Electronic Supplementary Material (ESI) for Chemical Communications
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Suzuki-Miyaura Cross–Couplings of Secondary Benzylic and Allylic Boronic Esters

Supplemental Information

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1. General Experimental Considerations

Unless otherwise noted, all reactions were performed under inert atmosphere using dried glassware. Solvents were dried by standard methods before being degassed by a minimum of three *freeze-pump-thaw* cycles and stored over 4 Å molecular sieves. Aryl iodides were purified before use following accepted protocols and Ag_2O was purified by continuous hot water extraction in a Soxhlet condenser over three days and dried under vacuum in the presence of P_2O_5.[1] Both $Pd_2(dba)_3$ and $Pd(PPh_3)_4$ were used as purchased from Aldrich and Strem, respectively. PPh_3 was purified by recrystallization from absolute ethanol. Cross-coupling reactions were assembled in the glovebox in 1-dram vials, sealed with air-tight Teflon caps and placed in an 85 °C oil bath for 24 h. Once cooled, the reactions were filtered through celite, washed with copious amounts of diethyl ether and hexanes and concentrated *in vacuo*. NMR spectra were recorded at 400 MHz (^{1}H), and 100 MHz (^{13}C) in $CDCl_3$ or CD_2Cl_2. GC analyses were performed on an HP 6850 network FID-GC with automatic injector. The column used was an HP-5 of 30 m in length with an internal diameter of 0.32 mm. The inlet conditions were 250 °C, 25 psi and a flow rate of 28.9 ml/min using a splitless injector with helium as the carrier gas. The method used had an initial temperature of 70 °C with an immediate increase to 240 °C using

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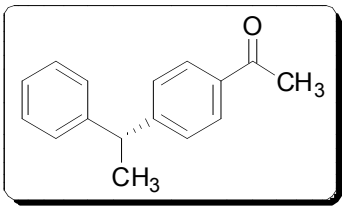
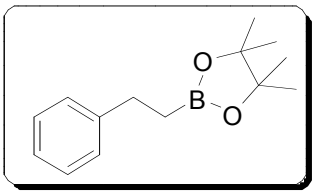
a 6 °/min ramp. Thin Layer Chromatography was performed on aluminum backed silica plates with F-254 indicator. Visualization was accomplished with a UV source (254, 365 nm) and by treatment with phosphomolybdic acid. Column chromatography was performed with flash grade silica (Silicycle, 50 μm particle size, 60 Å porosity) and reagent grade solvents. Determination of stereochemistry was performed by analysis on a supercritical fluid chromatograph. Analytical Supercritical Fluid Chromatography (SFC) was performed on a Berger SFC HPLC using the specified chiracel Berger Silica column and specified conditions of co-eluent, flow rate and pressure.

2. Chemoselectivity of the Enantiospecific Suzuki-Miyaura Reaction

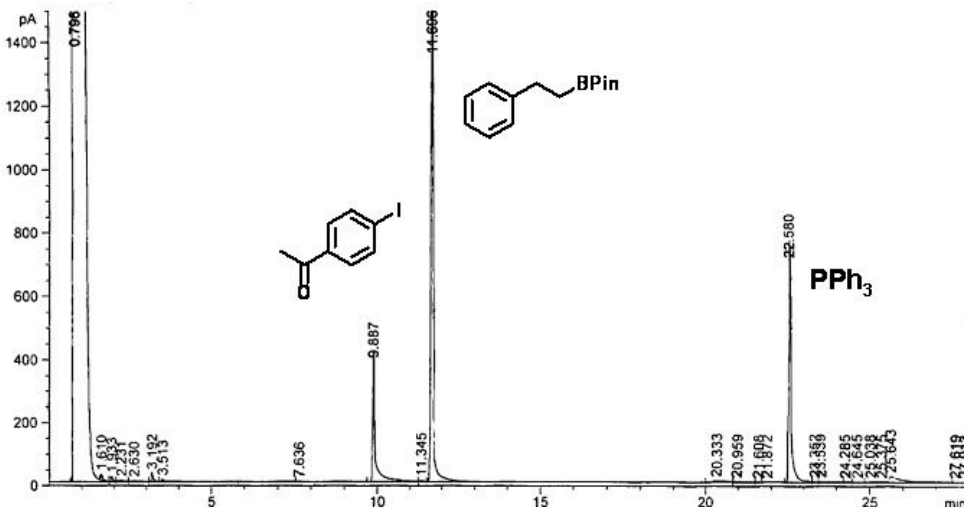


Synthesis of (*R*)-1-phenyl, 1-(4-acetylphenyl)ethane ((*R*)-2). In a nitrogen-filled glovebox, 4-iodoacetophenone (12.45 mg, 245.9 g/mol, 0.051 mmol), (*R*)-pinacol(1-phenylethyl)boronate (**(R)-1)** (17.41 mg, 232 g/mol, 0.075 mmol, er = 93.3:6.7) Ag_2O (17.68 mg, 232 g/mol, 0.076 mmol), $Pd_2(dba)_3$ (1.l86 mg, 915.7 g/mol, 0.0020 mmol, 8.1 mol% Pd), PPh_3 (8.54 mg, 262 g/mol, 0.033 mmol) were taken up in DME (1.0 mL). The reaction was sealed, and stirred at 85 °C for 24 h. The desired product was isolated by column chromatography (gradient 20:1 to 10:1 hexanes: ethyl acetate) in 63% yield. The enantiomeric ratio was determined by SFC analysis (AD-H Column, 5% MeOH, 2 mL, 200 bar) to be 91.5:8.5, a 98% retention of er. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, 2H), 7.35-7.22 (m, 7H) 4.23 (q, *J* = 7.2, 1H), 2.59 (s, 3H), 1.68 (d, *J* = 7.2, 3H). **^{13}C NMR:** (100 MHz, $CDCl_3$): δ 197.8, 152.4, 146.0, 135.7, 128.9, 128.8, 128.1, 127.9,

126.7, 45.2, 26.8, 21.6. **HRMS (EI-TOF):** calcd for $[M]^+$ ($C_{16}H_{16}O$) *m/z* 224.1201; found 224.1197.



Linear Boronic Ester (3) Subjected to Branched Coupling Conditions. In a nitrogen-filled glovebox, iodoacetophenone (13.3 mg, 0.054 mmol), (2-phenylethyl)boronic acid pinacol ester (**3**) (17.7 mg, 0.076 mmol), Ag_2O (17.7 mg, 0.076 mmol), $Pd_2(dba)_3$ (1.76 mg, 0.0019 mmol, 7.1 mol% Pd), PPh_3 (9.28 mg, 0.035 mmol) were taken up in THF (1.2 g). The vial was sealed, and stirred at 70 ^oC for 18 h after which it was cooled to room temperature before being filtered through celite and washed with copious amounts of diethyl ether. Analysis by GC (aliquot taken up in dichloromethane) indicates no coupling product and the preservation of the linear boronic ester.



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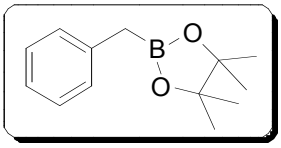
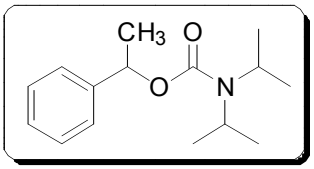


Cross-Coupling of *primary* Benzylboronic acid pinacol ester (5). In a nitrogen-filled glovebox, 4-iodoacetophenone (12.47 mg, 245.9 g/mol, 0.051 mmol), Ag_2O (19.09 mg, 234 g/mol, 0.0816 mmol, 1.60 equiv.), $Pd(PPh_3)_4$ (4.79 mg, 1155.6 g/mol, 0.0042 mmol, 8.1 mol% Pd), PPh_3 (4.75 mg, 262 g/mol, 0.018 mmol, 8.3:1 P:Pd) and K_2CO_3 (10.89 mg, 138 g/mol, 0.079 mmol) were taken up in DME (1.0 g). The reaction was sealed with a teflon cap complete with a rubber septum and removed from the glovebox. Outside the glovebox, benzylboronic acid pinacolate ester (**5)** (15.5 mg, 218 g/mol, 0.071 mmol, 1.4 equiv.) was added *via* syringe through the septum. The solution was then stirred at 85 °C for 20 h. Once cooled, the reaction was filtered through celite and washed with copious amounts of diethyl ether. The solvents were evaporated *in vacuo* and an internal NMR standard was added (hexamethylbenzene, HMB, 7.80 mg). The NMR yield of the reaction was determined to be 69%. The cross-coupled product was then purified by silica gel chromatography (20:1 hexanes:ethyl acetate) to yield 6.3 mg of clear oil, representing a 59% isolated yield. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8 Hz, 2H), 7.20 (m, 5H), 7.10 (d, J = 7.2 Hz, 2H), 3.96 (s, 2H), 2.50 (s, 3H). **^{13}C NMR:** (100 MHz, $CDCl_3$) δ 197.8, 146.8, 140.1, 135.3, 129.1, 129.0, 128.7, 126.4, 41.9, 26.7. (One aromatic peak doubled). **HRMS (EI-TOF):** calcd for $[M]^+$ ($C_{15}H_{14}O$) *m/z* 210.1045; found 210.1049.



Synthesis of *N,N*-Diisopropyl carbamic acid (1-phenylethyl) ester. *N,N*-diisopropylcarbamoyl chloride (1.011 g, 163.65 g/mol, 6.18 mmol, 1.0 equiv.) and freshly distilled triethylamine (0.9 mL, 0.726 g/mL, 101.2 g/mol, 6.45 mmol, 1.05 equiv.) were taken up in 20 mL of CH_2Cl_2. *sec*-Phenethanol (0.753 g, 122 g/mol, 6.1 mmol, 1.0 equiv.) was added and the solution was stirred under

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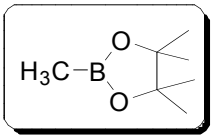
refluxing conditions for 24 h, with salts eventually precipitating out of solution. The solution was washed with H_2O and the aqueous layer was extracted with 3 x 25 mL CH_2Cl_2. The crude oil was purified by silica gel chromatography (6:1 hexanes:ethyl acetate, 2 inch by 5 inch column). No yield was recorded, though an NMR of the crude mixture indicated that the ratio of product to starting secondary alcohol was ~ 1:1 after 24 h of reflux. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 7.38 (m, 4 H), 7.28 (m, 1 H), 5.87 (q, *J* = 6.4 Hz, 1 H), 4.3-3.6 (d, br, 2 H), 1.57 (d, *J* = 6.4 Hz, 3 H), 1.23 (d, *J* = 6.4 Hz, 12 H). **^{13}C NMR:** (100 MHz, $CDCl_3$) δ 155.1, 142.8, 128.4, 127.4, 126.0, 72.7, 45.9 (br), 22.9, 22.2 (br). **HRMS (EI-TOF):** calcd for $[M]^+$ ($C_{15}H_{23}O_2N$) *m/z* 249.1729; found 249.1719.



Synthesis of methyl boronic acid pinacolate ester. 1.5066 g of methylboronic acid (60 g/mol, 25.11 mmol, 1.0 equiv.) and 3.282 g of pinacol (118 g/mol, 27.8 mmol, 1.1 equiv.) were taken up in 70 mL of diethyl ether. Once dissolved, 3.03 g of $MgSO_4$ (120 g/mol, 25.3 mmol, 1.0 equiv.) was dispersed in the solution, which was stirred at 25 °C for 48 h. The dispersion was filtered by vacuum and washed with copious amounts of diethyl ether. The homogeneous solution was then concentrated *in vacuo* to a volume of 10 mL and passed through a silica plug. The desired boronic acid was obtained in 87% yield. Contamination by pinacol caused future esterifications to be performed with equivalent stoichiometries of boronic acid and diols. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 1.26 (s, 12 H), 0.26 (s, 3 H). **^{11}B NMR:** (160 MHz, $CDCl_3$): δ 33. **^{13}C NMR:** (100 MHz, $CDCl_3$) δ 83.0, 24.9 (Methyl peak, broadened by B, not assigned). **HRMS (EI-TOF):** calcd for $[M]^+$ ($C_7H_{15}O_2B$) *m/z* 142.1165; found 142.1169.

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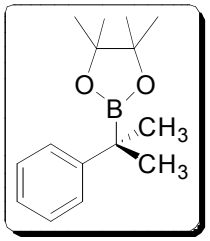

Synthesis of (1-methyl, 1-phenyl)ethyl boronic acid pinacolate ester (6). *N,N*-Diisopropyl carbamic acid (1-phenylethyl) ester (280 mg, 279 g/mol, 1.00 mmol, 1.0 equiv.) was taken up in diethyl ether and cooled to -78 °C in a dry ice/acetone bath. *s*-Butyllithium (1.4 mL, 1.16 M, 1.62 mmol, 1.6 equiv.) was added dropwise to the cold solution. After 5 h of lithiation, an ethereal solution of methylboronic acid pinacolate ester (186.6 mg, 142 g/mol, 1.31 mmol, 1.3 equiv., 1.5 mL Et_2O) was added dropwise to give a bright yellow solution, which faded to an orange colour over time. After 1 h borylation, commercially available $MgBr_2$ diethyl etherate (1.3 equiv.) was added to the cold solution in solid form by removing the septum and adding the solid at once. After addition of the $MgBr_2$, the solution is allowed to warm slowly before being heated to reflux overnight. After aqueous workup, the tertiary benzylic boronic ester was purified by silica gel chromatography (loaded with 50:1 hexanes:ethyl acetate, eluted with 20:1 hexanes:ethyl acetate $R_f = 1/7$) in 50% yield. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 7.36-7.28 (m, 4 H), 7.17 (m, 1 H), 1.37 (s, 6 H), 1.23 (s, 12 H). **^{11}B NMR:** (160 MHz, $CDCl_3$): δ 34. **^{13}C NMR:** (100 MHz, $CDCl_3$) δ 148.6, 128.1, 126.3, 125.0, 83.3, 25.6, 24.5 (One aromatic peak not assigned). **HRMS (EI-TOF):** calcd for $[M]^+$ ($C_{15}H_{24}O_2B$) *m/z* 247.1869; found 247.1865.

Attempted cross-coupling of a *Tertiary* Benzylic Boronic Ester (6). In a nitrogen-filled glovebox, 4-iodoacetophenone (26.07 mg, 245.9 g/mol, 0.104 mmol), (1-methyl, 1-phenyl)ethyl boronic acid pinacolate ester **(6)** (41.0 mg, 246 g/mol, 0.166 mmol, 1.6 equiv.), Ag_2O (40.59 mg, 232 g/mol, 0.173 mmol, 1.7 equiv.), $Pd_2(dba)_3$ (3.84 mg, 915 g/mol, 0.0042 mmol, 8.1 mol% Pd), and PPh_3 (21.44 mg, 262 g/mol, 0.081 mmol, 0.79 equiv., 9.6:1 P:Pd) were taken up in THF (2.2 g). The reaction was sealed in the glovebox with a teflon cap, removed, and placed in a 70

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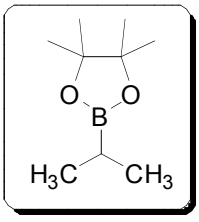
°C oil bath for 22 h. Once cooled, the reaction was filtered through celite and washed with copious amounts of diethyl ether. The crude reaction solution was analyzed by GC, which indicated that no product had been formed and that the tertiary benzylic boronic ester had survived the reaction conditions.

Attempted cross-coupling of a *Tertiary* Benzylic Boronic Ester under modified conditions. In a nitrogen-filled glovebox, 4-iodoacetophenone (9.15 mg, 245.9 g/mol, 0.036 mmol), (1-methyl, 1-phenyl)ethyl boronic acid pinacolate ester **(6)** (13.2 mg, 246 g/mol, 0.054 mmol, 1.5 equiv.), Ag_2O (12.35 mg, 232 g/mol, 0.053 mmol, 1.5 equiv.), $Pd_2(dba)_3$ (1.26 mg, 915 g/mol, 0.0014 mmol, 7.6 mol% Pd), and PPh_3 (6.89 mg, 262 g/mol, 0.026 mmol, 0.73 equiv., 9.3:1 P:Pd) were taken up in DME (0.75 g). The reaction was sealed in the glovebox with a teflon cap, removed, and placed in a 75 °C oil bath for 16 h. Once cooled, the reaction was filtered through celite and washed with copious amounts of diethyl ether and an internal NMR standard (hexamethylbenzene, HMB, 3.93 mg) was added. GC analysis of the filtered reaction indicated that no product had been formed and that the starting boronic ester was left unconsumed.



Synthesis of isopropylboronic acid pinacolate ester (7). 0.837 g of 1-isopropylboronic acid (87.9 g/mol, 9.52 mmol, 1.0 equiv.) and 1.124 g of pinacol (118 g/mol, 9.52 mmol, 1.0 equiv.) were taken up in 10 mL of diethyl ether. Once dissolved, 1.151 g of $MgSO_4$ (120 g/mol, 9.59 mmol, 1.0 equiv.) was dispersed in the solution, which was stirred at 25 °C for 22 h. The dispersion was filtered by vacuum and washed with copious amounts of diethyl ether. The homogeneous solution was then concentrated *in vacuo* to yield a crude oil which was purified by silica gel chromatography (20:1

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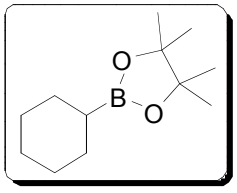
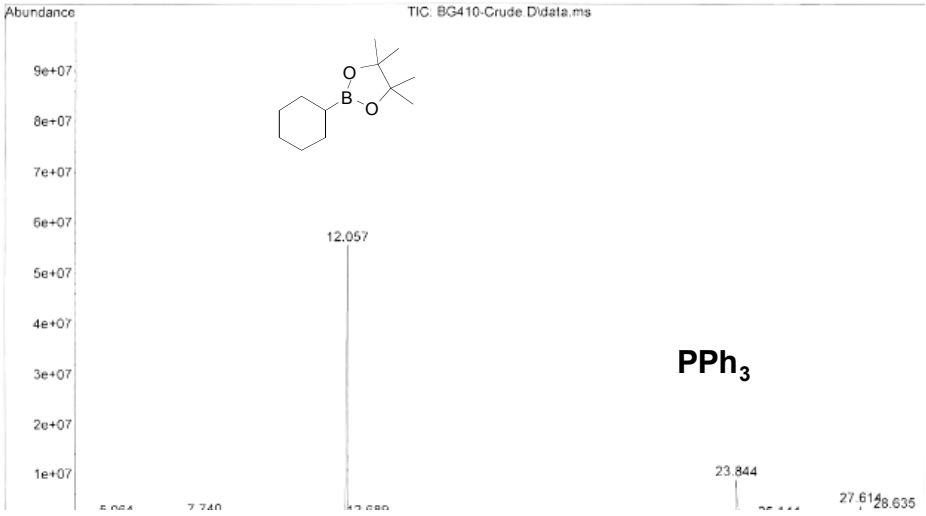
hexanes:ethyl acetate). The high volatility of the product boronic ester led to reduced yields, especially after removal of trace amounts of solvent by high vacuum. Ultimately, 563 mg of pure product were obtained, representing a 35% isolated yield. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 1.26 (s, 12H), 1.13-1.04 (m, br, 1H), 1.00 (d, *J* = 7.2 Hz, 6H). **^{11}B NMR:** (160 MHz, $CDCl_3$): δ 35. **^{13}C NMR:** (100 MHz, $CDCl_3$) δ 82.8, 24.7, 18.0.

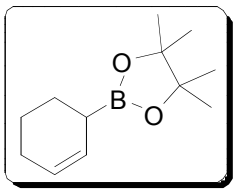
Attempted Cross-Coupling of isopropylboronic acid pinacolate ester (7). In a nitrogen-filled glovebox, iodobenzene (20.9 mg, 203.9 g/mol, 0.103 mmol), isopropylboronic acid pinacolate ester **(7)** (38.1 mg, 170 g/mol, 0.224 mmol, 2.2 equiv., excess used to offset high volatility of the short-chain boronic ester), Ag_2O (38.0 mg, 232 g/mol, 0.162 mmol, 1.6 equiv.), $Pd_2(dba)_3$ (3.60 mg, 915 g/mol, 0.0039 mmol, 7.6 mol% Pd), and PPh_3 (26.8 mg, 262 g/mol, 0.102 mmol, 1.0 equiv., 12.8:1 P:Pd) were taken up in diethyl ether (1.0 g). The reaction was sealed in the glovebox with a teflon cap, removed, and placed in a 65 °C oil bath for 14 h. Once cooled, the reaction was filtered through celite and washed with copious amounts of diethyl ether. A GC comparison of the crude reaction mixture and an authentic sample of cumene indicated that the cross-coupling reaction did not occur to any appreciable degree, but that the isopropylboronic acid pinacolate ester survived the reaction conditions.



Attempted Cross-Coupling of cyclohexylboronic acid pinacolate ester (8). In a nitrogen-filled glovebox, 4-iodoacetophenone (12.23 mg, 245.9 g/mol, 0.050 mmol), cyclohexylboronic acid pinacolate ester **(8)** (Frontier Chemical, 15.44 mg, 210 g/mol, 0.074 mmol, 1.48 equiv), Ag_2O (17.83 mg, 232 g/mol, 0.076 mmol, 1.5 equiv.), $Pd(PPh_3)_4$ (4.65 mg, 1155.6 g/mol, 0.0040 mmol, 8.0 mol% Pd), and PPh_3

(9.40 mg, 262 g/mol, 0.036 mmol, 0.72 equiv., 13:1 P:Pd) were taken up in DME (1.1 g). The reaction was sealed in the glovebox with a teflon cap, removed, and placed in a 85 °C oil bath for 18 h. Once cooled, the reaction was filtered through celite and washed with copious amounts of diethyl ether. GC analysis of the crude reaction solution indicates that no cross-coupling occurred and that the secondary boronic ester had survived intact.





Synthesis of 1-(boronic acid pinacolate ester)-2-cyclohexene ((±)-9). *p*-Toluene sulfonic acid (0.0247g, 0.1 eq.), bis(pinacolato)diboron (B_2pin_2, 1.397 g, 4 eq.) and Pd catalyst (di-μ-chlorobis[2-[(dimethylamino)methyl]phenyl-C-N]-dipalladium(II)) (0.0422 g, 0.05 eq) were taken up in a flame dried Schlenk flask under a positive pressure of $Ar_{(g)}$. DMSO (3 mL) and MeOH (3 mL) were added *via* syringe and the reaction solution was stirred at 50 °C for 24 h. The reaction was then extracted with 3x10mL of diethyl ether and dried over $MgSO_4$ before purification by column chromatography (40:1 Hexanes: ethyl acetate). The product was isolated in 42% yield and matched published the characterization data.[2]

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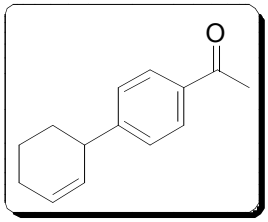
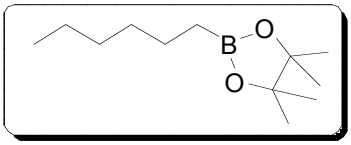


Cross-Coupling of 1-(boronic acid pinacolate ester)-2-cyclohexene ((±)-9). In a nitrogen filled glove box, 4-iodoacetophenone (12.5 mg, 0.051 mmol), 1-(boronic acid pinacolate ester)-2-cyclohexene (16.5 mg, 0.079 mmol), Ag_2O (19.34 mg, 0.083 mmol), K_2CO_3 (11.16 mg, 0.081 mmol), $Pd(PPh_3)_4$ (5.82 mg, 0.005 mmol) and PPh_3 (8.55 mg, 0.033 mmol) were weighed into a dried vial and taken up in 1 mL of DME. The reaction was sealed and stirred at 85 °C for 24 h. The reaction mixture was then cooled and filtered through a celite plug. The desired product was isolated by column chromatography (20:1-10:1 hexanes:ethyl acetate) in a 58% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8 Hz, 2H), 7.24 (d, *J* = 8 Hz, 2H), 5.85 (m, *J* = inc. 2.4 Hz, 1H), 5.62 (dd, *J* = 10 Hz, 2 Hz, 1H), 3.98 (m, 1H), 2.52 (s, 3H), 2.04 (m, 2H), 1.95 (m, 1H), 1.72-1.62 (m, 1H), 1.61-1.53 (m, 1H), 1.50-1.42 (m, 1H) **^{13}C NMR:** (100 MHz, $CDCl_3$): δ 197.9, 152.5, 135.2 (2C), 129.1, 128.5, 128.0, 41.9, 32.4, 26.6, 25.0, 21.1.

3. Synthesis of Secondary Allylic Boronic Esters



Synthesis of 1-hexylboronic acid pinacolate ester. 1.514 g of 1-hexylboronic acid (130 g/mol, 11.64 mmol, 1.0 equiv.) and 1.374 g of pinacol (118 g/mol, 11.64 mmol, 1.0 equiv.) were taken up in 10 mL of diethyl ether. Once dissolved, 1.415 g of $MgSO_4$ (120 g/mol, 11.8 mmol, 1.0 equiv.) was dispersed in the solution, which was stirred at 25 °C for 24 h. The dispersion was filtered by vacuum and washed with copious amounts of diethyl ether. The homogeneous solution was then concentrated *in vacuo* to

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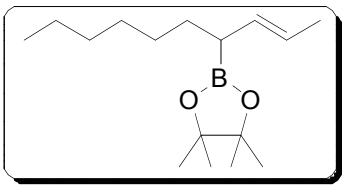
yield the pure boronic ester in 98% isolated yield. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 1.37-1.28 (m, 2 H), 1.23-1.19 (m, 6 H), 1.17 (s, 12H), 0.80 (m, 3 H), 0.69 (t, *J* = 7.6 Hz, 2 H) **^{11}B NMR:** (160 MHz, $CDCl_3$): δ 34.1. **^{13}C NMR:** (100 MHz, $CDCl_3$) δ 82.8, 32.1, 31.6, 24.8, 23.9, 22.5, 14.0 12-11 (br.). **HRMS (EI-TOF):** calcd for $[M]^+$ ($C_{12}H_{25}O_2B$) *m/z* 212.1948; found 212.1956.



4-(Boronic acid pinacolate ester)-2-decene (10a). Drisolv dichloromethane (0.9 mL, 14.2 mmol, 15 equiv.), stored under $Ar_{(g)}$, was added to 3.5 mL of freshly distilled THF. While under $Ar_{(g)}$, the solution was dropped to an internal temperature of -90 °C by cooling in an N_2/MeOH bath. *s*-butyllithium (1.1 mL, 1.3 M, 1.4 equiv.) was added dropwise to the stirring solution, with care given to keep the internal temperature below -85 °C. Lithiation was allowed to proceed at -90 °C for 60 min prior to the dropwise addition of the 1-hexyboronic acid pinacolate ester solution (161.6 mg, 0.762 mmol, 0.8 equiv., 1 mL THF). The solution was kept at -90 °C for 30 min to ensure complete borylation before addition of $ZnCl_2$ (0.95 mL, 1.0 M, 0.95 mmol, 1 equiv.). After addition of $ZnCl_2$, the solution was slowly warmed to 0 °C at which point the reaction was quenched with 2x 5 mL sat. $NH_4Cl_{(aq.)}$ aliquots. The aqueous layers were washed with 3 x 10 mL Et_2O. The organic layers were combined and dried with anhydrous $MgSO_4$ and filtered by vacuum. The ethereal solution was concentrated *in vacuo* to yield a slightly yellow crude oil. This oil was then taken up in 4 mL of freshly distilled Et_2O and cooled to 0 °C. To this solution was added 1-propenylmagnesium bromide (2.3 mL, 0.5 M, 1.22 equiv.). The solution was allowed to warm to 25 °C before aqueous quench and workup. The resultant yellow oil was purified by silica gel chromatography (80:1 hexanes:ethyl acetate, R_f = 7/20) to give 104.0 mg (51% isolated yield) of a clear, viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.50-5.26 (m, 2 H),

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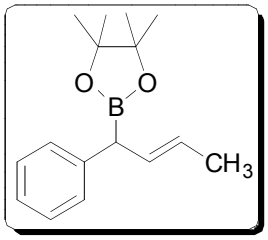
2.12-2.01 (m, 1 H), 1.66-1.56 (dd, J = 6.6 Hz, 1.4 Hz, 3 H), 1.32-1.17 (m, 22 H), 0.92-0.82 (m, 3 H) **^{11}B NMR:** (160 MHz, $CDCl_3$): δ 33.1 **^{13}C NMR:** (100 MHz, $CDCl_3$): δ 132.1, 123.2, 83.2, 32.1, 31.5, 29.7, 29.5, 25.0, 24.9, 22.9, 14.4, 13.4.



Synthesis of 4-(Boronic acid pinacolate ester)-4-phenyl-2-butene (10b). Drisolv dichloromethane (0.65 mL, 10.1 mmol, 3 equiv.) was added to 18.4 mL of freshly distilled THF. While under $Ar_{(g)}$, the solution was dropped to an internal temperature of -90 °C by cooling in an N_2/MeOH bath. *n*-butyllithium (1.75 mL, 2.5 M, 4.38 mmol, 1.3 equiv.) was added dropwise to the stirring solution, with care given to keep the internal temperature below -85 °C. Lithiation was allowed to proceed at -90 °C for 40 min. prior to the dropwise addition of the Phenylboronic acid pinacolate ester solution (686 mg, 3.37 mmol, 1.0 equiv., 3 mL THF). The reaction was allowed to warm slowly to room temperature overnight. The reaction was then quenched with 2x 5 mL sat. $NH_4Cl_{(aq.)}$ aliquots. The aqueous layers were washed with 3x 10 mL Et_2O. The organic layers were combined and dried with anhydrous $MgSO_4$ and filtered by vacuum. The ethereal solution was concentrated *in vacuo* to yield a slightly yellow crude oil. This oil was then taken up in 8 mL of freshly distilled Et_2O and cooled to 0 °C. To this solution was added 1-propenylmagnesium bromide (7.4 mL, 0.5 M, 1.1 equiv.). The solution was kept at 0 °C for 1.5 h before being allowed to warm to 25 °C over the course of 16 h and worked up as above. The crude oil was purified by silica gel chromatography (4:1 CH_2Cl_2:hexanes) to yield 262 mg of non isolable *Z* and *E* (major) isomer of the desired product, representing a 30.1% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) (for *E* isomer) δ 7.36-7.11 (m, 5 H), 5.78-5.68 (m, 1 H), 5.51-5.40 (m, 1 H), 3.17 (d, J = 8.1 Hz, 1 H), 1.75-1.66 (m, 3 H), 1.21 (s, 12 H). **^{13}C NMR:** (100 MHz, $CDCl_3$)

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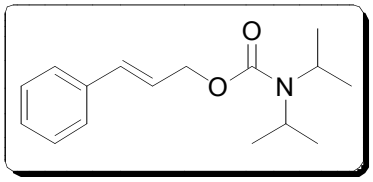
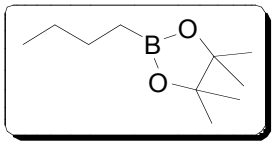
(mixture of *E* and *Z* isomers): δ 142.22, 142.20, 131.0, 130.6, 128.4, 128.33, 128.29, 128.1, 125.4, 125.30, 125.27, 123.6, 83.4, 24.59, 24.56, 24.54, 24.45, 18.1, 13.0. **HRMS (EI-TOF):** calcd for $[M]^+$ ($C_{16}H_{23}BO_2$) *m/z* 258.1791; found 258.1787.



***N,N*-Diisopropyl carbamic acid cinnamanyl ester.** *N,N*-Diisopropylcarbamoyl chloride (1.953 g, 163.65 g/mol, 11.94 mmol, 1.05 equiv.) and freshly distilled triethylamine (1.6 mL, 0.726 g/mL, 101.2 g/mol, 11.5 mmol, 1.0 equiv.) were taken up in 20 mL of CH_2Cl_2. Cinnamyl alcohol (semi-solid, 1.57 g, 134.2 g/mol, 11.7 mmol, 1 equiv.) was added and the solution was stirred under refluxing conditions for 21 h, with salts eventually precipitating out of solution. The solution was washed with sat. $NH_4Cl_{(aq.)}$ and the aqueous layer was extracted with 3 x 25 mL CH_2Cl_2. The crude oil was purified by silica gel chromatography (Load 20:1 hexanes:ethyl acetate, elute 10:1 hexanes:ethyl acetate, 2 inch by 5 inch column) to yield 1.928 g of the desired carbamate, or 63% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.6 Hz, 2 H), 7.25-7.15 (m, 5 H), 6.55 (d, *J* = 16 Hz, 1 H), 6.25 (dt, *J* = 15.6 Hz, 6.4 Hz, 1 H), 4.67 (dd, *J* = 6.8 Hz, 1.2 Hz, 2 H), 4.0-3.6 (d, br, 2 H), 1.14 (d, *J* = 6.8 Hz, 12 H). **^{13}C NMR:** (100 MHz, $CDCl_3$): δ 155.4, 136.6, 133.0, 128.6, 127.8, 126.6, 124.7, 65.2, 46 (br), 21.0 (br). **HRMS (EI-TOF):** calcd for $[M]^+$ ($C_{16}H_{23}O_2N$) *m/z* 261.1729; found 261.1733.



Synthesis of 1-butylboronic acid pinacolate ester. 1.519 g of 1-hexylboronic acid (101.8 g/mol, 14.9 mmol, 1.0 equiv.) and 1.763 g of pinacol (118 g/mol, 14.9 mmol, 1.0 equiv.) were taken up in 15 mL of diethyl ether. Once dissolved, 1.783 g of $MgSO_4$ (120 g/mol, 14.9 mmol, 1.0 equiv.) was dispersed in the solution,

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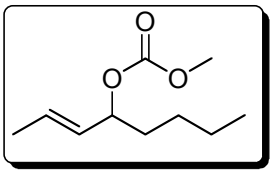
which was stirred at 25 °C for 24 h. The dispersion was filtered by vacuum and washed with copious amounts of diethyl ether. The homogeneous solution was then concentrated *in vacuo* to yield 2.105 g of the pure boronic ester, or 77% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.36 (m, 4 H), 1.25 (s, 12 H), 0.89 (t, J = 9.6 Hz, 3 H), 0.78 (m, 2 H). **^{11}B NMR:** (160 MHz, $CDCl_3$): δ 21. **^{13}C NMR:** (100 MHz, $CDCl_3$): δ 82.8, 26.2, 25.4, 24.8, 13.9, 10 (br). **HRMS (EI-TOF):** calcd for $[M]^+$ ($C_{10}H_{21}O_2B$) *m/z* 184.1635; found 184.1642.



Synthesis of (E)-methyl oct-2-en-4-yl carbonate. Under an argon atmosphere, to a stirred solution of crotonaldehyde (4 mL, 48.3 mmol) in THF (80 mL) at -78 °C, *n*-BuLi (2.5 M in hexane; 22 mL, 54 mmol) was added dropwise over 40 min. the mixture stirred at -78 °C for 2 h and then was allowed to warm slowly to –30 °C over 2 h. Water was added to quench the reaction, followed by acidification with 1 M HCl, and the mixture was stirred. The phases were then separated and the aqueous phase was extracted with Et_2O. The combined organic layers were washed with saturated, aqueous $NaHCO_3$ solution, then with brine, and dried with anhydrous $MgSO_4$ and filtered. Evaporation of the solvents *in vacuo* provided a yellow liquid, 2-Octen-4-ol, as crude product (5.63 g, 91 %). The crude product was subjected to the next reaction without further purification. The ^{1}H NMR was identical to those reported in the literature.[3]

Methyl chloroformate (5.0 g, 53 mmol) was added dropwise at 0 ^{o}C, to a solution 2-Octen-4-ol (2 g, 15.6 mmol) in dichloromethane (31 mL) and pyridine (4.8 mL, 60 mmol) and 4-(dimethylamino)pyridine (31 mg, 0.26 mmol) and the reaction was stirred at r.t for 4 h after which water was added to the reaction mixture and organic layer was separated. The aqueous layer was extracted twice with diethyl ether. The combined organic layers were washed brine and dried with anhydrous $MgSO_4$ and filtered. After removal of volatile materials, the residue was purified by silica gel chromatography (97:3 hexane:ethyl acetate) to give desired carbonate (2.27 g, 93 %) as a colorless oil. **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 5.81-5.70 (m, 1

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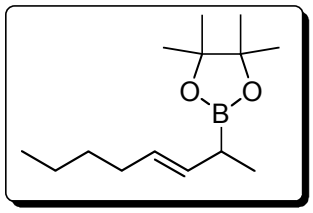
H), 5.46-5.36 (m, 1 H), 5.01-4.93 (q, *J* = 7.1 Hz, 1 H), 3.74 (s, 3 H), 1.72-1.63 (m, 4 H), 1.60-1.49 (m, 1 H), 1.36-1.24 (m, 4 H), 0.87 (t, *J* = 7.1 Hz, 3 H). **^{13}C NMR:** (100 MHz, $CDCl_3$) δ 155.3, 129.9, 129.2, 79.4, 54.3, 34.1, 27.2, 22.3, 17.6, 13.8. **HRMS (EI-TOF):** calcd for $[M]^+$ ($C_{10}H_{18}O_3$) *m/z* 186.1256; found 186.1252.



Synthesis of 2-(Boronic acid pinacolate ester)-3-octene (10c). Into a reaction vial, bis(pinacolato)diboron (254 mg, 1.0 mmol), copper(II) acetate (4.5 mg, 0.025 mmol), and 1,3-Bis(diphenylphosphino)propane (dppp) (10.31 mg, 0.025 mmol) were placed. After the vial was sealed with a rubber septum, the vial was evacuated and filled with nitrogen gas using a vacuum line through a needle. A THF solution of K(O-t-Bu) (1.0 M, 0.50 mL, 0.50 mmol) and THF (0.5 mL) were added to the vial. The mixture was allowed to stir at r.t for 30 min prior to the dropwise addition of (E)-methyl oct-2-en-4-yl carbonate solution (93.1 mg, 0.5 mmol, 0.1 mL THF). After 6 h stirring at r.t the reaction mixture was passed through a silica plug with an eluent (CH2Cl2/pentane 50:50) and the solvents were removed under reduced pressure with a rotary evaporator (3-4 bar). It should be noted that the **10c** is highly volatile compound and heating or using high vacuum line will result in the complete loss of **10c**. Using cold water during evaporating of solvents with rotary evaporator can help to prevent the loss of the desired component. The crude reaction mixture was directly loaded to silica gel column and was purified by CH_2Cl_2/pentane (20:80) to yield 74 mg of clear liquid representing a 62% isolated yield. **^{1}H NMR:** (400 MHz, CD_2Cl_2) δ 5.51-5.40 (m, 1 H), 5.39-5.26 (m, 1 H), 2.06-1.90 (m, 2 H), 1.81-1.68 (q, *J* = 7.3 Hz, 1 H), 1.38-1.25 (m, 4 H), 1.19 (s, 12 H), 1.01 (d, *J* = 7.3 Hz, 3 H), 0.94-0.82

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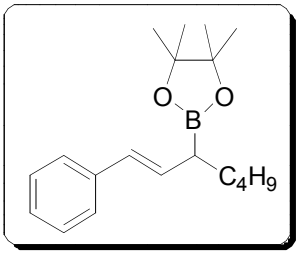
(m, 3 H). **^{13}C NMR:** (100 MHz, CD_2Cl_2) δ 133.0, 128.7, 83.6, 54.4, 33.0, 32.6, 25.11, 25.06, 22.7, 15.6, 14.3. **HRMS (EI-TOF):** calcd for $[M]^+$ ($C_{14}H_{27}BO_2$) *m/z* 238.2104; found 238.2101.



3-(Boronic acid pinacolate ester)-1-phenyl-1-heptene (10d). *N,N*-Diisopropyl carbamic acid cinnamyl ester (282.7 mg, 261 g/mol, 1.083 mmol, 1.15 equiv.) and (-)-sparteine (0.3 mL, 1.02 g/mL, 234.4 g/mol, 1.4 mmol, 1.45 equiv.) were taken up in diethyl ether and cooled to -78 °C in a dry ice/acetone bath. *s*-Butyllithium (1.1 mL, 1.3 M, 1.4 mmol, 1.45 equiv.) was added dropwise to the cold solution, creating a bright yellow solution, which eventually turned to dark green. After 4 h of lithiation, an ethereal solution of 1-butylboronic acid pinacolate ester (177.1 mg, 184 g/mol, 0.94 mmol, 1.0 equiv., 1 mL Et_2O) was added dropwise. No colour change was observed. After 5 h borylation, freshly prepared $MgBr_2$ diethyl etherate (3.0 equiv.) was added to the cold solution as an ethereal solution. $MgBr_2$ diethyl etherate is prepared by adding a necessary amount of 1,2-dibromoethane, in this case, 3 equivalents per boronic ester to an excess of Mg turnings in dry ether. The contents of the dense layer that dissociates from the ether are added to the reaction solution *via* syringe. After addition of the $MgBr_2$, the solution is allowed to warm slowly before being heated to reflux overnight. After aqueous workup, two silica gel chromatography steps (20:1 hexanes:ethyl acetate) were required and only 50.3 mg (18% yield) of white solid was isolated. The process was also performed with the achiral TMEDA ligand and gave similar yields. In the interest of obtaining a useable amount of product, the two batches were combined. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.2 Hz, 2 H), 7.28 (t, *J* = 7.6 Hz, 2 H), 7.17 (m, 1 H), 6.37 (d, *J* = 15.6 Hz, 1 H), 6.21 (dd, *J* = 16.0 Hz, 9.2 Hz, 1 H), 1.98 (q, *J* = 8.0 Hz, 1 H), 1.71-1.58 (m, 1 H), 1.55-1.45 (m, 1 H), 1.48-1.28 (m, 4 H), 1.25 (s, 12 H), 0.89 (t, *J*=

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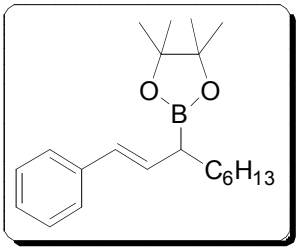
6.8 Hz, 3 H). **^{13}C NMR:** (100 MHz, $CDCl_3$): δ 138.3, 132.1, 128.9, 128.4, 126.5, 125.9, 83.2, 31.4, 30.5, 24.7, 24.6, 22.7, 14.1.



Synthesis of 3-(boronic acid pinacolate ester)-1-phenyl-1-nonene (10e). Freshly distilled dichloromethane (0.7 mL, 1.33 g/mL, 85 g/mol, 10.7 mmol, 15 equiv.) was taken in 5 mL of freshly distilled THF. The solution was cooled to -90 °C and *s*-BuLi (0.9 mL, 1.3 M, 1.15 mmol, 1.6 equiv.) was added dropwise with vigorous stirring maintaining an internal temperature below -85 °C. After 1 h of cold-temperature lithiation, 1-hexylboronic acid pinacolate ester (144.3 mg, 212 g/mol, 0.688 mmol, 1.0 equiv.) in 1 mL of THF was added to the solution. After 0.5 h of borylation, $ZnCl_2$ (0.8 mL, 1.0 M, 1.1 equiv.) was added dropwise and the solution was allowed to warm to room temperature overnight. The reaction was then quenched with 2 x 10 mL aqueous $NH_4Cl_{(sat.)}$ and washed with 3 x 20 mL of diethyl ether. The combined organic layers were dried over $MgSO_{4(anhydr.)}$, filtered and concentrated *in vacuo*. The crude oil was then taken in 5 mL of dry THF and cooled to 0 °C. Freshly prepared stryrenylmagnesium bromide (2.8 mL, 0.5 M, 1.42 mmol, 2.1 equiv.) was then added under vigorous stirring and the reaction was allowed to warm to room temperature. The crude reaction mixture was quenched and worked up as above, and 93.1 mg of an isomeric mixture of the desired product was isolated by silica gel chromatography (50:1 hexanes: diethyl ether), corresponding to a 42% yield. The product isomers are separable under the given chromatographic conditions, and ultimately, 62.1 mg of the *trans*-olefin product was isolated. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (d, J = 7.6 Hz, 2 H), 7.30 (t, J = 7.2 Hz, 2 H), 7.19 (t, J = 7.2 Hz, 1 H), 6.37 (d, J = 16 Hz, 1 H), 6.24 (dd, J = 16 Hz, 8.8 Hz, 1 H), 2.00 (q, J = 8.4 Hz, 1 H), 1.71-1.60 (m, 1 H), 1.59-1.47 (m, 1 H), 1.39-1.28 (m, 8

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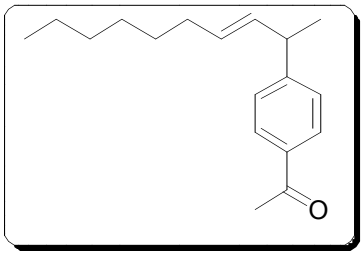
H), 1.27 (s, 12 H), 0.94-0.86 (m, 3 H). **^{11}B NMR:** (160 MHz, $CDCl_3$): δ 33.1. **^{13}C NMR:** (100 MHz, $CDCl_3$): δ 138.3, 132.1, 128.9, 128.4, 126.4, 125.9, 83.2, 31.8, 30.8, 29.3, 29.1, 24.7, 24.6, 22.6, 14.1. **HRMS (EI-TOF):** calcd for $[M]^+$ ($C_{21}H_{33}O_2B$) *m/z* 328.2574; found 328.2584.

4. Cross-Coupling of Secondary Allylic Boronic Esters with Aryl Iodides



Synthesis of 2-(4-acetylphenyl)-3-decene (12aa). In a nitrogen-atmosphere glovebox, 4-iodoacetophenone (12.68 mg, 245.9 g/mol, 0.052 mmol, 1.0 equiv.), 4-(boronic acid pinacolate ester)-2-decene (**10a**, 22.65 mg, 266 g/mol, 0.085 mmol, 1.6 equiv.), Ag_2O (18.80 mg, 232 g/mol, 0.081 mmol, 1.6 equiv.), $Pd(PPh_3)_4$ (4.55 mg, 1155.6 g/mol, 0.004 mmol, 7.6 mol% Pd), PPh_3 (5.03 mg, 262 g/mol, 0.019 mmol, 0.37 equiv., 8.75:1 P:Pd) and K_2CO_3 (12.65 mg, 138 g/mol, 0.092 mmol, 1.76 equiv.) were added to a tared 1 dram vial and taken up in 980 mg of DME. The reaction solution was sealed in the glovebox, removed, and placed in an 85 °C oil bath for 24 h. Once cooled, the reaction solution was passed through a celite plug and washed with copious amounts of diethyl ether. The solution was concentrated *in vacuo* to dryness and an NMR internal standard was added (hexamethylbenzene, HMB, 6.68 mg). NMR yield of the major isomer was determined to be 78% and the ratio of major (γ) to minor (α) isomers was 92:8 prior to isolation. Peak assignments for major and minor isomers were performed using 2D COSY-NMR correlations. The crude mixture was purified by silica gel chromatography (20:1 hexanes:ethyl acetate) and 11.2 mg of a mixture of isomers (γ:α = 87:13) was obtained, representing an 84% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.4

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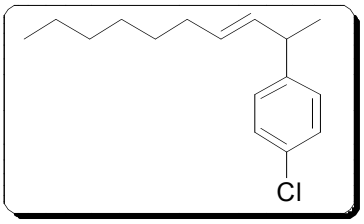
Hz, 2 H), 7.32 (d, *J* = 8.4 Hz, 2 H), 5.64-5.43 (m, 2 H), 3.55-3.45 (m, inc. *J* = 7.2 Hz, 1 H), 2.60 (s, 3 H), 2.08-1.99 (m, 2 H), 1.37 (d, *J* = 7.2 Hz, 3 H), 1.34-1.19 (m, 8 H), 0.93-0.85 (m, 3 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.8, 152.3, 135.2, 133.9, 130.3, 128.6, 127.4, 42.3, 32.5, 31.7, 29.4, 28.8, 26.6, 22.6, 21.3, 14.1. (13.1) **HRMS (EI-TOF):** calcd for $[M]^+$ ($C_{18}H_{26}O$) *m/z* 258.1984; found 258.1977.



Synthesis of 2-(4-chlorophenyl)-3-decene (12ab). In a nitrogen-atmosphere glovebox, 4-chloroiodobenzene (12.62 mg, 238.4 g/mol, 0.053 mmol, 1.0 equiv.), 4-(boronic acid pinacolate ester)-2-decene (**10a**, 23.35 mg, 266 g/mol, 0.088 mmol, 1.67 equiv.), Ag_2O (18.60 mg, 232 g/mol, 0.080 mmol, 1.50 equiv.), $Pd(PPh_3)_4$ (4.50 mg, 1155.6 g/mol, 0.0039 mmol, 7.3 mol% Pd), PPh_3 (4.23 mg, 262 g/mol, 0.016 mmol, 0.30 equiv., 8.10:1 P:Pd) and K_2CO_3 (10.66 mg, 138 g/mol, 0.077 mmol, 1.46 equiv.) were added to a tared 1 dram vial and taken up in 1.10 g of DME. The reaction solution was sealed in the glovebox, removed, and placed in an 85 °C oil bath for 24 h. Once cooled, the reaction solution was passed through a celite plug and washed with copious amounts of diethyl ether. The solution was concentrated *in vacuo* to dryness and an NMR internal standard was added (*p*- dimethoxybenzene, DMB, 10.42 mg). The NMR yield of the major isomer was determined to be 72% and the ratio of major (γ) to minor (α) isomers (assigned by 2D-COSY NMR correlations) was 83:17 prior to isolation. The crude mixture was purified by silica gel chromatography (20:1 hexanes:ethyl acetate) and 13.25 mg of a mixture of isomers (γ:α = 79:21) was obtained, representing an 83% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 6 Hz, 2 H), 7.06 (d, *J* = 8.4 Hz, 2 H), 5.50-5.40 (m, 1 H), 5.40-5.28 (m, 1 H), 3.32 (dq, *J* = 6.8 Hz, 1 H), 1.93 (m, 2 H), 1.3-1.15 (m, 8 H),1.23 (d, *J* = 6.8 Hz, 3 H), 0.81 (m, 3 H). **^{13}C NMR**

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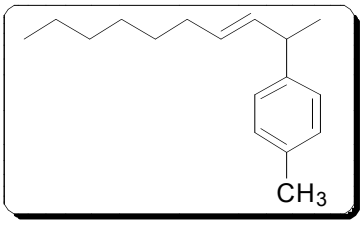
(100 MHz, $CDCl_3$) δ 145.0, 134.4, 129.8, 128.6, 128.4, 124.9, 41.7, 32.5, 31.7, 29.4, 28.8, 22.6, 21.5, 14.1. **HRMS (EI-TOF):** calcd for $[M]^+$ ($C_{16}H_{23}Cl$) *m/z* 250.1488; found 250.1483.



Synthesis of 2-(4-tolyl)-3-decene (12ac). In a nitrogen-atmosphere glovebox, 4-iodotoluene (11.80 mg, 217.9 g/mol, 0.054 mmol, 1.0 equiv.), 4-(boronic acid pinacolate ester)-2-decene (**10a**, 20.14 mg, 266 g/mol, 0.076 mmol, 1.41 equiv.), Ag_2O (17.50 mg, 232 g/mol, 0.075 mmol, 1.38 equiv.), $Pd(PPh_3)_4$ (4.52 mg, 1155.6 g/mol, 0.0039 mmol, 7.2 mol% Pd), PPh_3 (4.52 mg, 262 g/mol, 0.017 mmol, 0.32 equiv., 8.36:1 P:Pd) and K_2CO_3 (11.97 mg, 138 g/mol, 0.087 mmol, 1.61 equiv.) were added to a tared 1 dram vial and taken up in 1.0 g of DME. The reaction solution was sealed in the glovebox, removed, and placed in an 85 °C oil bath for 24 h. Once cooled, the reaction solution was passed through a celite plug and washed with copious amounts of diethyl ether. The solution was concentrated *in vacuo* to dryness. The crude mixture (γ:α = 90:10, assigned by 2D-COSY NMR correlation) was purified by silica gel chromatography (20:1 hexanes:ethyl acetate) and 8.7 mg of a mixture of isomers was obtained, representing an 70% isolated yield. The ratio of the major (γ) and minor (α) products after isolation was determined to be 86:14 by ^{1}H NMR. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27-7.05 (m, 4 H), 5.59 (dd, *J* = 6.8 Hz, 1 H), 5.51-5.38 (m, 1 H), 3.45-3.34 (m, 1 H), 2.33 (s, 3 H), 2.06-1.96 (m, 2 H), 1.41-1.21 (m, 11 H), 0.94-0.84 (m, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.6, 135.3, 135.1, 129.1, 129.0, 127.0, 41.8, 32.5, 31.7, 29.5, 28.8, 22.6, 21.6, 21.0, 14.1. **HRMS (EI-TOF):** calcd for $[M]^+$ ($C_{17}H_{26}$) *m/z* 230.2035; found 230.2036.

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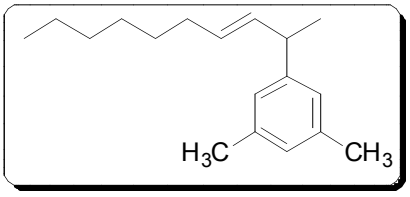

Synthesis of 2-(3,5-dimethylphenyl)-3-decene (12ad). In a nitrogen-atmosphere glovebox, 3,5-dimethyliodobenzene (13.73 mg, 232.9 g/mol, 0.059 mmol, 1.0 equiv.), 4-(boronic acid pinacolate ester)-2-decene (**10a**, 24.94 mg, 266 g/mol, 0.094 mmol, 1.59 equiv.), Ag_2O (23.88 mg, 232 g/mol, 0.10 mmol, 1.73 equiv.), $Pd(PPh_3)_4$ (5.68 mg, 1155.6 g/mol, 0.0049 mmol, 8.3 mol% Pd), PPh_3 (5.85 mg, 262 g/mol, 0.022 mmol, 0.38 equiv., 8.49:1 P:Pd) and K_2CO_3 (12.00 mg, 138 g/mol, 0.087 mmol, 1.47 equiv.) were added to a tared 1 dram vial and taken up in 1.05 g of DME. The reaction solution was sealed in the glovebox, removed, and placed in an 85 °C oil bath for 24 h. Once cooled, the reaction solution was passed through a celite plug and washed with copious amounts of diethyl ether. The solution was concentrated *in vacuo* to dryness and an NMR internal standard was added (*p*- dimethoxybenzene, DMB, 7.90 mg). NMR yield of the major isomer was determined to be 78% and the ratio of major (γ) to minor (α) isomers (assigned by 2D-COSY-NMR correlations) was 91:9 prior to isolation. The crude mixture was purified by silica gel chromatography (20:1 hexanes:ethyl acetate) and 10.4 mg of a mixture of isomers (γ:α = 90:10) was obtained, representing an 72% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.84 (s, 3 H), 5.59 (dd, *J* = 6.8 Hz, 1 H), 5.52-5.39 (m, 1 H), 3.41-3.30 (m, 1 H), 2.31 (s, 6 H), 2.07-1.96 (m, 2 H), 1.36-1.21 (m, 11 H), 0.94-0.83 (m, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.6, 137.7, 135.1, 129.1, 127.5, 125.0, 42.2, 32.5, 31.8, 29.4, 28.8, 22.7, 21.6, 21.3, 14.1. **HRMS (EI-TOF):** calcd for $[M]^+$ ($C_{18}H_{28}$) *m/z* 244.2191; found 244.2199.

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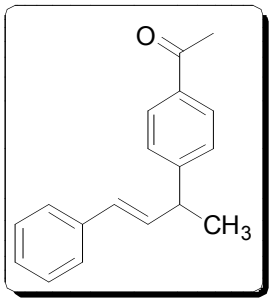
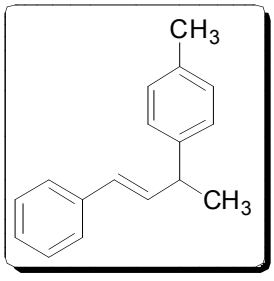


Synthesis of 3-(4-acetylphenyl)-1-phenyl-1-butene (12ba). In a nitrogen-atmosphere glovebox, 4-iodoacetophenone (12.46 mg, 245.9 g/mol, 0.051 mmol, 1.0 equiv.), 4-(boronic acid pinacolate ester)-4-phenyl-2-butene (**10b**, 19.61 mg, 258.16 g/mol, 0.076 mmol, 1.5 equiv.), Ag_2O (17.6 mg, 232 g/mol, 0.076 mmol, 1.5 equiv.), $Pd(PPh_3)_4$ (4.68 mg, 1155.6 g/mol, 0.004 mmol, 8 mol% Pd), PPh_3 (4.25 mg, 262.3 g/mol, 0.016 mmol, 0.32 equiv.) and K_2CO_3 (10.5 mg, 138.2 g/mol, 0.076 mmol, 1.5 equiv.) were added to a tared 1 dram vial and taken up in 1.0 g of DME. The reaction solution was sealed in the glovebox, removed, and placed in an 85 °C oil bath for 24 h. Once cooled, the reaction solution was passed through a celite plug and washed with copious amounts of diethyl ether. The crude mixture was purified by silica gel chromatography (96:4 hexanes:ethyl acetate) and 1.6 mg of a α of isomers and 8.6 mg of a γ of isomer (γ:α = 84:16) was obtained, representing a total 81% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.9 Hz, 2 H), 7.40-7.33 (m, 4 H), 7.29 (t, *J* = 6.0 Hz, 2 H), 7.21 (t, *J* = 7.6 Hz, 1 H), 6.43 (d, *J* = 15.7 Hz, 1 H), 6.35 (dd, *J* = 7.4 Hz, 4 Hz, 1 H), 3.77-3.66 (m, 1 H), 2.59 (s, 3 H), 1.48 (d, *J* = 6.8 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.8, 151.3, 137.2, 135.4, 134.0, 129.3, 128.7, 128.5, 127.5, 127.3, 126.2, 42.6, 29.7, 26.6, 21.0. **HRMS (EI-TOF):** calcd for $[M]^+$ ($C_{18}H_{18}O$) *m/z* 250.1358; found 250.1352.



Synthesis of 3-(4-tolyl)-1-phenyl-1-butene (12bc). In a nitrogen-atmosphere glovebox, 4-iodotoluene (11.0 mg, 217.9 g/mol, 0.051 mmol, 1.0 equiv.), 4-(boronic acid pinacolate ester)-4-phenyl-2-butene (**10b**,

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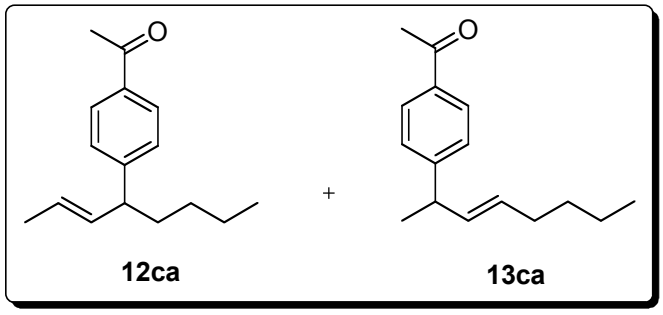
19.61 mg, 258.16 g/mol, 0.076 mmol, 1.5 equiv.), Ag_2O (17.6 mg, 232 g/mol, 0.076 mmol, 1.5 equiv.), $Pd(PPh_3)_4$ (4.68 mg, 1155.6 g/mol, 0.004 mmol, 8 mol% Pd), PPh_3 (4.25 mg, 262.3 g/mol, 0.016 mmol, 0.32 equiv.) and K_2CO_3 (10.5 mg, 138.2 g/mol, 0.076 mmol, 1.5 equiv.) were added to a tared 1 dram vial and taken up in 1.0 g of DME. The reaction solution was sealed in the glovebox, removed, and placed in an 85 °C oil bath for 24 h. Once cooled, the reaction solution was passed through a celite plug and washed with copious amounts of diethyl ether. The crude mixture was purified by silica gel chromatography (99:1 hexanes:CH_2Cl_2) and 0.9 mg of a α of isomers and 8.4 mg of a γ of isomer (γ:α = 91:9) was obtained, representing a total 82% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42-7.32 (m, 2 H), 7.31-7.27 (m, 2 H), 7.22-7.11 (m, 5 H), 6.44-6.36 (m, 2 H), 3.60 (m, 1 H), 2.33 (s, 3 H,), 1.45 (d, *J* = 6.8 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.6, 137.6, 135.5, 129.2, 128.4, 128.3, 127.2, 127.0, 126.1, 42.1, 21.3, 21.0. The characterization data were identical to those reported in the literature.[4]



Synthesis of 4-(4-acetylphenyl)-3-octene (12ca). and 2-(4-acetylphenyl)-3-octene (13ca).

In a nitrogen-atmosphere glovebox, 4-iodoacetophenone (24.92 mg, 245.9 g/mol, 0.1 mmol, 1.0 equiv.), 2-(Boronic acid pinacolate ester)-3-octene (**10c**) (36.2 mg, 238.2 g/mol, 0.15 mmol, 1.5 equiv.), Ag_2O (35.2 mg, 232 g/mol, 0.081 mmol, 1.5 equiv.), $Pd(PPh_3)_4$ (9.36 mg, 1155.6 g/mol, 0.008 mmol), PPh_3 (8.5 mg, 262 g/mol, 0.032 mmol) and K_2CO_3 (21 mg, 138 g/mol, 0.15 mmol, 1.5 equiv.) were added to a tared 1 dram vial and taken up in 2.3 ml of DME. The reaction solution was sealed in the glovebox, removed, and placed in an 85 °C oil bath for

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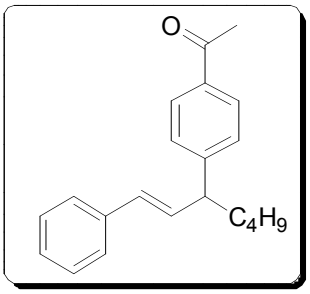
24 h. Once cooled, the reaction solution was passed through a celite plug and washed with copious amounts of diethyl ether. The solution was concentrated *in vacuo* and the crude mixture was purified by silica gel chromatography (98:2 hexanes:ethyl acetate) and 15.2 mg of a non separable mixture of α and γ product (α: γ = 50:50) was obtained. (ratio of α and γ was determined by crude ^{1}H NMR and GC-Mass analysis), representing a total 65% isolated yield. GC-MS analysis indicated that both α and γ products have *E* and *Z* isomers.

12ca: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.1 Hz, 2 H), 7.30 (d, *J* = 8.1 Hz, 2 H), 5.61-5.40 (m, 2H), 3.30-3.20 (m, 1H), 2.59 (s, 3H), 1.73-1.61 (m, 5H), 1.34-1.11 (m, 4H), 0.94-0.83 (m, 3 H). **13ca: ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.1 Hz, 2 H), 7.30 (d, *J* = 8.1 Hz, 2 H), 5.61-5.40 (m, 2H), 3.54-3.44 (m, 1H), 2.59 (s, 3H), 2.08-1.98 (m, 2H), 1.39-1.30 (m, 7H), 0.94-0.83 (m, 3 H). **^{13}C NMR** (mixture of α and γ products which both have *E* and *Z* isomers) (100 MHz, $CDCl_3$) δ 197.82, 197.81, 152.3, 151.4, 135.1, 134.4, 133.85, 133.79, 133.7, 130.2, 129.8, 128.62, 128.60, 128.57, 128.55, 127.7, 127.5, 127.4, 127.1, 125.31, 124.4, 79.0, 43.1, 42.3, 36.4, 35.6, 32.2, 31.7, 31.6, 29.7, 29.6, 26.53, 26.51, 22.6, 22.2, 21.3, 17.9, 14.0, 13.9, 13.1. **HRMS (EI-TOF):** calcd for $[M]^+$ ($C_{16}H_{22}O$) *m/z* 230.1671; found 230.1663.



Synthesis of 3-(4-acetylphenyl)-1-phenylheptene (13da). In a nitrogen-atmosphere glovebox, 4-iodoacetophenone (6.00 mg, 245.9 g/mol, 0.0244 mmol, 1.0 equiv.), 3-(boronic acid pinacolate ester)-1-phenyl-1-heptene (**10d**,12 mg, 300 g/mol, 0.04 mmol, 1.64 equiv.), Ag_2O (9.30 mg, 232 g/mol, 0.04 mmol, 1.62 equiv.), $Pd(PPh_3)_4$ (2.17 mg, 1155.6 g/mol, 0.0018 mmol, 7.7 mol% Pd), PPh_3 (2.09 mg, 262 g/mol, 0.008 mmol, 0.33 equiv., 8.44:1 P:Pd) and K_2CO_3 (5.94 mg, 138 g/mol, 0.043 mmol, 1.76 equiv.) were added to a tared 1 dram vial and

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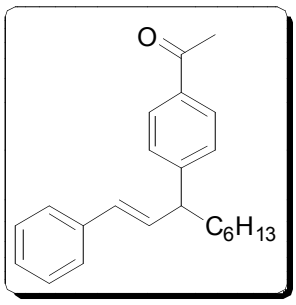
taken up in 0.6 g of DME. The reaction solution was sealed in the glovebox, removed, and placed in an 85 °C oil bath for 24 h. Once cooled, the reaction solution was passed through a celite plug and washed with copious amounts of diethyl ether. The solution was concentrated *in vacuo* to dryness. The crude mixture (α *:* γ = 88:12, assigned by 2D-COSY NMR correlations) was then purified by silica gel chromatography (20:1 hexanes:ethyl acetate) and 4.1 mg of a mixture of isomers (α: γ = 92:8) was obtained, representing an 58% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 2 H), 7.38-7.19 (m, 7 H), 6.41 (d, *J* = 16 Hz, 1 H), 6.31 (dd, *J* = 15.6 Hz, 7.6 Hz, 1 H), 3.48 (m, inc. *J* = 7.6 Hz, 1 H), 2.60 (s, 3 H), 1.89-1.77 (m, 2 H), 1.40-1.22 (m, 4 H), 0.92-0.85 (m, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.5, 137.3, 135.4, 133.3, 130.0, 128.7, 128.5, 127.9, 127.2, 126.2, 49.2, 35.5, 29.8, 26.6, 22.6, 14.0, (Carbonyl peak not assigned). **HRMS (EI-TOF):** calcd for $[M]^+$ ($C_{21}H_{24}O$) *m/z* 292.1827; found 292.1819.



Synthesis of 3-(4-acetylphenyl)-1-phenyl-1-nonene (13ea). In a nitrogen-atmosphere glovebox, 4-iodoacetophenone (12.46 mg, 245.9 g/mol, 0.051 mmol, 1.0 equiv.), 3-(boronic acid pinacolate ester)-1-phenyl-1-nonene (**10e**, 24.9 mg, 328.3 g/mol, 0.076 mmol, 1.5 equiv.), Ag_2O (17.6 mg, 232 g/mol, 0.076 mmol, 1.5 equiv.), $Pd(PPh_3)_4$ (4.68 mg, 1155.6 g/mol, 0.004 mmol, 8 mol% Pd), PPh_3 (4.25 mg, 262.3 g/mol, 0.016 mmol, 0.32 equiv.) and K_2CO_3 (10.5 mg, 138.2 g/mol, 0.076 mmol, 1.5 equiv.) were added to a tared 1 dram vial and taken up in 1.0 g of DME. The reaction solution was sealed in the glovebox, removed, and placed in an 85 °C oil bath for 24 h. Once cooled, the reaction solution was passed through a celite plug and washed with copious amounts of diethyl ether. The crude mixture was purified by silica gel chromatography (99:1 hexanes:CH_2Cl_2) and 6.9 mg of a α of isomers and 1.6 mg of a γ

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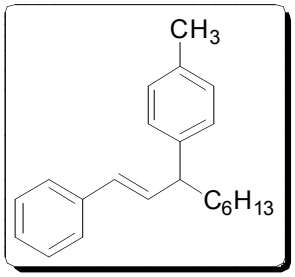
of isomer (γ:α = 19:81) was obtained, representing a total 53% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 2 H), 7.34 (d, *J* = 7.8 Hz, 4 H), 7.29 (t, *J* = 7.2 Hz, 2 H), 7.2 (t, *J* = 7.1 Hz, 1 H), 6.4 (d, *J* = 15.7 Hz, 1 H), 6.3 (dd, *J* = 7.6 Hz, 7.3 Hz, 1 H), 3.51-3.43 (m, 1 H), 2.59 (s, 3 H), 1.91-1.75 (m, 2H), 1.44-1.16 (m, 8H), 0.86 (t, *J* = 6.8 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.8, 150.5, 137.3, 135.3, 133.3, 130.0, 128.7, 128.5, 127.9, 127.2, 126.2, 49.2, 35.7, 31.7, 29.7, 29.2, 27.5, 26.6, 22.6, 14.0. **HRMS (ESI)** calcd for $[M+H]^+$ ($C_{23}H_{29}O$) *m/z* 321.2218; found 321.2214.



Synthesis of 3-(4- tolyl)-1-phenyl-1-nonene (13ec). In a nitrogen-atmosphere glovebox, 4-iodotoluene (11.0 mg, 217.9 g/mol, 0.051 mmol, 1.0 equiv.), 3-(boronic acid pinacolate ester)-1-phenyl-1-nonene (**10d**, 24.9 mg, 328.3 g/mol, 0.076 mmol, 1.5 equiv.), Ag_2O (17.6 mg, 232 g/mol, 0.076 mmol, 1.5 equiv.), $Pd(PPh_3)_4$ (4.68 mg, 1155.6 g/mol, 0.004 mmol, 8 mol% Pd), PPh_3 (4.25 mg, 262.3 g/mol, 0.016 mmol, 0 .32 equiv.) and K_2CO_3 (10.5 mg, 138.2 g/mol, 0.076 mmol, 1.5 equiv.) were added to a tared 1 dram vial and taken up in 1.0 g of DME. The reaction solution was sealed in the glovebox, removed, and placed in an 85 °C oil bath for 24 h. Once cooled, the reaction solution was passed through a celite plug and washed with copious amounts of diethyl ether. The crude mixture was purified by silica gel chromatography (hexanes) and 6.9 mg of a α of isomers and 1.3 mg of a γ of isomer (γ:α = 16:84) was obtained, representing a total 55% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36-7.09 (m, 9 H), 6.44-6.26 (m, 2 H), 3.38 (q, *J* = 6.6 Hz, 1 H), 2.34 (s, 3 H), 1.85-1.71 (m, 2 H), 1.38-1.19 (m, 8 H), 0.88 (t, *J* = 6.8 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.7, 137.7, 135.6, 134.8, 129.2,

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129.0, 128.4, 127.5, 126.9, 126.1, 48.8, 35.9, 31.8, 29.7, 29.3, 27.6, 22.6, 21.0, 14.1. **HRMS (EI-TOF):** calcd for $[M]^+$ ($C_{22}H_{28}$) *m/z* 292.2191; found 292.2187.

5. Ligand-Based Regioselectivity and Control Reactions

Attempted Ligand-Based Regioselectivity Switch in the Cross-Coupling of Secondary Allylic Boronic Esters. In a nitrogen-atmosphere glovebox, 4-iodoacetophenone (12.29 mg, 245.9 g/mol, 0.050 mmol, 1.0 equiv.), 3-(boronic acid pinacolate ester)-2-decene (19.43 mg, 266 g/mol, 0.073 mmol, 1.46 equiv.), Ag_2O (17.55 mg, 232 g/mol, 0.075 mmol, 1.50 equiv.), Pd_2dba_3 (1.95 mg, 915.7 g/mol, 0.0021 mmol, 8.5 mol% Pd), dppp (diphenylphosphine propane, 5.38 mg, 262 g/mol, 0.013 mmol, 0.26 equiv., 6.2:1 P:Pd) and K_2CO_3 (11.55 mg, 138 g/mol, 0.084 mmol, 1.67 equiv.) were added to a tared 1 dram vial and taken up in 1.1 g of DME. The reaction solution was sealed in the glovebox, removed, and placed in an 85 °C oil bath for 21 h. Once cooled, the reaction solution was passed through a celite plug and washed with copious amounts of diethyl ether. Analysis by GC-MS indicates that the boronic ester was the major species present in solution, with only trace amounts of arylated product detected.

Attempted cross-coupling of allylic boronate esters in the absence of silver oxide.

In a nitrogen-atmosphere glovebox, 4-iodotoluene (11.0 mg, 217.9 g/mol, 0.051 mmol, 1.0 equiv.), 4-(boronic acid pinacolate ester)-4-phenyl-2-butene (**10b**, 19.61 mg, 258.16 g/mol, 0.076 mmol, 1.5 equiv.), $Pd(PPh_3)_4$ (4.68 mg, 1155.6 g/mol, 0.004 mmol, 8 mol% Pd), PPh_3 (4.25 mg, 262.3 g/mol, 0.016 mmol, 0.32 equiv.) and K_2CO_3 (10.5 mg, 138.2 g/mol, 0.076 mmol, 1.5 equiv.) were added to a tared 1 dram vial and taken up in 1.0 g of DME. The reaction solution

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was sealed in the glovebox, removed, and placed in an 85 °C oil bath for 24 h. Once cooled, the reaction solution was passed through a celite plug and washed with copious amounts of diethyl ether. ^{1}H NMR, GC and TLC analysis of the filtered reaction indicated that no desired product had been formed.

Attempted cross-coupling of allylic boronate esters using Pd(dba)$_2$ as catalyst.

In a nitrogen-atmosphere glovebox, 4-iodotoluene (11.0 mg, 217.9 g/mol, 0.051 mmol, 1.0 equiv.), 4-(boronic acid pinacolate ester)-2-decene (**10a**, 20.2 mg, 266.2 g/mol, 0.076 mmol, 1.5 equiv.), Ag_2O (17.6 mg, 231.7 g/mol, 0.076 mmol, 1.5 equiv.), Pd(dba)$_2$ (2.3 mg, 575.0 g/mol, 0.004 mmol, 8 mol% Pd), and K_2CO_3 (10.5 mg, 138.2 g/mol, 0.086 mmol, 1.5 equiv.) were added to a tared 1 dram vial and taken up in 1.0 g of DME. The reaction solution was sealed in the glovebox, removed, and placed in an 85 °C oil bath for 24 h . Once cooled, the reaction solution was passed through a celite plug and washed with copious amounts of diethyl ether. ^{1}H NMR, GC and TLC analysis of the filtered reaction indicated that no desired product had been formed.

6. References

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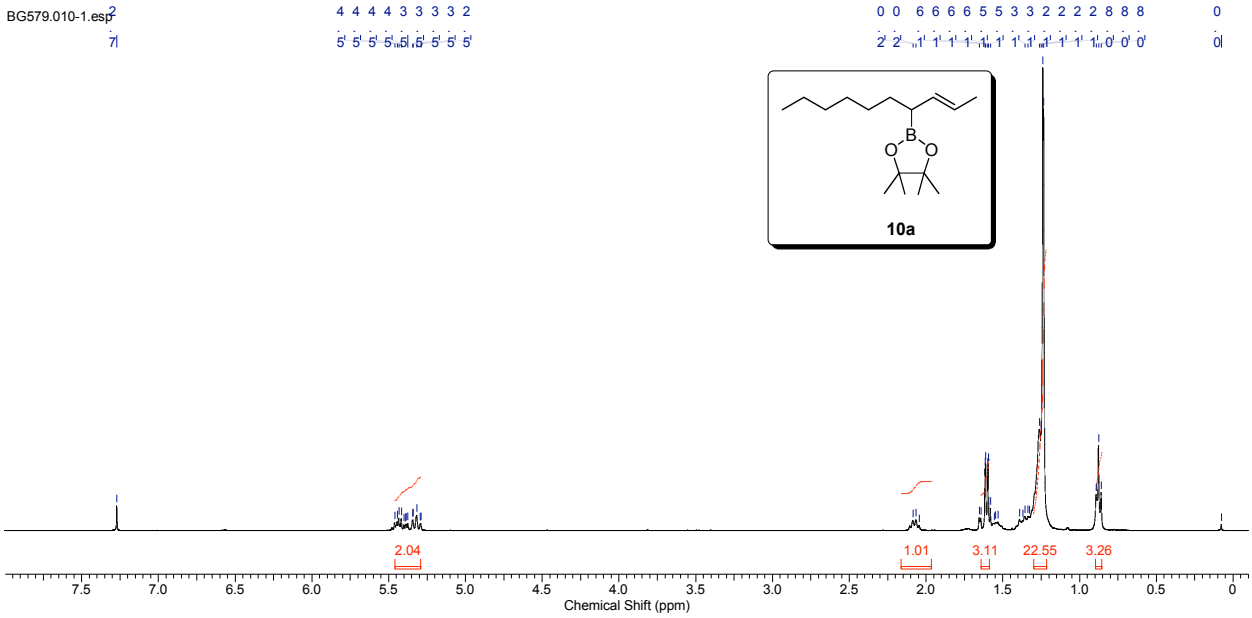
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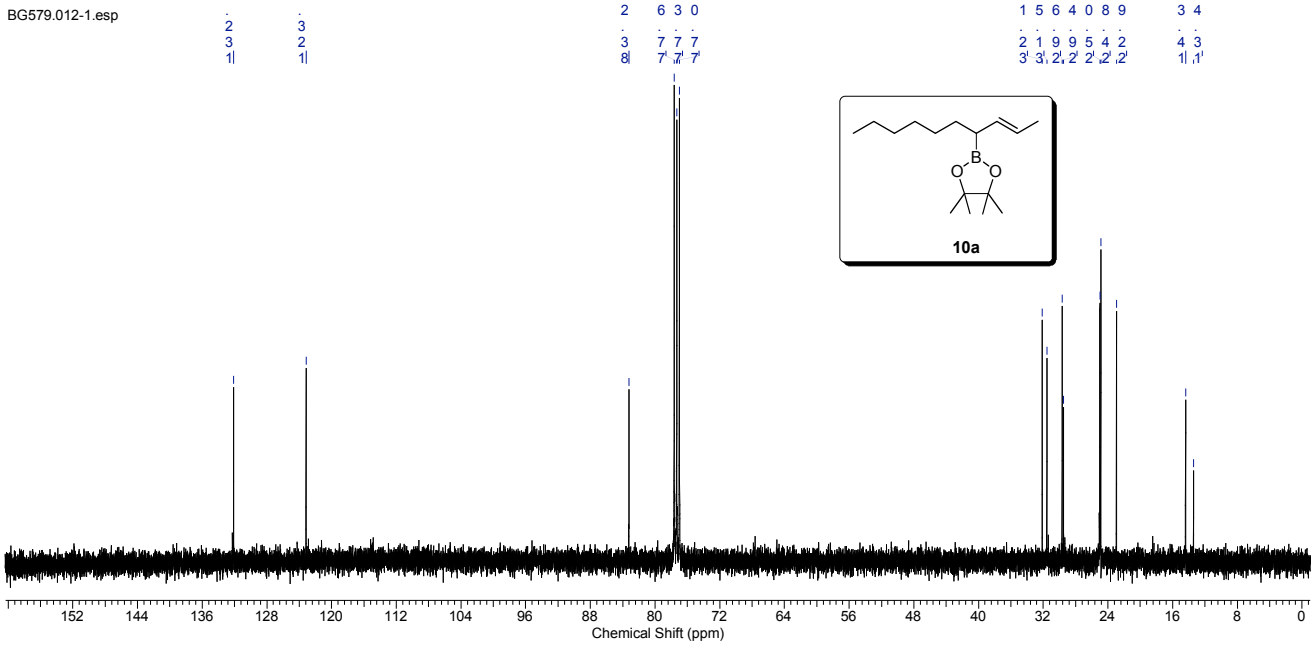
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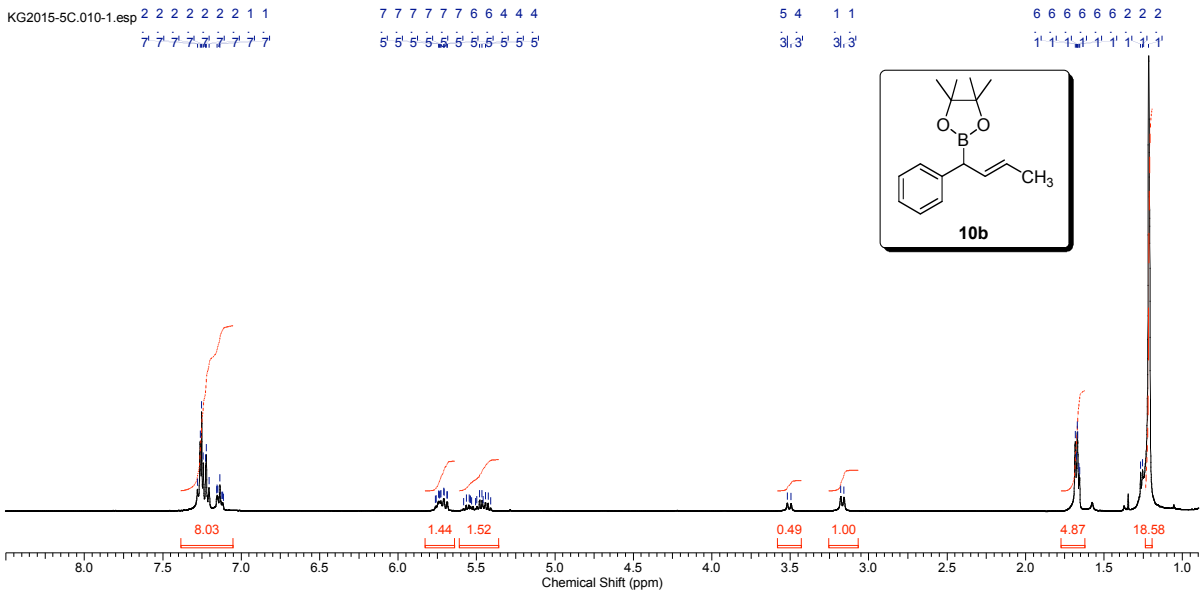
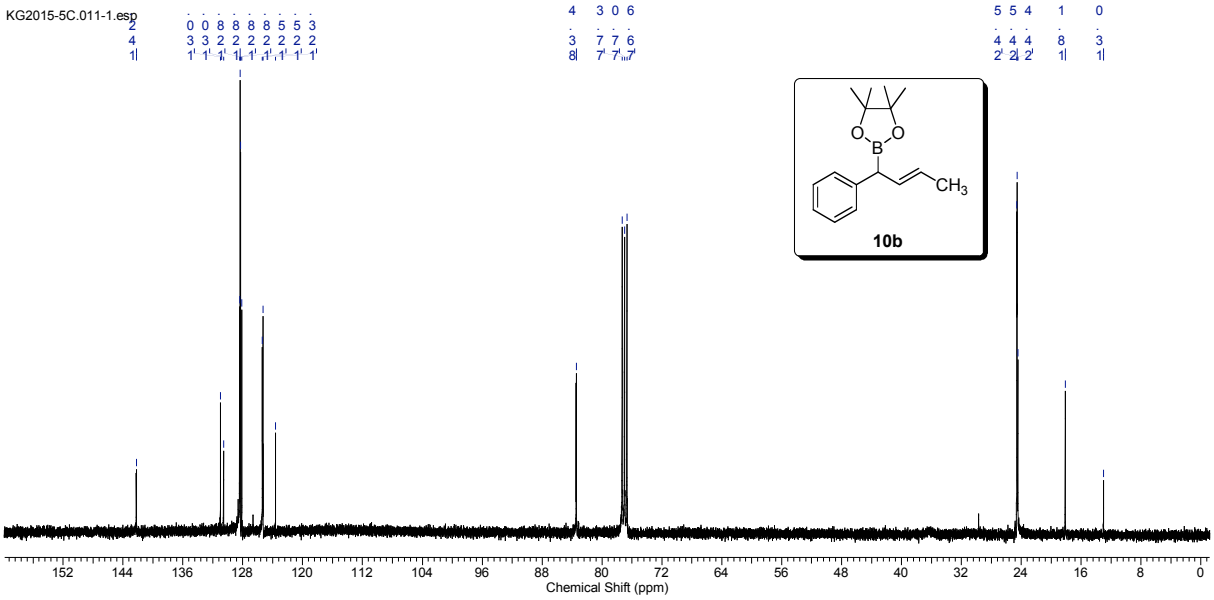
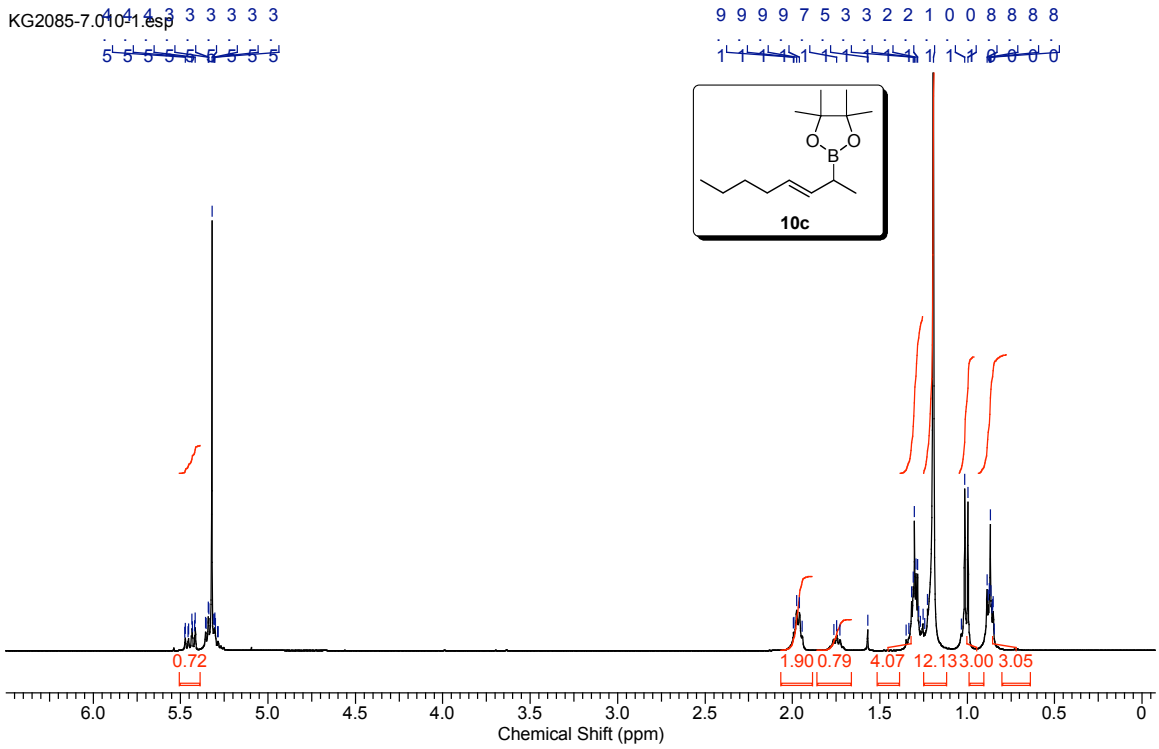
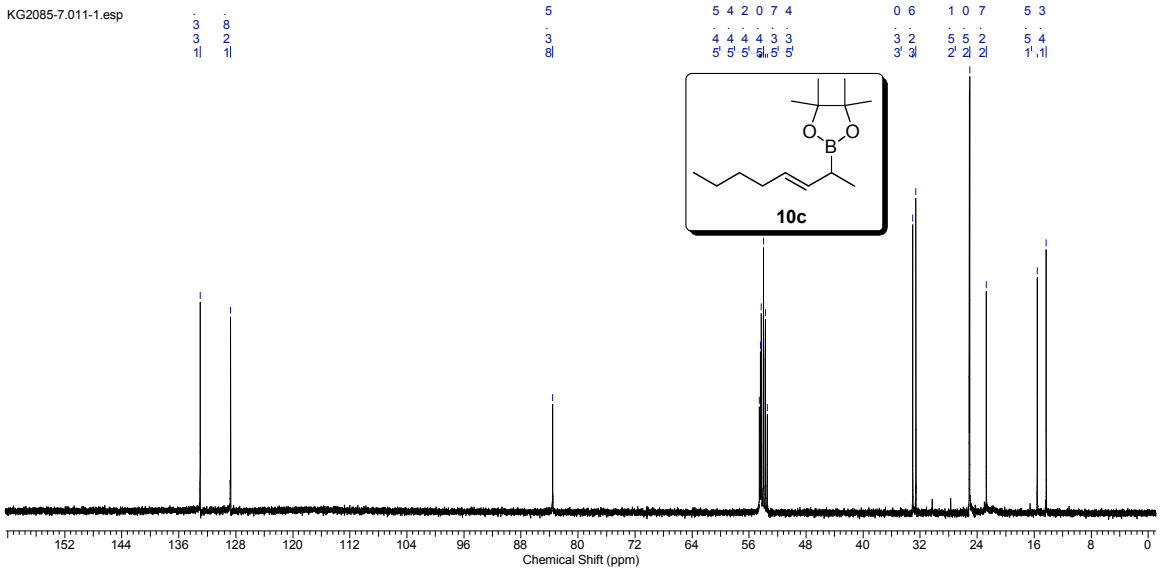
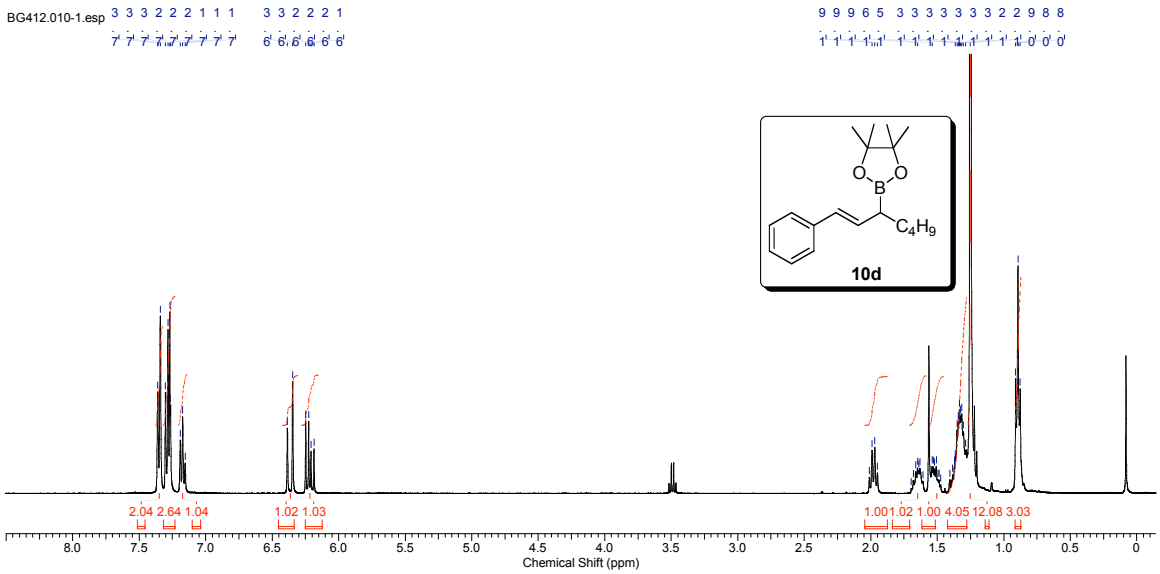
10a
Chemical Shift (ppm)

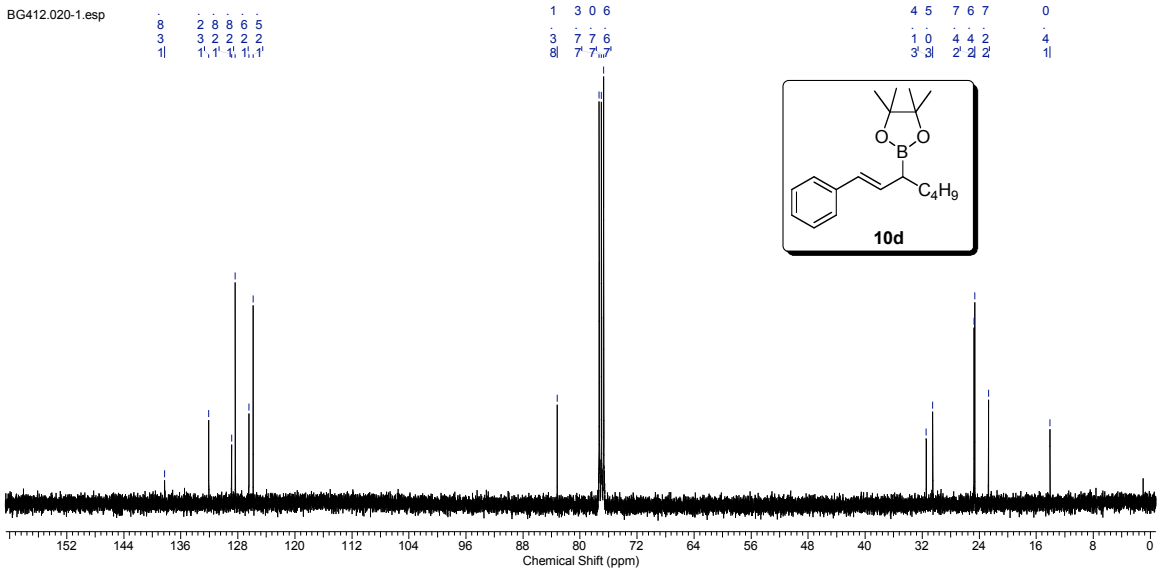

KG2015-5C.010-1.esp
10b
8.03
1.44
1.52
0.49
1.00
4.87
18.58
Chemical Shift (ppm)

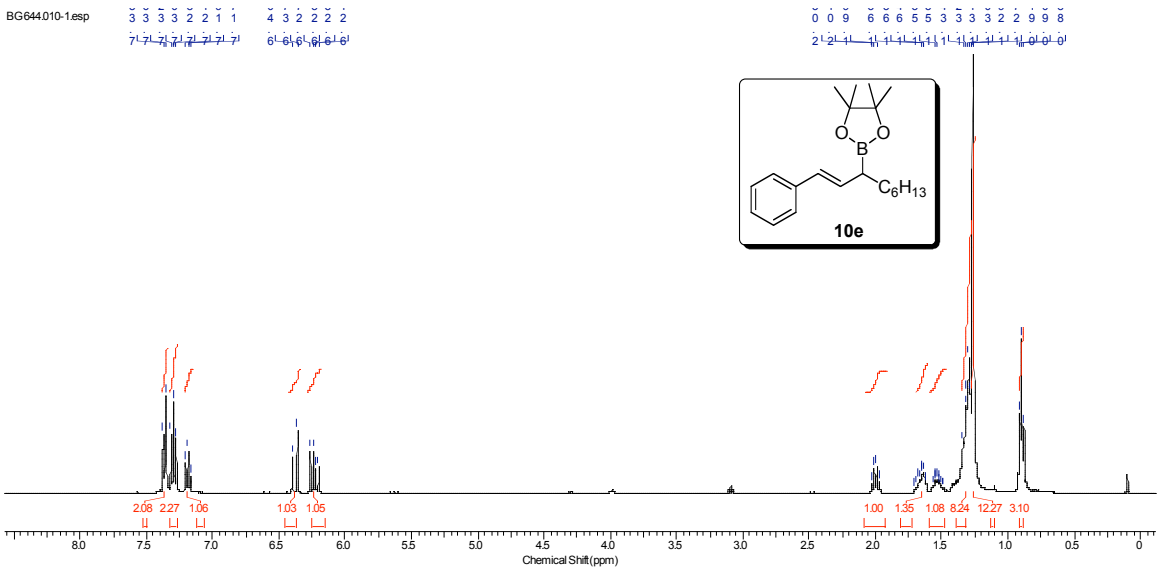

KG2015-5C.011-1.esp
10b
Chemical Shift (ppm)

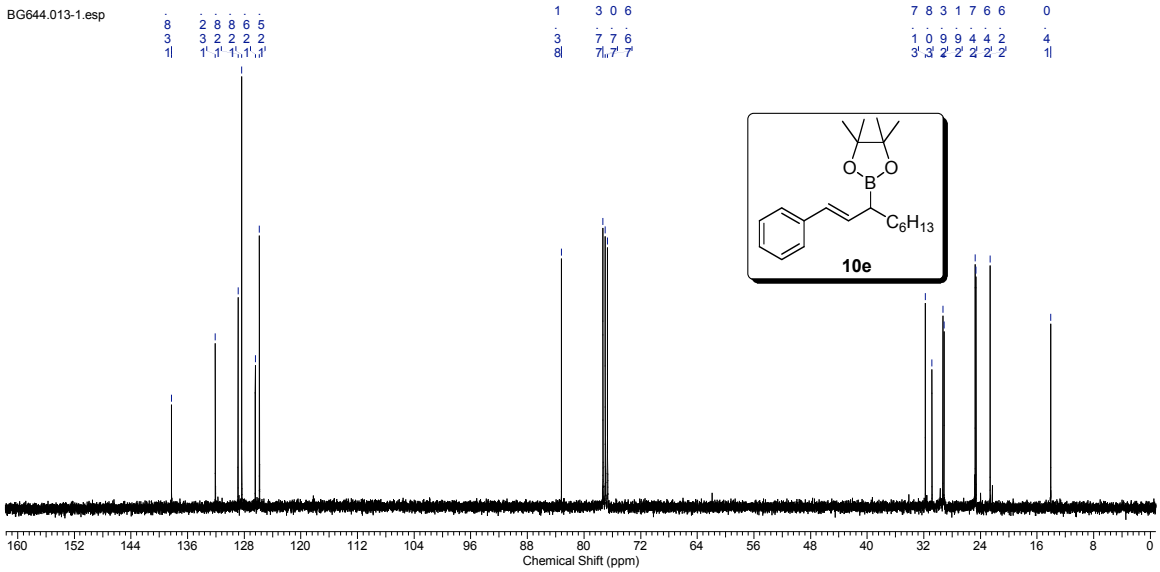

KG2085-7.010-1.esp
10c
0.72
1.90 0.79 4.07 12.13 3.00 3.05
Chemical Shift (ppm)

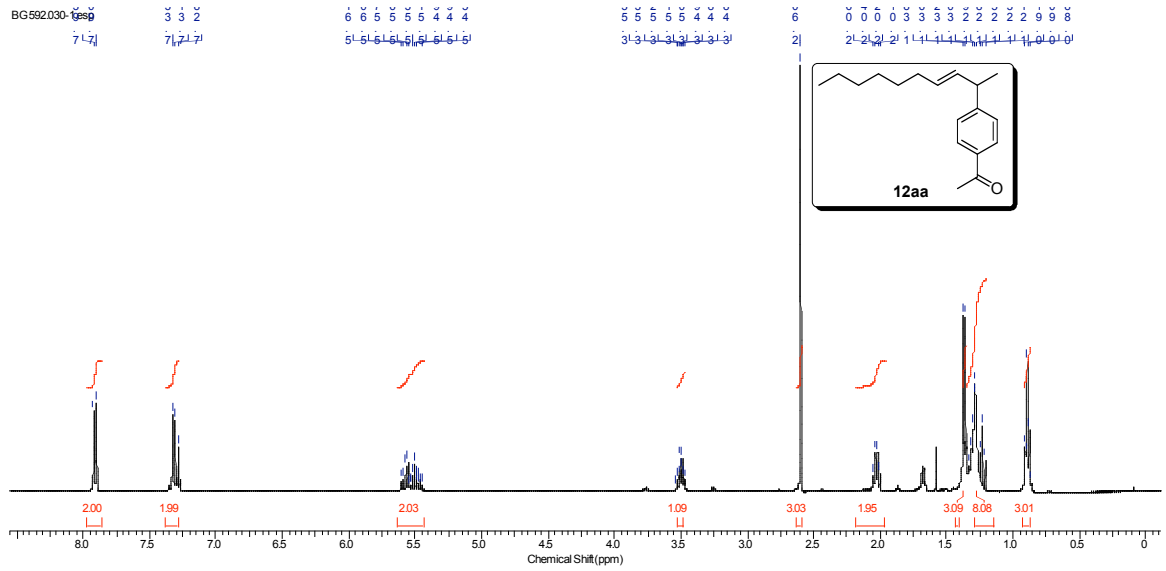

KG2085-7.011-1.esp
10c
Chemical Shift (ppm)

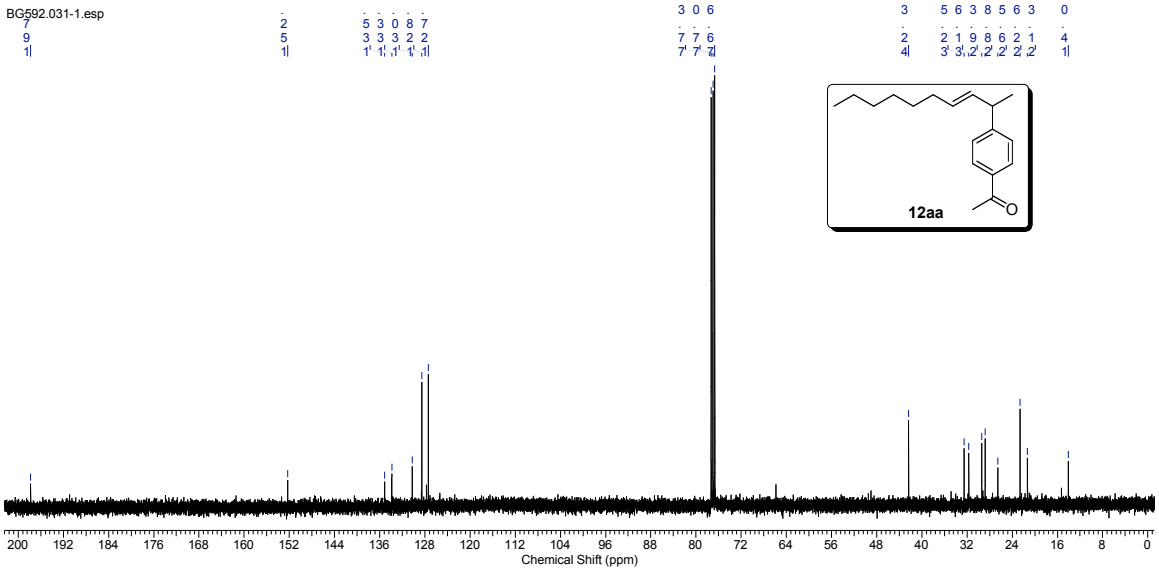

BG412.010-1.esp
10d
2.04 2.64 1.04
1.02 1.03
1.00 1.02 1.00 4.05 12.08 3.03
Chemical Shift (ppm)

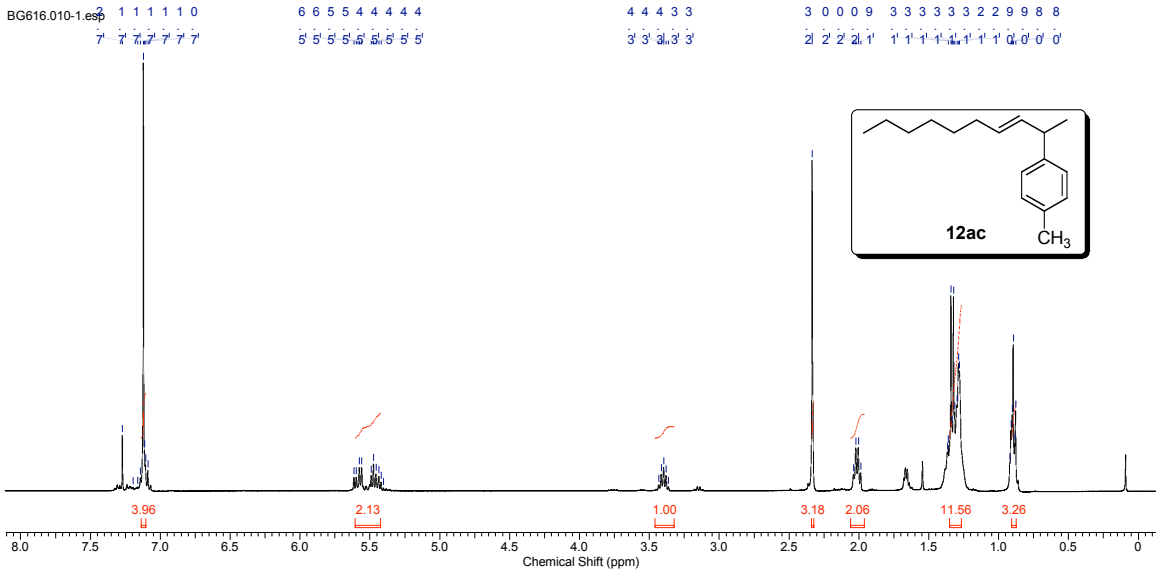

BG412.020-1.esp
10d
Chemical Shift (ppm)

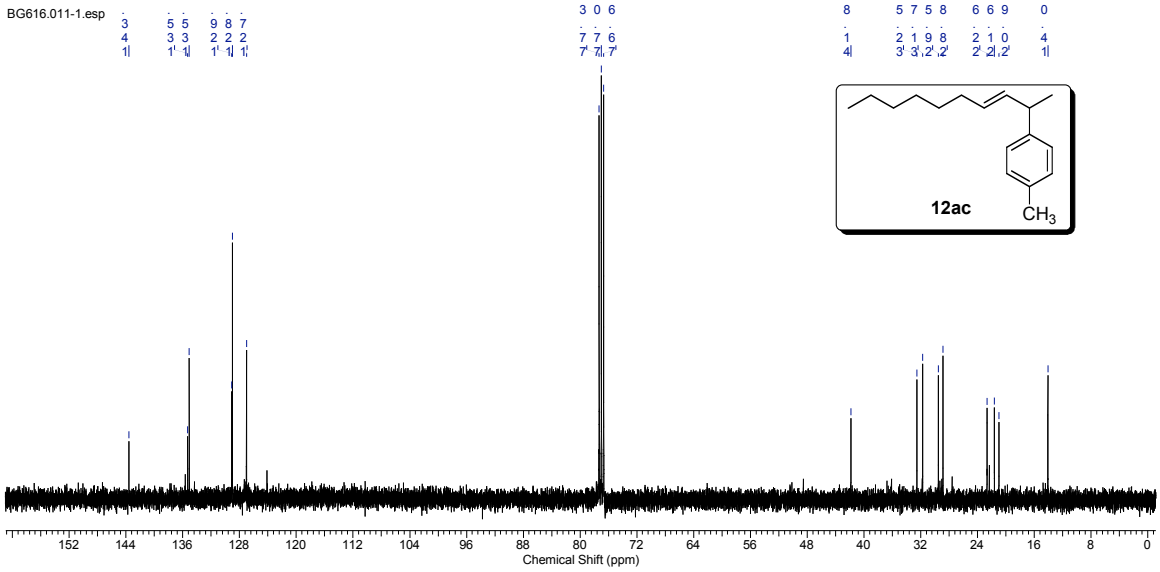

BG644.010-1.esp
10e
2.08 2.27 1.06 1.03 1.05 1.00 1.35 1.08 8.24 12.27 3.10
Chemical Shift(ppm)

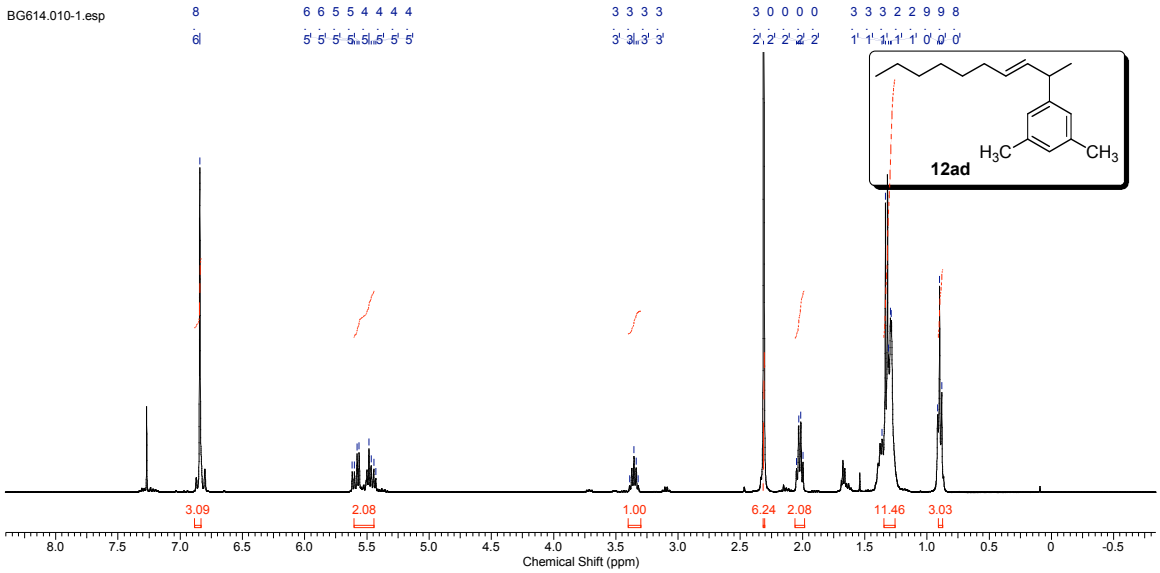

BG644.013-1.esp
10e
Chemical Shift (ppm)

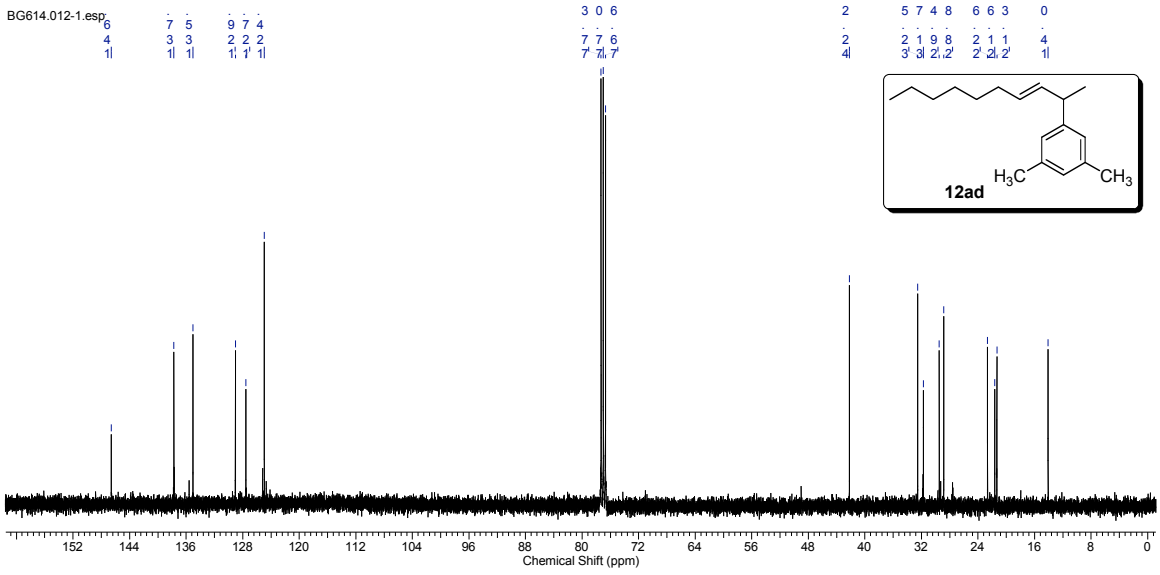

BG592.030-1.esp
12aa
O
2.00
1.99
2.03
1.09
3.03
1.95
3.09
8.08
3.01
Chemical Shift (ppm)

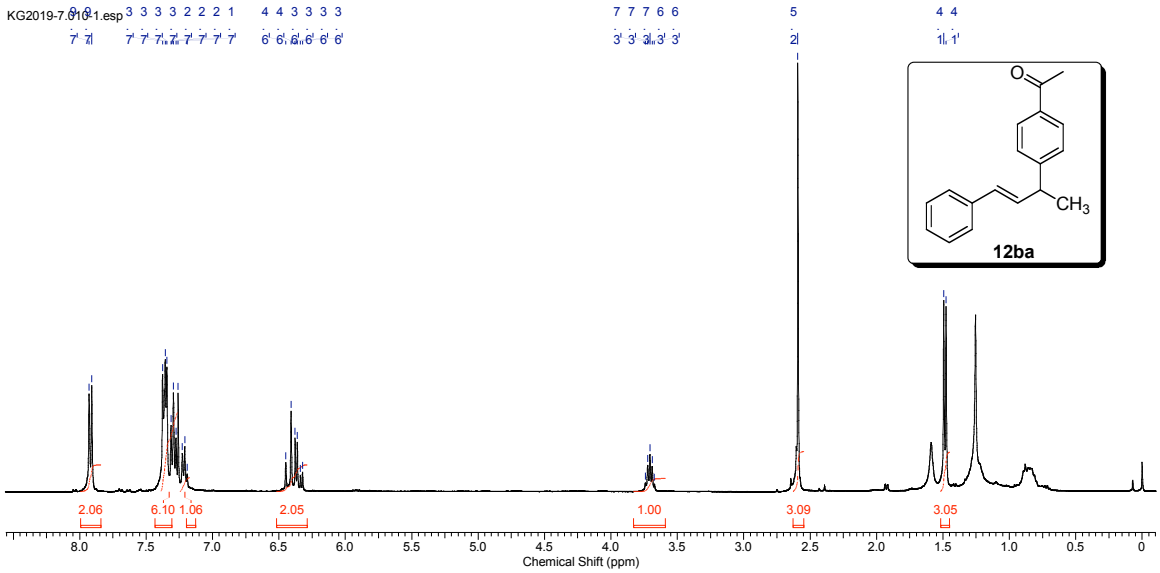

BG592.031-1.esp
12aa
O
Chemical Shift (ppm)

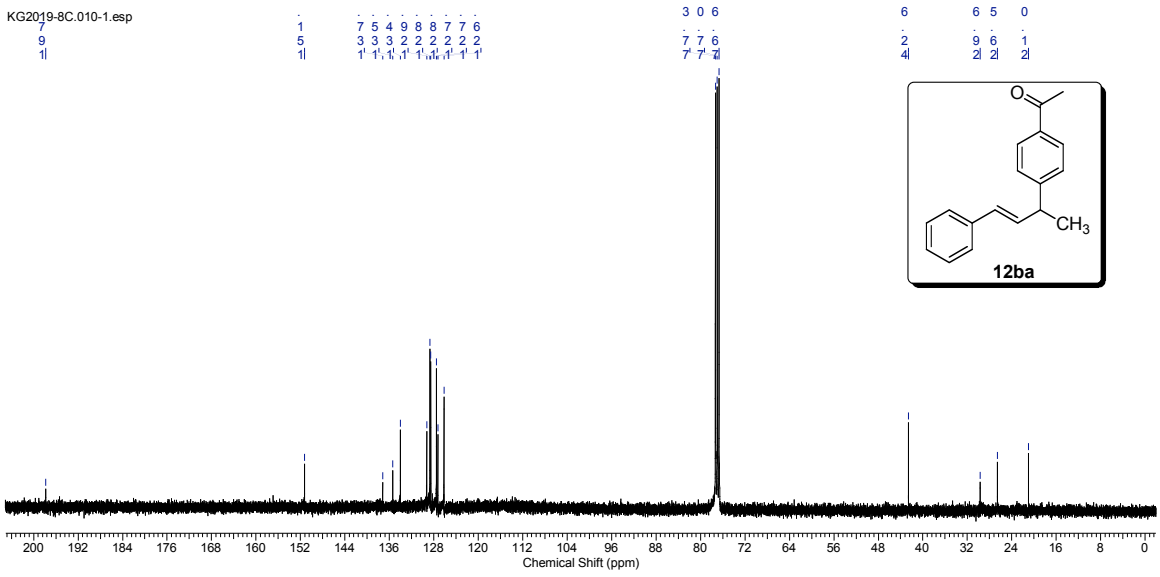

BG616.010-1.esp
12ac
CH3
3.96
2.13
1.00
3.18
2.06
11.56
3.26
Chemical Shift (ppm)

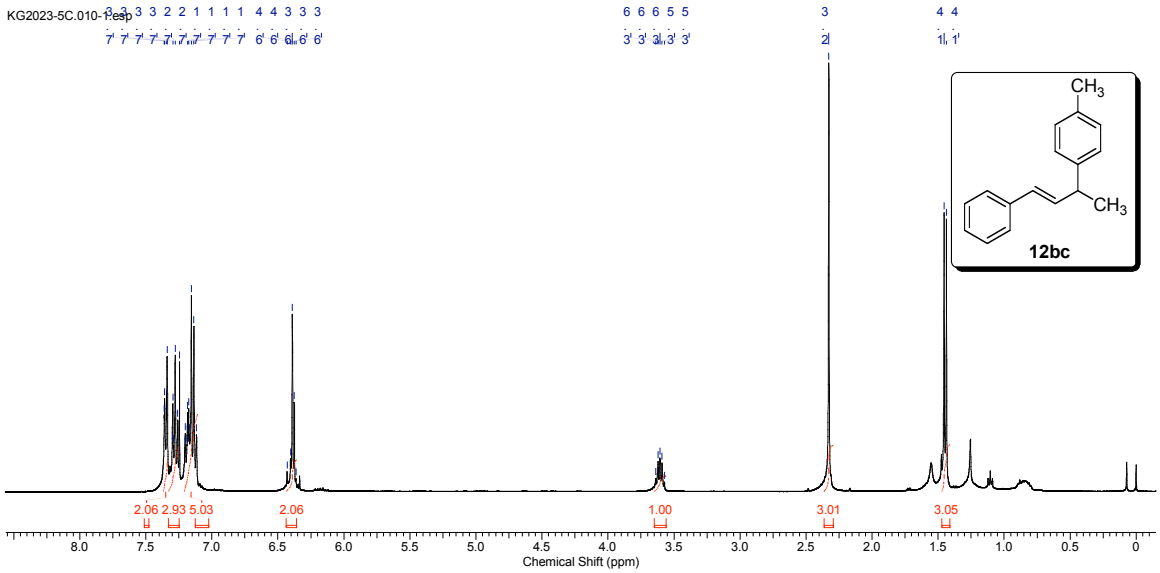

BG616.011-1.esp
12ac
CH3
Chemical Shift (ppm)

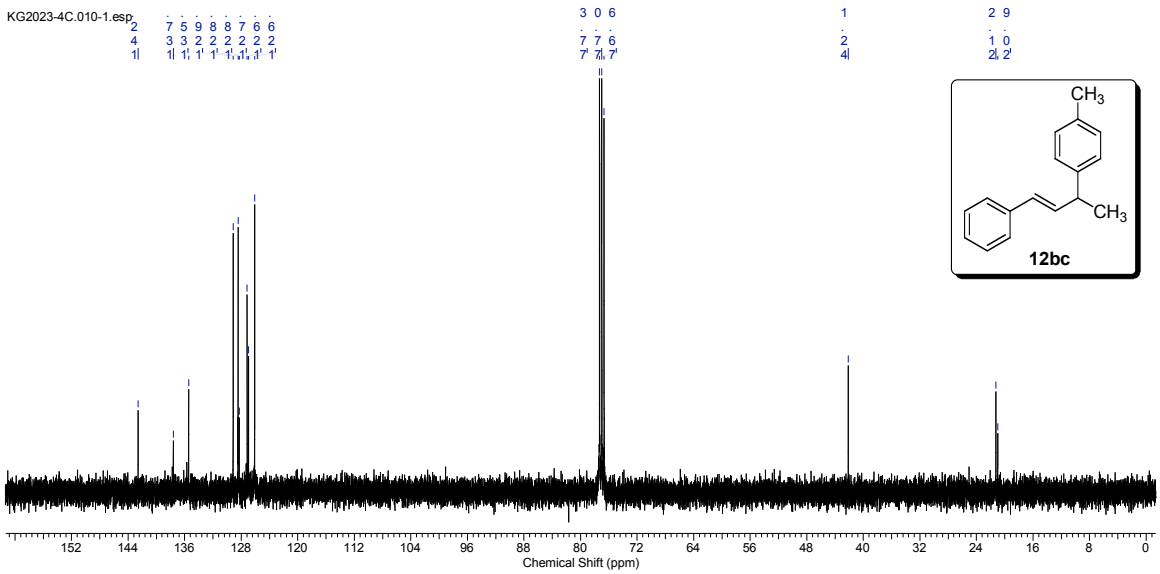

BG614.010-1.esp
12ad
3.09
2.08
1.00
6.24
2.08
11.46
3.03
Chemical Shift (ppm)

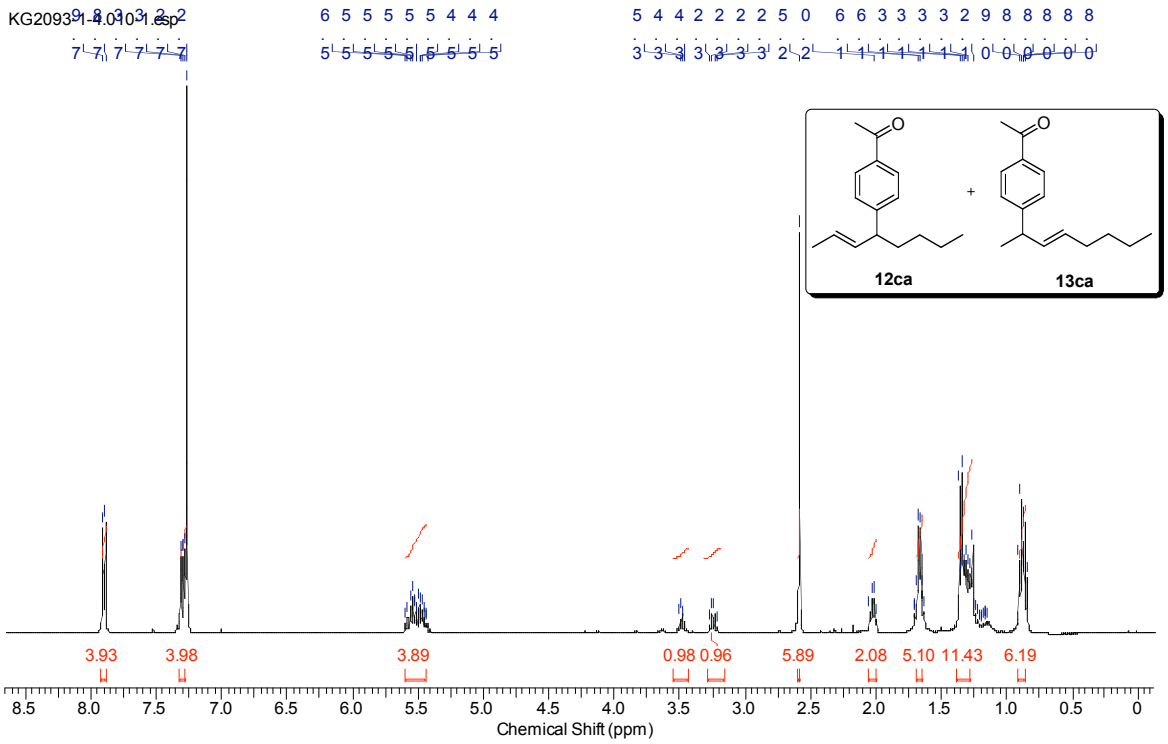

BG614.012-1.esp
12ad
Chemical Shift (ppm)

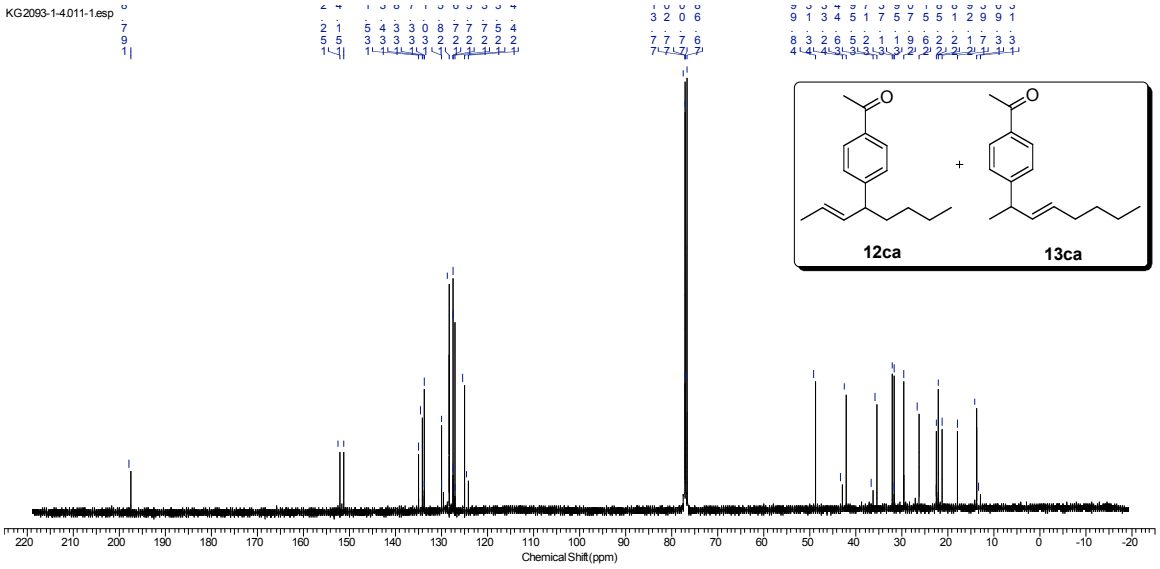

KG2019-7.010-1.esp
12ba
2.06
6.10
1.06
2.05
1.00
3.09
3.05
Chemical Shift (ppm)

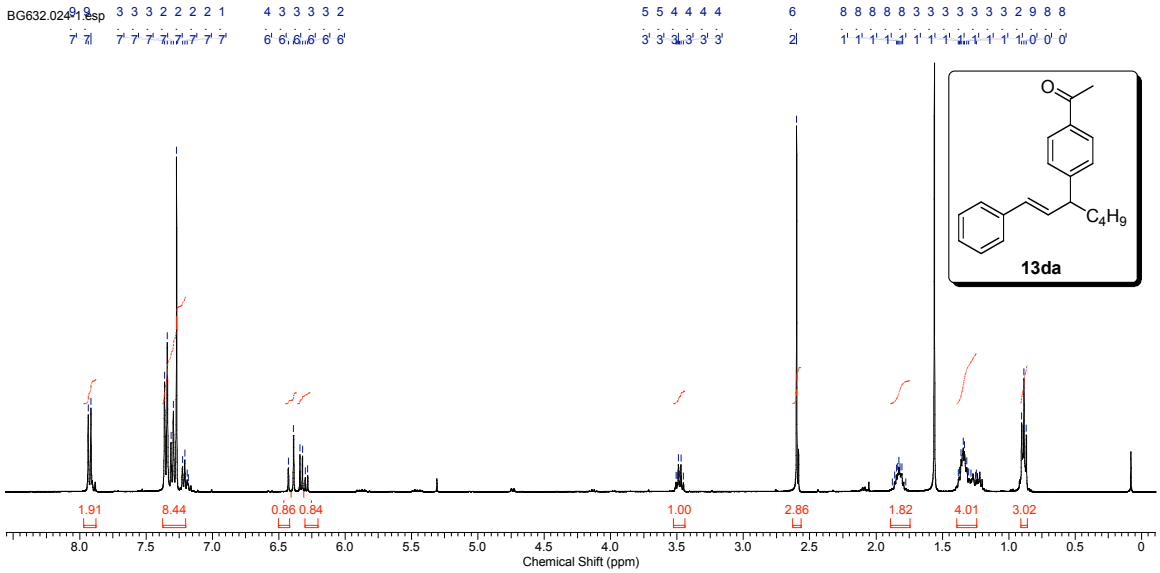

KG2019-8C.010-1.esp
12ba
Chemical Shift (ppm)

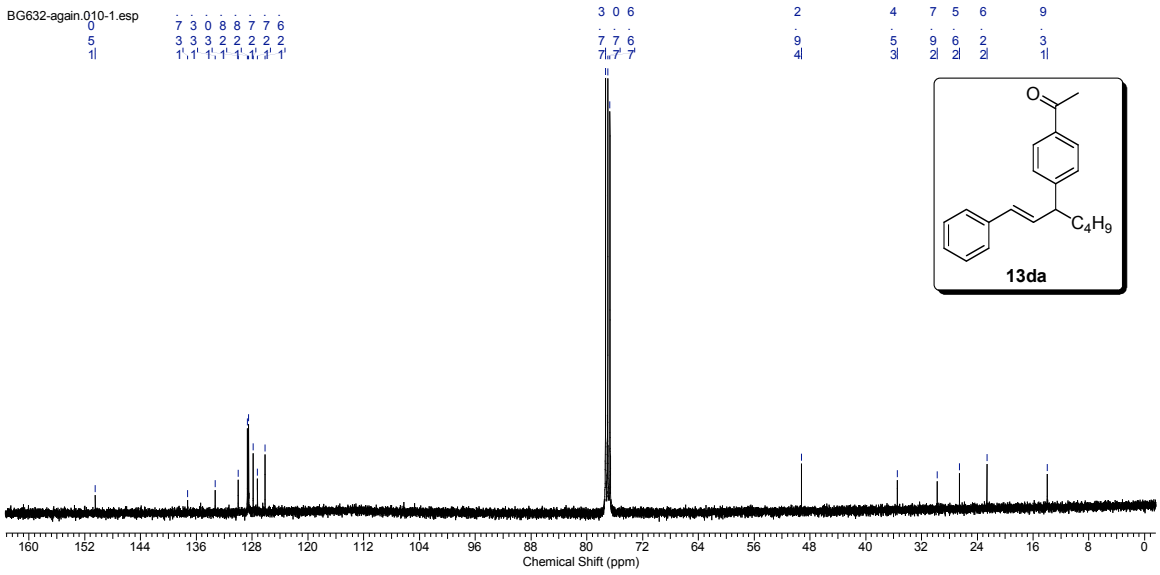

KG2023-5C.010-1.esp
12bc
2.06
2.93
5.03
2.06
1.00
3.01
3.05
Chemical Shift (ppm)

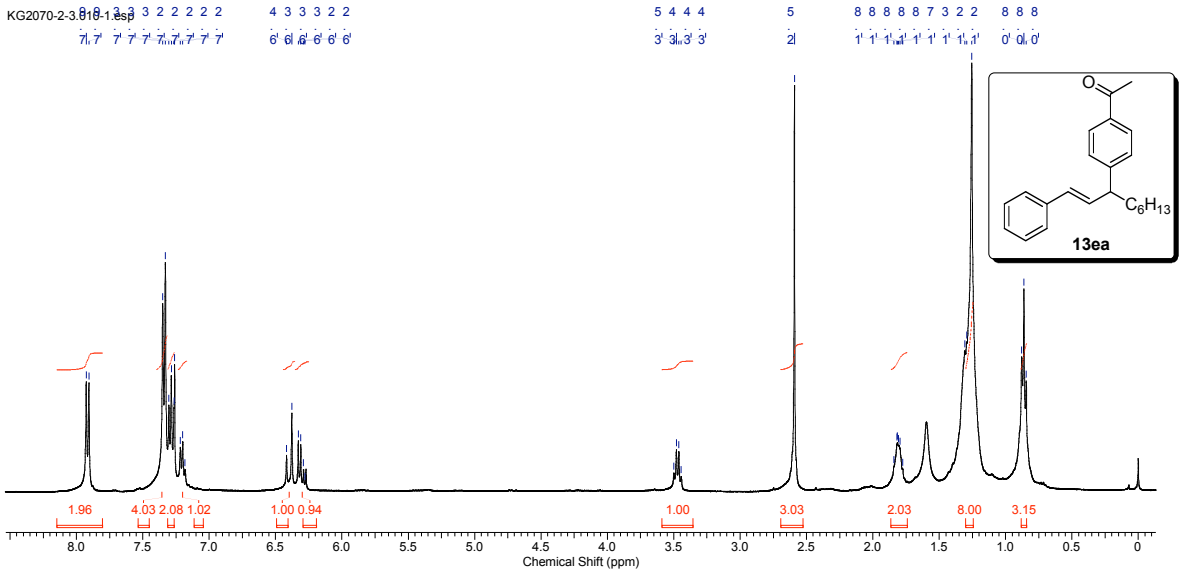

KG2023-4C.010-1.esp
12bc
Chemical Shift (ppm)

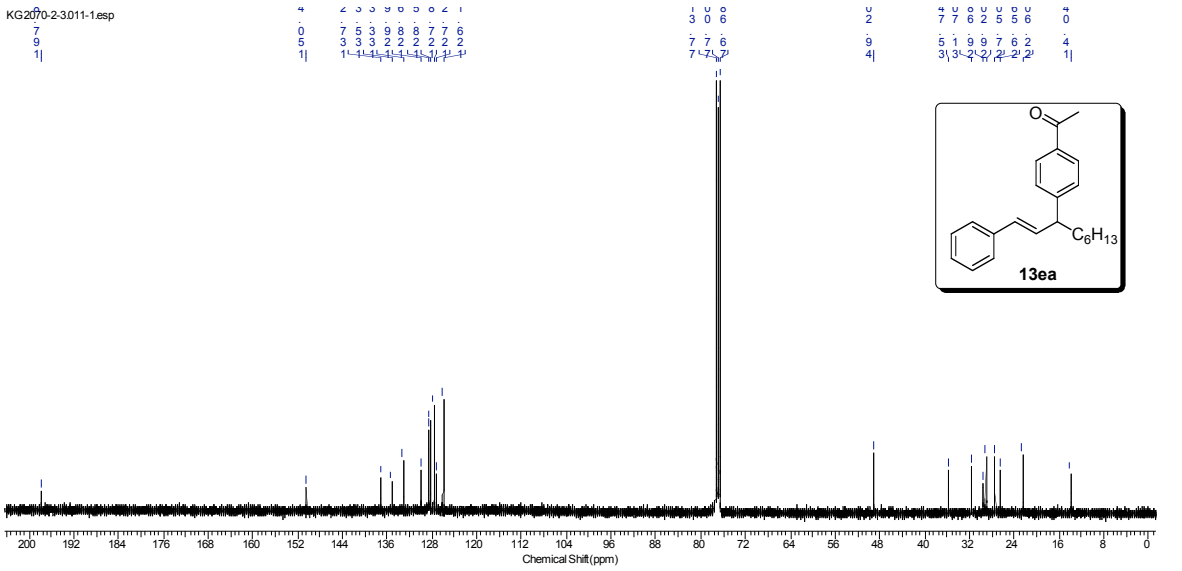

KG2093-1-4.010-1.esp
12ca
13ca
3.93
3.98
3.89
0.98
0.96
5.89
2.08
5.10
11.43
6.19
Chemical Shift (ppm)

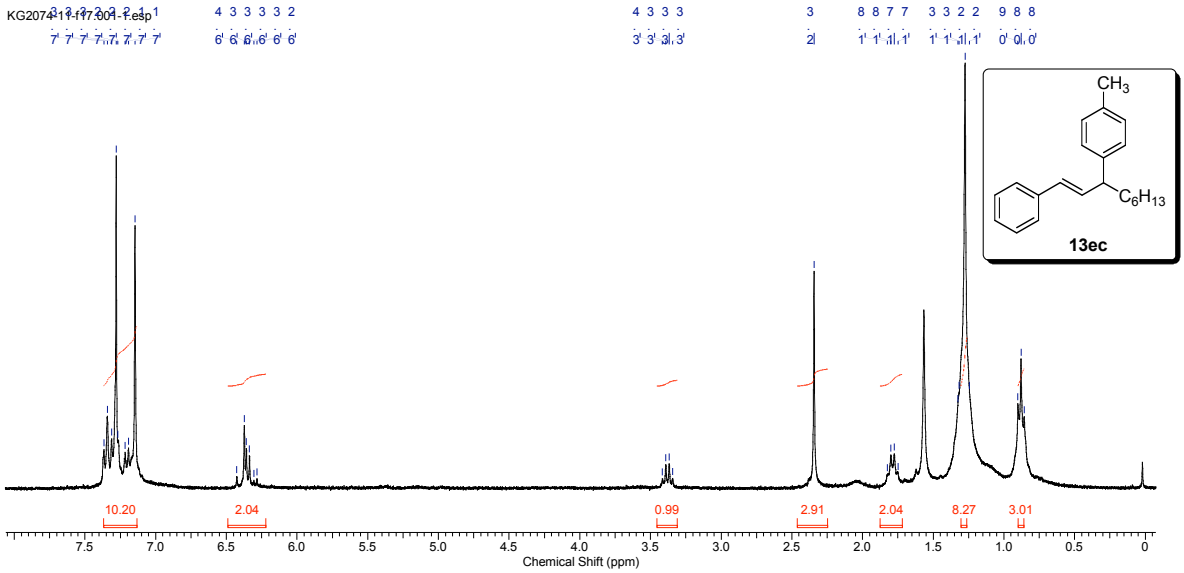

KG2093-1-4.011-1.esp
12ca
13ca
Chemical Shift (ppm)

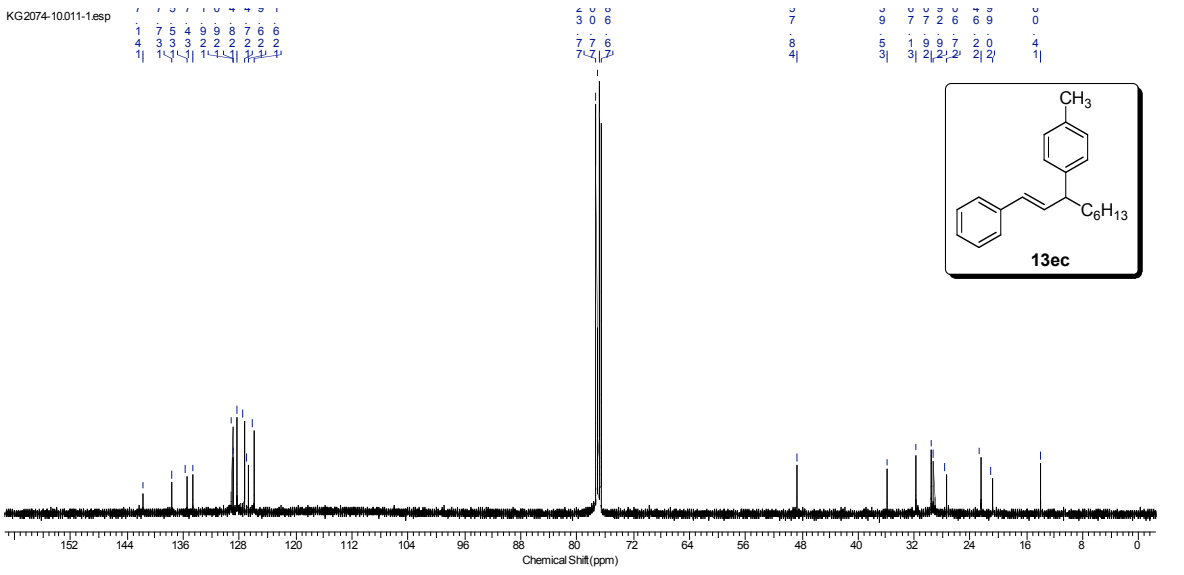

BG632.024-1.esp
13da
1.91
8.44
0.86
0.84
1.00
2.86
1.82
4.01
3.02
Chemical Shift (ppm)


BG632-again.010-1.esp
13da
Chemical Shift (ppm)


KG2070-2-3.010-1.esp
1.96
4.03
2.08
1.02
1.00
0.94
1.00
3.03
2.03
8.00
3.15
Chemical Shift (ppm)
13ea


KG2070-2-3.011-1.esp
Chemical Shift(ppm)
13ea


KG2074-11-1-H7.001-1.esp
10.20
2.04
0.99
2.91
2.04
8.27
3.01
Chemical Shift (ppm)
CH3
C6H13
13ec


KG2074-10.011-1.esp
Chemical Shift(ppm)
CH3
C6H13
13ec