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Conflict of Interest: The authors declare that they have no conflict of interest.

Abstract:
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Pd-Catalyzed Transfer Hydrogenation of Alkenes Using Tetrahydroxydiboron as the Sole Hydrogen Donor

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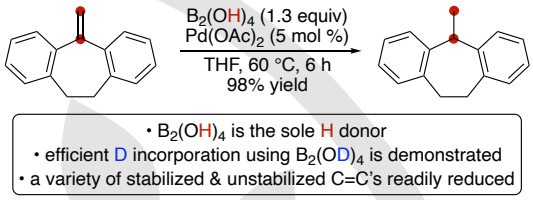

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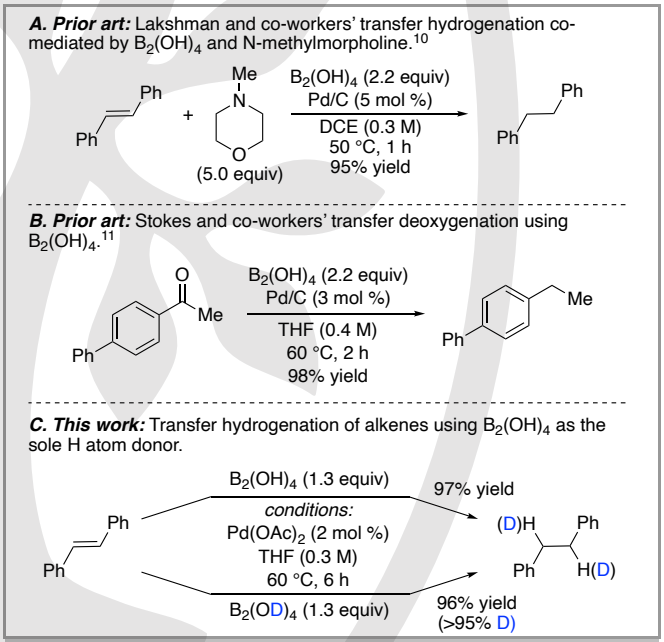
Abstract Tetrahydroxydiboron-mediated catalytic transfer hydrogenations have typically involved co-additives that, like tetrahydroxydiboron itself, are H atom donors. Herein we report an alkene transfer hydrogenation method with tetrahydroxydiboron as the sole source of H atoms. The reaction uses $Pd(OAc)_2$ as a convenient putative colloid pre-catalyst, and cyclic monoethers are competent solvents. Highly efficient alkene deuteration is demonstrated using tetradeuteroxydiboron.

Key words tetrahydroxydiboron, transfer hydrogenation, palladium catalysis, alkene reduction, deuterium, catalytic hydrogenation

Transition metal-catalyzed hydrogenation is one of the most important reactions in synthetic chemistry and is widely used and studied in both industry and academia.[1] Catalytic hydrogenation is often accomplished by direct application of H_2 gas, which is formally "byproductless," but safety and environmental concerns arise due to H_2 production, transportation, storage, and handling. To avoid these and other inconveniences associated with the direct application of H_2, transfer hydrogenation (TH) allows in situ generation of stoichiometric H_2, with the expense of stoichiometric byproduct generation from the transfer reagent.[2] Longstanding transfer reagents include formic acid,[3] primary alcohols,[4] ammonia borane,[5] and silanes.[6]

Since 2016, we and others have developed methods for transition metal-catalyzed transfer hydrogenation and hydrogenolysis reactions of a variety of organic functional groups using tetrahydroxydiboron-mediated processes with water or alcohols serving as H atom co-donors.[7] Among the common diborane reagents,[8] $B_2(OH)_4$ is the most atom-economical, and is being used industrially for the transition metal-catalyzed synthesis of aryl boronic acids.[9] More recently there have been examples of transfer hydrogenation or hydrogenolysis using $B_2(OH)_4$ without a polar protic additive. For example, in 2020,



Scheme 1 Relevant Examples of Catalytic Transfer Reductions Mediated by Tetrahydroxydiboron.

Lakshman and coworkers reported the Pd/C- catalyzed reduction of aryl halides, aldehydes, alkenes, and alkynes using $B_2(OH)_4$ and 4-methylmorpholine (Scheme 1A).[10] Interestingly, 4-methylmorpholine served as a formally aprotic co-donor of H atoms. More recently, our lab described a Pd/C-catalyzed transfer deoxygenation of benzylic ketones using $B_2(OH)_4$ as the sole H atom source in THF.[11] Herein, we report a Pd-catalyzed $B_2(OH)_4$-mediated alkene transfer hydrogenation method using $Pd(OAc)_2$ as a precatalyst and no H-atom co-donor (Scheme 1C).

The optimized conditions[12] are similar to those we recently published for the ketone deoxygenation.[11] In either case,

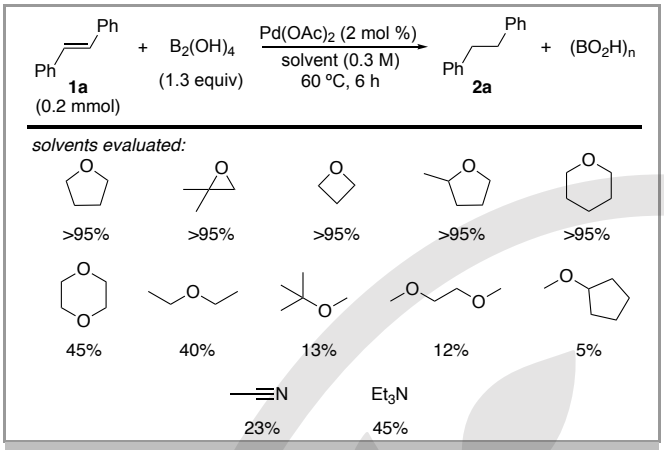
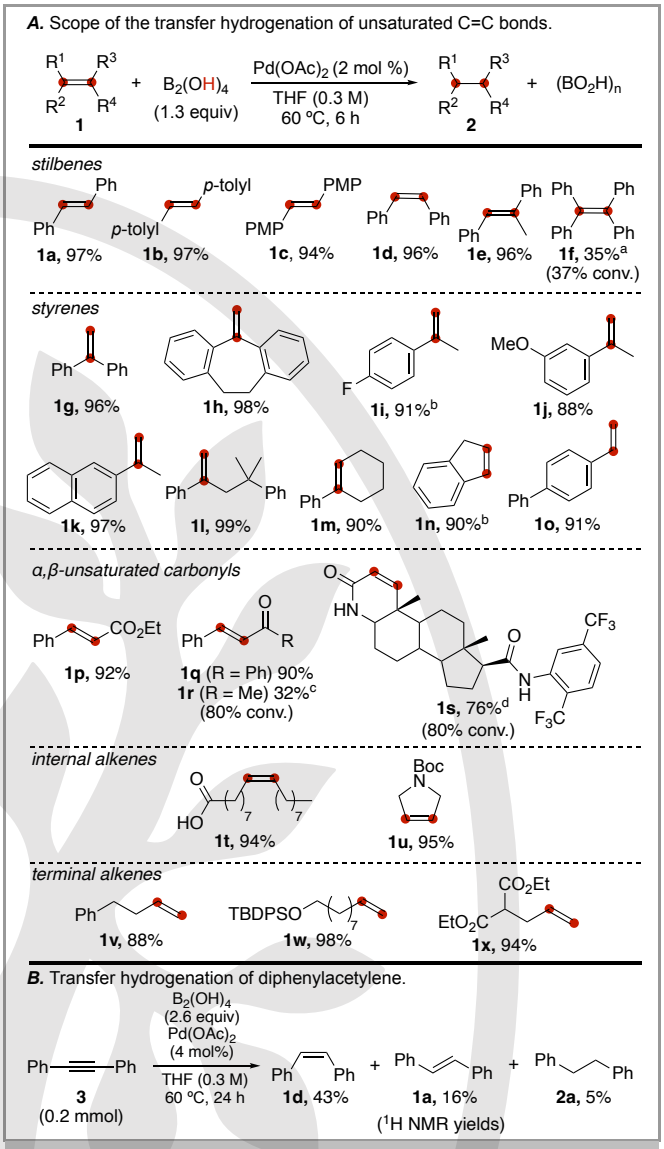


Table 1 Solvent effects on hydrogenation yield. Yields of **2a** determined by ^{1}H NMR analysis of the crude reaction mixture compared to 1,3,5-trimethoxybenzene as an internal standard.

common aprotic diboron reagents B_2pin_2 and B_2cat_2 afford no substrate conversion (see the Supporting Information for details). We evaluated a variety of polar solvents and found that amongst ethers, cyclic monoethers (Table 1, first row) are suitable for the reduction of *trans*-stilbene, whereas 1,4-dioxane and acyclic ethers (row 2) are less so. This may be due to the attenuated polarity of 1,4-dioxane and cyclic monoethers compared to the cyclic monoethers, which, beyond their ability to stabilize the putative metaboric acid byproduct,[11,13] may limit their ability to dissolve $B_2(OH)_4$. Acetonitrile and triethylamine (row 3) also exhibit some efficacy, while 1,2-dichloroethane, toluene, and DMSO yield no product.[12]

We then investigated the scope of the transfer hydrogenation of various alkenes as substrates using the optimized conditions and THF as solvent (Scheme 2A). Di- and tri-substituted stilbenes **1a**–**1e** are efficiently reduced, regardless of alkene geometry (cf., **1a** and **1d**). In contrast, tetraphenylethylene (**1f**) reacts incompletely even after heating for a full day. Interestingly the water-mediated variant, performed at ambient temperature in dichloromethane, rapidly reduces tetraphenylethylene at room temperature.[7a] A variety of styrenes (**1g**–**1o**) were evaluated and all afford yields greater than 90%. Furthermore, ethyl cinnamate (**1p**) undergoes efficient reduction of its α,β-unsaturation, as does chalcone (**1q**), whereas benzylideneacetone (**1r**), featuring an enolizable ketone, affords a low C=C reduction yield of 32% due to observed competing carbonyl reduction. Excitingly, dutasteride (**1s**), a prescription active pharmaceutical ingredient for the treatment of benign prostatic hyperplasia, undergoes selective reduction of its α,β-unsaturation position, albeit at a slow rate. We also evaluated the reduction of a few isolated alkenes using compounds **1t**–**1x**. Oleic acid (**1t**), a Boc-protected dihydropyrrole (**1u**), and three terminal alkenes (**1v**, **1w**, and **1x**) were all efficiently hydrogenated. Diphenylacetylene (**3**), was also subjected to similar reduction conditions although with twice the amount of additive and catalyst (Scheme 2B). The major product is *cis*-stilbene (**1d**, 43% yield), with *trans*-stilbene (**1a**) observed in 16% yield, and just 5% of bibenzyl (**2a**) produced.

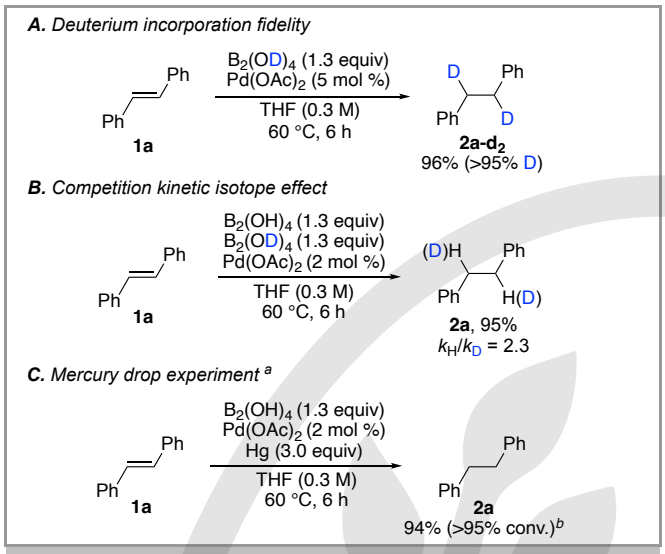
As shown in Scheme 3 below, we performed additional experiments on *trans*-stilbene (**1a**) to assess the fidelity of deuterium isotope incorporation, evaluate a deuterium kinetic isotope effect, and determine the influence of mercury on the catalysis. Excitingly, Scheme 3A shows that *trans*-stilbene



Scheme 2 Substrate scope of the transfer hydrogenation. These reactions were conducted on 0.5 mmol scale. Unless otherwise noted, full conversion was observed and reported yields are of isolated products. [a] Reaction time was 24 hours. [b] Due to product volatility, ^{1}H NMR yield is reported (compared to 1,3,5-trimethoxybenzene as an internal standard). [c] ^{1}H NMR yield compared to 1,3,5-trimethoxybenzene as an internal standard. [d] Conducted on 0.2 mmol scale. (PMP = *para*-methoxyphenyl)

incorporates deuterium from $B_2(OD)_4$ virtually quantitatively. This is exciting because deuterium-enriched compounds are valuable medicinally[14,15] and as probes of organic reaction mechanisms.[16] This also validates the hypothesis that the diboron reagent is the sole source of hydrogen atoms. A competition kinetic isotope effect (KIE) study[17,18] was performed using equimolar amounts of $B_2(OH)_4$ and $B_2(OD)_4$ (Scheme 3B), resulting in a KIE of 2.3 as determined from the ratio of products **1a**/**1a-d2**. Although the transfer of the H atom to form the putative palladium hydride is not likely the rate-determining step, this result informs about the formation of the putative palladium hydride, and especially interesting compared to the competition KIE previously reported for the B_2cat_2-mediated reduction of diphenylacetylene using equimolar H_2O and D_2O in dichloromethane, which resulted in a competition KIE of 5.6.[7a]

Lastly, a mercury drop test was performed (Scheme 3C). Near-complete conversion is achieved when mercury is added



Scheme 3 Applications and mechanistic studies on *trans*-stilbene. These reactions were conducted on 0.2 mmol scale. Isolated yields are reported and conversion matched the yield unless otherwise noted. [a] Mercury was added after eight minutes to allow for catalyst induction. [b] Yield and % conv. determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

following an eight-minute induction period.[19] In contrast, the yield and conversion decrease slightly (92% each) if mercury is added immediately, suggesting some inhibition of catalyst induction from $Pd(OAc)_2$ (not shown). Considering the putative colloidal ligandless nature of this reaction, the outcome of these mercury drop experiments—perhaps limited in their utility—is difficult to interpret.;

In conclusion, we have developed a method for the Pd-catalyzed transfer hydrogenation of a variety of unsaturated C–C bonds mediated by $B_2(OH)_4$ using $Pd(OAc)_2$ as a convenient precatalyst,[20,21] and quantitative alkene deuteration has been demonstrated using $B_2(OD)_4$.

Acknowledgment

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Supporting Information

YES (this text will be updated with links prior to publication)

Primary Data

NO.

Conflict of Interest

The authors declare no conflict of interest.

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(20) **General Transfer Hydrogenation Procedure.** An oven-dried one-dram disposable borosilicate vial is charged with a magnetic stir bar, 58.3 mg of tetrahydroxydiboron (0.65 mmol, 1.3 equiv), 2.3 mg of $Pd(OAc)_2$ (0.01 mmol, 0.02 equiv), and substrate if solid (0.5 mmol, 1.0 equiv). The vial is capped and purged with argon or nitrogen gas, then charged with 1.7 mL of degassed anhydrous THF and heated to 60 °C for six hours with stirring at 600 rpm. After cooling to ambient temperature, the solution is filtered through a plug of silica gel and rinsed with dichloromethane.

(21) Characterization data of representative product **2a**: Yield (0.5 mmol scale): 88 mg (97%); colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.25 (m, 4H), 7.21–7.16 (m, 6H), 2.92 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.1, 128.6, 128.4, 126.0, 38.0.

(22) Yaghoubi, M.; Reyes, I. C.; Stokes, B. J. *ChemRxiv* **2024**, DOI: 10.26434/chemrxiv-2024-k2qdm.

Pd-Catalyzed Transfer Hydrogenation of Alkenes Using Tetrahydroxydiboron as the Sole Hydrogen Donor

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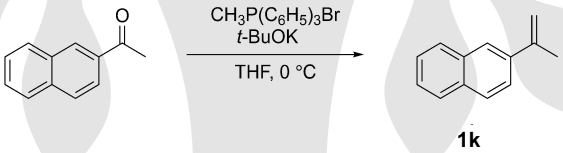
Table of Contents

I. General Considerations

Solvents were obtained from either Sigma-Aldrich or Fisher Scientific either anhydrous and inhibitor-free or dried by known procedure.[1] Water content of solvents were determined by Karl-Fisher titration to be less than 20 ppm. Sources of $B_2(OH)_4$ included AK Scientific and Boron Molecular. $Pd(OAc)_2$, 1,3,5-trimethoxybenzene, diphenylacetylene (**3**), and chalcone (**1q**) were purchased from Acros Organics. Bis(catecholato) diboron and bis(pinacolato) diboron were purchased from AK Scientific. *Cis*-stilbene (**1d**), α-methyl stilbene (**1e**), and 1,1-diphenylethylene (**1g**) were purchased from Alfa Aesar and used as received after confirming purity by ^{1}H NMR. *Trans*-stilbene (**1a**), tetraphenylethylene (**1f**), 4-fluoro-α-methyl styrene (**1i**), 2,4-diphenyl-4-methyl-1-pentene (**1l**), 1-phenyl-1-cyclohexene (**1m**), indene (**1n**), ethyl cinnamate (**1p**), dutasteride (**1s**), N-Boc-2,5-dihydro-1H-pyrrole (**1u**), 4-phenyl-1-butene (**1v**), and diethyl allylmalonate (**1x**) were used as purchased from Sigma-Aldrich. Oleic acid (**1t**) was purchased from Strem Chemicals. Palladium on carbon was obtained from Sigma-Aldrich (unreduced, 30 wt. %). All compounds were used as received. Solids were weighed using a MettlerToledo XS105 balance repeatable to 0.1 mg. NMR spectra were obtained on Agilent spectrometers, with ^{1}H NMR spectra obtained at 500 MHz or 400 MHz and referenced to the residual $CHCl_3$ singlet at 7.26 ppm, or CH_2Cl_2 at 5.32 ppm, or THF at 1.84 and 3.72 ppm. ^{13}C NMR spectra were obtained at 126 MHz or 100 MHz and referenced to the center line of the residual $CHCl_3$ triplet at 77.16 ppm. ^{11}B NMR spectra were obtained at 160 MHz in d_6-DMSO. ^{19}F NMR spectra were obtained at 470 MHz in $CDCl_3$. The abbreviations s, d, t, q, quint, dd, dt, and m stand for the resonance multiplicities singlet, doublet, triplet, quartet, quintet (pentet), doublet of doublets, doublet of triplets, and multiplet, respectively. GC analysis was obtained on a Thermo Trace 1300 with a 30m X 0.25 mm X 0.25μm column. FT-IR analysis was obtained on a Thermo-Nicolet 380 using a diamond GladiATR from Pike technologies; the abbreviations w, m, and s for the characteristic peaks stand for relative intensities of weak, medium, and strong, respectively, as determined by 0-25%, 25-50% and greater than 50% absorbance.

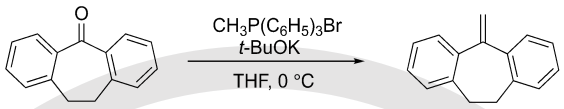
II. Preparation of **1b**, **1c**, **1h**, **1j**, **1k**, **1o**, **1w**, and $B_2(OD)_4$

A. Synthesis of 1h, 1j, 1k, and 1o via Wittig olefination of ketones or aldehydes



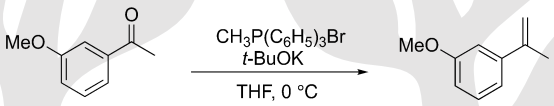
1k

2-Isopropenylnaphthalene 1k. In a dry 50 mL round bottom flask charged with PTFE coated magnetic stir bar, 2.63 g (1.25 equiv) of methyl triphenylphosphonium bromide was dissolved in 20.0 mL of anhydrous THF (0.3 M). The reaction flask was then sealed with a rubber septum before 4.8 mL (1.3 equiv) of a 1.6 M solution of *t*-BuOK in THF was added drop-wise under argon, upon which the reaction mixture had turned yellow and was continuously stirred for an additional 30 minutes before it was chilled to 0 °C. Then, 1.00 g (5.9 mmol) of 2-acetonaphthone in a minimal amount of THF was then added to the solution dropwise via syringe. The reaction was then brought to room temperature and allowed to stir for 18 hours. After TLC analysis showed all the ketone was consumed, the reaction was quenched with saturated aqueous NH_4Cl solution. The alkene was extracted with ethyl acetate three times. The combined organic solution was collected and dried over anhydrous sodium sulfate before it was concentrated under reduced pressure to afford the crude alkene product. Purification by silica gel chromatography using hexanes as the eluent and removal of the solvent by rotavap afforded the desired alkene (0.764 g, 77% yield) as a white solid. The spectral data matched those reported by Liu and co-workers.[2] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89–7.79 (m, 4H), 7.70 (dd, J = 8.7, 1.8 Hz, 1H), 7.51–7.44 (m, 2H), 5.56 (s, 1H), 5.22 (t, J = 1.5 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.0, 138.3, 134.6, 133.4, 128.2, 127.7, 127.5, 126.1, 125.8, 124.3, 123.9, 113.0, 21.9.



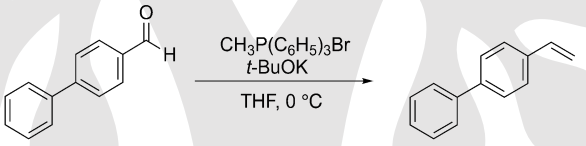
1h

10,11-Dihydro-5-methylene-5H-dibenzo[a,d]cycloheptene 1h. The general procedure was followed using 1.000 g (4.8 mmol) of 10,11-dihydro-5H-dibenzo[a,d]cyclohepten-5-one as substrate. Purification by column chromatography (100% hexane) afforded **1h** (0.792 g, 88% yield) as a white solid. The spectral data matched those reported by Lamanec and co-workers.[3] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (dd, J = 7.3, 1.3 Hz, 2H), 7.24–7.16 (m, 4H), 7.16–7.12 (m, 2H), 5.43 (s, 2H), 3.17 (s, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.8, 141.2, 138.4, 128.9, 128.2, 127.6, 126.2, 117.5, 33.3.



1j

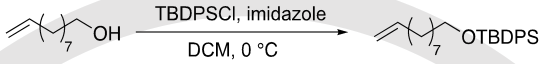
3-methoxy-α-methyl styrene 1j. The general procedure was followed using 1.000 g (6.7 mmol) of 3-methoxyacetophenone as substrate. Purification by column chromatography (100% hexane) afforded **1j** (0.814 g, 82% yield) as a colorless oil. The spectral data matched those reported by Martin and co-workers.[4] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.26 (t, J = 7.9 Hz, 1H), 7.12–7.08 (m, 1H), 7.05–7.03(m, 1H), 6.86 (ddd, J = 8.2, 2.6, 0.9 Hz, 1H), 5.41 (q, J = 0.9 Hz, 1H), 5.12 (p, J = 1.5 Hz, 1H), 3.85 (s, 3H), 2.18 (dd, J = 1.5, 0.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.5, 143.2, 142.8, 129.1, 118.1, 112.6, 111.5, 55.2, 21.8 (one carbon obscured).



1o

4-Ethenylbiphenyl 1o. The general procedure was followed was followed using 1.000 g (5.5 mmol) of 4-biphenylcarboxaldehyde as substrate. Finally, solvent removal resulted in 68% yield of a white solid. The spectral data matched those reported by Yoon and co-workers.[5] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64–7.56 (m, 4H), 7.52–7.49 (m, 2H), 7.48–7.43 (m, 2H), 7.38–7.33 (m, 1H), 6.78 (dd, J = 17.6, 10.9 Hz, 1H), 5.81 (dd, J = 17.6, 0.8 Hz, 1H), 5.29 (dd, J = 10.9, 0.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.7, 140.6, 136.6, 136.4, 128.8, 127.3, 127.2, 127.0, 126.6, 113.9.

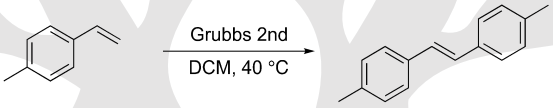
B. Synthesis of 1w via silyl TBDPS protection



1w

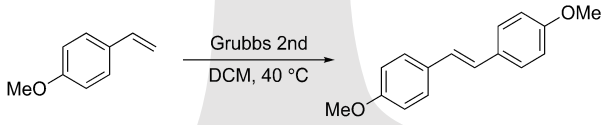
***tert*-butyl(dec-9-en-1-yloxy) diphenylsilane 1w.** Using a modified literature procedure,[6] to a solution of 9-decen-1-ol (0.500 g, 3.2 mmol) in anhydrous dichloromethane (3.2 mL) cooled to 0 °C, imidazole (0.283 g, 4.2 mmol) was added, followed by drop wise addition of *tert*-butyl(chloro)diphenylsilane (0.968 g, 3.5 mmol). The reaction mixture was allowed to warm to room temperature and stirred overnight and then quenched by the addition of water and dichloromethane. The layers were separated, and the organic layer was dried over Na_2SO_4. The solvent was evaporated under reduced pressure to afford the crude product which was purified by column chromatography on silica gel using (95:5) hexanes/EtOAc as the eluent to get the compound **1w** (1.035 g, 82%) as a colorless oil. The spectral data matched those reported by Stephan and co-workers.[7] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75–7.67 (m, 4H), 7.50–7.37 (m, 6H), 5.91–5.78 (m, 1H), 5.07–4.92 (m, 2H), 3.74–3.66 (m, 2H), 2.12–2.03 (m, 2H), 1.58 (m, 2H), 1.45–1.34 (m, 4H), 1.34–1.25 (m, 6H), 1.13–1.05 (m, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.2, 135.6, 134.2, 129.5, 127.6, 114.1, 64.0, 33.9, 32.6, 29.5, 29.3, 29.1, 29.0, 26.9, 25.8, 19.3.

C. Synthesis of 1b and 1c via olefin metathesis



1b

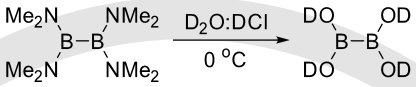
4,4'-dimethylstilbene 1b. A round bottom flask was charged with 64 mg of Grubbs 2nd generation catalyst and then capped with a septum, degassed under vacuum, and backfilled with nitrogen. To the flask, 4.0 mL of DCM and 0.3 mL (2.0 mmol) of 4-methylstyrene were added. The reaction was stirred under nitrogen gas at 40 °C for 5 hours, at which time all the solvent was removed *in vacuo*. The product was then collected by filtering through a silica plug to remove the catalyst, followed by column chromatography using (9:1) hexanes/EtOAc to get 68% of **1b** as a white solid. The spectral data matched those reported by Hassine and co-workers.[8] ^{1}H NMR (300 MHz, $CDCl_3$): 7.42 (m, 4H), 7.17 (m, 4H), 7.05 (s, 2H), 2.37 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): 137.3, 134.8, 129.4, 127.7, 126.4, 21.3.



1c

4,4'-dimethoxystilbene 1c. The procedure for **1b** was followed using 0.3 mL (2.0 mmol) of 4-methoxystyrene. The pure product was isolated as a white solid (127.3 mg, 53% yield). The spectral data matched those reported by Nolan and co-workers.[9] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48–7.40 (m, 4H), 6.94 (s, 2H), 6.92–6.87 (m, 4H), 3.84 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0, 130.5, 127.4, 126.2, 114.1, 55.3.

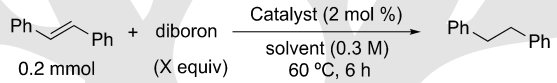
D. Synthesis of $B_2(OD)_4$



Tetradeuteroxydiboron: All Schlenk manipulations were carried out under nitrogen. Compounds were used as received, unless stated otherwise. Deuterium oxide (99.9% D) and 35% deuterium chloride in D_2O (99% D) were obtained from Sigma Aldrich. We employed the same procedure as our previous study,[10] resulting in 1.36 g (58%) of a white solid with no detectable proton inclusion by ^{1}H NMR. ^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ none detected; ^{11}B NMR (160 MHz, $(CD_3)_2SO$); δ 31.3. ATR-FTIR (neat): 2477 (s - OD sym. st); 2399 (s - OD assym. st); 1286 (s); 1147 (s); 926 (s); 804 (s); 634 (s) cm^{-1}.

III. Pd-Catalyzed Alkene Transfer Hydrogenation Mediated by Tetrahydroxydiboron

A. General Procedure for Reaction Optimization



General Optimization Procedure: To a 4 mL vial equipped with a stir bar, 23.3 mg of tetrahydroxydiboron (0.26 mmol), 0.9 mg of $Pd(OAc)_2$ (0.004 mmol) and 36 mg of *trans*-stilbene (0.2 mmol) were added. The vial was capped with a septum, degassed and backfilled with nitrogen for 15 minutes. Lastly, the vial was charged with 0.66 mL of degassed anhydrous THF and stirring at 60 °C and 600 rpm. After 6 hours, the solution was filtered through a silica plug and thoroughly washed with DCM. Solvent was removed and the reaction yield determined by ^{1}H NMR yield using 1,3,5-trimethoxybenzene as an internal standard.

B. Optimization Experiments

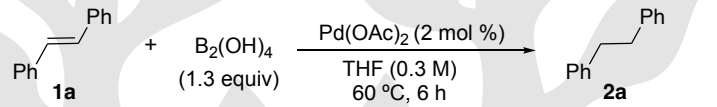
Trial[a]	Diboron	Diboron (eq.)	Solvent	Catalyst	% Yield
1[b]	$B_2(OH)_4$	1.7	MeCN	Pd/C	94
2[c]	$B_2(OH)_4$	1.5	THF	Pd/C	99
3[c]	$B_2(cat)_2$	1.5	THF	Pd/C	0
4[c]	$B_2(pin)_2$	1.5	THF	Pd/C	0
5	$B_2(OH)_4$	1.3	THF	$Pd(OAc)_2$	99
6[d]	$B_2(OH)_4$	1.3	DCE	$Pd(OAc)_2$	3
7[e]	$B_2(OH)_4$	1.3	DCE	$Pd(OAc)_2$	5
8	$B_2(OH)_4$	1.3	DMSO	$Pd(OAc)_2$	0
9[f]	$B_2(OH)_4$	1.3	DMSO	$Pd(OAc)_2$	5
10	$B_2(OH)_4$	1.5	THF	-	0
11[g]	$B_2(OH)_4$	1.3	THF	Pt/C	19
12[h]	$B_2(OH)_4$	1.3	THF	$NiCl_2$.glyme	0
13	$B_2(OH)_4$	1.3	MeCN	$Pd(OAc)_2$	23
14	$B_2(OH)_4$	1.3	Et_3N	$Pd(OAc)_2$	45
15	-	-	THF	$Pd(OAc)_2$	0
16	$B_2(OH)_4$	1.5	THF	$Pd_3(OAc)_6$	86
17[i]	$B_2(OH)_4$	1.5	MeCN	$Pd(OAc)_2$	95
18	$B_2(OH)_4$	1.3	epoxide	$Pd(OAc)_2$	97
19	$B_2(OH)_4$	1.3	oxetane	$Pd(OAc)_2$	96
20	$B_2(OH)_4$	1.3	2Me-THF	$Pd(OAc)_2$	98
21	$B_2(OH)_4$	1.3	THP	$Pd(OAc)_2$	95
22	$B_2(OH)_4$	1.3	dioxane	$Pd(OAc)_2$	45
23	$B_2(OH)_4$	1.3	DEE	$Pd(OAc)_2$	40
24	$B_2(OH)_4$	1.3	DME	$Pd(OAc)_2$	12
25	$B_2(OH)_4$	1.3	MTBE	$Pd(OAc)_2$	13
26	$B_2(OH)_4$	1.3	CPME	$Pd(OAc)_2$	5
27	PinBH	1.3	THF	$Pd(OAc)_2$	55

[a] 0.2 mmol trans-stilbene, X eq. diboron, 2 mol% catalyst loading, and 0.66 mL of degassed anhydrous solvent were reacted in a vial at 60 °C for 6 hours, unless otherwise noted. [b] 7.5 mol% catalyst and 7 eq. THF. [c] 5 mol% catalyst for 20 hours. [d] 5 eq. THF was added. [e] 10 eq. THF added. [f] 0.5 eq. THF was added. [g] 5 mol% catalyst loading. [h] 5 mol% catalyst loading overnight. [i] 6 mol% catalyst loading.

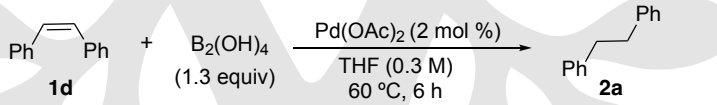
C. Optimized General Procedure

General Optimization Procedure: To a 1 dram vial (3.7 mL) equipped with a micro stir bar was added 58.3 mg of tetrahydroxydiboron (1.3 equiv, 0.65 mmol) and 2.3 mg $Pd(OAc)_2$ (2 mol%, 0.01 mmol). The vial was capped with a septum, degassed and backfilled with argon. If the starting material was solid, it was degassed along with diboron and catalyst, otherwise, it should be degassed and added later on. Lastly, the vial was charged with 1.7 mL of degassed anhydrous THF and allowed it to stir at 60 °C and 600 rpm. After 6 hours, the solution was filtered through a silica plug and washed with DCM or ethyl acetate, and the product was isolated by solvent removal *in vacuo* unless otherwise noted. (For the volatile products **2i** and **2n**, ^{1}H NMR yield was determined by adding a known amount of 1,3,5-trimethoxybenzene as an internal standard.)

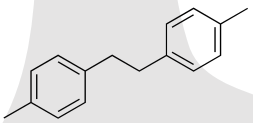
D. Scope of the Transfer Hydrogenation of Alkenes



Reduction of *trans*-stilbene (1a) to bibenzyl (2a). The general procedure was followed using 58.3 mg of tetrahydroxydiboron (0.65 mmol), 2.3 mg of $Pd(OAc)_2$ (0.01 mmol), 90.1 mg of *trans*-stilbene **1a** (0.5 mmol) and 1.7 mL of THF. ^{1}H NMR spectroscopy (400 MHz, $CDCl_3$) revealed complete consumption of **1a** and 97% isolated yield of **2a** as a colorless solid. The spectral data obtained are consistent with previous literature.[10] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.25 (m, 4H), 7.21–7.16 (m, 6H), 2.92 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.1, 128.6, 128.4, 126.0, 38.0.

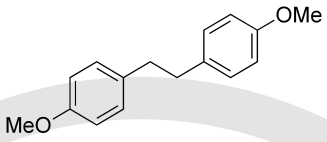


Reduction of *cis*-stilbene (1d) to bibenzyl (2a). The general procedure was followed using 58.3 mg of tetrahydroxydiboron (0.65 mmol), 2.3 mg $Pd(OAc)_2$ (0.01 mmol), 90.1 mg of *cis*-stilbene **1d** (0.5 mmol) and 1.7 mL of THF. ^{1}H NMR spectroscopy (500 MHz, $CDCl_3$) revealed complete consumption of **1d** and 96% isolated yield of **2a** as a colorless solid. The spectral data obtained are consistent with previous literature.[10] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29–7.25 (m, 4H), 7.21–7.16 (m, 6H), 2.91 (s, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.8, 128.5, 128.4, 126.0, 38.0.



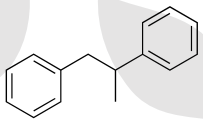
2b

4,4'-dimethylbibenzyl 2b. The general procedure was followed using 58.3 mg of tetrahydroxydiboron (0.65 mmol), 2.3 mg $Pd(OAc)_2$ (0.01 mmol), 104.2 mg of 4,4'-dimethylstilbene **1b** (0.5 mmol) and 1.7 mL of THF. ^{1}H NMR spectroscopy (400 MHz, $CDCl_3$) revealed complete consumption of **1b** and 97% isolated yield of **2b** as a colorless solid. The spectral data matched those reported by McNab and co-workers.[11] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (s, 8H), 2.91 (s, 4H), 2.37 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.9, 135.3, 129.0, 128.3, 37.7, 21.1.



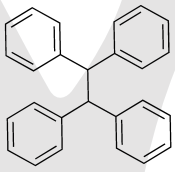
2c

4,4'-dimethoxylbibenzyl 2c. The general procedure was followed using 58.3 mg of tetrahydroxydiboron (0.65 mmol), 2.3 mg $Pd(OAc)_2$ (0.01 mmol), 120 mg of 4,4'-dimethoxylstileben **1c** (0.5 mmol) and 1.7 mL of THF. ^{1}H NMR spectroscopy (400 MHz, $CDCl_3$) revealed complete consumption of **1c** and 94% isolated yield of **2c** as a colorless solid. The spectral data matched those reported by Kim and co-workers.[12] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12–7.06 (m, 4H), 6.86–6.80 (m, 4H), 3.80 (s, 6H), 2.84 (s, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.8, 134.0, 129.4, 113.7, 55.3, 37.3.



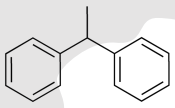
2e

1,2-Diphenylpropane 2e. The general procedure was followed using 58.3 mg of tetrahydroxydiboron (0.65 mmol), 2.3 mg $Pd(OAc)_2$ (0.01 mmol), 97 mg of *trans*-α-methylstilbene **1e** (0.5 mmol) and 1.7 mL of THF. ^{1}H NMR spectroscopy (400 MHz, $CDCl_3$) revealed complete consumption of **1e** and 96% isolated yield of **2e** as a colorless oil. The spectral data obtained are consistent with previous literature.[10] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.29 (m, 4H), 7.29–7.23 (m, 4H), 7.20– 7.14 (m, 2H), 3.13–3.00 (m, 2H), 2.85 (dd, J = 13.1, 8.1 Hz, 1H), 1.33 (d, J = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.0, 140.9, 129.2, 128.4, 128.2, 127.1, 126.1, 125.9, 45.1, 41.9, 21.2.



2f

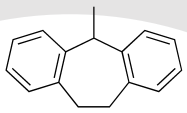
1,1,2,2-Tetraphenylethane 2f. The general procedure was followed using 58.3 mg of tetrahydroxydiboron (0.65 mmol), 2.3 mg $Pd(OAc)_2$ (0.01 mmol), 166.2 mg of tetraphenylethylene **1f** (0.5 mmol) and 1.7 mL of THF. After 18 hours, ^{1}H NMR spectroscopy (400 MHz, $CDCl_3$) revealed 38% consumption of **1f** and a 35% isolated yield of **2f** using 9:1 (hexanes/benzene) as the eluent by column chromatography. The spectral data obtained are consistent with previous literature.[10] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20–7.14 (m, 8H), 7.14–7.08 (m, 8H), 7.05–6.98 (m, 4H), 4.77 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 128.5, 128.1, 125.8, 56.3.



2g

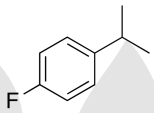
1,1- Diphenylethane (2g). The general procedure was followed using 58.3 mg of tetrahydroxydiboron (0.65 mmol), 2.3 mg $Pd(OAc)_2$ (0.01 mmol), 90.1 mg of 1,1-diphenylethylene **1g** (0.5 mmol) and 1.7 mL of THF. ^{1}H NMR spectroscopy (400 MHz, $CDCl_3$) revealed complete consumption of **1g**. Solvent was then removed *in vacuo* to afford 96% **2g** as a colorless oil. The spectral data obtained are consistent with previous literature.[10] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.34 (m, 4H), 7.33–7.29 (m, 4H), 7.28–7.24 (m, 2H), 4.24

(q, J = 7.2 Hz, 1H), 1.73 (d, J = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.4, 128.4, 127.7, 126.1, 44.8, 22.0.



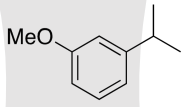
2h

10,11-Dihydro-5-methyl-5H-dibenzo[a,d]cycloheptene 2h. The general procedure was followed using 58.3 mg of tetrahydroxydiboron (0.65 mmol), 2.3 mg $Pd(OAc)_2$ (0.01 mmol), 103.1 mg of 10,11-Dihydro-5-methylene-5H-dibenzo[a,d]cycloheptene **1h** (0.5 mmol) and 1.7 mL of THF. Solvent was then removed *in vacuo* to yield 98 % of **2h**. The spectral data matched those reported by Muñiz and co-workers.[13] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28–7.24 (m, 2H), 7.19–7.11 (m, 6H), 4.47 (q, J = 7.4 Hz, 1H), 3.31–3.19 (m, 4H), 1.75 (d, J = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.2, 139.2, 130.0, 127.4, 126.3, 126.2, 43.7, 33.2, 22.0.



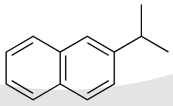
2i

1-Fluoro-4-isopropylbenzene 2i. The general procedure was followed using 58.3 mg of tetrahydroxydiboron (0.65 mmol), 2.3 mg $Pd(OAc)_2$ (0.01 mmol), 68.1 mg of 4-Fluoro-α-methylstyrene **2i** (0.5 mmol) and 1.7 mL of THF. Solvent was then removed *in vacuo* to yield 68 % of **2i**. Due to low boiling point, the reaction yield was determined by ^{1}H NMR yield using 1,3,5-trimethoxybenzene as an internal standard and 91% NMR yield of **2i** was obtained. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23–7.13 (m, 2H), 7.08–6.91 (m, 2H), 2.96–2.84 (sep, J = 6.9 Hz, 1H), 1.25 (d, J = 7.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.1 (d, J = 243.6 Hz), 144.4 (d, J = 3.2 Hz), 127.7 (d, J = 7.7 Hz), 114.9 (d, J = 20.9 Hz), 33.5, 24.1. ^{19}F NMR (470 MHz, $CDCl_3$) δ -118.1 ppm.



2j

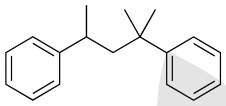
1-Isopropyl-3-methoxybenzene 2j. The general procedure was followed using 58.3 mg of tetrahydroxydiboron (0.65 mmol), 2.3 mg $Pd(OAc)_2$ (0.01 mmol), 74.1 of mg 3-methoxy-α-methyl styrene **1j** (0.5 mmol) and 1.7 mL of THF. Solvent was then removed *in vacuo* to yield 88 % of **2j**. ^{1}H NMR spectroscopy (400 MHz, $CDCl_3$) revealed complete consumption of **1j**. The spectral data matched those reported by Biscoe and co-workers.[14] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (t, J = 9.8, 5.9 Hz, 1H), 6.90 (d, J = 7.6 Hz, 1H), 6.86 (s, 1H), 6.79 (dd, J = 8.2, 2.2 Hz, 1H), 3.86 (s, 3H), 3.00 (sep, J = 6.9 Hz, 1H), 1.32 (d, J = 7.0 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.7, 150.7, 129.3, 118.9, 112.5, 110.8, 55.1, 34.2, 24.00.



2k

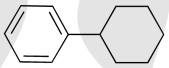
2-Isopropylnaphthalene 1k. The general procedure was followed using 58.3 mg of tetrahydroxydiboron (0.65 mmol), 2.3 mg $Pd(OAc)_2$ (0.01 mmol), 84.1 mg of 2-isopropenylnaphthalene **1k** (0.5 mmol) and 1.7

mL of THF. ^{1}H NMR spectroscopy (400 MHz, $CDCl_3$) revealed complete consumption of **1k** and 97% isolated yield of **2k**. The spectral data matched those reported by Liu and co-workers.[15] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (t, *J* = 7.6 Hz, 3H), 7.74 (br s,1H), 7.58–7.47 (m, 3H), 3.18 (sep, *J* = 6.9 Hz, 1H), 1.46 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 133.8, 132.2, 127.9, 127.7, 127.6, 125.9, 125.8, 125.2, 124.2, 34.3, 24.1.



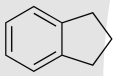
2l

2-Methyl-2,4-diphenyl-pentane 2l. The general procedure was followed using 58.3 mg of tetrahydroxydiboron (0.65 mmol), 2.3 mg $Pd(OAc)_2$ (0.01 mmol), 118.2 mg of 2,4-diphenyl-4-mthyl-1-pentene **1l** (0.5 mmol) and 1.7 mL of THF. ^{1}H NMR spectroscopy (400 MHz, $CDCl_3$) revealed complete consumption of **1l** and 99% isolated yield of **2l**. The spectral data matched those reported by Kobayashi and co-workers.[16] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42–7.35 (m, 4H), 7.33–7.29 (m, 2H), 7.28–7.19 (m, 2H), 7.16–7.12 (m, 2H), 2.69–2.60 (m, 1H), 2.17 (dd, *J* = 14.1, 7.1 Hz, 1H), 2.07 (dd, *J* = 14.1, 5.0 Hz, 1H), 1.36 (s, 3H), 1.27 (s, 3H), 1.15 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.4, 149.3, 128.3, 128.1, 127.1, 126.1, 125.6, 125.4, 52.8, 37.2, 31.1, 28.3, 25.2.



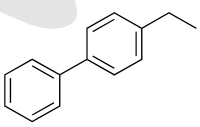
2m

Phenylcyclohexane 2m. The general procedure was followed using 58.3 mg of tetrahydroxydiboron (0.65 mmol), 2.3 mg $Pd(OAc)_2$ (0.01 mmol), 79.1 mg of 1-phenyl-1-cyclohexene **1m** (0.5 mmol) and 1.7 mL of THF. ^{1}H NMR spectroscopy (400 MHz, $CDCl_3$) revealed complete consumption of **1m** and 90% isolated yield of **2m**. The spectral data matched those reported by Fu and co-workers.[17] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 (t, *J* = 7.5 Hz, 2H), 7.27–7.19 (m, 3H), 2.58–2.50 (m, 1H), 1.96–1.86 (m, 4H), 1.83–1.75 (m, 1H), 1.52–1.38 (m, 4H), 1.35–1.26 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 128.3, 126.8, 125.8, 44.6, 34.5, 27.0, 26.2.



2n

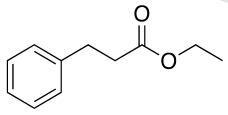
Indane 2n. The general procedure was followed using 58.3 mg of tetrahydroxydiboron (0.65 mmol), 2.3 mg $Pd(OAc)_2$ (0.01 mmol), 58.1 mg of indene **1n** (0.5 mmol) and 1.7 mL of THF. Solvent was then removed *in vacuo* to yield 66% of **2n**. Due to slightly low boiling point, the reaction yield also determined by ^{1}H NMR yield using 1,3,5-trimethoxybenzene as an internal standard and 90% NMR yield of **2n** as a colorless oil was obtained. The spectral data matched those reported by Clive and co-workers.[18] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.24 (m, 2H), 7.24–7.13 (m, 2H), 2.97 (t, *J* = 7.4 Hz, 4H), 2.12 (quint, *J* = 7.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 126.0, 124.4, 32.9, 25.4.



2o

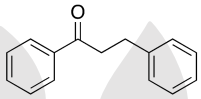
4-Ethyl-biphenyl 2o. The general procedure was followed using 58.3 mg of tetrahydroxydiboron (0.65 mmol), 2.3 mg $Pd(OAc)_2$ (0.01 mmol), 90.1 mg of 4-ethenylbiphenyl **1o** (0.5 mmol) and 1.7 mL of THF. Solvent was then removed *in vacuo* to yield 91 % of **2o**. The spectral data matched those reported by

Tsubouchi and co-workers.[19] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.56 (m, 2H), 7.55–7.50 (m, 2H), 7.46–7.40 (m, 2H), 7.36–7.26 (m, 3H), 2.70 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 141.2, 138.6, 128.7, 128.3, 127.1, 127.0, 126.9, 28.5, 15.6.



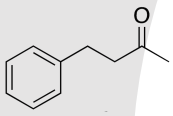
2p

Ethyl 3-phenylproponate 2p. The general procedure was followed using 58.3 mg of tetrahydroxydiboron (0.65 mmol), 2.3 mg $Pd(OAc)_2$ (0.01 mmol), 88 mg of ethyl cinnamate **1p** (0.5 mmol) and 1.7 mL of THF. ^{1}H NMR spectroscopy (400 MHz, $CDCl_3$) revealed complete consumption of **1q** and 90% isolated yield of **2q** as a colorless oil. The spectral data obtained are consistent with the previous literature.[10] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.28 (m, 2H), 7.26–7.20 (m, 3H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.97 (t, *J* = 7.7 Hz, 2H), 2.65 (t, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.9, 140.6, 128.5, 128.3, 126.2, 60.4, 36.00, 31.0, 14.2.



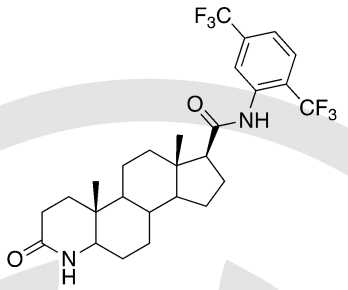
2q

Dihydrochalcone 2q. The general procedure was followed using 58.3 mg of tetrahydroxydiboron (0.65 mmol), 2.3 mg $Pd(OAc)_2$ (0.01 mmol), 104 mg of *trans*-chalcone **1q** (0.5 mmol) and 1.7 mL of THF. ^{1}H NMR spectroscopy (400 MHz, $CDCl_3$) revealed complete consumption of **1q** and 90% isolated yield of **2q**. The spectral data matched those reported by Fox and co-workers.[20] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04–7.98 (m, 2H), 7.99 (tt, *J* = 7.6, 1.7 Hz, 1H), 7.52–7.46 (m, 2H), 7.38–7.28 (m, 4H), 7.26 (tt, *J* = 7.1, 1.6 Hz, 1H), 3.34 (t, *J* = 7.9 Hz, 2H), 3.12 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.2, 141.4, 136.9, 133.1, 128.7, 128.6, 128.5, 128.1, 126.2, 40.5, 30.2.



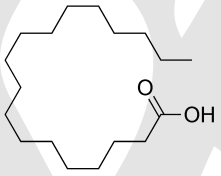
2r

4-Phenyl-2-butanone 2r. The general procedure was followed using 58.3 mg of tetrahydroxydiboron (0.65 mmol), 2.3 mg $Pd(OAc)_2$ (0.01 mmol), 73 mg of 4-phenyl-3-buten-2-one **1r** (0.5 mmol) and 1.7 mL of THF. ^{1}H NMR spectroscopy (400 MHz, $CDCl_3$) revealed 80% consumption of **1r** and a 32% NMR yield of **2r**. ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.29-7.25 (2H, m), 7.19- 7.16 (3H, m), 2.89 (t, *J* = 7.5 Hz, 2H), 2.75 (t, *J* = 7.5, 2H), 2.13 (s, 3H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 207.8, 140.9, 128.4, 128.2, 126.1, 45.1, 30.0, 29.7. By GC-MS and comparison to the literature, the remaining inseparable products are mixture of 1-phenyl-1-butene, butylbenzene and 4-phenyl-2-butanol.



2s

Dihydrodutasteride 2s. The general procedure was followed using 23.3 mg of tetrahydroxydiboron (0.26 mmol), 1 mg $Pd(OAc)_2$ (0.004 mmol), 106 mg of dutasteride (0.2 mmol) and 0.66 mL of THF. ^{1}H NMR spectroscopy (400 MHz, $CDCl_3$) revealed 80% consumption of **1s** and 76% of dihydrodutasteride **2s** as a white solid. The spectral data matched those reported by Górecki and co-workers.[21] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (s, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.51 (s, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 6.31 (s, 1H), 3.08 (dd, *J* = 12.3, 3.4 Hz, 1H), 2.47–2.38 (m, 2H), 2.35 (t, *J* = 9.1 Hz, 1H), 2.32–2.23 (m, 1H), 2.10–2.03 (m, 1H), 1.94–1.85 (m, 2H), 1.81–1.72 (m, 2H), 1.69–1.63 (m, 1H), 1.62–1.54 (m, 1H), 1.53–1.44 (m, 2H), 1.43–1.30 (m, 4H), 1.26–1.17 (m, 1H), 1.08–0.97 (m, 1H), 0.91 (s, 3H), 0.84 (td, *J* = 11.5, 3.7 Hz, 1H), 0.78 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.5, 171.4, 136.4 (q, *J* = 1.4 Hz), 135.2, 134.9, 126.8 (q, *J* = 5.4 Hz), 124.6, 124.2, 121.8 (q, *J* = 31 Hz), 120.3 (q, *J* = 8.1 Hz), 60.7, 58.5, 55.7, 51.1, 44.8, 37.9, 35.7, 35.1, 33.2, 29.5, 28.4, 27.2, 24.3, 23.6, 21.1, 13.4, 11.4; ^{19}F NMR (470 MHz, $CDCl_3$) δ –61.0, –63.4.

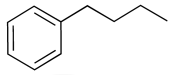


2t

Stearic acid 2t. The general procedure was followed using 58.3 mg of tetrahydroxydiboron (0.65 mmol), 2.3 mg $Pd(OAc)_2$ (0.01 mmol), 141 mg of oleic acid **1t** (0.5 mmol) and 1.7 mL of THF. ^{1}H NMR spectroscopy (400 MHz, $CDCl_3$) revealed complete consumption of **1t** and 94% isolated yield of **2t** as a colorless solid. The spectral data are consistent those reported by Jia and co-workers.[22] ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (t, *J* = 7.5 Hz, 2H), 1.68–1.58 (m, 2H), 1.39–1.19 (m, 28H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.4, 33.7, 31.9, 29.7–29.1 (12 carbons), 24.7, 22.7, 14.1.

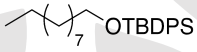
2u

N-Boc-pyrrolidine 2u. The general procedure was followed using 58.3 mg of tetrahydroxydiboron (0.65 mmol), 2.3 mg $Pd(OAc)_2$ (0.01 mmol), 85 mg of N-Boc-2,5-dihydropyrrole **1u** (0.5 mmol) and 1.7 mL of THF. ^{1}H NMR spectroscopy (400 MHz, $CDCl_3$) revealed complete consumption of **1u** and 95% isolated yield of **2u** as a colorless solid. The spectral data obtained are consistent with previous literature.[10] ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.23 (br s, 4H), 1.78 (br s, 4H), 1.40 (s, 9H); 13C NMR (100 MHz, $CDCl_3$): δ 154.5, 78.6, 46.1, 45.8, 28.4, 25.9, 25.1.



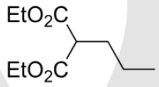
2v

1-Butylbenzene 2v. The general procedure was followed using 58.3 mg of tetrahydroxydiboron (0.65 mmol), 2.3 mg $Pd(OAc)_2$ (0.01 mmol), 66.1 of mg 4-phenyl-1-butene **1v** (0.5 mmol) and 1.7 mL of THF. ^1H NMR spectroscopy (400 MHz, $CDCl_3$) revealed complete consumption of **1v**and 88% yield of **2v** as a colorless liquid. The spectral data matched those reported by Ackermann and co-workers.[23] ^1H NMR (400 MHz, $CDCl_3$) δ 7.31–7.25 (m, 2H), 7.21–7.15 (m, 3H), 2.61 (t, J = 7.6, 2H), 1.6–1.5 (m, 2H), 1.4–1.3(m, 2H), 0.94 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 128.4, 128.2, 125.5, 35.7, 33.7, 22.4, 14.0.



2w

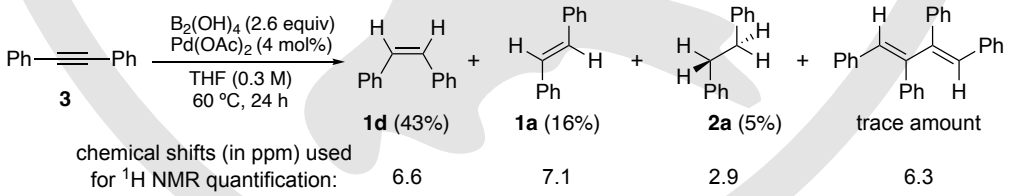
1-[tert-Butyl(diphenyl)silyloxy]decane 2w. The general procedure was followed using 58.3 mg of tetrahydroxydiboron (0.65 mmol), 2.3 mg $Pd(OAc)_2$ (0.01 mmol), 155.3 of mg tert-butyl(dec-9-en-1-yloxy) diphenylsilane **1w** (0.5 mmol) and 1.7 mL of THF. ^1H NMR spectroscopy (400 MHz, $CDCl_3$) revealed complete consumption of **1w** and 98% yield of **2w** as a colorless oil. The spectral data matched those reported by Yus and co-workers.[24] ^1H NMR (500 MHz, $CDCl_3$) δ 7.78–7.73 (m, 4H), 7.51–7.41 (m, 6H), 3.74 (t, J = 6.5 Hz, 2H), 1.67–1.60 (m, 2H), 1.45–1.29 (m, 14H), 1.13 (s, 9H), 0.96 (t, J = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.6, 134.3, 129.5, 127.6, 64.1, 32.7, 32.0, 29.7, 29.7, 29.5, 29.4, 26.9, 25.9, 22.8, 19.3, 14.2.



2x

Diethyl 2-propylmalonate 2x. The general procedure was followed using 58.3 mg of tetrahydroxydiboron (0.65 mmol), 2.3 mg $Pd(OAc)_2$ (0.01 mmol), 100.1 of mg Diethyl allylmalonate **1x** (0.5 mmol) and 1.7 mL of THF. ^1H NMR spectroscopy (400 MHz, $CDCl_3$) revealed complete consumption of **1x** and 94% yield of **2x** as a colorless oil. The spectral data obtained are consistent with the literature.[10] ^1H NMR (500 MHz, $CDCl_3$) δ 4.18 (q, J = 7.1 Hz, 4H), 3.33 (t, J = 7.6 Hz, 1H), 1.87 (dt, J = 9.9, 7.7 Hz, 2H), 1.40–1.30 (m, 2H), 1.26 (t, J = 7.1 Hz, 6H), 0.93 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 61.3, 51.9, 30.9, 20.7, 14.0, 13.7.

E. Hydrogenation of diphenylacetylene

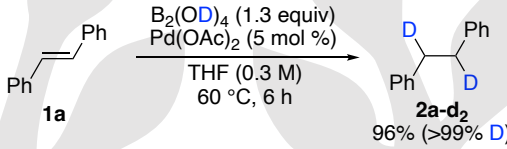


Hydrogenation of diphenylacetylene 3. A modified procedure of alkene reduction was employed using 47 mg of tetrahydroxydiboron (0.52 mmol), 1.8 mg of $Pd(OAc)_2$ (0.008 mmol), 0.66 mL of DCM, 35.6 mg of diphenylacetylene (0.2 mmol) over 24 hours. In spite of applying double amount of diboron and catalyst in a longer time, ^1H NMR spectroscopy (400 MHz, $CDCl_3$) revealed a combination of different products including *cis*-stilbene, *trans*- stilbene, bibenzyl and 1,2,3,4-tetraphenylbutadiene.[25]

IV. Deuteriation and Mercury Drop Experiments

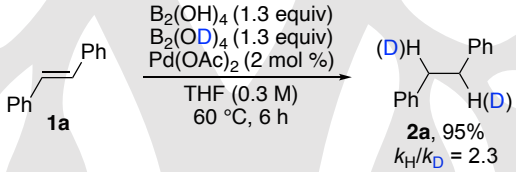
A. General Procedure for Deuterium Incorporation

Reactions were carried out in a 4 mL vial equipped with a stir bar and evaluation of THF by Karl Fisher titration revealed 4.1 ppm H_2O; To the vial, 24.4 mg of tetradeuteroxydiboron (0.26 mmols), 0.9 mg of $Pd(OAc)_2$ (0.004 mmol) and 36 mg of *trans*-stilbene **1a** (0.20 mmols) were added. The vial was capped with a septum, degassed and backfilled with nitrogen for 15 mintues. The vial was then charged with 0.66 mL of degassed anhydrous THF and stirring at 60 °C. After 6 hours, the solution was filtered through a silica plug and thoroughly washed with DCM. After removal of solvent, ^{1}H NMR and ^{13}C NMR were obtained using $CDCl_3$.



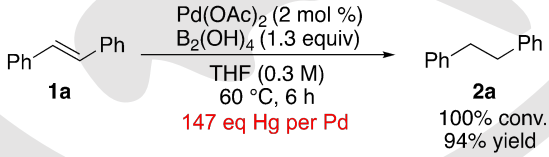
Deuteriation of *trans*- stilbene 1a to bibenzyl using $B_2(OD)_4$. The general deuteriation procedure was followed. After 6 hours, the solution was filtered through a silica plug and thoroughly washed with DCM. After removal of solvent, ^{1}H NMR and ^{13}C NMR were obtained using $CDCl_3$. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.29 (m, 4H), 7.25–7.19 (m, 6H), 2.96–2.91 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.8, 128.5, 128.3, 125.9, 38.0–37.2 (m). 100% deuterium incorporation is observed as indicated by 50% deuterium and 50% hydrogen on the benzylic positions.

B. Kinetic Isotope Effect Experiment



Kinetic isotope effect: competitive hydrogenation/deuteriation of trans-stilbene 1a. A modified deuteriation procedure was followed using 23.3 and 24.4 mg of tetrahydroxydiboron and tetradeuteroxydiboron, (0.26 mmol) respectively, 0.9 mg of $Pd(OAc)_2$ (0.004 mmol), 36 mg of diphenylacetylene (0.20 mmol) and 0.66 mL THF. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.28 (m, 4H), 7.23–7.19 (m, 6H), 2.94–2.92 (m, 3.4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 128.5, 128.3, 125.9, 38.0 (m). A kinetic isotope effect of 2.3 was observed.

C. Mercury Poisoning Experiment



Mercury poisoning experiment: Reactions were carried out in an argon purged glove box with O_2 < 15 ppm and water < 20 ppm. An oven dried, screw cap equipped reaction vial with a magnetic stir bar was charged with 36 mg of *trans*-stilbene (0.20 mmol), 0.9 mg of $Pd(OAc)_2$ (0.004 mmol), 23.3 mg of $B_2(OH)_4$ and 0.66 mL THF and then stirred at 60 °C and 600 rpms for 8 minutes. A drop of mercury (118 mg) was then added to the reaction mixture and stirred at 60 °C for 6 hours. Crude mixture was then filtered through

a silica plug and thoroughly washed with DCM. After removal of solvent, ^{1}H NMR and ^{13}C NMR were obtained using $CDCl_3$ which revealed complete consumption of **1a** and 94% isolated yield of bibenzyl **2a**.

V. References

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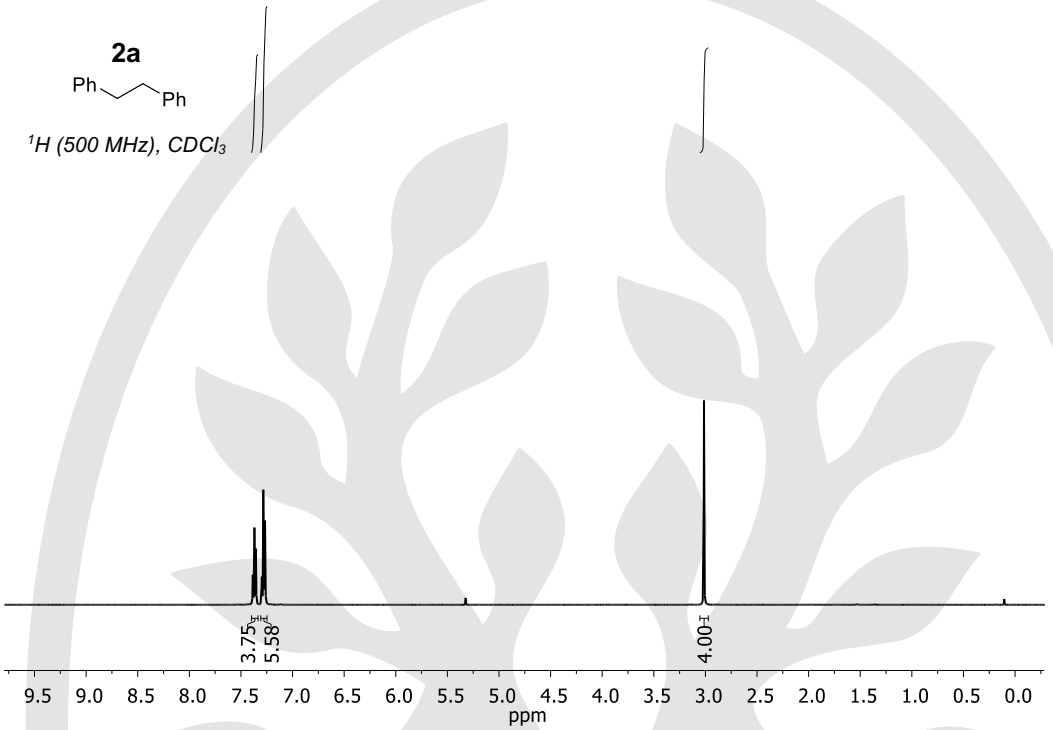
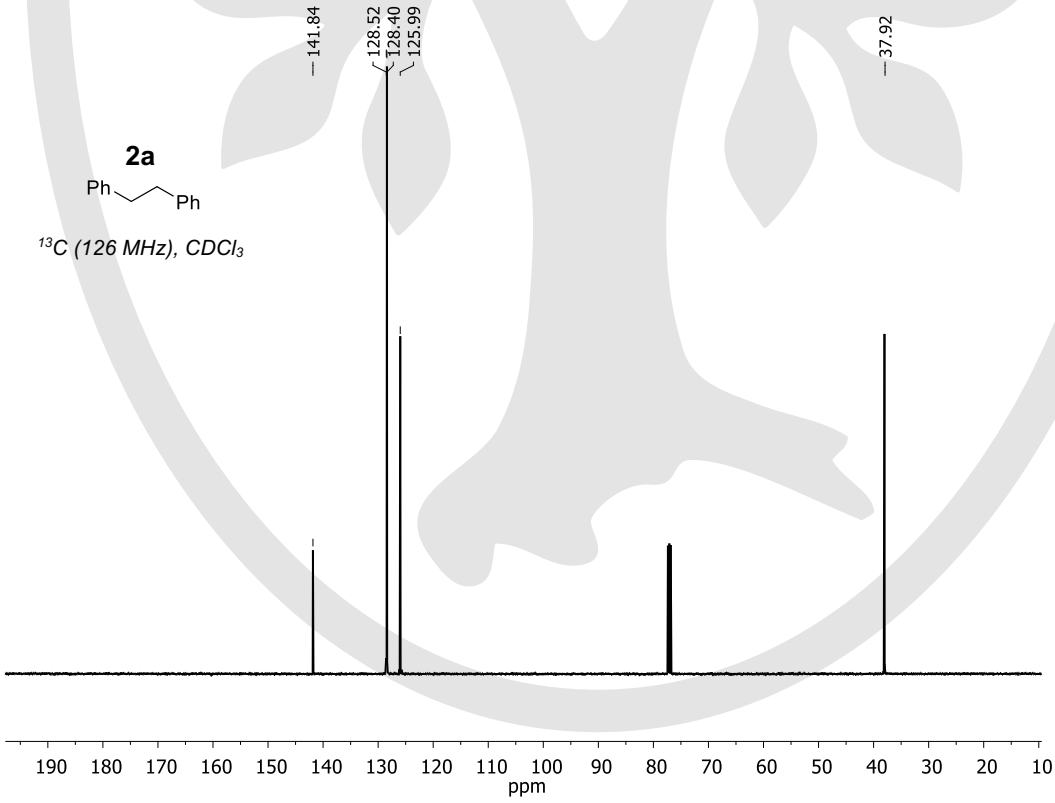
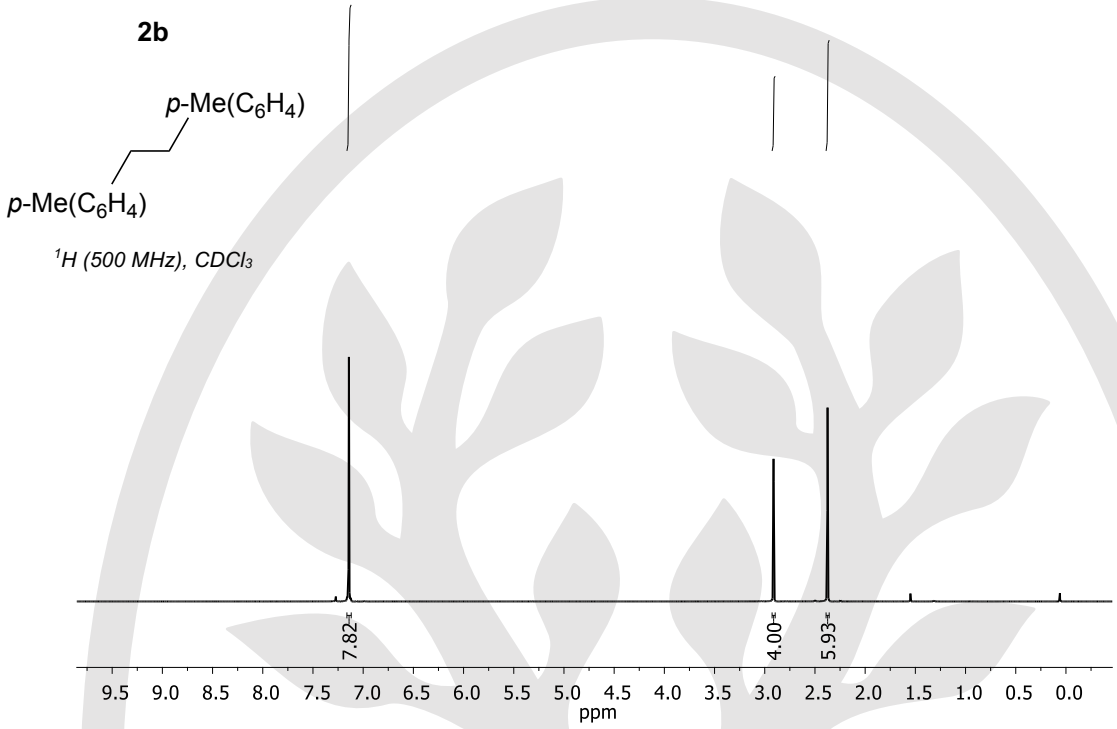
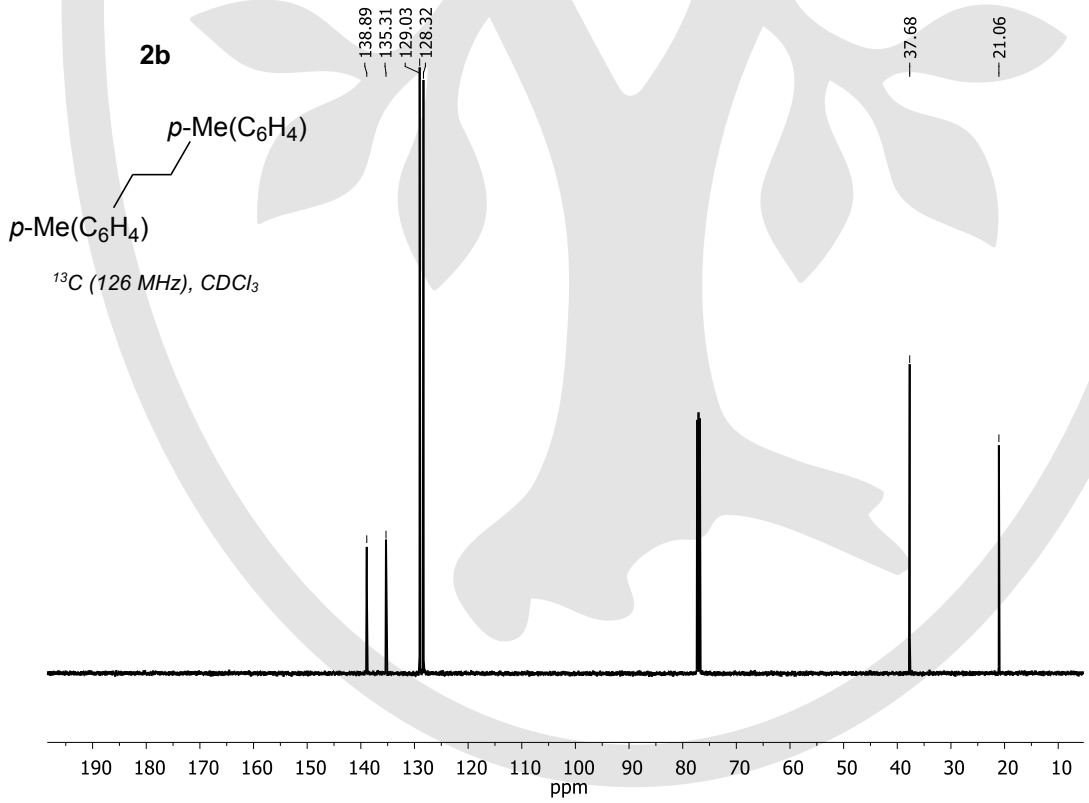
VI. NMR Spectra







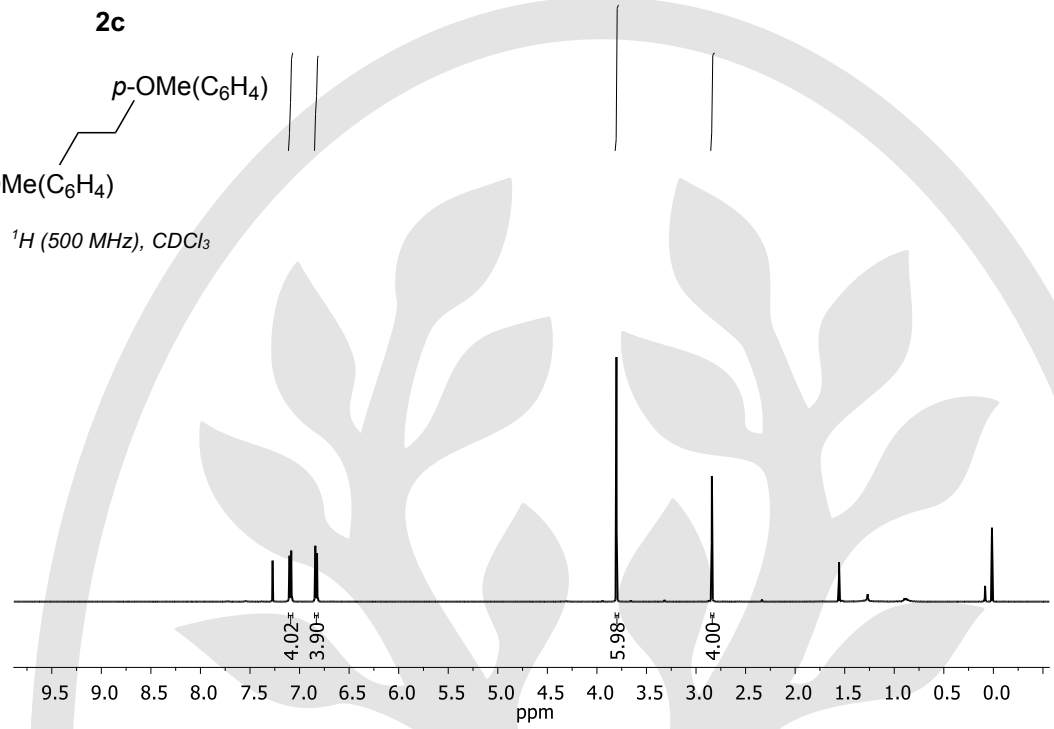


2c

p-OMe(C_6H_4)

p-OMe(C_6H_4)

^{1}H (500 MHz), $CDCl_3$



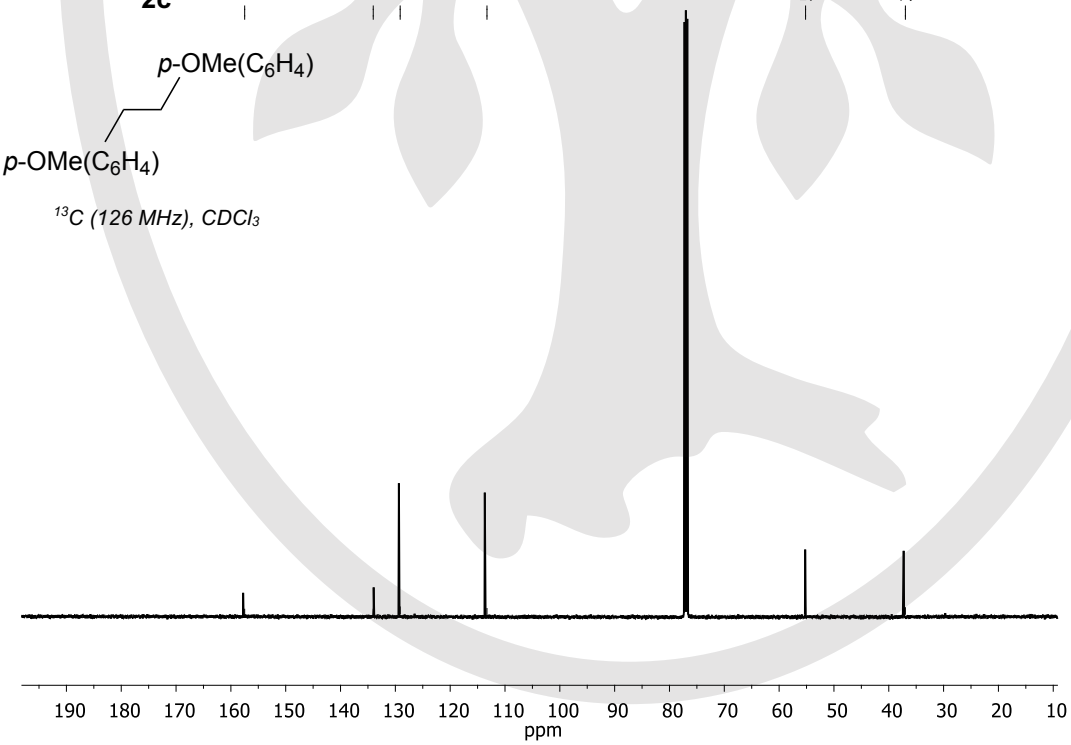
2c

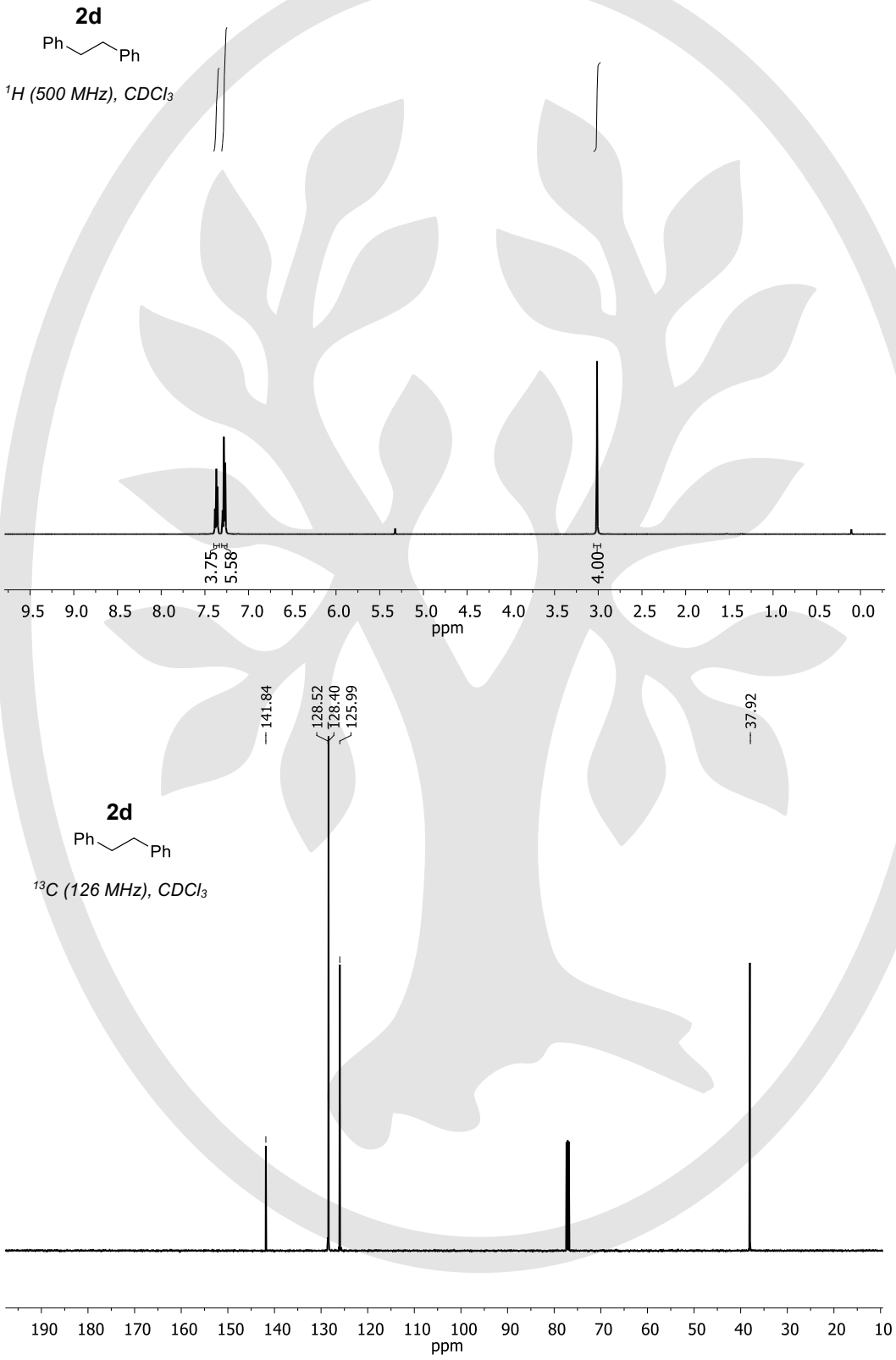
157.48
134.03
129.12
113.29
55.17
36.97

p-OMe(C_6H_4)

p-OMe(C_6H_4)

^{13}C (126 MHz), $CDCl_3$





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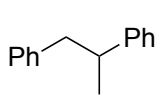

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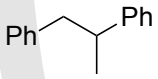
2e



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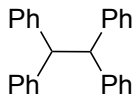
2f



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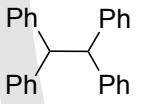
2f



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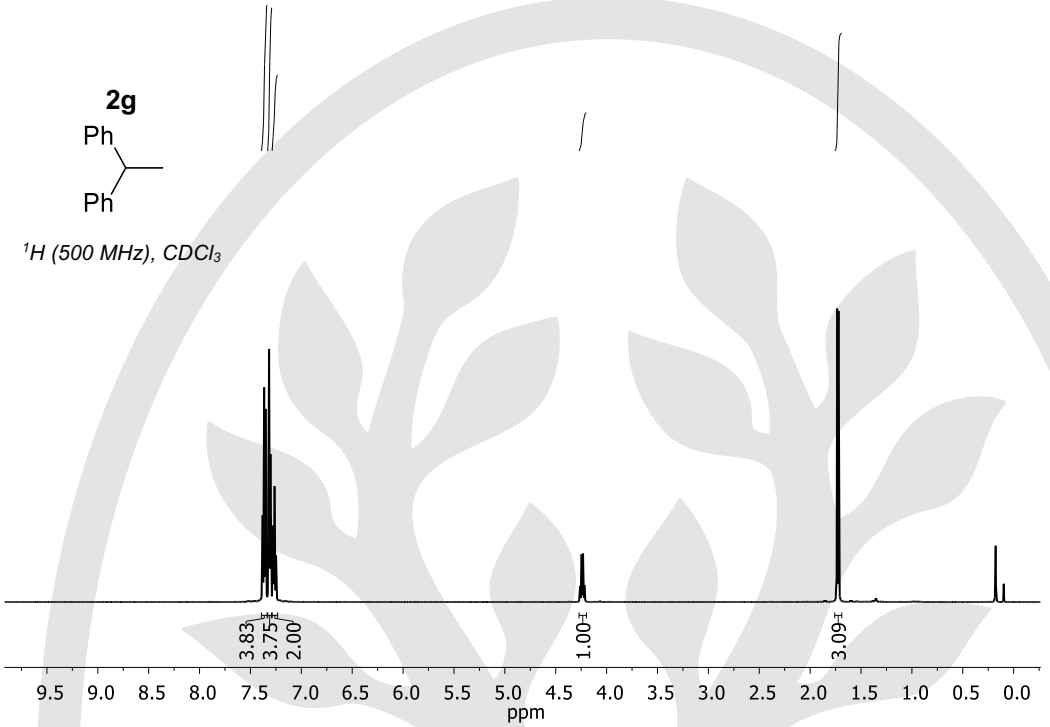

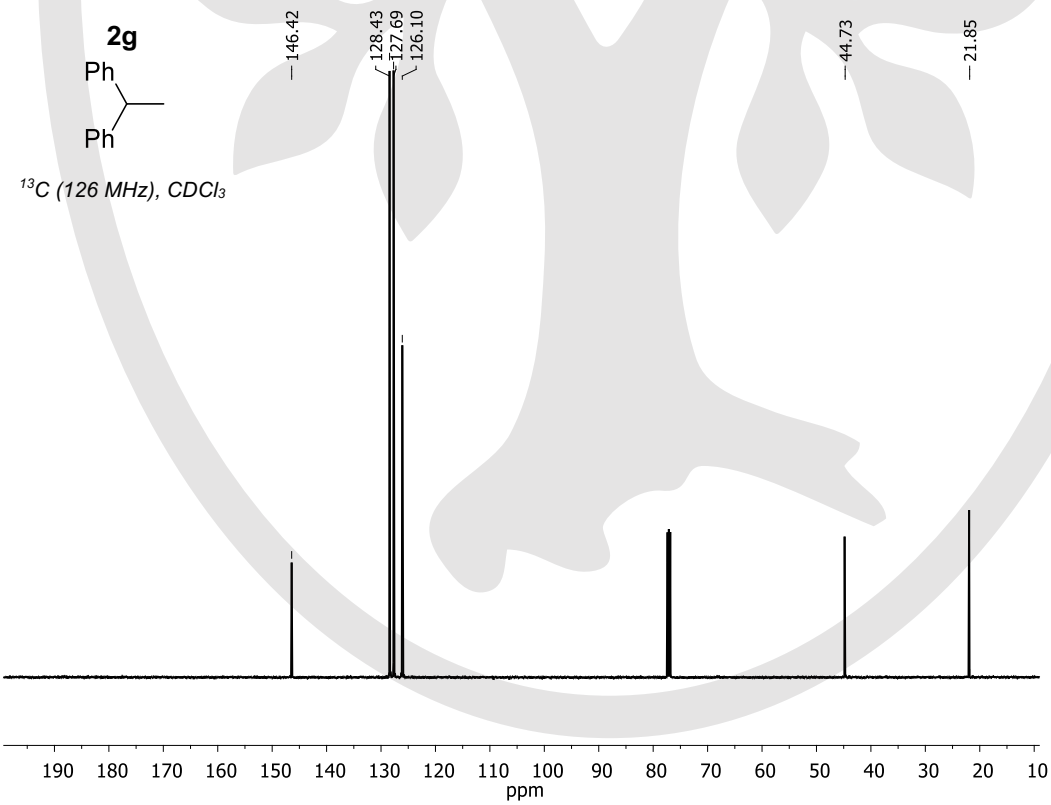

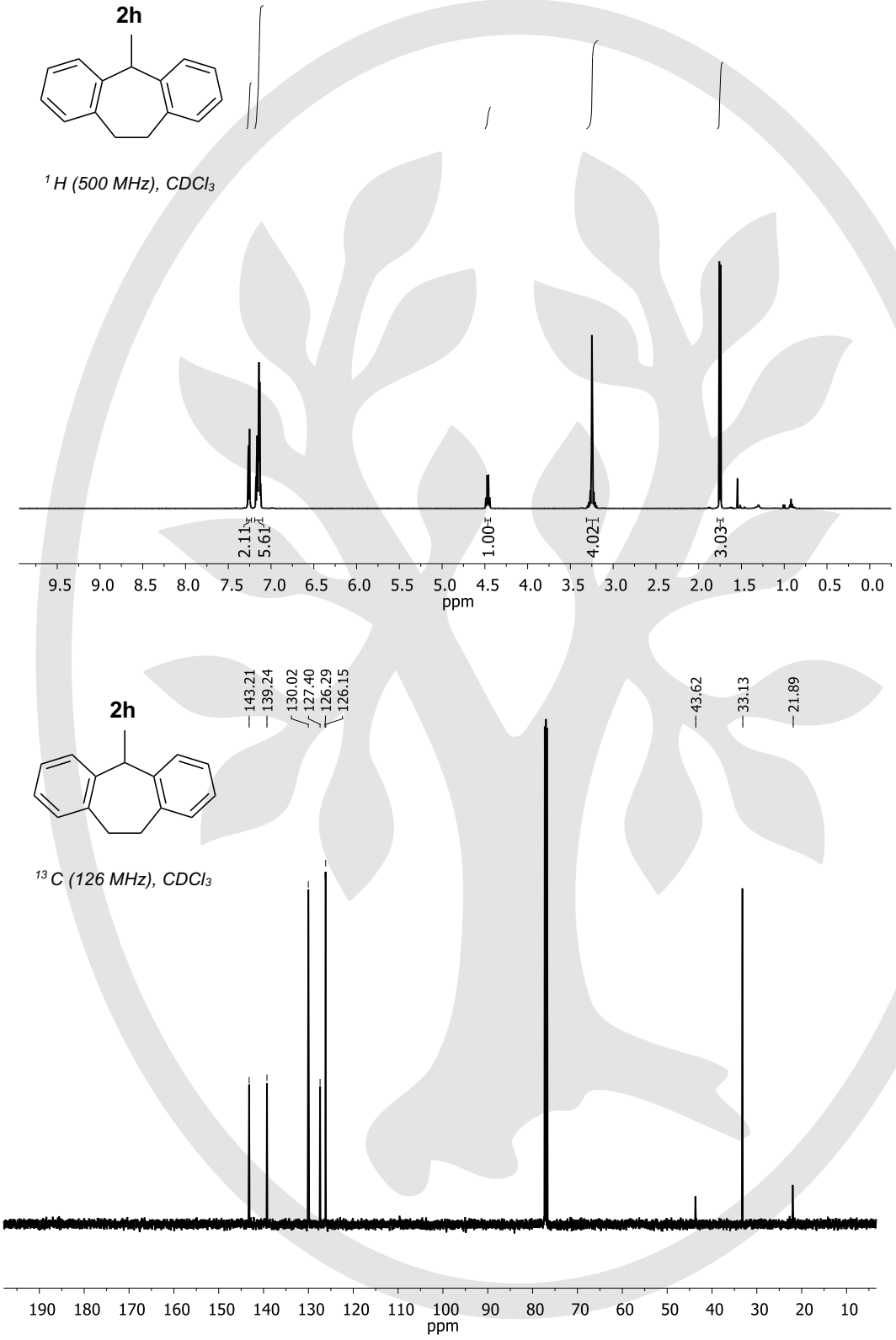

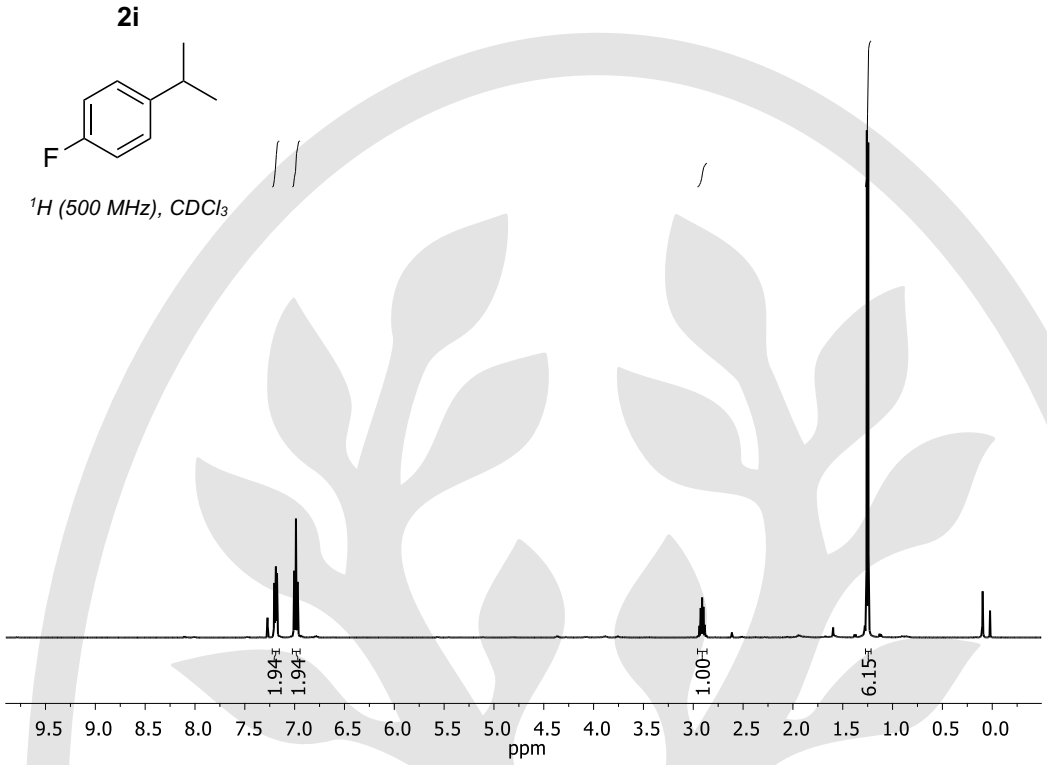

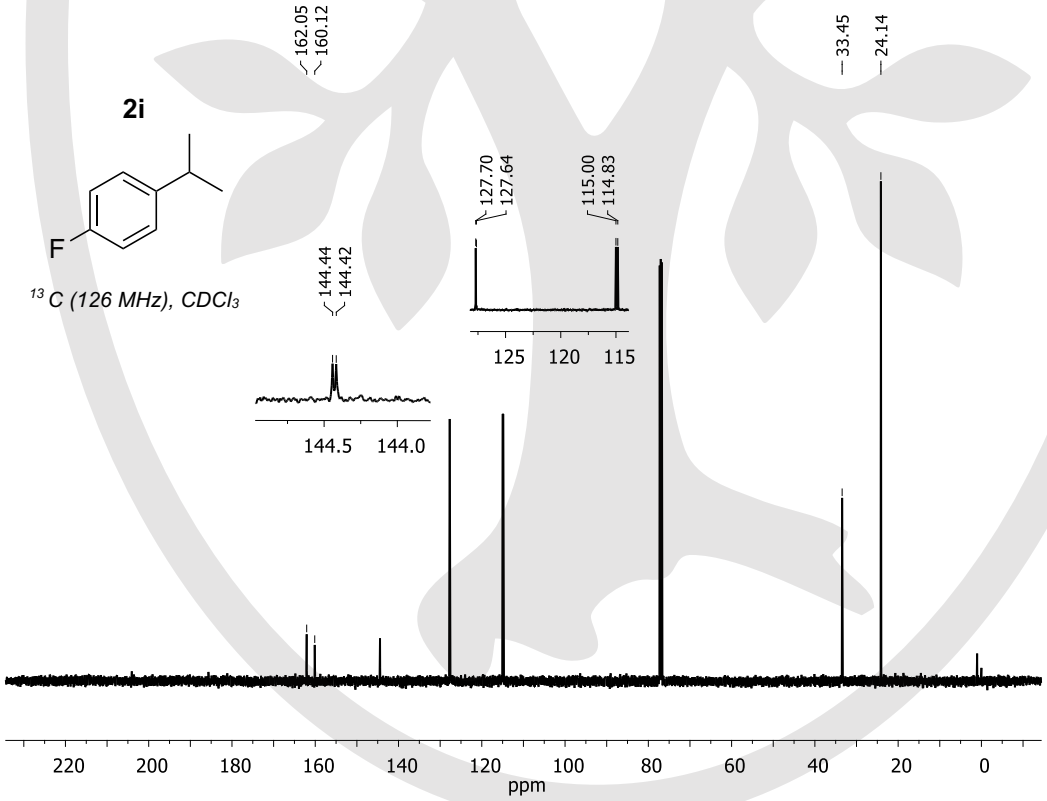

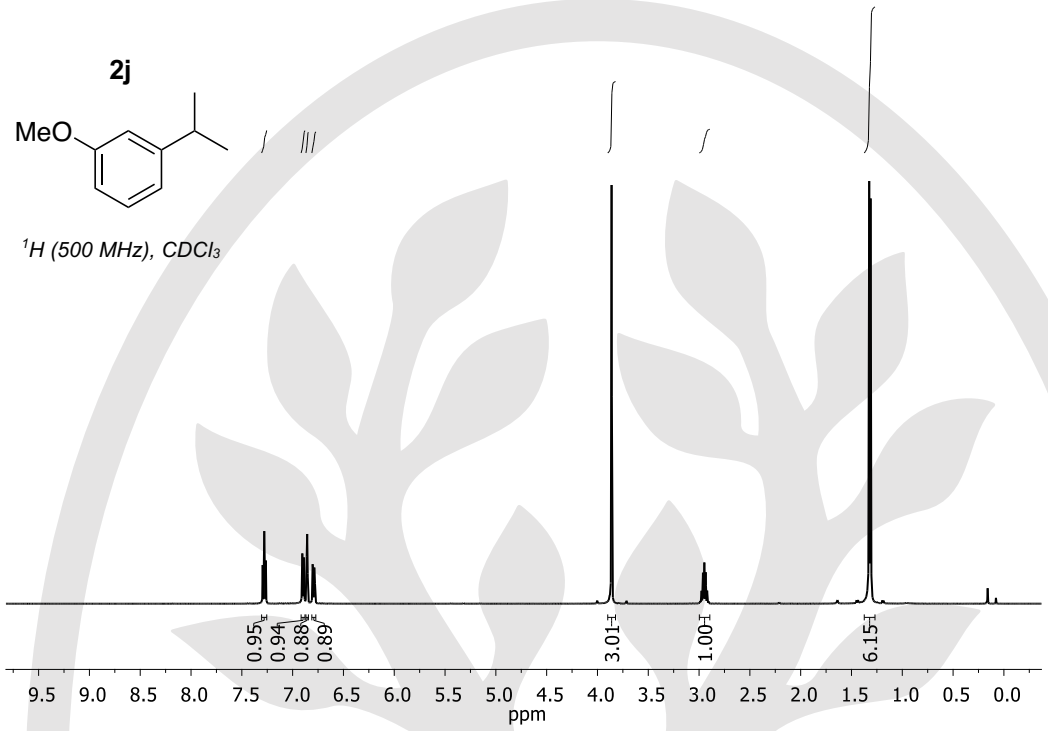

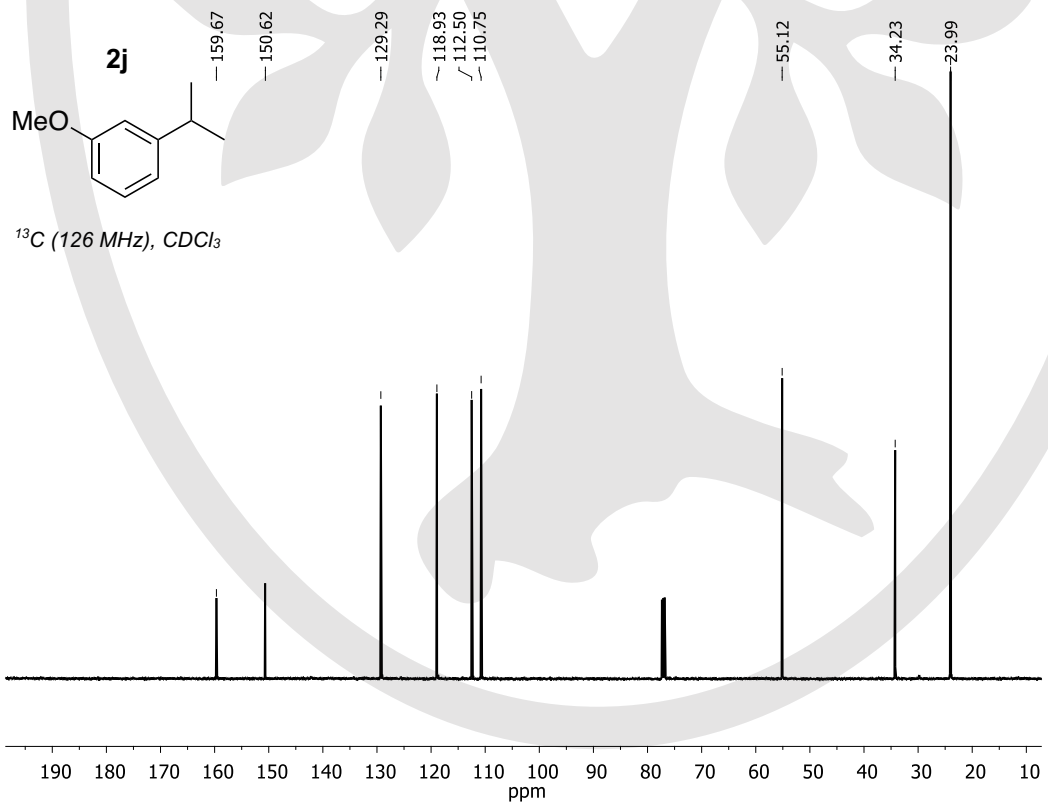

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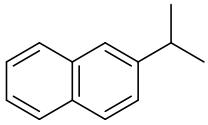

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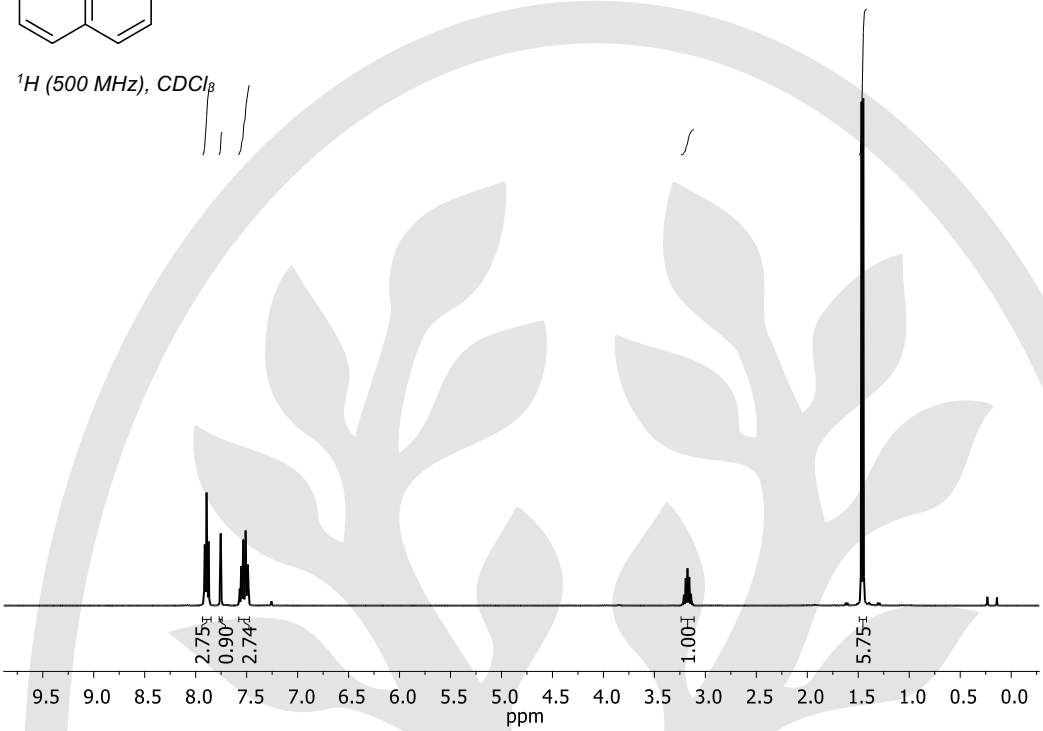

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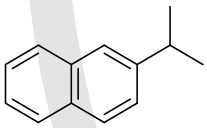

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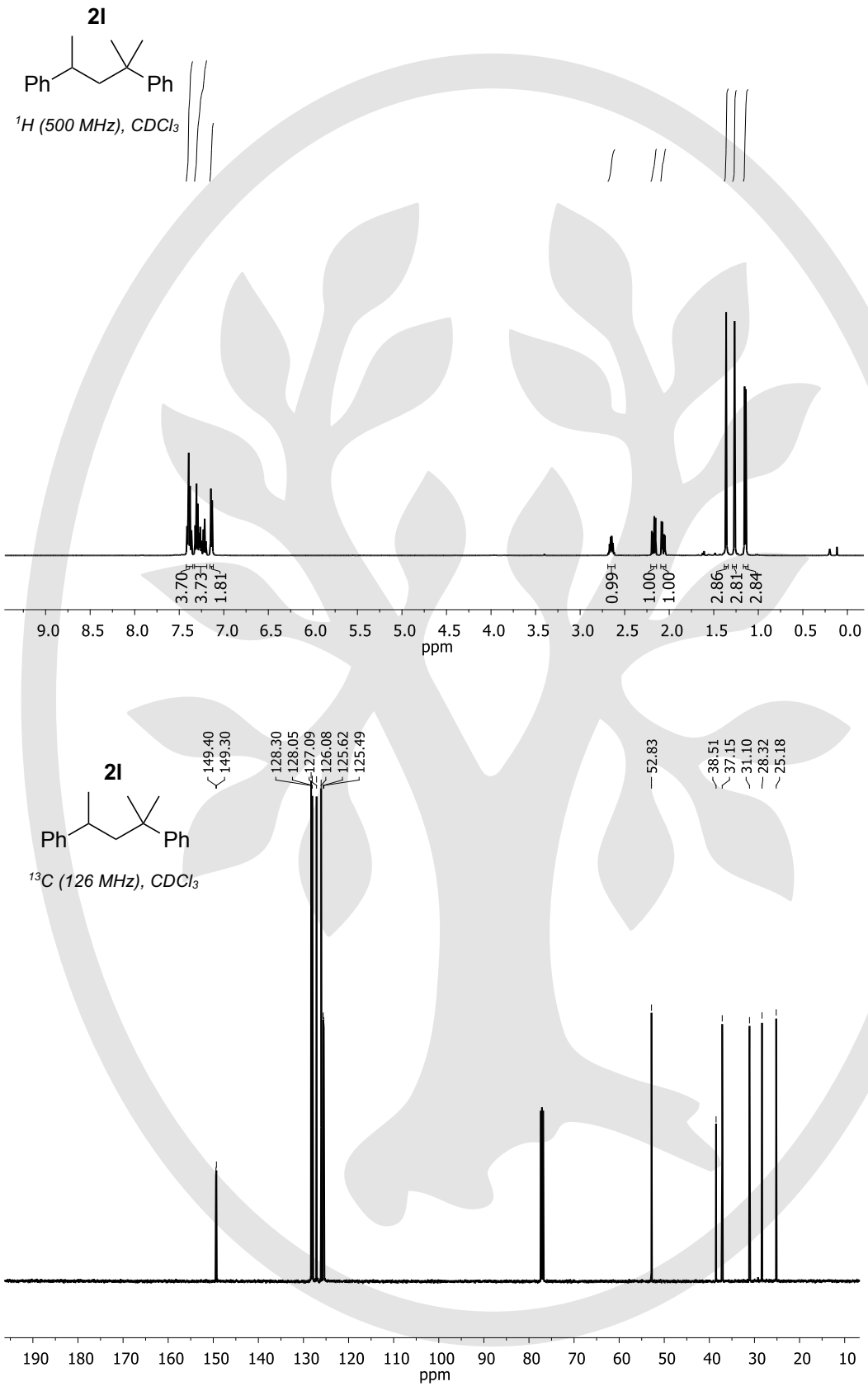

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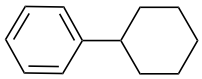

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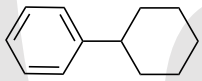

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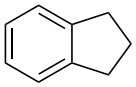

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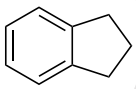

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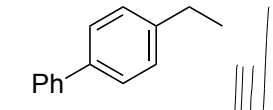

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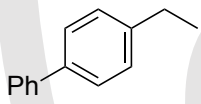

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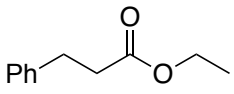

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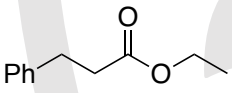

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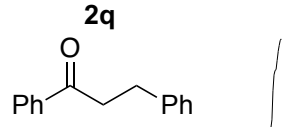

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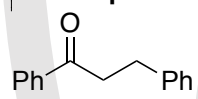

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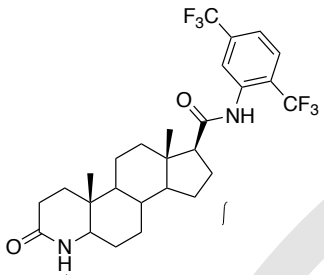

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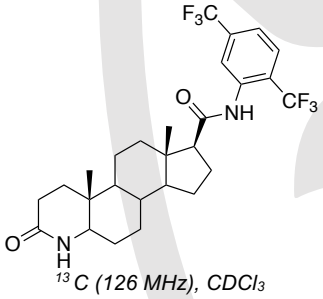

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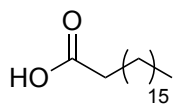

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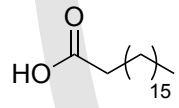

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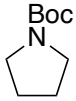
2u



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2u

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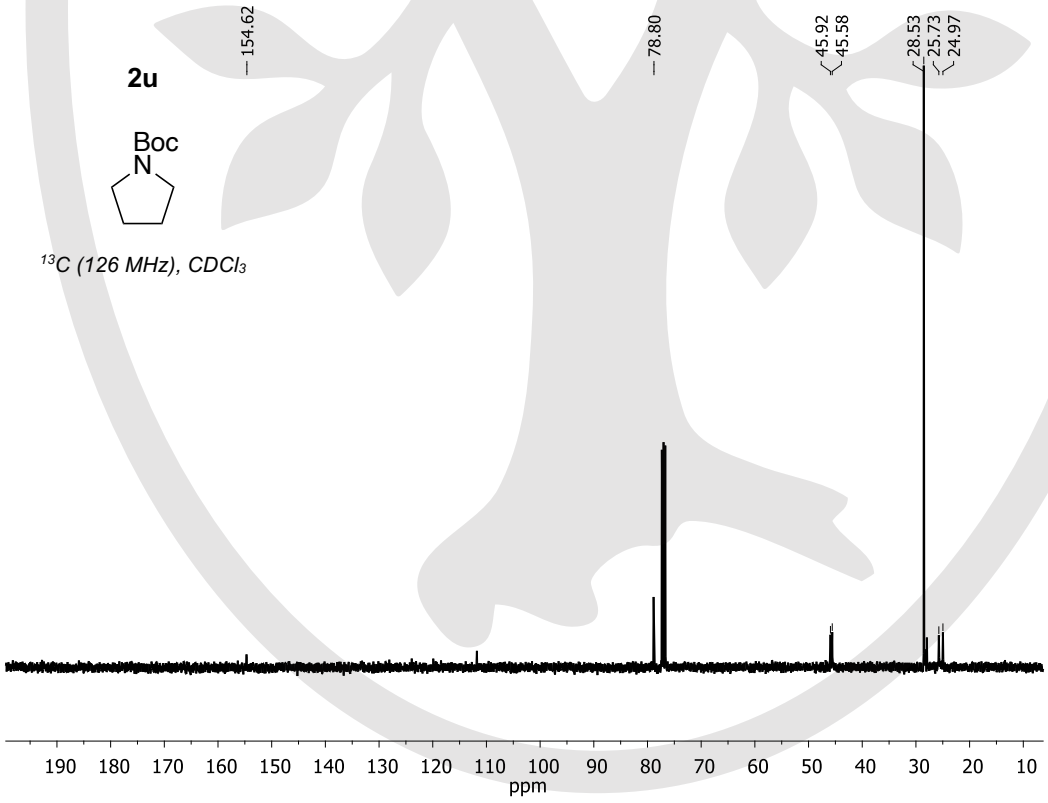

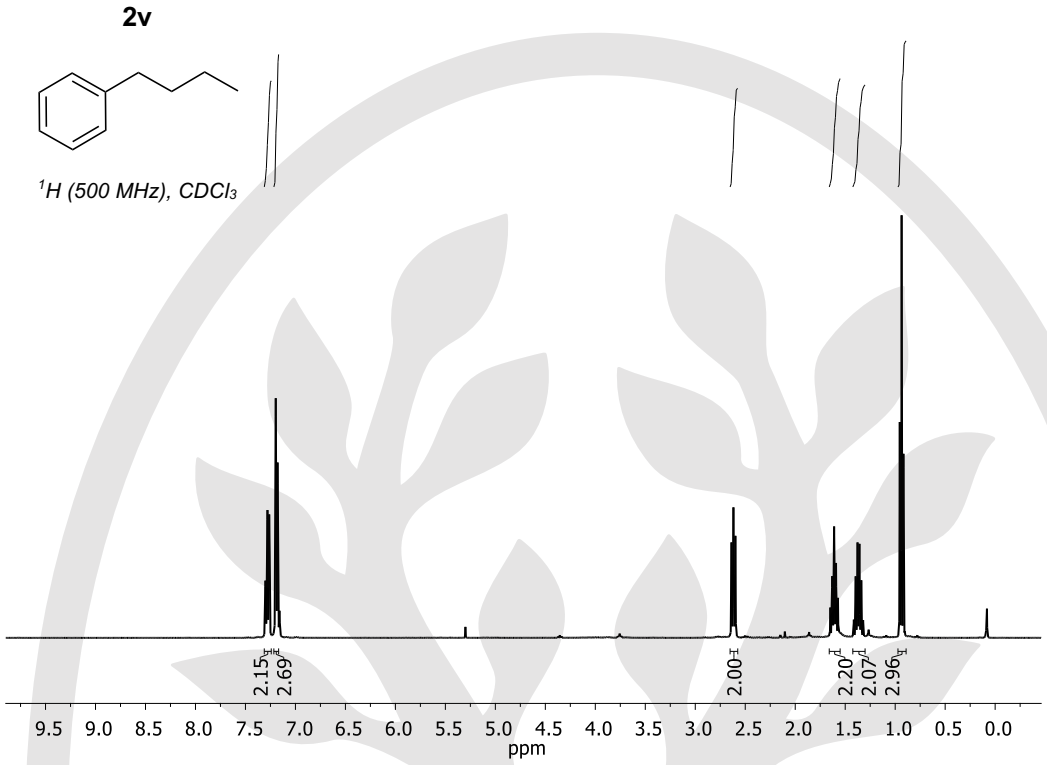

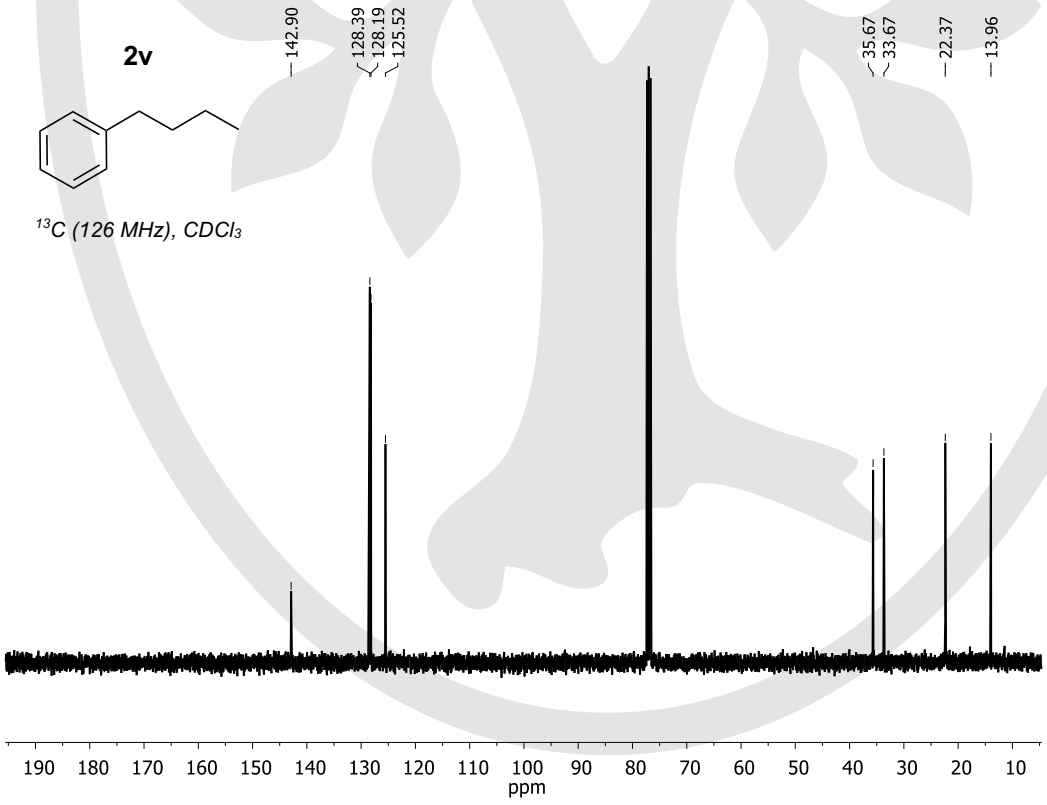

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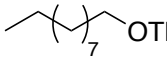

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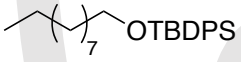

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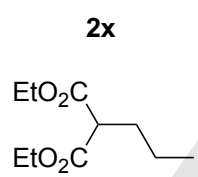
2x



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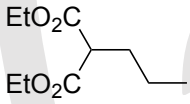
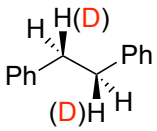
2x



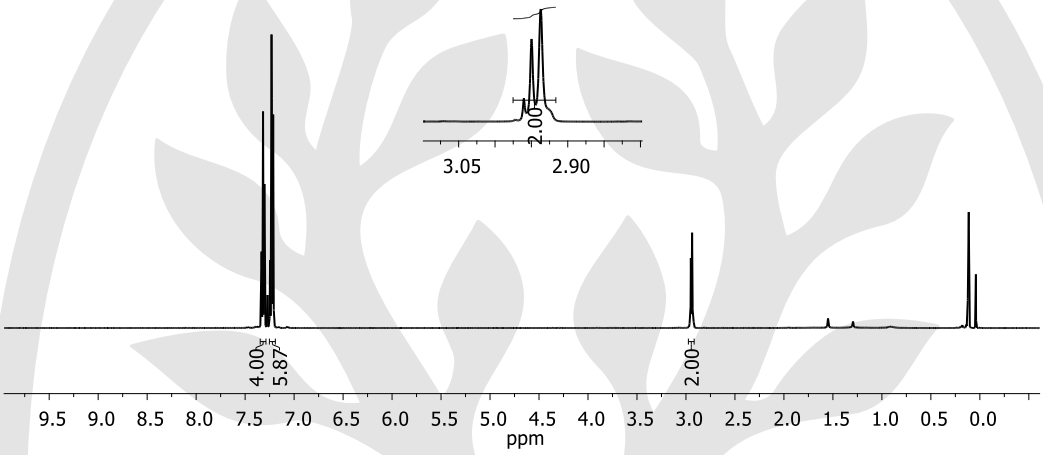
^{13}C (126 MHz), $CDCl_3$

D fidelity experiment

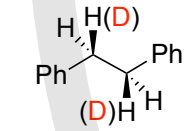
2a-d$_2$



^{1}H (500 MHz), CDCl$_3$

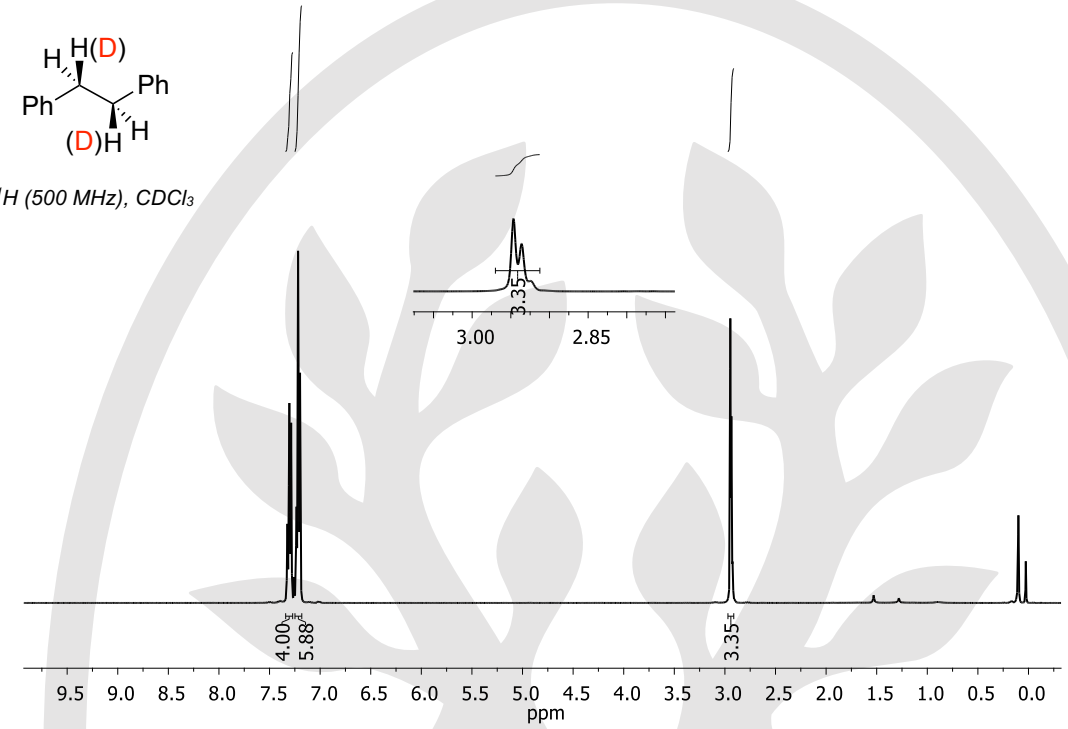


2a-d$_2$

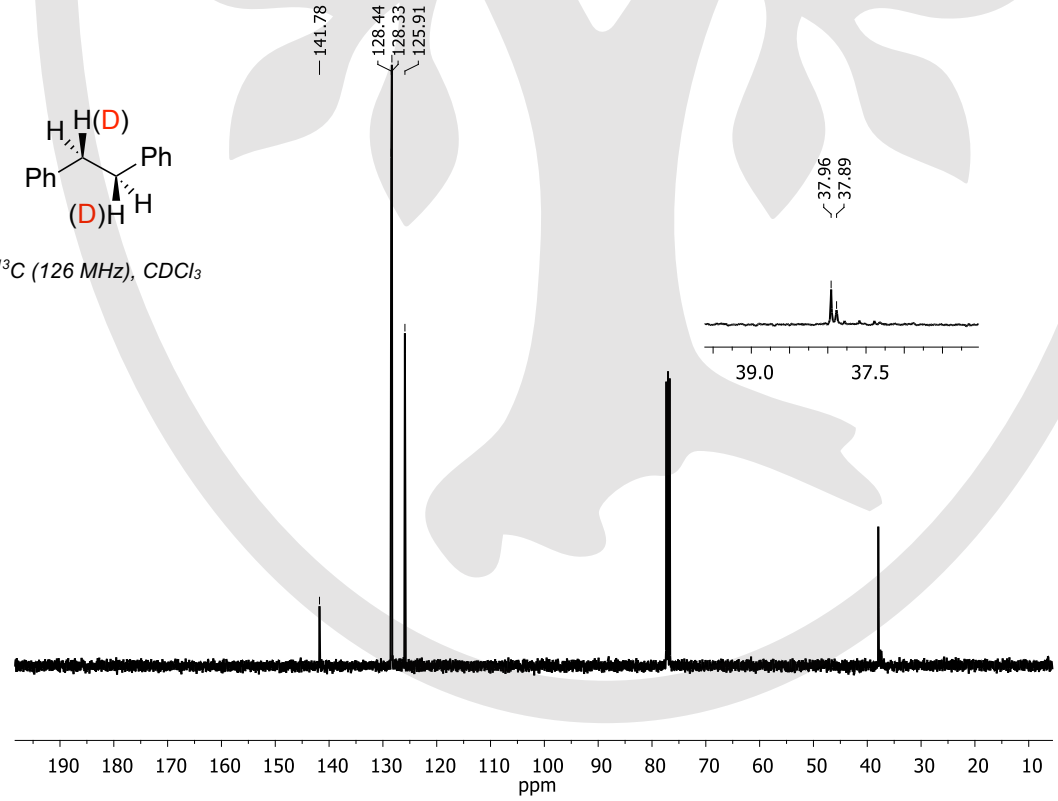


^{13}C (126 MHz), CDCl$_3$

Kinetic isotope effect



^{1}H (500 MHz), $CDCl_3$



^{13}C (126 MHz), $CDCl_3$