Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

Electrochemical Fluorination of Vinyl Boronates through Donor-Stabilized Vinyl Carbocation Intermediates

B. Wigman, W. Lee, W. Wei, K. N. Houk, H. M. Nelson**

Table of Contents

1. Materials and Methods.....2
2. Preparation of Vinyl Boronic Ester and Boronate Substrates 3
3. Electrochemical Fluorination Reactions of Vinyl Boronates 24
    3.1 General Procedure for Fluorination Reactions 24
    3.2 Mass Balance, Observed Byproducts, and Unsuccessful Substrates.....38
4. Mechanistic Studies 40
    4.1 ^{11}B NMR TBAF Titration Studies.....40
    4.2 Cyclic Voltammetry of Vinyl Trifluoroborates SI-18 and SI-13 41
    4.3 Elimination Reaction of Di- and Tri-substituted Vinyl Boronic Ester 42
    4.4 Friedel-Crafts Reaction with N-Me Pyrrole 43
    4.5 C–H Insertion Reactivity 45
    4.6 Coulometry Experiment 51
    4.7 Divided Cell Control Experiment 53
    4.8 Vinyl Radical Trapping Experiments 53
    4.9 Unsymmetrical Vinyl Boronate Fluorination 56
    4.10 Observation of BPin–F Side Product 58
5. HOMO Calculations/Computational Studies 60
    5.1 HOMO/Oxidation Potential Calculations 61
    5.2 Cartesian coordinates for structures 61
6. ^{1}H, ^{13}C, ^{19}F, ^{11}B NMR Spectral Data 64
7. References 208

1. Materials and Methods

All glassware and stir-bars were dried in a 160 °C oven for at least 12 hours and allowed to cool *in vacuo* or a desiccator before use. Acetonitrile was freshly distilled over CaH_2 before use. Benzene, dichloromethane, tetrahydrofuran, dimethylformamide, and toluene were degassed and dried in a JC Meyer solvent system. TBAF•$(H_2O)_3$ was purchased from Acros Organics and stored in a Drierite desiccator purged with nitrogen. $TBABF_4$ was purchased from Oakwood chemical and dried over P_2O_5 *in vacuo* before use. Thin layer chromatography (TLC) was performed using Millipore silica gel 60 F_{254} pre-coated plates (0.25 mm) and visualized by UV fluorescence quenching. SiliaFlash P60 silica gel (230-400 mesh) was used for flash chromatography. NMR spectra were recorded on a Bruker AV-300 (^{1}H, ^{19}F), Bruker AV-400 (^{1}H, ^{13}C, ^{19}F), Bruker DRX-500 (^{1}H), and Bruker AV-500 (^{1}H, ^{13}C). ^{1}H NMR spectra are reported relative to $CDCl_3$ (7.26 ppm) unless noted otherwise. Data for ^{1}H NMR spectra are as follows: chemical shift (ppm), multiplicity, coupling constant (Hz), integration. Multiplicities are as follows: s = singlet, d = doublet, t = triplet, dd = doublet of doublet, dt = doublet of triplet, ddd = doublet of doublet of doublet, td = triplet of doublet, m = multiplet. ^{13}C NMR spectra are reported relative to $CDCl_3$ (77.0 ppm) unless noted otherwise. GCMS spectra were recorded on a Shimadzu GCMS-QP2010 using a Restek XTI-5 (50 m, 0.25 mm ID, 0.25 □m DF) column interface at room temperature. IR Spectra were record on a Perkin Elmer 100 spectrometer and are reported in terms of frequency absorption (cm^{-1}). High resolution mass spectra (HR-MS) were recorded on a Waters (Micromass) GCT Premier spectrometer, a Waters (Micromass) LCT Premier, or an Agilent GC EI-MS, and are reported as follows: m/z (% relative intensity).

2. Preparation of Vinyl Boronic Ester and Boronate Substrates

Representative synthesis of vinyl boronic esters

(dibromomethylene)cyclohexane (SI-1). Synthesized according to known procedure, spectral data matched those known in the literature.[1]

2,2'-(cyclohexylidenemethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (SI-2). Synthesized according to known procedure, spectral data matched those known in the literature.[2]

Note: The cross-couplings performed to synthesize the substrates are not optimized.

Cross-Coupling Condition A:

Condition A Scheme

To schlenk flask was added 2,2'-(cyclohexylidenemethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(SI-2)** (1 equiv), aryl iodide (1 equiv), 1,4-dioxane (0.15 M), and the aqueous KOH solution (3 molar, 1.7 equiv). The flask was freeze-pump thawed three cycles of 15 minutes. Tetrakis(triphenylphosphine)palladium(0) (4 mol %) was added to the frozen solution and the flask was evacuated under vacuum and backfilled with nitrogen three times. The solution was heated to 80 ºC for 12 hours. The solution was cooled to room temperature and quenched with saturated aqueous NH_4Cl and extracted with ethyl acetate. The combined organics were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography.

Cross-Coupling Condition B:

Condition B Scheme

To schlenk flask was added 2,2'-(cyclohexylidenemethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(SI-2)** (1 equiv), aryl iodide (1 equiv), tetrahydrofuran (0.15 M), and the aqueous KOH solution (3 molar, 1.7 equiv). The flask was freeze-pump thawed three cycles of 15 minutes. Tris(dibenzylideneacetone)dipalladium(0) (3 mol %) was added to the frozen solution and the flask was evacuated under vacuum and backfilled with nitrogen three times. Tri-tertbutyl phosphine (12 mol %) was added to the frozen solution under a stream of nitrogen and the flask was evacuated under vacuum and backfilled with nitrogen three times. The solution was allowed to thaw and stirred at room temperature. The reaction was monitored carefully by TLC. The solution was quenched with saturated aqueous NH_4Cl and extracted with ethyl acetate. The combined organics were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography.

2-(cyclohexylidene(4-methoxyphenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. (SI-3)

Synthesized according to condition B.

To schlenk flask was added 2,2'-(cyclohexylidenemethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(SI-2)** (750 mg, 2.15 mmol, 1 equiv), 4-iodoanisole (504 mg, 2.15 mmol, 1 equiv), tetrahydrofuran (12 mL), and the aqueous KOH solution (2.15 mL, 3 molar, 3.0 equiv). The flask was freeze-pump thawed three cycles of 15 minutes. Tris(dibenzylideneacetone)dipalladium(0) (59 mg, 0.06 mmol, 3 mol %) was added to the frozen solution and the flask was evacuated under vacuum and backfilled with nitrogen three times. Tri-tertbutyl phosphine (52 mg, 0.26 mmol, 12 mol %) was added to the frozen solution under a stream of nitrogen and the flask was evacuated under vacuum and backfilled with nitrogen three times. The solution was allowed to thaw and stirred at room temperature. The reaction was monitored carefully by TLC (~3 hours). The solution was quenched with saturated aqueous NH_4Cl (10 mL) and extracted with ethyl acetate (3 x 12 mL). The combined organics were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (35% dichloromethane in hexanes) to yield 463 mg of an off-white solid (66% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.01 (d, J = 8.8 Hz, 2H), 6.82 (d, J = 8.7 Hz, 2H), 3.79 (s, 3H), 2.78 – 2.24 (m, 2H), 2.23 – 2.04 (m, 2H), 1.71 – 1.42 (m, 6H), 1.25 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.6, 154.6, 134.7, 130.3, 113.5, 83.4, 55.4, 35.7, 32.1, 29.1, 28.7, 27.0, 24.9. *Note*: Carbon attached to boron not seen due to relaxation on B.
^{11}B NMR (128 MHz, $CDCl_3$) δ 31.6.
FT-IR (neat film NaCl): 2976, 2926, 2852, 2835, 1606, 1507, 1464, 1354, 1238, 1104, 1006, 925, 856 cm^{-1}.
HR-MS (EI-MS) m/z: [M]+ Calculated for $C_{20}H_{29}BO_3$: 328.2209; Measured: 328.2213.
Melting Point: 75–76 ºC

4-(cyclohexylidene(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-*N*,*N*-dimethylaniline. (SI-4)
Synthesized according to condition A.
To a schlenk flask was added 2,2'-(cyclohexylidenemethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(SI-2)** (700 mg, 2.0 mmol, 1 equiv), 4-iodo-N,N-dimethylaniline (497 mg, 2.0 mmol, 1 equiv), 1,4-dioxane (14 mL, 0.15 M), and the aqueous KOH solution (1.2 mL, 3 molar, 1.7 equiv). The flask was freeze-pump thawed three cycles of 15 minutes. Tetrakis(triphenylphosphine)palladium(0) (93.0 mg, 0.08 mmol, 4 mol %) was added to the frozen solution and the flask was evacuated under vacuum and backfilled with nitrogen three times. The solution was heated to 90 ºC for 12 hours. The solution was cooled to room temperature and quenched with saturated aqueous NH_4Cl (14 mL) and extracted with ethyl acetate (3 x 14 mL) The combined organics were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (70% dichloromethane in hexanes) to yield the 120 mg (20% yield) of an off-white solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 – 6.82 (m, 2H), 6.69 (bs, 2H), 2.94 (s, 3H), 2.45 (t, J = 6.0 Hz, 2H), 2.17 (d, J = 6.5 Hz, 2H), 1.65 – 1.46 (m, 6H), 1.25 (s, 12H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 153.3, 148.6, 130.1, 112.5, 83.3, 41.0, 35.9, 32.0, 29.1, 28.7, 27.1, 25.0. *Note*: Carbon attached to boron not seen due to relaxation on B.
^{11}B NMR (161 MHz, $CDCl_3$) δ 29.85.
FT-IR (neat film NaCl): 2978, 2929, 2851, 1610, 1517, 1446, 1348, 1328, 1298, 1223, 1142, 973, 856 cm^{-1}.
HR-MS (EI-MS) m/z: [M]+ Calculated for $C_{21}H_{32}BNO_2$: 341.2526; Measured: 341.2530.
Melting Point: 122–124 ºC

2-(cyclohexylidene(2,4,6-trimethoxyphenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. (SI-5)

Synthesized according to condition B.

To schlenk flask was added 2,2'-(cyclohexylidenemethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(SI-2)** (235 mg, 0.675 mmol, 1 equiv), 2-iodo-1,3,5-trimethoxybenzene (199 mg, 0.675 mmol, 1 equiv), tetrahydrofuran (5 mL), and the aqueous KOH solution (0.68 mL, 3 molar, 3.0 equiv). The flask was freeze-pump thawed three cycles of 15 minutes. Tris(dibenzylideneacetone)dipalladium(0) (19 mg, 0.02 mmol, 3 mol %) was added to the frozen solution and the flask was evacuated under vacuum and backfilled with nitrogen three times. Tri-tertbutyl phosphine (17 mg, 0.08 mmol, 12 mol %) was added to the frozen solution under a stream of nitrogen and the flask was evacuated under vacuum and backfilled with nitrogen three times. The solution was allowed to thaw and stirred at room temperature. The reaction was monitored carefully by TLC (~3 hours). The solution was quenched with saturated aqueous NH_4Cl (5 mL) and extracted with ethyl acetate (3 x 10 mL). The combined organics were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (7→12% ethyl acetate in hexanes) to yield 193 mg of a white solid (73% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.13 (s, 2H), 3.80 (s, 3H), 3.73 (s, 6H), 2.83 – 2.34 (m, 2H), 1.92 (t, J = 5.7 Hz, 2H), 1.65 – 1.50 (m, 6H), 1.22 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.5, 158.3, 157.9, 113.2, 91.1, 82.8, 56.0, 55.5, 34.9, 33.9, 29.0, 27.8, 27.2, 25.1. *Note*: Carbon attached to boron not seen due to relaxation on B.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.03.

FT-IR (neat film NaCl): 2975, 2928, 2851, 1603, 1583, 1464, 1353, 1326, 1223, 1124, 953 cm^{-1}.

HR-MS (EI-MS) m/z: [M]+ Calculated for $C_{22}H_{33}BO_5$: 388.2421; Measured: 388.2425.

Melting Point: 112–114 ºC

2-(cyclohexylidene(thiophen-2-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. (SI-6)

Synthesized according to condition A.

To a schlenk flask was added 2,2'-(cyclohexylidenemethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(SI-2)** (600 mg, 1.7 mmol, 1 equiv), 2-bromo-thiophene (280 mg, 1.7 mmol, 1 equiv), 1,4-dioxane (11 mL, 0.15 M), and the aqueous KOH solution (1.0 mL, 3 molar, 1.7 equiv). The flask was freeze-pump thawed three cycles of 15 minutes. Tetrakis(triphenylphosphine)palladium(0) (100 mg, 0.09 mmol, 5 mol %) was added to the frozen solution and the flask was evacuated under vacuum and backfilled with nitrogen three times. The solution was heated to 90 ºC for 20 hours. The solution was cooled to room temperature and quenched with saturated aqueous NH_4Cl (11 mL) and extracted with ethyl acetate (3 x 12 mL) The combined organics were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (5% diethyl ether in hexanes) to yield 63 mg (12% yield) of a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 – 7.14 (m, 1H), 6.95 (dd, *J* = 5.2, 3.5 Hz, 1H), 6.71 (d, *J* = 3.5 Hz, 1H), 2.48 (t, *J* = 6.2 Hz, 2H), 2.32 (t, *J* = 5.8 Hz, 2H), 1.69 – 1.56 (m, 6H), 1.27 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 143.9, 127.0, 125.6, 124.1, 83.8, 35.9, 32.6, 29.1, 28.7, 26.9, 25.0. *Note*: Carbon attached to boron not seen due to relaxation on B.

^{11}B NMR (96 MHz, $CDCl_3$) δ 31.27.

FT-IR (neat film NaCl): 2977, 2926, 2853, 1608, 1446, 1354, 1300, 1144, 995, 854, 699 cm^{-1}.

HR-MS (EI-MS) m/z: [M]+ Calculated for $C_{17}H_{25}BO_2S$: 304.1668; Measured: 304.1663.

Melting Point: 48–50 ºC

2-(cyclohexylidene(2-methoxyphenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. (SI-7)

Synthesized according to condition B.

To schlenk flask was added 2,2'-(cyclohexylidenemethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(SI-2)** (500 mg, 1.44 mmol, 1 equiv), 1-iodo-2-methoxybenzene (336 mg, 1.44 mmol, 1 equiv), tetrahydrofuran (8 mL), and the aqueous KOH solution (1.44 mL, 3 molar, 3.0 equiv). The flask was freeze-pump thawed three cycles of 15 minutes. Tris(dibenzylideneacetone)dipalladium(0) (40 mg, 0.04 mmol, 3 mol %) was added to the frozen solution and the flask was evacuated under vacuum and backfilled with nitrogen three times. Tri-tertbutyl phosphine (35 mg, 0.17 mmol, 12 mol %) was added to the frozen solution under a stream of nitrogen and the flask was evacuated under vacuum and backfilled with nitrogen three times. The solution was allowed to thaw and stirred at room temperature. The reaction was monitored carefully by TLC (~3 hours). The solution was quenched with saturated aqueous NH_4Cl (10 mL) and extracted with ethyl acetate (3 x 15 mL). The combined organics were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (50% dichloromethane in hexanes) to yield 394 mg of an off-white solid (83% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (ddd, J = 8.2, 7.4, 1.8 Hz, 1H), 7.03 (dd, J = 7.4, 1.8 Hz, 1H), 6.89 (td, J = 7.4, 1.1 Hz, 1H), 6.82 (dd, J = 8.1, 1.1 Hz, 1H), 3.76 (s, 3H), 2.60 (t, J = 6.0 Hz, 2H), 2.13 (bs, 2H), 1.67 – 1.42 (m, 6H), 1.24 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.2, 156.5, 131.9, 127.2, 120.4, 110.3, 83.2, 55.5, 35.4, 33.0, 29.2, 28.9, 27.1, 25.0. *Note*: Carbon attached to boron not seen due to relaxation on B.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.29.

FT-IR (neat film NaCl): 2976, 2925, 2852, 1616, 1487, 1354, 1297, 1241, 1146, 972, 857, 750 cm^{-1}.

HR-MS (EI-MS) m/z: [M]+ Calculated for $C_{20}H_{39}BO_3$: 328.2209; Measured: 328.2213.

Melting Point: 119–121 ºC

***tert*-butyl (4-(cyclohexylidene(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)phenyl)carbamate. (SI-8)**

Synthesized according to condition A.

To a schlenk flask was added 2,2'-(cyclohexylidenemethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(SI-2)** (700 mg, 2.1 mmol, 1 equiv), tert-butyl (4-iodophenyl)carbamate (669 mg, 2.1 mmol, 1 equiv), 1,4-dioxane (12 mL, 0.15 M), and the aqueous KOH solution (1.2 mL, 3 molar, 1.7 equiv). The flask was freeze-pump thawed three cycles of 15 minutes. Tetrakis(triphenylphosphine)palladium(0) (97.0 mg, 0.08 mmol, 4 mol %) was added to the frozen solution and the flask was evacuated under vacuum and backfilled with nitrogen three times. The solution was heated to 90 ºC for 20 hours. The solution was cooled to room temperature and quenched with saturated aqueous NH_4Cl (10 mL) and extracted with ethyl acetate (3 x 10 mL) The combined organics were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (3→5% ethyl acetate in hexanes) to yield 84 mg (10% yield) of a white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 2H), 7.01 (d, J = 8.5 Hz, 2H), 6.39 (s, 1H), 2.58 – 2.37 (m, 2H), 2.24 – 2.00 (m, 2H), 1.65 – 1.42 (m, J = 6.1 Hz, 6H), 1.51 (s, 9H), 1.24 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.2, 153.2, 137.4, 135.9, 129.9, 118.6, 83.5, 35.8, 32.3, 29.1, 28.7, 27.0, 25.0. *Note*: Carbon attached to boron not seen due to relaxation on B.

^{11}B NMR (96 MHz, $CDCl_3$) δ 29.52.

FT-IR (neat film NaCl): 3335, 2976, 2927, 2852, 1726, 1588, 1521, 1448, 1390, 1354, 1270, 1227, 1161, 1052, 972, 855 cm^{-1}.

HR-MS (ESI-MS) m/z: [M–Boc]+ Calculated for $C_{14}H_{28}BNO_2$: 313.2313; Measured: 313.2315.

Melting Point: 145–147 ºC

2-((4-(*tert*-butylthio)phenyl)(cyclohexylidene)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. (SI-9)

Synthesized according to condition B.

To schlenk flask was added 2,2'-(cyclohexylidenemethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(SI-2)** (400 mg, 1.15 mmol, 1 equiv), (4-bromophenyl)(tert-butyl)sulfane (281 mg, 1.15 mmol, 1 equiv), tetrahydrofuran (8 mL), and the aqueous KOH solution (1.15 mL, 3 molar, 3.0 equiv). The flask was freeze-pump thawed three cycles of 15 minutes. Tris(dibenzylideneacetone)dipalladium(0) (52 mg, 0.06 mmol, 5 mol %) was added to the frozen solution and the flask was evacuated under vacuum and backfilled with nitrogen three times. Tri-tertbutyl phosphine (46.5 mg, 0.23 mmol, 20 mol %) was added to the frozen solution under a stream of nitrogen and the flask was evacuated under vacuum and backfilled with nitrogen three times. The solution was allowed to thaw and stirred at room temperature. The reaction was monitored carefully by TLC (~3 hours). The solution was quenched with saturated aqueous NH_4Cl (10 mL) and extracted with ethyl acetate (3 x 15 mL). The combined organics were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (20→25% dichloromethane in hexanes) to yield 187 mg of an yellow solid solid (42% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, J = 8.4 Hz, 2H), 7.04 (d, J = 8.2 Hz, 2H), 2.62 – 2.37 (m, 2H), 2.26 – 1.94 (m, 2H), 1.60 – 1.42 (m, 6H), 1.29 (s, 9H), 1.24 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.5, 143.1, 137.2, 129.5, 83.6, 46.0, 35.8, 32.3, 31.3, 29.1, 28.8, 27.0, 24.9. *Note*: Carbon attached to boron not seen due to relaxation on B.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.44.

FT-IR (neat film NaCl): 2974, 2925, 2854, 1614, 1482, 1448, 1352, 1300, 1145, 972, 856, 764 cm^{-1}.

HR-MS (EI-MS) m/z: [M]+ Calculated for $C_{23}H_{35}BO_2S$: 386.2451; Measured: 386.2455.

Melting Point: 77–79 ºC

2-(cyclohexylidene(phenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. (SI-10)
Synthesized according to condition A.
To a schlenk flask was added 2,2'-(cyclohexylidenemethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(SI-2)** (500 mg, 1.4 mmol, 1 equiv), iodobenzene (293 mg, 1.4 mmol, 1 equiv), 1,4-dioxane (12 mL, 0.15 M), and the aqueous KOH solution (0.7 mL, 3 molar, 1.7 equiv). The flask was freeze-pump thawed three cycles of 15 minutes. Tetrakis(triphenylphosphine)palladium(0) (50.0 mg, 0.04 mmol, 3 mol %) was added to the frozen solution and the flask was evacuated under vacuum and backfilled with nitrogen three times. The solution was heated to 90 ºC for 18 hours. The solution was cooled to room temperature and quenched with saturated aqueous NH_4Cl (10 mL) and extracted with ethyl acetate (3 x 10 mL) The combined organics were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (6% diethyl ether in hexanes) to yield 140 mg (32% yield) of a white solid. This material matched reported literature ^{1}H NMR data.[3]

2-(cyclohexylidene(3,4-dimethoxyphenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. (SI-11)
Synthesized according to condition B.
To schlenk flask was added 2,2'-(cyclohexylidenemethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(SI-2)** (400 mg, 1.15 mmol, 1 equiv), 4-iodo-1,2-dimethoxybenzene (316 mg, 1.15 mmol, 1 equiv), tetrahydrofuran (7 mL), and the aqueous KOH solution (1.2 mL, 3 molar, 3.0 equiv). The flask was freeze-pump thawed three cycles of 15 minutes. Tris(dibenzylideneacetone)dipalladium(0) (33 mg, 0.03 mmol, 3 mol %) was added to the frozen solution and the flask was evacuated under vacuum and backfilled with nitrogen three times. Tri-tertbutyl phosphine (29 mg, 0.14 mmol, 12 mol %) was added to the frozen solution under a stream of nitrogen and the flask was evacuated under vacuum and backfilled with nitrogen three times. The solution was allowed to thaw and stirred at room temperature (24 h). The solution was quenched with saturated aqueous NH_4Cl (10 mL) and extracted with ethyl acetate (3 x 15 mL). The combined organics were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (15→20% diethyl ether in hexanes) to yield 70 mg of a yellow solid (16% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.86 – 6.72 (m, 1H), 6.64 (d, J = 7.5 Hz, 3H), 3.86 (s, 3H), 3.84 (s, 3H), 2.59 – 2.37 (m, 2H), 2.27 – 2.09 (m, 2H), 1.72 – 1.46 (m, 6H), 1.26 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.6, 148.5, 147.0, 135.0, 121.3, 112.7, 111.0, 83.5, 56.1, 56.0, 35.9, 32.3, 29.1, 28.8, 27.0, 25.0. *Note*: Carbon attached to boron not seen due to relaxation on B.
^{11}B NMR (128 MHz, $CDCl_3$) δ 30.10.
FT-IR (neat film NaCl): 2975, 2925, 2852, 1603, 1510, 1463, 1445, 1352, 1296, 1249, 1142, 1030, 858 cm^{-1}.
HR-MS (EI-MS) m/z: [M]+ Calculated for $C_{21}H_{31}BO_4$: 358.2315; Measured: 358.2319.
Melting Point: 77–80 ºC

2-(cyclohexylidene(2-methoxy-5-methylphenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. (SI-12)
Synthesized according to condition B.
To schlenk flask was added 2,2'-(cyclohexylidenemethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(SI-2)** (400 mg, 1.15 mmol, 1 equiv), 2-iodo-1-methoxy-4-methylbenzene (285 mg, 1.15 mmol, 1 equiv), tetrahydrofuran (7 mL), and the aqueous KOH solution (1.2 mL, 3 molar, 3.0 equiv). The flask was freeze-pump thawed three cycles of 15 minutes. Tris(dibenzylideneacetone)dipalladium(0) (32 mg, 0.03 mmol, 3 mol %) was added to the frozen solution and the flask was evacuated under vacuum and backfilled with nitrogen three times. Tri-tertbutyl phosphine (28 mg, 0.14 mmol, 12 mol %) was added to the frozen solution under a stream of nitrogen and the flask was evacuated under vacuum and backfilled with nitrogen three times. The solution was allowed to thaw and stirred at room temperature. The reaction was monitored carefully by TLC (~1 h). The solution was quenched with saturated aqueous NH_4Cl (10 mL) and extracted with ethyl acetate (3 x 15 mL). The combined organics were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (30→40% diethyl ether in hexanes) to yield 378 mg of a brown solid (96% yield).
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.96 (dd, J = 8.2, 2.3 Hz, 1H), 6.85 (bs, 1H), 6.71 (d, J = 8.2 Hz, 1H), 3.72 (s, 3H), 2.59 (bs, 2H), 2.25 (bs, 3H), 2.15 (s, 3H), 1.67 – 1.52 (m, 6H), 1.24 (s, 12H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 156.2, 155.2, 132.1, 131.5, 129.3, 127.6, 110.3, 83.2, 55.7, 35.5, 33.0, 29.2, 28.9, 27.1, 25.0, 21.0. *Note*: Carbon attached to boron not seen due to relaxation on B.
^{11}B NMR (128 MHz, $CDCl_3$) δ 30.81.
FT-IR (neat film NaCl): 2976, 2924, 2852, 1617, 1495, 1447, 1350, 1297, 1146, 1036, 856, 801 cm^{-1}.
HR-MS (EI-MS) m/z: [M]+ Calculated for $C_{21}H_{31}BO_3$: 342.2366; Measured: 342.2370.
Melting Point: 75–77 ºC

2-(cyclohexylidene(3-methoxyphenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. (SI-13)

Synthesized according to condition B.

To schlenk flask was added 2,2'-(cyclohexylidenemethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(SI-2)** (370 mg, 1.06 mmol, 1 equiv), 1-iodo-3-methoxybenzene (249 mg, 1.06 mmol, 1 equiv), tetrahydrofuran (7 mL), and the aqueous KOH solution (1.0 mL, 3 molar, 3.0 equiv). The flask was freeze-pump thawed three cycles of 15 minutes. Tris(dibenzylideneacetone)dipalladium(0) (29 mg, 0.03 mmol, 3 mol %) was added to the frozen solution and the flask was evacuated under vacuum and backfilled with nitrogen three times. Tri-tertbutyl phosphine (26 mg, 0.13 mmol, 12 mol %) was added to the frozen solution under a stream of nitrogen and the flask was evacuated under vacuum and backfilled with nitrogen three times. The solution was allowed to thaw and stirred at room temperature (18 h). The solution was quenched with saturated aqueous NH_4Cl (10 mL) and extracted with ethyl acetate (3 x 15 mL). The combined organics were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (20→35% dichloromethane in hexanes) to yield 203 mg of a brown solid (61% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 8.2, 7.5 Hz, 1H), 6.78 – 6.52 (m, 3H), 3.78 (s, 3H), 2.53 – 2.41 (m, 2H), 2.21 – 2.02 (m, 2H), 1.83 – 1.50 (m, 6H), 1.25 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.6, 155.2, 143.6, 129.3, 121.5, 114.0, 111.4, 83.6, 55.1, 35.3, 32.1, 29.9, 28.3, 27.5, 25.2. *Note*: Carbon attached to boron not seen due to relaxation on B.

^{11}B NMR (128 MHz, $CDCl_3$) δ 31.27.

FT-IR (neat film NaCl): 2977, 2925, 2851, 1618, 1487, 1353, 1297, 1135, 970, 857 cm^{-1}.

HR-MS (EI-MS) m/z: [M]+ Calculated for $C_{20}H_{39}BO_3$: 328.2209; Measured: 328.2211.

Melting Point: 75–77 ºC

General scheme for synthesis of SI-16

4,4',4''-(ethene-1,1,2-triyl)tris(methoxybenzene). (SI-14)

(**SI-14**) was synthesized according to known procedures, and the ^{1}H NMR data matched spectra reported in the literature.[4]

4,4',4''-(2-bromoethene-1,1,2-triyl)tris(methoxybenzene). (SI-15)

(**SI-15**) was synthesized according to known procedures, and the ^{1}H NMR data matched spectra reported in the literature.[5]

4,4,5,5-tetramethyl-2-(1,2,2-tris(4-methoxyphenyl)vinyl)-1,3,2-dioxaborolane. (SI-16)

(**SI-16**) was prepared by Miyaura-borylation.

To a flame dried schlenk flask with a stir bar was added 4,4',4''-(2-bromoethene-1,1,2-triyl)tris(methoxybenzene) (**SI-15**) (300 mg, 0.70 mmol, 1 equiv), potassium phenolate (140 mg, 1.05 mmol, 1.5 equiv), 4,4,4',4'5,5,5',5'-octamethyl-2,2'bi(1,3,2-dioxaborolane) (197 mg, 0.775 mmol, 1.1 equiv) and triphenylphosphine (11.1 mg, 0.04 mmol, 6 mol %). To this was added dry toluene (5 mL). The solution was freeze pump-thawed three cycles of 15 minutes. To the frozen solution was added bis(triphenylphosphine)palladium chloride (15 mg, 0.02 mmol, 3 mol %), and the flask was evacuated and back filled with nitrogen three times. The solution was thawed and heated to 70 ºC (1.5 h). The solution was diluted with diethyl ether (10 mL) and quenched with satd. Aqueous NH_4Cl (10 mL). The aqueous solution was extracted with diethyl ether (3 x 15 mL), and the organic layer was dried over Na_2SO_4. The organic solution was filtered and concentrated *in vacuo*. The crude yellow material was purified flash column chromatography (18% diethyl ether in hexanes) to yield 260 mg of a yellow solid (78% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.7 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 6.68 (d, *J* = 8.8 Hz, 2H), 6.62 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 3.74 (s, 3H), 3.73 (s, 3H), 1.14 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.5, 158.5, 157.8, 150.3, 138.2, 135.0, 135.1, 132.7, 131.3, 130.9, 113.8, 113.5, 113.2, 83.8, 55.6, 55.4, 55.4, 24.9.*Note*: Carbon attached to boron not seen due to relaxation on B.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.93.

FT-IR (neat film NaCl): 2977, 2930, 2885, 1605, 1508, 1346, 1292, 1244, 1173, 1140, 1034, 852, 832 cm^{-1}.

HR-MS (EI-MS) m/z: [M]+ Calculated for $C_{29}H_{33}BO_5$: 427.2421; Measured: 427.2426.

Melting Point: 117–119 ºC

SI-17 SI-18

SI-17 was prepared according to known literature procedures.[6]

2,2'-(2-butylhex-1-ene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (SI-18)

To a flame dried schlenk flask equipped with a stir bar was added 5-(dibromomethylene)nonane **(SI-17)** (1.63 g, 5.47 mmol, 1 equiv) followed by dry THF (14 mL) and diethyl ether (14 mL). This solution was cooled to –110 ºC with a liquid nitrogen/pentane cooling bath. To this solution was added n-butyllithium (3.76 mL, 1.60 M, 6.0 mmol, 1.1 equiv), and the solution was stirred at –110 ºC for 30 minutes. To this solution was added a –110 ºC chilled solution of bis(pinacolato)diboron (1.53 g, 6.0 mmol, 1.1 equiv) in 14 mL of THF dropwise *via* cannula. This solution was stirred at –110 ºC for an additional 15 minutes and then allowed to warm to room temperature overnight. To this solution was added saturated aqueous NH_4Cl (20 mL), and the aqueous layer was extracted with ethyl acetate (3 x 20 mL). The organic layer was dried over Na_2SO_4, filtered, concentrated, and purified by flash column chromatography (100% hexanes→ 3% ether:hexanes →5% ether:hexanes) to yield **(SI-18)** as a colorless oil (830 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 – 2.18 (m, 4H), 1.47 – 1.34 (m, 4H), 1.34 – 1.26 (m, 4H), 0.88 (t, J = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 82.9, 38.2, 32.3, 25.1, 23.4, 14.3.

Note: Carbon attached to boron not seen due to relaxation on B.

^{11}B NMR (128 MHz, $CDCl_3$) δ 31.6.

FT-IR (neat film NaCl): 2976, 2957, 2930, 2860, 1609, 1466, 1378, 1355, 1319, 1283, 1142, 1010, 987, 856 cm^{-1}.

HR-MS (CI-MS) m/z: [M+H]+ Calculated for $C_{22}H_{42}BO_4$: 393.3347; Measured: 393.3356.

2-(2-butyl-1-(4-methoxyphenyl)hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (SI-19)

Synthesized according to condition B.

To schlenk flask was added 2,2'-(2-butylhex-1-ene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (SI-18) (400 mg, 1.02 mmol, 1 equiv), 1-iodo-4-methoxybenzene (239 mg, 1.02 mmol, 1 equiv), tetrahydrofuran (7 mL), and the aqueous KOH solution (1.0 mL, 3 molar, 3.0 equiv). The flask was freeze-pump thawed three cycles of 15 minutes. Tris(dibenzylideneacetone)dipalladium(0) (46 mg, 0.05 mmol, 5 mol %) was added to the frozen solution and the flask was evacuated under vacuum and backfilled with nitrogen three times. Tri-tertbutyl phosphine (41 mg, 0.20 mmol, 20 mol %) was added to the frozen solution under a stream of nitrogen and the flask was evacuated under vacuum and backfilled with nitrogen three times. The solution was allowed to thaw and stirred at room temperature (18 h). The solution was quenched with saturated aqueous NH_4Cl (10 mL) and extracted with ethyl acetate (3 x 15 mL). The combined organics were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (10→50% dichloromethane in hexanes) to yield 267 mg of a brown oil (70% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.98 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 3H), 2.47 – 2.23 (m, 2H), 2.10 – 1.81 (m, 2H), 1.50 – 1.26 (m, 6H), 1.21 (s, 12H), 1.13 (d, *J* = 7.0 Hz, 2H), 0.94 (t, *J* = 7.1 Hz, 3H), 0.77 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 157.6, 155.7, 135.3, 130.1, 113.5, 83.3, 55.4, 35.4, 32.5, 32.3, 31.0, 25.0, 23.4, 23.2, 14.4, 14.2. *Note*: Carbon attached to boron not seen due to relaxation on B.
^{11}B NMR (128 MHz, $CDCl_3$) δ 29.12.
FT-IR (neat film NaCl): 2957, 2930, 2860, 1602, 1508, 1465, 1352, 1282, 1242, 1173, 1145, 1116, 1036, 973, 857, 829 cm^{-1}.
HR-MS (EI-MS) m/z: [M]+ Calculated for $C_{23}H_{37}BO_3$: 372.2835; Measured: 378.2840.

2-(2-butyl-1-(2,4-dimethylphenyl)hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (SI-20)
Synthesized according to condition B.

To schlenk flask was added 2,2'-(2-butylhex-1-ene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (SI-18) (400 mg, 1.02 mmol, 1 equiv), 1-iodo-2,4-dimethylbenzene (237 mg, 1.02 mmol, 1 equiv), tetrahydrofuran (7 mL), and the aqueous KOH solution (1.0 mL, 3 molar, 3.0 equiv). The flask was freeze-pump thawed three cycles of 15 minutes. Tris(dibenzylideneacetone)dipalladium(0) (46 mg, 0.05 mmol, 5 mol %) was added to the frozen solution and the flask was evacuated under vacuum and backfilled with nitrogen three times. Tri-tertbutyl phosphine (41 mg, 0.20 mmol, 20 mol %) was added to the frozen solution under a stream of nitrogen and the flask was evacuated under vacuum and backfilled with nitrogen three times. The solution was allowed to thaw and stirred at room temperature (4 h). The solution was quenched with saturated aqueous NH_4Cl (10 mL) and extracted with ethyl acetate (3 x 15 mL). The combined organics were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (10→80% dichloromethane in hexanes) to yield 314 mg of a brown oil (83% yield).
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.94 (s, 1H), 6.89 (d, *J* = 7.7 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 2.49 (d, *J* = 7.9 Hz, 1H), 2.40 (d, *J* = 7.6 Hz, 1H), 2.29 (s, 3H), 2.10 (s, 3H), 1.97 – 1.64 (m, 2H), 1.47 (p, *J* = 7.4 Hz, 2H), 1.39 (p, *J* = 7.1 Hz, 2H), 1.20 (s, 12H), 1.14 – 1.02 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H), 0.72 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 157.5, 139.9, 135.6, 134.9, 130.4, 129.3, 126.2, 83.0, 34.4, 32.9, 32.7, 30.5, 25.1, 24.9, 23.3, 23.1, 21.4, 20.3, 14.4, 14.2. *Note*: Carbon attached to boron not seen due to relaxation on B.
^{11}B NMR (96 MHz, $CDCl_3$) δ 30.00.
FT-IR (neat film NaCl): 2976, 2956, 2928, 2871, 2859, 1604, 1496, 1465, 1378, 1348, 1294, 1145, 1007, 973, 857 cm^{-1}.
HR-MS (EI-MS) m/z: [M]+ Calculated for $C_{24}H_{39}BO_2$: 370.3043; Measured: 370.3047.

2,2'-(cyclopentylidenemethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (SI-21)
SI-21 was prepared according to known procedures, the ^{1}H NMR spectrum matched the reported spectra.[13]

***tert*-butyl (4-(cyclopentylidene(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)phenyl)(methyl)carbamate (SI-22)**
Synthesized according to condition B.

To schlenk flask was added 2,2'-(cyclopentylidenemethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(SI-21)** (850 mg, 2.5 mmol, 1 equiv), tert-butyl (4-iodophenyl)(methyl)carbamate (848 mg, 2.5 mmol, 1 equiv), tetrahydrofuran (15 mL), and the aqueous KOH solution (2.5 mL, 3 molar, 3.0 equiv). The flask was freeze-pump thawed three cycles of 15 minutes. Tris(dibenzylideneacetone)dipalladium(0) (70 mg, 0.076 mmol, 3 mol %) was added to the frozen solution and the flask was evacuated under vacuum and backfilled with nitrogen three times. Tri-tertbutyl phosphine (61.7 mg, 0.30 mmol, 12 mol %) was added to the frozen solution under a stream of nitrogen and the flask was evacuated under vacuum and backfilled with nitrogen three times. The solution was allowed to thaw and stirred at room temperature (24 h). The solution was quenched with saturated aqueous NH_4Cl (10 mL) and extracted with ethyl acetate (3 x 15 mL). The combined organics were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (10→20% diethyl ether in hexanes followed by 90% DCM:Hexanes) to yield 268 mg of a colorless oil (25% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (d, J = 8.4 Hz, 2H), 7.11 – 6.97 (m, 2H), 3.25 (s, 3H), 2.68 – 2.54 (m, 2H), 2.27 (tt, J = 7.1, 1.2 Hz, 2H), 1.70 (p, J = 7.0 Hz, 2H), 1.63 – 1.49 (m, 2H), 1.45 (s, 9H), 1.26 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.6, 155.3, 141.1, 140.7, 129.2, 124.9, 83.3, 80.3, 37.6, 34.3, 34.1, 28.7, 26.7, 26.4, 25.1.

Note: Carbon attached to boron not seen due to relaxation on B.

^{11}B NMR (96 MHz, $CDCl_3$) δ 31.76.

FT-IR (neat film NaCl): 2975, 2867, 1699, 1606, 1509, 1477, 1452, 1389, 1357, 1305, 1145, 980, 858 cm^{-1}.

HR-MS (CI-MS) m/z: [M]+ Calculated for $C_{24}H_{36}BNO_4$: 413.2737; Measured: 413.2742.

2-(cyclopentylidene(2,2-dimethylbenzo[*d*][1,3]dioxol-5-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (SI-23)

Synthesized according to condition B.

To schlenk flask was added 2,2'-(cyclopentylidenemethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(SI-21)** (400 mg, 1.2 mmol, 1 equiv), 5-iodo-2,2-dimethylbenzo[d][1,3]dioxole (331 mg, 1.2 mmol, 1 equiv), tetrahydrofuran (8 mL), and the aqueous KOH solution (1.2 mL, 3 molar, 3.0 equiv). The flask was freeze-pump thawed three cycles of 15 minutes. Tris(dibenzylideneacetone)dipalladium(0) (54.8 mg, 0.06 mmol, 5 mol %) was added to the frozen solution and the flask was evacuated under vacuum and backfilled with nitrogen three times. Tri-tertbutyl phosphine (48.4 mg, 0.24 mmol, 20 mol %) was added to the frozen solution under a stream of nitrogen and the flask was evacuated under vacuum and backfilled with nitrogen three times. The solution was allowed to thaw and stirred at room temperature (1.5 h). The solution was quenched with saturated aqueous NH_4Cl (10 mL) and extracted with ethyl acetate (3 x 15 mL). The combined organics were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (100% hexanes→2% diethyl ether in hexanes) to yield **(SI-23)** 130 mg of a brown oil (30% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.64 (d, *J* = 7.9 Hz, 1H), 6.56 (d, *J* = 1.5 Hz, 1H), 6.53 (dd, *J* = 7.8, 1.6 Hz, 1H), 2.62 (t, *J* = 7.2 Hz, 2H), 2.29 (t, *J* = 7.1 Hz, 2H), 1.76 – 1.67 (m, 4H), 1.67 (s, 6H), 1.27 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.9, 147.1, 145.2, 136.8, 121.4, 117.5, 109.6, 107.8, 83.3, 34.2, 34.2, 26.7, 26.4, 26.3, 25.1.

Note: Carbon attached to boron not seen due to relaxation on B.

^{11}B NMR (96 MHz, $CDCl_3$) δ 30.63.

FT-IR (neat film NaCl): 2976, 2953, 2866, 1611, 1493, 1438, 1369, 1304, 1245, 1232, 1144, 977, 854, 840, 753 cm^{-1}.

HR-MS (EI-MS) m/z: [M]+ Calculated for $C_{21}H_{29}BO_4$: 356.2158; Measured: 356.2163.

4-(cyclopentylidene(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-*N*-methylaniline (SI-24)

To a 20 mL scintillation vial containing *tert*-butyl (4-(cyclopentylidene(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)phenyl)(methyl)carbamate (230 mg, 0.56 mmol, 1 equiv) **(SI-21)** and a stir bar was added dichloromethane (5.1 mL). This solution was cooled to 0 ºC in an ice bath. To this solution was added dropwise trifluoroacetic acid (214 uL, 2.78 mmol, 5 equiv). This solution was allowed to warm to room temperature and stirred for 4 hours (monitored for consumption of the starting material by LC-MS). To this solution was slowly added triethylamine (0.5 mL) followed by saturated aqueous NH_4Cl (3 mL). This solution was extracted with dichloromethane (3 x 5 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated. This essentially pure material was purified by flash column chromatography to yield a **SI-23** as a white solid (135 mg, 77%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.01 (d, *J* = 8.5 Hz, 2H), 6.56 (d, *J* = 8.5 Hz, 2H), 2.83 (s, 3H), 2.63 (tt, *J* = 7.3, 1.4 Hz, 2H), 2.32 (tt, *J* = 7.1, 1.4 Hz, 2H), 1.82 – 1.62 (m, 2H), 1.59 – 1.47 (m, 2H), 1.27 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.4, 147.1, 132.7, 129.9, 112.3, 83.2, 34.2, 34.0, 31.2, 26.7, 26.4, 25.1. *Note*: Carbon attached to boron not seen due to relaxation on B.
^{11}B NMR (96 MHz, $CDCl_3$) δ 29.91.
Melting Point: 78–80 ºC
HR-MS (ESI-MS) m/z: [M]+ Calculated for $C_{19}H_{28}BNO_2$: 313.2213; Measured: 313.2217.

(cyclohexylidene(4-methoxyphenyl)methyl)trifluoro-λ^4-borane, potassium salt. (SI-25)
To 25 mL round bottom flask with a stir bar was added 2-(cyclohexylidene(4-methoxyphenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(SI-3)** (286 mg, 0.87 mmol, 1 equiv). This was dissolved in a mixture of methanol/water (7.1mL methanol:1.0 mL water). Diethyl ether was added to the solution until it was homogeneous (~1 mL). To this stirring solution was added KHF_2 (340 mg, 4.35 mmol, 5 equiv). The solution was stirred vigorously and monitored by TLC. Once the starting pinacol boronic ester had been consumed (~25 minutes) the solution was stirred an additional 15 minutes. The solution was concentrated *in vacuo*. The remaining solid was dissolved in hot acetone (~15 mL) and filtered. The filtrate was concentrated *in vacuo*. The resulting off-white solid was washed with cold hexanes (15 mL), cold diethyl ether (5 mL), and finally cold hexanes (10 mL). The white solid remaining white solid was dried *in vacuo* to give the (**SI-7**) as a white powder (180 mg, 67% yield). *Note:*This solid should be stored in a freezer for long term storage.
^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 6.91 (d, J = 8.6 Hz, 2H), 6.72 (d, J = 8.6 Hz, 2H), 3.75 (s, 3H), 2.54 (t, J = 5.8 Hz, 2H), 1.91 (t, J = 6.0 Hz, 2H), 1.64 – 1.48 (m, 4H), 1.42 (q, J = 6.0 Hz, 2H).
^{13}C NMR (126 MHz, $(CD_3)_2CO$) δ 157.6, 143.3, 141.3, 131.2, 116.6, 113.5, 55.9, 34.8, 34.1, 29.0, 26.0, 25.9. *Note*: Carbon attached to boron not seen due to relaxation on B.
^{11}B NMR (96 MHz, $(CD_3)_2CO$) δ 3.89 – 2.43 (m).
^{19}F NMR (282 MHz, $(CD_3)_2CO$) δ -133.6 – 133.5 (m).
FT-IR (neat film NaCl): 2921, 2849, 1603, 1505, 1276, 1236, 1177, 1135, 1119, 1079, 975, 830, 797 cm^{-1}.
HR-MS (ESI): Calculated for $[M]^-$ $C_{14}H_{17}BF_3O$: 269.1324; Measured: 269.1320.
Melting Point: 75–85 ºC decomposition

(cyclohexylidene(4-methoxyphenyl)methyl)trifluoro-λ^4-borane, tetrabutylammonium salt. (SI-26)

To a 10 mL round bottom flask equipped with a stir bar was added (cyclohexylidene(4-methoxyphenyl)methyl)trifluoro-λ^4-borane, potassium salt **(SI-25)** (50 mg, 0.16 mmol, 1 equiv). This was covered in dichloromethane (1.5 mL). To this solution was added tetrabutylammonium hydroxide 55% aqueous solution w/w (77 mg, 0.16 mmol, 1 equiv). The solution was stirred until homogeneous (~5 minutes). The solution was diluted with dichloromethane (15 mL) and washed with water (1 x 5 mL). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo* to give the pure product as a yellow oil (75 mg, 90% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (d, *J* = 8.4 Hz, 2H), 6.74 (d, *J* = 8.3 Hz, 2H), 3.75 (s, 3H), 3.19 – 3.01 (m, 8H), 2.57 (t, *J* = 6.0 Hz, 2H), 1.96 (t, *J* = 6.0 Hz, 2H), 1.66 – 1.60 (m, 2H), 1.58 – 1.49 (m, 10H), 1.45 – 1.40 (m, 2H), 1.38 (q, *J* = 7.4 Hz, 8H), 0.98 (t, *J* = 7.3 Hz, 12H).

^{13}C NMR (126 MHz, CD_2Cl) δ 155.9, 141.6, 141.3, 129.7, 112.1, 77.5, 58.6, 33.3, 32.5, 29.1, 19.6, 13.3. *Note*: Carbon attached to boron not seen due to relaxation on B.

^{11}B NMR (96 MHz, $CDCl_3$) δ 4.87.

^{19}F NMR (282 MHz, $CDCl_3$) δ -132.55.

FT-IR (neat film NaCl): 2962, 2920, 2876, 2848, 1603, 1504, 1463, 1381, 1233, 1172, 1113, 1050, 979, 858, 827, 795 cm^{-1}.

HR-MS (ESI): Calculated for $[M]^-$ $C_{14}H_{17}BF_3O$: 269.1324; Measured: 269.1319.

2-(1-(4-methoxyphenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. (SI-27)

(**SI-27**) was prepared according to known procedures, and matched the reported 1H NMR spectral data.[8]

potassium 2-(4-methoxyphenyl)acrylate. (SI-28)

(**SI-28**) was prepared according to known procedures, and matched the reported 1H NMR spectral data.[9]

1,3-dioxoisoindolin-2-yl 2-(4-methoxyphenyl)acrylate. (SI-29)
(**SI-29**) was prepared according to known procedures, and matched the reported ^{1}H NMR spectral data.[10]

(*Z*)-2-(1-(4-methoxyphenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. (SI-29.1) was prepared according to known procedures, and matched the reported ^{1}H NMR spectral data.[11]

(2-butyl-1-(2,4-dimethylphenyl)hex-1-en-1-yl)trifluoro-λ^4-borane, potassium salt (SI-30)
To a scintillation vial containing **SI-20** (100 mg, 0.27 mmol, 1 equiv) and a stir bar was added methanol (3.4 mL) and water (1.7 mL). To this was added solid KHF_2 (127 mg, 1.62 mmol, 6 equiv). This solution was stirred vigorously (rpm~1300) for 8 hours. This solution was filtered through a kimwipe pipette to remove solids. The filtrate was concentrated **<u>at or below</u>** room temperature using rotary evaporation followed by high-vac. This was then dissolved in room temperature acetone and decanted away from the solids. The acetone solution was concentrated to yield a low-melting colorless solid of **SI-30** (89 mg, 94% yield). *Note:* This solid was stable in the freezer (–20ºC) for only a few days at a time without signification decomposition to the styrene, presumably through protodeboronation.
^{1}H NMR (300 MHz, $(CD_3)_2O$) δ 6.79 (d, *J* = 0.8 Hz, 1H), 6.71 (d, *J* = 0.9 Hz, 2H), 2.69 – 2.47 (m, 1H), 2.29 – 2.22 (m, 1H), 2.19 (s, 3H), 2.15 (d, *J* = 7.2 Hz, 1H), 2.10 (s, 3H), 2.07 (bs, 1H), 1.66 (q, *J* = 6.9, 6.3 Hz, 2H), 1.48 (qd, *J* = 6.8, 6.4, 2.8 Hz, 2H), 1.42 – 1.26 (m, 2H), 1.10 – 0.98 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H), 0.71 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (126 MHz, $(CD_3)_2O$) δ 147.1, 139.1,135.6 132.0, 129.7, 129.0, 125.1, 33.0, 32.8, 32.7, 31.4, 24.9, 23.7, 23.4, 20.8, 20.33, 14.4, 14.0.
^{19}F NMR (282 MHz, $(CD_3)_2O$) δ -134.99.

^{11}B NMR (96 MHz, $(CD_3)_2O$) δ 4.83.
FT-IR (neat film NaCl): 2955, 2928, 2858, 1613, 1492, 1465, 1377, 1140, 1072, 932, 857, 818 cm^{-1}.
HR-MS (ESI): $[M]^-$ Calculated for $C_{18}H_{27}BF_3$: 311.2157; Measured: 311.2149.

(*E*)-2-(1-(4-methoxyphenyl)-2-phenylprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (SI-30.1). was prepared according to known procedures, and matched the reported ^{1}H NMR spectral data.[12]

3. Electrochemical Fluorination Reactions of Vinyl Boronates

3.1 General procedure for fluorination reactions

To an oven dried 2 dram vial equipped with an oven dried stir bar was added the vinyl boronic ester or boronate (0.05–0.025 mmol, 1 equiv). To this was added the $TBABF_4$ (99.0 mg, 0.300 mmol, 6 equiv) and the TBAF•(H_2O) (79.0 mg, 0.25 mmol, 5 equiv). The electrodes [Pt(–)/C(+)] held in place by a septum cap were put in place. The vial was placed under a nitrogen atmosphere. Freshly distilled acetonitrile was added (2.5 mL). The solution was degassed by bubbling nitrogen with stirring (~400 rpm) for 20 minutes. *Degassing showed no effect on yield for this reaction with several substrates, but for consistency was performed before each reaction.* After degassing the potentiostat (TACKLife MDC01 DC power supply) was connected to the electrodes and a constant working potential *vs.* a CHI-50 SCE electrode of +1.8 V (measured with a multimeter between the C(+) and reference CHI-150 SCE electrode (*usually ~3.5V E_{cell} required, this can allow further ease of use without a reference electrode*) was applied for 15 minutes, or until the starting material was consumed. (*Constant voltage gave optimal yields for this reaction, particularly for substrates that contained redox sensitive moieties such as unprotected anilines and thiols).* Upon completion the applied potential was halted and the electrodes were removed from solution and rinsed with dichloromethane (3 x 4 mL). The resulting solution was concentrated *in vacuo* to yield a brown oil. The crude material was purified by flash column chromatography to give the resulting vinyl fluoride.

Typical TLC indicating complete reaction: (reaction, cospot, starting material)

Image of electrodes and reaction vial (2 electrode set-up [left] with no reference and 3-electrode reference electrode set-up [right]):

Size of Electrodes

Platinum: 1cm × 1cm × 0.1cm. C felt: approximately 1cm × 1cm × 0.5cm. C felt electrodes were connected to a 2B pencil graphite (see above image for accurate scaling information). A new piece of carbon felt was used in every reaction.

Platinum electrodes were washed between use by rinsing with acetone and water, followed by sonication in a 1:1 acetone/water bath, and finally scraped with a razor to remove any remaining solids. 2B pencil graphite was rinsed with acetone and water, and then scraped with a razor to remove any remaining solids between use. After two uses the pencil graphite was replaced, or if visible deposition/discoloration was observed.

1-(cyclohexylidenefluoromethyl)-4-methoxybenzene. (SI-31)

To an oven dried 2 dram vial equipped with an oven dried stir bar was added 2-(cyclohexylidene(4-methoxyphenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(SI-3)** (16.4 mg, 0.05 mmol, 1 equiv). To this was added the $TBABF_4$ (99.0 mg, 0.300 mmol, 6 equiv) and the TBAF•(H_2O) (79.0 mg, 0.25 mmol, 5 equiv). The electrodes [Pt(–)/C(+)] held in place by a septum cap were put in place. The vial was placed under a nitrogen atmosphere. Freshly distilled acetonitrile was added (2.5 mL). The solution was degassed by bubbling nitrogen with stirring (~400 rpm) for 20 minutes. After degassing the potentiostat (TACKLife MDC01 DC power supply) was connected to the electrodes and a constant working potential *vs.* a CHI-50 SCE electrode of +1.8 V (measured with a multimeter between the C(+) and reference CHI-150 SCE electrode) was applied for 15

minutes, or until the starting material was consumed. Upon completion the applied potential was halted and the electrodes were removed from solution and rinsed with dichloromethane (3 x 4 mL). The resulting solution was concentrated *in vacuo* to yield a brown oil. The crude material was purified by flash column chromatography (50% dichloromethane in hexanes) to give the resulting vinyl fluoride as a colorless oil (7.7 mg, 70% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 9.0, 1.0 Hz, 2H), 6.95 – 6.84 (m, 2H), 3.82 (s, 3H), 2.43 – 2.28 (m, 2H), 2.19 (t, *J* = 5.6 Hz, 2H), 1.69 – 1.47 (m, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.7 (d, *J* = 1.6 Hz), 150.0 (d, *J* = 237.2 Hz), 130.2 (d, *J* = 3.5 Hz), 125.9 (d, *J* = 31.7 Hz), 117.7 (d, *J* = 17.9 Hz), 113.7, 55.6, 29.1 (d, *J* = 4.2 Hz), 27.9 (d, *J* = 2.3 Hz), 27.3, 26.8, 26.6 (d, *J* = 7.7 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ -107.71.
FT-IR (neat film NaCl): 2927, 2852, 1609, 1510, 1444, 1302, 1247, 1174, 1031, 834 cm^{-1}.
HR-MS (EI-MS) m/z: [M]+ Calculated for $C_{14}H_{17}FO$: 220.1263; Measured: 220.1267.

4-(cyclohexylidenefluoromethyl)-*N*,*N*-dimethylaniline. (SI-32)
To an oven dried 2 dram vial equipped with an oven dried stir bar was added 4-(cyclohexylidene(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-*N*,*N*-dimethylaniline **(SI-4)** (17.1 mg, 0.05 mmol, 1 equiv). To this was added the $TBABF_4$ (99.0 mg, 0.300 mmol, 6 equiv) and the TBAF•(H_2O) (79.0 mg, 0.25 mmol, 5 equiv). The electrodes [Pt(–)/C(+)] held in place by a septum cap were put in place. The vial was placed under a nitrogen atmosphere. Freshly distilled acetonitrile was added (2.5 mL). The solution was degassed by bubbling nitrogen with stirring (~400 rpm) for 20 minutes. After degassing the potentiostat (TACKLife MDC01 DC power supply) was connected to the electrodes and a constant working potential *vs.* a CHI-150 SCE electrode of +1.8 V (measured with a multimeter between the C(+) and reference CHI-50 SCE electrode) was applied for 15 minutes, or until the starting material was consumed. Upon completion the applied potential was halted and the electrodes were removed from solution and rinsed with dichloromethane (3 x 4 mL). The resulting solution was concentrated *in vacuo* to yield a brown oil. The crude material was purified by flash column chromatography (50% dichloromethane in hexanes) to give the resulting vinyl fluoride **(SI-32)** as a colorless oil (9.5 mg, 81% yield).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.21 (m, 2H), 6.70 (d, *J* = 8.5 Hz, 2H), 2.98 (s, 6H), 2.37 (dt, *J* = 6.8, 3.3 Hz, 2H), 2.21 (t, *J* = 5.6 Hz, 2H), 1.56 (dq, *J* = 24.2, 6.5, 5.7 Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 150.3 (d, *J* = 237.5 Hz), 150.2, 130.1, 129.5, 116.2 (d, *J* = 18.6 Hz), 111.5, 40.3, 28.8 (d, *J* = 4.3 Hz), 27.6 (d, *J* = 2.2 Hz), 27.0, 26.5, 26.3 (d, *J* = 7.6 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ -107.69.

FT-IR (neat film NaCl): 2923, 2851, 1611, 1523, 1446, 1356, 1288, 1191, 1038, 817 cm^{-1}.

HR-MS (EI-MS) m/z: [M]+ Calculated for $C_{15}H_{20}FN$: 233.1579; Measured: 233.1576.

2-(cyclohexylidenefluoromethyl)-1,3,5-trimethoxybenzene. (SI-33)

To an oven dried 2 dram vial equipped with an oven dried stir bar was added 2-(cyclohexylidene(2,4,6-trimethoxyphenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(SI-5)** (19.4 mg, 0.05 mmol, 1 equiv). To this was added the $TBABF_4$ (99.0 mg, 0.300 mmol, 6 equiv) and the TBAF•(H_2O) (79.0 mg, 0.25 mmol, 5 equiv). The electrodes [Pt(–)/C(+)] held in place by a septum cap were put in place. The vial was placed under a nitrogen atmosphere. Freshly distilled acetonitrile was added (2.5 mL). The solution was degassed by bubbling nitrogen with stirring (~400 rpm) for 20 minutes. After degassing the potentiostat (TACKLife MDC01 DC power supply) was connected to the electrodes and a constant working potential *vs.* a CHI-150 SCE electrode of +1.8 V (measured with a multimeter between the C(+) and reference CHI-50 SCE electrode) was applied for 15 minutes, or until the starting material was consumed. Upon completion the applied potential was halted and the electrodes were removed from solution and rinsed with dichloromethane (3 x 4 mL). The resulting solution was concentrated *in vacuo* to yield a brown oil. The crude material was purified by flash column chromatography (50% dichloromethane in hexanes) to give the resulting vinyl fluoride **(SI-33)** as a colorless oil (11.5 mg, 82% yield).

Note: Reaction was also performed on 0.25 mmol scale with 3 equiv of TBAF.

To an oven dried test tube equipped with an oven dried stir bar was added 2-(cyclohexylidene(2,4,6-trimethoxyphenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(SI-5)** (97.1 mg, 0.25 mmol, 1 equiv). To this was added the $TBABF_4$ (493.9 mg, 1.50 mmol, 6 equiv) and the TBAF•(H_2O) (236.6 mg, 0.75 mmol, 3 equiv). The electrodes [Pt(–)/C(+)] held in place by a septum cap were put in place. The vial was placed under a nitrogen atmosphere. Freshly distilled acetonitrile was added (12.5 mL). The solution was degassed by bubbling nitrogen with stirring (~400 rpm) for 20 minutes. After degassing the potentiostat (TACKLife MDC01 DC power supply) was connected to the electrodes and a constant working potential *vs.* a CHI-150 SCE electrode of +1.8 V (measured with a multimeter between the C(+) and reference CHI-50 SCE electrode) was applied for 1 hr. Upon completion the applied potential was halted and the electrodes were removed from solution and rinsed with dichloromethane (5 x 4 mL). The resulting solution was concentrated *in vacuo* to yield a brown oil. The crude material was purified by flash column chromatography (50% dichloromethane in hexanes) to give the resulting vinyl fluoride **(SI-33)** as a colorless oil (56.0 mg, 79% yield).

Note: Reaction was also performed on 1 mmol scale with 3 equiv of TBAF.

To an oven dried 100 mL round bottom flask equipped with an oven dried stir bar was added 2-(cyclohexylidene(2,4,6-trimethoxyphenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(SI-5)** (388 mg, 1.0 mmol, 1 equiv). To this was added the $TBABF_4$ (1.98 g, 1.50 mmol, 6 equiv) and the TBAF•(H_2O) (947 mg, 0.75 mmol, 3 equiv). The electrodes [Pt(–)/C(+)] held in place by a septum cap were put in place. The vial was placed under a nitrogen atmosphere. Freshly distilled acetonitrile was added (50 mL). The solution was degassed by bubbling nitrogen with stirring (~400 rpm) for 20 minutes. After degassing the potentiostat (TACKLife MDC01 DC power supply) was connected to the electrodes and a constant cell potential (E_{cell}=3.5 V) was applied for 5 hr. Upon completion the applied potential was halted and the electrodes were removed from solution and rinsed with dichloromethane (5 x 4 mL). The resulting solution was concentrated *in vacuo* to yield a brown oil. The crude material was purified by flash column chromatography (100% hexanes→50% dichloromethane in hexanes) to give the resulting vinyl fluoride **(SI-33)** as a colorless oil (201 mg, 71% yield).

1 mmol scale reaction without use of reference electrode

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.12 (s, 2H), 3.83 (s, 3H), 3.80 (s, 6H), 2.41 (td, *J* = 6.2, 2.1 Hz, 2H), 1.85 – 1.73 (m, 2H), 1.65 – 1.59 (m, 2H), 1.51 (ddq, *J* = 14.4, 11.4, 5.9 Hz, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.4 (d, *J* = 2.2 Hz), 160.1, 142.7 (d, *J* = 238.7 Hz), 120.8 (d, *J* = 18.8 Hz), 104.2 (d, *J* = 29.5 Hz), 90.8, 56.2, 55.6, 29.5 (d, *J* = 3.6 Hz), 27.4 (d, *J* = 2.4 Hz), 27.3, 26.9, 26.2 (d, *J* = 5.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -108.75.

FT-IR (neat film NaCl): 2928, 2841, 1605, 1584, 1466, 1413, 1226, 1205, 1156, 1128, 1030, 812 cm^{-1}.

HR-MS (EI-MS) m/z: [M]+ Calculated for $C_{16}H_{21}FO_3$: 280.1474; Measured: 280.1478.

2-(cyclohexylidenefluoromethyl)thiophene. **(SI-34)**
To an oven dried 2 dram vial equipped with an oven dried stir bar was added 2-(cyclohexylidene(thiophen-2-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(SI-6)** (15.2 mg, 0.05 mmol, 1 equiv). To this was added the $TBABF_4$ (99.0 mg, 0.300 mmol, 6 equiv) and the TBAF•(H_2O) (79.0 mg, 0.25 mmol, 5 equiv). The electrodes [Pt(–)/C(+)] held in place by a septum cap were put in place. The vial was placed under a nitrogen atmosphere. Freshly distilled acetonitrile was added (2.5 mL). The solution was degassed by bubbling nitrogen with stirring (~400 rpm) for 20 minutes. After degassing the potentiostat (TACKLife MDC01 DC power supply) was connected to the electrodes and a constant working potential *vs.* a CHI-150 SCE electrode of +1.8 V (measured with a multimeter between the C(+) and reference CHI-50 SCE electrode) was applied for 15 minutes. Upon completion the applied potential was halted and the electrodes were removed from solution and rinsed with dichloromethane (3 x 4 mL). The resulting solution was concentrated *in vacuo* to yield a brown oil. The crude material was purified by flash column chromatography (100% hexaness→35% dichloromethane in hexanes) to give the resulting vinyl fluoride **(SI-34)** as a colorless oil (6.0 mg, 61% yield) as a 9:1 mix with the styrene product.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, J = 5.1 Hz, 1H), 7.19 – 7.10 (m, 1H), 7.02 (q, J = 3.9, 2.8 Hz, 1H), 2.71 – 2.14 (m, 4H), 1.63 – 1.56 (m, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 144.7 (d, J = 232.2 Hz), 134.9 (d, J = 36.3 Hz), 127.3 (d, J = 5.1 Hz), 126.9, 126.1, 120.5 (d, J = 18.1 Hz), 29.2 (d, J = 4.1 Hz), 27.7 (d, J = 2.3 Hz), 27.2, 26.9 (d, J = 7.7 Hz), 26.6.
^{19}F NMR (282 MHz, $CDCl_3$) δ -104.80.
FT-IR (neat film NaCl): 2926, 2854, 1719, 1630, 1449, 1413, 1278, 1258, 1038, 799 cm^{-1}.
HR-MS (EI-MS) m/z: [M]+ Calculated for $C_{11}H_{13}FS$: 196.0722; Measured: 196.0722.

1-(cyclohexylidenefluoromethyl)-2-methoxybenzene. (SI-35)
To an oven dried 2 dram vial equipped with an oven dried stir bar was added 2-(cyclohexylidene(2-methoxyphenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(SI-7)** (16.4 mg, 0.05 mmol, 1 equiv). To this was added the $TBABF_4$ (99.0 mg, 0.300 mmol, 6 equiv) and the TBAF•(H_2O) (79.0 mg, 0.25 mmol, 5 equiv). The electrodes [Pt(–)/C(+)] held in place by a septum cap were put in place. The vial was placed under a nitrogen atmosphere. Freshly distilled acetonitrile was added (2.5 mL). The solution was degassed by bubbling nitrogen with stirring (~400 rpm) for 20 minutes. After degassing

the potentiostat (TACKLife MDC01 DC power supply) was connected to the electrodes and a constant working potential *vs.* a CHI-150 SCE electrode of +1.8 V (measured with a multimeter between the C(+) and reference CHI-50 SCE electrode) was applied for 15 minutes. Upon completion the applied potential was halted and the electrodes were removed from solution and rinsed with dichloromethane (3 x 4 mL). The resulting solution was concentrated *in vacuo* to yield a brown oil. The crude material was purified by flash column chromatography (50% dichloromethane in hexanes) to give the resulting vinyl fluoride **(SI-35)** as a colorless oil (5.5 mg, 50% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (ddt, *J* = 8.2, 7.5, 1.7 Hz, 1H), 7.26 – 7.20 (m, 1H), 7.05 – 6.83 (m, 2H), 3.85 (s, 3H), 2.52 – 2.33 (m, 2H), 2.02 – 1.80 (m, 2H), 1.67 – 1.45 (m, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 158.0, 147.3 (d, *J* = 239.3 Hz), 132.0 (d, *J* = 2.3 Hz), 130.6 (d, *J* = 2.4 Hz), 122.3 (d, *J* = 28.9 Hz), 120.4, 119.7 (d, *J* = 16.9 Hz), 55.9, 29.3 (d, *J* = 4.0 Hz), 27.8 (d, *J* = 2.4 Hz), 27.3, 26.8, 26.3 (d, *J* = 6.7 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ -107.51.
FT-IR (neat film NaCl): 2927, 2852, 1701, 1600, 1580, 1491, 1463, 1435, 1299, 1272, 1247, 1209, 1111, 1033, 936, 752 cm^{-1}.
HR-MS (EI-MS) m/z: [M]+ Calculated for $C_{14}H_{17}FO$: 220.1263; Measured: 220.1261.

***tert*-butyl (4-(cyclohexylidenefluoromethyl)phenyl)carbamate. (SI-36)**
To an oven dried 2 dram vial equipped with an oven dried stir bar was added *tert*-butyl (4-(cyclohexylidene(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)phenyl)carbamate **(SI-8)** (20.7 mg, 0.05 mmol, 1 equiv). To this was added the $TBABF_4$ (99.0 mg, 0.300 mmol, 6 equiv) and the TBAF•(H_2O) (79.0 mg, 0.25 mmol, 5 equiv). The electrodes [Pt(–)/C(+)] held in place by a septum cap were put in place. The vial was placed under a nitrogen atmosphere. Freshly distilled acetonitrile was added (2.5 mL). The solution was degassed by bubbling nitrogen with stirring (~400 rpm) for 20 minutes. After degassing the potentiostat (TACKLife MDC01 DC power supply) was connected to the electrodes and a constant working potential *vs.* a CHI-150 SCE electrode of +1.8 V (measured with a multimeter between the C(+) and reference CHI-50 SCE electrode) was applied for 15 minutes. Upon completion the applied potential was halted and the electrodes were removed from solution and rinsed with dichloromethane (3 x 4 mL). The resulting solution was concentrated *in vacuo* to yield a brown oil. The crude material was purified by flash column chromatography (70% dichloromethane in hexanes) to give the resulting vinyl fluoride **(SI-36)** as a white solid (6.0 mg, 39% yield) as well as recovered the unreacted starting material **(SI-8)** (6.2 mg, 30% recovered s.m.).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 6.50 (s, 1H), 2.37 (bs, 2H), 2.19 (t, *J* = 5.8 Hz, 2H), 1.63 – 1.55 (m, 6H), 1.52 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.9, 149.8 (d, *J* = 237.0 Hz), 138.6 (d, *J* = 1.9 Hz), 129.6 (d, *J* = 3.8 Hz), 128.0 (d, *J* = 31.5 Hz), 118.3 (d, *J* = 17.6 Hz), 118.1, 81.1, 29.1 (d, *J* = 4.2 Hz), 28.6, 27.9 (d, *J* = 2.2 Hz), 27.3, 26.8, 26.6 (d, *J* = 7.9 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ -108.84.
FT-IR (neat film NaCl): 3330, 2967, 2927, 2852, 1731, 1702, 1590, 1523, 1405, 1367, 1315, 1234, 1159, 1054, 842 cm^{-1}.
HR-MS (ESI): Calculated for $[M]^+$ $C_{18}H_{24}FNO_2$: 305.1791; Measured: 305.1795.

***tert*-butyl(4-(cyclohexylidenefluoromethyl)phenyl)sulfane. (SI-37)**
To an oven dried 2 dram vial equipped with an oven dried stir bar was added 2-((4-(*tert*-butylthio)phenyl)(cyclohexylidene)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(SI-9)** (19.3 mg, 0.05 mmol, 1 equiv). To this was added the $TBABF_4$ (99.0 mg, 0.300 mmol, 6 equiv) and the TBAF•(H_2O) (79.0 mg, 0.25 mmol, 5 equiv). The electrodes [Pt(–)/C(+)] held in place by a septum cap were put in place. The vial was placed under a nitrogen atmosphere. Freshly distilled acetonitrile was added (2.5 mL). The solution was degassed by bubbling nitrogen with stirring (~400 rpm) for 20 minutes. After degassing the potentiostat (TACKLife MDC01 DC power supply) was connected to the electrodes and a constant working potential *vs.* a CHI-150 SCE electrode of +1.8 V (measured with a multimeter between the C(+) and reference CHI-50 SCE electrode) was applied for 15 minutes. Upon completion the applied potential was halted and the electrodes were removed from solution and rinsed with dichloromethane (3 x 4 mL). The resulting solution was concentrated *in vacuo* to yield a brown oil. The crude material was purified by flash column chromatography (100% hexanes→20% dichloromethane in hexanes) to give the resulting vinyl fluoride **(SI-37)** as a colorless oil (2.8 mg, 20% yield) as well as recovered the unreacted starting material **(SI-9)** (11.3 mg, 59% recovered s.m.).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 – 7.47 (m, 2H), 7.41 – 7.30 (m, 2H), 2.39 (d, *J* = 6.4 Hz, 2H), 2.24 (d, *J* = 6.1 Hz, 2H), 1.68 – 1.55 (m, 6H), 1.30 (s, 9H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 149.2 (d, *J* = 236.9 Hz), 136.9, 133.2 (d, *J* = 31.0 Hz), 132.8, 128.4 (d, *J* = 3.8 Hz), 119.4 (d, *J* = 16.9 Hz), 46.2, 30.9, 28.7 (d, *J* = 4.3 Hz), 27.5 (d, *J* = 2.2 Hz), 27.0, 26.4 (d, *J* = 7.9 Hz), 26.4.
^{19}F NMR (282 MHz, $CDCl_3$) δ -109.95.
FT-IR (neat film NaCl): 2962, 2927, 2854, 1447, 1393, 1363, 1291, 1214, 1164, 1042, 839 cm^{-1}.
HR-MS (EI-MS) m/z: [M]+ Calculated for $C_{17}H_{23}FS$: 278.1504; Measured: 278.1506.

4-(cyclohexylidenefluoromethyl)-1,2-dimethoxybenzene. (SI-38)

To an oven dried 2 dram vial equipped with an oven dried stir bar was added 2-(cyclohexylidene(3,4-dimethoxyphenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(SI-11)** (17.9 mg, 0.05 mmol, 1 equiv). To this was added the $TBABF_4$ (99.0 mg, 0.300 mmol, 6 equiv) and the TBAF•(H_2O) (79.0 mg, 0.25 mmol, 5 equiv). The electrodes [Pt(–)/C(+)] held in place by a septum cap were put in place. The vial was placed under a nitrogen atmosphere. Freshly distilled acetonitrile was added (2.5 mL). The solution was degassed by bubbling nitrogen with stirring (~400 rpm) for 20 minutes. After degassing the potentiostat (TACKLife MDC01 DC power supply) was connected to the electrodes and a constant working potential *vs.* a CHI-150 SCE electrode of +1.8 V (measured with a multimeter between the C(+) and reference CHI-50 SCE electrode) was applied for 15 minutes. Upon completion the applied potential was halted and the electrodes were removed from solution and rinsed with dichloromethane (3 x 4 mL). The resulting solution was concentrated *in vacuo* to yield a brown oil. The crude material was purified by flash column chromatography (15% diethyl ether in hexanes) to give the resulting vinyl fluoride **(SI-38)** as colorless oil (7.4 mg, 59% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00 – 6.89 (m, 2H), 6.85 (d, *J* = 8.2 Hz, 1H), 3.90 (s, 3H), 3.89 (s, 3H), 2.38 (t, *J* = 5.0 Hz, 2H), 2.21 (t, *J* = 5.8 Hz, 2H), 1.64 – 1.51 (m, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 149.0 (d, *J* = 237.9 Hz), 148.4 (d, *J* = 1.6 Hz), 125.7 (d, *J* = 31.4 Hz), 121.6 (d, *J* = 4.3 Hz), 117.6 (d, *J* = 17.8 Hz), 111.5 (d, *J* = 2.9 Hz), 110.4, 55.8, 28.8 (d, *J* = 4.2 Hz), 27.6 (d, *J* = 2.3 Hz), 27.0, 26.4, 26.3 (d, *J* = 7.7 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ -107.48.
FT-IR (neat film NaCl): 2928, 2852, 1604, 1513, 1463, 1447, 1409, 1256, 1233, 1169, 1140, 1027, 812 cm^{-1}.
HR-MS (EI-MS) m/z: [M]+ Calculated for $C_{15}H_{19}FO_2$: 250.1369; Measured: 250.1359.

2-(cyclohexylidenefluoromethyl)-1-methoxy-4-methylbenzene. (SI-39)
To an oven dried 2 dram vial equipped with an oven dried stir bar was added 2-(cyclohexylidene(2-methoxy-5-methylphenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(SI-12)** (17.1 mg, 0.05 mmol, 1 equiv). To this was added the $TBABF_4$ (99.0 mg, 0.300 mmol, 6 equiv) and the TBAF•(H_2O) (79.0 mg, 0.25 mmol, 5 equiv). The electrodes [Pt(–)/C(+)] held in place by a septum cap were put in place. The vial was placed under a nitrogen atmosphere. Freshly distilled acetonitrile was added (2.5 mL). The solution was degassed by bubbling nitrogen with stirring (~400 rpm) for 20 minutes. After degassing the potentiostat (TACKLife MDC01 DC power supply) was connected to the electrodes and a constant working potential *vs.* a CHI-150 SCE electrode of +1.8 V (measured with a multimeter between the C(+) and reference CHI-50 SCE electrode) was applied for 15 minutes. Upon completion the applied potential was halted and the electrodes were removed from solution and rinsed with dichloromethane (3 x 4 mL). The resulting solution was concentrated *in vacuo* to yield a brown oil. The crude material was

purified by flash column chromatography (20% dichloromethane in hexanes) to give the resulting vinyl fluoride **(SI-39)** as colorless oil (5.7 mg, 47% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.5 Hz, 1H), 7.05 (s, 1H), 6.82 (d, *J* = 8.3 Hz, 1H), 3.81 (s, 3H), 2.46 – 2.32 (m, 2H), 2.29 (s, 3H), 1.93 (t, *J* = 5.6 Hz, 2H), 1.65 – 1.46 (m, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 155.8, 147.3 (d, *J* = 239.3 Hz), 132.4 (d, *J* = 2.0 Hz), 131.0 (d, *J* = 2.4 Hz), 129.7, 122.0 (d, *J* = 29.1 Hz), 119.6 (d, *J* = 17.2 Hz), 111.5, 56.1, 29.3 (d, *J* = 3.9 Hz), 27.8 (d, *J* = 2.4 Hz), 27.3, 26.8, 26.3 (d, *J* = 6.7 Hz), 20.7.
^{19}F NMR (282 MHz, $CDCl_3$) δ -107.18.
FT-IR (neat film NaCl): 2926, 2852, 1501, 1463, 1448, 1273, 1251, 1147, 1112, 1040, 807 cm^{-1}.
HR-MS (EI-MS) m/z: [M]+ Calculated for $C_{15}H_{19}FO$: 234.1419; Measured: 234.1420.

4,4',4''-(2-fluoroethene-1,1,2-triyl)tris(methoxybenzene). (SI-40)
To an oven dried 2 dram vial equipped with an oven dried stir bar was added **4**,4,5,5-tetramethyl-2-(1,2,2-tris(4-methoxyphenyl)vinyl)-1,3,2-dioxaborolane **(SI-16)** (23.6 mg, 0.05 mmol, 1 equiv). To this was added the $TBABF_4$ (99.0 mg, 0.300 mmol, 6 equiv) and the TBAF•(H_2O) (79.0 mg, 0.25 mmol, 5 equiv). The electrodes [Pt(–)/C(+)] held in place by a septum cap were put in place. The vial was placed under a nitrogen atmosphere. Freshly distilled acetonitrile was added (2.5 mL). The solution was degassed by bubbling nitrogen with stirring (~400 rpm) for 20 minutes. After degassing the potentiostat (TACKLife MDC01 DC power supply) was connected to the electrodes and a constant working potential *vs.* a CHI-150 SCE electrode of +1.8 V (measured with a multimeter between the C(+) and reference CHI-50 SCE electrode) was applied for 15 minutes. Upon completion the applied potential was halted and the electrodes were removed from solution and rinsed with dichloromethane (3 x 4 mL). The resulting solution was concentrated *in vacuo* to yield a brown oil. The crude material was purified by flash column chromatography (5% acetone in hexanes) to give the resulting vinyl fluoride **(SI-40)** as a yellow solid (10.9 mg, 60% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 2H), 7.17 (d, *J* = 8.9 Hz, 2H), 7.05 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 6.74 – 6.67 (m, 2H), 3.82 (s, 3H), 3.80 (s, 3H), 3.77 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.6, 159.0, 158.8, 153.4 (d, *J* = 249.5 Hz), 132.5 (d, *J* = 3.2 Hz), 132.0 (d, *J* = 7.4 Hz), 131.6, 131.4 (d, *J* = 4.8 Hz), 130.0 (d, *J* = 6.1 Hz), 126.2 (d, *J* = 29.6 Hz), 120.2 (d, *J* = 18.7 Hz), 114.2, 113.7, 113.6, 55.5, 55.5.
^{19}F NMR (282 MHz, $CDCl_3$) δ -104.48.
FT-IR (neat film NaCl): 2002, 2932, 2836, 1738, 1607, 1512, 1462, 1365, 1297, 1247, 1175, 1033, 831 cm^{-1}.
HR-MS (EI-MS) m/z: [M]+ Calculated for $C_{23}H_{21}FO_3$: 364.1474; Measured: 364.1475.
Melting Point: 78–80 ºC

1-(2-butyl-1-fluorohex-1-en-1-yl)-4-methoxybenzene (SI-41)

To an oven dried 2 dram vial equipped with an oven dried stir bar was added 2-(2-butyl-1-(4-methoxyphenyl)hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(SI-19)** (18.6 mg, 0.05 mmol, 1 equiv). To this was added the $TBABF_4$ (99.0 mg, 0.300 mmol, 6 equiv) and the TBAF•(H_2O) (79.0 mg, 0.25 mmol, 5 equiv). The electrodes [Pt(–)/C(+)] held in place by a septum cap were put in place. The vial was placed under a nitrogen atmosphere. Freshly distilled acetonitrile was added (2.5 mL). The solution was degassed by bubbling nitrogen with stirring (~400 rpm) for 20 minutes. After degassing the potentiostat (TACKLife MDC01 DC power supply) was connected to the electrodes and a constant working potential *vs.* a CHI-150 SCE electrode of +1.8 V (measured with a multimeter between the C(+) and reference CHI-50 SCE electrode) was applied for 15 minutes, or until the starting material was consumed. Upon completion the applied potential was halted and the electrodes were removed from solution and rinsed with dichloromethane (3 x 4 mL). The resulting solution was concentrated *in vacuo* to yield a brown oil. The crude material was purified by flash column chromatography (100% hexanes→30% dichloromethane in hexanes) to give the resulting vinyl fluoride **(SI-41)** as a colorless oil (9.5 mg, 72% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2H), 7.04 – 6.82 (m, 2H), 3.83 (s, 3H), 2.35 – 2.13 (m, 2H), 2.11 – 1.92 (m, 2H), 1.52 – 1.32 (m, 6H), 1.27 (q, *J* = 7.2 Hz, 2H), 0.94 (t, *J* = 7.1 Hz, 3H), 0.86 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4, 152.6 (d, *J* = 238.5 Hz), 129.7 (d, *J* = 3.8 Hz), 125.9 (d, *J* = 31.5 Hz), 118.6 (d, *J* = 17.2 Hz), 113.4, 55.2, 30.5 (d, *J* = 3.1 Hz), 30.2, 29.5 (d, *J* = 4.3 Hz), 27.3, 27.2, 22.6, 14.0.
^{19}F NMR (282 MHz, $CDCl_3$) δ -103.34.
FT-IR (neat film NaCl): 2956, 2927, 2858, 1726, 1681, 1610, 1512, 1464, 1378, 1301, 1250, 1175, 1108, 1033, 834 cm^{-1}.
HR-MS (EI-MS) m/z: [M]+ Calculated for $C_{17}H_{25}FO$: 264.1889; Measured: 264.1901.

1-(2-butyl-1-fluorohex-1-en-1-yl)-2,4-dimethylbenzene (SI-42)

To an oven dried 2 dram vial equipped with an oven dried stir bar was added 2-(2-butyl-1-(2,4-dimethylphenyl)hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(SI-20)** (18.5 mg, 0.05 mmol, 1 equiv). To this was added the $TBABF_4$ (99.0 mg, 0.300 mmol, 6 equiv) and the TBAF•(H_2O) (79.0 mg, 0.25 mmol, 5 equiv). The electrodes [Pt(–)/C(+)] held in place by a septum cap were put in place. The vial was placed under a nitrogen atmosphere. Freshly distilled acetonitrile was added (2.5 mL). The solution was degassed by bubbling nitrogen with stirring (~400 rpm) for 20 minutes. After degassing the potentiostat (TACKLife MDC01 DC power supply) was connected to the electrodes and a constant working potential *vs.* a CHI-150 SCE electrode of +1.8 V (measured with a multimeter between the C(+) and reference CHI-50 SCE electrode) was applied for 15 minutes, or until the starting material was consumed. Upon completion the applied potential was halted and the electrodes were removed from solution and rinsed with dichloromethane (3 x 4 mL). The resulting solution was concentrated *in vacuo* to yield a brown oil. The crude material was purified by flash column chromatography (100% hexanes) to give the resulting vinyl fluoride **(SI-42)** as a colorless oil (7.2 mg, 55% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (d, J = 8.0 Hz, 1H), 7.04 (s, 1H), 6.97 (d, J = 7.6 Hz, 1H), 2.33 (s, 3H), 2.27 (d, J = 2.4 Hz, 3H), 2.24 (d, J = 6.8 Hz, 2H), 1.82 (t, J = 7.8 Hz, 2H), 1.47 (q, J = 7.7 Hz, 2H), 1.39 (dt, J = 15.0, 7.5 Hz, 2H), 1.31 (p, J = 7.5 Hz, 2H), 1.17 (h, J = 7.4 Hz, 2H), 1.01 – 0.89 (m, 3H), 0.85 – 0.73 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.6 (d, J = 242.2 Hz), 138.7 (d, J = 2.9 Hz), 137.7, 130.8, 130.4, 129.9 (d, J = 28.0 Hz), 126.0, 119.3 (d, J = 15.9 Hz), 114.9, 30.1 (d, J = 3.0 Hz), 29.6 (d, J = 5.5 Hz), 29.1 (d, J = 3.7 Hz), 26.3 (d, J = 5.9 Hz), 22.6, 22.4, 21.2, 19.4, 14.0, 13.9.

^{19}F NMR (282 MHz, $CDCl_3$) δ -100.07.

FT-IR (neat film NaCl): 2956, 2926, 2859, 1737, 1693, 1498, 1458, 1378, 1349, 1288, 1261, 1121, 1034 cm^{-1}.

HR-MS (EI-MS) m/z: [M]+ Calculated for $C_{18}H_{27}F$: 262.2096; Measured: 262.2097.

5-(cyclopentylidenefluoromethyl)-2,2-dimethylbenzo[*d*][1,3]dioxole (SI-43)

To an oven dried 2 dram vial equipped with an oven dried stir bar was added 2-(cyclopentylidene(2,2-dimethylbenzo[*d*][1,3]dioxol-5-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(SI-22)** (17.8 mg, 0.05 mmol, 1 equiv). To this was added the $TBABF_4$ (99.0 mg, 0.300 mmol, 6 equiv) and the TBAF•(H_2O) (79.0 mg, 0.25 mmol, 5 equiv). The electrodes [Pt(–)/C(+)] held in place by a septum cap were put in place. The

vial was placed under a nitrogen atmosphere. Freshly distilled acetonitrile was added (2.5 mL). The solution was degassed by bubbling nitrogen with stirring (~400 rpm) for 20 minutes. After degassing the potentiostat (TACKLife MDC01 DC power supply) was connected to the electrodes and a constant working potential *vs.* a CHI-150 SCE electrode of +1.8 V (measured with a multimeter between the C(+) and reference CHI-50 SCE electrode) was applied for 15 minutes, or until the starting material was consumed. Upon completion the applied potential was halted and the electrodes were removed from solution and rinsed with dichloromethane (3 x 4 mL). The resulting solution was concentrated *in vacuo* to yield a brown oil. The crude material was purified by flash column chromatography (1%DCM:hexanes + 0.1% triethylamine on triethylamine deactivated silica gel) to give the resulting vinyl fluoride **(SI-43)** as a yellow oil (8.3 mg, 68% yield). This material was sensitive to mild acids, and decomposition was observed in $CDCl_3$. The NMR spectra are reported in $(CD_3)_2CO$.

^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 6.95 (dd, *J* = 8.2, 1.8 Hz, 1H), 6.87 (d, *J* = 1.8 Hz, 1H), 6.79 (dt, *J* = 8.2, 0.6 Hz, 1H), 2.49 (dt, *J* = 6.9, 3.5 Hz, 4H), 1.76 – 1.67 (m, 4H), 1.66 (s, 6H).

^{13}C NMR (126 MHz, $(CD_3)_2CO$) δ 148.8 (d, *J* = 232.5 Hz), 147.0 (d, *J* = 47.4 Hz), 126.8 (d, *J* = 30.9 Hz), 121.5, 120.3 (d, *J* = 21.6 Hz), 119.2 (d, *J* = 7.4 Hz), 118.0, 107.5, 105.5 (d, *J* = 7.2 Hz), 33.5, 33.1, 29.8 (d, *J* = 4.6 Hz), 27.1, 25.3, 24.7.

^{19}F NMR (282 MHz, $(CD_3)_2CO$) δ -105.33.

FT-IR (neat film NaCl): 2980, 2853, 1698, 1495, 1446, 1384, 1359, 1259, 1243, 1151, 1016, 804 cm^{-1}.

HR-MS (EI-MS) m/z: [M]+ Calculated for $C_{15}H_{17}FO_2$: 248.1212; Measured: 248.1213.

***tert*-butyl (4-(cyclopentylidenefluoromethyl)phenyl)(methyl)carbamate (SI-44)**

To an oven dried 2 dram vial equipped with an oven dried stir bar was added 2 *tert*-butyl (4-(cyclopentylidene(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)phenyl)(methyl)carbamate (**SI-23**) (20.6 mg, 0.05 mmol, 1 equiv). To this was added the $TBABF_4$ (99.0 mg, 0.300 mmol, 6 equiv) and the TBAF•(H_2O) (79.0 mg, 0.25 mmol, 5 equiv). The electrodes [Pt(–)/C(+)] held in place by a septum cap were put in place. The vial was placed under a nitrogen atmosphere. Freshly distilled acetonitrile was added (2.5 mL). The solution was degassed by bubbling nitrogen with stirring (~400 rpm) for 20 minutes. After degassing the potentiostat (TACKLife MDC01 DC power supply) was connected to the electrodes and a constant working potential *vs.* a CHI-150 SCE electrode of +1.8 V (measured with a multimeter between the C(+) and reference CHI-50 SCE electrode) was applied for 15 minutes. Upon completion the applied potential was halted and the electrodes were removed from solution and rinsed with dichloromethane (3 x 4 mL). The resulting solution was concentrated *in vacuo* to yield a

brown oil. The crude material was purified by flash column chromatography (70% dichloromethane:hexanes) to give the resulting vinyl fluoride **(SI-44)** as a colorless oil (7.9 mg, 52% yield). 4.0 mg of **SI-22** was also recovered.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.7 Hz, 2H), 7.24 (d, *J* = 8.7 Hz, 2H), 3.27 (s, 3H), 2.66 – 2.43 (m, 4H), 1.85 – 1.61 (m, 2H), 1.46 (s, 9H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 154.9, 149.2 (d, *J* = 232.9 Hz), 143.2, 130.8 (d, *J* = 30.4 Hz), 126.2 (d, *J* = 6.9 Hz), 125.1, 123.0 (d, *J* = 21.5 Hz), 80.8, 37.4, 30.8 (d, *J* = 4.6 Hz), 29.8 (d, *J* = 4.6 Hz), 28.6, 28.0, 26.1.
^{19}F NMR (282 MHz, $CDCl_3$) δ -110.47.
FT-IR (neat film NaCl): 2957, 2928, 2868, 1703, 1608, 1513, 1477, 1366, 1355, 1285, 1152, 1110, 1054, 11013, 840 cm^{-1}.
HR-MS (EI-MS) m/z: [M]+ Calculated for $C_{18}H_{24}FNO_2$: 305.1791; Measured: 305.1805.

4-(cyclopentylidenefluoromethyl)-*N*-methylaniline (SI-45)
To an oven dried 2 dram vial equipped with an oven dried stir bar was added 2-(cyclopentylidene(2,2-dimethylbenzo[*d*][1,3]dioxol-5-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(SI-22)** (17.8 mg, 0.05 mmol, 1 equiv). To this was added the $TBABF_4$ (99.0 mg, 0.300 mmol, 6 equiv) and the TBAF•(H_2O) (79.0 mg, 0.25 mmol, 5 equiv). The electrodes [Pt(–)/C(+)] held in place by a septum cap were put in place. The vial was placed under a nitrogen atmosphere. Freshly distilled acetonitrile was added (2.5 mL). The solution was degassed by bubbling nitrogen with stirring (~400 rpm) for 20 minutes. After degassing the potentiostat (TACKLife MDC01 DC power supply) was connected to the electrodes and a constant working potential *vs.* a CHI-150 SCE electrode of +0.8 V (measured with a multimeter between the C(+) and reference CHI-50 SCE electrode) was applied for 15 minutes, or until the starting material was consumed. Upon completion the applied potential was halted and the electrodes were removed from solution and rinsed with dichloromethane (3 x 4 mL). The resulting solution was concentrated *in vacuo* to yield a brown oil. The crude material was purified by flash column chromatography (100% hexanes→6% ether:hexanes) to give the resulting vinyl fluoride **(SI-44)** as a yellow oil (4.7mg, 45% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.7 Hz, 2H), 6.60 (d, *J* = 8.4 Hz, 2H), 2.86 (s, 3H), 2.58 – 2.43 (m, 4H), 1.80 – 1.62 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 150.0 (d, *J* = 232.7 Hz), 148.9, 127.3 (d, *J* = 6.6 Hz), 123.2 (d, *J* = 30.6 Hz), 119.2 (d, *J* = 22.3 Hz), 112.1, 30.9, 30.6 (d, *J* = 4.9 Hz), 29.5 (d, *J* = 4.4 Hz), 28.0, 26.3.
^{19}F NMR (282 MHz, $CDCl_3$) δ -109.47.
FT-IR (neat film NaCl): 3417, 2954, 2868, 2890, 2816, 1680, 1613, 1523, 1318, 1261, 1189, 1046, 952, 824 cm^{-1}.
HR-MS (EI-MS) m/z: [M]+ Calculated for $C_{13}H_{10}FN$: 205.1266; Measured: 205.1267.

3.2 Mass Balance, Observed Byproducts, and Unsuccessful Substrates

Initial optimization of the electrochemical fluorination with **SI-13** revealed ~18% total yield (by ^{1}HNMR) of the following ketone **cyclohexyl(4-methoxyphenyl)methanone (SI-46)** (16% yield) and enone **cyclohex-1-en-1-yl(4-methoxyphenyl)methanone (SI-47)** (~3% yield)**.** These were further purified from the reaction mixture as previously described using flash column chromatography (50% → 80% dichloromethane in hexanes). The resultant ^{1}HNMR spectra were consistent with those reported in the literature.[13,14] Running the reaction at both 0 and –20 ºC did not increase the yield, and these water trapping products were still observed. Higher temperatures resulted in some protodeboronation to form the styrene.

(SI-46) **(SI-47)**

Additionally, initial reactions in dichloromethane solvent yielded **1-(chloro(cyclohexylidene)methyl)-4-methoxybenzene (SI-48)** as well as the desired vinyl fluoride. This could be synthesized by substituting the TBAF with TBACl.

1-(chloro(cyclohexylidene)methyl)-4-methoxybenzene. (SI-48)

To an oven dried 2 dram vial equipped with an oven dried stir bar was added 2-(cyclohexylidene(4-methoxyphenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(SI-3)** (16.4 mg, 0.05 mmol, 1 equiv). To this was added the $TBABF_4$ (99.0 mg, 0.300 mmol, 6 equiv) and the TBACl (79.0 mg, 0.35 mmol, 7 equiv). The electrodes [Pt(–)/C(+)] held in place by a septum cap were put in place. The vial was placed under a nitrogen atmosphere. Freshly distilled acetonitrile was added (2.5 mL). The solution was degassed by bubbling nitrogen with stirring (~400 rpm) for 20 minutes. After degassing the potentiostat (TACKLife MDC01 DC power supply) was connected to the electrodes and a constant working potential *vs.* a CHI-150 SCE electrode of +1.8 V (measured with a multimeter between the C(+) and reference CHI-50 SCE electrode) was applied for 25 minutes. Upon completion the applied potential was halted and the electrodes were removed from solution and rinsed with dichloromethane (3 x 4 mL). The resulting solution was concentrated *in vacuo* to yield a brown oil. The crude material was purified by flash column chromatography (50% dichloromethane in hexanes) to give the resulting vinyl chloride **(SI-48)** as a colorless oil (8.0 mg, 68% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 3.82 (s, 3H), 2.52 (dd, J = 7.0, 5.3 Hz, 2H), 2.15 (dd, J = 7.0, 5.2 Hz, 2H), 1.78 – 1.43 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.3, 137.7, 132.0, 130.8, 122.9, 113.8, 55.6, 32.3, 32.2, 28.2, 27.5, 26.6.

FT-IR (neat film NaCl): 2927, 2852, 1606, 1508, 1442, 1293, 1243, 1173, 1034, 831, 800cm^{-1}.
HR-MS (EI-MS) m/z: [M]+ Calculated for $C_{14}H_{17}ClO$: 236.0967; Measured: 236.0968.

1-(bromo(cyclohexylidene)methyl)-4-methoxybenzene. (SI-49)
To an oven dried 2 dram vial equipped with an oven dried stir bar was added (cyclohexylidene(4-methoxyphenyl)methyl)trifluoro-λ^4-borane, potassium salt (**SI-25)** (15.4 mg, 0.05 mmol, 1 equiv). To this was added the TBABr (97.0 mg, 0.300 mmol, 6 equiv). The electrodes [Pt(–)/C(+)] held in place by a septum cap were put in place. The vial was placed under a nitrogen atmosphere. Freshly distilled acetonitrile was added (2.5 mL). The solution was degassed by bubbling nitrogen with stirring (~400 rpm) for 20 minutes. After degassing the potentiostat (TACKLife MDC01 DC power supply) was connected to the electrodes and a constant working potential *vs.* a CHI-150 SCE electrode of +1.8 V (measured with a multimeter between the C(+) and reference CHI-50 SCE electrode) was applied for 15 minutes. Upon completion the applied potential was halted and the electrodes were removed from solution and rinsed with dichloromethane (3 x 4 mL). The resulting solution was concentrated *in vacuo* to yield a brown oil. The crude material was purified by flash column chromatography (50% dichloromethane in hexanes) to give the resulting vinyl bromide **(SI-49)** as a colorless oil (8.0 mg, 57% yield). ^{1}H NMR data were in matched those reported in the literature.[15]

Electrolysis of **SI-28, SI-29,** and **SI-29.1** yielded no desired product even at higher applied voltages. Presumably the ease of oxidation of the alkenyl boronates and the correct substitution pattern to form a stabilized vinyl carbocation are important for this transformation.

4. Mechanistic Studies

4.1 ^{11}B NMR TBAF titration

To a flame dried 1 dram vial equipped with a stir bar was added 2-(cyclohexylidene(4-methoxyphenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(SI-3)** (3.3 mg, 0.01 mmol, 1 equiv). To this was added a freshly distilled acetonitrile (0.4 mL, 0.3 mL, or 0.2 mL). To this was added a freshly prepared (0.1M) solution of TBAF•(H_2O) (0.1 mL, 0.2 mL, or 0.3 mL). Each solution was stirred for 5 minutes, and then transferred to an oven dried NMR tube for analysis. The resulting spectra were observed, the free boronic ester is the peak on the left ~33ppm while the proposed borate is depicted on the right around ~8ppm. Full consumption of the boronic ester was observed at 3 equiv of TBAF.

4.2 Cyclic Voltammetry of Vinyl Trifluoroborate SI-25

Cyclic voltammetry was performed under nitrogen with a Gamry Instruments Interface 1000-E potentiostat. $TBABF_4$ and **SI-25** (noted as $TBABF_3$ in voltammogram below) were dried under vacuum overnight prior to any testing. Freshly distilled acetonitrile (over CaH_2) was used. Each solution was degassed with nitrogen for 20 minutes before any potential was applied. A platinum (Pt) S6 wire was used as the counter electrode and a Ag+/Ag wire was used as the pseudo-reference electrode equipped with a glass frit. A 3 mm diameter glassy carbon working electrode was used. Voltammograms were recorded at 100mV/s. The reported data are after iR correction. Cyclic voltammograms of ferrocene were also conducted to calibrate the potentials of the Ag+/Ag pseudo-reference electrode, based on the reported standard potential of ferrocene (conversion to SCE was performed by adding +0.380V).[16]

Cyclic voltammogram of **SI-25**. Oxidative events at +1.12 and +1.56 V *vs* SCE.

<u>Additionally cyclic voltammetry was performed on the tetrabutylammonium salt of **SI-13**.</u>

Oxidative events were observed at +1.42 and +1.90 V *vs*. SCE. These higher potentials indicate the difficulty performing the second oxidation is likely why no vinyl fluoride products were observed. At higher applied potentials to reach this second oxidation, deleterious side reactions occurred yielding intractable mixtures of products.

4.3 Elimination Reaction of Disubstituted Vinyl Boronic Ester

Alkyne **(SI-50)** can be produced from the E1 elimination of a putative intermediate vinyl carbocation.

1-ethynyl-4-methoxybenzene. (SI-50)

To an oven dried 2 dram vial equipped with an oven dried stir bar was added 2-(1-(4-methoxyphenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**SI-27**) (13.0 mg, 0.05 mmol, 1 equiv). To this was added the $TBABF_4$ (99.0 mg, 0.300 mmol, 6 equiv) and the TBAF•(H_2O) (79.0 mg, 0.25 mmol, 5 equiv). The electrodes [Pt(–)/C(+)] held in place by a septum cap were put in place. The vial was placed under a nitrogen atmosphere. Freshly distilled acetonitrile was added (2.5 mL). The solution was degassed by bubbling nitrogen with stirring (~400 rpm) for 20 minutes. After degassing the potentiostat (TACKLife MDC01 DC power supply) was connected to the electrodes and a constant working potential *vs.* a CHI-150 SCE electrode of +1.8 V (measured with a multimeter between the C(+) and reference CHI-50 SCE electrode) was applied for 15 minutes. Upon completion the applied potential was halted and the electrodes were removed from solution and rinsed with dichloromethane (3 x 4 mL). The resulting solution was concentrated *in vacuo* to yield a brown oil. The crude material was purified by flash column chromatography (5% acetone in hexanes) to give the resulting alkyne **(SI-40)** as a colorless oil (2.8 mg, 43% yield). The ^{1}H NMR spectrum was in agreement with the reported specta.[17]

Additionally, **1-(1-fluorovinyl)-4-methoxybenzene (SI-51)** was prepared according to known methods, and matched the reported ^{1}H NMR spectra.[18] This was further subjected to the above reaction conditions, and full recovery of the starting material was observed by an added internal ^{1}H NMR standard.

1-(1-fluorovinyl)-4-methoxybenzene (SI-51)

1-methoxy-4-(prop-1-yn-1-yl)benzene (SI-51.1)
The same procedure was followed as above yielding alkyne SI-51.1

To an oven dried 2 dram vial equipped with an oven dried stir bar was added (*Z*)-2-(1-(4-methoxyphenyl)prop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14.0 mg, 0.05 mmol, 1 equiv). To this was added the $TBABF_4$ (99.0 mg, 0.300 mmol, 6 equiv) and the TBAF•(H_2O) (79.0 mg, 0.25 mmol, 5 equiv). The electrodes [Pt(–)/C(+)] held in place by a septum cap were put in place. The vial was placed under a nitrogen atmosphere. Freshly distilled acetonitrile was added (3.0 mL). The solution was degassed by bubbling nitrogen with stirring (~400 rpm) for 20 minutes. After degassing the potentiostat (TACKLife MDC01 DC power supply) was connected to the electrodes and a constant working potential *vs.* a CHI-150 SCE electrode of +1.8 V (measured with a multimeter between the C(+) and reference CHI-50 SCE electrode) was applied for 15 minutes. Upon completion the applied potential was halted and the electrodes were removed from solution and rinsed with dichloromethane (3 x 4 mL). The resulting solution was concentrated *in vacuo* to yield a brown oil. The crude material was purified by flash column chromatography (2% ether in hexanes) to give the resulting alkyne **(SI-51.1)** as a colorless oil (4.5 mg, 62% yield). The ^{1}H NMR spectrum was in agreement with the reported specta.[17]

4.4 Friedel-Crafts Reaction with N-Me Pyrrole

Additional evidence supporting the intermediacy of a vinyl cation is the Friedel-Crafts reactivity with N-Me pyrrole to produce **2-(cyclohexylidene(4-methoxyphenyl)methyl)-1-methyl-1*H*-pyrrole (SI-52)** and **3-(cyclohexylidene(4-methoxyphenyl)methyl)-1-methyl-1*H*-pyrrole (SI-53)**.

(SI-52)

(SI-53)

To an oven dried 2 dram vial equipped with an oven dried stir bar was added (cyclohexylidene(4-methoxyphenyl)methyl)trifluoro-λ^4-borane, potassium salt **(SI-25)** (15.4 mg, 0.05 mmol, 1 equiv). To this was added the $TBABF_4$ (99.0 mg, 0.300 mmol, 6 equiv) and water (15 uL, 15 equiv). The electrodes [Pt(–)/C(+)] held in place by a septum cap were put in place. The vial was placed under a nitrogen atmosphere. Freshly distilled acetonitrile was added (2.5 mL) followed by N-Me pyrrole (41 mg, 0.50 mmol, 10 equiv). The solution was degassed by bubbling nitrogen with stirring (~400 rpm) for 20 minutes. After degassing the potentiostat (TACKLife MDC01 DC power supply) was connected to the electrodes and a constant working potential *vs.* a CHI-150 SCE electrode of +1.8 V (measured with a multimeter between the C(+) and reference CHI-50 SCE electrode) was applied for 15 minutes. Upon completion the applied potential was halted and the electrodes were removed from solution and rinsed with dichloromethane (3 x 4 mL). The resulting solution was concentrated *in vacuo* to yield a brown oil. The crude material was purified by flash column chromatography (2% diethyl ether in hexanes) to give the resulting Friedel-Crafts products **(SI-52)** and **(SI-53)** as colorless oils (6.8 mg, 48% combined yield, 2.7:1 ratio). Analytical samples of each were obtained by further flash column chromatography (100% hexanes → 2% diethyl ether in hexanes).

(SI-52) Characterization Data:
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 6.53 (dd, *J* = 2.7, 1.8 Hz, 1H), 6.10 (dd, *J* = 3.5, 2.7 Hz, 1H), 5.99 (dd, *J* = 3.5, 1.8 Hz, 1H), 3.78 (s, 3H), 3.21 (s, 3H), 2.34 (bs, 2H), 2.23 (t, *J* = 5.6 Hz, 2H), 1.60 (bs, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 158.1, 143.6, 134.5, 134.1, 131.0, 125.4, 121.4, 113.5, 108.9, 106.9, 55.5, 34.5, 33.7, 32.1, 29.0, 29.0, 27.1.
FT-IR (neat film NaCl): 2923, 2850, 1605, 1507, 1447, 1290, 1244, 1174, 1036, 833 cm^{-1}.
HR-MS (ESI): [M]+ Calculated for $C_{19}H_{23}NO$: 281.1779; Measured: 281.1780.

(SI-53) Characterization Data:
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 6.48 (t, *J* = 2.5 Hz, 1H), 6.25 (t, *J* = 2.0 Hz, 1H), 5.95 (dd, *J* = 2.7, 1.7 Hz, 1H), 3.80 (s, 3H), 3.57 (s, 3H), 2.53 (s, 2H), 2.27 – 1.95 (m, 2H), 1.81 – 1.48 (m, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 157.9, 137.4, 136.6, 131.0, 128.1, 126.3, 121.9, 121.1, 113.3, 110.3, 55.5, 36.4, 33.1, 32.5, 29.0, 28.8, 27.3.
FT-IR (neat film NaCl): 2921, 2851, 1606, 1507, 1463, 1289, 1242, 1159, 1102, 1037, 830, 799 cm^{-1}.
HR-MS (ESI): [M]+ Calculated for $C_{19}H_{23}NO$: 281.1779; Measured: 281.1771.

4.5 C–H Insertion Reactivity

In order to probe for C–H insertion reactivity without halide nucleophilic attack, trifluoroborate salt of **SI-30** was oxidized electrochemically in a divided cell according to the following procedure.

To both cells of an oven dried divided cell (fine glass frit) with an oven dried stir bar in each half-cell was added freshly dried under P_2O_5 $TBABF_4$ (395 mg, 1.20 mmol, 24 equiv) as the electrolyte (increased concentration of electrolyte was used due to the increased resistance of the divided cell). To each half-cell was added freshly distilled acetonitrile (3.0 mL). To the cathodic side was added water (20uL, 1.1 mmol, 22 equiv). To the anodic side was added (2-butyl-1-(2,4-dimethylphenyl)hex-1-en-1-yl)trifluoro-λ^4-borane, potassium salt **(SI-30)** (17.5 mg, 0.050 mmol, 1 equiv). To the cathodic side was quickly placed the platinum electrode. To the anodic side was quickly placed the carbon electrode. Each solution was degassed by bubbling nitrogen with stirring (~300 rpm) for 20 minutes. After degassing the potentiostat (TACKLife MDC01 DC power supply) was connected to the electrodes and a cell potential of 3.5V was applied (enough potential to observe 1-2 mA of current) for 1 hour. After electrolysis was halted, a small aliquot from the anodic chamber (~20 uL) was taken, diluted with hexanes and water (1 mL hexanes:0.25mL water). The hexanes layer was analyzed by GC-FID (indicating a 5.5:1 ratio of desired product). The anode was rinsed with dichloromethane (3 x 4 mL) into the anodic solution, and the solution was concentrated to yield a yellow oil. This yellow oil was plugged through silica gel with diethyl ether. The diethyl ether was concentrated, and analyzed by ^{1}H NMR with added 2.5uL of nitromethane as an internal standard (indicating a 12% yield of desired product). The ratio of these olefin isomers was further confirmed by GC-FID. Attempts to purify the mixture by chromatography failed, and so standards of the olefinic products were synthesized.

Additionally subjection of a mixture of **SI-56** and **SI-57** to the reaction mixtures showed ~65% consumption of the material (10 mg of the mixture/0.04 mmol). 1.25 uL of nitromethane was added as an internal standard indicating ~35% remaining material. (see spectrum below).

Crude 1H NMR indicating 12% NMR yield. (protons at 2.8–2.9 ppm correspond to tertiary allylic protons of **SI-56** and **SI-57**.

GC-FID Trace of pure **SI-56** (top) and **SI-57** (middle) and crude reaction (bottom).

Crude 1H NMR with added 1.25uL of nitromethane as an internal standard of resubjected **(SI-57)** and **(SI-58)** to the reaction conditions after 15 minutes, indicating ~35% remaining starting material.

Additionally two control experiments were performed. The previous procedure for the divided cell electrolysis of **SI-30** were replicated with the addition of 15uL of nonane as an internal standard to the anodic chamber. The solution was prestirred for 30 minutes after degassing and no production of **SI-57** and **SI-58** was observed (See GC-FID trace below). Then electrolysis was performed for 1 hour (See GC-FID below). To show that this process is promoted only by electrolysis and not BF_3 generated during the reaction an additional 0.05 mmol of **SI-30** was added to the cathodic chamber after electrolysis was halted. This solution was stirred for an additional 2 hours, and the ratio of **SI-57** and **SI-58** remained unchanged relative to the added nonane internal standard (See GC-FID trace below)

Top GC-FID trace: aliquot after stirring for 30 minutes after degassing
2nd to top GC-FID trace: aliquot after electrolysis for 1 hour
2nd to bottom GC-FID trace: aliquot after addition of more starting material and stirring for 2 hours.
Bottom GC-FID trace: diethyl ether blank (peak at 6.37 is the BHT stabilizer present in commercial samples of diethyl ether)

General scheme for synthesis of authentic C–H insertion products:

2-butyl-1-(2,4-dimethylphenyl)hexan-1-one (SI-54)

To a 20 mL scintillation vial containing 2-(2-butyl-1-(2,4-dimethylphenyl)hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(SI-20)** (345 mg, 0.93 mmol, 1 equiv) and a stir bar was added acetone (4.1 mL) followed by an aqueous solution of sodium perborate

tetrahydrate (2.6 mL, 0.9 M, 2.5 equiv). This solution was stirred vigorously (~1300 rpm) for 18 hours. (the reaction was carefully monitored for consumption of the s.m. by TLC 10% ether:hexanes to produce a more non-polar spot). The reaction was concentrated *in vacuo* and purified by flash column chromatography (100% hexanes→ 2% ether:hexanes) to yield **SI-54** as a colorless oil (200 mg, 82% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.3 Hz, 2H), 7.10 – 6.85 (m, 2H), 3.22 (tt, *J* = 7.7, 5.5 Hz, 1H), 2.45 (s, 3H), 2.35 (s, 3H), 1.71 (dq, *J* = 13.1, 7.4 Hz, 2H), 1.51 – 1.36 (m, 2H), 1.35 – 1.20 (m, 8H), 0.85 (t, *J* = 6.8 Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 208.6, 141.6, 138.7, 136.7, 128.7, 126.4, 49.3, 32.2, 30.1, 23.2, 21.6, 21.4, 14.3.
FT-IR (neat film NaCl): 2956, 2928, 2859, 1680, 1612, 1566, 1456, 1378, 1349, 1286, 1225, 1205, 1145, 1035, 972, 950, 857, 818 cm^{-1}.
HR-MS (ESI): [M+H]+ Calculated for $C_{18}H_{29}O$: 261.2218; Measured: 261.2220.

2-butyl-1-(2,4-dimethylphenyl)hex-1-en-1-yl 4-methylbenzenesulfonate (SI-55)
To a flamed dried schlenk flask equipped with a stir bar was added lithium hexamethyldisilazide (257 mg, 1.54 mmol, 2.0 equiv) and dry toluene (1 mL). To this was added dry N,N-dimethylethylamine (166 uL, 1.54 mmol, 2.0 equiv). This solution was placed in a room temperature water bath, and to it was added dropwise a solution of 2-butyl-1-(2,4-dimethylphenyl)hexan-1-one **(SI-54)** (200 mg, 0.77 mmol, 1 equiv) in toluene (4 mL). This solution was allowed to stir for 20 minutes at room temperature, and to it was added toluenesulfonic anhydride (501 mg, 1.54 mmol, 2.0 equiv) as a solution in DCM (5 mL). The viscous solution was stirred for 1.5 hours. The solution was diluted with ethyl acetate (5 mL) and 1M aqueous NaOH (10mL). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, concentrated *in vacuo*, and purified by flash column chromatography (100% hexanes→ 2% ether:hexanes) to yield the vinyl tosylate **SI-55** as a colorless oil (130 mg, 41 %).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.4 Hz, 2H), 7.09 – 6.95 (m, 3H), 6.86 – 6.80 (m, 1H), 6.74 – 6.68 (m, 1H), 2.45 – 2.36 (m, 1H), 2.33 (s, 3H), 2.24 (s, 3H), 2.23 – 2.17 (m, 1H), 2.02 (s, 3H), 1.93 (ddd, *J* = 13.6, 9.1, 6.5 Hz, 1H), 1.83 (ddd, *J* = 13.6, 8.9, 6.6 Hz, 1H), 1.51 – 1.43 (m, 2H), 1.42 – 1.35 (m, 2H), 1.29 (dddd, *J* = 12.5, 10.0, 7.1, 4.1 Hz, 2H), 1.19 – 1.07 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H), 0.76 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 143.9, 141.7, 138.7, 137.8, 135.1, 134.2, 131.9, 130.7, 130.3, 129.1, 127.8, 125.9, 30.2, 28.7, 23.2, 22.8, 21.8, 21.4, 19.7, 14.3, 14.2.
FT-IR (neat film NaCl): 2956, 2928, 2861, 1613, 1598, 1495, 1457, 1368, 1188, 1176, 1094, 998, 980, 829, 811, 784, 742, 558 cm^{-1}.
HR-MS (ESI): Calculated for [M+Na]+ $C_{25}H_{34}O_3SNa$: 437.2126; Measured: 437.2118.

(SI-56) (SI-57)

1-(2-butyl-5-methylcyclopent-1-en-1-yl)-2,4-dimethylbenzene (SI-56) + 1-(2-butyl-5-methylcyclopent-1-en-1-yl)-2,4-dimethylbenzene (SI-57)

In a well kept glovebox, (H2O, O2 < 0.5 ppm), an oven dried dram vial equipped with a stir bar was charged with $LiB(C_6F_5)_4$ (3.4 mg, 0.005 mmol, 10 mol %), LiH (2.0 mg, 0.25 mmol, 5 equiv) and this was 1,2-difluorobenzene. To this solution was added vinyl tosylate **(SI-55)** (21.0 mg, 0.05 mmol, 1 equiv). The vial was sealed and heated to 70 ºC for 20 minutes. After this time the vial was removed from the glove box and quenched with diethyl ether and the contents passed through silica gel with diethyl ether. The filtrate was concentrated *in vacuo* to yield a yellow oil as a mixture of **(SI-56)** and **(SI-57)** (NMR yield 80% yield combined isomers). Analytically pure samples of each isomer were obtained by flash column chromatography on $AgNO_3$ impregnated silica gel (100% hexanes). ($AgNO_3$-Impregnated silica gel was prepared by mixing with a solution of $AgNO_3$ (150% v/w [v/w $AgNO_3$ solution/silica gel] of 10% w/v solution in acetonitrile), removing solvent under reduced pressure, and drying *in vacuo* at 120 °C).

Characterization Data:

1-(2-butyl-5-methylcyclopent-1-en-1-yl)-2,4-dimethylbenzene (SI-56)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.01 – 6.98 (m, 1H), 6.94 (d, *J* = 7.4 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 2.95 – 2.87 (m, *j*1H), 2.46 – 2.33 (m, 2H), 2.31 (s, 3H), 2.23 – 2.15 (m, 1H), 2.13 (s, 3H), 1.86 (t, *J* = 7.7 Hz, 2H), 1.46 (ddd, *J* = 15.5, 12.9, 7.0 Hz, 1H), 1.30 (p, *J* = 7.6 Hz, 2H), 1.23 – 1.10 (m, *J* = 6.7 Hz, 2H), 0.85 (d, *J* = 6.9 Hz, 3H), 0.79 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.9, 136.4, 135.9, 135.6, 130.7, 126.1, 34.1, 32.3, 30.4, 30.0, 29.4, 22.9, 21.4, 20.0, 14.3.

FT-IR (neat film NaCl): 2953, 2926, 2859, 1499, 1455, 1376, 815 cm^{-1}.

HR-MS (CI): Calculated for $C_{18}H_{26}$: [M]+ 242.2034; Measured: 242.2041.

1-(5-butyl-2-methylcyclopent-1-en-1-yl)-2,4-dimethylbenzene (SI-57)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00 (s, 1H), 6.95 (d, J = 7.7 Hz, 1H), 6.86 (d, J = 7.6 Hz, 1H), 2.83 (s, 1H), 2.45 – 2.33 (m, 2H), 2.31 (s, 3H), 2.18 – 2.14 (m, 1H), 2.13 (s, 3H), 2.11 – 2.0 (m, 1H), 1.54 – 1.49 (m, 1H), 1.48 (s, 3H), 1.36 – 0.96 (m, 6H), 0.80 (t, J = 7.0 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 136.4, 135.9, 135.6, 134.9, 130.8, 126.2, 37.3, 34.4, 30.4, 29.7, 23.2, 21.4, 20.0, 15.3, 14.5.
FT-IR (neat film NaCl): 2954, 2923, 2855, 1497, 1456, 1376, 817 cm^{-1}.
HR-MS (CI): Calculated [M]+ $C_{18}H_{26}$: 242.2034; Measured: 242.2043.

4.6 Coulometry Experiment
In order to determine the number of electrons required to generate the vinyl fluoride product, **SI-5** was subjected to bulk electrolysis with coulometry using a CHI600E potentiostat.

To an oven dried 20 mL scintillation vial equipped with a septum cap and stir bar was added **SI-5** (38.8 mg, 0.10 mmol, 1 equiv), $TBABF_4$ (198 mg, 0.6 mmol, 6 equiv), and TBAF•$(H_2O)_3$ (158 mg, 0.5 mmol, 5 equiv). To this was added freshly distilled MeCN (6 mL). The Pt(–), C(+), and SCE reference electrode were placed into the solution through the septum cap under nitrogen. The solution was degassed by bubbling nitrogen for 20 minutes with stirring (400 rpm). The electrodes were connected to the CHI600E potentiostat and a bulk electrolysis with coulometry was carried out at +1.8V *vs* SCE. The reaction was monitored carefully by TLC for full consumption of the starting material. After 32 minutes of electrolysis it was determined that the starting material had been consumed and the data collection and applied potential was halted. The electrodes were rinsed into the solution with dichloromethane and the reaction contents were concentrated *in vacuo*. The material was purified by flash column chromatography (50% dichloromethane:hexanes) to yield the vinyl fluoride **SI-33** (21.6 mg, 77% yield).

20.2 coulombs had been passed, corresponding to 0.21 mmol of electrons at a Faradaic efficiency of 73%. (See graphs of current/charge vs. time below).

Electrochemical Fluorination: Charge vs. Time
2.50E+01
2.00E+01
1.50E+01
1.00E+01
5.00E+00
0.00E+00
Charge (C)
0
500
1000
1500
2000
2500
Time (s)
Charge/C

Electrochemical Fluorination: Current vs. Time
4.50E-02
4.00E-02
3.50E-02
3.00E-02
2.50E-02
2.00E-02
1.50E-02
1.00E-02
5.00E-03
0.00E+00
Current (A)
0
500
1000
1500
2000
2500
Time (s)
Current/A

4.7 Divided Cell Control Experiment

To ensure that this is an oxidative process vinyl boronic ester **SI-5** was subjected to divided cell electrolysis in both the cathode and the anode chamber. To each half-cell of an oven dried divided cell (fine glass frit) was added **SI-5** (9.7 mg, 0.025 mmol, 1 equiv), $TBABF_4$ (296 mg, 0.90mmol, 36 equiv), and $TBAF\bullet(H_2O)_3$ (39.4 mg, 5 equiv, 0.125 mmol). To each half-cell was added freshly distilled MeCN (3 mL). The electrodes Pt(–) and C(+) were put into place, and each side was degassed by bubbling with nitrogen for 20 minutes. The electrodes were connected to the potentiostat (TACKLife MDC01 DC power supply) a constant cell potential of 3.5 V (enough to pass 1-2mA) was applied for 1 hour. Upon completion the applied potential was halted and the electrodes were removed from solution and rinsed with dichloromethane (3 x 4 mL). The resulting solution of each half-cell was concentrated *in vacuo* and plugged through silica gel with ether. The anodic half-cell reaction indicated 80% yield of the vinyl fluoride product by ^{1}H NMR as determined by an internal standard, and the cathodic half-cell solution showed unreacted starting material.

4.8 Vinyl Radical Trapping Experiments.

To an oven dried 2 dram vial equipped with an oven dried stir bar was added (cyclohexylidene(4-methoxyphenyl)methyl)trifluoro-λ^4-borane, potassium salt **(SI-25)** (15.4 mg, 0.05 mmol, 1 equiv). To this was added the $TBABF_4$ (99.0 mg, 0.300 mmol, 6 equiv), water (15 uL, 15 equiv), deuterated propane thiol (77 mg, 20 equiv) as prepared by known methods.[19] The electrodes [Pt(–)/C(+)] held in place by a septum cap were put in place. The vial was placed under a nitrogen atmosphere. Freshly distilled acetonitrile was added (2.5 mL). The solution was degassed by bubbling nitrogen with stirring (~400 rpm) for 20 minutes. After degassing the potentiostat (TACKLife MDC01 DC power supply) was connected to the electrodes and a constant working potential *vs.* a CHI-150 SCE electrode of +1.8 V (measured with a multimeter between the C(+) and reference CHI-50 SCE electrode) was applied for 5 minutes. Upon completion the applied potential was halted and the electrodes were removed from solution and rinsed with dichloromethane (3 x 4 mL). The resulting solution was concentrated *in vacuo* to yield a brown oil. The crude material was purified by flash column chromatography (2% ether in hexanes) to yield **SI-58.D** (6.0 mg, 60% yield) with 25% deuterium incorporation as determined by ^{1}H NMR and ^{2}D NMR. (See attached NMR spectra at end of SI section 6).

Additionally control experiments were also performed. The same reaction was performed without electrolysis and no styrene product was formed. Additionally, with 20 equivalents of added sodium propanethiolate and no electrolysis, the styrene product was also not formed indicating that electrolysis is necessary and this is likely not a simple protodeboronation process.

To an oven dried 2 dram vial equipped with an oven dried stir bar was added (cyclohexylidene(4-methoxyphenyl)methyl)trifluoro-λ^4-borane, potassium salt **(SI-25)** (15.4 mg, 0.05 mmol, 1 equiv). To this was added the $TBABF_4$ (99.0 mg, 0.300 mmol, 6 equiv) and water (15 uL, 15 equiv). The electrodes [Pt(–)/C(+)] held in place by a septum cap were put in place. The vial was placed under a nitrogen atmosphere. Freshly distilled acetonitrile was added (2.5 mL) followed by N-Me pyrrole (41 mg, 0.50 mmol, 10 equiv). The solution was degassed by bubbling nitrogen with stirring (~400 rpm) for 20 minutes. After degassing the potentiostat (TACKLife MDC01 DC power supply) was connected to the electrodes and a constant working potential *vs.* a CHI-150 SCE electrode of ***+1.1 V*** (measured with a multimeter between the C(+) and reference CHI-50 SCE electrode) was applied for 15 minutes. Upon completion the applied potential was halted and the electrodes were removed from solution and rinsed with dichloromethane (3 x 4 mL). The resulting solution was concentrated *in vacuo* to yield a brown oil. The crude material was plugged through a pipette of silica gel with ether. ^{1}H NMR analysis of this mixture with added 1.5 uL of nitromethane as an internal standard showed product **(SI-52)** and styrene **(SI-58)** in 11% and 78% yield respectively (See spectrum below). **(SI-58)** was isolated by flash column chromatography (2% ether in hexanes) and matched known literature spectra.[20] Styrene product integration at ~6.2 ppm and pyrrole addition product integration ~7.2 ppm.

Zoomed in view of crude ^{1}H NMR showing no production of the C-3 arylation product. Highlighting allylic protons around 2.0–2.5 ppm. (top 3-addition product, middle 2-addition product, bottom-crude reaction mix).

Additionally TEMPO trapping experiments were attempted, however only the alpha-keto TEMPO adduct was successfully isolated.

To an oven dried 2 dram vial equipped with an oven dried stir bar was added (cyclohexylidene(4-methoxyphenyl)methyl)trifluoro-λ^4-borane, potassium salt **(SI-25)** (15.4 mg, 0.05 mmol, 1 equiv). To this was added the $TBABF_4$ (99.0 mg, 0.300 mmol, 6 equiv), water (15 uL, 15 equiv), TEMPO (78 mg, 10 equiv). The electrodes [Pt(–)/C(+)] held in place by a septum cap were put in place. The vial was placed under a nitrogen atmosphere. Freshly distilled acetonitrile was added (2.5 mL). The solution was degassed

by bubbling nitrogen with stirring (~400 rpm) for 20 minutes. After degassing the potentiostat (TACKLife MDC01 DC power supply) was connected to the electrodes and a constant working potential *vs.* a CHI-150 SCE electrode of +1.8 V (measured with a multimeter between the C(+) and reference CHI-50 SCE electrode) was applied for 5 minutes. Upon completion the applied potential was halted and the electrodes were removed from solution and rinsed with dichloromethane (3 x 4 mL). The resulting solution was concentrated *in vacuo* to yield a brown oil. The crude material was purified by flash column chromatography (5% ether in hexanes) to yield **SI-59** as a colorless oil (5.5 mg, 30% yield). This material underwent decomposition upon standing at room temperature over several days.

This product does not show evidence for the vinyl radical, but it does potentially support spin trapping of the incipient radical cation calculated to exist after the initial oxidation.

At the same time an identical solution was prepared that was not subjected to electrolysis. No formation of the TEMPO adduct was observed.

(4-methoxyphenyl)(1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)cyclohexyl)methanone (SI-59)

^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.27 (d, *J* = 9.1 Hz, 2H), 6.91 (d, *J* = 9.1 Hz, 2H), 3.85 (s, 3H), 2.34 (d, *J* = 13.3 Hz, 2H), 1.91 (td, *J* = 13.5, 4.3 Hz, 2H), 1.65 – 1.55 (m, 4H), 1.51 – 1.38 (m, 4H), 1.37 – 1.24 (m, 3H), 1.17 – 1.07 (m, 1H), 1.19 – 1.07 (m, 1H), 1.03 (d, *J* = 7.5 Hz, 12H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 200.0, 163.1, 133.6, 129.0, 113.4, 88.4, 60.1, 55.9, 41.3, 34.4, 30.2, 29.7, 26.2, 24.3, 21.7, 17.7.

FT-IR (neat film NaCl): 2931, 2853, 1726, 1683, 1604, 1579, 1537, 1510, 1463, 1429, 1375, 1307, 1257, 1169, 1075, 843, 772 cm^{-1}.

HR-MS (ESI): Calculated for $[C_{23}H_{36}NO_3+H]^+$: 374.2689; Measured: 374.2684.

4.9 Unsymmetric vinyl boronate experiment

Further evidence for the intermediacy of a vinyl carbocation is the mixture of vinyl fluorides (6.25:1 Z:E) starting from a single isomer of alkenyl boronic ester **SI-30.1**.

To an oven dried 2 dram vial equipped with an oven dried stir bar was added (*E*)-2-(1-(4-methoxyphenyl)-2-phenylprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(SI-30.1)** (17.5 mg, 0.05 mmol, 1 equiv). To this was added the $TBABF_4$ (99.0 mg, 0.300 mmol, 6 equiv) and the TBAF•(H_2O) (79.0 mg, 0.25 mmol, 5 equiv). The electrodes [Pt(–)/C(+)] held in place by a septum cap were put in place. The vial was placed under a nitrogen atmosphere. Freshly distilled acetonitrile was added (2.5 mL). The solution was degassed by bubbling nitrogen with stirring (~400 rpm) for 20 minutes. After degassing the potentiostat (TACKLife MDC01 DC power supply) was connected to the electrodes and a constant working potential *vs.* a CHI-150 SCE electrode of +1.8 V (measured with a multimeter between the C(+) and reference CHI-50 SCE electrode) was applied for 15 minutes. Upon completion the applied potential was halted and the electrodes were removed from solution and rinsed with dichloromethane (3 x 4 mL). The resulting solution was concentrated *in vacuo* to yield a brown oil. This material was then plugged through silica gel with diethyl ether and concentrated. ^{1}H NMR analysis of this crude material indicated 30% yield of the Z-vinyl fluoride product (*Z*)-1-(1-fluoro-2-phenylprop-1-en-1-yl)-4-methoxybenzene **(SI-60).** ^{19}F NMR analysis indicated a 6.25:1 mixture of this material with E isomer.

The crude material was purified by flash column chromatography (40% dichloromethane in hexanes) to give the resulting vinyl fluoride **(SI-60)**. This matched published literature spectral data.[21] The ^{19}F NMR spectrum of the crude mixture is shown below indicating a 6.25:1 ratio.

4.10 Observation of BPin–F side product

To further validate that BPin–F is produced as a side product in the reaction, a reaction was run using tetrabutyl ammonium hexfluorophosphate ($TBAPF_6$) as opposed to $TBABF_4$ and the crude reaction was placed into a sealed NMR tube to analyze by ^{11}B and ^{19}F NMR.

To an oven dried 2 dram vial equipped with an oven dried stir bar was added 2-(cyclohexylidene(2,4,6-trimethoxyphenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(SI-5)** (19.4 mg, 0.05 mmol, 1 equiv). To this was added the $TBAPF_6$ (116.2 mg, 0.300 mmol, 6 equiv) and the TBAF•(H_2O) (40 mg, 0.125 mmol, 2.5 equiv). The electrodes [Pt(–)/C(+)] held in place by a septum cap were put in place. The vial was placed under a nitrogen atmosphere. Freshly distilled acetonitrile was added (2.5 mL). The solution was degassed by bubbling nitrogen with stirring (~400 rpm) for 20 minutes. After degassing the potentiostat (TACKLife MDC01 DC power supply) was connected to the electrodes and a constant working potential *vs.* a CHI-150 SCE electrode of +1.8 V (measured with a multimeter between the C(+) and reference CHI-50 SCE electrode) was applied for 15 minutes, or until the starting material was consumed. Upon completion the applied potential was halted and to the crude solution was added 10uL of dry trifluorotoluene. This solution was quickly transferred to a dry sealed NMR tube by syringe. ^{19}F NMR spectra indicated 44% yield of BPin–F and 74% yield of the vinyl fluoride product. ^{11}B NMR spectra also indicated production of BPin–F, both spectra matched literature reports.[22]

-62.4079
-70.6471
-73.1509
-107.3747
-112.6426
-150.6231
TBAPF6
PhCF3
TBAF
Vinyl
fluoride
BPin–F
3.00
0.74
0.44
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
ppm

5. Computational mechanistic studies

Density functional theory (DFT) calculations were performed by using Gaussian 16.[23] Geometry optimization and frequency calculations were performed using the uM06-2X functional at 6-31+G(d,p) level of theory with the CPCM solvation model for acetonitrile.[24–28] Single point energy calculations were conducted using the uM06-2X functional at the 6-311++G(d,p) basis set. The default algorithm criteria and integration grids were used for Gaussian 16 calculations. Normal mode analysis of the harmonic vibrational frequencies confirmed that optimized structures are minima (no imaginary frequency). Zero point energy (ZPE), enthalpy and free energy corrections were obtained using a standard state of 1 atmosphere of pressure and 298 K. All of 3D structures were generated using CYLview.[29] In order to calculate electrochemical potentials of the intermediates in the proposed mechanism, the computational methods studied by Nicewicz et al. were utilized.[30]

5.1 HOMO/Oxidation Potential Calculations

The experimental redox potential of vinyl trifluoroborate **30**, which held the potassium counter ion in the actual experiment, was observed at +1.12 V *vs* SCE. Based on the computational studies, the redox potential from **30** to **31** was 1.04 V *vs* SCE.

Figure S1. Calculated redox potential (uM06-2X/6-311++G(d,p) cpcm=acetonitrile // uM06-2X/6-31+G(d,p) cpcm=acetonitrile)

Intermediate	Electronic Energy (EE)	Zero-Point Energy Correction (ZPE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
30	-943.329406 Hartree	0.291981 Hartree	-943.018678 Hartree	-943.084409 Hartree
31	-943.131918 Hartree	0.292935 Hartree	-942.820389 Hartree	-942.885658 Hartree

Table S1. Energies for the intermediates of Figure S1 (uM06-2X/6-31+G(d,p) in CPCM=acetonitrile)

Intermediate	Electronic Energy (EE)	EE + Thermal Free Energy Correction (6-31+G(d,p)) (G)
30	-943.554296 Hartree	-943.309299 Hartree
31	-943.354815 Hartree	-943.108555 Hartree

Table S2. Single point energies for the intermediates of Figure S1 (uM06-2X/6-311++G(d,p) in CPCM=acetonitrile)

Figure S2. HOMO of vinyl trifluoroborate anion (**30**) (uM06-2X/6-31+G(d,p) cpcm=acetonitrile)

5.2 Cartesian coordinates for structures of Figure S1, Figure S2, Table S1, & Table S2. (optimized with uM06-2X/6-31+G(d,p) in CPCM=acetonitrile)

Vinyl trifluoroborate anion (30)
Charge: -1

C	3.44265900	-0.45088400	0.21190900
C	2.84105800	0.08002700	-0.93120400
C	1.47870300	0.39252800	-0.90736700
C	0.68260700	0.17618600	0.22129900
C	1.31865300	-0.35061500	1.35810400
C	2.67326400	-0.66175500	1.36103400
H	3.15401000	-1.06893000	2.24549600
H	0.73330400	-0.52037400	2.25868300
C	-0.76761300	0.53371900	0.22222100
C	-1.70599100	-0.41875300	0.41348500
C	-3.18852300	-0.10584700	0.45174600
H	-3.57901400	-0.39222100	1.44167600
C	-3.96022800	-0.90389600	-0.61066300
C	-3.70126300	-2.40463500	-0.47014700
C	-2.20234900	-2.70355200	-0.51766800
C	-1.43390400	-1.90403400	0.54871900
H	-1.76956200	-2.24334100	1.54131900
H	-0.36572900	-2.12161100	0.47855400
H	-2.02055700	-3.77557000	-0.38033100
H	-1.81217600	-2.43582400	-1.50946600
H	-4.10568700	-2.75038400	0.49207100
H	-4.22674300	-2.96046600	-1.25494900
H	-3.63859700	-0.57267800	-1.60778600
H	-5.03265700	-0.69149300	-0.53246700
H	-3.36364400	0.96386500	0.33004800
B	-1.15141900	2.10473400	-0.00066000
F	0.00989700	2.90734600	-0.18214000
F	-1.85737500	2.64550900	1.11831300
F	-1.97759800	2.30302700	-1.14985200
H	1.02431900	0.81645500	-1.79930600
H	3.41191600	0.25825000	-1.83501900
O	4.76388000	-0.78724800	0.30203900
C	5.57053800	-0.58254600	-0.84572400
H	5.20979700	-1.17719100	-1.69216700
H	6.57326700	-0.90858400	-0.57312100
H	5.59382100	0.47581600	-1.12759100

There are no imaginary frequencies

Vinyl trifluoroborate radical (INT31)

Charge: 0

C	3.50461900	-0.55980300	0.16630800
C	3.04586200	0.50767200	-0.62991700
C	1.70721900	0.84295800	-0.61058700
C	0.75732800	0.10226200	0.14828300

C	1.26263200	-0.97334100	0.94595000
C	2.59541000	-1.28964100	0.96742100
H	2.98020400	-2.08994000	1.58979300
H	0.58054400	-1.52620300	1.58360300
C	-0.63172500	0.44941700	0.16745000
C	-1.61113100	-0.53189400	0.39272400
C	-2.97069100	-0.20863200	0.93149900
H	-3.10764500	-0.83404200	1.82626900
C	-4.07375600	-0.58115000	-0.08433400
C	-3.94846800	-2.03794600	-0.52217700
C	-2.55011900	-2.31987600	-1.06687700
C	-1.45797700	-1.96475700	-0.03047000
H	-1.59905400	-2.60992100	0.84896600
H	-0.47108000	-2.16023700	-0.45114300
H	-2.43769800	-3.37333900	-1.33839100
H	-2.37993000	-1.72921800	-1.97562100
H	-4.14589900	-2.69769600	0.33309600
H	-4.69868900	-2.26693700	-1.28605200
H	-3.98414800	0.08264500	-0.95142400
H	-5.04818300	-0.39195100	0.37583500
H	-3.04838100	0.83389200	1.23350000
B	-1.17708000	2.02203700	0.00573200
F	-0.23100600	2.87447600	-0.58483300
F	-1.46463900	2.49573800	1.30567300
F	-2.35099300	2.04759600	-0.77157200
H	1.36242600	1.66764000	-1.21921300
H	3.72914100	1.07170800	-1.25200400
O	4.77623000	-0.94989700	0.23522100
C	5.75799500	-0.25915600	-0.54129500
H	5.53146300	-0.34571400	-1.60696800
H	6.70257400	-0.75074900	-0.32119400
H	5.80646800	0.79208700	-0.24676500

There are no imaginary frequencies

---

6. NMR Spectra

^{1}H NMR (300 MHz, $CDCl_3$) of compound **SI-1**.

^{1}H NMR (300 MHz, $CDCl_3$) of compound **SI-2**.

^{1}H NMR (300 MHz, $CDCl_3$) of compound **SI-3**.

^{13}C NMR (126 MHz, $CDCl_3$) of compound **SI-3**.

^{11}B NMR (128 MHz, $CDCl_3$) of compound **SI-3.**

^{1}H NMR (400 MHz, $CDCl_3$) of compound **SI-4**.

^{13}C NMR (126 MHz, $CDCl_3$) of compound **SI-4**.

^{11}B NMR (161 MHz, $CDCl_3$) of compound **SI-4**.

^{1}H NMR (400 MHz, $CDCl_3$) of compound **SI-5**.

^{13}C NMR (126 MHz, $CDCl_3$) of compound **SI-5**.

^{11}B NMR (129 MHz, $CDCl_3$) of compound **SI-5**.

^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI-6**.

^{13}C NMR (126 MHz, $CDCl_3$) of compound **SI-6**.

^{11}B NMR (96 MHz, $CDCl_3$) of compound **SI-6**.

^{1}H NMR (400 MHz, $CDCl_3$) of compound **SI-7**.

^{13}C NMR (126 MHz, $CDCl_3$) of compound **SI-7**.

^{11}B NMR (96 MHz, $CDCl_3$) of compound **SI-7.**

^{1}H NMR (300 MHz, $CDCl_3$) of compound **SI-8**.

^{13}C NMR (126 MHz, $CDCl_3$) of compound **SI-8**.

^{11}B NMR (96 MHz, $CDCl_3$) of compound **SI-8.**

^{1}H NMR (300 MHz, $CDCl_3$) of compound **SI-9.**

^{13}C NMR (126 MHz, $CDCl_3$) of compound **SI-9**.

^{11}B NMR (96 MHz, $CDCl_3$) of compound **SI-9.**

^{1}H NMR (300 MHz, $CDCl_3$) of compound **SI-10.**

^{1}H NMR (300 MHz, $CDCl_3$) of compound **SI-11.**

^{13}C NMR (126 MHz, $CDCl_3$) of compound **SI-11.**

^{11}B NMR (96 MHz, $CDCl_3$) of compound **SI-11.**

^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI-12.**

^{13}C NMR (126 MHz, $CDCl_3$) of compound **SI-12.**

^{11}B NMR (96 MHz, $CDCl_3$) of compound **SI-12.**

^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI-13.**

^{13}C NMR (126 MHz, $CDCl_3$) of compound **SI-13.**

^{11}B NMR (96 MHz, $CDCl_3$) of compound **SI-13.**

^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI-14.**

^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI-15.**

^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI-16.**

^{13}C NMR (126 MHz, $CDCl_3$) of compound **SI-16.**

^{11}B NMR (96 MHz, $CDCl_3$) of compound **SI-16.**

^{1}H NMR (400 MHz, $CDCl_3$) of compound **SI-18.**

^{13}C NMR (126 MHz, $CDCl_3$ of compound **SI-18.**

^{11}B NMR (96 MHz, $CDCl_3$) of compound **SI-18.**

^{1}H NMR (300 MHz, $CDCl_3$) of compound **SI-19.**

^{11}B NMR (96 MHz, $CDCl_3$) of compound **SI-19.**

^{13}C NMR (126 MHz, $CDCl_3$) of compound **SI-19**

^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI-20.**

^{13}C NMR (126 MHz, $CDCl_3$) of compound **SI-20.**

^{11}B NMR (96 MHz, ($CDCl_3$ of compound **SI-20.**

j1H NMR (300 MHz, $CDCl_3$) of compound **SI-21.**

^{1}H NMR (300 MHz, $CDCl_3$) of compound **SI-22.**

^{13}C NMR (126 MHz, $CDCl_3$) of compound **SI-22.**

^{11}B NMR (96 MHz, (CDCl$_3$ of compound **SI-22.**

^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI-23.**

^{13}C NMR (126 MHz, $CDCl_3$) of compound **SI-23.**

^{11}B NMR (96 MHz, ($CDCl_3$ of compound **SI-23.**

^{1}H NMR (300 MHz, $CDCl_3$) of compound **SI-24.**

^{13}C NMR (126 MHz, $CDCl_3$) of compound **SI-24.**

^{11}B NMR (96 MHz, ($CDCl_3$ of compound **SI-24.**

^{1}H NMR (500 MHz, $(CD_3)_2CO$) of compound **SI-25.**

^{13}C NMR (126 MHz, $(CD_3)_2CO$) of compound **SI-25.**

^{11}B NMR (96 MHz, $(CD_3)_2CO$) of compound **SI-25.**

^{19}F NMR (282 MHz, $(CD_3)_2CO$) of compound **SI-25.**

^{1}H NMR (500 MHz, ($CDCl_3$) of compound **SI-26.**

Removal of DCM under high-vacuum was never achieved (5.3 ppm)

^{13}C NMR (126 MHz, (CD_2Cl_2) of compound **SI-26.**

^{11}B NMR (96 MHz, ($CDCl_3$) of compound **SI-26.**

^{19}F NMR (282 MHz, (CD_3Cl) of compound **SI-26.**

^{1}H NMR (300 MHz, ($CDCl_3$) of compound **SI-27.**

^{1}H NMR (300 MHz, ($CDCl_3$) of compound **SI-28.**

^{1}H NMR (300 MHz, ($CDCl_3$) of compound **SI-29.**

^{1}H NMR (300 MHz, ($CDCl_3$) of compound **SI-29.1.**

^{1}H NMR (300 MHz, $(CD_3)_2CO$) of compound **SI-30.**

^{13}C NMR (126 MHz, $(CD_3)_2CO$) of compound **SI-30.**

^{19}F NMR (282 MHz, ((CD$_3$)$_2$CO) of compound **SI-30.**

^{11}B NMR (96 MHz, $(CD_3)_2CO$) of compound **SI-30.**

^{1}H NMR (300 MHz, ($CDCl_3$) of compound **SI-30.1.**

^{1}H NMR (300 MHz, ($CDCl_3$) of compound **SI-31.**

^{13}C NMR (126 MHz, ($CDCl_3$) of compound **SI-31.**

^{19}F NMR (282 MHz, (CD_3Cl) of compound **SI-31.**

^{1}H NMR (500 MHz, ($CDCl_3$) of compound **SI-32.**

^{13}C NMR (126 MHz, ($CDCl_3$) of compound **SI-32.**

^{19}F NMR (376 MHz, (CD_3Cl) of compound **SI-32.**

^{1}H NMR (400 MHz, ($CDCl_3$) of compound **SI-33.**

^{13}C NMR (126 MHz, ($CDCl_3$) of compound **SI-33.**

^{19}F NMR (376 MHz, (CD_3Cl) of compound **SI-33.**

^{1}H NMR (500 MHz, ($CDCl_3$) of compound **SI-34.**
(Note: styrene impurity not integrated)

^{13}C NMR (126 MHz, ($CDCl_3$) of compound **SI-34.**
(Note: styrene impurity peaks not selected for clarity)

^{19}F NMR (282 MHz, (CD_3Cl) of compound **SI-34.**

^{1}H NMR (300 MHz, ($CDCl_3$) of compound **SI-35.**

^{13}C NMR (126 MHz, ($CDCl_3$) of compound **SI-35.**

^{19}F NMR (282 MHz, (CD_3Cl) of compound **SI-35.**

^{1}H NMR (400 MHz, ($CDCl_3$) of compound **SI-36.**

^{13}C NMR (126 MHz, ($CDCl_3$) of compound **SI-36.**

^{19}F NMR (376 MHz, (CD_3Cl) of compound **SI-36.**

^{1}H NMR (300 MHz, ($CDCl_3$) of compound **SI-37.**

^{13}C NMR (126 MHz, ($CDCl_3$) of compound **SI-37.**

^{19}F NMR (282 MHz, ($CDCl_3$) of compound **SI-37.**

^{1}H NMR (500 MHz, ($CDCl_3$) of compound **SI-38.**

^{13}C NMR (126 MHz, ($CDCl_3$) of compound **SI-38.**

^{19}F NMR (282 MHz, ($CDCl_3$) of compound **SI-38.**

^{1}H NMR (300 MHz, ($CDCl_3$) of compound **SI-39.**

^{13}C NMR (126 MHz, ($CDCl_3$) of compound **SI-39.**

^{19}F NMR (282 MHz, ($CDCl_3$) of compound **SI-39.**

^{1}H NMR (500 MHz, ($CDCl_3$) of compound **SI-40.**

^{13}C NMR (126 MHz, ($CDCl_3$) of compound **SI-40.**

^{19}F NMR (282 MHz, ($CDCl_3$) of compound **SI-40.**

^{1}H NMR (300 MHz, ($CDCl_3$) of compound **SI-41.**

^{13}C NMR (126 MHz, ($CDCl_3$) of compound **SI-41.**

^{19}F NMR (282 MHz, ($CDCl_3$) of compound **SI-41.**

^{1}H NMR (500 MHz, ($CDCl_3$) of compound **SI-42.**

^{13}C NMR (126 MHz, ($CDCl_3$) of compound **SI-42.**

^{19}F NMR (282 MHz, ($CDCl_3$) of compound **SI-42.**

^{1}H NMR (300 MHz, $(CD_3)_2CO$ of compound **SI-43.**

^{13}C NMR (126 MHz, $(CD_3)_2CO$ of compound **SI-43.**

^{19}F NMR (282 MHz, $(CD_3)_2CO$ of compound **SI-43.**

^{1}H NMR (300 MHz, ($CDCl_3$) of compound **SI-44.**

^{13}C NMR (126 MHz, ($CDCl_3$) of compound **SI-44.**

^{19}F NMR (282 MHz, $CDCl_3$) of compound **SI-44.**

^{1}H NMR (300 MHz, ($CDCl_3$) of compound **SI-45.**

^{13}C NMR (126 MHz, ($CDCl_3$) of compound **SI-45.**

^{19}F NMR (282 MHz, $CDCl_3$) of compound **SI-45.**

^{1}H NMR (300 MHz, ($CDCl_3$) of compound **SI-46.**

^{1}H NMR (300 MHz, ($CDCl_3$) of compound **SI-47.**

^{1}H NMR (500 MHz, ($CDCl_3$) of compound **SI-48.**

^{13}C NMR (126 MHz, ($CDCl_3$) of compound **SI-48.**

^{1}H NMR (300 MHz, ($CDCl_3$) of compound **SI-49.**

^{1}H NMR (300 MHz, ($CDCl_3$) of compound **SI-50.**

^{1}H NMR (300 MHz, ($CDCl_3$) of compound **SI-51.**

^{1}H NMR (300 MHz, ($CDCl_3$) of compound **SI-51.1**

^{1}H NMR (300 MHz, ($CDCl_3$) of compound **SI-52.**

^{13}C NMR (126 MHz, ($CDCl_3$) of compound **SI-52.**

^{1}H NMR (300 MHz, ($CDCl_3$) of compound **SI-53.**

^{13}C NMR (126 MHz, ($CDCl_3$) of compound **SI-53.**

^{1}H NMR (300 MHz, ($CDCl_3$) of compound **SI-54.**

^{13}C NMR (126 MHz, ($CDCl_3$) of compound **SI-54.**

^{1}H NMR (500 MHz, ($CDCl_3$) of compound **SI-55.**

^{13}C NMR (126 MHz, ($CDCl_3$) of compound **SI-55.**

^{1}H NMR (500 MHz, ($CDCl_3$) of compound **SI-56.**

^{13}C NMR (126 MHz, ($CDCl_3$) of compound **SI-56.**

^{1}H NMR (500 MHz, ($CDCl_3$) of compound **SI-57.**

^{13}C NMR (126 MHz, ($CDCl_3$) of compound **SI-57.**

^{1}H NMR (300 MHz, ($CDCl_3$) of compound **SI-58.**

^{1}H NMR (300 MHz, ($CDCl_3$) of compound **SI-58.D. Indicating ~25% deuterium incorporation**

^{2}H NMR (77 MHz, ($CHCl_3$)) of compound **SI-58.D.**

^{1}H NMR (500 MHz, (CD_2Cl_2) of compound **SI-59.**

^{13}C NMR (126 MHz, (CD_2Cl_2) of compound **SI-59.**

^{1}H NMR (300 MHz, ($CDCl_3$) of compound **SI-60.**

7. References

1. S. Datta, A. Odedra; R. –S. Liu, *J. Am. Chem. Soc.* **2005**, *127*, 11606–11607.
2. T. Hata, H. Kitagawa, H. Masai, T. Kurahashi, M. Shimizu, T. Hiyama, *Angew. Chem., Int. Ed.* **2001**, *40*, 790–792.
3. Y. Hu, W. Sun, T. Zhang, N. Xu, J. Xu, Y. Lan, C. Liu, *Angew. Chem., Int. Ed.* **2019**, *58*, 15813–15818.
4. M. –J. Wu, L. –M. Wei, C. –F. Lin, S.–P. Leou, L.–L. Wei, *Tetrahedron* **2001**, *57*, 7839–7844.
5. R. S. Shelton, M. G. Van Campen, US Patent 2430891. November 18, 1947.
6. Y. R. Bhorge, C. –T. Chang, S. –H. Chang, T. –H. Yan, *Eur. J. Org. Chem.* **2012**, 4805–4810.
7. T. Kurahashi, T. Hata, H. Masai, H. Kitagawa, M. Shimizu, T. Hiyama, *Tetrahedron* **2002**, *58*, 6381–6395
8. A. Paptchikhine, P. Cheruku, M. Engman, P. G. Andersson, P. G. *Chem. Comm.* **2009**, *40*, 5996–5998.
9. S. R. Kandukuri, J. A. Schiffner, M. Oestreich, *Angew. Chem., Int. Ed.* **2012**, *51*, 1265–1269.
10. L. Candish, M. Teders, F. Glorius, *J. Am. Chem. Soc.* **2017**, *139*, 7440–7443.
11. H. R. Kim, J. Yun *Chem. Commun.* **2011**, *47*, 2943–2945.
12. M. Shimizu, C. Nakamaki, K. Shimono, M. Schelper, T. Kurahashi, T. Hiyama *J. Am. Chem. Soc.* **2005**, *127*, 12506–12507.
13. C.–G. Yu, Y. Matsuo, *Org. Lett.* **2020**, *22*, 950–955.
14. F. –F. Pan, P. Guo, C. –L. Li, P. Su, X. –Z. Shu, *Org. Lett*. **2019**, *21*, 3701–3705.
15. S. Kobayashi, Y. Hori, T. Hasako, K. –i. Koga, H. Yamtaka, *J. Org. Chem.* **1996**, 5274–5279.
16. V. V. Pavlishchuk, A. W. Addison, *Inorganica Chimica Acta* **2000**, *298*, 97–102.
17. (a) V. A. Rassadin, V. P. Boyarskiy, V. Y. Kukushkin. *Org. Lett.* **2015**, *17*, 3502–3505. (b) J. Renner, A. Thakur, P. M. Rutz, J. M. Cowley, J. L. Evangelista, P. Kumar, M. B. Prater, R. M. Stolley, J. Louie, *Org. Lett.* **2020**, *22*, 924–928.
18. C. J. Thomson, Q. Zhang, N. Al-Maharik, M. Bühl, D. B. Cordes, A. M. Z. Slawin, D. O'hagan, *Chem. Comm.* **2018**, *54*, 8415–8418.
19. S. –K. Lin, B. Jaun, *Helv. Chim. Acta.* **1992**, *75*, 1478–1490.
20. S. Zhou, F. Yuan, M. Guo, G. Wang, X. Tang, W. Zhao, *Org. Lett.* **2018**, *20*, 6710–6714.
21. C. Chen, K. Wilcoxen, Y.–F Zhu, K.–i. Kim, J. R. McCarthy *J. Org. Chem.* **1999**, *64*, 3476–3482.
22. G. Iakobson, J. Du, A. M. Z. Slawin, P. Beier, *Beilstein J. Org. Chem.* **2015**, *11*, 1494–1502.
23. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T.

Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M.; Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, *Gaussian 16*; Gaussian, Inc., Wallingford, CT, **2016**.

24. Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215–241.
25. R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys.* **1971**, *54*, 724–728.
26. W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1971**, *54*, 2257–2261.
27. P. C. Hariharan, J. A. Pople, J. *Theor. Chim. Acta.* **1973**, *28*, 213–222.
28. (a) V. Barone, M. Cossi, *J. Phys. Chem. A* **1998**, *102*, 1995−2001. (b) M. Cossi, N. Rega, G. Scalmani, V. Barone, V. *J. Comput. Chem.* **2003**, *24*, 669−681.
29. C. Y. Legault, CYLview, 1.0b; Université de Sherbrooke, **2009**; http://www.cylview.org.
30. H. G. Roth, N. A. Romero, D. A. Nicewicz, *Synlett* **2016**, *27*, 714–723.