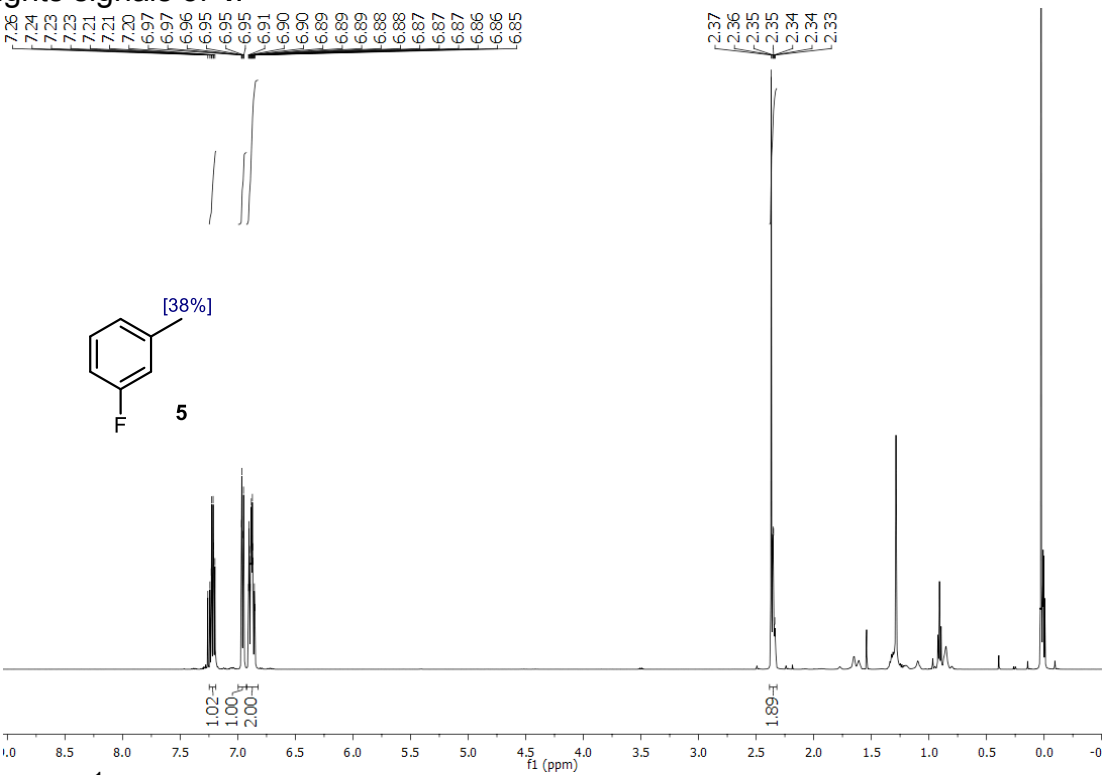


Figure S4. ^{1}H NMR spectrum (500 MHz, chloroform-*d*, 23 ºC) of labeled 3-fluorotoluene **5**. Dodecane, TMS-d_1, and reduced arene also present.

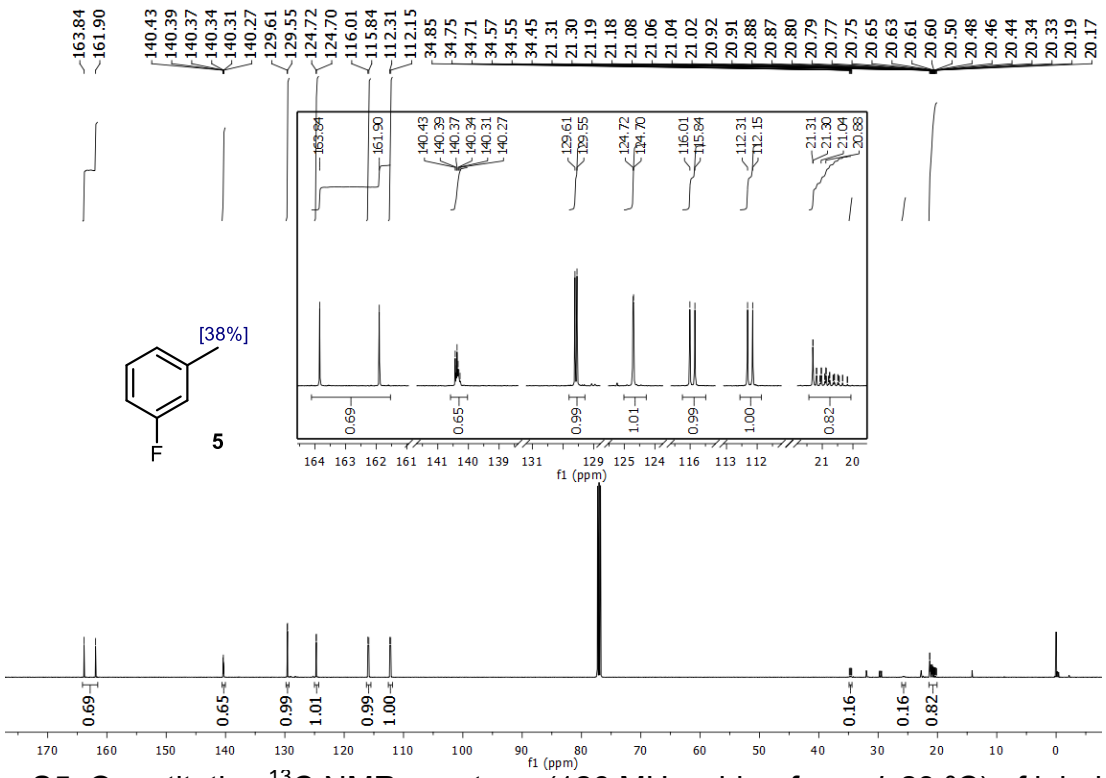


Figure S5. Quantitative ^{13}C NMR spectrum (126 MHz, chloroform-*d*, 23 ºC) of labeled 3-fluorotoluene **5**. Dodecane, TMS-d_1, and reduced arene also present. Inset spectrum highlights signals of **5**.

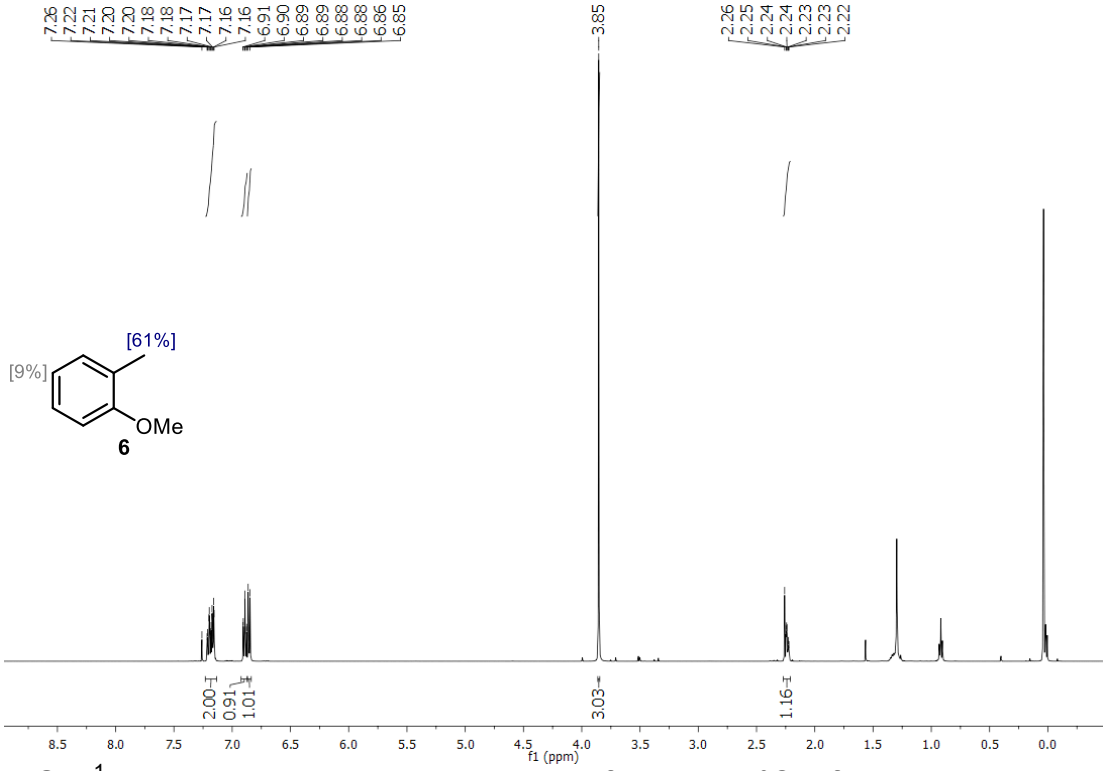


Figure S6. ^{1}H NMR spectrum (500 MHz, chloroform-*d*, 23 ºC) of labeled 2-methylanisole **6**. Dodecane and TMS-d_1 also present.

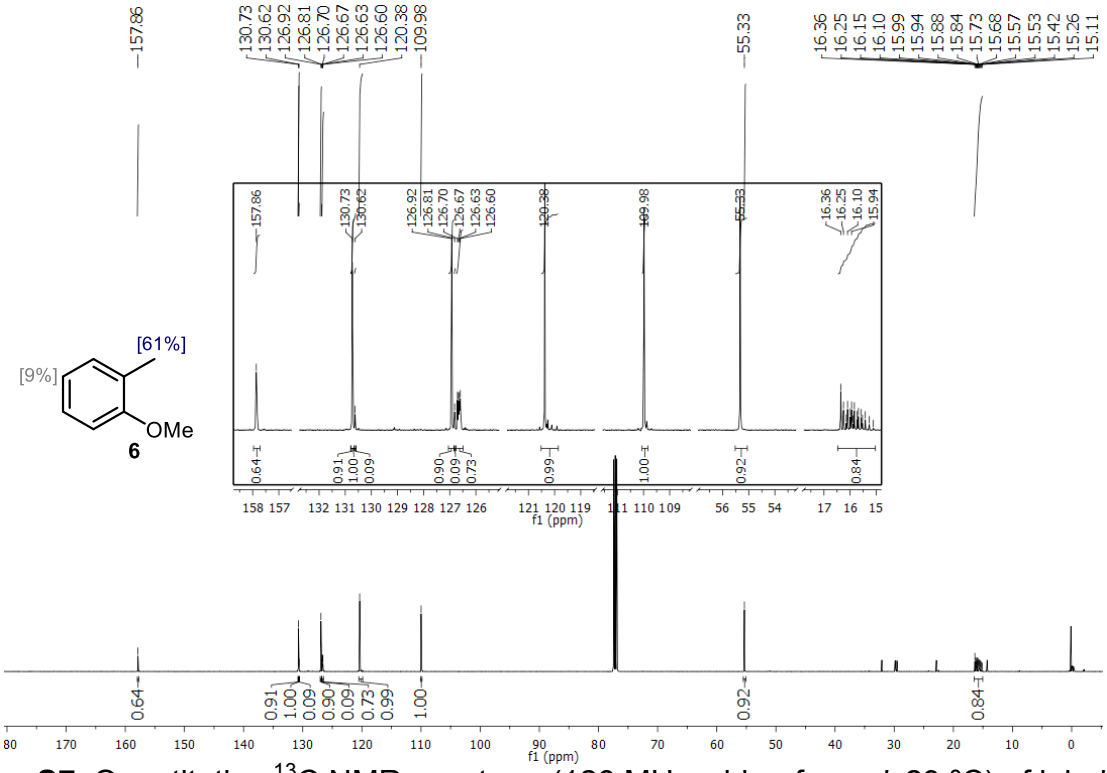


Figure S7. Quantitative ^{13}C NMR spectrum (126 MHz, chloroform-*d*, 23 ºC) of labeled 2-methylanisole **6**. Dodecane and TMS-d_1 also present. Inset spectrum highlights signals of **6**.

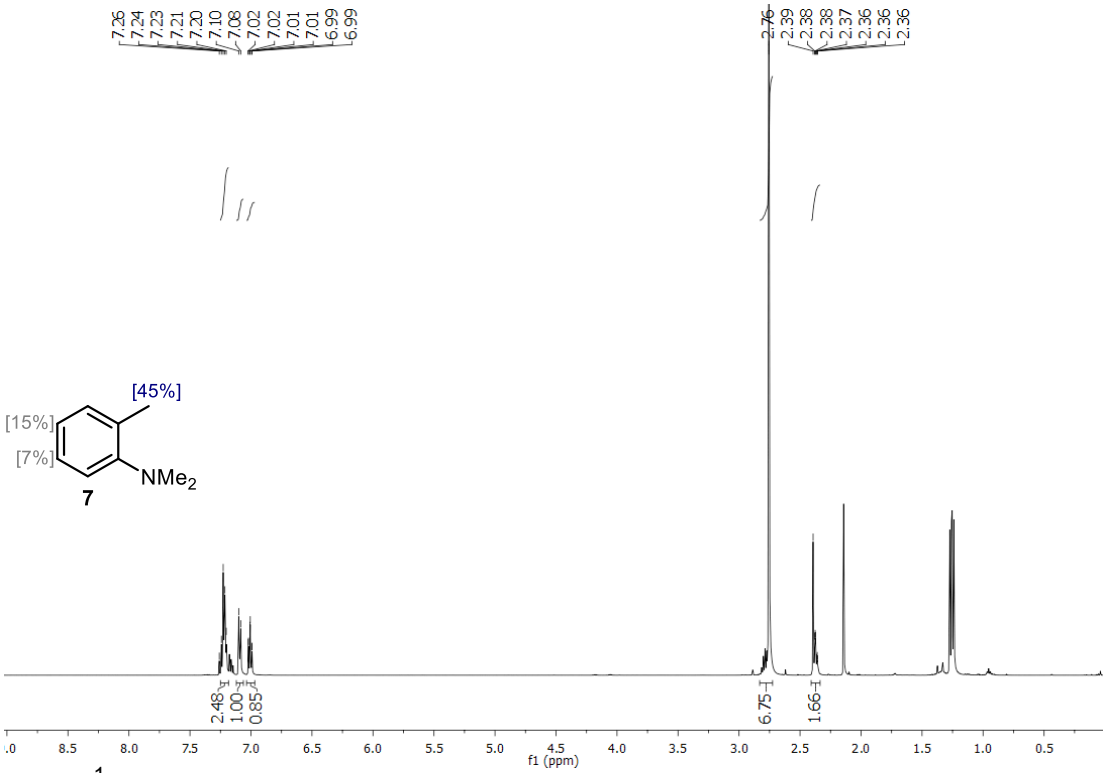


Figure S8. ^{1}H NMR spectrum (500 MHz, chloroform-*d*, 23 ºC) of labeled *N,N*-dimethyl-*o*-toluidine **7**. Free ^{iPr}DI ligand also present.

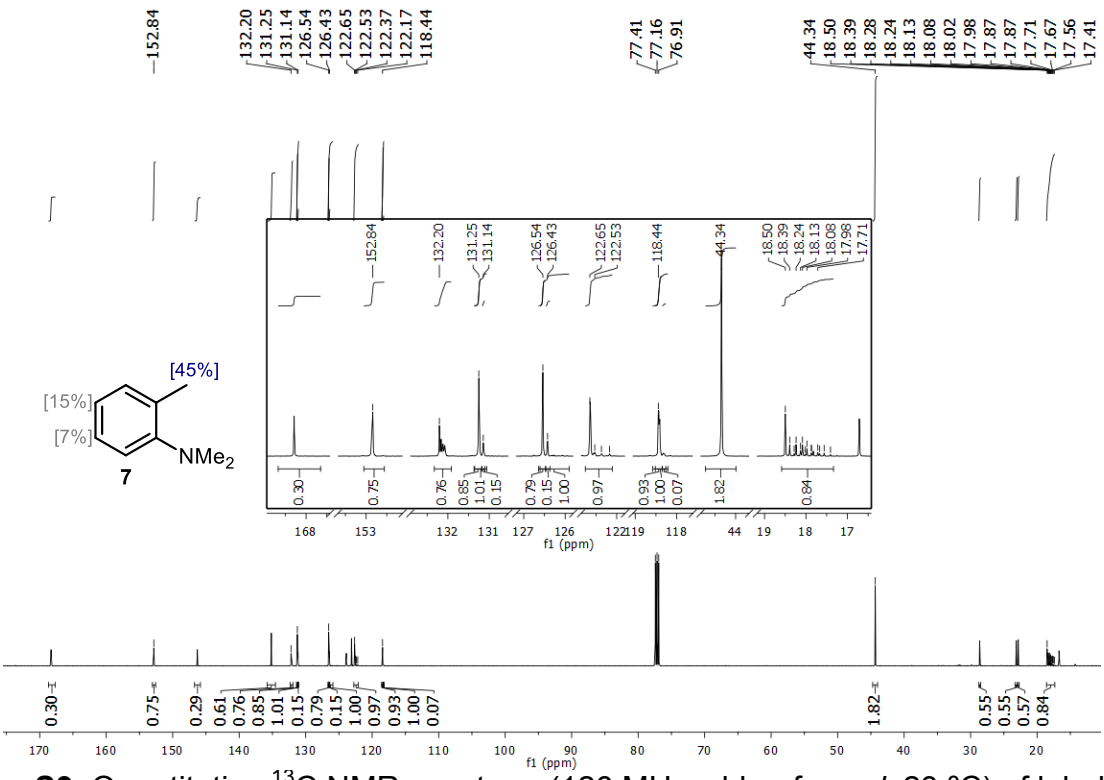


Figure S9. Quantitative ^{13}C NMR spectrum (126 MHz, chloroform-*d*, 23 ºC) of labeled *N,N*-dimethyl-*o*-toluidine **7**. Free ^{iPr}DI ligand also present. Inset spectrum highlights signals of **7**.

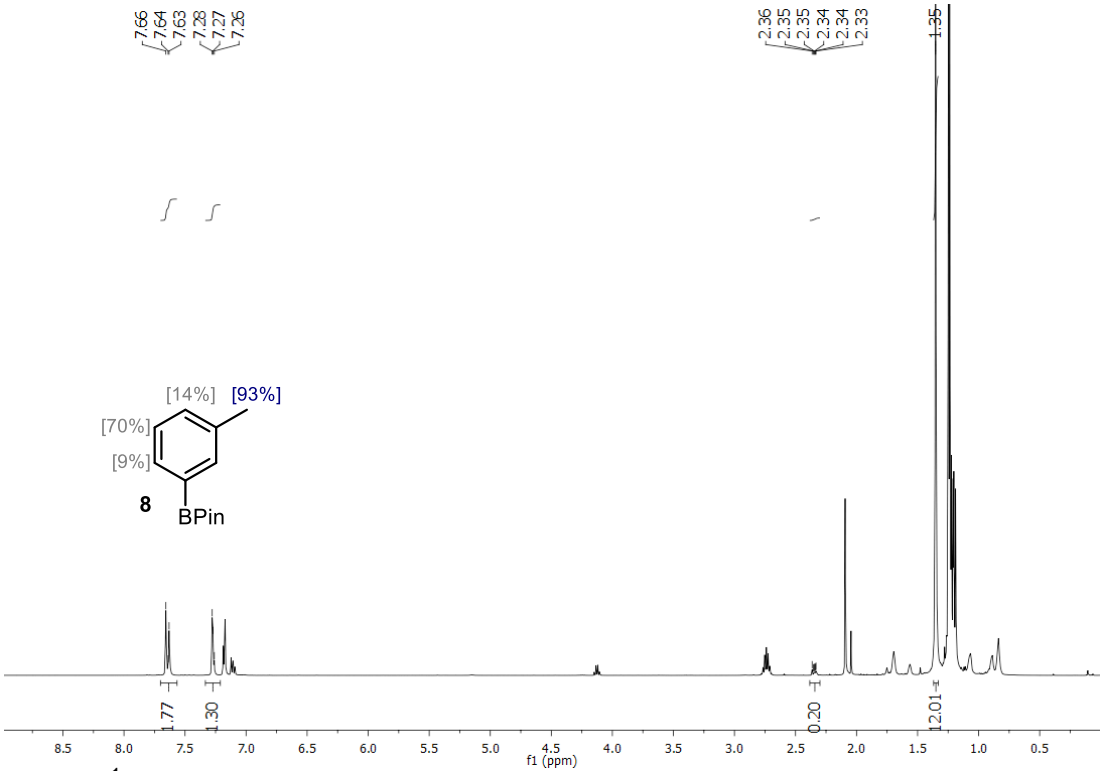


Figure S10. ^{1}H NMR spectrum (500 MHz, chloroform-*d*, 23 ºC) of labeled *m*-tolylboronic acid pinacol ester **8**. Ethyl acetate, ^{iPr}DI ligand, and reduced arene present.

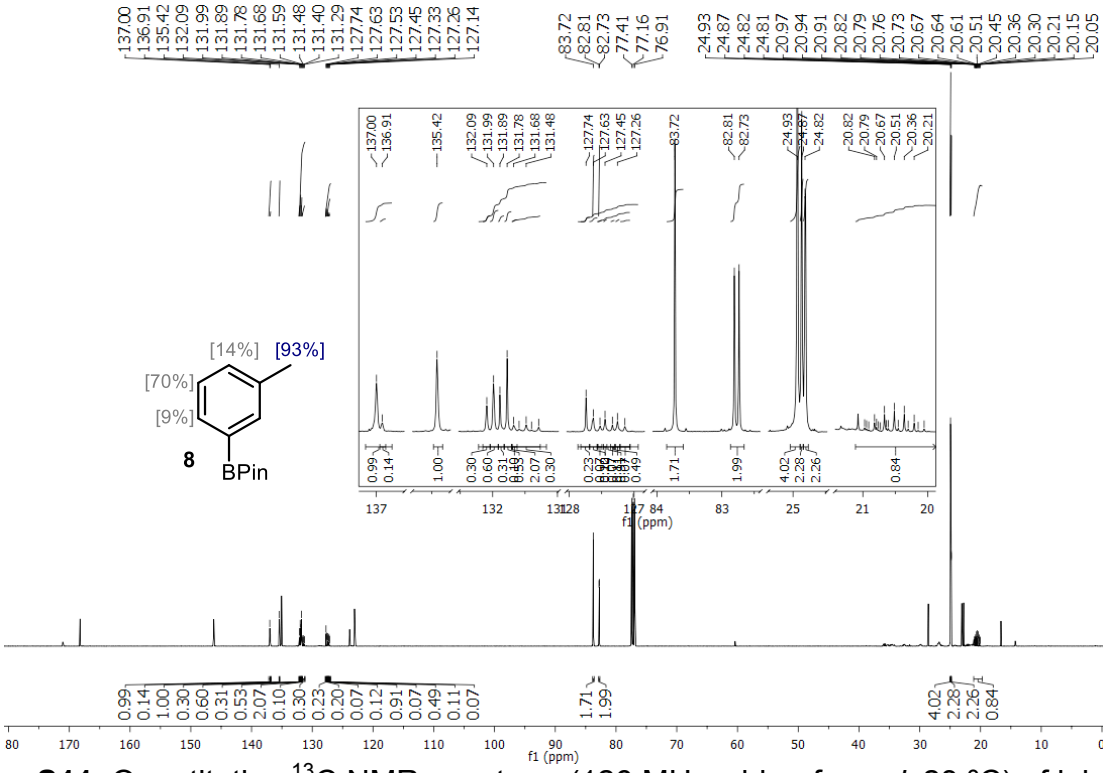


Figure S11. Quantitative ^{13}C NMR spectrum (126 MHz, chloroform-*d*, 23 ºC) of labeled *m*-tolylboronic acid pinacol ester **8**. Ethyl acetate, ^{iPr}DI ligand, and reduced arene also present. Inset spectrum highlights signals of **8**.

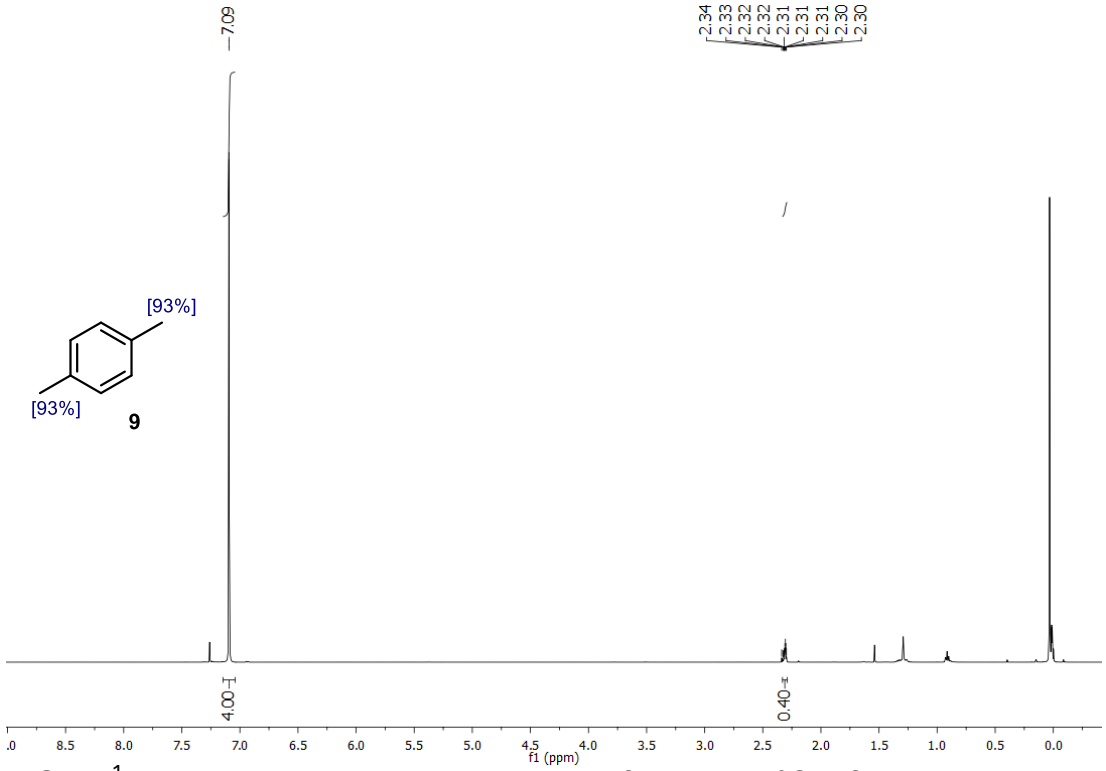


Figure S12. ^{1}H NMR spectrum (500 MHz, chloroform-*d*, 23 ºC) of labeled *p*-xylene **9**. Dodecane and TMS-d_1 also present.

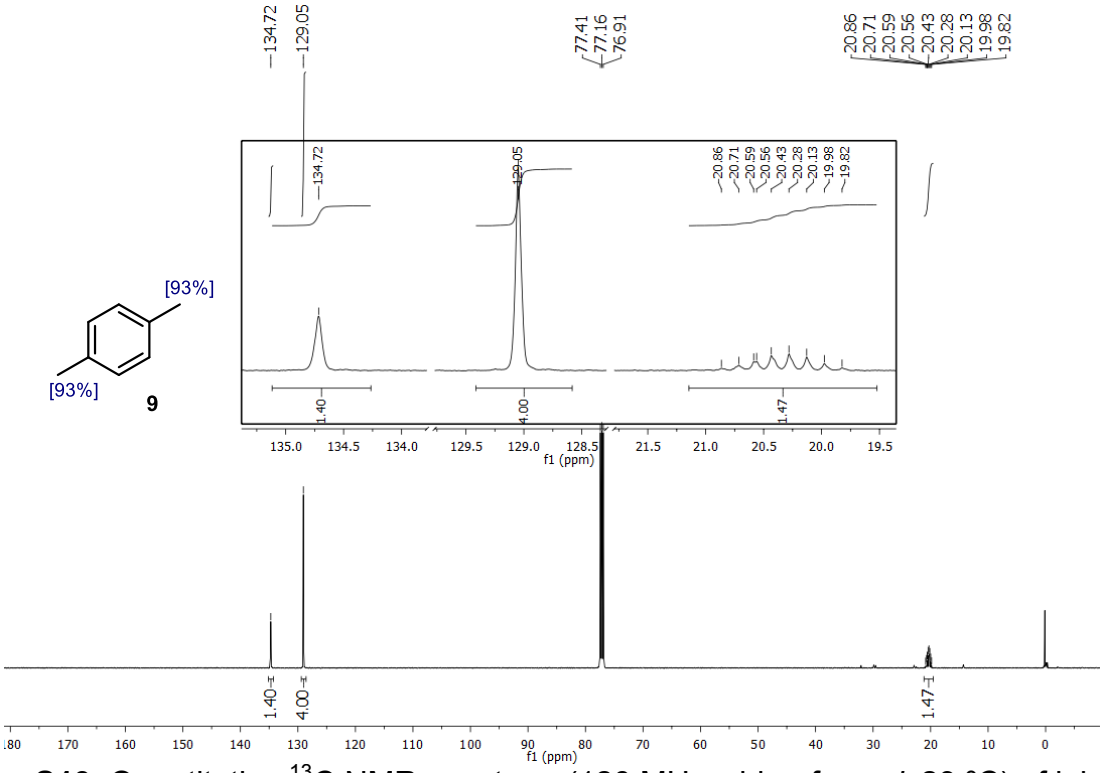


Figure S13. Quantitative ^{13}C NMR spectrum (126 MHz, chloroform-*d*, 23 ºC) of labeled *p*-xylene **9**. Dodecane and TMS-d_1 also present. Inset spectrum highlights signals of **9**.

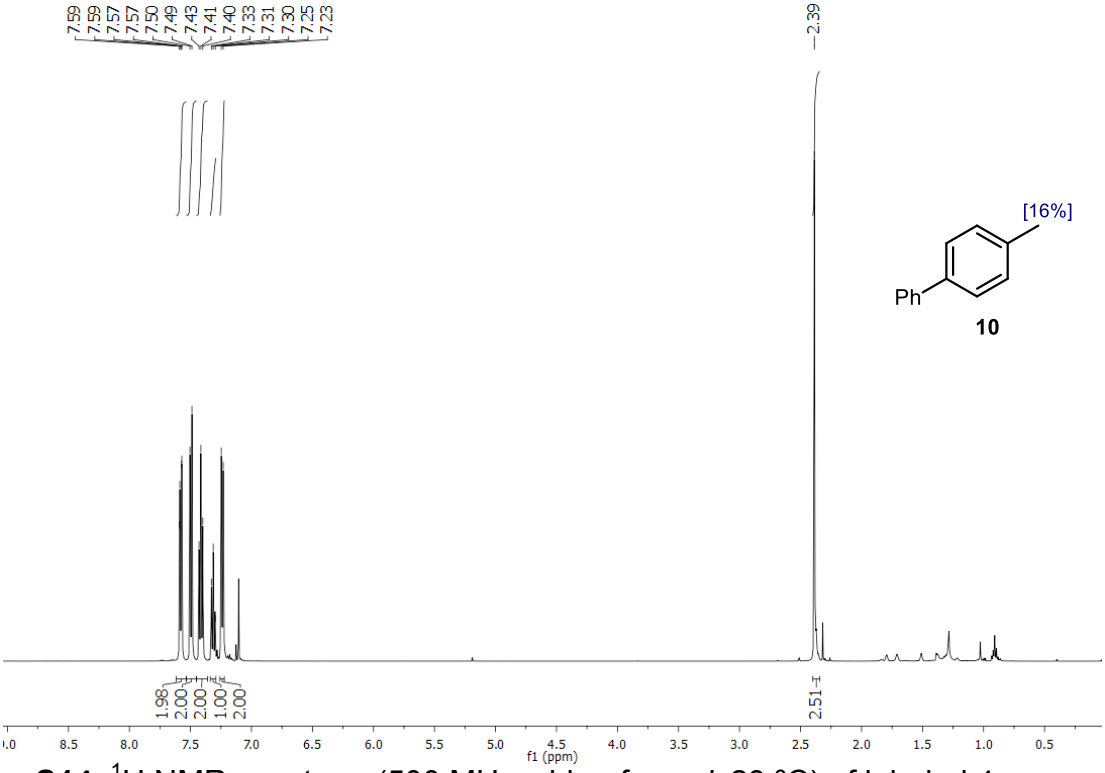


Figure S14. ^{1}H NMR spectrum (500 MHz, chloroform-*d*, 23 ºC) of labeled 4-phenyltoluene **10**. Reduced arene and hexanes also present.

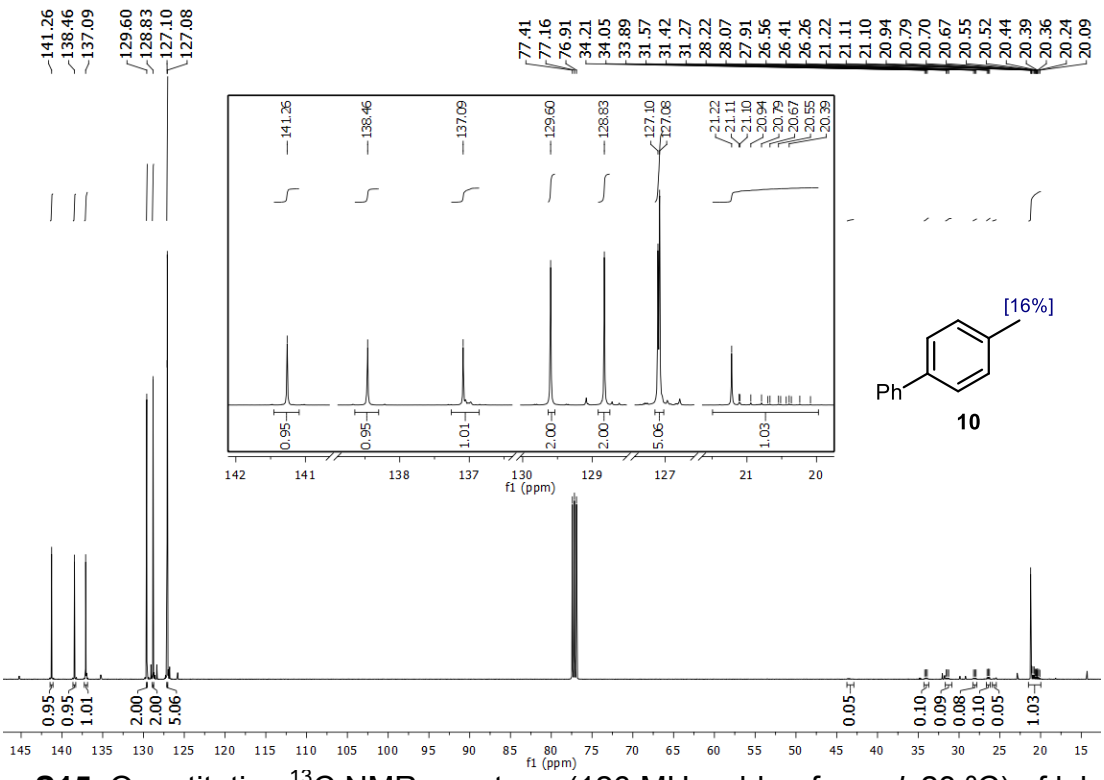


Figure S15. Quantitative ^{13}C NMR spectrum (126 MHz, chloroform-*d*, 23 ºC) of labeled 4-phenyltoluene **10**. Reduced arene and hexanes also present. Inset spectrum highlights signals of **10**.

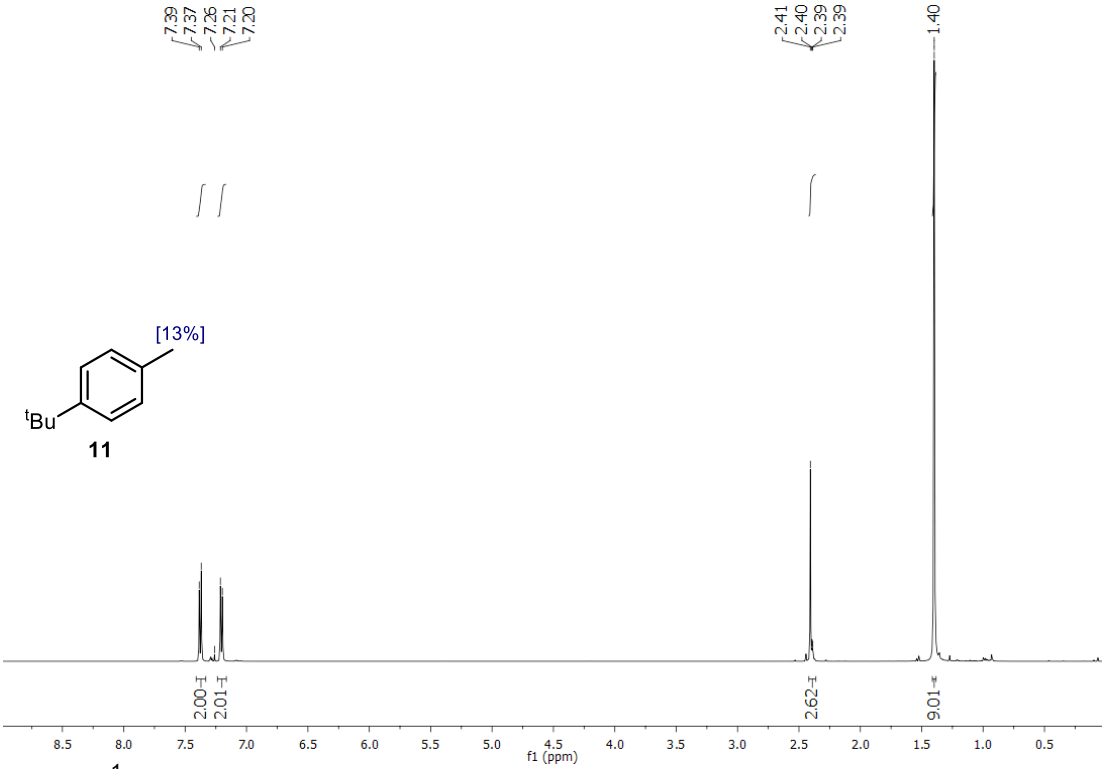


Figure S16. ^{1}H NMR spectrum (500 MHz, chloroform-*d*, 23 ºC) of labeled 4-*tert*-butyltoluene **11**.

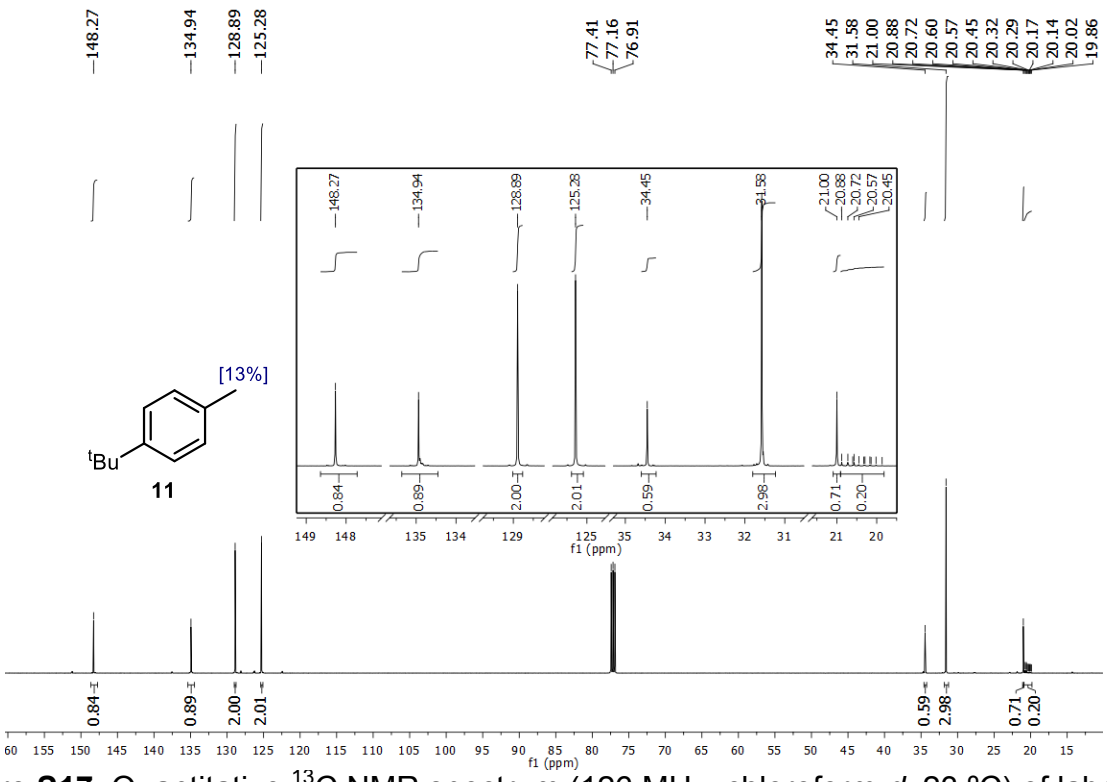


Figure S17. Quantitative ^{13}C NMR spectrum (126 MHz, chloroform-*d*, 23 ºC) of labeled 4-*tert*-butyltoluene **11**. Inset spectrum highlights signals of **11**.

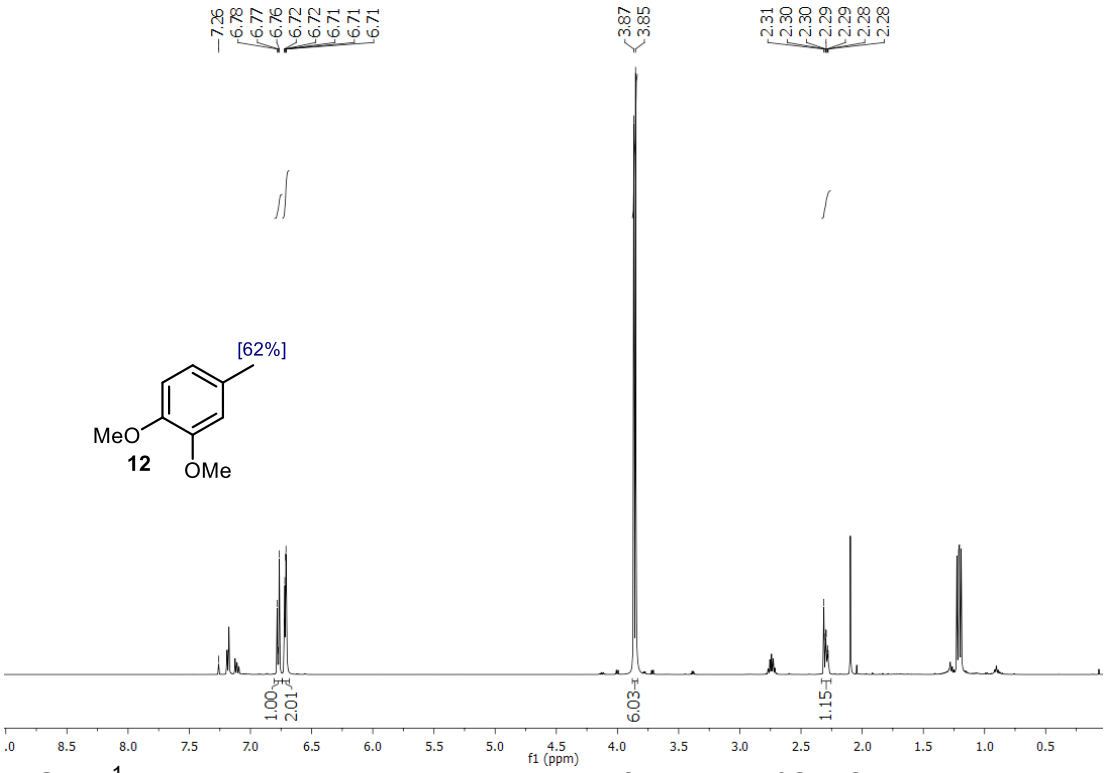


Figure S18. ^{1}H NMR spectrum (500 MHz, chloroform-*d*, 23 ºC) of labeled 3,4-dimethoxytoluene **12**. Free ^{iPr}DI ligand also present.

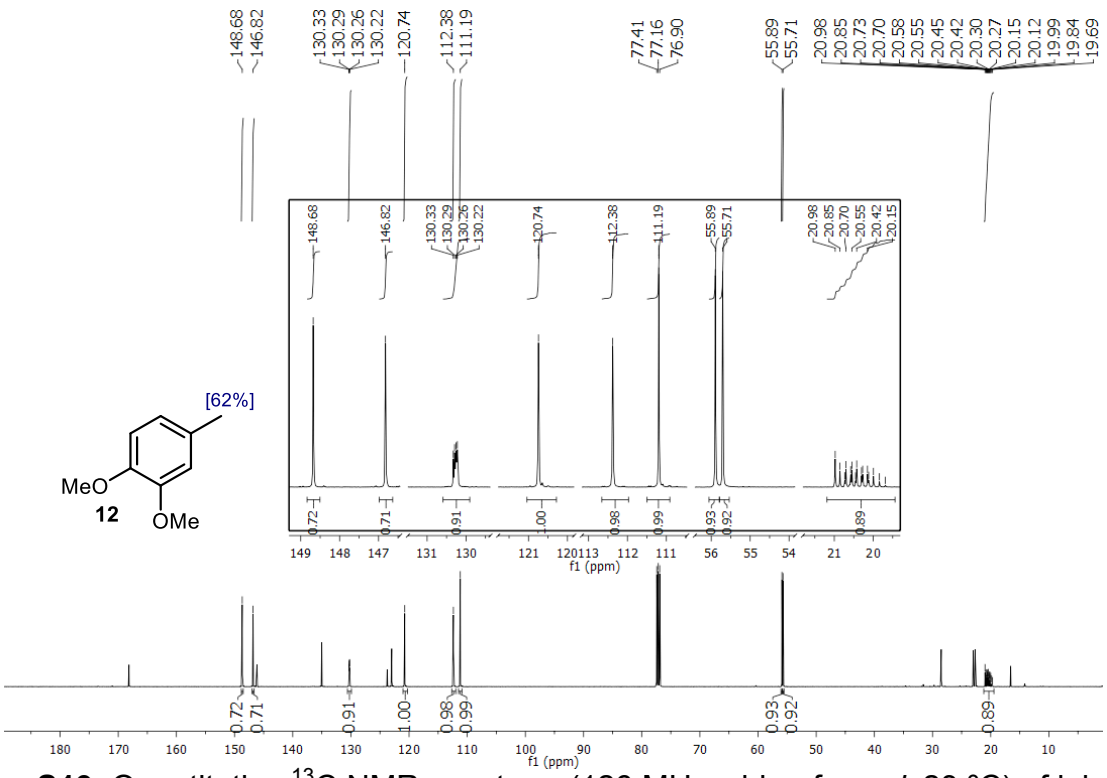


Figure S19. Quantitative ^{13}C NMR spectrum (126 MHz, chloroform-*d*, 23 ºC) of labeled 3,4-dimethoxytoluene **12**. Free ^{iPr}DI ligand also present. Inset spectrum highlights signals of **12**.

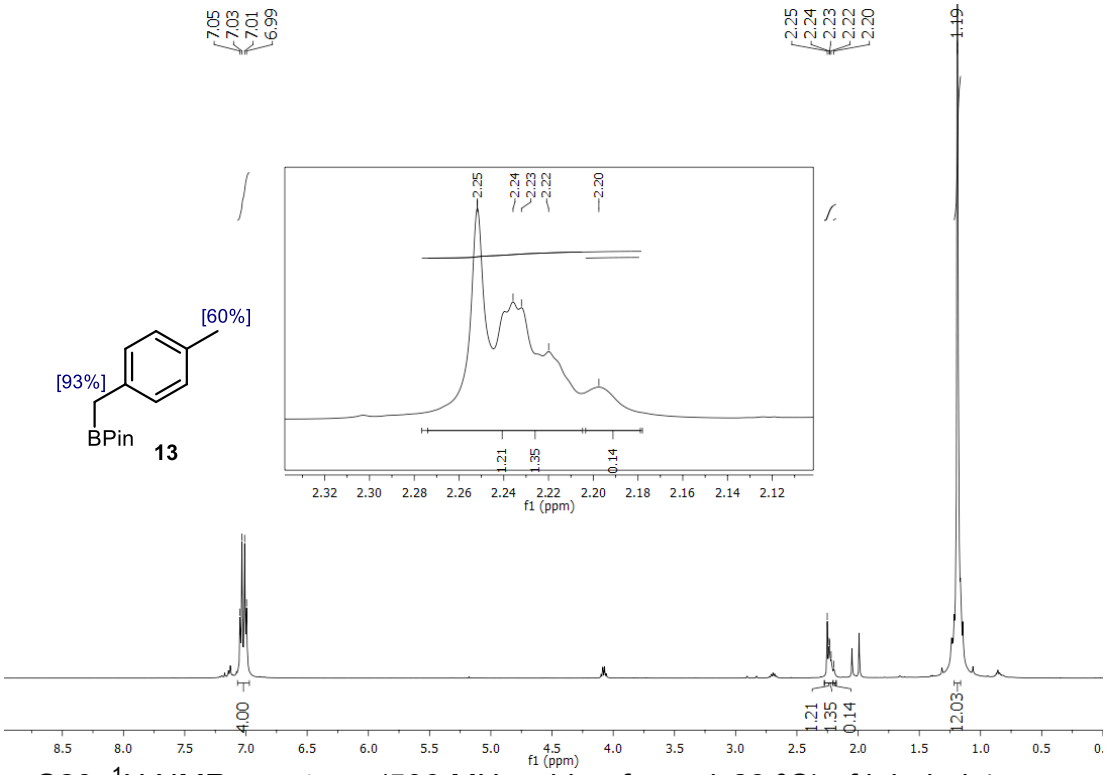


Figure S20. ^{1}H NMR spectrum (500 MHz, chloroform-*d*, 23 ºC) of labeled 4-methylbenzylboronic acid pinacol ester **13**. Free ^{iPr}DI ligand and ethyl acetate present.

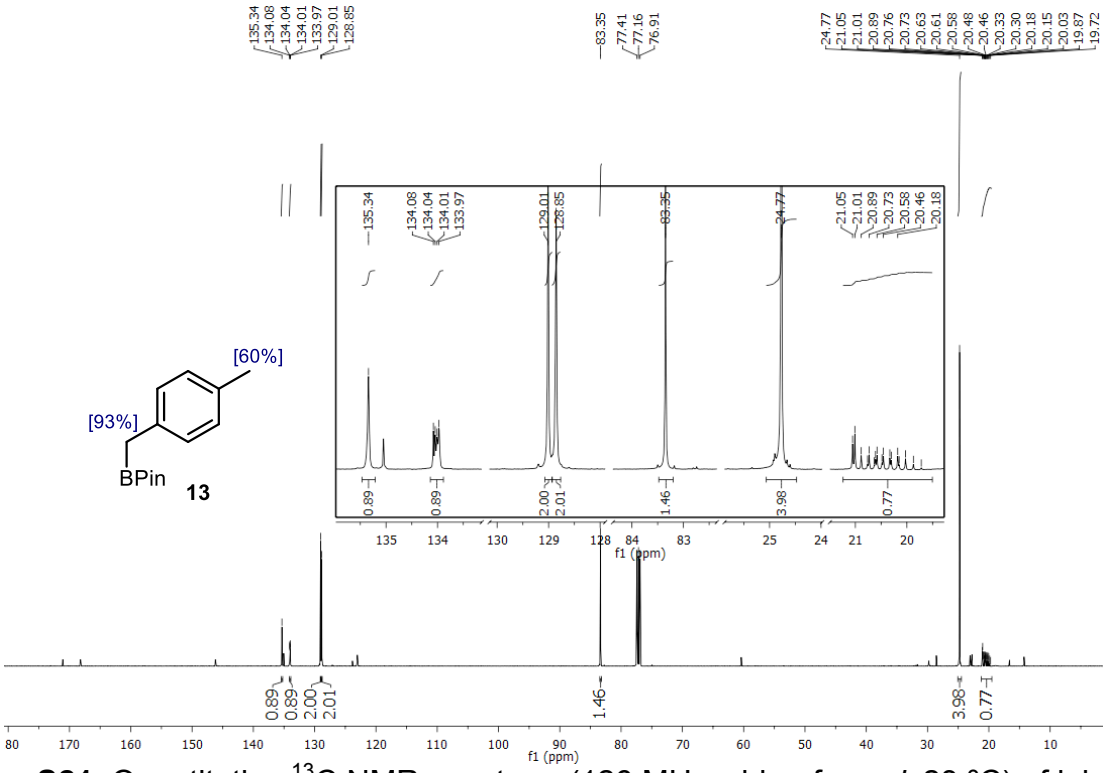


Figure S21. Quantitative ^{13}C NMR spectrum (126 MHz, chloroform-*d*, 23 ºC) of labeled methylbenzylboronic acid pinacol ester **13**. Free ^{iPr}DI ligand and ethyl acetate present. Inset spectrum highlights signals of **13**.

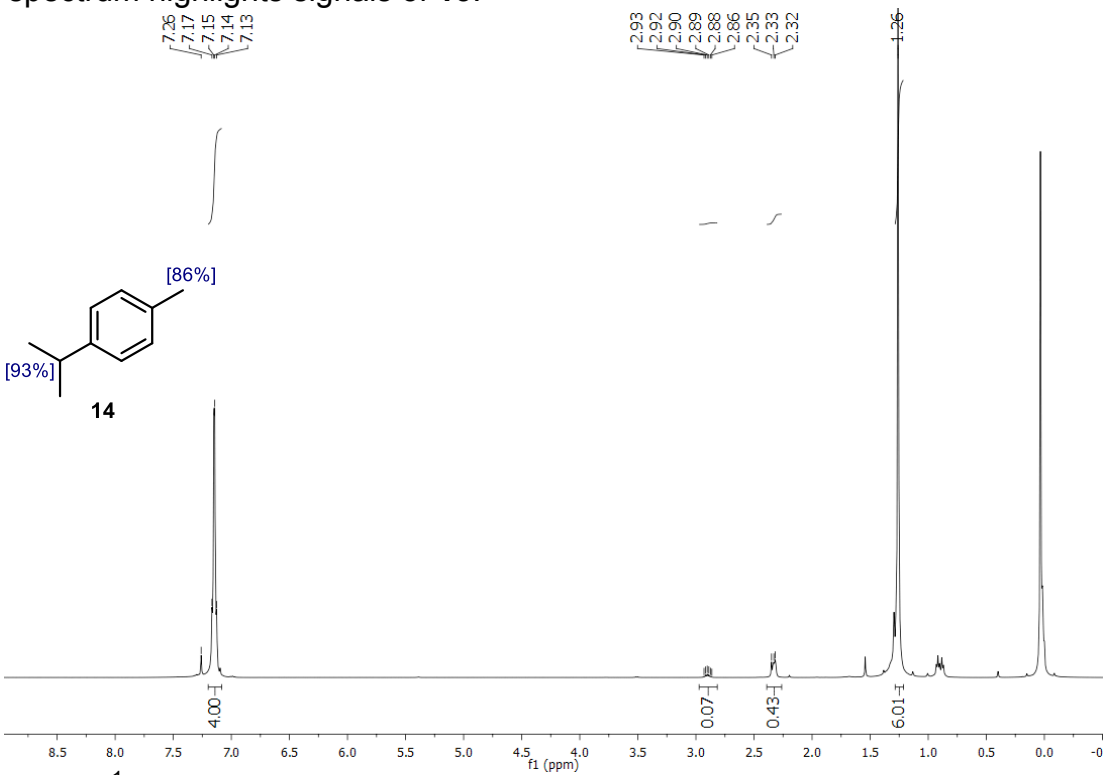


Figure S22. ^{1}H NMR spectrum (500 MHz, chloroform-*d*, 23 ºC) of labeled *p*-cymene **14**. Dodecane and TMS-d_1 also present.

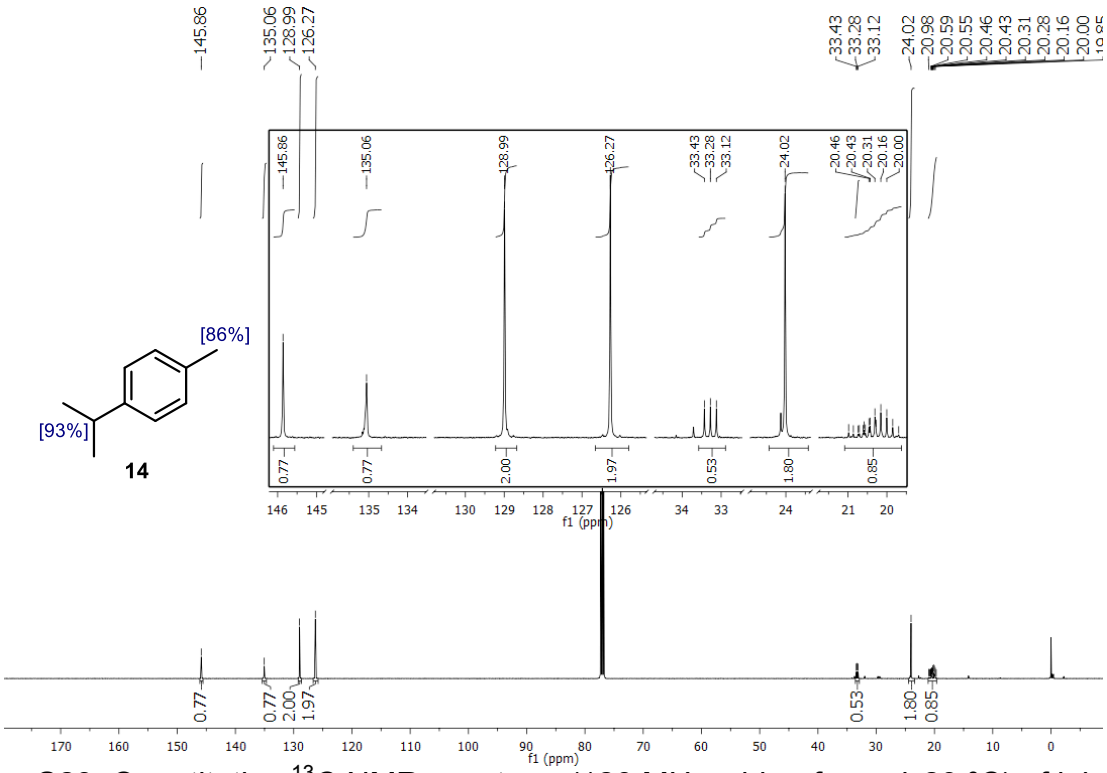


Figure S23. Quantitative ^{13}C NMR spectrum (126 MHz, chloroform-*d*, 23 ºC) of labeled *p*-cymene **14**. Dodecane and TMS-d_1 also present. Inset spectrum highlights signals of **14**.

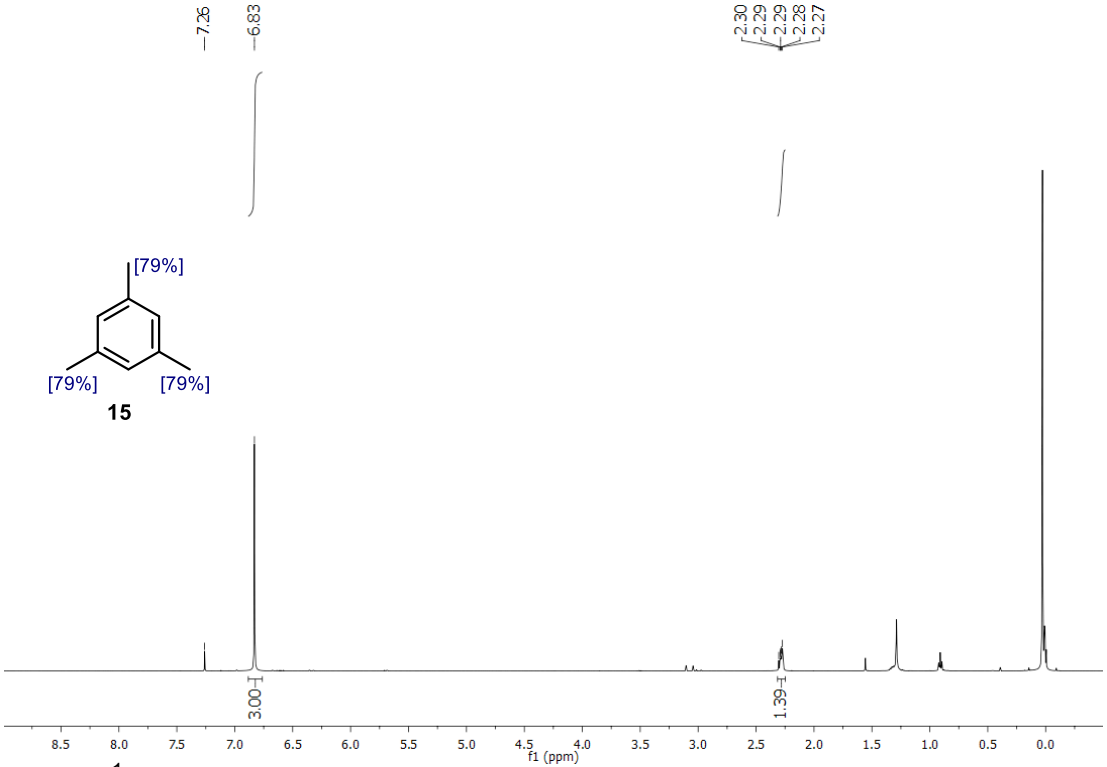


Figure S24. ^{1}H NMR spectrum (500 MHz, chloroform-*d*, 23 ºC) of labeled mesitylene **15**. Dodecane and TMS-d_1 also present.

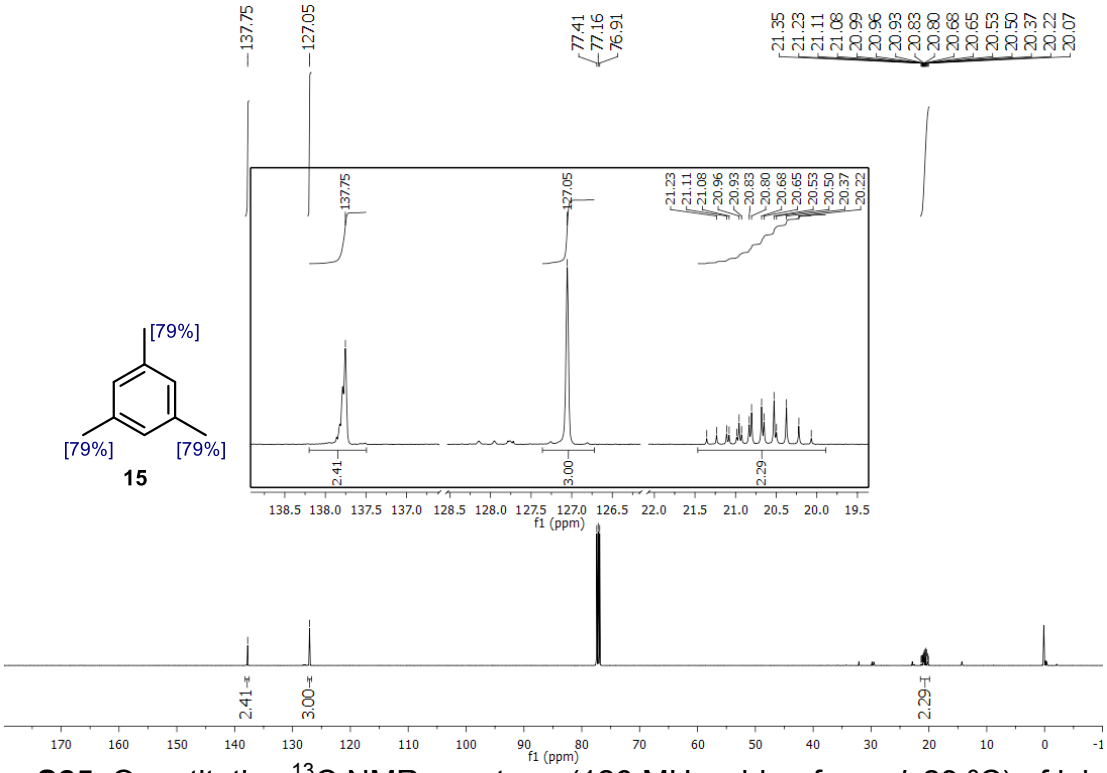


Figure S25. Quantitative ^{13}C NMR spectrum (126 MHz, chloroform-*d*, 23 ºC) of labeled mesitylene **15**. Dodecane and TMS-d_1 also present. Inset spectrum highlights signals of **15**.

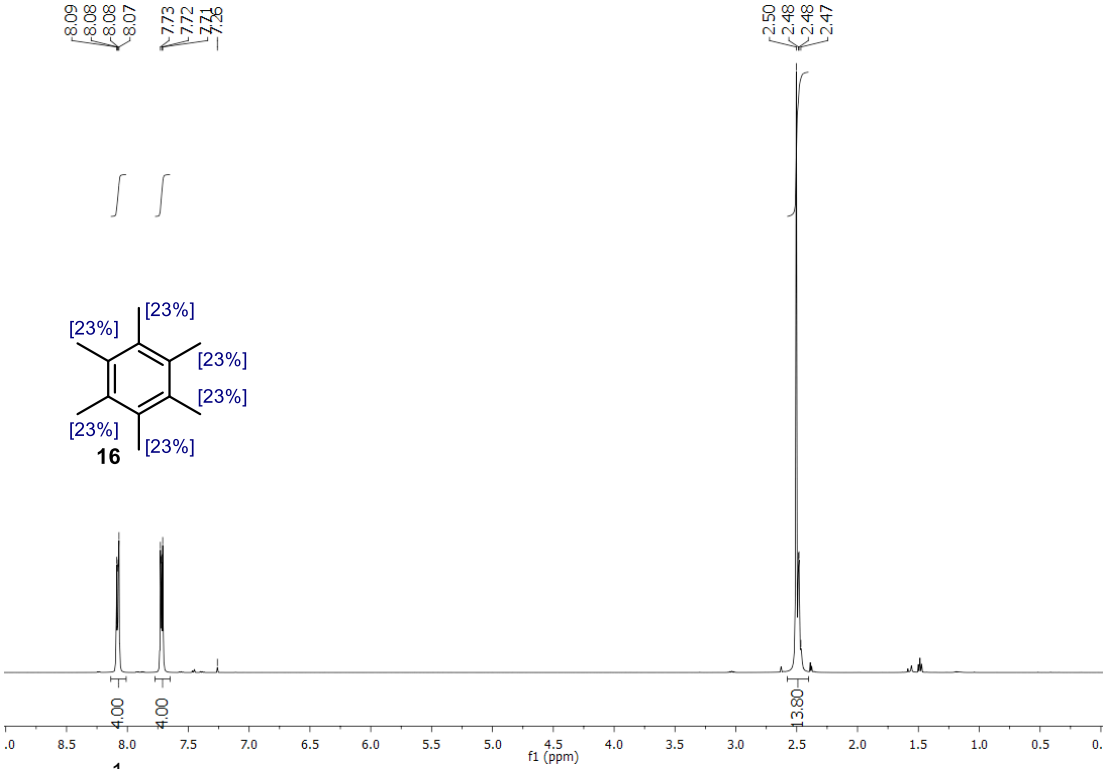


Figure S26. ^{1}H NMR spectrum (500 MHz, chloroform-*d*, 23 ºC) of labeled hexamethylbenzene **16**. Naphthalene (internal NMR standard) also present.

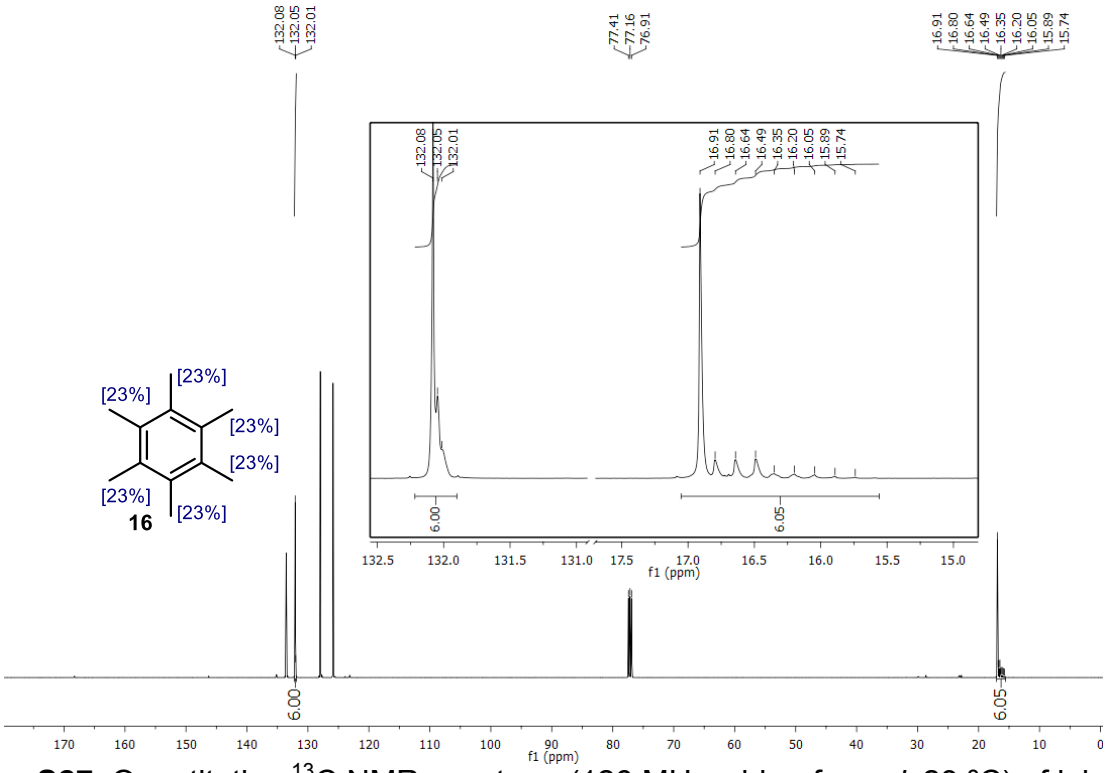


Figure S27. Quantitative ^{13}C NMR spectrum (126 MHz, chloroform-*d*, 23 ºC) of labeled hexamethylbenzene **16**. Naphthalene (internal NMR standard) also present. Inset spectrum highlights signals of **16**.

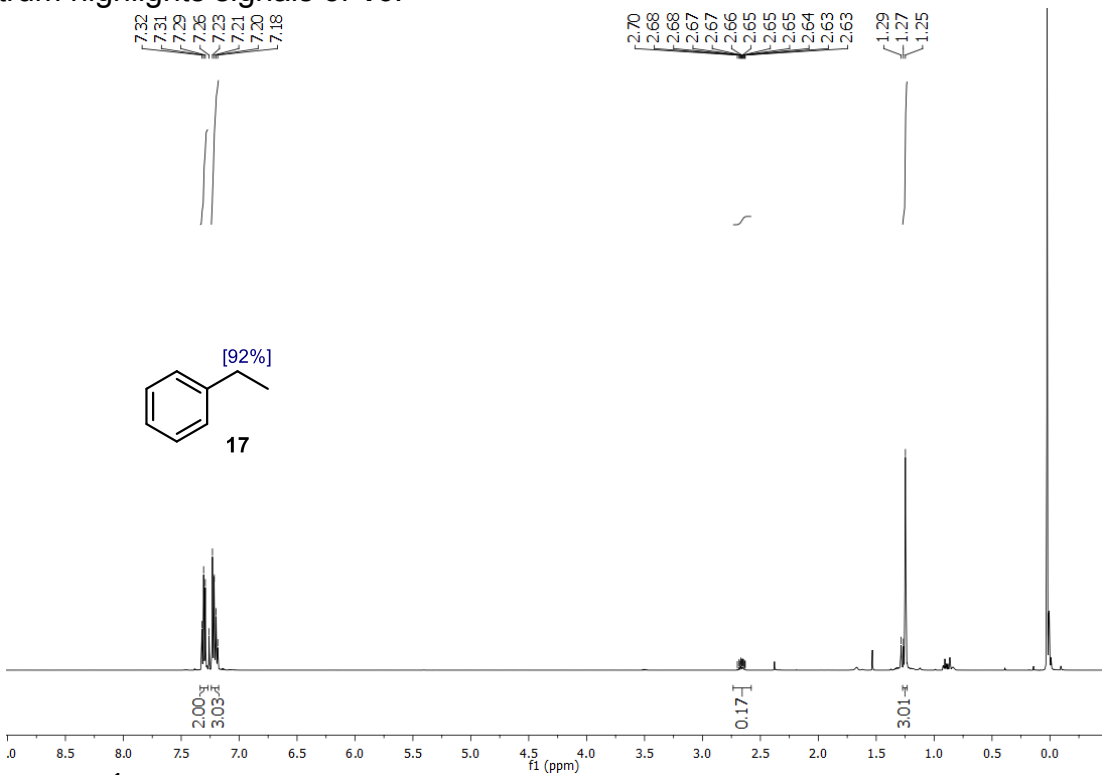


Figure S28. ^{1}H NMR spectrum (500 MHz, chloroform-*d*, 23 ºC) of labeled ethylbenzene **17**. Dodecane and TMS-d_1 also present.

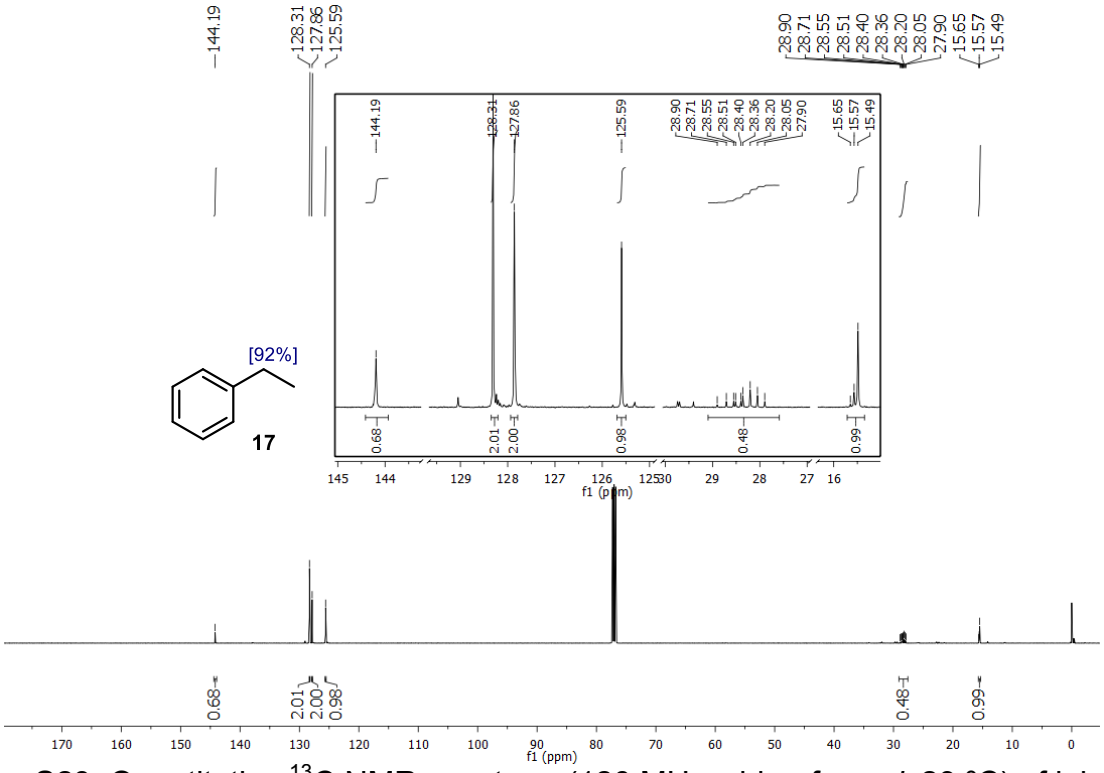


Figure S29. Quantitative ^{13}C NMR spectrum (126 MHz, chloroform-*d*, 23 ºC) of labeled ethylbenzene **17**. Dodecane and TMS-d_1 also present. Inset spectrum highlights signals of **17**.

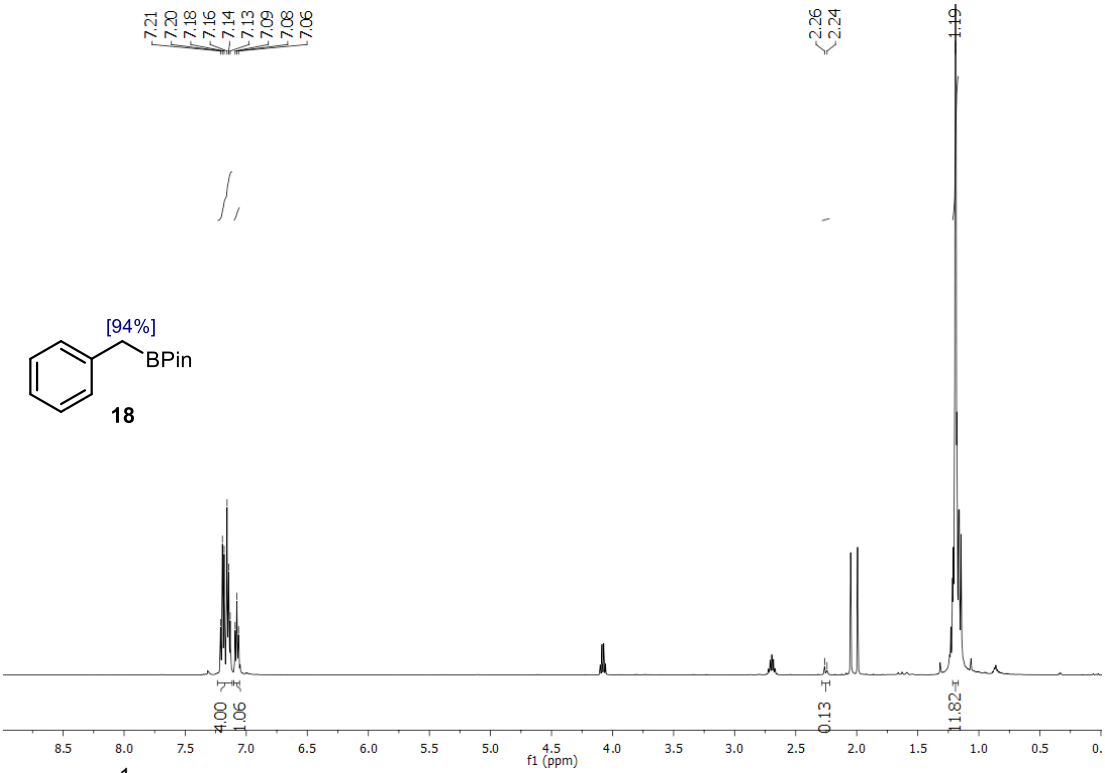


Figure S30. ^{1}H NMR spectrum (500 MHz, chloroform-*d*, 23 ºC) of labeled benzylboronic acid pinacol ester **18**. Free ^{iPr}DI ligand and ethyl acetate also present.

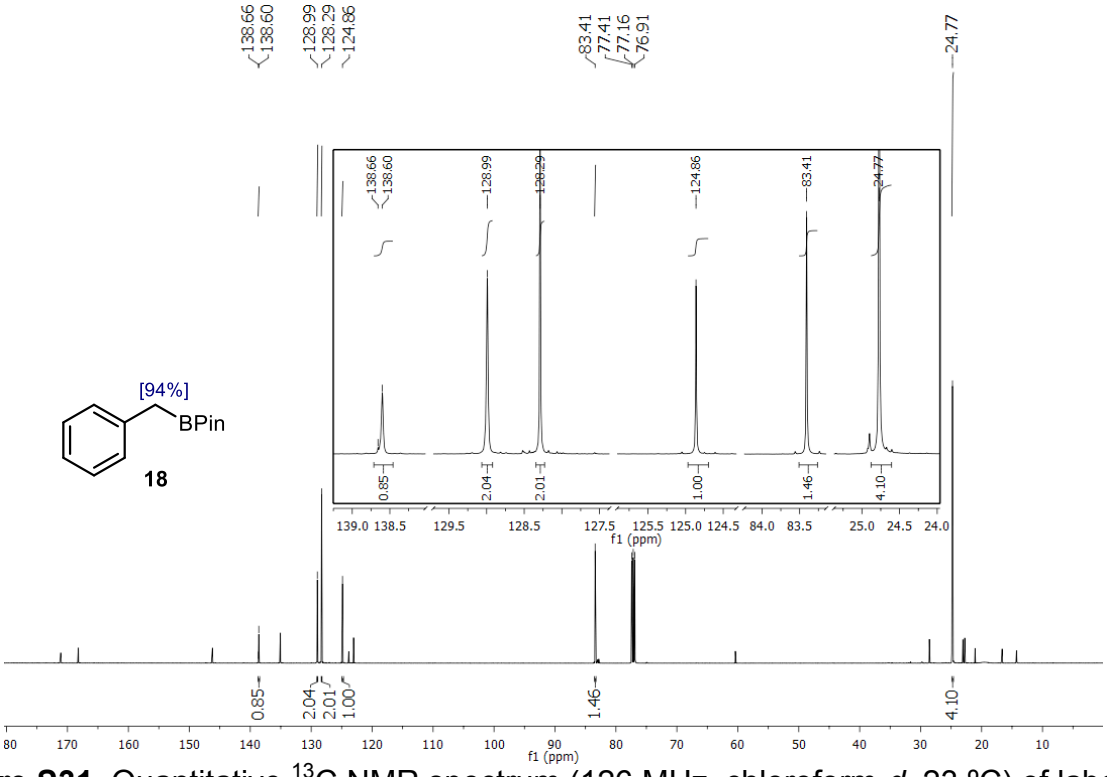


Figure S31. Quantitative ^{13}C NMR spectrum (126 MHz, chloroform-*d*, 23 ºC) of labeled benzylboronic acid pinacol ester **18**. Free ^{iPr}DI ligand and ethyl acetate also present. Inset spectrum highlights signals of **18**.

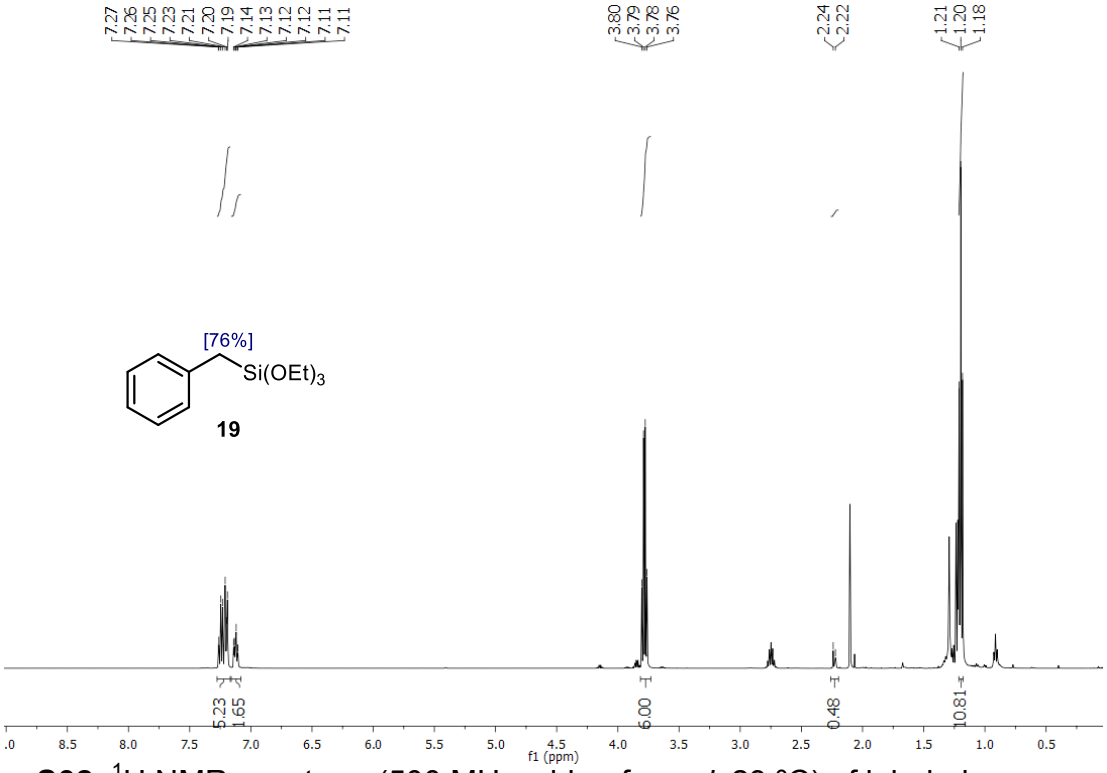


Figure S32. ^{1}H NMR spectrum (500 MHz, chloroform-*d*, 23 ºC) of labeled benzyltriethoxysilane **19**. Free ^{iPr}DI ligand also present.

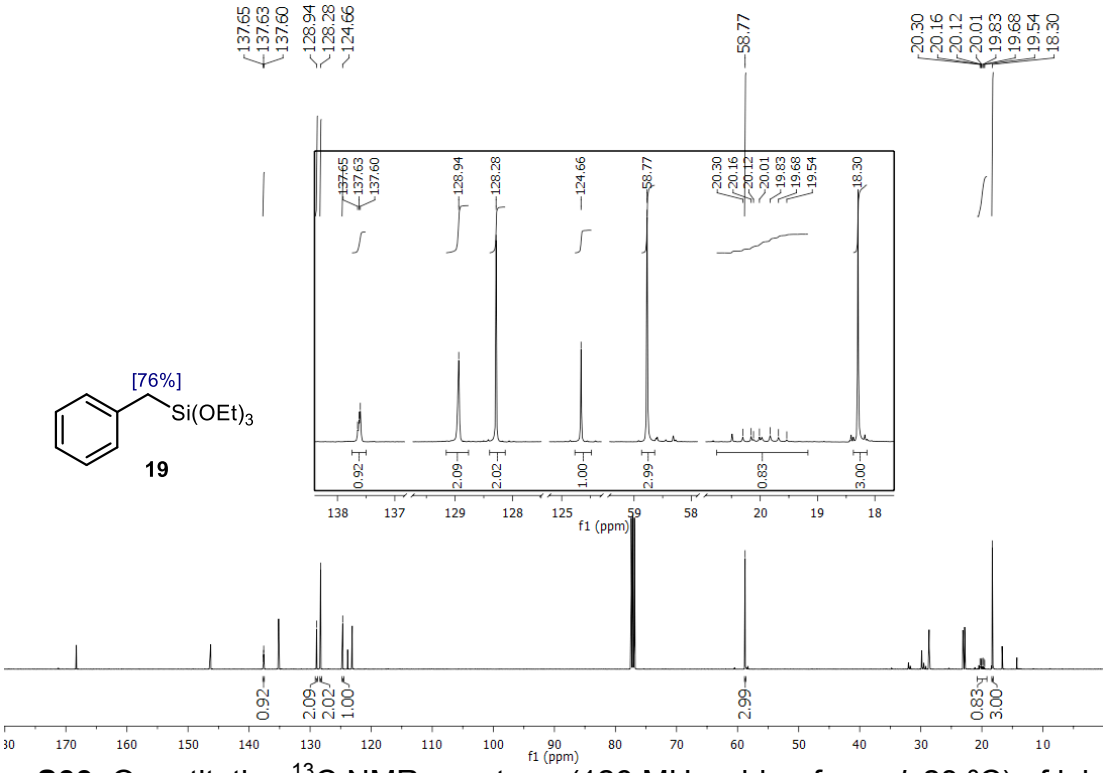


Figure S33. Quantitative ^{13}C NMR spectrum (126 MHz, chloroform-*d*, 23 ºC) of labeled benzyltriethoxysilane **19**. Free ^{iPr}DI ligand also present. Inset spectrum highlights signals of **19**.

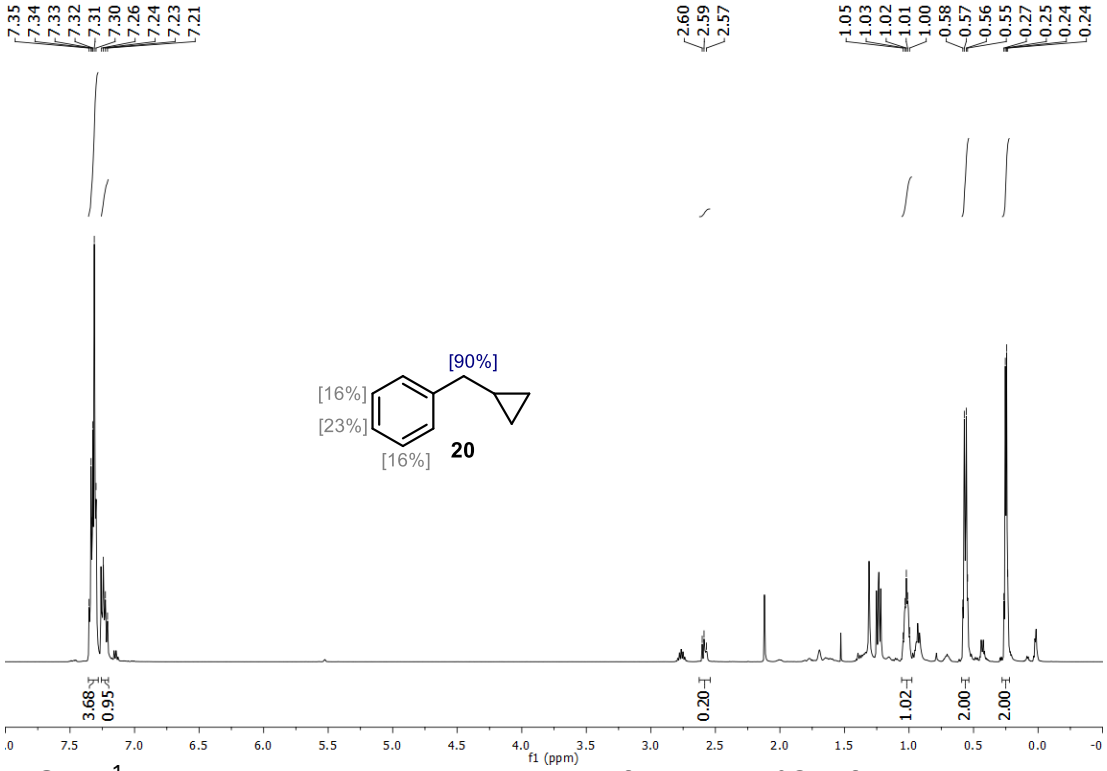


Figure S34. ^{1}H NMR spectrum (500 MHz, chloroform-*d*, 23 ºC) of labeled benzylcyclopropane **20**. Free ^{iPr}DI ligand, hexanes, and reduced arene also present.

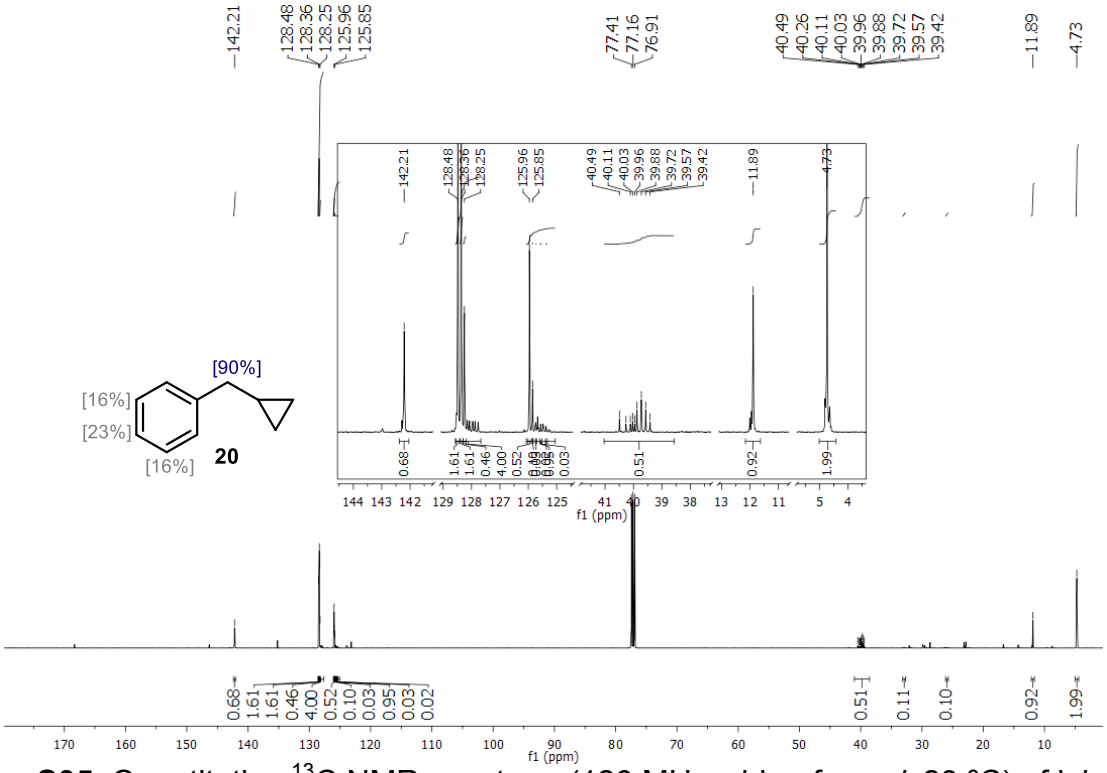


Figure S35. Quantitative ^{13}C NMR spectrum (126 MHz, chloroform-*d*, 23 ºC) of labeled benzylcyclopropane **20** Free ^{iPr}DI ligand, hexanes, and reduced arene also present. Inset spectrum highlights signals of **20**.

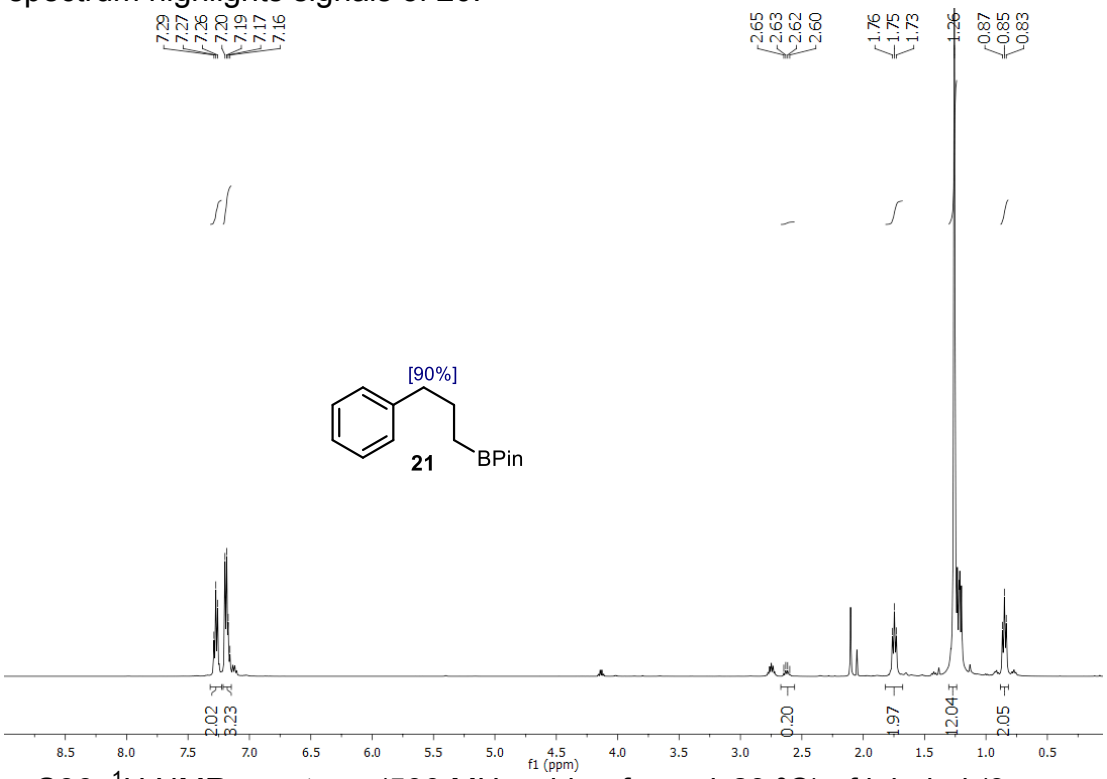


Figure S36. ^{1}H NMR spectrum (500 MHz, chloroform-*d*, 23 ºC) of labeled (3-phenylpropyl)boronic acid pinacol ester **21**. Free ^{iPr}DI ligand and ethyl acetate present.

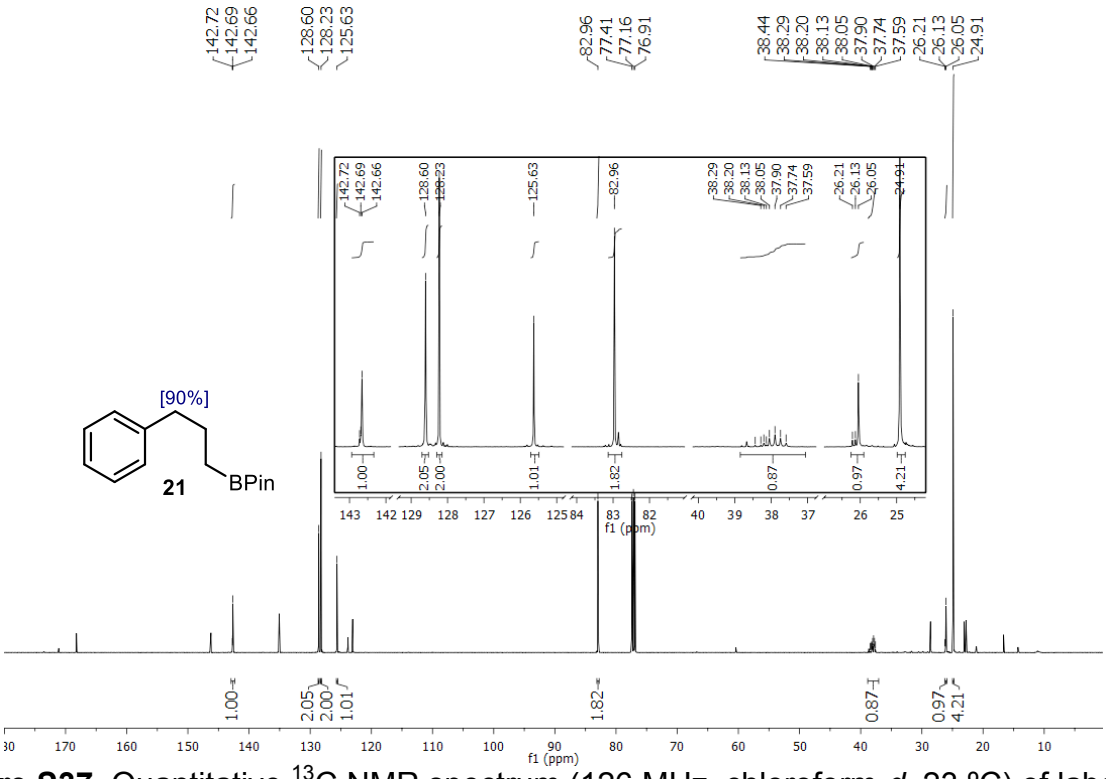


Figure S37. Quantitative ^{13}C NMR spectrum (126 MHz, chloroform-*d*, 23 ºC) of labeled (3-phenylpropyl)boronic acid pinacol ester **21**. Free ^{iPr}DI ligand and ethyl acetate also present. Inset spectrum highlights signals of **21**.

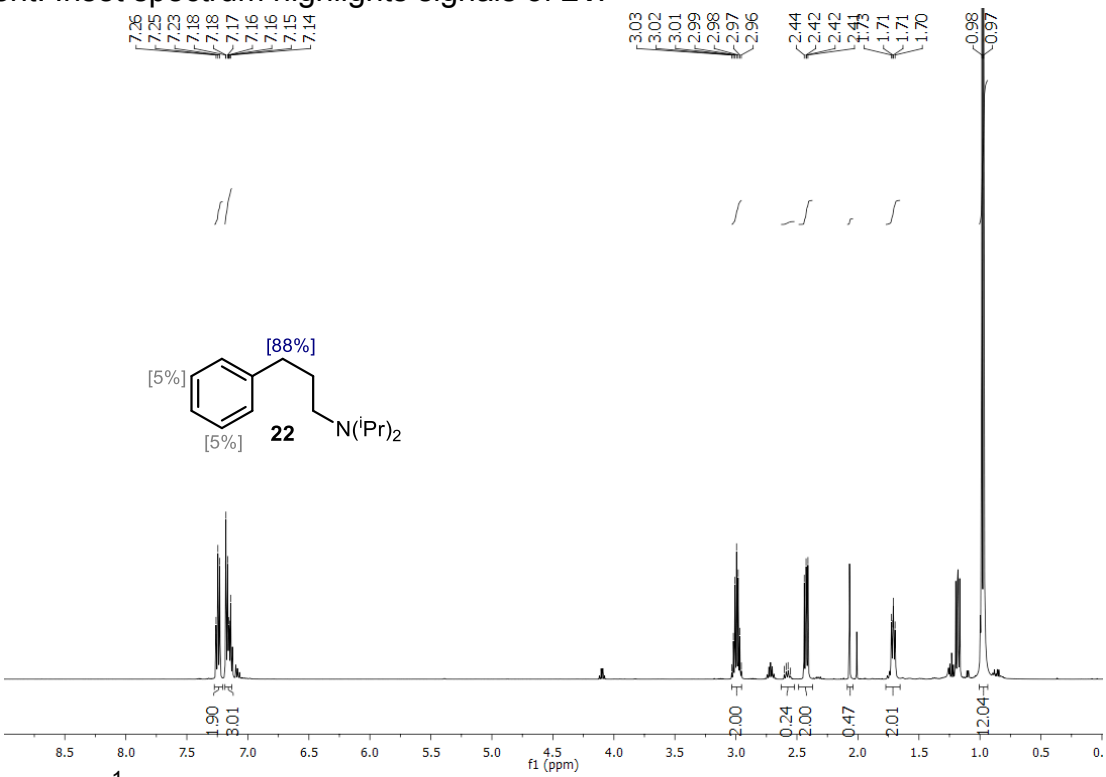


Figure S38. ^{1}H NMR spectrum (500 MHz, chloroform-*d*, 23 ºC) of labeled diisopropyl(3-phenylpropyl)amine **22**. Free ^{iPr}DI ligand and ethyl acetate present.

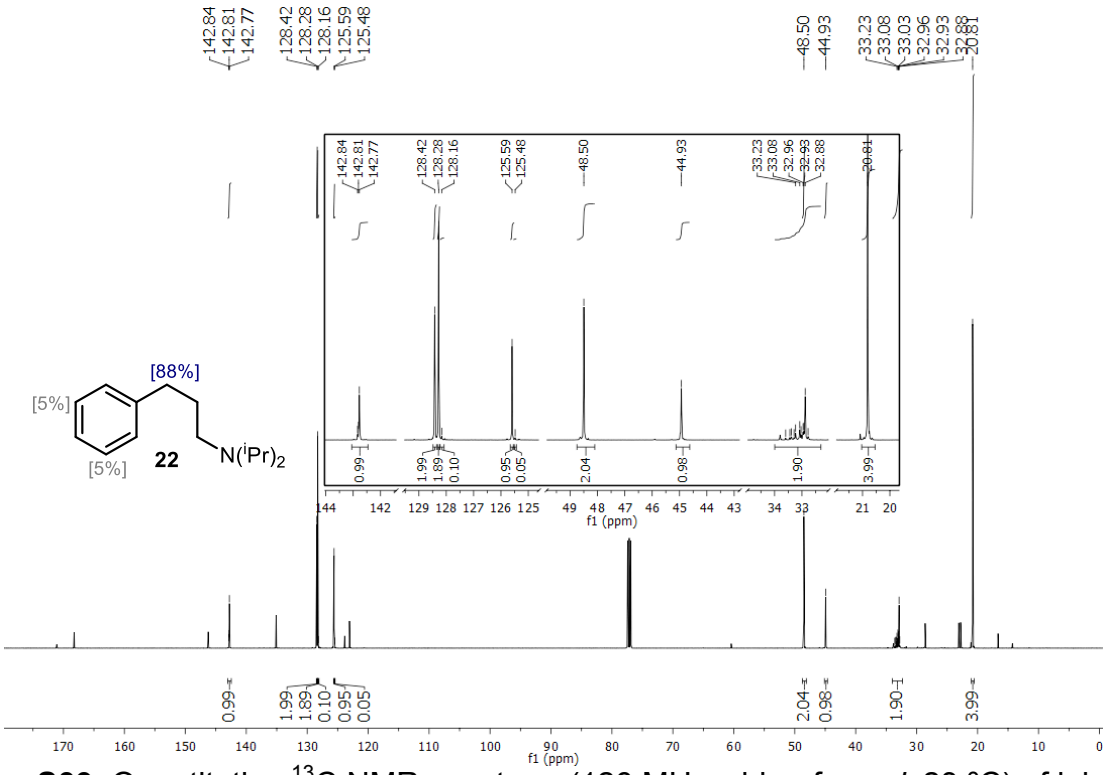


Figure S39. Quantitative ^{13}C NMR spectrum (126 MHz, chloroform-*d*, 23 ºC) of labeled diisopropyl(3-phenylpropyl)amine **22**. Free ^{iPr}DI ligand and ethyl acetate also present. Inset spectrum highlights signals of **22**.

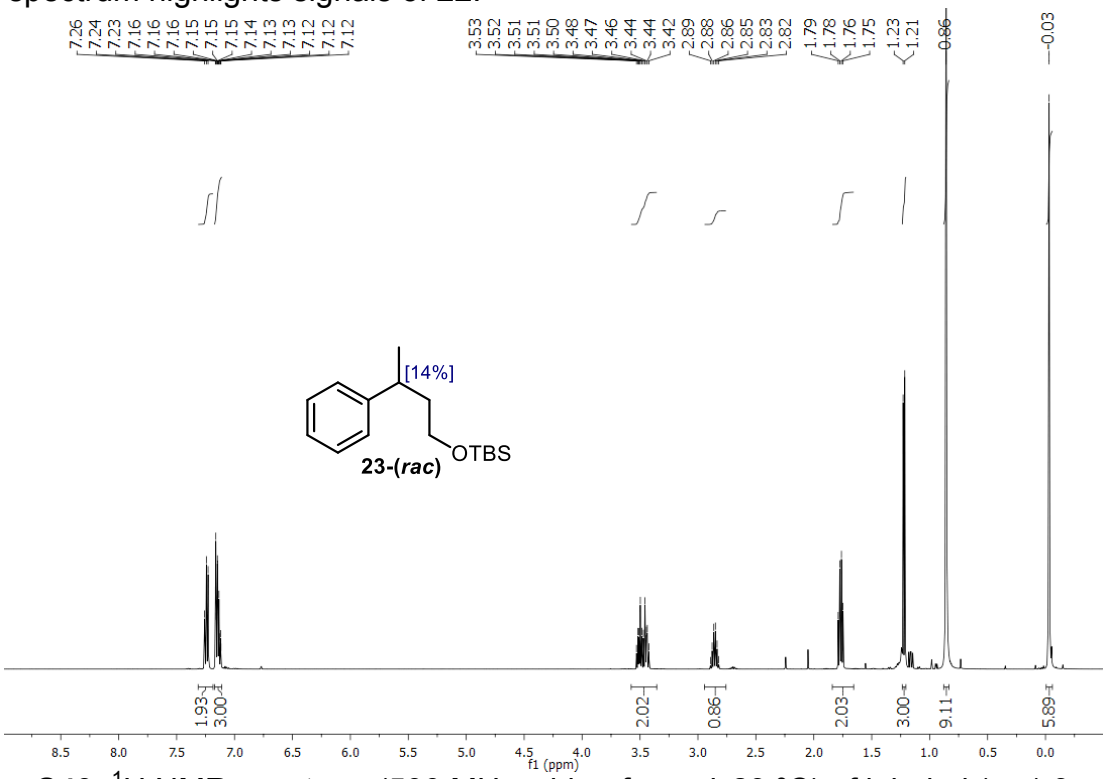


Figure S40. ^{1}H NMR spectrum (500 MHz, chloroform-*d*, 23 ºC) of labeled (*rac*) 3-Phenylbutan-1-ol *tert*-butyldimethylsilyl ether **23-(*rac*)**.

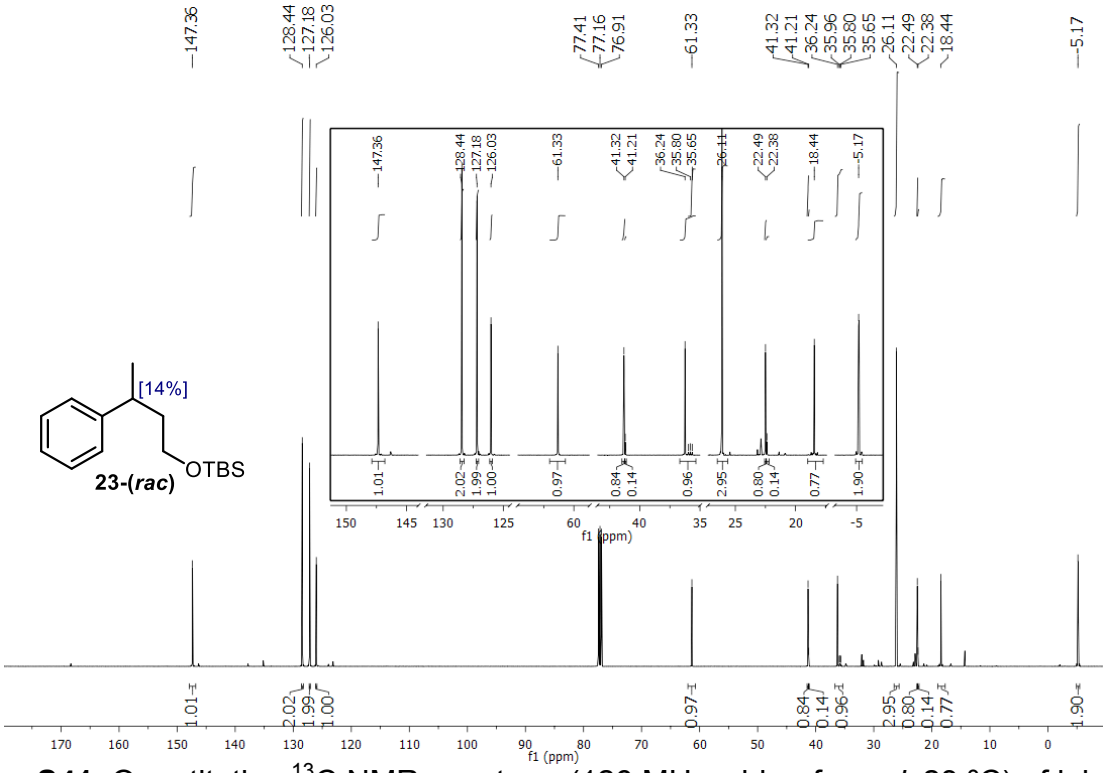


Figure S41. Quantitative ^{13}C NMR spectrum (126 MHz, chloroform-*d*, 23 ºC) of labeled (*rac*) 3-Phenylbutan-1-ol *tert*-butyldimethylsilyl ether **23-(*rac*)**. Inset spectrum highlights signals of **23-(*rac*)**.

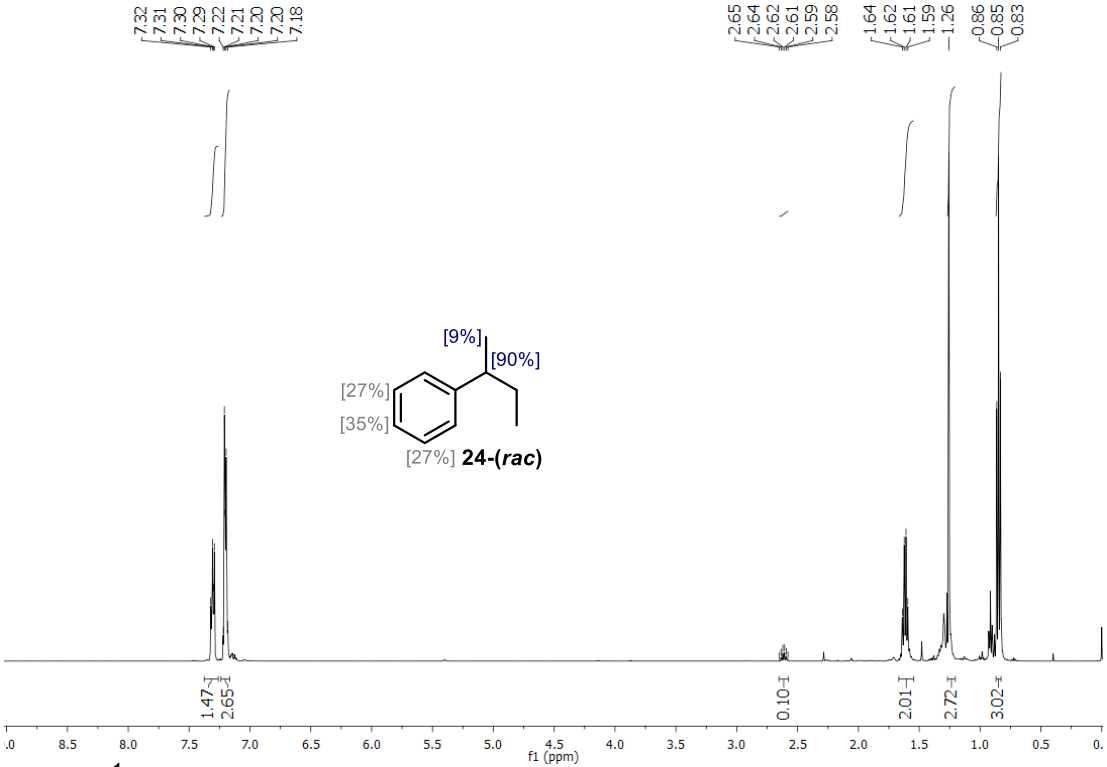


Figure S42. ^{1}H NMR spectrum (500 MHz, chloroform-*d*, 23 ºC) of labeled (*rac*) *sec*-butylbenzene **24-(*rac*)**.

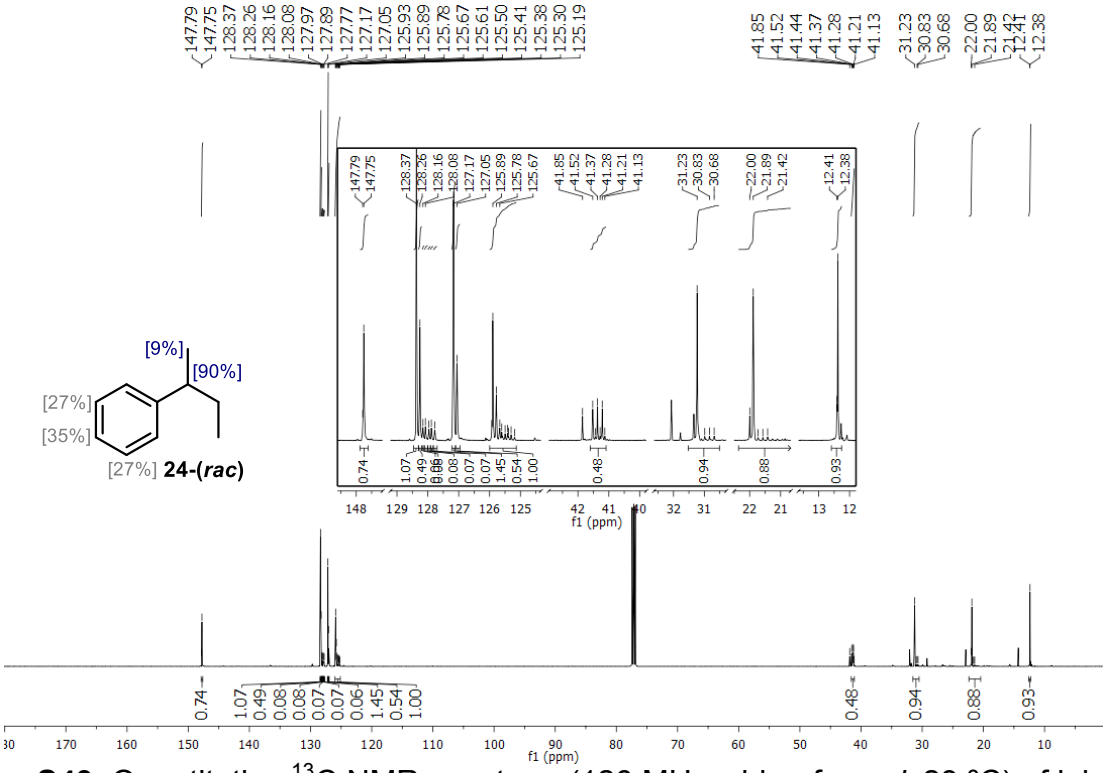


Figure S43. Quantitative ^{13}C NMR spectrum (126 MHz, chloroform-*d*, 23 ºC) of labeled (*rac*) *sec*-butylbenzene **24-(*rac*)**. Inset spectrum highlights signals of **24-(*rac*)**.

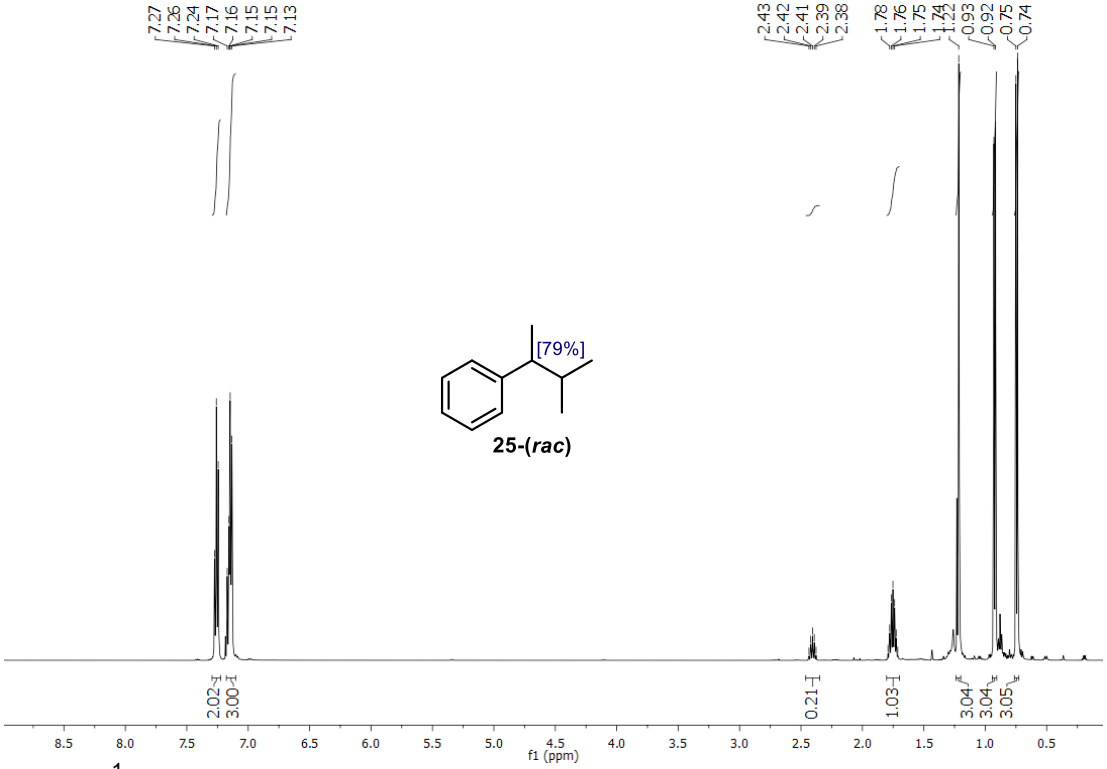


Figure S44. ^{1}H NMR spectrum (500 MHz, chloroform-*d*, 23 ºC) of labeled (*rac*) 2-phenyl-3-methylbutane **25-(*rac*)**.

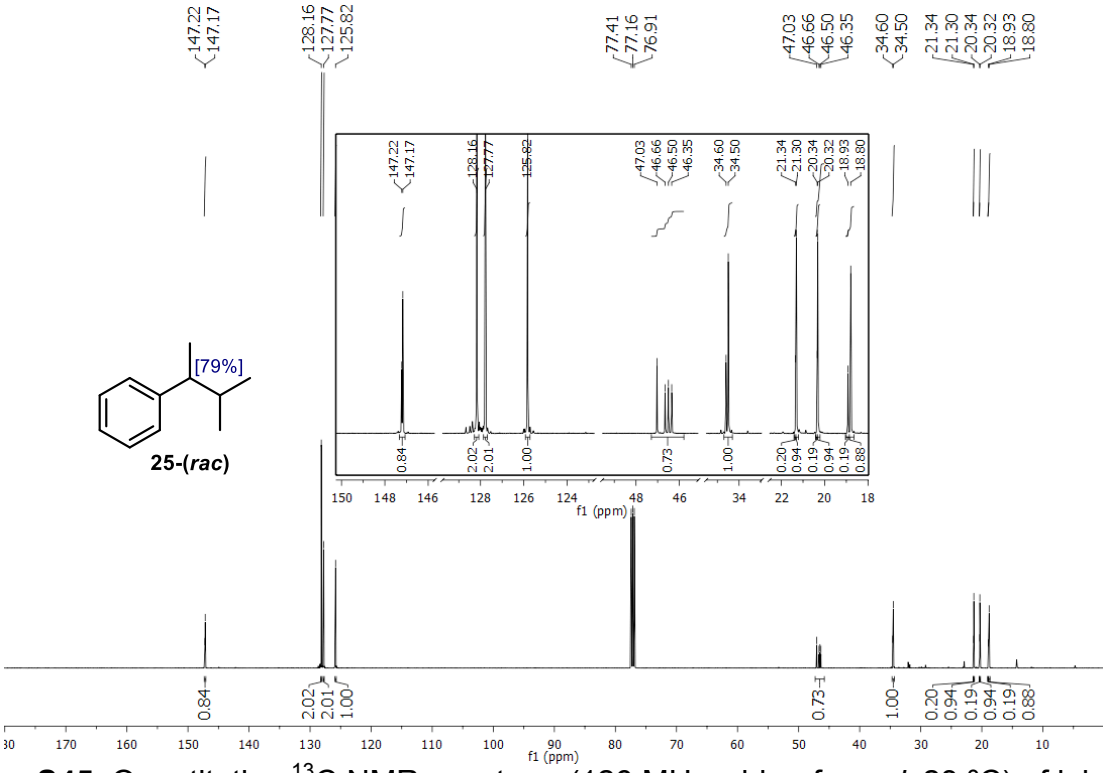


Figure S45. Quantitative ^{13}C NMR spectrum (126 MHz, chloroform-*d*, 23 ºC) of labeled (*rac*) 2-phenyl-3-methylbutane **25-(*rac*)**. Inset spectrum highlights signals of **25-(*rac*)**.

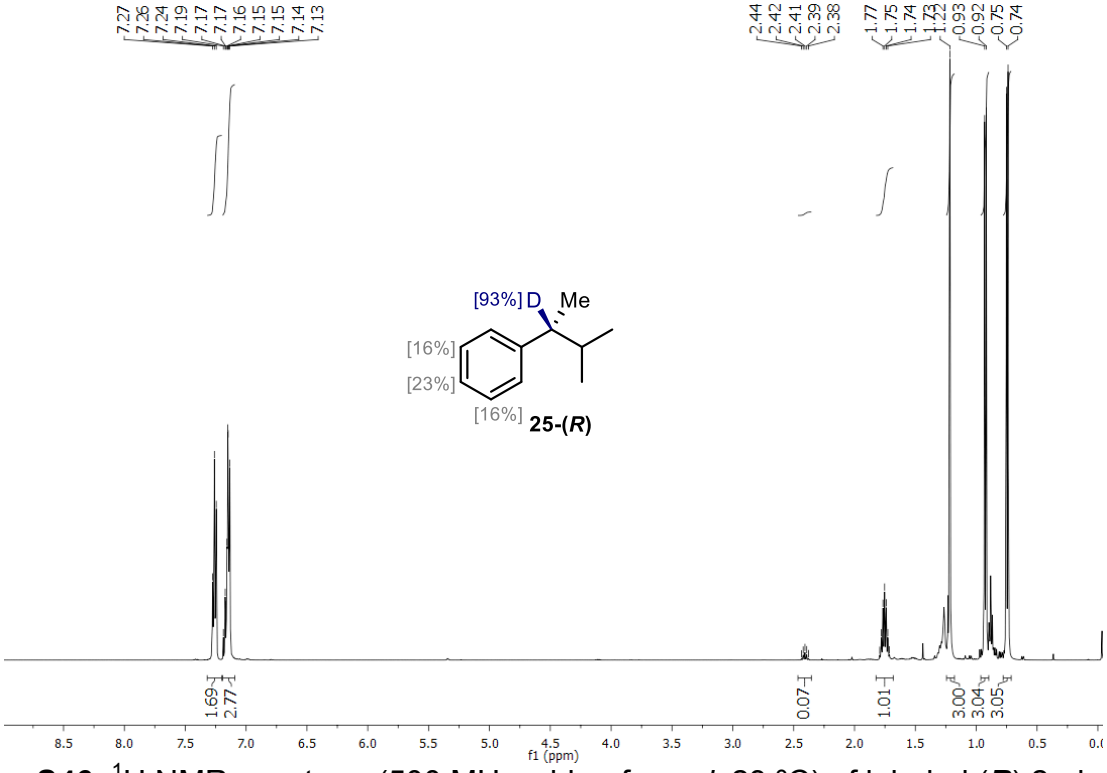


Figure S46. ^{1}H NMR spectrum (500 MHz, chloroform-*d*, 23 ºC) of labeled (*R*) 2-phenyl-3-methylbutane **25-(*R*)**.

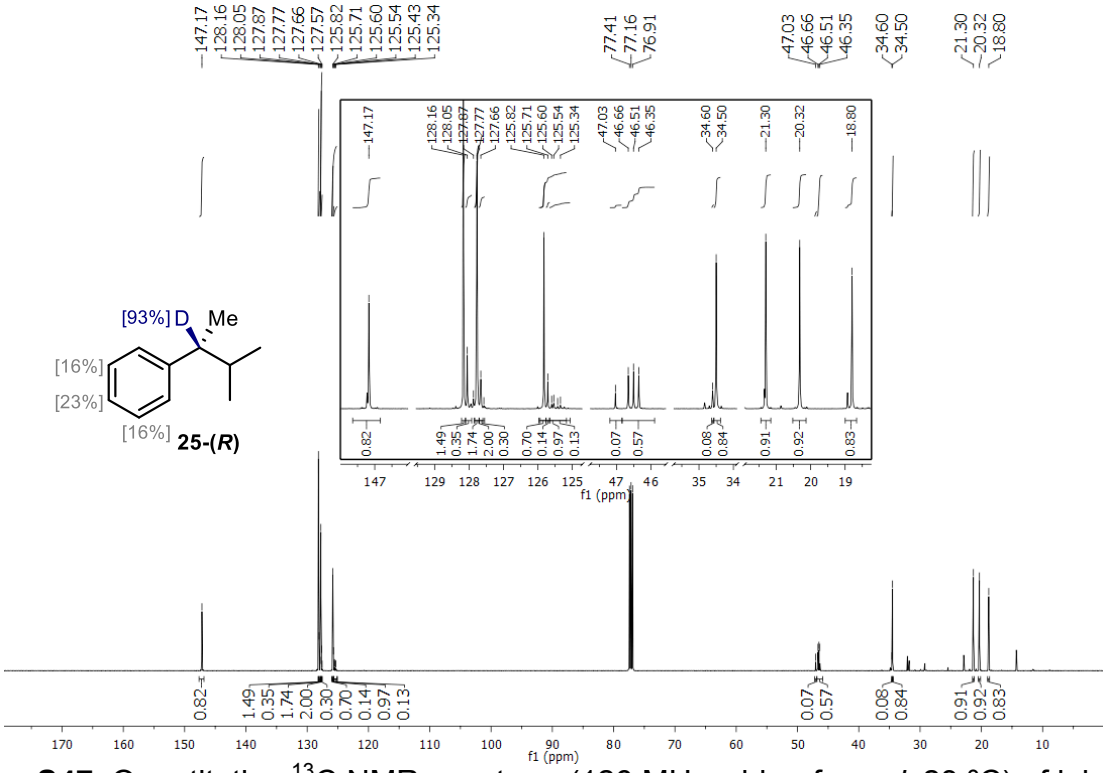


Figure S47. Quantitative ^{13}C NMR spectrum (126 MHz, chloroform-*d*, 23 ºC) of labeled (*R*) 2-phenyl-3-methylbutane **25-(*R*)**. Inset spectrum highlights signals of **25-(*R*)**.

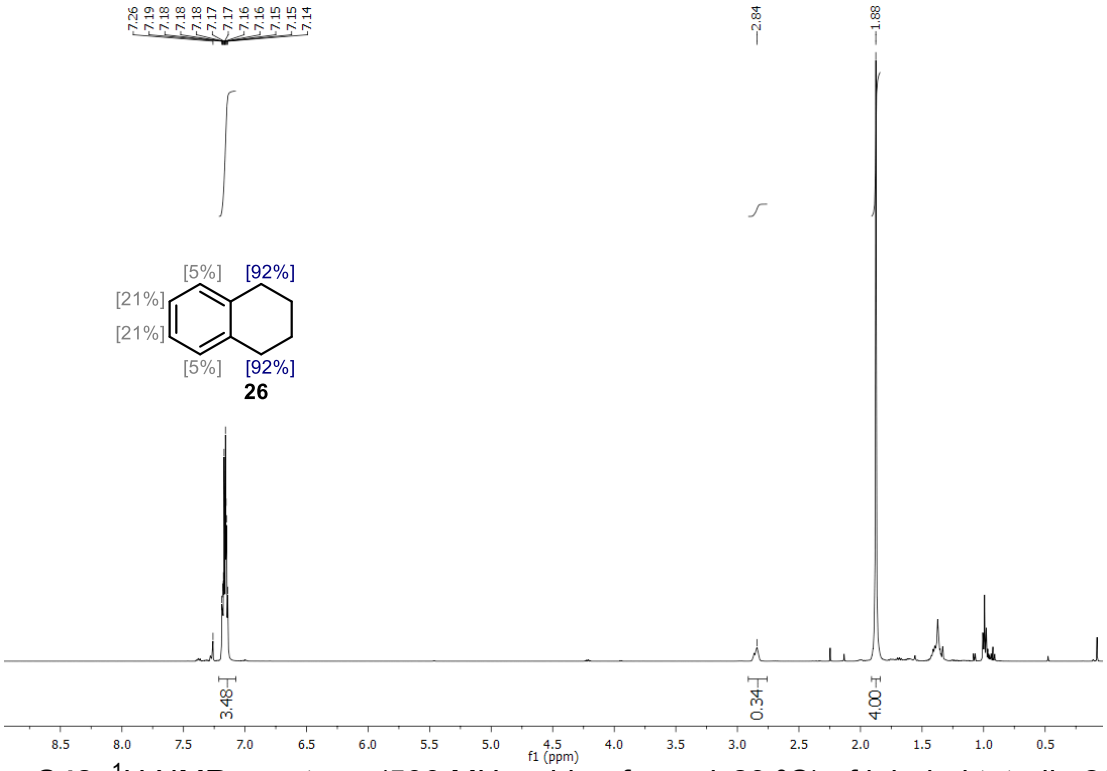


Figure S48. ^{1}H NMR spectrum (500 MHz, chloroform-*d*, 23 ºC) of labeled tetralin **26**. Hexanes also present.

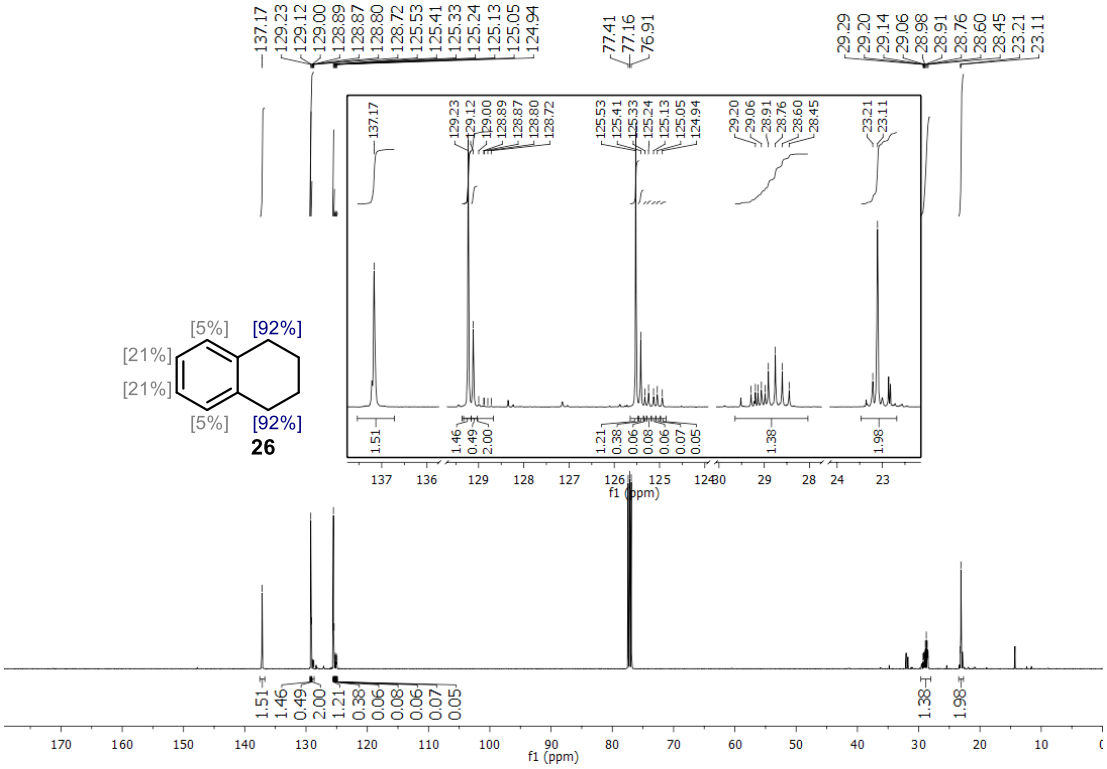


Figure S49. Quantitative ^{13}C NMR spectrum (126 MHz, chloroform-*d*, 23 ºC) of labeled tetralin **26**. Hexanes also present. Inset spectrum highlights signals of **26**.

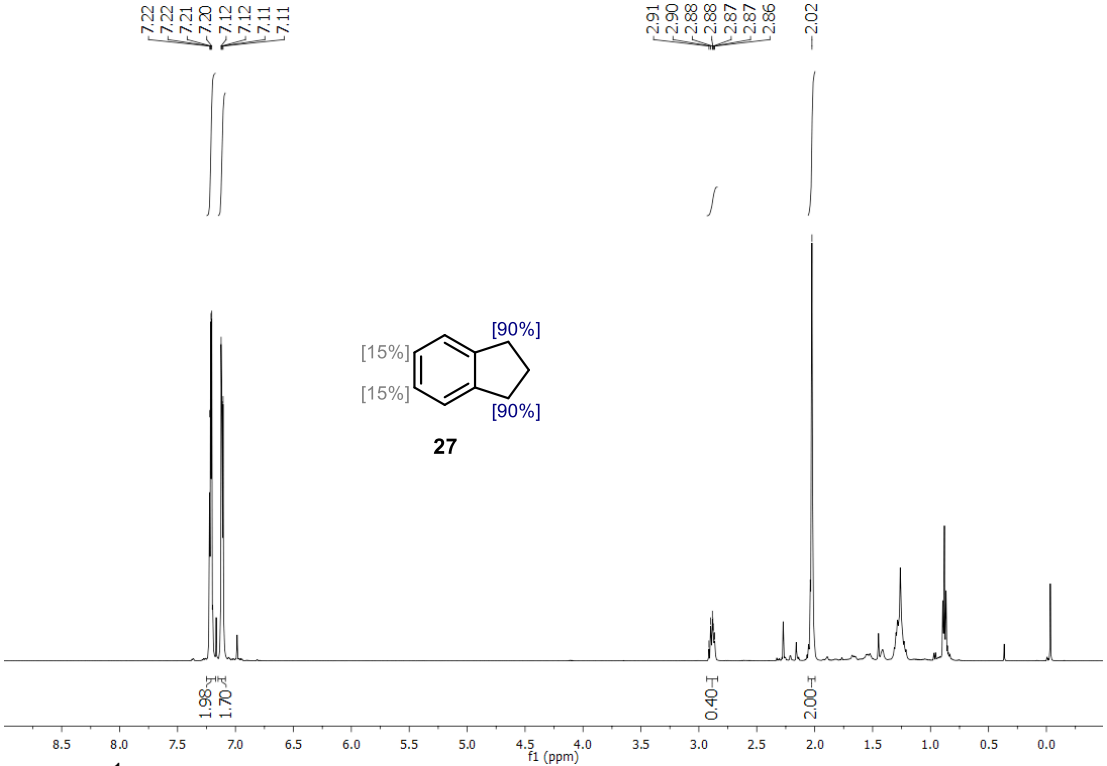


Figure S50. ^{1}H NMR spectrum (500 MHz, chloroform-*d*, 23 ºC) of labeled indan **27**. Hexanes also present.

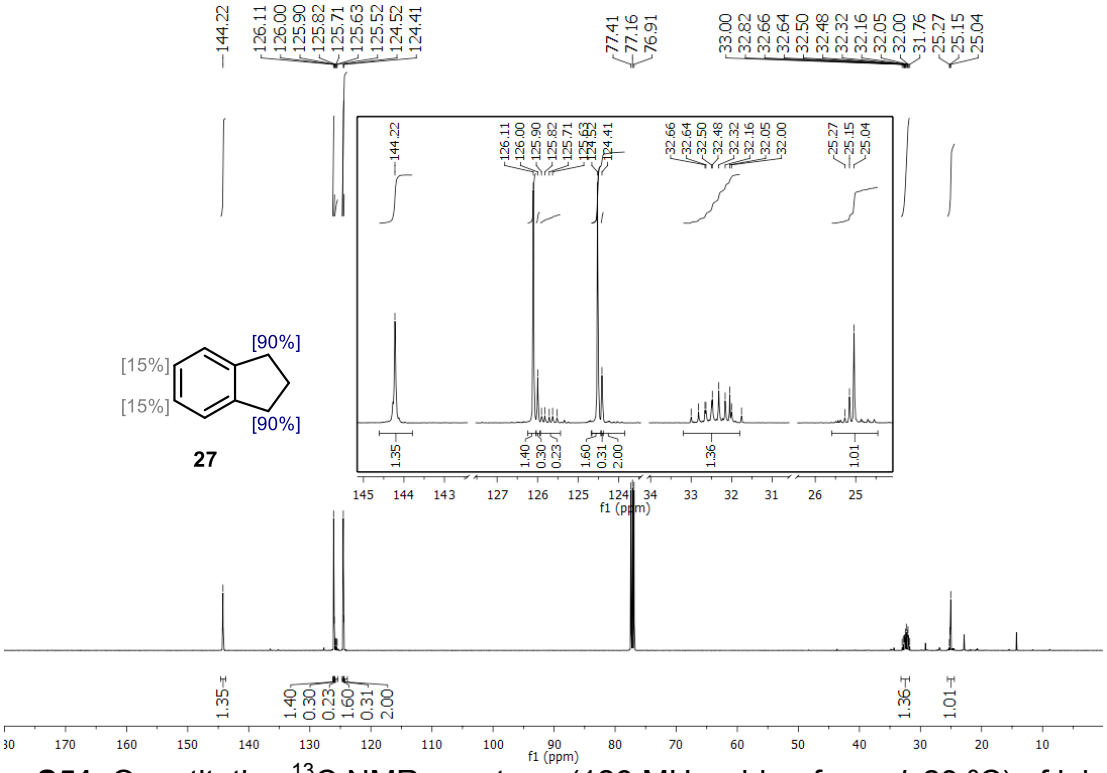


Figure S51. Quantitative ^{13}C NMR spectrum (126 MHz, chloroform-*d*, 23 ºC) of labeled indan **27**. Hexanes also present. Inset spectrum highlights signals of **27**.

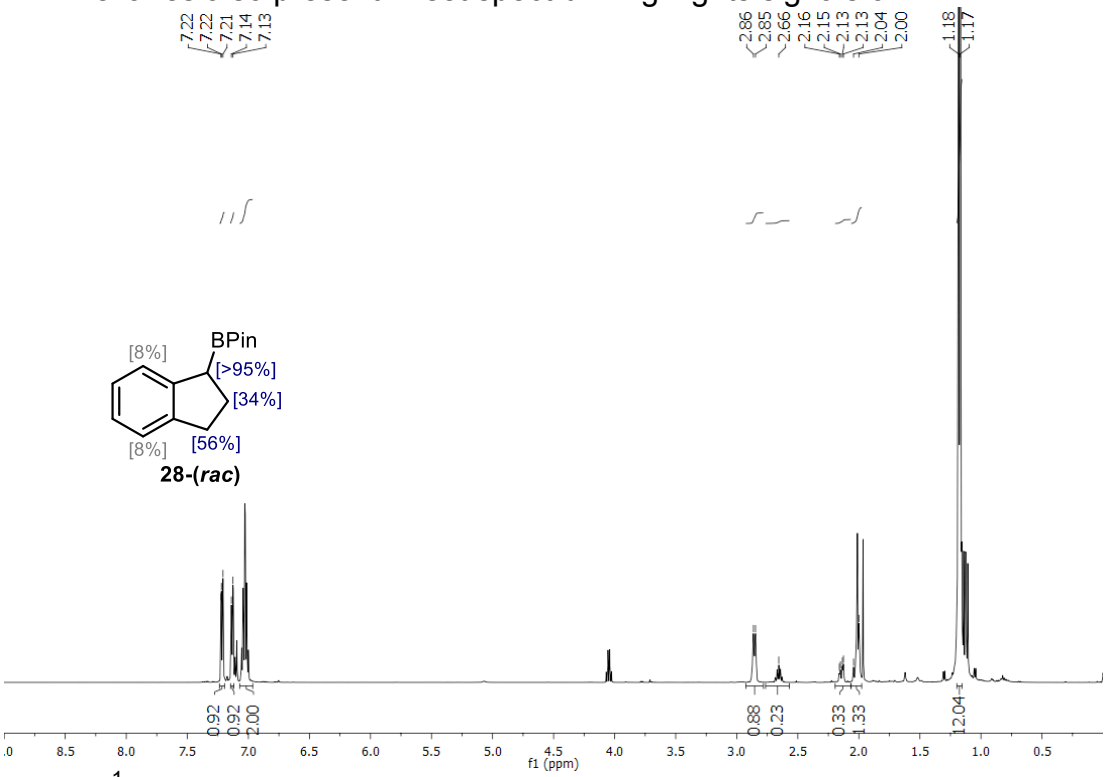


Figure S52. ^{1}H NMR spectrum (500 MHz, chloroform-*d*, 23 ºC) of labeled racemic 1-indanylboronic acid pinacol ester **28-(*rac*)**. Free ^{iPr}DI ligand and ethyl acetate present.

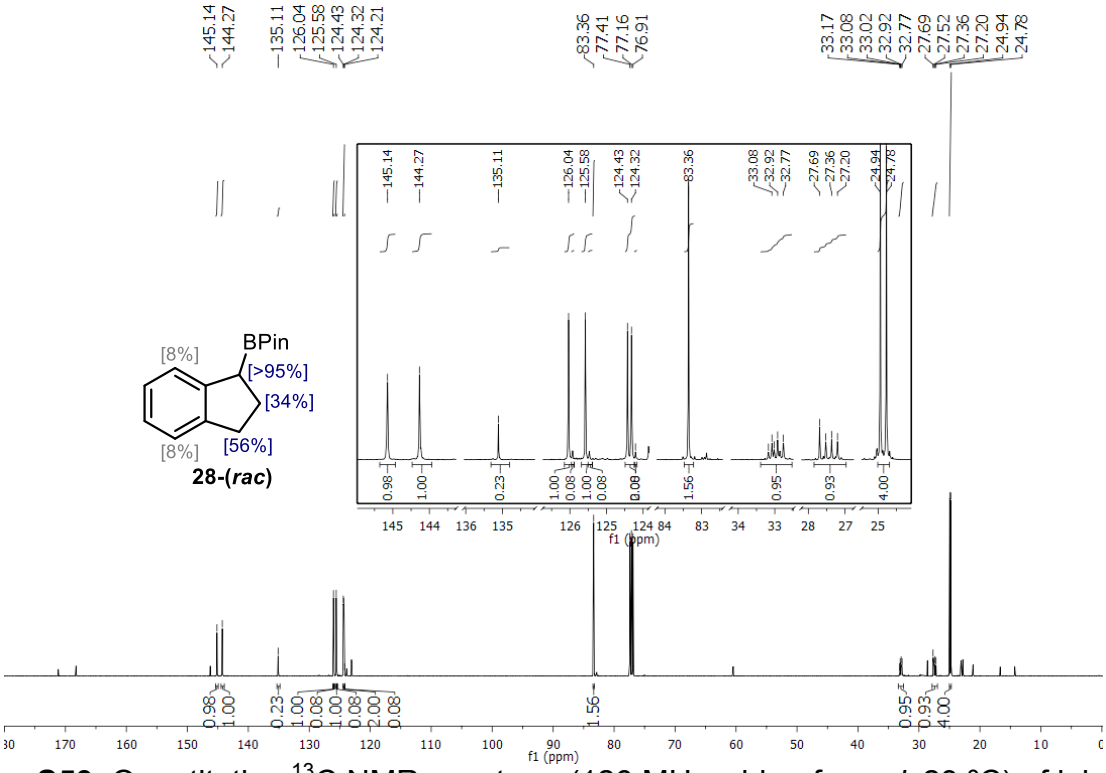


Figure S53. Quantitative ^{13}C NMR spectrum (126 MHz, chloroform-*d*, 23 ºC) of labeled racemic 1-indanylboronic acid pinacol ester **28-(*rac*)**. Free ^{iPr}DI ligand and ethyl acetate also present. Inset spectrum highlights signals of **28-(*rac*)**.

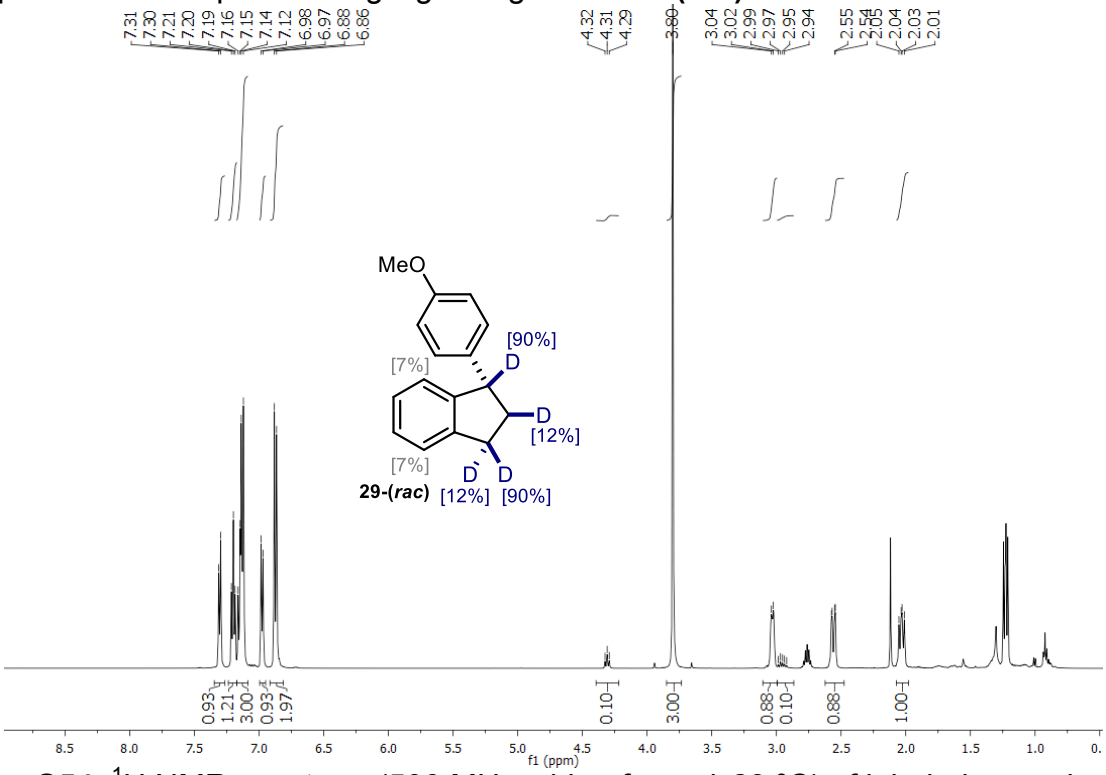


Figure S54. ^{1}H NMR spectrum (500 MHz, chloroform-*d*, 23 ºC) of labeled racemic arylindan **29-(*rac*)**. Free ^{iPr}DI ligand also present.

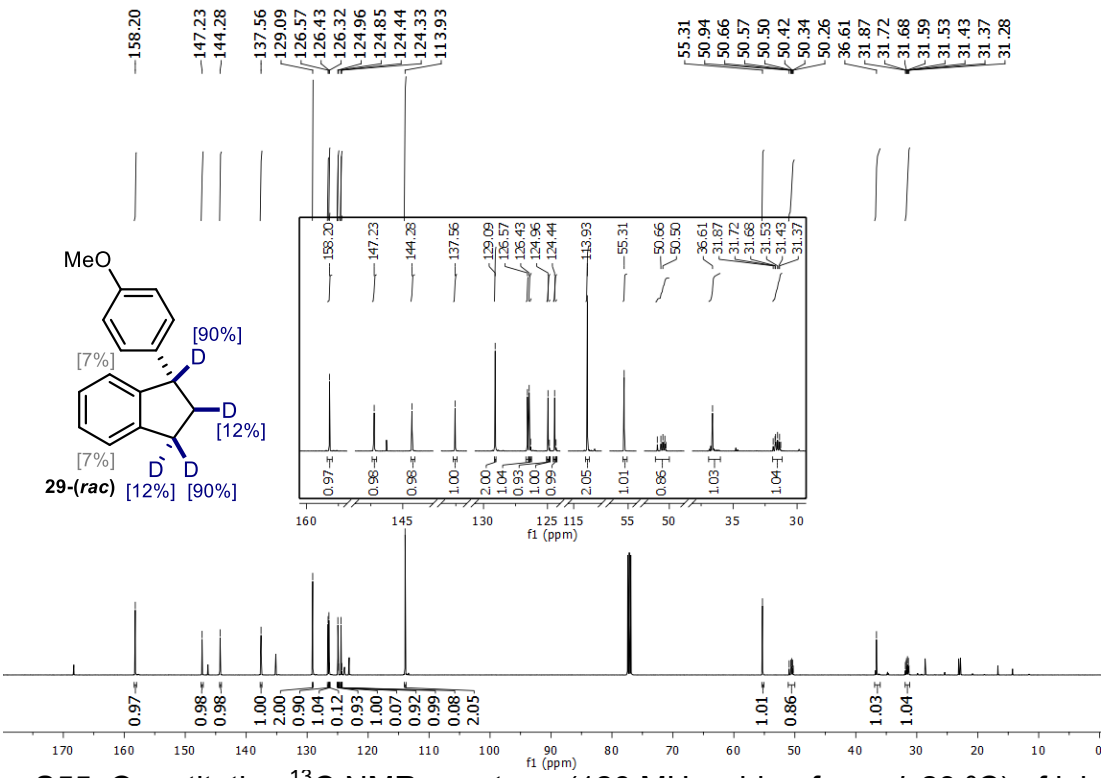


Figure S55. Quantitative ^{13}C NMR spectrum (126 MHz, chloroform-*d*, 23 ºC) of labeled racemic arylindan **29-(*rac*)**. Free ^{iPr}DI ligand also present. Inset spectrum highlights signals of **29-(*rac*)**.

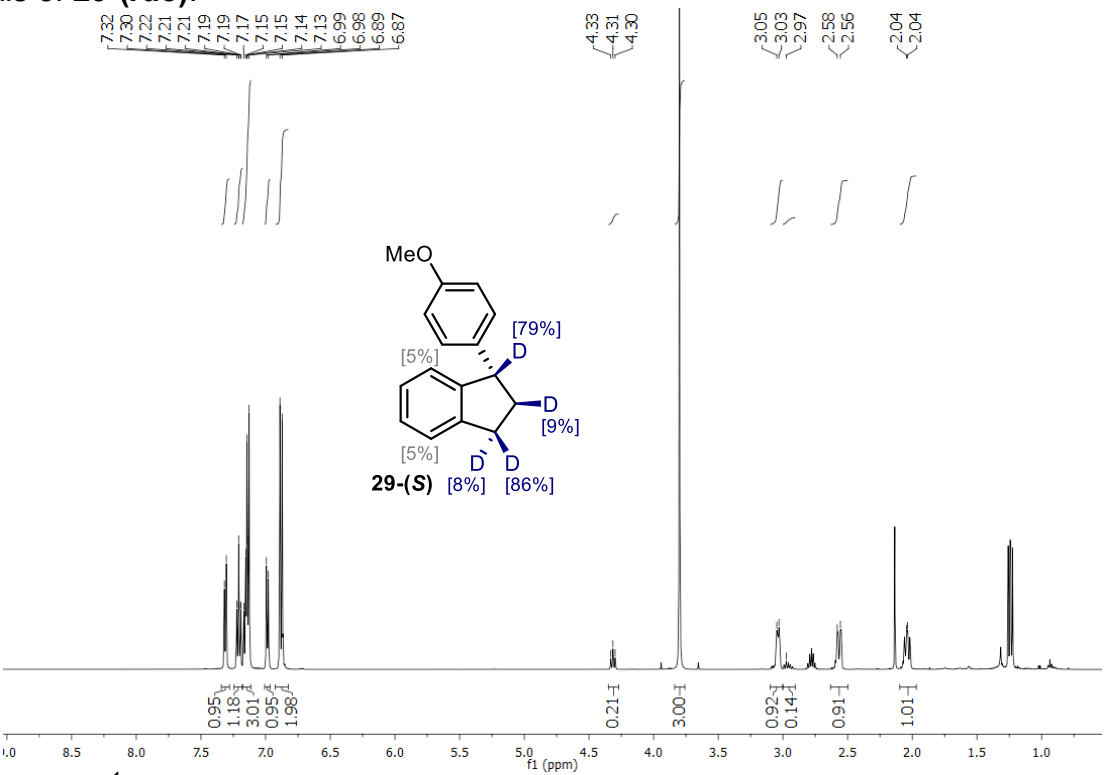


Figure S56. ^{1}H NMR spectrum (500 MHz, chloroform-*d*, 23 ºC) of labeled (*S*) arylindan **29-(*S*)**. Free ^{iPr}DI ligand also present.

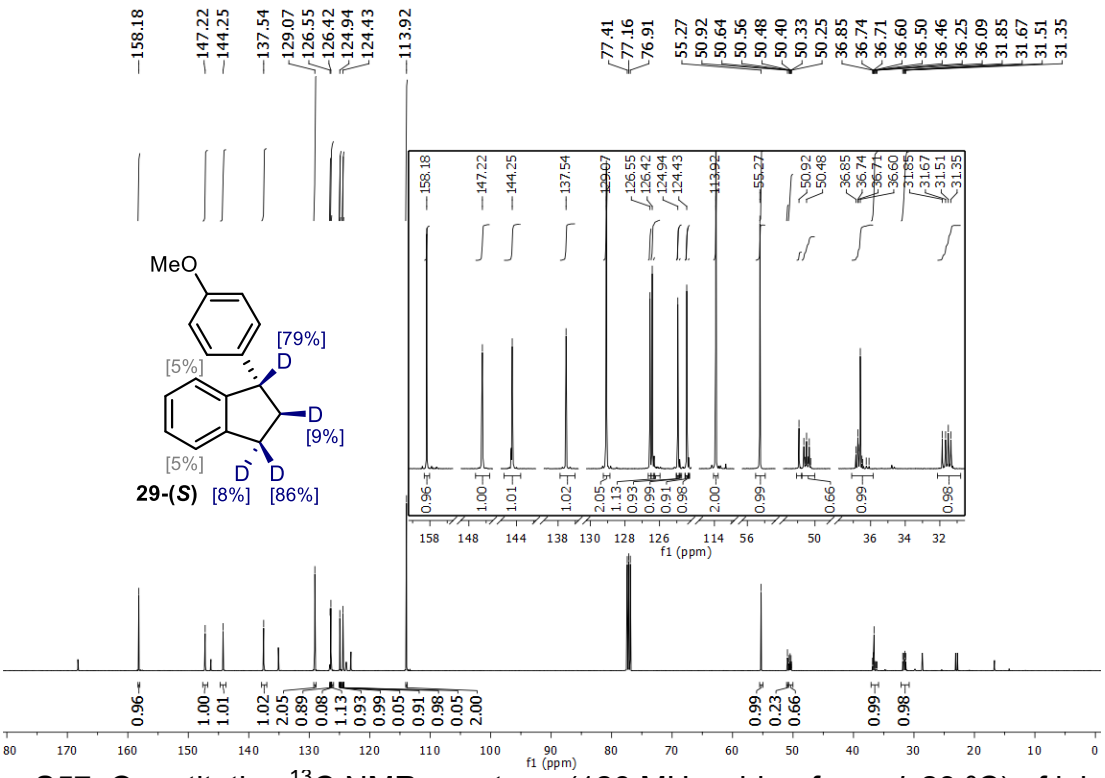


Figure S57. Quantitative ^{13}C NMR spectrum (126 MHz, chloroform-*d*, 23 ºC) of labeled (*S*) arylindan **29-(*S*)**. Free ^{iPr}DI ligand also present. Inset spectrum highlights signals of **29-(*S*)**.

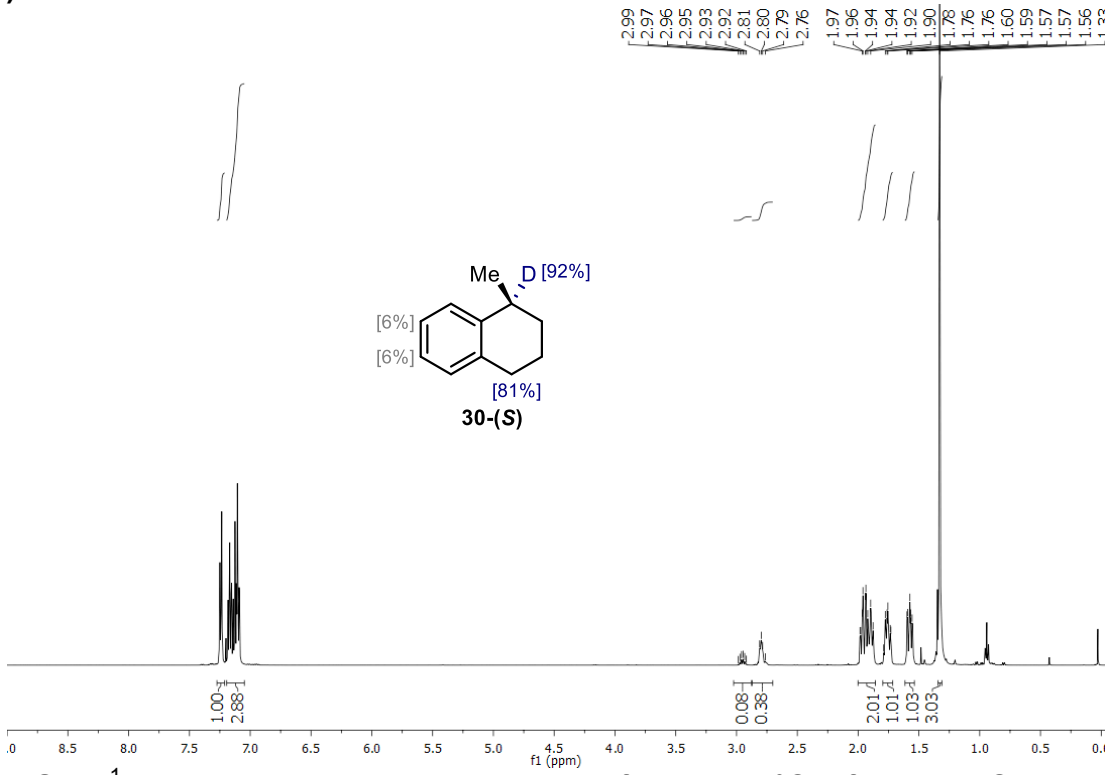


Figure S58. ^{1}H NMR spectrum (500 MHz, chloroform-*d*, 23 ºC) of labeled (*S*)-1-methyltetralin **30-(*S*)**.

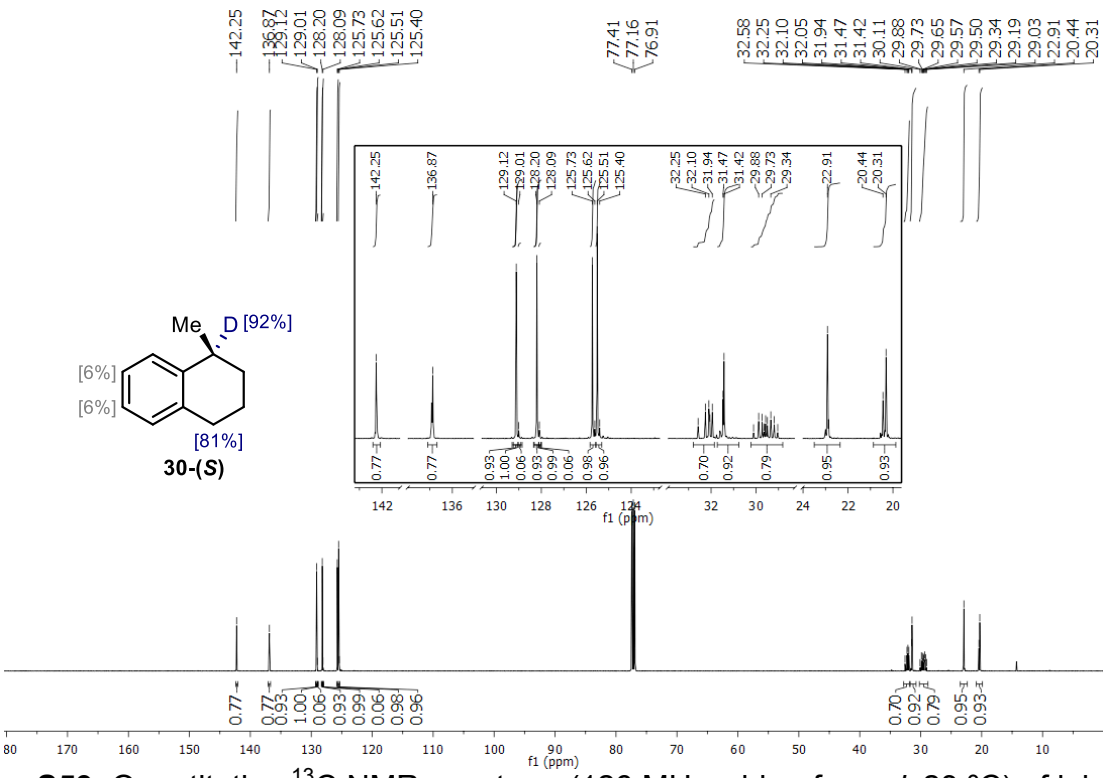


Figure S59. Quantitative ^{13}C NMR spectrum (126 MHz, chloroform-*d*, 23 ºC) of labeled (*S*)-1-methyltetralin **30-(*S*)**. Inset spectrum highlights signals of **30-(*S*)**.

VIII. References.

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