nature portfolio

https://doi.org/10.1038/s41586-022-04540-4

Supplementary information

Electrochemically driven cross-electrophile coupling of alkyl halides

In the format provided by the authors and unedited

Supplementary Information for

Electrochemically Driven Cross-Electrophile Coupling of Alkyl Halides

Wen Zhang[1], Lingxiang Lu[1], Wendy Zhang[2], Yi Wang[1], Skyler D. Ware[2], Jose Mondragon[1], Jonas Rein[1], Neil Strotman[3], Dan Lehnherr[3], Kimberly A. See[2]*, Song Lin[1]*

[1]Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853, USA
[2]Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, USA
[3]Process Research and Development, Merck & Co., Inc., Rahway, New Jersey 07065, USA
*Correspondence to: songlin@cornell.edu, ksee@caltech.edu

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1. General Considerations

All reactions were conducted under a nitrogen atmosphere unless otherwise noted. Flash chromatography was performed using silica gel 60 (230-400 mesh) from SiliCycle. Commercial reagents were purchased from Sigma Aldrich, Alfa Aesar, Acros, TCI, AK Scientific, Combi-Blocks and Oakwood and used as received. Tetrahydrofuran (THF) was purchased from Fisher, dried over microwave oven dried 4 Å molecular sieves and stored in glove box. Anhydrous DME was purchased from Sigma Aldrich (catalog: 259527) and used without further purification. The electrolyte tetrabutylammonium perchlorate ($TBAClO_4$) was purchased from TCI (catalog: T0836) and stored in glove box. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Mercury-300 (300 MHz), Inova-400 (400 MHz) and Inova-500 (500 MHz) spectrometers. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$ = δ 77.16). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration. Infrared (IR) spectra were obtained using a Bruker Hyperion Tensor 27 FTIR spectrometer. Enantiomeric ratios of isolated material were determined by chiral HPLC using a SHIMADZU system with a CHIRALPAK® column. Cyclic voltammetry data were measured with a BASi Epsilon potentiostat. The mass spectral (MS) data were obtained on a Thermo Fisher Scientific Exactive series DART Mass Spectrometer and Agilent 8860 GC System with an Agilent 5977B Mass Selective Detector. GC analyses were performed on a Shimadzu Nexus GC-2030 gas chromatograph with an FID detector and Agilent 8860 GC System. All electrolysis reactions were performed on ElectraSyn 2.0 with oven-dried vial (5 mL) unless otherwise noted. The Mg electrode was cut into 5.25 x 0.8 x 0.2 cm^3 plate. The Mg plate should be polished with spatula to remove the stains and insoluble salts in the surface before use. Graphite plate (5.25 x 0.8 x 0.2 cm^3) was bought from IKA and could recyclable use. General procedure to recycle the graphite: after reaction, the graphite was sequentially washed with water and acetone (sometimes, it requires using dilute HCl aqueous to remove the precipitated Mg). Then the graphite was immersed in acetone and ultrasonic cleaning for 5 minutes. After that, the graphite was rinsed with acetone and polished with sand paper. Finally, the graphite was dried over in oven before use.

2. General Procedure for e-XEC Reaction

General Procedure A for e-XEC reaction with alkyl bromides

In glove box, $TBAClO_4$ (3 mmol, 3 equiv.) and dried THF (2.5 mL) was added into the flame dried undivided ElectraSyn vial (5 mL) equipped with a stir bar. The resulting suspension was pre-stirred for about 1 min to dissolve the electrolyte (If the substrate was solid, it would be added to the vial before adding the solvent. If the substrate was sticky oil, it would be added as a solution in THF). Then the substrate with anion-stabilizing group (1 mmol, 1 equiv.) and alkyl bromide (3 mmol, 3 equiv.) was sequentially added to the mixture. The vial was sealed with the ElectraSyn vial cap equipped with anode (Mg plate) and cathode (graphite plate), and then bring it out of glove box. Pre-stirring the resulting mixture for 2 minutes, and then the reaction mixture was electrolyzed at a constant current of 5 mA (current density = 1.03 mA/cm^2) until passing 2 F/mol of charge at room temperature. After electrolysis, disconnect the reaction vial from ElectraSyn 2.0, gently remove the cap with electrodes from the vial and transfer the reaction media to a separatory funnel. Both electrodes were rinsed with saturated NH_4Cl (aq) and Et_2O. Then, the crude mixture was further diluted with Et_2O. The resulting mixture was washed with brine. The organic layer was dried over with anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to furnish the desired product.

General Procedure B for e-XEC reaction of tertiary-α-bromo pinacol boronic ester with chorosilane

In glove box, $TBAClO_4$ (3 mmol, 3 equiv.) and dried THF (2.5 mL) was added into the flame dried undivided ElectraSyn vial (5 mL) equipped with a stir bar. The resulting suspension was pre-stirred for about 1 min to dissolve the electrolyte (If the substrate or electrophile was solid, it would be added to the vial before adding the solvent. If the substrate was sticky oil, it would be added as a solution in THF). Then the substrate (1 mmol, 1 equiv) and chlorosilane (3 mmol, 3 equiv) was sequentially added to the mixture. The vial was sealed with the ElectraSyn vial cap equipped with anode (Mg plate) and cathode (graphite plate), and then bring it out of glove box. Pre-stirring the resulting mixture for 2 minutes, and then the reaction mixture was

electrolyzed at a constant current of 5 mA (current density = 1.03 mA/cm^2) until passing 2 F/mol of charge at room temperature. After electrolysis, disconnect the reaction vial from ElectraSyn 2.0, gently remove the cap with electrodes from the vial and transfer the reaction media to a separatory funnel. Both electrodes were rinsed with saturated NH_4Cl (aq) and Et_2O. Then, the crude mixture was further diluted with Et_2O. The resulting mixture was washed with brine. The organic layer was dried over with anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to furnish the desired product.

General Procedure C for e-XEC reaction of secondary-α-chloro pinacol boronic ester with chorosilane

In glove box, $TBAClO_4$ (2 mmol, 4 equiv.), TBAB (0.5 mmol, 1 equiv.), dried THF (2.5 mL) and DME (0.5 mL) was sequentially added into the flame dried undivided ElectraSyn vial (5 mL) equipped with a stir bar. The resulting suspension was pre-stirred for about 1 min to dissolve the electrolyte (If the substrate or electrophile was solid, it would be added to the vial before adding the solvent. If the substrate was sticky oil, it would be added as a solution in THF). Then the substrate (0.5 mmol, 1 equiv) and chlorosliane (1.5 mmol, 3 equiv) was sequentially added to the mixture. The vial was sealed with the ElectraSyn vial cap equipped with anode (Mg plate) and cathode (graphite plate), and then bring it out of glove box. Pre-stirring the resulting mixture for 2 minutes, and then the reaction mixture was electrolyzed at a constant current of 5 mA (current density = 1.03 mA/cm^2) until passing 2 F/mol of charge at room temperature. After electrolysis, disconnect the reaction vial from ElectraSyn 2.0, gently remove the cap with electrodes from the vial and transfer the reaction media to a separatory funnel. Both electrodes were rinsed with saturated NH_4Cl (aq) and Et_2O. Then, the crude mixture was further diluted with Et_2O. The resulting mixture was washed with brine. The organic layer was dried over with anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to furnish the desired product.

General Procedure D for e-XEC reaction of benzyl chloride with CO_2

In glove box, $TBAClO_4$ (2 mmol, 4 equiv.), dried THF (2.5 mL) and DME (0.5 mL) was sequentially added into the flame dried undivided ElectraSyn vial (5 mL) equipped with a stir bar. The resulting suspension was pre-stirred for about 1 min to dissolve the electrolyte (If the substrate or electrophile was solid, it would be added to

the vial before adding the solvent. If the substrate was sticky oil, it would be added as a solution in THF). Then the substrate (0.5 mmol, 1 equiv) was added to the mixture. The vial was sealed with the ElectraSyn vial cap equipped with anode (Mg plate) and cathode (graphite plate), and then bring it out of glove box. The resulting mixture was purged with CO_2 for 10 min, and then CO_2-filled balloon was adapted through the septum to sustain a CO_2 atmosphere. Then the reaction mixture was electrolyzed at a constant current of 5 mA (current density = 1.03 mA/cm^2) until passing 2.2 F/mol of charge at room temperature. After electrolysis, disconnect the reaction vial from ElectraSyn 2.0, gently remove the cap with electrodes from the vial and transfer the reaction media to a separatory funnel. Both electrodes were rinsed with saturated NH_4Cl (aq) and Et_2O. The crude mixture was acidified with HCl (1M, aq) to PH = 2, and then further diluted with Et_2O (40 mL). The resulting mixture was washed with saturated NH_4Cl (aq, 30 mL) and brine (30 mL x 3 times). The organic layer was dried over with anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to furnish the desired product.

General Procedure E for e-XEC reaction with TsOMe or $TsOCD_3$

In glove box, $TBAClO_4$ (2 mmol, 4 equiv.), TBAB (0.5 mmol, 1 equiv.), dried THF (2.5 mL) and DME (0.5 mL) was sequentially added into the flame dried undivided ElectraSyn vial (5 mL) equipped with a stir bar. The resulting suspension was pre-stirred for about 1 min to dissolve the electrolyte (If the substrate or electrophile was solid, it would be added to the vial before adding the solvent. If the substrate was sticky oil, it would be added as a solution in THF). Then the substrate (0.5 mmol, 1 equiv) and TsOMe or $TsOCD_3$ (1.5 mmol, 3 equiv) was sequentially added to the mixture. The vial was sealed with the ElectraSyn vial cap equipped with anode (Mg plate) and cathode (graphite plate), and then bring it out of glove box. Pre-stirring the resulting mixture for 2 minutes, and then the reaction mixture was electrolyzed at a constant current of 5 mA (current density = 1.03 mA/cm^2) until passing 2.2 F/mol of charge at room temperature. After electrolysis, disconnect the reaction vial from ElectraSyn 2.0, gently remove the cap with electrodes from the vial and transfer the reaction media to a separatory funnel. Both electrodes were rinsed with saturated NH_4Cl (aq) and Et_2O. Then, the crude mixture was further diluted with Et_2O. The resulting mixture was washed with brine. The organic layer was dried over with anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to furnish the desired product.

Note: (1) $TBAClO_4$ is classified as an oxidizer that should be handled with care and avoid heat or ignition. An example of a Safety Data Sheet can be found here: https://www.sigmaaldrich.com/US/en/sds/aldrich/86885.

(2) Although 3 equivalents of alkyl bromides or clorosilane were used for investigating the substrate scope of this reaction in most cases, the reaction using 2 equivalents of electrophiles still can give desired product in satisfied yield.

(3) As we have mentioned in the main text that the incorporation of DME as cosolvent can alleviate the passivation of electrode and decrease the use of electrolyte (usually 2 equivalents of $TBAClO_4$ is enough). Meanwhile, the use of DME can inhibit the background reaction. Therefore, we highly recommend to use a mixture of THF and DME (5/1, v/v) as solvent. Even for our reported results using THF as single solvent, especially for large scale reaction, these reactions using a mixture of THF and DME as solvent can give a very similar reaction results.

3. Extended Substrate Scope

Figure S1. Extended Substrate Scope

4. Suboptimal and Unsuccessful Substrates

Figure S2. Suboptimal and Unsuccessful Substrates

5. Optimization of Reaction Parameters for e-XEC Reaction

Optimization of electrode material

Entry	Electrode variation	Yield[a]
1	standard condition	70%
2	Al(+) instead of Mg(+)	15%
3	Zn(+) instead of Mg(+)	0%[b]
4	Fe (+) instead of Mg(+)	0%
5	Ni (+) instead of Mg(+)	0%
6	Sn (+) instead of Mg(+)	0%
7	C (+) + Amine (2.5 equiv.)[c] instead of Mg(+)	16%
8	Pt (-) instead of C (-)	28%
9	Ag (-) instead of C (-)	21%
10	Sn (-) instead of C (-)	32%
11	Al (-) instead of C (-)	8%
12	Zn (-) instead of C (-)	10%
13	Fe (-) instead of C (-)	12%
14	Cu (-) instead of C (-)	20%

[a] Reaction condition: **7-Cl** (1 mmol), **31** (3 mmol), $TBAClO_4$ (3 mmol), THF (2.5 mL),Mg anode, graphite cathode, undivided cell (5 mL, ElectraSyn 2.0), constant current i = 5 mA (current density = 1.03 mA/cm^2), Q = 2 F/mol, 22 °C. Yield determined by ^{1}H-NMR using CH_2Br_2 as internal standard. [b] Zn was precipitated on the graphite cathode. [c] Amine = 1,2,2,6,6-pentamethylpiperidine

Table S1. Optimization of electrode material

Optimization of electrolyte and other parameters

1 or 7-Cl 31 32 or 125

Entry	Variation from above conditions	Yield[a]
	7-Cl	
1	standard condition	70%
2	$TBAPF_6$ instead of $TBAClO_4$	0%[b]
3	$TBABF_4$ instead of $TBAClO_4$	30%
4	TBAOTf instead of $TBAClO_4$	22%
5	DMF as solvent	50%
6	TBAB, TBAI, TBAOTf, $TBABF_4$, $TBAPF_6$, Et_4NOTs, $LiNTf_2$, LiOTf, or $LiClO_4$ instead of $TBAClO_4$	12-20%[c]
	1	
7	standard condition	86%
8	THF/DME (2.5 mL/0.5 mL) as solvent	83%[d]
9	THF/DME (2.5 mL/0.5 mL) as solvent	91%[e]
10	$^nBu_3MeNOSO_3Me$ instead of $TBAClO_4$	14%[f]
11	$TBABPh_4$ instead of $TBAClO_4$	9%[f]
12	$LiBPh_4$ or $NaBPh_4$ instead of $TBAClO_4$	18-33%[f,g]
13	TBAOTs	28%[f]
14	$^nBu_4N^+(PhO)_2P(O)O^-$	0%[f,h]
15	THF, w/o electricity	17%[i]
16	THF/DME, w/o electricity	0%[j]
17	Mg powder	0%[k]
18	Mg powder	20%[l]
19	Mg (+), divided cell, I = 2.5 mA	72%[m]
20	C (+)+ Amine (2.5 equiv)[n], divided cell, I = 2.5 mA	75%[m]
21	Mg (+), divided cell, I = 2.5 mA, Alternating electrode polarity per 1s	0%[m]
22	Mg (+), divided cell, I = 2.5 mA, Alternating electrode polarity per 5s	0%[m]

[a] Reaction condition: **7-Cl** or **1** (1 mmol), **31** (3 mmol), $TBAClO_4$ (3 mmol), THF (2.5 mL),Mg anode, graphite cathode, undivided cell (5 mL, ElectraSyn 2.0), constant current i = 5 mA (current density = 1.03 mA/cm^2), Q = 2 F/mol, 22 °C. Yield determined by ^{1}H-NMR using CH_2Br_2 as internal standard. [b] initial cell votage too high. [c] DMF (3 mL) as solvent. [d] Less passivation on Anode. [e] $TBAClO_4$ (2 equiv.). [f] THF/DME (2.5 mL/0.5 mL) as solvent, electrolyte (2 equiv.). [g] cell voltage was too high after passing 0.5-0.7 F/mol of charge. [h] Mg was precipitated on graphite cathode. [i] 48% of **1** was recovered. [j] 95% of **1** wa recovered. [k] 100% of **1** was consumed. [l] $PhSCH_2CH_2CH_2Br$ (**2**) instead of **31** as electrophile. [m] Cathodic part: **1** (0.5 mmol), **31** (1.5 mmol), $TBAClO_4$ (2 mmol), THF (3.5 mL); Anodic part: $TBAClO_4$ (2 mmol), THF (3.5 mL). The detail of divided cell, see Figure S3. [n] Amine = 1,2,2,6,6-pentamethylpiperidine

Table S2. Optimization of electrolyte and other parameters

Figure S3: Divided cell before electrolysis (left), reaction mixture after electrolysis (middle), electrode after electrolysis (right).

6. e-XEC with Unactivated Alkyl Bromides

In glove box, $TBAClO_4$ (3 mmol, 3 equiv.) and dried THF (2.5 mL)) was added into the flame dried undivided ElectraSyn vial (5 mL) equipped with a stir bar. The resulting suspension was pre-stirred for about 1 min to dissolve the electrolyte. Then the (3-bromo-3-methylbutyl)benzene (1 mmol, 1 equiv.), alkyl bromide **2** (2 mmol, 2 equiv.), and internal standard tetradecane (1 mmol, 1 equiv.) was sequentially added to the mixture. The vial was sealed with the ElectraSyn vial cap equipped with anode (Mg plate) and cathode (graphite plate), and then bring it out of glove box. Pre-stirring the resulting mixture for 2 minutes, and then the reaction mixture was electrolyzed at a constant current of 5 mA until passing 2.1 F/mol of charge at room temperature. After electrolysis, disconnect the reaction vial from ElectraSyn 2.0, gently remove the cap with electrodes from the vial. 5 µl aliquots were drawn from the reaction and diluted with 2 mL of HPLC grade hexanes. The resultant solution was then flushed through a pipette filled with cotton and analyzed on GC and GC-MS.

The reaction was conducted as the procedure described above using *tert*-butyl bromide (1 mmol, 1 equiv.) and (3-bromopropoxy)benzene (2 equiv.) under constant current condition. After electrolysis, disconnect the reaction vial from ElectraSyn 2.0, gently remove the cap with electrodes from the vial. 5 µl aliquots were drawn from the reaction and diluted with 2 mL of HPLC grade hexanes. The resultant solution was then flushed through a pipette filled with cotton and analyzed on GC-MS. Then the remaining reaction mixture was worked up following the general procedure. The yield of the propoxybenzene was determined by ^{1}H NMR with CH_3NO_2 as internal standard.

The reaction was conducted as the procedure described above using (3-bromopropyl)benzene (1 mmol, 1 equiv.) and bromocyclopentane (3 equiv.) under constant current of 10 mA condition. After electrolysis, disconnect the reaction vial from ElectraSyn 2.0, gently remove the cap with electrodes from the vial. 5 μl aliquots were drawn from the reaction and diluted with 2 mL of HPLC grade hexanes. The resultant solution was then flushed through a pipette filled with cotton and analyzed on GC-MS. Then the remaining reaction mixture was worked up following the general procedure. The yield of the product was determined by ^{1}H NMR with CH_3NO_2 as internal standard.

7. Cyclic Voltammetry of Alkyl Halides

All cyclic voltammetry studies were conducted inside the glovebox with the BASi Epsilon. Measurements were performed in 0.5 M $TBAClO_4$ in THF using a divided three-compartment cell. $Mg(OTf)_2$, which bears a redox innocent anion, was used as the Mg^{2+} source instead of $MgCl_2$ due to its higher solubility in THF. Control experiments revealed no difference of $Mg(OTf)_2$ and $MgCl_2$ in the scan range of –3.0 ~ 0.5 V vs $Zn^{2+/0}$. Scan rate is 100 mV/s unless specified.

Supporting Electrolyte: $TBAClO_4$ was recrystallized in ethyl acetate for three times and dried under vacuum at 65 ℃ overnight.

Solvents: THF was first dried overnight with potassium hydroxide. Then reflux in sodium metal and benzophenone under nitrogen for 5 hours. The quality of the

solvent was verified by the deep purple color when acetophenone was added and the water concentration was titrated by a Karl Fischer Titrator to be 6.2 (±1.3) ppm.

Working electrode: The working electrode is a 3 mm diameter glassy carbon working electrode. Polished with 1.0, 0.3 and 0.05 µm aluminum oxide and then sonicated in distilled water and acetone before air drying and transferring into the glovebox.

Reference electrode: The reference electrode consisted of a zinc wire submerged in a saturated solution of zinc triflate ($Zn(OTf)_2$) and THF. The Zn wire was polished with sandpaper and washed with acetone before transferring into the glovebox. After each set of scans, ferrocene was added to reference the final potential to ferrocenium/ferrocene redox couple ($Fc^{+/0}$).

Counter electrode: The counter electrode is a platinum wire that was previous burnt for 30 seconds with a butane torch.

Figure S4. Cyclic voltammetry of **1** (tertiary α-bromo Bpin). The on-set potential for the reduction of **1** is around –2.1 V and the $E_{p1/2}$ is approximately –2.6 V.

Figure S5. Cyclic voltammetry of **2** (primary alkyl bromide). The on-set potential for the reduction of **2** is around –2.7 V.

Figure S6. Cyclic voltammetry of **7-Cl** (secondary α-chloro Bpin). The on-set potential for the reduction of **7-Cl** is around –2.8 V and the $E_{p1/2}$ is approximately –3.2 V.

Figure S7. Cyclic voltammetry of **7-Br** (secondary α-bromo Bpin). The on-set potential for the reduction of **7-Br** is around –2.5 V and the $E_{p1/2}$ is approximately –2.75 V.

Figure S8. Cyclic voltammetry of **51-sub** (primary allyl chloride). The on-set potential for the reduction of **51-sub** is around –2.5 V and the $E_{p1/2}$ is approximately –3.0 V.

Figure S9. Cyclic voltammetry of **58-sub** (primary propargyl chloride). The on-set potential for the reduction of **58-sub** is around –2.4 V and the $E_{p1/2}$ is approximately –2.8 V.

Figure S10. Cyclic voltammetry of **63-sub** (secondary α-silyl benzyl chloride). The on-set potential for the reduction of **63-sub** is around –2.2 V and the $E_{p1/2}$ is approximately –2.75 V.

Figure S11. Cyclic voltammetry of **65-sub** (tertiary α-bromo silane). The on-set potential for the reduction of **65-sub** is around –2.4 V and the $E_{p1/2}$ is approximately –2.8 V.

Figure S12. Cyclic voltammetry of **87** (secondary benzyl chloride). The on-set potential for the reduction of **87** is around –2.5 V and the $E_{p1/2}$ is approximately –2.8 V.

Figure S13. Cyclic voltammetry of $Mg(OTf)_2$. The on-set potential for the reduction of $Mg(OTf)_2$ is around –3.0 V.

Figure S14. Cyclic voltammetry of **1**, **2**, **7-Cl** and **7-Br**. The reduction of **1** is the easiest and **7-Br** are significantly easier to be reduced, compared to the **2** and **7-Cl**.

Figure S15. Cyclic voltammetry of **58-sub**, **51-sub**, **87** and **2**. The reduction of **58-sub**, **51-sub** and **87** is significantly easier compared to the **2**.

63–sub **65–sub** **2**

Figure S16. Cyclic voltammetry of **63-sub**, **65-sub** and **2**. The reduction of **63-sub** and **65-sub** is significantly easier compared to the **2**.

8. DFT Calculations

General Information: All density functional theory (DFT) calculations were performed with Gaussian 09[1]. Geometry optimizations were carried out in the gas phase using the B3LYP functional[2,3] and the 6-31+G(d) basis set[4]. Unscaled harmonic frequency calculations at the same level were performed to validate each structure as a minimum and to evaluate its zero-point energy and thermal corrections at 298 K. Quasiharmonic corrections[5,6] were applied during the entropy calculations by setting all positive frequencies that are less than 100 cm^{-1} to 100 cm^{-1}. On the basis of the optimized structures, single-point energy refinements were performed at the (U)B3LYP/maug-cc-pVTZ[7–12] level and the Gibbs energies of solvation were computed at the SMD[13]/(U)B3LYP/6-31+G(d) level. The computed standard reduction potentials were referenced to either aqueous saturated calomel electrode (SCE) or ferrocenium/ferrocene (Fc^+/Fc) couple in THF. Standard state concentration of 1.0 M was used. The thermodynamics of the electron was computed according to the Fermi−Dirac statistics[14].

The standard reduction potentials of ^{t}BuBr in DMF have been estimated experimentally (Table S3): E_1^o and E_2^o are −1.04 V[15] and −1.60 to −1.48 V[16] (vs aqueous SCE), respectively. While the DFT-computed E_1^o (−1.00 V) is quite similar to the experimental data (−1.04 V), the absolute deviation of the DFT-computed E_2^o (−2.18 V) from the experimental value (−1.60 to −1.48 V) is more than 500 mV. We attribute such a deviation to the following reasons: (1) The error of the computed Gibbs energy of solvation for charged species is large; (2) The uncertainty due to the reproducibility of the experiments may reach 200 mV; (3) The ion-pairing effect was not taken into account. Despite these issues, we could expect that the trend for the relative ease of the reduction of alkyl halides won't change much. The predicted potentials in THF are substantially more negative than those in DMF.

$$^t\mathrm{BuBr} + e^- \longrightarrow {}^t\mathrm{Bu}^\bullet + \mathrm{Br}^- \qquad E_1^\circ$$

$$^t\mathrm{Bu}^\bullet + e^- \longrightarrow {}^t\mathrm{Bu}^- \qquad E_2^\circ$$

Solvent	Reference	E_1^o (V)		E_2^o (V)	
		DFT	expt	DFT	expt
DMF	aqueous SCE[a]	−1.00	−1.04[15]	−2.18	−1.60 to −1.48[16]
THF	Fc^+/Fc in THF	−2.03	N.D.[b]	−3.30	N.D.[b]

[a] The absolute potential of aqueous SCE is 4.522 V[17]. The liquid junction potential for

DMF | H_2O junction is 0.172 V[18]. [b] Not available from the literature.

Table S3. Standard reduction potentials of ^{t}BuBr in DMF and THF.

The DFT-computed standard reduction potential of alkyl halides and the corresponding carboradicals in THF are listed as follows:

Figure S17. DFT-computed standard reduction potential of alkyl halides in THF.

The substituent effect on the standard reduction potentials (E_1^o and E_2^o) of alkyl halides was investigated for a broad scope of substituents (Figure S17). Simple alkyl halides (i.e., **RX-1**, **RX-2** and **RX-3**) without stabilizing groups that allow for delocalization *via* p−p or p−π conjugation had significantly lower (more negative) reduction potentials. This is especially true for E_2^o: the reduction of *tert*-butyl and isopropyl radicals to the corresponding carbanions requires potentials of −3.30 V and −3.22 V vs Fc^+/Fc, respectively. This gives a good rationale for why tertiary and secondary alkyl halides without an anion-stabilizing substituent are not component coupling partners. Further, the computed E_1^o is significantly higher (less negative) than E_2^o for all alkyl halides investigated. Despite this, reaction conditions enable selective formation of the alkyl anion *via* an ECE mechanism, suggesting that the

initial reduction has a significant overpotential. This is also evident by the cyclic voltammetry studies, which show a single reduction wave for the alkyl halides that does not resolve both electron transfers despite the calculated differences.[19] It suggests that the reaction is most selective for the radical–polar cross-over for electrodes with a large overpotential for the first reduction. This is further supported by the electrode screening which revealed that electrode materials that are electrocatalytic for alkyl halide reduction (silver, copper, platinum) (Table S4) provide diminished yields and lower selectivity with increased amounts of side products derived from radical side reactions. We supposed that graphite imparts a substantial overpotential for the initial reduction of **1**, thereby rendering the first electron transfer in the ECEC mechanism slower than the second and ensuring high reaction selectivity.

Entry	Cathode	Results
1	graphite	**3** (79%)+**4** (5%)+**5** (3%)+**6** (3%)
2	Ag	**3** (38%)+**4** (9%)+**5** (4%)+**6** (19%)
3	Cu	**3** (58%)+**4** (3%)+**6** (5%)
4	Pt	**3** (61%)+**4** (2%)+**6** (18%)

Table S4. Cathode effect on the chemoselectivity of e-XEC reaction

	TCG[a,b] (a.u.)	SPE[a] (a.u.)	SPE[c] (a.u.)	SPE[d] (a.u.)	SPE[e] (a.u.)
ferrocene (Fc)	0.138670	-1650.731084	-1651.013196	-1650.743434	
ferrocenium (Fc^+)	0.138089	-1650.471296	-1650.754580	-1650.550919	
Cl^-	-0.015023	-460.274726	-460.310516	-460.367485	
Br^-	-0.016176	-2571.803183	-2574.318372	-2571.879325	-2571.888107
RX-1	0.038968	-2650.952911	-2653.492316	-2650.959908	
carboradical	0.035259	-79.162850	-79.192657	-79.163979	
carbanion	0.034817	-79.149242	-79.182434	-79.242912	
RX-2	0.065660	-2690.275635	-2692.822851	-2690.283311	
carboradical	0.061017	-118.483732	-118.526627	-118.486420	
carbanion	0.060589	-118.468560	-118.514138	-118.555816	
RX-3	0.093538	-2729.596874	-2732.152127	-2729.604781	-2729.604572
carboradical	0.088569	-157.804493	-157.860124	-157.807819	-157.807024
carbanion	0.087686	-157.794918	-157.852662	-157.874358	-157.885068
28-sub	0.173984	-910.808028	-910.998746	-910.821100	
carboradical	0.171085	-450.553910	-450.706793	-450.560751	

carbanion	0.169953	-450.591691	-450.747660	-450.671908	
RX-4	0.200701	-950.125287	-950.328648	-950.139144	
carboradical	0.196499	-489.874917	-490.040848	-489.883607	
carbanion	0.194785	-489.902376	-490.071000	-489.979239	
1	0.226414	-3100.978717	-3103.653624	-3100.992568	
carboradical	0.223452	-529.196061	-529.374811	-529.205178	
carbanion	0.221774	-529.219316	-529.400114	-529.291393	
87	0.114773	-770.488628	-770.624884	-770.501693	
carboradical	0.110729	-310.245718	-310.345280	-310.254981	
carbanion	0.108492	-310.269292	-310.371459	-310.344211	
51-sub	0.043735	-577.508508	-577.587837	-577.516162	
carboradical	0.041751	-117.267924	-117.309878	-117.270379	
carbanion	0.039247	-117.281082	-117.326341	-117.363473	
RX-5	0.139931	-1024.272049	-1024.435914	-1024.280727	
carboradical	0.135405	-564.035498	-564.161962	-564.040417	
carbanion	0.133768	-564.067179	-564.195579	-564.138615	
63-sub	0.181087	-1139.848781	-1140.046576	-1139.860619	
carboradical	0.177971	-679.609323	-679.769518	-679.617422	
carbanion	0.175799	-679.653152	-679.816094	-679.719295	
RX-5	0.130707	-3059.637888	-3062.243405	-3059.644786	
carboradical	0.127540	-487.848938	-487.952795	-487.850771	
carbanion	0.124994	-487.862533	-487.969451	-487.931174	
RX-6	0.157590	-3098.956152	-3101.570082	-3098.963198	
carboradical	0.153991	-527.167508	-527.284205	-527.170196	
carbanion	0.151304	-527.176078	-527.295128	-527.240329	

[a] Computed at the (U)B3LYP/6-31+G(d) level. [b] Computed at 1 atm and 298 K with quasiharmonic corrections. [c] Computed at the (U)B3LYP/maug-cc-pVTZ//(U)B3LYP/6-31+G(d) level. [d] Computed at the SMD(THF)/(U)B3LYP/6-31+G(d)//(U)B3LYP/6-31+G(d) level. [e] Computed at the SMD(DMF)/(U)B3LYP/6-31+G(d)//(U)B3LYP/6-31+G(d) level.

Table S5. Thermal corrections to Gibbs energies (TCGs) and single-point energies (SPEs)

Cartesian coordinates for ^{t}BuBr (**RX-3**)

Br	0.000000	0.000000	1.168765
C	0.000000	0.000000	-0.855575
C	0.000000	1.463917	-1.285186
C	-1.267789	-0.731959	-1.285186
C	1.267789	-0.731959	-1.285186
H	-0.887650	1.985812	-0.915069
H	0.000000	1.518936	-2.383187
H	0.887650	1.985812	-0.915069
H	-1.275938	-1.761633	-0.915069
H	-1.315437	-0.759468	-2.383187
H	-2.163588	-0.224179	-0.915069

H	2.163588	-0.224179	-0.915069
H	1.315437	-0.759468	-2.383187
H	1.275938	-1.761633	-0.915069

Cartesian coordinates for **1**

Br	2.418170	-0.816920	-0.425261
O	-0.723967	0.801704	-0.878710
O	-0.695084	-0.229651	1.168144
C	1.546747	0.835566	0.394850
C	2.024116	0.898300	1.841403
C	2.014263	2.024831	-0.435976
C	-2.113171	0.436282	-0.609361
C	-1.964275	-0.620936	0.557495
C	-2.726854	-0.102196	-1.900063
C	-2.830663	1.723949	-0.182628
C	-3.050636	-0.564958	1.628923
C	-1.784867	-2.061439	0.060776
B	0.017472	0.460347	0.222089
H	1.560367	1.763084	2.337574
H	3.112208	1.019241	1.890833
H	1.745084	-0.000254	2.396858
H	1.551324	2.942497	-0.045319
H	1.726488	1.922182	-1.485105
H	3.102570	2.139963	-0.379434
H	-2.754910	0.694257	-2.651140
H	-3.754565	-0.444347	-1.729142
H	-2.145131	-0.931062	-2.310002
H	-2.395743	2.146235	0.729421
H	-3.897756	1.548608	-0.007384
H	-2.730838	2.467637	-0.980029
H	-2.834547	-1.304641	2.407005
H	-4.031989	-0.800970	1.200392
H	-3.104409	0.417563	2.104121
H	-0.987724	-2.133555	-0.685588
H	-2.710768	-2.451892	-0.375685
H	-1.508508	-2.696890	0.908325

Cartesian coordinates for the other structures are available upon request from one of the corresponding authors (Song Lin: songlin@cornell.edu).

9. Kinetic Studies

The reactions were setup as described protocol in general procedure A in 0.5 mmol scale under constant current of 2.5 mA condition. Tetradecane (0.5 mmol) was added as an internal standard. A nitrogen filled balloon was connected to the reaction vessel to sustain a nitrogen atmosphere. About 5 μl aliquots of reaction mixture were drawn from the reaction at various charges passed and diluted with 2 mL HPLC grade hexanes. The resultant solution was then flushed through a pipette filled with cotton and analyzed on GC. Signals were identified by comparison with the retention time of

authentic samples. Area of the product was calibrated about the internal standard tetradecane.

Figure S18. Monitor the reaction of **1** with 3 equiv. of **2**

Figure S19. Monitor the reaction of **1** with 2 equiv. of **2**

Figure S20. Monitor the reaction of **1** with 1.05 equiv. of **2**

Figure S21. Monitor the reaction of **1** with **2** under constant current of 4 mA condition

Figure S22. Monitor the reaction of **7-Br** with **2**

Figure S23. Monitor the reaction of **7-Cl** with **2**

Discussion: Secondary α-chloro Bpin **7-Cl** can also undergo e-XEC with **2** to afford **8** in 53%isolated yield, in addition to 5% of dimer **10**. However, we also obtained a significant amount (22%) of alkane **6** from hydrodehalogenation of **2.** During the time course, we observed an induction period as well as the formation of a new compound, which was assigned as halogen-exchange product **7-Br** by a comparison of NMR, GC-MS, and GC retention time with authentic **7-Br**, respectively. The concentration of **7-Br** was gradually increased before consuming the first 1 F/mol of charge, and then decreased. Further CV study revealed that substrate **7-Cl** shows a similar reduction potential to its coupling partner **2**, whereas the corresponding bromide **7-Br** is substantially easier to reduce than **7-Cl** (by ~400 mV). These findings suggest that **7-Br** is likely the actual reactant in the e-XEC, with the observed induction period stemming from slow generation of **7-Br** upon unproductive consumption of **2** to release Br^-. To increase the yield and selectivity of the e-XEC reaction between **7-Cl** and **2**, we proposed to add a catalytic amount of tetrabutylammonium bromide (TBAB) to promote the in-situ halogen exchange. The results are listed as follows:

Figure S24. Monitor the reaction of **7-Cl** with **2** in the presence of TBAB (0.3 equiv.)
Discussion: The e-XEC reaction between **7-Cl** with **2** in the presence of TBAB (0.3 equiv.) can provide the product **8** in an improved yield (60%) and chemoselectivity (12% **6**), which is similar to the results for the reaction with **7-Br**.

10. Control Reactions under Previously Reported XEC Conditions

10.1 Reaction under Metallaphotoredox Condition

The reaction was performed according to the literature reference with slight modification[20]. In glove box, to an 8 mL vial equipped with a stir bar was added photocatalyst $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.3 mg, 0.01 equiv.), the substrate with anion-stabilizing group (0.2 mmol, 1 equiv.) , supersilanol (159 mg, 0.6 mmol, 3 equiv.), anhydrous potassium phosphate (127 mg, 0.6 mmol, 3.0 equiv.) and MeCN (2 mL). To a separate vial was added $NiCl_2{\bullet}6H_2O$ (2.5 mg, 0.05 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (2.8, 0.05 equiv.). The precatalyst vial was sealed, dissolved in MeCN (0.5 mL) and then sonicated until it became homogeneous. Subsequently, the precatalyst solution was syringed into the reaction vessel and the solution was degassed by sparging with nitrogen for 20 minutes. The alkyl bromide **2** was then added (231 mg, 1.0 mmol, 5.0 equiv) was then added before sealing with parafilm. The reaction was stirred and irradiated using 2 x 15 W blue LED lamps (5 cm away, with cooling fan to keep the reaction at room temperature) for 24 hours. The reaction was quenched by exposure to air. Thereafter, tetradecane (38.0 mg, 0.2 mmol)

was added to the reaction mixture, and stirred the mixture for 10 min. About 5 µl aliquots of reaction mixture were drawn from the reaction and diluted with 2 mL HPLC grade hexanes. The resultant solution was then flushed through a pipette filled with cotton and analyzed on GC.

10.2 Reaction under Ni-Catalyzed XEC Reaction Condition with Zn as Reductant

The reaction was performed according to the literature reference with slight modification[21]. To a flame-dried seal tube equipped with a magnetic stir bar was added (4-Cl)-H-Pybox (3.2 mg, 0.013 mmol, 8 mol%). The tube was moved into a glove box, at which point $Ni(COD)_2$ (4.4 mg, 0.016 mmol, 10 mol%), activated Zn powder (31.0 mg, 0.48 mmol, 3 equiv.), and substrate with anion-stabilizing group (0.16 mmol, 1 equiv.) was added. The tube was moved out of the glove box, and alkyl bromide **2** (111 mg, 0.48 mmol, 3 equiv.) and DMA (1.0 mL) were then added via syringe under N_2 atmosphere. After the reaction mixture was allowed to stir for 16 h

under N_2 atmosphere at room temperature, tetradecane (29.6 mg, 0.16 mmol) was added to the reaction mixture. The resulting mixture was stirred for 10 minutes. Then the mixture was diluted with brine (5 mL) and ethyl acetate (5 mL). The organic layer was washed with brine (5 mLx2), dried over Na_2SO_4. About 10 µl aliquots of the mixture were drawn from the organic layer and diluted with 2 mL HPLC grade hexanes. The resultant solution was then flushed through a pipette filled with cotton and analyzed on GC.

10.3 Reaction under Ni-catalyzed XEC Reaction Condition with B_2pin_2 as Reductant

The reaction was performed according to the literature reference with slight modification[22]. To a flame-dried seal tube equipped with a magnetic stir bar was added 2-(2-Pyridyl)imidazoline (2.4 mg, 0.016 mmol, 10 mol %), (pin)B–B(pin) (81.3 mg, 0.32 mmol, 2 equiv.). The tube was moved into a glove box, at which point NiI_2 (5.0 mg, 0.016 mmol, 10 mol %), LiOMe (15.2 mg, 0.40 mmol, 2.5 equiv.), and substrate with anion-stabilizing group (0.16 mmol, 1 equiv.) was sequentially added. The tube was moved out of the glove box, then alkyl bromide **2** (0.24 mmol, 1.5 equiv.) and NMP (0.5 mL) were then added via a syringe. After the reaction mixture was allowed to stir for 16 h at 40 ℃, recovered the reaction mixture to room

temperature, and tetradecane (29.6 mg, 0.16 mmol) was added to the reaction mixture. The resulting mixture was stirred for 10 minutes. Then the mixture was diluted with brine (5 mL) and ethyl acetate (5 mL). The organic layer was washed with brine (5 mLx2), dried over Na_2SO_4. About 10 µl aliquots of the mixture were drawn from the organic layer and diluted with 2 mL HPLC grade hexanes. The resultant solution was then flushed through a pipette filled with cotton and analyzed on GC.

11. Synthetic Application

11.1 Iterative e-XEC for the Synthesis of a Polysubstituted Alkylboronic Ester

2-(1-Chlorooctan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**32**): Followed general procedure A and purified using silica gel chromatography (Hexanes:Et_2O = 50:1) to give 186.4 mg (68% yield) of **32** as a colorless oil.^{1}H NMR: (500 MHz,

$CDCl_3$) δ 3.51 (t, *J* = 7.0 Hz, 2H), 1.83-1.72 (m, 2H), 1.55-1.46 (m, 2H), 1.45-1.38 (m, 1H), 1.37-1.32 (m, 1H), 1.31-1.26 (m, 4H), 1.24 (s, 12H), 1.01-0.92 (m, 1H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 83.1, 45.5, 32.5, 31.5, 31.0, 25.0, 24.9, 23.1, 14.2, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.4 (br). IR (neat): 2978, 2956, 1460, 1371, 1314, 1142, 967, 852, 770, 687 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{14}H_{32}BClNO_2$) m/z 292.2209, found m/z 292.2210.

2-(4-Bromo-1-chlorooctan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**33**): In a three-necked round bottom flask with a magnetic stir bar and equipped with a saturated $NaHCO_3$ (aq) scrubber, bromine (0.14 mL, 2.87 mmol, equiv) was dropwise added to a solution of **32** (830 mg, 2.87 mmol, 1 equiv., accumulated by parallelly set up the XEC reaction for 5 times) in CCl_4 (8 mL) under N_2. The reaction was stirred at room temperature under N_2 for 8 hours. The stir bar was removed and the reaction was concentrated *in vacuo* to afford the crude product (1.00 g).Considering the potential elimination reaction of the product during the purification, the afforded crude mixture was directly used in the next e-XEC reaction without purification. The purity of product (70%) was determined by ^{1}H NMR with internal standard.

2-(1-Chloro-4-(3-phenoxypropyl)octan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (35): Followed general procedure A and purified using silica gel chromatography (Hexanes:DCM = 1:1) to give 245.0 mg (60% yield) of **35** as a white solid.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.28-7.21 (m, 2H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 7.5 Hz, 2H), 3.90 (t, *J* = 7.0 Hz, 2H), 3.48 (t, *J* = 7.0 Hz, 2H), 1.75-1.63 (m, 4H), 1.51-1.42 (m, 4H), 1.37-1.32 (m, 2H), 1.30-1.24 (m, 2H), 1.21 (s, 12H), 1.19-1.13 (m, 2H), 0.87 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 159.2, 129.5, 120.5, 114.6, 83.3, 68.6, 46.1, 30.2, 28.4, 27.2, 25.0, 24.6, 23.7, 14.3, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.8 (br). IR (neat): 2928, 2869, 1601, 1586, 1461, 1408, 1379, 1235, 1081, 895, 755, 695, 596 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{23}H_{42}BClNO_3$) m/z 426.2941, found m/z 426.2948.

11.2 Formal Benzylic C–H (d_3-)Methylation of Bioactive Molecules

Step 1: The approach to chlorination the benzylic C-H bonds was performed according to Leonori's report[23]. A 20 mL screw-cap culture tube equipped with a septum and a magnetic stir bar was charged with NCS (267 mg, 2 mmol, 1.0 equiv.), evacuated and refilled with N_2. The degassed DCM (5 mL) (degassed by bubbling through with N_2 for 20 min.) and the amine (226 mg, 2 mmol, 1.0 equiv.) were added and the mixture was stirred for 30 min at room temperature (In order to minimize

direct exposure the mixture to visible light at this stage, the tube was fully covered with aluminum foil). Then the reaction mixture was cooled to 0 ℃ and stirred at this temperature for 10 minutes. After that, the benzylic C-H substrate (2 mmol, 1.0 equiv., in the case of solid substrates, they were added as a 2 M solution in the DCM) and $HClO_4$ (70 % in H_2O, 3.0 equiv.) was sequentially added to the mixture. After taking off the aluminum foil covered on the surface of the tube, the blue LEDs were immediately switched on and the mixture was stirred under blue LED irradiation for 2 h at 0 ℃. Then turn off the light, the mixture was allowed warmed to r.t. The reaction mixture was diluted with H_2O and DCM. The organic layer was washed with brine, dried over MgSO4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography to afford the desire product.

Step 2: In glove box, $TBAClO_4$ (2 mmol, 4 equiv.), TBABr (0.5 mmol, 1 equiv.), dried THF (2.5 mL) and DME (0.5 mL) was sequentially added into the flame dried undivided ElectraSyn vial (5 mL) equipped with a stir bar. The resulting suspension was pre-stirred for about 1 min to dissolve the electrolyte (If the substrate was solid, it would be added to the vial before adding the solvent. If the substrate was sticky oil, it would be added as a solution in THF). Then the substrate (0.5 mmol, 1 equiv) and TsOMe or $TsOCD_3$ (1.5 mmol, 3 equiv) was sequentially added to the mixture. The vial was sealed with the ElectraSyn vial cap equipped with anode (Mg plate) and cathode (graphite plate), and then bring it out of glove box. Pre-stirring the resulting mixture for 2 minutes, and then the reaction mixture was electrolyzed at a constant current of 5 mA (current density = 1.03 mA/cm^2) until passing 2.2 F/mol of charge at room temperature. After electrolysis, disconnect the reaction vial from ElectraSyn 2.0, gently remove the cap with electrodes from the vial and transfer the reaction media to a separatory funnel. Both electrodes were rinsed with saturated NH_4Cl (aq) and Et_2O. Then, the crude mixture was further diluted with Et_2O. The resulting mixture was washed with brine. The organic layer was dried over with anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to furnish the desired product.

77-Cl

methyl (1R,4aS,10aR)-9-chloro-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydro phenanthrene-1-carboxylate (77-Cl): Prepared from methyl (1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene -1-carboxylate (2 mmol, 1 equiv.) following the procedure in step 1. When we try to purify the crude mixture by flash chromatography, the product was decomposed to the alkene (438 mg, 70% yield). ^{1}H NMR: (300 MHz, $CDCl_3$) δ 7.11-7.03 (m, 2H), 6.90

(s, 1H), 6.50 (dd, J = 9.6 Hz, 3.0 Hz, 1H), 5.70 (dd, J = 9.6 Hz, 2.4 Hz, 1H), 3.63 (s, 3H), 2.91 (t, J = 3.0 Hz, 1H), 2.89-2.78 (m, 1H), 2.20 (d, J = 12.3 Hz, 1H), 1.88-1.62 (m, 2H), 1.38 (s, 3H), 1.23 (s, 3H), 1.21 (s, 3H), 1.07 (s, 3H). Then the alkene was transformed to **77-Cl** according the following procedure: Acetyl chloride (864 mg, 11 mmol, 8 equiv) was dropwise added to a solution of the alkene (428 mg, 1.37 mmol) in EtOH (0.64 mL, 11 mmol, 8 equiv) at room temperature (*Caution: Anhydrous HCl gas was generated by the reaction of acetyl chloride with EtOH. To avoid the high pressure of the reaction vessel, we recommend to use a lage reaction flask and to tie the rubber cap with the flask by PTFE tape*). The mixture was stirred at 30 ^{o}C for 3 hours. After the reaction, the mixture was diluted with water and ethyl acetate. The organic layer dried over $MgSO_4$, filtered, and concentrated in vacuo. The resulting white solid (483 mg, dr~2.7:1, 75% purity, 76% yield) containing 25% of alkene was directly used in e-XEC reaction without further purification.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.21-7.09 (m, 3H), 5.39-5.31 (m, 1H), 3.70 (s, 2.2 H), 3.68 (s, 0.8H), 2.91-2.81 (m, 1.3H), 2.74 (dd, J = 12.5 Hz, 1.5 Hz, 0.7H), 2.38-2.25 (m, 2H), 2.11-1.94 (m, 1H), 1.87-1.53 (m, 6H), 1.34-1.16 (m, 12H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 178.6/178.3, 147.4/146.7, 146.6/146.3, 134.6/134.0, 129.0/128.0, 127.4/126.4, 124.6/124.0, 60.0/59.6, 52.3/52.1, 47.4/47.3, 45.1/40.5, 38.0/37.6, 37.46/37.44, 36.8/35.8, 34.3/33.6, 31.8, 25.2/24.9, 24.11/24.06, 23.95/23.91, 18.7/18.4, 16.9/16.5 . HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{21}H_{33}ClNO_2$) m/z 366.2194, found m/z 366.2203.

77

Methyl (1R,4aS,10aR)-7-isopropyl-1,4a,9-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (77): Followed the procedure in step 2 and purified using silica gel chromatography (Hexanes:EA = 25:1) to give product (152.0mg, 92% purity, 85% yield, dr = 1:1) as a white solid. The afford product is a mixture of **77** (92%) and unknown side product (8%), which was hard to be purified by column chromatography due to the same polarity to **77**. The purity was determined by ^{1}H-NMR with internal standard. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.16 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 7.07 (s, 0.5H), 7.02 (s, 0.5 H), 7.00 (s, 0.5H), 6.95 (s, 0.5H), 3.67/3.66 (s, 3H), 3.06-2.94 (m, 1H), 2.93-2.79 (m, 1H), 2.40-2.24 (m, 1.5H), 2.07 (td, J = 13.0 Hz, 6.5 Hz, 0.5H), 1.88-1.45 (m, 7H), 1.34-1.17 (m, 15H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 179.3/179.1, 147.0/146.6, 145.90/145.87, 140.03/139.95, 127.5/125.9, 124.3/124.2, 124.1/123.9, 52.0/51.9, 47.9/47.6, 44.4/40.5, 38.4/38.2, 37.6/37.4, 36.7/36.5, 34.2/33.8, 33.7/33.0, 31.6/29.1, 25.7/25.2, 24.7/24.2, 24.16/23.4, 24.11, 18.8/18.7, 16.61/16.55. IR (neat): 2951, 2865, 1719, 1493, 1454, 1383, 1361, 1246, 1108, 987,

870, 752, 643 cm^{-1}.HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{22}H_{36}NO_2$) m/z 346.2741, found m/z 346.2742.

78-Cl

Methyl 2-(4-(1-chloro-2-methylpropyl)phenyl)propanoate (78-Cl): Prepared from methyl 2-(4-isobutylphenyl)propanoate (2 mmol, 1 equiv.) following the procedure in step 1. The resulting mixture was purified by flash column chromatography to afford the product **78-Cl** (442 mg, 87% yield, dr = 1:1) as a colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7. 32-7.24 (m, 4H), 4.62 (d, *J* = 7.5 Hz, 1H), 3.72 (q, *J* = 7.0 Hz, 1H), 3.66 (s, 3H), 2.28-2.17 (m, 1H), 1.49 (d, *J* = 7.0 Hz, 3H), 1.10 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 175.00/174.99, 140.31/140.29, 140.0, 127.9, 127.6, 70.6, 52.2, 45.2, 36.7, 20.3, 19.7, 18.7. HRMS (DART) calculated for $[M+H]^+$ ($C_{20}H_{24}ClO_2$) m/z 331.1465, found m/z 331.1459.

78

Methyl 2-(4-(3-methylbutan-2-yl-1,1,1-d3)phenyl)propanoate (78): Followed the procedure in step 2 and purified using silica gel chromatography (Hexanes:EA = 25:1) to give product (89.0 mg, 88% purity, 66% yield, dr = 1:1) as a colorless oil. The afford product is a mixture of **78** (88%) and unknown side product (12%), which was hard to be purified by column chromatography due to the same polarity to **78**. The purity was determined by ^{1}H-NMR with internal standard. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 3.70 (q, *J* = 7.0 Hz, 1H), 3.66 (s, 3H), 2.39 (d, *J* = 7.5 Hz, 1H), 1.79-1.70 (m, 1H), 1.49 (d, *J* = 7.0 Hz, 3H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.75 (d, *J* = 6.5 Hz, 3H) ; ^{13}C NMR: (126 MHz, $CDCl_3$) δ 175.4, 146.0, 137.8, 128.0, 127.2, 52.1, 46.3, 45.2, 34.5, 21.3, 20.2, 18.8. IR (neat): 2954, 2872, 1735, 1511, 1456, 1434, 1383, 1248, 1207, 1162, 1062, 934, 829, 767, 555 cm^{-1}.HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{15}H_{23}D_3NO$) m/z 255.2146, found m/z 255.2153.

79-Cl

Methyl 4'-(1-chlorohexyl)-[1,1'-biphenyl]-4-carboxylate (79-Cl): Prepared from methyl 4'-hexyl-[1,1'-biphenyl]-4-carboxylate (2 mmol, 1 equiv.) following the

procedure in step 1. The resulting mixture was purified by flash column chromatography to afford the product **79-Cl** (514 mg, 78% yield) as a white solid. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.13-8.09 (m, 2H), 7.68-7.64 (m, 2H), 7.63-7.59 (m, 2H), 7.50-7.46 (m, 2H), 4.90 (t, *J* = 7.2 Hz, 1H), 3.94 (s, 3H), 2.21-2.13 (m, 1H), 2.11-2.01 (m, 1H), 1.58-1.46 (m, 1H), 1.36-1.28 (m, 5H), 0.92-0.87 (m, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 167.1, 145.1, 142.1, 140.0, 130.3, 129.2, 127.7, 127.6, 127.1, 63.6, 52.3, 40.0, 31.3, 26.9, 22.6, 14.1. HRMS (DART) calculated for $[M+H]^+$ ($C_{20}H_{24}ClO_2$) m/z 331.1459, found m/z 331.1465 .

79

Methyl 4'-(heptan-2-yl-1,1,1-*d*$_3$)-[1,1'-biphenyl]-4-carboxylate (79): Followed the procedure in step 2 and purified using silica gel chromatography (Hexanes:EA = 25:1) to give product (125.2 mg, 80% purity, 64% yield) as a colorless oil. The afford product is a mixture of **79** (80%) and unknown side product (20%), which was hard to be purified by column chromatography due to the same polarity to **79**. The purity was determined by ^{1}H-NMR with internal standard. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.12-8.07 (m, 2H), 7.68-7.64 (m, 2H), 7.58-7.54 (m, 2H), 7.30-7.26 (m, 2H), 3.94 (s, 3H), 2.72 (t, *J* = 7.5 Hz, 1H), 1.68-1.57 (m, 2H), 1.36-1.17 (m, 6H), 0.89-0.93 (m, 3H) ; ^{13}C NMR: (126 MHz, $CDCl_3$) δ 167.2, 148.4, 145.7, 137.5, 130.2, 129.1, 127.7, 127.3, 127.0, 52.2, 39.6, 38.4, 32.1, 27.5, 22.7, 14.2. IR (neat): 2953, 2924, 2854, 1719, 1607, 1435, 1274, 1109, 827, 770 cm^{-1}.HRMS (DART) calculated for $[M+H]^+$ ($C_{21}H_{24}D_3O_2$) m/z 314.2194, found m/z 314.2203.

12. Control Experiments

12.1 Radical Probe Experiment

In glove box, $TBAClO_4$ (3 mmol, 3 equiv.) and dried THF (2.5 mL)) was added into the flame dried undivided ElectraSyn vial (5 mL) equipped with a stir bar. The resulting suspension was pre-stirred for about 1 min to dissolve the electrolyte. Then the substrate **80** (1 mmol, 1 equiv.) and alkyl bromide **31** (3 mmol, 3 equiv.) was sequentially added to the mixture. The vial was sealed with the ElectraSyn vial cap equipped with anode (Mg plate) and cathode (graphite plate), and then bring it out of glove box. Pre-stirring the resulting mixture for 2 minutes, and then the reaction

mixture was electrolyzed at a constant current of 5 mA (current density = 1.03 mA/cm^2) until passing 2 F/mol of charge at room temperature. After electrolysis, disconnect the reaction vial from ElectraSyn 2.0, gently remove the cap with electrodes from the vial and transfer the reaction media to a separatory funnel. Both electrodes were rinsed with saturated NH_4Cl (aq) and Et_2O. Then, the crude mixture was further diluted with Et_2O. The resulting mixture was washed with brine. The organic layer was dried over with anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (Hexanes:Et_2O = 30:1) to give colorless oil a mixture of desire product **81** and ring-opened protonation product (141.2 mg) as a colorless oil. The yield of **81** (35%) was further determined by ^{1}H-NMR with CH_3NO_2 as internal standard after column chromatography purification.(Note: the minor peak in ^{1}H-NMR is protonation product). ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.21-7.17 (m, 1H), 7.16-7.12 (m, 2H), 6.51 (dt, *J* = 18.0 Hz, 6.5 Hz, 1H), 5.43 (d, *J* = 17.5 Hz, 1H), 3.43 (t, *J* = 6.5 Hz, 2H), 2.71-2.63 (m, 1H), 2.54-2.40 (m, 2H), 1.90-1.80 (m, 1H), 1.70-1.51 (m, 4H), 1.24 (s, 12H) ; ^{13}C NMR: (126 MHz, $CDCl_3$) δ 152.2, 144.7, 128.6, 128.5, 127.6, 126.4, 83.2, 45.2, 44.8, 43.7, 33.2, 30.7, 24.9, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 29.7 (br). IR (neat): 2977, 2928, 1637, 1452, 1358, 1320, 1142, 969, 848, 734, 648 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{19}H_{32}BClNO_2$) m/z 352.2209, found m/z 352.2213.

12.2 Reaction with Chiral Alkyl Bromide

In glove box, $TBAClO_4$ (3 mmol, 3 equiv.), dried THF (2.5 mL) and DME (0.5 mL) was added into the flame dried undivided ElectraSyn vial (5 mL) equipped with a stir bar. The resulting suspension was pre-stirred for about 1 min to dissolve the electrolyte. Then the substrate **1** (1 mmol, 1 equiv) and **82** (3 mmol, 3 equiv) was sequentially added to the mixture. The vial was sealed with the ElectraSyn vial cap equipped with anode (Mg plate) and cathode (graphite plate), and then bring it out of glove box. Pre-stirring the resulting mixture for 2 minutes, and then the reaction mixture was electrolyzed at a constant current of 5 mA (current density = 0.97 mA/cm^2) until passing 2.1 F/mol of charge at room temperature. After electrolysis, disconnect the reaction vial from ElectraSyn 2.0, gently remove the cap with electrodes from the vial and transfer the reaction media to a separatory funnel. Both electrodes were rinsed with saturated NH_4Cl (aq) and Et_2O. Then, the crude mixture was further diluted with Et_2O. The resulting mixture was washed with brine. The organic layer was dried over with anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified using silica gel chromatography (Hexanes:Et_2O = 33:1) to give 91.4 mg (30% yield, 92% ee) of **83** as a colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.29-7.25 (m, 2H), 7.20-7.16 (m, 3H), 2.77-2.69 (m,

1H), 2.52-2.43 (m, 1H), 1.73-1.65 (m, 1H), 1.55-1.48 (m, 1H), 1.37-1.29 (m, 1H), 1.22 (s, 12H), 0.92 (d, J = 6.5 Hz, 3H), 0.87 (d, J = 4.0 Hz, 6H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 143.5, 128.5, 128.4, 125.6, 82.9, 39.7, 35.7, 35.1, 24.9, 24.8, 21.8, 20.8, 14.7, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.9 (br). IR (neat): 2975, 2867, 1604, 1471, 1455, 1304, 1139, 850, 744, 697 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{19}H_{35}BNO_2$) m/z 320.2755, found m/z 320.2761. (*Note: the absolute configuration of* ***83*** *was assumed according to the stereochemistry characteristic of* S_N2 *reaction*)

In order to determine the enantiomer excess of the product **83**, the pinacol boronic ester was efficiently oxidized to corresponding alcohol according to the following procedure.

H_2O_2 (30% in water, 0.2 mL) was dropwise added to a solution of **83** (30 mg), NaOH (3.0 M in water, 0.2 mL), THF (0.5 mL) and EtOH (0.2 mL) at 0 ^{o}C. The resulting mixture was stirred at 0 ^{o}C for 3 hours. The reaction mixture was quenched by $Na_2S_2O_3$ (aq), the aqueous layer was extracted by ether. The organic layer was dried over $MgSO_4$, filtered and concentrated in reduced pressure. The resulting mixture was purified by prepared TLC to afford the product (14 mg, 74% yield, 92% ee) as a colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.31-7.25 (m, 2H), 7.23-7.14 (m, 3H), 2.82-2.75 (m, 1H), 2.55-2.46 (m, 1H), 1.99-1.92 (m, 1H), 1.50-1.43 (m, 1H), 1.39 (br, 1H), 1.34-1.27 (m, 1H), 1.16 (d, J = 9.0 Hz, 6H), 0.99 (d, J = 7.0 Hz, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 142.9, 128.52, 128.46, 125.8, 73.6, 44.0, 34.7, 33.8, 27.3, 26.3, 14.6. IR (neat): 3389 (br), 2968, 2868, 1604, 1496, 1454, 1371, 1137, 1030, 944, 745, 697, 586 cm^{-1}.HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{13}H_{24}NO$) m/z 210.1852, found m/z 210.1856. HPLC (IA, 0.46 cm x 25 cm, hexane / isopropanol = 99.5/0.5, flow 1.0 mL/min, detection at 254 nm) retention time = 8.27 min (major), 8.45 min (minor).

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.202	159524	24953	47.499
2	8.377	176324	25398	52.501
Total		335848	50351	100.000

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.274	330573	55596	95.773
2	8.448	14590	3192	4.227
Total		345162	58788	100.000

12.3 Electrochemical Reduction of 1 in the Absence of Alkyl Bromide

Procedure: In glove box, $TBAClO_4$ (3 mmol, 3 equiv, 1.02 g) and dry THF or THF-*d8* (2.5 mL) was added into the flame dried undivided ElectraSyn vial (5 mL) with a stir bar. Then **1** (1 mmol, 249 mg, 1 equiv) and tetradecane (1 mmol, 198 mg, 1 equiv) were sequentially added to the mixture. The vial was sealed with the ElectraSyn vial cap equipped with anode (Mg plate) and cathode (graphite plate) (the submerged exterior surface of the electrode approximately 2.90 x 0.8 x 0.2 cm), and then bring it out of glove box. A nitrogen-filled balloon was used to sustain a nitrogen atmosphere. Pre-stirring the resulting mixture for 1 minutes, and then the reaction mixture was electrolyzed at a constant current of 2.5 mA until passing 1 F/mol of charge (usually require 10h45min) at room temperature. During electrolysis, 10 µl aliquots were drawn from the reaction at various charges passed (0.05, 0.1, 0.15, 0.25, 0.5, 0.75, 1.0) and diluted with 2 mL HPLC grade hexanes. The resultant solution was then flushed through a syringe filter and analyzed on a GC-FID instrument. Signals were identified by comparison with the retention time of authentic samples. Areas of the starting material and products were calibrated about the tetradecane internal standard. Strong linearity (R^2 > 0.999) was found for (**1**, **4** and **5**), indicating a zero-order rate in reactants **1** consumption and products (**4**, **5**) formation.

Figure S25. Electrolysis of **1** and the formation of **4** and **5** versus different charges. a) In 4Å molecular sieves dried THF; b) in commercial THF-d_8

Discussion: It is worth noting that only product **4** and **5** was detected with less than 0.5% dimerization product of **1** detected. We hereby proposed a plausible mechanism:

Tertiary α-bromo Bpin initially undergo a single electron reduction to generate the carbon centred radical **Int-4**, which was sequentially reduced to carbanion intermediate **Int-5**. **Int-5** could act as a base to abstract one hydrogen from the methyl group in **1**, affording product **4** and triggering the E2 elimination of **1** to give product **5**. On this basis, the ratio of product 4 and 5 was expected to be 1:1 since it is a bimolecular reaction. Although a nearly 1:1 ratio was obtained, the 11% more of **4** suggests the possibility of other alternative pathways. We first hypothesize it is from the radical pathway that **Int-4** could abstract a hydrogen from THF to afford product **4**, especially at the end of the reaction stage where the concentration of **1** is too low to undergo a bimolecular reaction. To test this hypothesis, we used THF-*d8* as the solvent and found out that the deuteration ratio of **4** was less than 1% determined by GC-MS with a similar ratio of product **4** and **5** observed. This result thus excludes the possibility of the HAT of **Int-4**. We then reasoned that the hydrogen atom is more likely to come from the Hoffman elimination process where **Int-5** acts as a strong base to react with tetrabutylammonium cation from the electrolyte to give **4**[24].

12.4 Divided Cell Reaction

In glove box, an oven-dried 10 mL H-type divided cell with glass frit was equipped with a stir bar respectively, $TBAClO_4$ (3 mmol), dried THF (5 mL), **1** (0.5 mmol), **2** (1.5 mmol), tetradecane (0.5 mmol), and w/ or w/o $Mg(OTf)_2$ (5 mol%) was sequentially added into cathode chamber while the anodic chamber was added with $TBAClO_4$ (3 mmol), dried THF (5 mL). The divided cell was equipped with graphite plate cathode and Mg plate anode, and then brings it out of glove box. Pre-stirring the resulting mixture for 2 minutes, the reaction mixture was electrolyzed at a constant current of 2.5 mA until passing 2 F/mol of charge at room temperature. During the electrolysis, about 5 μl aliquots of reaction mixture were drawn from the reaction at various charges passed and diluted with 2 mL HPLC grade hexanes. The resultant solution was then flushed through a pipette filled with cotton and analyzed on GC.

Figure S26. Initial reaction rate comparison of the divided cell reaction of **1** with **2** in the presence and absence of $Mg(OTf)_2$

13. Determination the Impurities in Electrodes by ICP-AES and XRF

To rule out the reaction, potentially, was catalyzed by the trace amount of transition metal (eg, Pd, Ni, Co, etc) in the electrode, Inductively Coupled Plasma−Atomic Emission Spectroscopy (ICP-AES) and/or X-ray fluorescence (XRF) were used to analyze the metal and non-metal impurities in the electrodes.

13.1 Determination the Impurities in Electrodes by ICP-AES

Sample preparation: A piece of Mg and graphite electrode was cut, polished and washed with acetone to clean the surface and remove the oxide layer. The resulting electrodes were dried over oven and then transferred to 20 mL glass vials. To the vials containing Mg (0.2971 g) and graphite (0.2362 g), a same amount of fresh prepared *aqua regia* was added to dissolve the pieces, respectively. For Mg, the reaction was rapid, and a colorless solution was obtained. For graphite, the solution was heated up to promote the reaction. A filtration may be necessary to remove the unreacted residue solids and a clear colorless solution was obtained. The resulting solution was transferred to 50 mL volumetric flask and diluted with deionized water, sealed and stored at room temperature overnight before submitting to ICP analysis. A blank sample was also prepared with *aqua regia* at the same concentration. The ICP results were shown as following table: (*Note: the unit for the concentration of each element is mg/L*)

Elements / Sample	**Al** 396.152	**B** 249.677	**Ca** 317.933	**Cd** 214.438	**Co** 228.616	**Cr** 267.716	**Cu** 324.754
Blank	0.065	0.255	0.118	0.000	0.000	0.000	0.000
Mg	183.367	0.493	0.121	0.000	0.000	0.000	0.022
Percentage in Mg%	**3.085**	**0.004**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**
Graphite	0.520	1.841	0.199	0.000	0.000	0.000	0.060
Percentage in C%	**0.010**	**0.034**	**0.002**	**0.000**	**0.000**	**0.000**	**0.001**

Elements / Sample	Fe 259.941	K 766.491	Mg 279.079	Mn 257.611	Na 330.298	Ni 231.604	P 213.618
Blank	0.044	0.771	0.000	0.000	0.389	0.000	0.000
Mg	0.177	60.409	4163.580*	13.320	50.488	0.017	0.000
Percentage in Mg%	**0.002**	**1.004**	**70.070***	**0.224**	**0.843**	**0.000**	**0.000**
Graphite	0.030	5.207	11.794	0.000	2.170	0.000	0.000
Percentage in C%	**0.000**	**0.094**	**0.250**	**0.000**	**0.038**	**0.000**	**0.000**

Elements / Sample	Pb 220.353	S 182.034	Zn 213.856	Pd 340.458	Pt 214.423	Ag 328.0_2	Rh 343.489
Blank	0.000	0.000	0.019	0.000	0.000	0.000	0.000
Mg	0.062	0.000	135.154	0.002	0.000	0.000	0.000
Percentage in Mg%	**0.001**	**0.000**	**2.274**	**0.000**	**0.000**	**0.000**	**0.000**
Graphite	0.000	0.316	0.111	0.000	0.000	0.000	0.000
Percentage in C%	**0.000**	**0.007**	**0.002**	**0.000**	**0.000**	**0.000**	**0.000**

***The concentration and mass percentage of Mg is inaccurate for Mg electrode due to the high concentration of Mg (>500 mg/L), which can affect the sensitivity of ICP-AES method. Therefore, the standard curve cannot be used to quantify the actual concentration of Mg in Mg electrodes. For a more accurate determination of Mg concentration, see XRF results.

Table S6. Analysis of Mg plate and graphite by ICP-AES

13.2 Determination the Impurities in Mg Plate by XRF

X-ray fluorescence (XRF) was used to determine the elemental composition of the Mg used for the e-XEC reaction. The samples were directly used for analysis without additional preparation.

XRF data were collected using a Bruker M4 TORNADO Micro-XRF Spectrometer with a MCBM 50-0.6B Rh X-ray tube and an XFlash 430 detector. The tube voltage and the tube current were set to 50 keV and 99 μA respectively.

Figure S27. XRF spectrum of a fresh Mg plate.

Element	AN	series	Net	[wt.%]	[norm. wt.%]	[norm. at.%]
Mg	12	K-series	740135	108.4069	97.12701	98.01432
Al	13	K-series	9935	1.908759	1.71015	1.554579
Mn	25	K-series	253726	0.255345	0.228776	0.102137
Zn	30	K-series	2017993	0.877414	0.786118	0.294864
Rh	45	K-series	84711	0	0	0
Pd	46	K-series	31975	0.165128	0.147946	0.034098
			Sum:	111.6135	100	100

Table S7. Analysis of Mg plate by XRF

Discussion: The ICP-AES analysis reveals the high purity of graphite electrodes and the impurities in Mg electrodes are consistent with our XRF data. Typical transition metals that can potentially catalyze XEC reactions, such as Cu, Fe, Pd, Ni, Rh, are either NOT found or found in very minute amounts in both graphite and magnesium electrodes. The impurities in Mg are unlikely to influence our XEC reactivity as our divided cell experiments still afford the desire product in satisfied yield.

14. Anode Passivation Analysis

14.1 Homemade Electrochemical Setup for e-XEC in a Low Volume Cell

e-XEC were conducted in a three-electrode configuration with a Mg counter electrode (CE, Anode), a graphite working electrode (WE, Cathode), and a Ag wire pseudo-reference. The pseudo-reference is used to observe and isolate the CE

potential changes from those at the WE. The Mg electrodes were mechanically ablated within the glovebox, prior to use, to remove any oxide layer on the surface. All experiments were carried out in a 10 mL low volume cell equipped with a low volume cell cap (Pine). The reaction, coupling **1** and **2** in 1.5 mmol scale, was electrolyzed at a constant current of -2.5 mA (j = 1.0 mA/cm^2) until passing 2 F/mol of charge (~33.5 h) at room temperature. The reaction using THF or THF/DME (5/1) as solvent provided the product **3** in 83% and 74% yield, respectively.

All e-XEC experiments were conducted in an Ar-filled glovebox on a VMP3 potentiostat (BioLogic).

Figure S28. The homemade electrochemical setup for the e-XEC reaction.

Figure S29. Mg CE after the e-XEC with homemade setup (Fig. S28) under mechanistic study conditions: (a) THF or (b) THF/DME (5:1, v/v) as the solvent, and with ElectraSyn 2.0 under synthetic conditions: (c) THF or (d) THF/DME (5:1, v/v) as the solvent. The synthetic conditions results show visible substantial suppression of passivation layer formation after addition of DME.

14.2 Electrochemical Impedance Spectroscopy

The electrochemical impedance spectroscopy (EIS) experiments were conducted in a two-electrode configuration with an Mg CE and a graphite WE. The data was collected from 10^6-10^{-1} Hz at 3 points per decade, with a 10 mV sinus amplitude. The high-frequency features of the resultant Nyquist plots were fit with an equivalent circuit composed of a resistor (R_1) in series with an Q_2/R_2 circuit (where Q_2 is a constant phase element, employed to describe non-ideal capacitance). The Q_2/R_2 circuit represents interfacial resistance on the Mg anode.

All EIS experiments were conducted in an Ar-filled glovebox on a VMP3 potentiostat (BioLogic).

Figure S30 Nyquist plot of the e-XEC reaction in THF/DME (5:1, v/v) at 0 h.

Figure S31. The voltage profile and EIS of the e-XEC reaction with (a) THF or (b) THF/DME (5:1, v/v) as the solvent.

14.3 Scanning Electron Microscope and Energy-Dispersive X-ray Spectroscopy

Samples for scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were prepared by collecting the passivation layers formed on the Mg CE after the e-XEC reaction. All samples were rinsed 3× with THF to remove any absorbed species and dried under vacuum for at least 48 h before analysis. The samples were brief exposed to air when loading into the instrument.

SEM data were collected on a ZEISS 1550VP field emission scanning electron microscope using a 10 kV acceleration voltage and an in-lens SE detector. EDS data were collected using an SSD EDS detector (Oxford X-MAX 80 mm^2) with a 30 kV acceleration voltage. The samples were brief exposed to air when loading into the instrument.

Figure S32. SEM image of the passivation layer formed on Mg CE after the e-XEC with (a) THF or (b) THF/DME (5:1, v/v) as the solvent.

Figure S33. EDS of the passivation layer formed on Mg CE after the e-XEC with (a) THF or (b) THF/DME (5:1, v/v) as the solvent.

14.4 Fourier-Transform Infrared Spectroscopy

Samples for Fourier-transform infrared spectroscopy (FT-IR) were prepared by pressing the passivation layer formed on the Mg CE with KCl to form a pellet. The

passivation layer samples were rinsed 3× with THF to remove any absorbed species and dried under vacuum for at least 48 h before being used for pellet preparation. The sample pellets were prepared by thoroughly mixing and grinding 0.9 mg passivation sample with 200 mg dry KCl with a mortar and pestle. The solid mixture was then pressed into a translucent pellet using a hydraulic press.

FT-IR data were collected using a Bruker Vertex 80 FT-IR spectrometer controlled by OPUS spectroscopy software with a resolution of 4 cm^{-1}.

Figure S34. FT-IR of the passivation layer formed on Mg CE after the e-XEC with (a) THF, or (b) THF/DME (5:1, v/v) as the solvent. The absorption at 1151 cm^{-1} and 1093 cm^{-1} are assigned as the asymmetric stretching of ClO_4^-.[25]

14.5 X-ray Photoelectron Spectroscopy

Samples for X-ray photoelectron spectroscopy (XPS) were prepared by collecting the passivation layers formed on the Mg CE after the e-XEC reaction. All samples were rinsed 3× with THF to remove any absorbed species and dried under vacuum for at least a week before analysis. The samples were mounted on a vacuum stage under an Ar atmosphere, then transferred to the XPS with brief exposure to air.

XPS data were collected using a Surface Science Instruments M-Probe ESCA controlled by Hawk Data Collection software. Low-resolution survey spectra were acquired between binding energies of 1−1100 eV. High-resolution detailed scans, with a resolution of 0.065 eV, were collected on individual XPS lines of interest. The sample chamber was maintained at $<2 \times 10^{-8}$ Torr. The XPS data were analyzed using CasaXPS analysis software, and individual peaks of interest were fit with Shirley backgrounds. Peaks were deconvoluted using asymmetric Gaussian-Lorentzian line shapes. Spectra were referenced to adventitious C at 285 eV.

Figure S35. The C 1s spectra of the passivation layer on Mg CE after the e-XEC with (a) THF and (b) THF/DME (5:1, v/v) as the solvent. The lowest binding energy peak in each spectrum was calibrated to 285 eV.

Figure S36. Mg, Br, Cl, and O regions of the XPS spectrum of the passivation layer on Mg CE after the e-XEC with THF as the solvent.

Figure	**Peak binding energy (eV)**	**Assignment**[26-29]
S34. O	532.9	ClO_4^-
	534.7	C−O
S34. Cl	208.1	ClO_4^-
S34. Br	68.0	$MgBr_2$

Table S8: Peak assignments of the XPS of the passivation layer on Mg CE after the e-XEC with THF as the solvent.

Figure S37. Mg, Br, Cl, and O regions of the XPS spectrum of the passivation layer on Mg CE after the e-XEC with THF/DME (5:1, v/v) as the solvent.

Figure	**Peak binding energy (eV)**	**Assignment**[26-28, 30]
S36. O	533.1	ClO_4^-
	533.6	ClO_3^-
S36. Cl	208.4	ClO_4^-
	206.7	ClO_3^-
S36. S	163.1	S-C
S36. Br	68.5	$MgBr_2$

Table S9: Peak assignments of the XPS of the passivation layer on Mg CE after the e-XEC with THF/DME (5:1, v/v) as the solvent as the solvent.

15. Gram Scale Reaction

In glove box, $TBAClO_4$ (10 mmol, 2 equiv.), dried THF (10 mL)) and DME (2 mL) was added into the flame dried undivided ElectraSyn vial (20 mL) equipped with a

stir bar. The resulting suspension was pre-stirred for about 1 min to dissolve the electrolyte. Then the substrate **84** (5 mmol, 1 equiv.) and alkyl bromide **85** (10 mmol, 2 equiv.) was sequentially added to the mixture. The vial was sealed with the ElectraSyn vial cap equipped with anode (Mg plate) and cathode (graphite plate), and then bring it out of glove box. Pre-stirring the resulting mixture for 2 minutes, and then the reaction mixture was electrolyzed at a constant current of 10 mA (current density: ~ 1.60 mA/cm^2) until passing 2 F/mol of charge at room temperature. After electrolysis, disconnect the reaction vial from ElectraSyn 2.0, gently remove the cap with electrodes from the vial and transfer the reaction media to a separatory funnel. Both electrodes were rinsed with saturated NH_4Cl (aq) and Et_2O. Then, the crude mixture was further diluted with Et_2O. The resulting mixture was washed with brine. The organic layer was dried over with anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified using silica gel chromatography (Hexanes:Et_2O = 10:1) to give **86** (1.072 g, 76% yield) as a white solid.^{1}H NMR: (500 MHz, $CDCl_3$) δ 3.31 (t, *J* = 7.0 Hz, 2H), 3.30 (s, 3H), 1.87 (d, *J* = 12.5 Hz, 2H), 1.66-1.59 (m, 3H), 1.58-1.50 (m, 2H), 1.32-1.19 (m, 4H), 1.24 (s, 12H), 1.17-1.07 (m, 1H), 0.90 (td, *J* = 13.0 Hz, 2.5 Hz, 2H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 83.1, 58.6, 37.2, 35.4, 26.9, 25.7, 25.4, 25.0, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.6 (br). IR (neat): 2977, 2919, 2836, 1451, 1302, 1136, 1112, 1013, 971, 856, 698, 669 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{16}H_{32}BO_3$) m/z 283.2439, found m/z 283.2443.

In glove box, $TBAClO_4$ (10 mmol, 2 equiv.), dried THF (10 mL)) and DME (2 mL) was added into the flame dried undivided ElectraSyn vial (20 mL) equipped with a stir bar. The resulting suspension was pre-stirred for about 1 min to dissolve the electrolyte. Then the substrate **87** (5 mmol, 1 equiv.) and alkyl bromide **31** (10 mmol, 2 equiv.) was sequentially added to the mixture. The vial was sealed with the ElectraSyn vial cap equipped with anode (Mg plate) and cathode (graphite plate), and then bring it out of glove box. Pre-stirring the resulting mixture for 2 minutes, and then the reaction mixture was electrolyzed at a constant current of 10 mA (current density: ~1.60 mA/cm^2) until passing 2 F/mol of charge at room temperature. After electrolysis, disconnect the reaction vial from ElectraSyn 2.0, gently remove the cap with electrodes from the vial and transfer the reaction media to a separatory funnel. Both electrodes were rinsed with saturated NH_4Cl (aq) and Et_2O. Then, the crude mixture was further diluted with Et_2O. The resulting mixture was washed with brine. The organic layer was dried over with anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified using silica gel chromatography (pentane) to give **88** (758.1 mg, 83% yield) as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.5 Hz, 2H), 7.23-7.15 (m, 3H), 3.54-3.43 (m, 2H), 2.76-2.66 (m, 1H), 1.79-1.59 (m, 4H), 1.27 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ

147.0, 128.6, 127.1, 126.2, 45.4, 39.6, 35.6, 31.0, 22.6. IR (neat): 2958, 2927, 2870, 1603, 1493, 1451, 1377, 1306, 1072, 1028, 761, 698 cm^{-1}. LRMS (EI) calculated for $[M]^+$ ($C_{11}H_{15}Cl$) m/z 182.1, found m/z 182.1.

20 mmol scale reaction with two-neck flask

In glove box, $TBAClO_4$ (40 mmol, 2 equiv) was added into a flame dried undivided cell equipped with a stir bar. The vial was sealed with a rubber septa, and a Teflon cap equipped with anode (Mg plate) and cathode (carbon felt), which was then brought out from the glove box. The substrate **87** (20 mmol, 1 equiv), alkyl bromide **31** (40 mmol, 2 equiv), dried THF (30 mL) and DME (30 mL) were then sequentially added to the cell. Pre-stirring the resulting mixture for 2 minutes, and then the reaction mixture was electrolyzed at a constant current of 25 mA (current density: ~ 1.62 mA/cm^2) until passing 2.1 F/mol of charge at room temperature. After electrolysis, disconnect the reaction vial from the power source, gently remove the cap with electrodes from the vial and transfer the reaction media to a separatory funnel. Both electrodes were rinsed with saturated NH_4Cl (aq) and Et_2O. Then, the crude mixture was further diluted with Et_2O. The resulting mixture was washed with brine. The organic layer was dried over with anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified using silica gel chromatography (hexanes) to give **88** (3.32 g, 91% yield) as a colorless oil.

Figure S38: Electrolysis setup(left), reaction mixture after electrolysis (middle), Mg electrode after electrolysis (right). While the formation of a solid layer on the Mg

electrode surface was observed, the Mg anode was not passivated with cell potential remaining stable (6~10 V) throughout the electrolysis.

20 mmol scale reaction with three-neck RBF

In glove box, $TBAClO_4$ (44 mmol, 2.2 equiv) was added into a flame dried three-necked flask (100 mL) with a stir bar. The flask was sealed with a rubber septa equipped with two anodes (Mg plate, 3 x 6 x 0.8 x 0.2 cm^3) on both sides neck and one cathode (carbon felt, 5 x 2.4 x 0.5 cm^3) on the middle neck, which was then brought out from the glove box. The substrate **87** (20 mmol, 1 equiv), alkyl bromide **31** (40 mmol, 2 equiv), dried THF (48 mL) and DME (12 mL) were then sequentially added to the cell. Pre-stirring the resulting mixture for 2 minutes, and then the reaction mixture was electrolyzed at a constant current of 25 mA (current density: ~ 1.30 mA/cm^2) until passing 2.05 F/mol of charge at room temperature. After electrolysis, disconnect the reaction vial from the power source, gently remove the cap with electrodes from the vial and transfer the reaction media to a separatory funnel. Both electrodes were rinsed with saturated NH_4Cl (aq) and Et_2O. Then, the crude mixture was further diluted with Et_2O. The resulting mixture was washed with brine. The organic layer was dried over with anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified using silica gel chromatography (hexanes) to give **88** (3.48 g, 95% yield) as a colorless oil.

Note: considering the large scale reaction will consume lots of Mg, so we use two Mg anode for this reaction, which are connect to the anode of electrasyn. Each Mg anode was fabricated by three Mg plates (6 x 0.8 x 0.2 cm^3) were tightly assembled by copper wire via the hole on the top of the plate.

Figure S39: Electrolysis setup (left), reaction mixture after electrolysis (middle), Mg electrode after electrolysis (right). While black stains were observed on Mg electrode, the Mg anode was not passivated with cell potential remaining stable (3.6~5.0 V) throughout the electrolysis.

16. Comparison between e-XEC and the Matteson Reaction

We have conducted several control experiments to compare our method with the Matteson reaction. This comparison helped to make a stronger case for the significance of our new method. We think our method is complementary and more favorable in the following scenarios. First, the Matteson reaction can only be used to synthesize alkylboronic esters. In contrast, our method can also cross couple alkyl halides without an alpha-Bpin group such as benzyl-, allyl-, and propargyl chloride as well as *alpha*-haloalkylsilanes. In addition, other electrophiles such as chlorosilanes, chlorogermanes, and CO_2 are also suitable electrophiles.

Second, our method could be applied to synthesize alkyboronic esters that cannot be obtained using the Matteson reaction. In general, alkyl halides that could be easily transformed into Grignard reagents can readily undergo Matteson reaction to give the desire product (e.g., **19**, **89**, **93**, **97**) in comparable yields to our method. However, several other types of alkyl halides are not compatible with the Matteson reaction due to instability of their corresponding Grignard reagents (e.g., prone to intramolecular S_N2 reaction, E1cb reaction, or radical dimerization; Table S10, eq 1-4). Our trials to synthesize the products (**14**, **90**, **94**, **95**) from these alkyl bromides via Matteson reaction were failed. In contrast, these alkyl bromides are suitable substrates for the e-XEC.

Finally, our method can couple *alpha*-haloalkylboronic esters with chlorosilane to synthesize *gem*-silyboryl products. To the best of our knowledge, the Matteson reaction has not been explored in this context. Our preliminary trials showed only less than 15% desired product can be obtained (Table S10, eq 5-7). We also note that using our method, the carbanion nucleophile is *in situ* generated via electrochemistry, thus circumventing the preparation of Grignard reagents that is necessary prior to the Matteson reaction.

Table S10: Comparison between e-XEC and the Matteson reaction.

17. Synthesis of Starting Materials

17.1 General Procedure to Synthesize Tertiary α-Bromopinacol Boronic Ester (GP-1)

The preparation of tertiary α-bromopinacol boronic ester was performed according to a literature reference with slight modification[31]. In a three-necked round bottom flask

with a magnetic stir bar and equipped with a saturated $NaHCO_3$ (aq) scrubber, bromine (1.1 equiv) was dropwise added to a solution of secondary alkyl pinacol boronic ester (1 equiv.) in CCl_4 (0.15~0.5 M) under N_2. The reaction was stirred at room temperature under N_2 for overnight (4 hours is enough for this reaction). The stir bar was removed and the reaction was concentrated *in vacuo* to afford the crude product. Usually, the crude product was pure enough for e-XEC reaction without further purification. The crude product can be purified by short path distillation under reduced pressure.

The following tertiary α-bromopinacol boronic esters were prepared according to this procedure:

1

2-(2-Bromopropan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1): Prepared from 2-isopropyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (40 mmol) and Br_2 (42 mmol) in CCl_4 (80 mL) following General Procedure 1. The crude residue was purified by short path distillation under reduced pressure to afford **1** (8.32 g, 83%) as a colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 1.77 (s, 6H), 1.28 (s, 12H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 84.4, 30.4, 24.5, carbon attached to boron not observed. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 31.3 (br). HRMS (DART) calculated for $[M+NH_4]^+$ ($C_9H_{22}BBrNO_2$) m/z 266.0921, found m/z 266.0926.

11-sub

2-(1-Bromocyclobutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11-sub) : Prepared from 2-cyclobutyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5 mmol) and Br_2 (5.5 mmol) in CCl_4 (12 mL) following General Procedure 1. The crude residue was purified by short path distillation under reduced pressure to afford **11-sub** (1.20 g, 85%) as a colorless oil with trace amount of starting material. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 2.69-2.62 (m, 2H), 2.61-2.52 (m, 2H), 2.14-2.06 (m, 1H), 1.82-1.72 (m, 1H), 1.30 (s, 12H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 84.6, 37.4, 24.6, 19.2, carbon attached to boron not observed. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 32.0 (br). HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{10}H_{22}BBrNO_2$) m/z 278.0921, found m/z 278.0927.

12-sub

2-(1-Bromocyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12-sub) :

Prepared from 2-cyclopentyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10 mmol) and Br_2 (11 mmol) in CCl_4 (30 mL) following General Procedure 1. The afforded brown solid **12-sub** (2.70 g, 93% yield) containing trace amount of starting material was directly used in e-XEC reaction without further purification. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 2.25-2.14 (m, 2H), 2.07-1.92 (m, 4H), 1.74-1.62 (m, 2H), 1.28 (s, 12H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 84.3, 40.1, 24.6, 23.8, carbon attached to boron not observed. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 31.3 (br). HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{11}H_{24}BBrNO_2$) m/z 292.1078, found m/z 292.1082.

13-sub

2-(1-Bromocyclohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13-sub) : Prepared from 2-cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10 mmol) and Br_2 (11 mmol) in CCl_4 (20 mL) following General Procedure 1. The afforded crude light yellow oil **13-sub** (2.56 g, 89% yield) was decomposed at above 100 ^{o}C under reduced pressure, so the residue containing about 10% of starting material was directly used in e-XEC reaction without further purification. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 2.24 (d, J = 8.5 Hz, 2H), 1.98-1.87 (m, 2H), 1.82-1.71 (m, 2H), 1.68-1.49 (m, 2H), 1.36-1.32 (m, 2H), 1.29 (s, 12H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 84.1, 38.9, 25.4, 24.9, 24.5, carbon attached to boron not observed. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 31.2 (br). HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{12}H_{26}BBrNO_2$) m/z 306.1234, found m/z 306.1243.

14-sub

2-(2-Bromobutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14-sub) : Prepared from 2-(sec-butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10 mmol) and Br_2 (11 mmol) in CCl_4 (15 mL) following General Procedure 1. The crude residue was purified by short path distillation under reduced pressure to afford **14-sub** (2.48 g, 93%) as a colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 2.05-1.91 (m, 2H), 1.73 (s, 3H), 1.28 (s, 12H), 0.98 (t, J = 7.5 Hz, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 84.3, 35.6, 26.8, 24.6, 24.5, 11.4, carbon attached to boron not observed. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{10}H_{24}BBrNO_2$) m/z 280.1078, found m/z 280.1083.

92-sub

2-(1-Bromocycloheptyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (92-sub) : Prepared from 2-cycloheptyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8 mmol) and Br_2 (8.8 mmol) in CCl_4 (20 mL) following General Procedure 1. The afforded brown

solid **92-sub** (2.19 g, 90% yield) containing trace amount of starting material was directly used in e-XEC reaction without further purification. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 2.40-2.33 (m, 2H), 2.19-2.11 (m, 2H), 1.75-1.68 (m, 2H), 1.62-1.50 (m, 4H), 1.46-1.37 (m, 2H), 1.29 (s, 12H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 84.1, 41.4, 28.0, 25.0, 24.5, carbon attached to boron not observed. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 31.2 (br). HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{13}H_{28}BBrNO_2$) m/z 320.1391, found m/z 320.1398.

17.2 General Procedure to Synthesize Secondary α-Chloropinacol Boronic Ester (GP-2)

The preparation of secondary α-chloropinacol boronic ester was performed according to a literature reference[32]. A solution of dichloromethane (1.55 equiv) in THF (0.2-0.6 M) was cooled to -100 ℃ in a 95% ethanol/liquid nitrogen slush bath and stirred magnetically during the dropwise addition of nBuLi (2.5 M in hexane, 1.05 equiv) by a syringe over a period of 10 min. The nBuLi must be chilled before contacting the dichloromethane solution, by running the nBuLi solution down the cold wall of the reaction flask. The solution should remain colorless or pale yellow. Darkening is a sign of overheating and decomposition. After 30 min, a solution of primary alkyl Bpin (1.0 equiv) in diethyl ether or THF (0.5 M) was in*J*ected in one portion, resulting in dissolution of the precipitate of (dichloromethyl)lithium. The solution was allowed to warm slowly to room temperature and stirred at RT for overnight. DCM were added to precipitate the lithium chloride, the solution was filtered and concentrated in vacuo, and the resulting residue was purified by short path distillation under reduced pressure to afford the desired product. For the product with high boiling point or heat sensitive, the product was purified by flash column chromatography with silica gel or determining the purity by ^{1}H NMR with internal standard and then directly used in the e-XEC reaction without further purification.

The following secondary α-chloropinacol boronic esters were prepared according to this procedure:

7-Cl

2-(1-Chloropentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7-Cl) : Prepared from 2-butyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (20 mmol) following General Procedure 2. The crude residue was purified by short path distillation under reduced pressure to afford **7-Cl** (3.39 g, 73%) as a colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 3.40 (dd, *J* = 8.0 Hz, 6.5 Hz, 1H), 1.88-1.74 (m, 2H), 1.52-1.41 (m, 1H), 1.41-1.31 (m, 3H), 1.28 (s, 12H), 0.90 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 84.5, 33.9, 29.6, 24.74, 24.71, 22.4, 14.1, carbon attached to boron not observed; ^{11}B NMR ($CDCl_3$, 160 MHz): δ 31.4 (br). HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{11}H_{26}BClNO$) m/z 250.1740, found m/z 250.1744.

15-sub

2-(1-Chlorobut-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15-sub) : Prepared from 2-allyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (20 mmol) following General Procedure 2. The crude residue was purified by short path distillation under reduced pressure to afford **15-sub** (3.27 g, 75%) as a colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 5.83 (ddt, *J* = 17.0 Hz, 10.0 Hz, 6.5 Hz, 1H), 5.14 (dq, *J* = 17.5 Hz, 1.5 Hz, 1H), 5.11-5.07 (m, 1H), 3.44 (t, *J* = 7.5 Hz, 1H), 2.68-2.49 (m, 2H), 1.28 (s, 12H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 134.9, 117.8, 84.6, 38.5, 24.8, 24.7, carbon attached to boron not observed. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 31.5 (br). HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{10}H_{22}BClNO_2$) m/z 234.1427, found m/z 234.1431.

2-(2-((*1R,5S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S2): The preparation of **S2** was performed according to a literature reference[33]. CuI (191 mg, 0.1 mmol, 0.1 equiv.), PPh_3 (341 mg, 0.13 mmol, 0.13 equiv.), LiOMe (760 mg, 20 mmol, 2 equiv.), and bis(pinacolato)diboron (3.81 g, 15 mmol, 1.5 equiv.) were added to a 50 mL Schlenk tube The vessel was evacuated and filled with N_2. Then anhydrous DMF(20 mL) and the **S1** (2.29 g, 10 mmol, 1 equiv) were sequentially added to the above mixture. The resulting reaction mixture was stirred vigorously at 25 ℃ for 18 h. The reaction mixture was then diluted with EtOAc and brine. The organic layer was washed by brine, dried over Na_2SO_4, concentrated under reduced pressure. The resulting mixture was purified by chromatography to give **S2** (2.16 g, 78%) as a colorless oil. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 5.18-5.11 (m, 1H), 2.32 (dt, *J* = 8.4 Hz, 6.0 Hz, 1H), 2.26-2.10 (m, 2H), 2.08-1.96 (m, 4H), 1.28-1.19 (m, 15H), 1.13 (d, *J* = 6.8 Hz, 1H), 0.88-0.77 (m, 5H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 150.3, 114.4, 83.0, 46.1, 41.1, 38.0, 31.7, 31.3, 30.9, 26.5, 25.0, 24.9, 21.3, carbon attached to boron not observed.

2-(1-Chloro-3-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (16-sub): Prepared from **S2** (3 mmol) following General Procedure 2. The afforded light yellow oil **16-sub** (1.01 g, 84% yield, dr ~ 1:1) was pure enough to use in the e-XEC reaction without further purification. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 5.25-5.19 (m, 1H), 3.42 (t, *J* = 7.0 Hz, 1H), 2.38-2.31 (m, 1H), 2.28-2.13 (m, 2H), 2.12-1.97 (m, 4H), 1.93-1.77 (m, 2H), 1.28 (s, 12H), 1.26 (s, 3H), 1.13 (t, *J* = 8.0 Hz, 1H), 0.81 (d, *J* = 9.0 Hz, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 147.2/147.1, 117.0/116.9, 84.502/84.496, 46.0/45.9, 41.0, 38.13/38.08, 34.63/34.58, 31.92/31.86, 31.82/31.81, 31.4, 26.4, 24.75/24.74/24.72, 21.4/21.3, carbon attached to boron not observed. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 31.2 (br). HRMS (DART) calculated for $[M+H]^+$ ($C_{18}H_{31}BClO_2$) m/z 325.2100, found m/z 325.2104.

4-(Bromomethyl)-2,2-dimethyl-1,3-dioxolane (S4): Bromine (1.84 mL, 36 mmol, 1.2 equiv) was added to a suspension of PPh_3 (9.44 g, 36 mmol, 1.2 equiv) in DCM (100 mL) at 0 ℃. The mixture was stirred for 10 min and a white solid will precipitate from the mixture. And then imidazole (2.45 g, 36 mmo, 1.2 equiv) was added to the mixture, the solution become clean again. After that, **S3** (3.96 g, 30 mmol, 1 equiv) was added slowly by syringe. The resulting mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with DCM. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel to afford **S4** (4.62 g, 79% yield) as colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 4.38-4.29 (m, 1H), 4.13 (dd, *J* = 8.5 Hz, 6.5 Hz, 1H), 3.87 (dd, *J* = 8.5 Hz, 5.0 Hz, 1H), 3.43 (dd, *J* = 10.0 Hz, 4.5 Hz, 1H), 3.31 (dd, *J* = 10.0 Hz, 8.5 Hz, 1H), 1.44 (s, 3H), 1.35 (s, 3H) ; ^{13}C NMR: (126 MHz, $CDCl_3$) δ

110.4, 75.4, 68.4, 32.9, 27.1, 25.5.

2-((2,2-Dimethyl-1,3-dioxolan-4-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S5): Prepared from **S4** (1.95 g, 10 mmol, 1 equiv.) and B_2pin_2 (3.81 g, 15 mmol, 1.5 equiv) following the procedure to synthesize **S2.** The residue was purified by flash column chromatography to afford the **S5** (1.78 g, 80% yield) as a white solid. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 4.35-4.22 (m, 1H), 4.08 (dd, *J* = 7.6 Hz, 5.6 Hz, 1H), 3.44 (t, *J* = 8.0 Hz, 1H), 1.40 (s, 3H), 1.34 (s, 3H), 1.27-1.20 (m, 14H) ; ^{13}C NMR: (100 MHz, $CDCl_3$) δ 108.5, 83.5, 73.7, 70.9, 27.2, 26.1, 25.0, 24.9.

2-(1-Chloro-2-(2,2-dimethyl-1,3-dioxolan-4-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (17-sub) : Prepared from **S5** (4.4 mmol) following General Procedure 2. The afforded residue was further purified by column chromatography to afford the **17-sub** (950 mg, 74% yield, dr~1:1, 80% purity) as a colorless oil. The afforded product was impure with 20% of starting material. The purity was determined by ^{1}H NMR with internal standard. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 4.35-4.23 (m, 1H), 4.13-4.04 (m, 1H), 3.63-3.48 (m, 2H), 2.21-1.90 (m, 2H), 1.40 (s, 3H), 1.34 (d, *J* = 6.5 Hz, 3H), 1.28 (s, 12H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 109.2/109.1, 84.7/84.6, 73.7/73.6, 69.5/69.2, 38.3/38.0, 27.2/27.1, 25.8, 24.9/24.8, 24.65/24.63, carbon attached to boron not observed. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 31.5 (br). HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{13}H_{28}BClNO_4$) m/z 308.1794, found m/z 308.1800.

1-(3-Bromopropyl)cyclohexane-1-carbonitrile (S7): The preparation of **S7** was performed according to a literature reference[34]. To a stirred solution of diisopropylamine (3.04 g, 30 mmol, 1 equiv.) in ether (30 mL) was added ^{n}BuLi (12.6 mL, 31.5 mmol, 1.05 equiv) at 0 ℃, and the mixture was stirred for 30 min at the same temperature. To this solution was then added the **S6** (3.28 g, 30.0 mmol, 1 equiv.) dropwise. After stirring for 30 min at 0 ℃, the reaction solution was cooled to –78 ℃, and 1,3-dibromopropane (12.11 g, 60 mmol, 2 equiv) was added. The reaction mixture was allowed to warm gradually to 0 ℃ over 1 h and quenched with NH_4Cl (aq.). The organic layer was extracted with ether, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel to give the desire **S7** (3.45 g, 50% yield) as a colorless oil. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 3.44 (t, *J* = 6.4 Hz, 2H), 2.12-2.02 (m, 2H), 2.01-1.91 (m, 2H), 1.81-1.53 (m, 7H), 1.31-1.10 (m, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 123.4, 39.2, 38.7, 35.8, 33.3, 27.8, 25.5, 23.1.

1-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)cyclohexane-1-carbonitrile (S8): Prepared from **S7** (1.73 g, 7.5 mmol, 1 equiv.) and B_2pin_2 (2.86 g, 11.25 mmol, 1.5 equiv) following the procedure to synthesize **S2.** The residue was purified by flash column chromatography to afford the **S8** (896 mg, 43% yield) as a white

solid. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 1.96 (d, *J* = 12.8 Hz, 2H), 1.77-1.47 (m, 10H), 1.24 (m, 12H), 1.23-1.12 (m, 2H), 0.79 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 124.0, 83.2, 43.3, 39.2, 35.8, 25.6, 25.0, 23.2, 19.1.

1-(4-Chloro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)cyclohexane-1-carbonitrile (18-sub): Prepared from **S8** (1.55 mmol) following General Procedure 2. The afforded light yellow solid **18-sub** (492 mg, 83% yield) containing trace amount of starting material was used for e-XEC reaction without further purification. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 3.42 (dd, *J* = 7.5 Hz, 6.5 Hz, 1H), 1.97 (d, *J* = 12.5 Hz, 2H), 1.89-1.82 (m, 2H), 1.77-1.67 (m, 4H), 1.66-1.57 (m, 4H), 1.56-1.47 (m, 2H), 1.28 (s, 12H), 1.23-1.13 (m, 2H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 123.7, 84.6, 40.0, 39.1, 35.8, 35.7, 34.1, 25.6, 25.0, 24.8, 24.7, 23.2, 22.4, carbon attached to boron not observed. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 31.3 (br). HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{17}H_{33}BClN_2O_2$) m/z 343.2318, found m/z 343.2326.

Ethyl 5-bromo-2,2-dimethylpentanoate (S10): Prepared from **S9** (3.48 g, 30 mmol, 1 equiv.), 1,3-dibromopropane (6.12 g, 30.3 mmol, 1.01 equiv) and THF (20 mL) following the procedure to synthesize **S7**. The residue was purified by column chromatography on silica gel to give the desire **S10** (5.29 g, 74% yield) as a colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 4.12 (q, *J* = 7.0 Hz, 2H), 3.37 (t, *J* = 7.0 Hz, 2H), 1.85-1.76 (m, 2H), 1.67-1.62 (m, 2H), 1.24 (t, *J* = 7.0 Hz, 3H), 1.17 (s, 6H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 177.6, 60.6, 41.9, 39.2, 34.0, 28.6, 25.3, 14.4.

Ethyl 2,2-dimethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (S11): Prepared from **S10** (2.37 g, 10 mmol, 1 equiv.) and B_2pin_2 (3.81 g, 15 mmol, 1.5 equiv) following the procedure to synthesize **S2.** The residue was purified by flash column chromatography to afford the product (2.01g, 71% yield) as a colorless oil. ^{1}H NMR: (300 MHz, $CDCl_3$) δ 4.10 (q, *J* = 7.2 Hz, 2H), 1.57-1.47 (m, 2H), 1.41-1.28 (m, 2H), 1.27-1.19 (m, 15H), 1.14 (s, 6H), 0.74 (t, *J* = 7.8 Hz, 2H).

Ethyl 6-chloro-2,2-dimethyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoate (19-sub): Prepared from ethyl **S11** (6.3 mmol) following General Procedure 2. The afforded light yellow oil **19-sub** (1.73 g, 82% yield) containing trace amount of starting material was used for e-XEC reaction without further purification. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 4.10 (q, *J* = 7.2 Hz, 2H), 3.40 (t, *J* = 7.2 Hz, 1H), 1.83-1.75 (m, 2H), 1.61-1.46 (m, 3H), 1.28 (s, 12H), 1.25-1.21 (m, 4H), 1.16 (s, 6H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 178.0, 84.5, 60.4, 42.2, 40.1, 34.6, 25.25, 25.20, 24.75, 24.71, 22.8, 14.4, carbon attached to boron not observed. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{16}H_{34}BClNO_4$) m/z 350.2264, found m/z 350.2271.

20-sub

9-(4-Chloro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)-9H-carbazole (20-sub) : Prepared from 9-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-9*H*-carbazole (6 mmol) following General Procedure 2. The crude residue was purified by column chromatography to afford **20-sub** (1.61 g, 70%) as light yellow solid. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.5 Hz, 2H), 7.50-7.44 (m, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 4.35 (t, *J* = 7.0 Hz, 2H), 3.46 (dd, *J* = 7.5 Hz, 6.5 Hz, 1H), 2.19-1.87 (m, 4H), 1.24 (s, 12H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 140.4, 125.8, 123.0, 120.5, 119.0, 108.7, 84.7, 42.6, 31.7, 26.8, 26.69, 26.66, carbon attached to boron not observed. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 31.1 (br). HRMS (DART) calculated for $[M+H]^+$ ($C_{22}H_{28}BClNO_2$) m/z 384.1896, found m/z 384.1904.

(4,4-Difluorocyclohexyl)methanol (S13): $LiAlH_4$ (988 mg, 26 mmol, 1.3 equiv.) was added portionwisely to a solution of **S12** (3.28 g, 20 mmol, 1 equiv.) in anhydrous THF at 0 ℃. The mixture was stirred overnight at r.t., then it was cooled to 0 ℃ and the reaction mixture was carefully quenched with 1M HCl (aq) at 0 ^{o}C until no bubbling. After that, the reaction mixture was dilute with ether and water. The aqueous layer was extracted by ether. The combined organic layer dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The afforded colorless oil **S13** (3.30 g, 100% yield) was pure enough for next step reaction without further purification. ^{1}H NMR: (300 MHz, $CDCl_3$) δ 3.52 (d, *J* = 6.6 Hz, 2H), 2.22-2.00 (m, 2H), 1.94-1.50 (m, 5H), 1.49-1.17 (m, 3H).

4-(Bromomethyl)-1,1-difluorocyclohexane (S14): Prepared from **S13** (3.30 g, 20 mmol, 1 equiv.) Br_2 (1.24 mL, 24 mmol, 1.2 equiv) and PPh_3 (6.29 g, 24 mmol, 1.2 equiv.) following the procedure to synthesize **S4.** The residue was purified by flash column chromatography to afford the **S14** (3.80 g, 89% yield) as a colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 3.31 (d, *J* = 6.5 Hz, 2H), 2.18-2.06 (m, 2H), 1.99-1.90 (m, 2H), 1.82-1.65 (m, 3H), 1.46-1.32 (m, 2H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 123.3 (dd, *J* = 241.0 Hz, 238.6 Hz), 38.4 (d, *J* = 1.5 Hz), 38.2 (d, *J* = 3.5 Hz), 33.4, 33.2 (d, *J* = 2.4 Hz), 33.0, 27.8 (d, *J* = 9.8 Hz).

2-((4,4-Difluorocyclohexyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S15): Prepared from **S14** (2.13 g, 10 mmol, 1 equiv.) and B_2pin_2 (3.81 g, 15 mmol, 1.5

equiv) following the procedure to synthesize **S2.** The residue was purified by flash column chromatography to afford the product (1.83 g, 70% yield) as a colorless oil. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 2.10-1.95 (m, 2H), 1.82-1.56 (m, 5H), 1.36-1.26 (m, 2H), 1.24 (s, 12H), 0.78 (d, *J* = 7.2 Hz); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 123.8 (t, *J* = 240.2 Hz), 83.2, 34.0, 33.8 (d, *J* = 3.1 Hz), 33.6, 32.3 (d, *J* = 1.2 Hz), 31.5 (d, *J* = 9.4 Hz), 25.0, carbon attached to boron not observed. ^{19}F NMR ($CDCl_3$, 376 MHz) δ -91.8 (d, *J* = 235.4 Hz), -101.9 (d, *J* = 235.0 Hz).

2-(1-Chloro-2-(4,4-difluorocyclohexyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (21-sub): Prepared from **S15** (4 mmol) following General Procedure 2. The afforded brown solid **21-sub** (1.05 g, 85% yield) containing 8% of starting material was used for e-XEC reaction without further purification. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 3.47 (dd, *J* = 11.0 Hz, 5.0 Hz, 1H), 2.12-2.02 (m, 2H), 1.89-1.80 (m, 2H), 1.78-1.63 (m, 5H), 1.37-1.25 (m, 13H), 1.22-1.14 (m, 1H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 123.7 (dd, *J* = 240.6 Hz, 238.2 Hz), 84.6, 39.4 (d, *J* = 2.4 Hz), 33.7 (d, *J* = 22.5 Hz), 33.5 (d, *J* = 22.4 Hz), 33.3 (d, *J* = 22.6 Hz), 33.1, 29.5 (d, *J* = 9.5 Hz), 27.5 (d, *J* = 9.6 Hz), 24.7 (d, *J* = 1.6 Hz), carbon attached to boron not observed. ^{19}F NMR ($CDCl_3$, 470 MHz) δ -91.7 (d, *J* = 234.5 Hz), -102.1 (d, *J* = 235.0 Hz). ^{11}B NMR ($CDCl_3$, 160 MHz): δ 31.3 (br). HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{14}H_{28}BClF_2NO_2$) m/z 326.1864, found m/z 326.1868.

4,4,5,5-Tetramethyl-2-(2-(thiophen-3-yl)ethyl)-1,3,2-dioxaborolane (S17): Prepared from **S16** (1.91 g, 10 mmol, 1 equiv.) and B_2pin_2 (3.81 g, 15 mmol, 1.5 equiv) following the procedure to synthesize **S2.** The residue was purified by flash column chromatography to afford the **S17** (1.65 g, 69% yield) as a colorless oil. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.21 (dd, *J* = 5.2 Hz, 3.2 Hz, 1H), 6.99-6.90 (m, 2H), 2.76 (t, *J* = 8.0 Hz, 2H), 1.22 (s, 12H), 1.15 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 145.0, 128.3, 125.1, 119.5, 83.2, 24.9, 24.7, carbon attached to boron not observed.

2-(1-Chloro-3-(thiophen-3-yl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (22-sub): Prepared from **S17** (3 mmol) following General Procedure 2. The afforded brown solid **22-sub** (745 g, 87% yield) containing trace amount of starting material was used for e-XEC reaction without further purification. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 4.5 Hz, 3.0 Hz, 1H), 7.00-6.97 (m, 1H), 6.97-6.94 (m, 1H), 3.41 (dd, *J* = 8.0 Hz, 6.0 Hz, 1H), 2.90-2.78 (m, 2H), 2.16-2.08 (m, 2H), 1.28 (s, 12H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 141.4, 128.4, 125.6, 120.9, 84.6, 34.9, 27.8, 24.76, 24.75, carbon attached to boron not observed. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 31.7 (br). HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{13}H_{24}BClNO_2S$) m/z 304.1304, found m/z 304.1311.

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)propyl 4-methoxybenzoate (S19): Prepared from **S18** (2.05 g, 7.5 mmol, 1 equiv.) and B_2pin_2 (2.56 g, 11.25 mmol, 1.5 equiv) following the procedure to synthesize **S2.** The residue was purified by flash column chromatography to afford the **S19** (1.60 g, 67% yield) as a colorless oil. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.02-7.95 (m, 2H), 6.94-6.88 (m, 2H), 4.25 (t, *J* = 6.8 Hz, 2H), 3.85 (s, 3H), 1.93-1.80 (m, 2H), 1.24 (s, 12H), 0.90 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 166.6, 163.3, 131.7, 123.2, 113.6, 83.3, 66.5, 55.5, 25.0, 23.5, carbon attached to boron not observed.

4-Chloro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl 4-methoxybenzoate (23-sub): Prepared from **S19** (3 mmol) following General Procedure 2. The afforded residue was further purified by column chromatography to afford the **23-sub** (651 mg, 59% yield, 78% purity) as a colorless oil. The afforded product is impure with 20% of starting material. The purity was determined by ^{1}H NMR with internal standard. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 9.0 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 4.30 (t, *J* = 6.0 Hz, 2H), 3.85 (s, 3H), 3.48 (dd, *J* = 8.0 Hz, 5.5 Hz, 1H), 2.07-1.81 (m, 4H), 1.28 (s, 12H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 166.4, 163.4, 131.7, 113.7, 84.6, 64.3, 55.6, 30.9, 26.8, 24.75, 24.71, carbon attached to boron not observed. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 31.7 (br). HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{18}H_{30}BClNO_5$) m/z 386.1900, found m/z 386.1905.

Methyl 4-(hydroxymethyl)bicyclo[2.2.2]octane-1-carboxylate (S21): To a stirred solution of **S20** (3.18 g, 15 mmol) in THF (20 mL), was added borane dimethyl sulfide complex (22.5 mL, 45 mmol, 3 equiv., 2.0 M in THF) at 0 °C.The reaction was warmed to rt and stirred. After 4 h, the reaction mixture was quenched with MeOH (dropwise addition over 15 mins with cooling) and stirred at rt for 2 h. The solvent was concentrated and the crude product was purified by flash column chromatography to afford the **S21** (2.06 g, 69% yield) as a colorless oil. ^{1}H NMR: (300 MHz, $CDCl_3$) δ 3.64 (s, 3H), 3.20 (s, 2H), 1.87-1.72 (m, 6H), 1.58-1.48 (m, 6H).

Methyl 4-(bromomethyl)bicyclo[2.2.2]octane-1-carboxylate (S22): To a 250 mL three-necked flash equipped with magnetic stir bar was added methyl **S21** (2.06 g, 10.4 mmol, 1 equiv), N-bromosuccinimide (1.94 g, 10.9 mmol, 1.05 equiv), triphenylphosphine (PPh_3, 2.86 g, 10.9 mmol, 1.05 equiv), anhydrous THF (30 mL). The resulting solution was stirred at 60 ^{o}C for 12 h. The reaction mixture was diluted with Et_2O and washed with brine. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure, the residue was purified by flash

chromatography to afford **S22** (1.68 g, 62% yield) as a sticky colorless oil. ^{1}H NMR: (300 MHz, $CDCl_3$) δ 3.64 (s, 3H), 3.28 (s, 2H), 1.92-1.64 (m, 6H), 1.56-1.32 (m, 6H).

Methyl 4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)bicyclo[2.2.2]octane-1-carboxylate (S23): Prepared from **S22** (1.65 g, 6.3 mmol, 1 equiv.) and B_2pin_2 (2.40 g, 9.4 mmol, 1.5 equiv) following the procedure to synthesize **S2.** The residue was purified by flash column chromatography to afford the **S23** (1.12 g, 58% yield) as a white solid. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 3.61 (s, 3H), 1.78-1.69 (m, 6H), 1.52-1.42 (m, 6H), 1.22 (s, 12H), 0.66 (s, 2H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 178.9, 82.9, 51.7, 38.7, 32.8, 29.6, 29.0, 25.0, carbon attached to boron not observed.

Methyl 4-(2-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)bicyclo[2.2.2]octane-1-carboxylate (24-sub): To an oven dried round flask equipped with a stirring bar was added CH_2Cl_2 (329 mg, 3.9 mmol, 1.55 equiv) and THF (8 mL) by syringe, and the solution was cooled to -100 ℃. Then nBuLi (1.1 mL, 2.6 mmol, 1.05 equiv, 2.5 M in hexanes) was added dropwise at -100 ^{o}C. After stirring for 30 min, a solution of **S23** (771 mg, 2.5 mmol, 1 equiv.) in THF (4 mL) was directly added via syringe. After that, a solution of anhydrous $ZnCl_2$ (3 mL, 3.0 mmol, 1.0 M in Et_2O, 1.25 equiv) was added to the reaction mixture. Then the reaction mixture was allowed to slowly warm to room temperature overnight. The reaction was quenched by NH_4Cl (aq). The aqueous phase was extracted with ether. The combined organic layer was washed with brine and dried over anhydrous $MgSO_4$, concentrated in vacuo. The residue was purified by column chromatography to give the **24-sub** (631 mg, 71% yield) as light yellow oil. The afforded product is impure with 35% of elimination side product, which is hard to purify by flash column chromatography. The afforded product was used for e-XEC reaction without further purification. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 3.62 (s, 3H), 3.42 (dd, *J* = 9.0 Hz, 6.0 Hz, 1H), 1.82-1.70 (m, 6H), 1.52-1.33 (m, 8H), 1.27 (s, 12H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 178.5, 84.4, 51.8, 45.6, 38.8, 30.6, 28.6, 28.5, 24.64, 24.61, carbon attached to boron not observed. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 30.8 (br). HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{18}H_{34}BClNO_4$) m/z 374.2264, found m/z 374.2269.

2-(Chloro((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (25-sub) : Prepared from 2-((1R,2R,5R)-2-isopropyl-5-methylcyclohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (800 mg, 3 mmol) following General Procedure 2. The residue was purified by flash column chromatography to afforded **25-sub** (802 mg, 85%, dr ~5:1) as a

colorless oil. The afforded product contains trace amount of unreactive starting material and elimination side product (about 90% purity). The purity of the product was determined by ^{1}H NMR with internal standard. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 3.81 (s, 0.16H), 3.73 (s, 0.84H), 2.06 (d, *J* = 13.0 Hz, 0.84H), 2.02-1.95 (m, 0.19H), 1.94-1.82 (m, 1H), 1.80-1.74 (m, 1H), 1.73-1.68 (m, 1H), 1.67-1.61 (m, 1H), 1.29/1.27 (s, 12H), 1.23-1.14 (m, 2H), 1.04-0.94 (m, 2H), 0.91-0.88 (m, 6H), 0.87-0.81 (m, 2H), 0.77 (d, *J* = 7.0 Hz, 3H); The ^{13}C NMR chemical shift of ma*J*or diastereomer was list in here.^{13}C NMR: (126 MHz, $CDCl_3$) δ 84.4, 45.8, 44.0, 38.9, 35.4, 32.8, 27.0, 24.9, 24.8, 24.5, 22.7, 21.6, 15.5, carbon attached to boron not observed. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{17}H_{36}BClNO_2$) m/z 332.2522, found m/z 332.2530.

5-(2,5-Dimethylphenoxy)-2,2-dimethylpentan-1-ol (S25): Prepared from **S24** (5.0 g, 20 mmol, 1 equiv.) and $LiAlH_4$ (2.28 g, 60 mmol, 3 equiv) following the procedure to synthesize **S13.** The afforded colorless oil **S25** (4.72 g, 100% yield) was directly used in next step without further purification. ^{1}H NMR: (300 MHz, $CDCl_3$) δ 7.00 (d, *J* = 5.7 Hz, 1H), 6.75-6.51 (m, 2H), 3.99-3.84 (m, 2H), 3.36 (s, 2H), 2.31 (s, 3H), 2.18 (s, 3H), 1.91-1.69 (m, 2H), 1.51-1.30 (m, 3H), 0.92 (d, *J* = 1.2 Hz, 6H).

2-((5-Bromo-4,4-dimethylpentyl)oxy)-1,4-dimethylbenzene (S26): Prepared from **S25** (4.72 g, 20 mmol, 1 equiv.) following the procedure to synthesize **S22.** The residue was purified by flash column chromatography to afford the **S26** (4.10 g, 68% yield) as a colorless oil. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 7.6 Hz, 1H), 6.67 (d, *J* = 7.6 Hz, 1H), 6.63 (s, 1H), 3.95 (t, *J* = 6.4 Hz, 2H), 3.33 (s, 2H), 2.32 (s, 3H), 2.20 (s, 3H), 1.83-1.71 (m, 2H), 1.59-1.48 (m, 2H), 1.06 (s, 6H). ^{13}C NMR: (126 MHz, $CDCl_3$) δ 157.1, 136.6, 130.4, 123.7, 120.8, 112.1, 68.2, 46.6, 36.4, 34.5, 25.9, 24.4, 21.5, 15.9.

2-(5-(2,5-Dimethylphenoxy)-2,2-dimethylpentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S27): Prepared from **S26** (2.99 g, 10 mmol) and B_2pin_2 (3.81 g, 15 mmol) following the procedure to synthesize A. The residue was purified by column chromatography to give the **S27** (1.70 g, 49% yield) as white solid. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.00 (d, *J* = 7.5 Hz, 1H), 6.65 (d, *J* = 7.5 Hz, 1H), 6.63 (s, 1H), 3.92 (t, *J* = 7.0 Hz, 2H), 2.32 (s, 3H), 2.19 (s, 3H), 1.83-1.74 (m, 2H), 1.46-1.40 (m, 2H), 1.25 (s, 12H), 1.01 (s, 6H), 0.84 (s, 2H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 157.3, 136.5, 130.3, 123.7, 120.6, 112.1, 82.9, 68.9, 41.0, 32.2, 29.5, 25.0, 24.9, 21.6, 15.9, carbon attached to boron not observed.

2-(1-Chloro-6-(2,5-dimethylphenoxy)-3,3-dimethylhexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (26-sub): Prepared from **S27** (866 mg, 2.5 mmol) following the

procedure to synthesize **24-sub** . The residue was purified over silica gel flash column chromatography to afford the **26-sub** (602 mg, 61%) as a colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.00 (d, *J* = 7.5 Hz, 1H), 6.65 (d, *J* = 7.5 Hz, 1H), 6.61 (s, 1H), 3.95-3.87 (m, 2H), 3.48 (dd, *J* = 9.0 Hz, 5.5 Hz, 1H), 2.31 (s, 3H), 2.18 (s, 3H), 1.98 (dd, *J* = 14.0 Hz, 9.5 Hz, 1H), 1.83 (dd, *J* = 14.0 Hz, 5.5 Hz, 1H), 1.80-1.71 (m, 2H), 1.47-1.37 (m, 2H), 1.27 (d, *J* = 1.5 Hz, 12H), 0.95 (d, *J* = 9.0 Hz, 6H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 157.2, 136.6, 130.4, 123.7, 120.7, 112.1, 84.4, 68.5, 46.2, 38.8, 33.7, 27.2, 24.64, 24.60, 24.4, 21.6, 16.0, carbon attached to boron not observed. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 30.9 (br). HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{22}H_{40}BClNO_3$) m/z 412.2784, found m/z 412.2792.

((*1R,4aS,10aR*)-7-Isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methanol (S29): Prepared from dehydroabietic acid **S27** (10.92 g, 20 mmol, 1 equiv., 55% purity) and $LiAlH_4$ (1.52 g, 40 mmol, 2.0 equiv) following the procedure to synthesize **S13**. The residue was purified by flash column chromatography to afford the **S29** (4.30 g, 75% yield) as sticky colorless oil. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.0 Hz, 1H), 7.00 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 6.90 (s, 1H), 3.48 (d, *J* = 10.8 Hz, 1H), 3.24 (d, *J* = 10.8 Hz, 1H), 2.97-2.77 (m, 3H), 2.34-2.24 (m, 1H), 1.88-1.62 (m, 5H), 1.50-1.34 (m, 4H), 1.24 (s, 3H), 1.23 (s, 3H), 1.22 (s, 3H), 0.90 (s, 3H).

(*1R,4aS,10aR*)-1-(Bromomethyl)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (S30): Prepared from **S29** (3.30 g, 15 mmol, 1 equiv.), NBS (2.80 g, 15.75 mmol, 1.05 equiv) and PPh_3 (4.13 g, 15.75 mmol, 1.05 equiv.) following the procedure to synthesize **S22.** The residue was purified by flash column chromatography to afford the **S30** (3.56 g, 68% yield) as sticky colorless oil. ^{1}H NMR: (300 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.1 Hz, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 6.89 (s, 1H), 3.49 (d, *J* = 10.2 Hz, 1H), 3.30 (d, *J* = 9.9 Hz, 1H), 2.97-2.75 (m, 3H), 2.35-2.20 (m, 1H), 1.87-1.63 (m, 5H), 1.59-1.33 (m, 3H), 1.24 (s, 3H), 1.22 (s, 6H), 1.06 (s, 3H).

2-(((*1R,4aS,10aS*)-7-Isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S31): Prepared from **S30** (3.32 g, 9.5 mmol, 1 equiv.) and B_2pin_2 (3.62 g, 14.25 mmol, 1.5 equiv) following the procedure to synthesize **S2.** The residue was purified by flash column

chromatography to afford the **S31** (2.45 g, 65% yield) as a white solid. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.4 Hz, 1H), 6.98 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 6.88 (s, 1H), 2.95-2.75 (m, 3H), 2.31-2.21 (m, 1H), 1.99-1.89 (m, 1H), 1.82-1.56 (m, 4H), 1.44-1.32 (m, 3H), 1.26-1.19 (m, 18H), 1.18 (s, 3H), 1.09 (d, *J* = 14.4 Hz, 1H), 1.02 (s, 3H), 0.73 (d, *J* = 14.4 Hz, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 147.9, 145.4, 135.2, 126.9, 124.4, 123.8, 82.9, 51.7, 40.5, 38.9, 38.0, 36.1, 33.6, 30.8, 25.3, 25.2, 25.0, 24.14, 24.10, 21.9, 19.5, 19.2, carbon attached to boron not observed.

2-(1-Chloro-2-((*1S,4aS,10aS*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (27-sub): Prepared from **S31** (1.33 g, 3.34 mmol) following the procedure to synthesize **24-sub**. The afforded brown oil **27-sub** (1.27 g) is a mixture of product and starting material. When we try to purified the afford product by column chromatography, the product was decomposed to the corresponding aldehyde. Therefore, the afforded residue, containing 40% of product, was directly used for e-XEC reaction without further purification.

4,4,5,5-Tetramethyl-2-styryl-1,3,2-dioxaborolane (S33): Pinacol (2.84 g, 24 mmol, 1.2 equiv.) was added to a solution of **S32** (2.96 g, 20 mmol) in THF (50 mL) at room temperature. After stirred for 3h, the reaction mixture was concentrated in vacuo and the residue was purified by flash chromatography to afford the **S33** (3.85 g, 84% yield) as a white solid.

4,4,5,5-Tetramethyl-2-(2-phenylcyclopropyl)-1,3,2-dioxaborolane (S34): The preparation of **S34** was performed according to a literature reference[35]. Et_2Zn (20 mL, 1M in hexane, 20 mmol, 2 equiv.) was added to anhydrous CH_2Cl_2 (17 mL) at 0 ℃ under N_2 atmosphere. To this solution was added (very slowly) trifluoroacetic acid (2.28 g, 20 mmol) dissolved in CH_2Cl_2 (7.7 mL). After the addition was completed, the reaction mixture was stirred for 30 minutes at 0 ℃. Next, a solution of diiodomethane (5.36 g, 20 mmol, 2 equiv.) dissolved in CH_2Cl_2 (7.7 mL) was added and the resulting reaction mixture was stirred for an additional 20 minutes at 0 ℃. To this reaction was added **S33** (2.30 g, 10 mmol, 1 equiv.) in CH_2Cl_2 (7.7 mL), and the reaction mixture was allowed to warm to rt and stirred for 12 h. The reaction was quenched with saturated NH_4Cl (aq) and diluted with EtOAc, filtered and washed with brine. The organic layer was dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified over silica gel flash column chromatography (PE/Et_2O = 20:1) to afford the **S34** (1.76 g, 72%) as a colorless oil.

2-(Chloro(2-phenylcyclopropyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (80): Prepared from **S34** (4 mmol) following General Procedure 2. The afforded brown oil **80** (1.01 g, 86% yield, dr ~ 1:1) was pure enough to use in the e-XEC reaction without further purification. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.25 (t, *J* = 7.5 Hz, 2H), 7.18-7.10 (m, 3H), 3.13 (t, *J* = 9.0 Hz, 1H), 2.05-1.97 (m, 1H), 1.61-1.53 (m,

1H), 1.31 (s, 6H), 1.27 (d, J = 5.0 Hz, 6H), 1.18-1.11 (m, 1H), 1.10-1.04 (m, 1H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 141.9/141.8, 128.3, 126.5, 125.91/125.89, 84.64/84.62, 26.3/26.1, 24.71/24.68/24.66, 24.1, carbon attached to boron not observed. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 30.9 (br). HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{16}H_{26}BClNO_2$) m/z 310.1740, found m/z 310.1746.

96-sub

2-(1-Chloro-4-methoxybutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (96-sub) : Prepared from 2-(3-methoxypropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8 mmol) following General Procedure 2. The crude residue was purified by short path distillation under reduced pressure to afford **96-sub** (1.57 g, 79%) as a colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 3.46-3.41 (m, 1H), 3.40 (t, J = 6.5 Hz, 2H), 3.32 (s, 3H), 1.98-1.89 (m, 1H), 1.89-1.74 (m, 2H), 1.73-1.63 (m, 1H), 1.28 (s, 12H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 84.5, 72.2, 58.6, 30.9, 27.4, 24.76, 24.72, carbon attached to boron not observed. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{11}H_{26}BClNO_3$) m/z 266.1689, found m/z 266.1693.

97-sub

2-(1-Chloro-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (97-sub) : Prepared from 4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane (8 mmol) following General Procedure 2. The crude residue was purified by using silica gel chromatography to give **97-sub** (1.57 g, 71% yield) as a colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.30-7.27 (m, 2H), 7.24-7.17 (m, 3H), 3.42 (t, J = 7.5 Hz, 1H), 2.89-2.81 (m, 1H), 2.80-2.72 (m, 1H), 2.12 (q, J = 7.5 Hz, 2H), 1.29 (s, 12H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 141.2, 128.8, 128.5, 126.1, 84.6, 35.8, 33.4, 24.76, 24.74, carbon attached to boron not observed; ^{11}B NMR ($CDCl_3$, 160 MHz): δ 31.6 (br). HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{15}H_{26}BClNO_2$) m/z 298.1740, found m/z 298.1746.

98-sub

2-(Chloro(cyclopropyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (98-sub) : Prepared from 2-cyclopropyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6 mmol) following General Procedure 2. The crude residue was purified by short path distillation under reduced pressure to afford **98-sub** (926 mg, 71%) as a colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 2.90 (d, J = 10.0 Hz, 1H), 1.29 (s, 12H), 1.27-1.24 (m, 1H), 0.72-0.60 (m, 2H), 0.45-0.33 (m, 2H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 84.5, 24.70, 24.69, 15.2, 6.5, 6.1, carbon attached to boron not observed. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 30.6 (br). HRMS (DART) calculated for $[M+H]^+$ ($C_{10}H_{19}BClO_2$) m/z

217.1161, found m/z 217.1166.

99-sub

2-(Chloro(tetrahydro-2H-pyran-4-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (99-sub) : Prepared from 4,4,5,5-tetramethyl-2-(tetrahydro-2H-pyran-4-yl)-1,3,2-dioxaborolane (909 mg, 4.3 mmol) following General Procedure 2. The crude residue was purified by short path distillation under reduced pressure to afford **99-sub** (786 mg, 70%) as white solid. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 4.04-3.94 (m, 2H), 3.38 (tdd, *J* = 12.0 Hz, 4.5 Hz, 2.0 Hz, 2H), 3.22 (d, *J* = 12.0 Hz, 1H), 1.98 (dtt, *J* = 19.5 Hz, 11.5 Hz, 3.5 Hz, 1H), 1.89-1.81 (m, 1H), 1.62-1.56 (m, 1H), 1.52-1.38 (m, 2H), 1.28 (s, 12H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 84.6, 68.0, 67.8, 38.9, 30.8, 30.7, 24.8, 24.7, carbon attached to boron not observed. HRMS (DART) calculated for $[M+H]^+$ ($C_{12}H_{23}BClO_3$) m/z 261.1423, found m/z 261.1429.

100-sub

2-(Chloro(2,3-dihydro-1H-inden-2-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (100-sub) : Prepared from 2-(2,3-dihydro-1H-inden-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.6 mmol) following General Procedure 2. The afforded brown oil **100-sub** (820 mg, 78%) containing 10% of starting material was used for e-XEC reaction without further purification. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.23-7.17 (m, 2H), 7.15-7.11 (m, 2H), 3.51 (d, *J* = 8.0 Hz, 1H), 3.21-3.12 (m, 1H), 3.10-3.03 (m, 1H), 3.02-2.91 (m, 2H), 2.86-2.79 (m, 1H), 1.28 (s, 12H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 142.65, 142.58, 126.5, 126.4, 124.7, 124.6, 84.6, 43.2, 37.5, 37.1, 24.75, 24.69, carbon attached to boron not observed. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 31.1 (br). HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{16}H_{26}BClNO_2$) m/z 310.1740, found m/z 310.1746.

(*3aR,4R,6R,7aS*)-3a,5,5-trimethyl-2-phenethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (S37): To a solution of phenethylboronic acid **S35** (1.50 g, 10 mmol, 1.0 eq) in anhydrous THF (20 mL) was added (+)-pinanediol **S36** (1.87 g, 11 mmol, 1.1 eq). The solution was stirred at room temperature overnight before the solvent was evaporated. The resulting residue was purified by flash column chromatography to obtain the desire **S37** (1.91 g, 67%) as a white solid. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.29-7.20 (m, 4H), 7.15 (t, *J* = 7.0 Hz, 1H), 4.26 (dd, *J* = 9.0 Hz, 2.0 Hz, 1H), 2.77 (t, *J* = 8.0 Hz, 2H), 2.32 (ddt, *J* = 15.0 Hz, 9.0 Hz, 2.5 Hz, 1H), 2.21-2.11 (m, 1H), 2.03

(t, J = 5.5 Hz, 1H), 1.93-1.86 (m, 1H), 1.82 (dt, J = 14.5 Hz, 2.5 Hz, 1H), 1.36 (s, 3H), 1.28 (s, 3H), 1.19 (t, J = 8.0 Hz, 2H), 1.01 (d, J = 11.0 Hz, 1H), 0.84 (s, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 144.6, 128.3, 128.1, 125.6, 85.7, 77.8, 51.4, 39.6, 38.3, 35.6, 30.2, 28.8, 27.2, 26.5, 24.1, carbon attached to boron not observed.

(*3aR,4R,6R,7aS*)-2-((R)-1-chloro-3-phenylpropyl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (101-sub): The preparation of **101-sub** was performed according to a literature reference[36]. To an oven dried round flask equipped with a stirring bar was added CH_2Cl_2 (722 mg, 8.5 mmol, 1.7 equiv) and THF (15 mL) by syringe, and the solution was cooled to -100 ℃. Then n-butyllithium (2.5 mL, 6.25 mmol, 1.25 equiv, 2.5 M in hexanes) was added dropwise at -100 ^{o}C. After stirring for 45 min, a solution of corresponding boronic ester (1.42 g, 5 mmol, 1 equiv.) in THF (5 mL) was directly added via syringe. After that, a solution of anhydrous $ZnCl_2$ (3.4 mL, 3.4 mmol, 1.0 M in Et_2O, 0.67 equiv) was added to the reaction mixture. Then the reaction mixture was allowed to slowly warm to room temperature overnight. The reaction was quenched by saturated ammonium chloride solution (30 mL). After stirring for 10 minutes, the aqueous phase was extracted with ether. The combined organic phases were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by flash column chromatography to give **101-sub** (1.21 g, 73% yield, dr = 1.8:1) as a colorless oil. The affored product containing traces of unreacted starting material was used for e-XEC reaction without further purification. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.31-7.27 (m, 2H), 7.24-7.17 (m, 3H), 4.38-4.34 (m, 1H), 3.51-3.42 (m, 1H), 2.93-2.83 (m, 1H), 2.82-2.71 (m, 1H), 2.39-2.32 (m, 1H), 2.28-2.22 (m, 1H), 2.18-2.12 (m, 2H), 2.09 (t, J = 5.5 Hz, 1H), 1.96-1.87 (m, 2H), 1.41 (s, 3H), 1.29 (s, 3H), 1.17 (dd, J = 11.0 Hz, 1.5 Hz, 1H), 0.84 (s, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 141.2, 128.80/128.79, 128.6, 87.0, 78.72/78.70, 51.3, 39.5, 38.4, 36.01/35.98, 35.4, 33.49/33.45, 28.6, 27.2, 26.5, 24.1, carbon attached to boron not observed. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{19}H_{30}BClNO_2$) m/z 350.2053, found m/z 350.2057.

17.3 General Procedure to Synthesize Benzyl Chloride (GP-3)

To a solution of benzyl alcohol (1 equiv.) in $CHCl_3$ was added thionyl chloride (1.6 eq.) at 0 ℃. The reaction mixture was stirred at room temperature for overnight. After that, the mixture was diluted with DCM and water, the organic layer was sequentially washed with saturated $NaHCO_3$, deionized water, dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum to afford the title product. Usually, the afforded product was pure enough for e-XEC reaction without further purification. For some case, the resulting product was not pure enough, then the resulting mixture was further purified by flash column chromatography purification or determining the purity by ^{1}H NMR with internal standard and then directly used in the e-XEC reaction without further purification. The following alkyl bromides were prepared according to

this procedure:

The NMR Spectral data of 4-chloro-2-(1-chloroethyl)-1-(difluoromethoxy)benzene (**39-sub**)[37], 3-(chloromethyl)benzo[b]thiophene (**48-sub**)[38], matched those in the literature.

2-Phenyladamantan-2-ol (S39): PhMgBr (1.0 M in THF, 12 mL, 12 mmol, 1.2 equiv.) was dropwise added to a solution of adamantanone **S38** (1.50 g, 10 mmol, 1 equiv.) in THF (20 ml) at 0 ^{o}C. After the addition, the mixture was stirred at room temperature for 1 hour. The reaction mixture was quenched by saturated NH_4Cl (aq), and then the aqueous layer was extracted with Et_2O. The combined organic layer dried with $MgSO_4$, filtered, concentrated under reduced pressure. The residue was purified by flash column chromatography to afford the **S39** (1.78 g, 80% yield) as a white solid. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.58-7.51 (m, 2H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.32-7.25 (m, 1H), 2.58 (s, 2H), 2.42 (d, *J* = 12.5 Hz, 2H), 1.91 (s, 1H), 1.79-1.66 (m, 9H), 1.52 (br, 1H); ^{13}C NMR: (126MHz, $CDCl_3$) δ 145.5, 128.8, 127.4, 125.5, 75.8, 37.8, 35.8, 35.0, 33.1, 27.6, 27.1.

2-Chloro-2-phenyladamantane (36-sub): Prepared from **S39** (685 mg, 3 mmol) following General Procedure 3. Considering the potential elimination reaction of the product, the reaction was stirred at 0 ^{o}C for 1h. After that, the reaction mixture was quenched with H_2O, the organic layer was washed with H_2O. Then the organic layer dried over $MgSO_4$, filtered, and concentrated in vacuo. The resulting white solid **36-sub** (710 mg, 96% yield) was pure enough for e-XEC reaction without further purification. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.0 Hz, 2H), 7.44-7.36 (m, 2H), 7.32-7.26 (m, 1H), 2.92 (s, 2H), 2.66 (d, *J* = 12.5 Hz, 2H), 2.00 (s, 1H), 1.88 (d,

J = 12.5 Hz, 4H), 1.82-1.72 (m, 5H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 144.2, 128.8, 127.6, 125.2, 79.7, 38.2, 37.3, 35.2, 34.0, 27.3, 26.9. GC-MS (EI) calculated for $[M]^+$ ($C_{16}H_{19}Cl$) m/z 246.1, found m/z 246.1.

4-Phenyltetrahydro-2H-thiopyran-4-ol (S41): Prepared from **S40** (2.32 g, 20 mmol) and PhMgBr (1.0 M in THF, 24 mL, 24 mmol, 1.2 equiv) following the procedure to synthesize **S39**. The residue was purified by flash column chromatography to afford the **S41** (2.91 g, 75% yield) as a light yellow solid. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.50-7.44 (m, 2H), 7.37 (t, J = 7.5 Hz, 2H), 7.30-7.24 (m, 1H), 3.21 (t, J = 13.0 Hz, 2H), 2.51-2.40 (m, 2H), 2.18 (t, J = 13.5 Hz, 2H), 2.01 (d, J = 14.0 Hz, 2H), 1.76 (br, 1H); ^{13}C NMR: (126MHz, $CDCl_3$) δ 149.1, 128.6, 127.2, 124.3, 72.0, 39.7, 24.3.

4-Chloro-4-phenyltetrahydro-2H-thiopyran (37-sub): Prepared from **S41** (971 mg, 5 mmol) following General Procedure 3. Considering the potential elimination reaction of the product, the reaction was stirred at 0 ^{o}C for 1h. After that, the reaction mixture was quenched with H_2O, the organic layer was washed with H_2O. Then the organic layer dried over $MgSO_4$, filtered, and concentrated in vacuo. The resulting yellow oil **37-sub** (996 mg, 94% yield) was pure enough for e-XEC reaction without further purification. ^{1}H NMR: (500 MHz, $CDCl_3$) δ7.50-7.45 (m, 2H), 7.31-7.26 (m, 2H), 7.24-7.19 (m, 2H), 3.28-3.17 (m, 2H), 2.54-2.41 (m, 4H), 2.32-2.20 (m, 2H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 146.1, 128.6, 128.1, 125.7, 73.6, 41.3, 24.9. GC-MS (EI) calculated for $[M]^+$ ($C_{11}H_{13}ClS$) m/z 212.0, found m/z 212.1.

38-sub

2-(1-Chloroethyl)biphenylene (38-sub): Prepared from 1-(biphenylen-2-yl)ethan-1-ol (1.0 g, 4.5 mmol) following General Procedure 3. The resulting yellow solid **38-sub** (821 mg, 76% yield,) was pure enough for e-XEC reaction without further purification. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 6.80-6.75 (m, 3H), 6.74-6.71 (m, 1H), 6.70-6.62 (m, 2H), 6.56 (dd, J = 6.8 Hz, 0.8 Hz, 1H), 4.88 (q, J = 7.2 Hz, 1H), 1.78 (d, J = 6.8 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 152.1, 151.4, 150.7, 150.6, 143.0, 128.7, 126.3, 117.9, 117.8, 117.0, 116.0, 59.7, 26.2. GC-MS (EI) calculated for $[M]^+$ ($C_{14}H_{11}Cl$) m/z 214.0, found m/z 214.1.

39-sub

4-Chloro-2-(1-chloroethyl)-1-(difluoromethoxy)benzene (39-sub): Prepared from

1-(5-chloro-2-(difluoromethoxy)phenyl)ethan-1-ol (1.0 g, 4.5 mmol) following General Procedure 3. The resulting light yellow oil **39-sub** (821 mg, 76% yield,) was pure enough for e-XEC reaction without further purification. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 2.4 Hz, 1H), 7.28 (dd *J* = 8.8 Hz, 2.8 Hz, 1H), 7.07 (d, *J* = 8.8 Hz, 1H), 6.52 (dd, *J* = 74.4 Hz, 72.4 Hz, 1H), 5.42 (q, *J* = 6.8 Hz, 1H), 1.81 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 146.1, 136.5, 131.7, 129.5, 128.3, 120.9, 116.0 (dd, *J* = 261.5 Hz, 259.4 Hz), 50.9, 25.6. ^{19}F NMR: (376MHz, CDCl3) δ -80.6 (m). GC-MS (EI) calculated for $[M]^+$ ($C_9H_8Cl_2F_2O$) m/z 240.0, found m/z 240.0.

1-(6-(Tert-butyl)-1,1-dimethyl-2,3-dihydro-1H-inden-4-yl)ethan-1-ol (S43): $NaBH_4$ (492 mg, 13 mmol) was portionwise added to a solution of celestolide **S42** (2.44 g, 10 mmol) in MeOH at 0 °C. Then the reaction mixture was stirred at room temperature for overnight. After reaction, the solvent was removed under reduced pressure. The resulting mixture was diluted with H_2O and DCM. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The resulting white solid **S43** (2.31 g, 94% yield) is pure enough for next step reaction without further purification. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 1.6 Hz, 1H), 7.10 (d, *J* = 2.0 Hz, 1H), 5.00 (q, *J* = 6.4 Hz, 1H), 2.98-2.72 (m, 2H), 1.94 (t, *J* = 7.2 Hz, 2H), 1.50 (d, *J* = 6.4 Hz, 3H), 1.34 (s, 9H), 1.26 (s, 6H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 152.9, 150.5, 140.8, 136.7, 119.5, 118.1, 68.8, 44.0, 41.6, 35.0, 31.8, 28.92, 28.87, 27.9, 23.9.

6-(Tert-butyl)-4-(1-chloroethyl)-1,1-dimethyl-2,3-dihydro-1H-indene (40-sub): Prepared from **S43** (1.23 g, 5 mmol) following General Procedure 3. The afforded white solid **40-sub** (1.21 g, 92% yield) was pure enough for e-XEC reaction without further purification. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 1.6 Hz, 1H), 7.12 (d, *J* = 1.6 Hz, 1H), 5.22 (q, *J* = 6.8 Hz, 1H), 3.04-2.83 (m, 2H), 2.00-1.92 (m, 2H), 1.88 (d, *J* = 7.2 Hz, 3H), 1.34 (s, 9H), 1.27 (s, 6H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 153.1, 150.5, 137.7, 137.4, 120.7, 119.1, 57.2, 44.2, 41.4, 35.0, 31.7, 28.9, 28.8, 27.9, 25.5. GC-MS (EI) calculated for $[M]^+$ ($C_{17}H_{25}Cl$) m/z 264.2, found m/z 264.2.

(1-Methylpiperidin-4-yl)(phenyl)methanone (S45): Thionyl chloride (2.5 ml) was added to a suspension of **S44** (716 mg, 5 mmol, 1 equiv.) in benzene (30 mL). The reaction mixture was refluxed at 80 °C for 2 hours. After that, the excess $SOCl_2$ and toluene was evaporated under reduced pressure. Then the resulting residue was re-dissolved in benzene (30 mL). Anhydrous $AlCl_3$ (1.67 g, 12.5 mmol, 2.5 equiv.)

was portionwise added to the mixture. The resulting mixture was refluxed at 80 ^{o}C for 3 hours. After the reaction cooled to room temperature, the reaction mixture was slowly quenched by saturated Na_2CO_3 (aq), and diluted with ethyl acetate. The aqueous layer was extracted with ethyl acetate. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting light yellow oil **S45** (728 mg, 72% yield) was directly used in next step without further purification. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.97-7.88 (m, 2H), 7.60-7.53 (m, 1H), 7.52-7.44 (m, 2H), 3.26 (s, 1H), 3.02-2.90 (m, 2H), 2.36 (s, 3H), 2.28-2.09 (m, 2H), 2.02-1.80 (m, 4H).

(1-Methylpiperidin-4-yl)(phenyl)methanol (S46): Prepared from **S45** (728 mg, 3.58 mmol, 1 equiv.) and $NaBH_4$ (203 mg, 5.37 mmol, 1.5 equiv.) following the procedure to synthesize **S43**. The resulting residue was purified by flash column chromatography to afford the **S46** (368 mg, 50% yield) as a colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.36-7.23 (m, 5H), 4.33 (d, *J* = 7.5 Hz, 1H), 2.91 (d, *J* = 11.5 Hz, 1H), 2.78 (d, *J* = 11.0 Hz, 1H), 2.56 (br, 1H), 2.22 (s, 3H), 2.07-1.98 (m, 1H), 1.92 (td, *J* = 11.5 Hz, 2.0 Hz, 1H), 1.82 (td, *J* = 11.5 Hz, 2.5 Hz, 1H), 1.63-1.52 (m, 1H), 1.44 (qd, *J* = 12.0 Hz, 4.0 Hz, 1H), 1.35-1.18 (m, 2H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 143.5, 128.4, 127.8, 126.8, 78.8, 55.7, 55.6, 46.2, 42.6, 28.7, 28.4.

4-(Chloro(phenyl)methyl)-1-methylpiperidine (41-sub): Prepared from **S46** (367 mg, 1.79 mmol) and $SOCl_2$ (2.15 mmol, 1.2 equiv.) following a modified General Procedure 3 using toluene (5 mL) instead of $CHCl_3$ as solvent. The resulting residue was purified by flash column chromatography to afford **41-sub** (245 mg, 61%) as a colorless oil. The afforded product containing trace amount of elimination side product was directly used in e-XEC reaction. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.37-7.27 (m, 5H), 4.59 (d, *J* = 8.5 Hz, 1H), 2.93 (d, *J* = 11.0 Hz, 1H), 2.78 (d, *J* = 11.5 Hz, 1H), 2.25 (s, 3H), 2.22-2.15 (m, 1H), 1.97-1.89 (m, 1H), 1.88-1.77 (m, 2H), 1.50-1.39 (m, 1H), 1.36-1.30 (m, 1H), 1.30-1.19 (m, 1H). HRMS (DART) calculated for $[M+H]^+$ ($C_{13}H_{19}ClN$) m/z 224.1201, found m/z 224.1204.

Chroman-4-ol (S48): Prepared from **S47** (2.96 g, 20 mmol) and $NaBH_4$ (983 mg, 26 mmol) following the procedure to synthesize **S43.** The resulting white solid **S48** (2.90 g, 97% yield) is pure enough for next step reaction without further purification. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.24-7.17 (m, 1H), 6.92 (td, *J* = 7.6 Hz, 1.2 Hz, 1H), 6.85 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 4.79 (t, *J* = 8.0 Hz, 1H), 4.32-4.23 (m, 2H), 2.18-2.08 (m, 1H), 2.07-1.99 (m, 1H), 1.90 (br, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 154.7, 129.9, 129.8, 124.4, 120.7, 117.2, 63.4, 62.0, 31.0.

4-Chlorochromane (42-sub): Prepared from **S48** (1.57 g, 10 mmol) following General Procedure 3. The afforded light yellow oil **42-sub** (1.57 g, 93% yield) was

pure enough for e-XEC reaction without further purification. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.24-7.18 (m, 1H), 6.92 (td, *J* = 7.6 Hz, 1.2 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 5.24 (t, *J* = 3.2 Hz, 1H), 4.48 (td, *J* = 11.6 Hz, 2.0 Hz, 1H), 4.38-4.30 (m, 1H), 2.55-2.43 (m, 1H), 2.34-2.26 (m, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 154.3, 130.8, 130.4, 122.2, 120.8, 117.5, 61.8, 53.1, 32.1. GC-MS (EI) calculated for $[M]^+$ (C_9H_9ClO) m/z 168.0, found m/z 168.1.

Tert-butyl 5-chloro-1,3,4,5-tetrahydro-2H-benzo[c]azepine-2-carboxylate (43-sub): To a solution of **S49** (1.0 g, 3.8 mmol) and pyridine (600 mg, 7.6 mmol, 2 equiv.) in $CHCl_3$ (10 mL) was added thionyl chloride (0.42 mL, 5.7 mml, 1.5 equiv.) at 0 ℃. The reaction mixture was stirred at room temperature for overnight. After that, the reaction mixture was quenched with H_2O, and the organic layer was washed with H_2O. Then the organic layer dried over $MgSO_4$, filtered, and concentrated in vacuo. The resulting reside was purified by flash column chromatography to afford **43-sub** (462 mg, 43% yield, a mixture of rotamers (~2:1)) as a colorless oil. The afforded product containing 10% of elimination product was directly used in e-XEC reaction without further purification. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.30-7.18 (m, 4H), 5.38-5.30 (m, 1H), 4.77-4.44 (m, 2H), 4.42-4.17 (m, 1H), 3.90-3.69 (m, 1H), 2.35-2.13 (m, 2H), 1.39/1.36 (s, 9H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 155.1, 139.9, 139.5, 131.0/130.6 (major), 129.75 (major)/129.66, 128.9/128.4 (major), 127.63 (major)/127.57, 79.92 (major)/79.88, 65.3 (major)/65.1, 51.7 (major)/51.2, 44.9/44.5 (major), 36.5/35.8 (major), 28.54/28.48 (major). HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{15}H_{24}ClN_2O_2$) m/z 299.1521, found m/z 299.1526.

44-sub

3-(1-Chloropropyl)benzo[b]thiophene (44-sub): Prepared from 1-(benzo[b]thiophen-3-yl)propan-1-ol (1.70 g, 8.9 mmol) following General Procedure 3. The afforded brown oil **44-sub** (1.71 g, 91% yield) was pure enough for e-XEC reaction without further purification. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.46 (s, 1H), 7.44 (td, *J* = 8.0 Hz, 1.0 Hz, 1H), 7.41-7.36 (m, 1H), 5.21 (t, *J* = 7.0 Hz, 1H), 2.39-2.28 (m, 2H), 1.13 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 140.8, 137.1, 136.3, 124.8, 124.3, 124.1, 123.1, 122.4, 59.3, 31.4, 12.0. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{11}H_{15}ClNS$) m/z 228.0608, found m/z 228.0610.

45-sub

2-(1-Chloro-2-phenylethyl)pyrazine (45-sub): Prepared from 2-phenyl-1-(pyrazin-2-yl)ethan-1-ol (340 mg, 1.7 mmol) following General Procedure 3. The resulting brown oil **45-sub** (351 mg, 94% yield, containing 8% of elimination product) was used for e-XEC reaction without further purification. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.54 (dd, *J* = 2.4 Hz, 1.6 Hz, 1H), 8.45 (d, *J* = 2.4 Hz, 1H), 8.42 (d, *J* = 1.2 Hz, 1H), 7.46-7.41 (m, 2H), 7.39-7.30 (m, 3H), 5.40 (dd, *J* = 9.2 Hz, 5.6 Hz, 1H), 3.62-3.43 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 153.3, 145.6, 144.4, 143.2, 140.8, 128.9, 128.8, 127.1, 61.9, 45.7. HRMS (DART) calculated for $[M+H]^+$ ($C_{12}H_{12}ClN_2$) m/z 219.0684, found m/z 219.0687.

1-(6-Methoxypyridin-3-yl)-2-methylpropan-1-ol (S51): Prepared from **S50** (1.37 g, 10 mmol, 1 equiv. and ^{i}PrMgBr (1.6 M in THF, 8.8 mL, 14 mmol, 1.4 equiv.) following the procedure to synthesize **S39**. The residue was purified by flash column chromatography to afford the **S51** (1.62 g, 89% yield) as light yellow oil. ^{1}H NMR: (300 MHz, $CDCl_3$) δ 8.04 (d, *J* = 1.8 Hz, 1H), 7.57 (dd, *J* = 6.3 Hz, 1.8 Hz, 1H), 6.73 (d, *J* = 6.3 Hz, 1H), 4.33 (d, *J* = 5.4 Hz, 1H), 1.93 (hept, *J* = 5.1 Hz, 1H), 1.88 (br, 1H), 1.01 (d, *J* = 4.8 Hz, 3H), 0.78 (d, *J* = 5.1 Hz, 3H).

5-(1-Chloro-2-methylpropyl)-2-methoxypyridine (46-sub): Prepared from **S51** (1.61 g, 8.9 mmol) following General Procedure 3. The afforded light yellow oil **46-sub** (1.46 g, 82% yield) was pure enough for e-XEC reaction without further purification. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 2.4 Hz, 1H), 7.61 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 4.60 (d, *J* = 7.6 Hz, 1H), 3.93 (s, 3H), 2.28-2.13 (m, 1H), 1.10 (d, *J* = 6.4 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 164.0, 145.7, 137.9, 129.7, 111.1, 67.9, 53.6, 36.7, 20.0, 19.9. HRMS (DART) calculated for $[M+H]^+$ ($C_{10}H_{15}ClNO$) m/z 200.0837, found m/z 200.0838.

(6-Methoxypyridin-3-yl)(phenyl)methanol (S52): Prepared from **S50** (1.10 g, 8 mmol, 1 equiv.) and PhMgBr (1 M in THF, 8.8 mL, 8.8 mmol, 1.1 equiv.) following the procedure to synthesize S**39**. The residue was purified by flash column chromatography to afford the **S52** (1.39 g, 79% yield) as a colorless oil. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 2.4 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 2.8 Hz, 1H),

7.40-7.32 (m, 4H), 7.31-7.26 (m, 1H), 6.70 (d, J = 8.8 Hz, 1H), 5.83 (s, 1H), 3.92 (s, 3H), 2.26 (br, 1H).

5-(Chloro(phenyl)methyl)-2-methoxypyridine (47-sub): Prepared from **S52** (1.52 g, 7 mmol) following General Procedure 3. The resulting yellow oil **47-sub** (1.51 g, 91% yield) was pure enough for e-XEC reaction without further purification. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.15 (d, J = 2.4 Hz, 1H), 7.65 (dd, J = 8.4 Hz, 2.4 Hz, 1H), 7.44-7.40 (m, 2H), 7.39-7.34 (m, 2H), 7.34-7.28 (m, 1H), 6.76 (d, J = 8.4 Hz, 1H), 6.11 (s, 1H), 3.95 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 163.8, 145.5, 140.3, 138.9, 130.2, 128.8, 128.5, 127.7, 111.4, 61.7, 54.0. HRMS (DART) calculated for $[M+H]^+$ ($C_{13}H_{13}ClNO$) m/z 234.0680, found m/z 234.0683.

Methyl 2-(10-oxo-10,11-dihydrodibenzo[b,f]thiepin-2-yl)propanoate (S54): To a solution of Zaltoprofen **S53** (2.98 g, 10 mmol, 1 equiv.) in MeOH (16 mL), sulfoxide chloride (1.78 g, 15 mmol, 1.5 equiv.) was added dropwise at 0 ^{o}C. After the addition, the reaction mixture was stirred at rt for 3h. The mixture was concentrated, quenched with ice water (20 mL), extracted with EtOAc (30 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting residue was purified by flash chromatography to afford the **S54** (3.12 g, 100% yield) as a colorless oil.

Methyl 2-(10-hydroxy-10,11-dihydrodibenzo[b,f]thiepin-2-yl)propanoate (S55): Prepared from **S54** (3.12 g, 10 mmol) and $NaBH_4$ (492 mg, 13 mmol, 1.3 equiv) following the procedure to synthesize **S43.** The resulting colorless sticky oil **S55** (2.98 g, 95% yield, dr = 1:1) was pure enough for next step reaction without further purification. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 8.0 Hz, 2H), 7.27 (t, J = 7.2 Hz, 1H), 7.20 (s, 1H), 7.15 (t, J = 7.6 Hz, 1H), 7.08 (d, J = 8.0 Hz, 1H), 5.38 (dd, J = 8.4 Hz, 2.8 Hz, 1H), 3.77-3.71 (m, 1H), 3.71-3.65 (m, 1H), 3.64 (s, 3H), 3.43-3.30 (m, 1H), 1.47 (d, J = 7.2 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 174.8, 143.0, 140.8, 139.4, 134.3, 133.1, 132.1, 131.5, 130.84/130.82, 130.67/130.64, 128.0, 127.8, 126.07/126.04, 69.9, 52.3, 45.1, 41.5, 18.7/18.6.

Methyl 2-(10-chloro-10,11-dihydrodibenzo[b,f]thiepin-2-yl)propanoate (50-sub): Prepared from **S55** (1.57 g, 5 mmol) following General Procedure 3. The afforded colorless oil **50-sub** (1.57 g, 95% yield, dr = 1:1) was pure enough for e-XEC reaction without further purification. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.54 (d, J = 8.0 Hz, 1H), 7.49 (dd, J = 8.0 Hz, 3.5 Hz, 1H), 7.43 (dd, J = 8.0 Hz, 1.0 Hz, 1H), 7.26-7.21 (m, 2H), 7.17-7.09 (m, 2H), 5.83 (dd, J = 9.0 Hz, 3.5 Hz, 1H), 3.96 (dd, J = 14.5 Hz, 3.0

Hz, 1H), 3.77-3.67 (m, 2H), 3.65 (d, J = 1.5 Hz, 3H), 1.48 (dd, J = 7.5 Hz, 1.0 Hz, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 174.73/174.71, 141.09/141.03, 140.1, 139.43/139.40, 134.6, 133.8, 133.25/133.22, 132.03/131.98, 131.88, 130.5/130.3, 128.3, 127.85/127.84, 126.6/126.4, 60.33/60.31, 52.3, 45.2/45.1, 42.30/42.26, 18.64/18.60. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{18}H_{21}ClNO_2S$) m/z 350.0976, found m/z 350.0981.

2-(3-Methoxyphenyl)propan-2-ol (S57): Prepared from **S56** (3.0 g, 20 mmol, 1 equiv.) and Bromomethylmagnesium (3 M in Et_2O, 8 mL, 24 mmol, 1.2 equiv.) following the procedure to synthesize **S39**. The residue was purified by flash column chromatography to afford the **S57** (2.78 g, 84% yield) as a colorless oil. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.264 (t, J = 8.0 Hz, 1H), 7.11-7.01 (m, 2H), 6.79 (ddd, J = 8.4 Hz, 2.8 Hz, 0.8 Hz, 1H), 3.82 (s, 3H), 1.58 (s, 6H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 159.7, 151.1, 129.4, 116.9, 111.9, 110.7, 72.7, 55.4, 31.8.

1-(2-Chloropropan-2-yl)-3-methoxybenzene (102-sub): Prepared from **S57** (1.0 g, 6 mmol) following General Procedure 3. Considering the potential elimination reaction of the product, the reaction was stirred at 0 ^{o}C for 1h. After that, the reaction mixture was quenched with H_2O, the organic layer was washed with H_2O. Then the organic layer dried over $MgSO_4$, filtered, and concentrated in vacuo. The resulting reside yellow oil **102-sub** (976 mg, 88% yield) was pure enough for e-XEC reaction without further purification. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.30-7.26 (m, 1H), 7.19-7.13 (m, 2H), 6.86-6.80 (m, 1H), 3.83 (s, 3H), 1.99 (s, 6H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 159.5, 148.0, 129.3, 117.9, 112.6, 112.2, 69.6, 55.4, 34.4. GC-MS (EI) calculated for $[M]^+$ ($C_{10}H_{13}ClO$) m/z 184.1, found m/z 184.1.

Tert-butyl 4-hydroxy-4-phenylpiperidine-1-carboxylate (S59): To a stirred solution of bromobenzene (4.24 g, 27 mmol, 1.35 equiv) in THF (30 mL) at −78 °C was added nBuLi (2.5 M in hexanes, 10.4 mL, 26 mmol, 1.30 equiv), and the reaction was maintained at −78 ℃ for 30 min. After that, a solution of **S58** (3.98 g, 20 mmol, 1 equiv) in THF (30 mL) was slowly added into the reaction and stirred at −78 °C for 2 h. The reaction was quenched with the addition of a saturated solution of NH_4Cl, and the reaction mixture was transferred to a separating funnel and extracted with ether. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography to afford

the **S59** (4.01 g, 72% yield) as a white solid. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.0 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.27 (t, *J* = 7.0 Hz, 1H), 4.01 (d, *J* = 12.0 Hz, 2H), 3.24 (t, *J* = 12.5 Hz, 2H), 1.99 (td, *J* = 13.5 Hz, 4.5 Hz, 2H), 1.81 (br, 1H), 1.72 (d, *J* = 12.5 Hz, 2H), 1.47 (s, 9H); ^{13}C NMR: (126MHz, $CDCl_3$) δ 155.0, 148.2, 128.6, 127.3, 124.6, 79.6, 71.6, 40.0, 38.2, 28.6.

Tert-butyl 4-chloro-4-phenylpiperidine-1-carboxylate (103-sub): To a solution of **S59** (416 mg, 1.5 mmol) and Et_3N (0.45 mL, 3.15 mmol, 2.1 equiv.) in $CHCl_3$ (10 mL) was added thionyl chloride (0.22 mL, 3 mml, 2 equiv.) at 0 ℃. The reaction mixture was stirred at 0 ℃ for 5 h. After that, the reaction mixture was quenched with H_2O, and the organic layer was washed with H_2O. Then the organic layer dried over $MgSO_4$, filtered, and concentrated in vacuo. The resulting white solid (431 mg) contains 72% of desire product **103-sub** and 25% of elimination side product. Considering the potential elimination of the **103-sub**, the residue was directly used in e-XEC reaction without further purification. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.57-7.51 (m, 2H), 7.42-7.35 (m, 2H), 7.35-7.28 (m, 1H), 4.11-4.02 (m, 2H), 3.36 (t, *J* = 12.5 Hz, 2H), 2.35-2.25 (m, 2H), 2.17-2.06 (m, 2H), 1.47 (s, 9H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 154.8, 145.2, 128.6, 128.5, 125.5, 79.9, 72.0, 39.3, 28.6. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{16}H_{23}ClNO_2$) m/z 296.1412, found m/z 296.1419.

105-sub

(Chloro(cyclohexyl)methyl)benzene (105-sub): Prepared from cyclohexyl(phenyl)methanol (1.90 g, 10 mmol) following General Procedure 3. The resulting white solid **105-sub** (1.96 g, 94% yield) was pure enough for e-XEC reaction without further purification. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.38-7.26 (m, 5H), 4.62 (d, *J* = 8.4 Hz, 1H), 2.20 (d *J* = 12.8 Hz, 1H), 1.95-1.75 (m, 2H), 1.73-1.58 (m, 2H), 1.45 (d, *J* = 12.8 Hz, 1H), 1.33-1.01 (m, 4H), 0.98-0.85 (m, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 141.1, 128.5, 128.1, 127.7, 70.0, 45.8, 30.6, 30.4, 26.3, 26.1, 26.0. GC-MS (EI) calculated for $[M]^+$ ($C_{13}H_{17}Cl$) m/z 208.1, found m/z 208.1.

106-sub

4-(1-Chloro-3-(4-(trifluoromethyl)phenyl)propyl)-1,2-dimethoxybenzene (106-sub): Prepared from 1-(3,4-dimethoxyphenyl)-3-(4-(trifluoromethyl)phenyl)propan-1-ol (0.65 g, 1.91 mmol) following General Procedure 3. The resulting white solid **106-sub** (612 mg, 89% yield) was pure enough for e-XEC reaction without further purification. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.93-6.87 (m, 2H), 6.85-6.80 (m, 1H), 4.77 (dd, *J* = 8.4 Hz, 6.0 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 2.92-2.83 (m, 1H), 2.83-2.72 (m, 1H), 2.54-2.41 (m, 1H), 2.39-2.25 (m, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 149.31, 149.30, 144.9, 133.9, .129.0, 125.5 (q, *J* = 3.7

Hz), 124.4 (q, J = 270.4 Hz), 119.5, 111.0, 110.1, 63.0, 56.0, 41.1, 33.2. ^{19}F NMR: (376MHz, $CDCl_3$) δ -62.3 (s). HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{18}H_{22}ClF_3NO_2$) m/z 376.1286, found m/z 376.1288.

108-sub

1-Chloro-2,3-dihydro-1H-indene (108-sub): Prepared from 2,3-dihydro-1*H*-inden-1-ol (2.01 g, 15 mmol) following General Procedure 3. The afforded light yellow oil **108-sub** (2.01 g, 88% yield) was pure enough for e-XEC reaction without further purification. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.48-7.42 (m, 1H), 7.32-7.23 (m, 3H), 5.45 (dd, J = 6.4 Hz, 3.2 Hz, 1H), 3.28-3.14 (m, 1H), 2.98-2.85 (m, 1H), 2.68-2.55 (m, 1H), 2.46-2.34 (m, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 143.5, 143.2, 129.0, 127.2, 125.1, 124.9, 63.3, 37.1, 30.4. GC-MS (EI) calculated for $[M]^+$ (C_9H_9Cl) m/z 152.0, found m/z 152.1.

109-sub

4-Chlorothiochromane (109-sub): Prepared from thiochroman-4-ol (1.0 g, 6 mmol) following General Procedure 3. The resulting light yellow solid **109-sub** (1.01 g, 91% yield) was pure enough for e-XEC reaction without further purification. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.28 (dd, J = 7.6 Hz, 1.6 Hz, 1H), 7.18-7.08 (m, 2H), 7.07-7.01 (m, 1H), 5.32 (t, J = 3.2 Hz, 1H), 3.62 (td, J = 12.8 Hz, 2.8 Hz, 1H), 2.93-2.83 (m, 1H), 2.67-2.56 (m, 1H), 2.44-2.31 (m, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 132.9, 132.3, 131.7, 129.0, 126.8, 124.4, 57.0, 31.3, 21.6. GC-MS (EI) calculated for $[M]^+$ (C_9H_9ClS) m/z 184.0, found m/z 184.0.

Isopropyl 2-(4-((4-chlorophenyl)(hydroxy)methyl)phenoxy)-2-methylpropanoate (S61): Prepared from fenofibrate **S60** (1.80 g, 5 mmol) and $NaBH_4$ (246 mg, 6.5 mmol, 1.3 equiv) following the procedure to synthesize **S43**. The resulting sticky colorless oil **S61** (1.69 g, 93% yield) was pure enough for next step reaction without further purification. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.29 (s, 4H), 7.22-7.13 (m, 2H), 6.83-6.75 (m, 2H), 5.74 (d, J = 3.2 Hz, 1H), 5.06 (hept, J = 6.4 Hz, 1H), 2.29 (d, J = 3.2 Hz, 1H), 1.56 (s, 6H), 1.20 (d, J = 6.4 Hz, 6H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 173.8, 155.3, 142.5, 137.0, 133.3, 128.6, 128.0, 127.6, 119.0, 79.3, 75.2, 69.1, 25.49, 25.48, 21.7.

Isopropyl 2-(4-(chloro(4-chlorophenyl)methyl)phenoxy)-2-methylpropanoate

(112-sub): Prepared from **S61** (1.09 g, 3 mmol) following General Procedure 3. The afforded colorless oil **112-sub** (1.04 g, 91% yield) was pure enough for e-XEC reaction without further purification. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.36-7.28 (m, 4H), 7.25-7.19 (m, 2H), 6.84-6.74 (m, 2H), 6.05 (s, 1H), 5.07 (hept, 6.4 Hz, 1H), 1.59 (s, 6H), 1.20 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 173.6, 155.7, 139.9, 134.0, 133.9, 129.3, 128.77, 128.76, 118.7, 79.3, 69.2, 63.3, 25.51, 25.49, 21.7. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{20}H_{26}Cl_2NO_3$) m/z 398.1284, found m/z 398.1289.

2-Phenylprop-2-en-1-ol (S63): A suspension of CuI (1.43 g, 7.5 mmol, 0.5 equiv) in toluene (20 mL) was cooled to -78 ℃. Then, propargyl alcohol **S62** (840 mg, 15 mmol, 1.0 equiv) and PhMgBr (15 mL, 45 mmol, 3.0 M in Et_2O, 3.0 equiv) were added, and the mixture was warmed to room temperature overnight. The reaction was quenched with saturated NH_4Cl (aq) and diluted with Et_2O. Then the aqueous layer was extracted with Et_2O. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography to give the **S63** (1.65 g, 82% yield) as a light yellow oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.48-7.43 (m, 2H), 7.39-7.34 (m, 2H), 7.33-7.29 (m, 1H), 5.49-5.46 (m, 1H), 5.37-5.46 (m, 1H), 4.55 (s, 2H), 1.76 (br, 1H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 147.4, 138.6, 128.6, 128.1, 126.2, 112.7, 65.1.

(3-Chloroprop-1-en-2-yl)benzene (53-sub): Prepared from **S63** (671 mg, 5 mmol) following General Procedure 3. The afforded light yellow oil **53-sub** (719 mg, 94% yield) was pure enough for e-XEC reaction without further purification. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.52-7.46 (m, 2H), 7.42-7.30 (m, 3H), 5.57 (d, *J* = 0.4 Hz, 1H), 5.49-5.45 (m, 1H), 4.48 (d, *J* = 0.8 Hz, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 144.1, 137.8, 128.7, 128.4, 126.3, 116.9, 46.7. GC-MS (EI) calculated for $[M]^+$ (C_9H_9Cl) m/z 152.0, found m/z 152.1.

17.4 General Procedure to Synthesize Propargyl Chloride (GP-4)

Step1: nBuLi (1.3 equiv.) was added dropwise into a solution of alkyne (1.3 equiv.) in anhydrous THF (0.4 M) at –78 ℃. The mixture was stirred at room temperature for 30 min and cooled to –78 ℃. Aldehyde (1.0 equiv.) was added dropwise. Then the mixture was warmed up to room temperature and stirred for overnight. The mixture was quenched by a saturated NH_4Cl (aq.), and the aqueous layer was extracted with Et_2O. The combined organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo. The resulting residue was purified by flash column chromatography to afford the desired propargyl alcohol.

Step 2: Last step synthesized propargyl alcohol (1.0 equiv.) was added to a solution of PPh_3 (1.2 equiv.) in THF (0.5 M). N-Chlorosuccinimide (1.3 equiv.) was added in portions over 10 minutes and the reaction mixture was refluxed at 60 ^oC for 20 hours. When the reaction mixture was cool to room temperature, a mixture of EA and H_2O was added to the solution. The aqueous layer was extracted by EA. The combined organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo. The resulting residue was purified by flash column chromatography to afford the desired propargyl chloride.

59-ol

1-(Triisopropylsilyl)pent-1-yn-3-ol (59-ol): Prepared from ethynyltriisopropylsilane (4.74 g, 26 mmol, 1.3 equiv.), nBuLi (10.4 mL, 26 mmol, 1.3 equiv.) and propionaldehyde (2.68 g, 20 mmol, 1.0 equiv.) following the step 1 of General Procedure 4. The crude residue was purified by flash chromatography to afford **59-ol** (3.71 g, 77%) as colorless oil. ^1H NMR: (300 MHz, $CDCl_3$) δ 4.34 (t, *J* = 4.8 Hz, 1H), 1.82-1.64 (m, 3H), 1.11-1.04 (m, 21 H), 1.03 (t, *J* = 5.7 Hz, 3H).

59-sub

(3-Chloropent-1-yn-1-yl)triisopropylsilane (59-sub): Prepared from **59-ol** (3.71 g, 15.4 mmol, 1.0 equiv.), NCS (2.88 g, 21.6 mmol, 1.4 equiv.) and PPh_3 (6.06 g, 23.1 mmol, 1.5 equiv) following the step 2 of General Procedure 4. The crude residue was purified by flash chromatography to afford **59-sub** (2.57 g, 64%) as a colorless oil. ^1H NMR: (400 MHz, $CDCl_3$) δ 4.53 (t, *J* = 6.4 Hz, 1H), 2.03-1.93 (m, 2H), 1.11 (t, *J* = 7.6 Hz, 3H), 1.09-1.04 (m, 21H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 105.3, 87.8, 50.5, 32.8, 18.7, 11.3, 10.6. GC-MS (EI) calculated for $[M]^+$ ($C_{14}H_{27}ClSi$) m/z 258.2, found m/z 258.2.

60-ol

1-Phenylnon-4-yn-3-ol (60-ol): Prepared from hex-1-yne (2.0 g, 24.3 mmol, 1.48 equiv.), nBuLi (8.3 mL, 20.6 mmol, 1.26 equiv.) and 3-phenylpropanal (2.20 g, 16.4 mmol, 1.0 equiv.) following the step 1 of General Procedure 4. The crude residue was purified by flash chromatography to afford **60-ol** (3.07 g, 86%) as yellow oil.

60-sub

(3-Chloronon-4-yn-1-yl)benzene (60-sub): Prepared from **60-ol** (2.16 g, 10 mmol, 1.0 equiv.), NCS (1.87 g, 14 mmol, 1.4 equiv.) and PPh_3 (3.93 g, 15 mmol, 1.5 equiv) following the step 2 of General Procedure 4. The crude residue was purified by flash chromatography to afford **60-sub** (1.81 g, 77%) as colorless oil. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.34-7.27 (m, 2H), 7.25-7.17 (m, 3H), 4.51 (tt, *J* = 6.8 Hz, 2.0 Hz, 1H), 2.86 (t, *J* = 7.6 Hz, 2H), 2.32-2.18 (m, 4H), 1.57-1.47 (m, 2H), 1.47-1.37 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 140.6, 128.69, 128.67, 126.3, 87.9, 78.5, 49.0, 41.3, 32.5, 30.7, 22.1, 18.6, 13.7. GC-MS (EI) calculated for $[M]^+$ ($C_{15}H_{19}Cl$) m/z 234.1, found m/z 234.1.

61-ol

8-Methoxy-2-methyloct-5-yn-4-ol: Prepared from 4-methoxybut-1-yne (1.0 g, 10 mmol, 1.2 equiv.), nBuLi (4 mL, 10 mmol, 1.0 equiv.) and 3-methylbutanal (0.86 g, 10 mmol, 1.0 equiv.) following the step 1 of General Procedure 4. The afforded crude **61-ol** (1.89 g, yellow oil) was directly used in next step without further purification. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 4.40 (tt, *J* = 7.6 Hz, 2.0 Hz, 1H), 3.49 (t, *J* = 7.2 Hz, 2H), 3.37 (s, 3H), 2.49 (td, *J* = 7.2 Hz, 2.0 Hz, 2H), 1.88-1.77 (m, 1H), 1.71 (br, 1H), 1.66-1.47 (m, 2H), 0.92 (t, *J* = 6.4 Hz, 6H).

61-sub

5-Chloro-1-methoxy-7-methyloct-3-yne (61-sub): Prepared from **61-ol** (10 mmol, 1.0 equiv.), NCS (1.74 g, 13 mmol, 1.3 equiv.) and PPh_3 (3.15 g, 12 mmol, 1.2 equiv) following the step 2 of General Procedure 4. The crude residue was purified by flash chromatography to afford **61-sub** (1.15 g, 61%) as colorless oil. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 4.56 (tt, *J* = 7.6 Hz, 2.0 Hz, 1H), 3.50 (t, *J* = 7.2 Hz, 2H), 3.37 (s, 3H), 2.52 (td, *J* = 7.2 Hz, 2.0 Hz, 2H), 1.95-1.86 (m, 1H), 1.85-1.76 (m, 2H), 0.95-0.90 (m, 6H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 83.7, 80.0, 70.7, 58.8, 48.5, 48.0, 25.8, 22.2, 22.0, 20.2. GC-MS (EI) calculated for $[M]^+$ ($C_{10}H_{17}ClO$) m/z 188.1, found m/z 188.0.

62-ol

3,7-Dimethyloct-5-yn-4-ol (62-ol): Prepared from 3-methylbut-1-yne (1.23 g, 18mmol, 1.2 equiv.), nBuLi (6 mL, 15 mmol, 1.0 equiv.) and 2-methylbutanal (1.29 g, 15 mmol, 1.0 equiv.) following the step 1 of General Procedure 4. The afforded crude **62-ol** (2.13 g, colorless oil, dr~1:1) was directly used in next step without further purification. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 4.30 (ddd, *J* = 6.8 Hz, 4.8 Hz, 2.0 Hz, 1H), 2.65-2.50 (m, 1H), 1.65 (br, 1H), 1.64-1.47 (m, 2H), 1.26-1.18 (m, 1H), 1.16 (d, *J* = 7.2 Hz, 6H), 0.97 (dd, *J* = 6.8 Hz, 0.8 Hz, 3H), 0.92 (td, *J* = 7.2 Hz, 3.2 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 92.0/91.7, 79.6/78.9, 67.0/66.9, 41.5/41.4, 25.6, 24.9, 23.2, 20.6, 14.6/14.2, 11.8/11.7.

62-sub

5-Chloro-2,6-dimethyloct-3-yne (62-sub): Prepared from **62-ol** (1.54 g, 10 mmol, 1.0 equiv.), NCS (1.74 g, 13 mmol, 1.3 equiv.) and PPh_3 (3.15g, 12 mmol, 1.2 equiv) following the step 2 of General Procedure 4. The crude residue was purified by flash chromatography to afford **62-sub** (858 mg, 50% yield, dr ~1:1) as a colorless oil. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 4.60-4.54 (m, 1H), 2.65-2.54 (m, 1H), 1.85-1.76 (m, 1H), 1.68-1.55 (m, 1H), 1.38-1.24 (m, 1H), 1.22-1.19 (m, 1H), 1.17 (d, *J* = 7.2 Hz, 6H), 1.06 (dd, *J* = 6.4 Hz, 5.2 Hz, 3H), 0.93 (td, *J* = 7.6 Hz, 2.4 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 104.7/103.9, 93.6/93.2, 77.3/76.2, 55.4/55.0, 42.7/42.4, 26.6/25.8, 22.96/22.94/22.92, 20.77/20.76, 15.5/15.1, 11.72/11.66. GC-MS (EI) calculated for $[M]^+$ ($C_{10}H_{17}Cl$) m/z 172.1, found m/z 172.1.

17.5 General Procedure to Synthesize α-Halosilane (GP-5)

General procedure to synthesize α-aryl-α-chlorosilane

The preparation of α-aryl-α-chlorosilane was performed according to a literature reference[39]. n-Butyllithium was added dropwise (8 mL, 2.5 M in hexane, 20 mmol, 1.0 equiv) to a solution of diisopropylamine (2.8 mL, 20 mmol, 1.0 equiv) in THF (0.5 M) at -78 °C under N_2 atmosphere, and the resulting mixture was stirred for another 10 minutes, at which time the solution was diluted with hexane (0.5 M) and cooled to –100 ℃. A mixture of the benzyl chloride (1.0 equiv) and silyl chloride (1.2 equiv) in THF (0.5 M) was added dropwise over the course of 30 minutes via syringe. The reaction was stirred for 20 minutes, then warmed to 0 ℃ and quenched with water. The aqueous layer was extracted with ether and the combined organic layers were washed with 1 M HCl, water, then dried with $MgSO_4$, filtered, and concentrated

under reduced pressure. The product was purified by column chromatography and/or by reduced pressure distillation.

Note: for the reaction with chloro(dimethyl)phenylsilane, the fresh prepared LDA solution was added dropwise to the solution of chloro(dimethyl)phenylsilane and benzyl chloride in THF.

The following α-aryl-α-chlorosilanes were prepared according to this procedure:

63-sub 66-sub 72-sub 114-sub

63-sub

(Chloro(phenyl)methyl)trimethylsilane (63-sub): Prepared from benzyl chloride (2.53 g, 20 mmol, 1.0 equiv.) and chlorotrimethylsilane (2.61 g, 24 mmol, 1.2 equiv.) following General Procedure 5. The crude residue was purified by short path distillation under reduced pressure to afford **63-sub** (3.12 g, 78%) as a colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.34-7.28 (m, 2H), 7.26-7.18 (m, 3H), 4.34 (s, 1H), 0.09 (s, 9H). ^{13}C NMR: (126 MHz, $CDCl_3$) δ 140.3, 128.3, 127.0, 126.7, 53.1, -3.4; ^{29}Si NMR (99 MHz, $CDCl_3$) δ -5.7. GC-MS (EI) calculated for $[M]^+$ ($C_{10}H_{15}ClSi$) m/z 198.1, found m/z 198.1.

66-sub

5-(Chloro(dimethyl(phenyl)silyl)methyl)-2-methoxypyridine (66-sub): Prepared from 5-(chloromethyl)-2-methoxypyridine (943 mg, 6 mmol, 1.0 equiv.) and Chlorodimethylphenylsilane (1.13 g, 6.6 mmol, 1.1 equiv.) following General Procedure 5. The crude residue was purified by flash column chromatography to afford **66-sub** (1.32 g, 75%) as colorless oil. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 2.8 Hz, 1H), 7.46-7.38 (m, 3H), 7.37-7.31 (m, 2H), 7.27 (dd, *J* = 8.4 Hz, 2.8 Hz, 1H), 6.61 (d, *J* = 8.8 Hz, 1H), 4.43 (s, 1H), 3.91 (s, 3H), 0.44 (s, 3H), 0.39 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 163.3, 145.1, 138.1, 134.53, 134.50, 130.1, 128.4, 128.0, 110.6, 53.6, 49.4, -4.9, -5.1. HRMS (DART) calculated for $[M+H]^+$ ($C_{15}H_{19}ClNOSi$) m/z 292.0919, found m/z 292.0924.

72-sub

(Chloro(phenyl)methyl)dimethyl(phenyl)silane (72-sub): Prepared from benzyl chloride (2.53 g, 20 mmol, 1.0 equiv.) and Chlorodimethylphenylsilane (22 mmol, 1.1

equiv.) following General Procedure 5. The crude residue was purified by short path distillation under reduced pressure to afford (3.29 g, 63%) as a colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.43-7.37 (m, 3H), 7.35-7.30 (m, 2H), 7.25-7.20 (m, 2H), 7.20-7.14 (m, 1H), 4.48 (s, 1H), 0.44 (s, 3H), 0.34 (s, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 139.7, 135.1, 134.5, 129.8, 128.2, 127.8, 127.3, 126.8, 52.4, -5.0. GC-MS (EI) calculated for $[M]^+$ ($C_{15}H_{17}ClSi$) m/z 260.1, found m/z 260.1.

114-sub

(Chloro(4-vinylphenyl)methyl)dimethyl(phenyl)silane (114-sub): Prepared from 1-(chloromethyl)-4-vinylbenzene (1.07 g, 7 mmol, 1.0 equiv.) and Chlorodimethylphenylsilane (1.31 g, 7.7 mmol, 1.1 equiv.) following General Procedure 5. The crude residue was purified by flash column chromatography to afford **114-sub** (1.65 g, 68%) as colorless oil. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.46-7.37 (m, 3H), 7.37-7.31 (m, 2H), 7.30-7.26 (m, 2H), 7.08-7.01 (m, 2H), 6.68 (dd, *J* = 17.6 Hz, 10.8 Hz, 1H), 5.72 (d, *J* = 17.7 Hz, 1H), 5.23 (d, *J* = 10.8 Hz, 1H), 4.48 (s, 1H), 0.45 (s, 3H), 0.35 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 139.4, 136.5, 136.1, 135.0, 134.6, 129.9, 127.8, 127.5, 126.0, 113.7, 52.3, -5.01, -5.03. GC-MS (EI) calculated for $[M]^+$ ($C_{17}H_{19}ClSi$) m/z 286.1, found m/z 286.1.

(Dibromomethyl)(methyl)diphenylsilane (S64): The preparation of **S64** was performed according to a literature reference[40]. The solution of LDA (1.0 M in hexanes/THF, 21 mL, 21 mmol, 1.05 equiv.) was added to a solution of dibromomethane (3.48 g, 20 mmol, 20 mL) and chlorodiphenylmethylsilane (4.66 g, 20 mmol, 1 equiv.) in THF (17 mL) dropwise at -78 ^{o}C. After stirring at -78 ^{o}C for 0.5 h, the resulting mixture was poured into 1M HCl and extracted with ether. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The crude residue was purified by flash column chromatography to afford **S64** (5.17 g, 70%) as colorless oil.

(1,1-Dibromoethyl)(methyl)diphenylsilane: A solution of **S64** (3.70 g, 10 mmol, 1 equiv) in THF (20 mL) was added dropwise to a solution of LDA (1.0 M in Hexanes/THF, 10.5 mL, 10.5 mmol, 1.05 equiv.) at -78 ^{o}C. The mixture was stirred at -78 ^{o}C for 0.5 h and then MeI (1.77 g, 12.5 mmol, 1.25 equiv.) was added. After stirring at -78 ^{o}C for another 0.5 h, the mixture was poured into 1M HCl and extracted with ether. The combined organic layers were dried over anhydrous Na_2SO_4, flitered and concentrated in vacuo. The residue was purified by flash column chromatography to afford **S65** (2.91 g, 76%) as a colorless oil.

(2-Bromopropan-2-yl)(methyl)diphenylsilane (65-sub): A solution of lithium

trimethylmagnesate, (prepared by mixing methylmagnesium bromide (3.0 M in ether, 2 mL, 6 mmol, 1 equiv.) and methyllithium (1.6 M in ether, 7.5 mL, 12 mmol, 2 equiv.) in THF (15 mL)) was added to a solution of **S65** (2.30 g, 6 mmol, 1 equiv) in THF (30 mL) at -78 ^{o}C under N_2 atmosphere. After stirring at -78 ^{o}C for 0.5 h, the mixture was carefully poured into 1 HCl and extracted with ether. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash column chromatography to afford **65-sub** (1.52 g, 79%) as a colorless oil. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.77-7.70 (m, 4H), 7.44-7.36 (m, 6H), 1.85 (s, 6H), 0.78 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 135.8, 134.1, 129.8, 127.9, 53.9, 31.5, -4.8. GC-MS (EI) calculated for $[M]^+$ ($C_{16}H_{19}BrSi$) m/z 318.0, found m/z 318.1.

1-(Methyldiphenylsilyl)hexan-1-ol (S66): The preparation of **S66** was performed according to a literature reference[41]. Chlorodiphenylmethylsilane (5.82 g, 25 mmol, 1 equiv.) was added to a suspension of Li pellet (399 mg, 57.5 mmol, 2.3 equiv) in anhydrous THF (25 mL) under Argon atmosphere. The resulting mixture was stirred at room temperature for 16 h (note: after ~20 min of stirring, the reaction mixture had turned dark green or brown). Next, a solution of the Hexanal (1.91 g, 19 mmol, 0.75 equiv) in THF (40 mL) was prepared in a flame-dried round-bottom flask under an atmosphere of nitrogen. The resulting solution was cooled to –78 ℃, and the solution of the lithiated silane was then added dropwise over 5 min. Next, the reaction mixture was warmed to room temperature and stirred for 16 h. The mixture was quenched by NH_4Cl (aq), and the resulting mixture was extracted three times with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under cacuum. The resulting residue was purified via flash chromatography to afford the desire **S66** (4.13 g, 55% yield) as a colorless oil. ^{1}H NMR: (300 MHz, $CDCl_3$) δ 7.68-7.56 (m, 2H), 7.48-7.30 (m, 6H), 3.97-3.85 (m, 1H), 1.68-1.54 (m, 2H), 1.38-1.16 (m, 7H), 0.87 (t, J = 4.8 Hz, 3H), 0.62 (s, 3H).

(1-Bromohexyl)(methyl)diphenylsilane (67-sub): Bromine (0.72 mL, 14.1 mmol, 1.5 equiv) was added to a suspension of PPh_3 (3.70 g, 14.1 mmol, 1.5 equiv) in DCM (30 mL) at 0 ℃. The mixture was stirred for 10 min and a white solid will precipitate from the mixture. And then imidazole (959 mg, 14.1 mmo, 1.5 equiv) was added to the mixture, the solution become clean again. After that, **S66** (2.83 g, 9.4 mmol, 1 equiv) was added slowly by syringe. The resulting mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with DCM. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel to afford **67-sub** (2.17 g, 64% yield) as colorless oil. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.65-7.60 (m, 2H), 7.59-7.55 (m, 2H), 7.45-7.33

(m, 6H), 3.76 (dd, J = 11.2 Hz, 3.6 Hz, 1H), 1.91-1.61 (m, 3H), 1.46-1.34 (m, 1H), 1.34-1.21 (m, 3H), 1.21-1.09 (m, 1H), 0.86 (t, J = 7.2 Hz, 3H), 0.74 (s, 3H) ; ^{13}C NMR: (100 MHz, $CDCl_3$) δ 135.16, 135.13, 134.7, 134.5, 129.86, 128.83, 128.1, 128.0, 42.0, 33.4, 31.0, 29.0, 22.6, 14.2, -5.4. GC-MS (EI) calculated for $[M]^+$ ($C_{19}H_{25}BrSi$) m/z 360.1, found m/z 360.2.

Tert-butyl 3-(hydroxymethyl)piperidine-1-carboxylate (S68): A solution of Boc_2O(8.82 g, 40.4 mmol, 1.01 equiv) in DCM (20 mL) was portionwise added to a solution of piperidin-3-ylmethanol (4.61 g, 40 mmol, 1 equiv) and Et_3N (11.4 mL, 80 mmol, 2 equiv) in DCM (60 mL). The mixture was stirred at room temperature for overnight. The solvent was evaporated and the residue was purified by flash column chromatography to afford the **S68** (8.01 g, 93% yield) as a sticky colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 3.73/3.58 (br, 2H), 3.48 (t, J = 6.0 Hz, 2H), 3.09/2.97/2.54/2.02 (br, 3H), 1.82-1.67 (m, 2H), 1.60 (br, 1H), 1.53-1.34 (m, 10H), 1.25 (br, 1H).

Tert-butyl 3-(bromomethyl)piperidine-1-carboxylate (13-Br): PPh_3 (7.87 g, 30 mmol, 1.2 equiv.) was portionwise added to a solution of **S68** (5.38 g, 25 mmol, 1 equiv.) and carbon tetrabromide (10.61 g, 32 mmol, 1.25 equiv.) in DCM (120 mL) at room temperature. The resulting mixture was stirred at RT for overnight. After that, the reaction solvent was evaporated under reduced pressure. The insoluble $OPPh_3$ was precipitated by addition of ether. The resulting suspension was vigorously stirred at rt for 20 min. Then the mixture was filtered through cotton, the solid pad was washed by ether. The filtrate was concentrated *in vacuo*, the residue was purified by flash column chromatography to give the **13-Br** (5.42 g, 78% yield) as a colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 4.02 (br, 1H), 3.84 (d, J = 13.0 Hz, 2H), 3.38-3.21 (m, 2H), 2.83 (s, 1H), 2.77-2.47 (br, 1H), 1.96-1.77 (m, 2H), 1.71-1.63 (m, 1H), 1.54-1.36 (m, 10H), 1.36-1.20 (m, 1H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 154.9, 79.7, 48.4, 44.3, 38.1, 36.1, 29.7, 28.5, 24.4. HRMS (DART) calculated for $[M+H]^+$ ($C_{11}H_{21}BrNO_2$) m/z 278.0750, found m/z 278.0755.

(*S*)-4-Phenylbutan-2-ol (S69): Benzylmagnesium chloride (1.0 M in Et_2O, 48 mL, 48 mmol, 1.5 equiv.) was added dropwise to a -30 ℃ suspension of CuI (9.14 g, 48mmol, 1.5 equiv.) in THF (38 mL) and stirred for 5 minutes. (*S*)-Propylene oxide (1.86 g, 32 mmol, 1 equiv.) was added and the reaction was warmed to 0 ℃ and stirred for an additional 2.5 hours. The reaction was then quenched with saturated NH_4Cl (aq) and warmed to room temperature. Ether was added and the mixture was filtered through celite before the layers were separated. The organic layer was washed sequentially with a saturated $NaHCO_3$ (aq.), and then brine, dried over $MgSO_4$, filtered, and

concentrated under reduced pressure. The crude product was purified by flash chromatography to afford the **S69** (4.65 g, 97% yield, 99% ee) as a colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.32-7.27 (m, 2H), 7.24-7.16 (m, 3H), 3.88-3.78 (m, 1H), 2.82-2.63 (m, 2H), 2.82-2.63 (m, 2H), 1.24 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 142.2, 128.5, 126.0, 67.7, 41.0, 32.3, 23.8. HPLC (OD, hexane/ isopropanol = 99/1, flow 1.0 mL/min, detection at 254 nm) retention time =9.81 min (minor) and 13.16 min (major).

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	9.894	96447	8068	50.290
2	13.188	95335	5971	49.710
Total		191782	14039	100.000

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	9.813	84	17	0.081
2	13.155	103772	6361	99.919
Total		103856	6378	100.000

(*R*)-(3-Bromobutyl)benzene (82): Bromine (0.54 mL, 30 mmol, 1.2 equiv) was added to a suspension of PPh_3 (7.87 g, 30 mmol, 1.2 equiv) in DCM (40 mL) at 0 ℃. The mixture was stirred for 10 min and a white solid will precipitate from the mixture.

And then imidazole (2.04 g, 30 mmol, 1.2 equiv) was added to the mixture, the solution become clean again. After that, **S69** (3.76 g, 25 mmol, 1 equiv) was added slowly by syringe. The resulting mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with DCM. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel to afford **82** (4.47 g, 84% yield) as colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.33-7.27 (m, 2H), 7.24-7.18 (m, 3H), 4.14-4.04 (m, 1H), 2.91-2.83 (m, 1H), 2.80-2.71 (m, 1H), 2.19-2.10 (m, 1H), 2.09-2.01 (m, 1H), 1.74 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 141.0, 128.7, 128.6, 126.2, 51.0, 42.8, 34.1, 26.7. Data are consistent with those reported in the literature[42].

18. Characterization of Products

3

4,4,5,5-Tetramethyl-2-(2-methyl-5-(phenylthio)pentan-2-yl)-1,3,2-dioxaborolane (3): Followed general procedure A and purified using silica gel chromatography (Hexanes : Et_2O = 50:1) to give 262.6 mg (82% yield) of **3** as a white solid.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.34-7.29 (m, 2H), 7.28-7.23 (m, 2H), 7.14 (t, *J* = 7.5 Hz, 1H), 2.88 (t, *J* = 7.5 Hz, 2H), 1.65-1.56 (m, 2H), 1.41-1.35 (m, 2H), 1.17 (s, 12H), 0.91 (s, 6H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 137.2, 129.0, 128.9, 125.7, 83.1, 40.6, 34.4, 26.5, 25.0, 24.8, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 35.0 (br). IR (neat): 2973, 2931, 1583, 1474, 1366, 1166, 1025, 897, 735, 690 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{18}H_{33}BNO_2S$) m/z 338.2320, found m/z 338.2326.

8

4,4,5,5-Tetramethyl-2-(1-(phenylthio)octan-4-yl)-1,3,2-dioxaborolane (8): Followed general procedure A and purified using silica gel chromatography (Hexanes : Et_2O = 50:1) to give 261.0 mg (75% yield) of **8** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.34-7.29 (m, 2H), 7.28-7.22 (m, 2H), 7.14 (t, *J* = 7.5 Hz, 1H), 2.90 (t, *J* = 7.5 Hz, 2H), 1.69-1.59 (m, 2H), 1.55-1.45 (m, 2H), 1.44-1.36 (m, 1H), 1.35-1.23 (m, 5H), 1.20 (s, 12H), 1.01-0.92 (m, 1H), 0.87 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 137.2, 129.0, 128.9, 125.7, 83.0, 33.9, 31.6, 31.1, 30.8, 29.0, 24.93, 24.90, 23.1, 14.2, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.3 (br). IR (neat): 2976, 2954, 2854, 1584, 1386, 1370, 1314, 1141, 966, 853, 736, 689 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{20}H_{34}BO_2S$) m/z 349.2367, found m/z 349.2370.

11

4,4,5,5-Tetramethyl-2-(1-(3-phenoxypropyl)cyclobutyl)-1,3,2-dioxaborolane (11): Followed general procedure A and purified using silica gel chromatography (Hexanes : Et_2O = 50:3) to give 221.0 mg (70% yield) of **11** as a white solid.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.29-7.24 (m, 2H), 6.94-6.87 (m, 3H), 3.98-3.89 (m, 2H), 2.18-2.09 (m, 2H), 1.99-1.84 (m, 2H), 1.76-1.64 (m, 6H), 1.26 (s, 12H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 159.2, 129.5, 120.5, 114.7, 83.2, 68.4, 36.1, 0.4, 26.8, 24.8, 18.3, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.9 (br). IR (neat): 2971, 2938, 2869, 1600, 1583, 1492, 1473, 1372, 1248, 887, 762, 709 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{19}H_{33}BNO_3$) m/z 334.2548, found m/z 334.2550.

12

2-(1-(But-3-en-1-yl)cyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12): Followed general procedure A and purified using silica gel chromatography (Hexanes : Et_2O = 50:1) to give 200.7 mg (80% yield) of **12** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 5.88-5.77 (m, 1H), 5.01-4.94 (m, 1H), 4.92-4.86 (m, 1H), 2.05-1.96 (m, 2H), 1.85-1.76 (m, 2H), 1.65-1.58 (m, 2H), 1.57-1.50 (m, 2H), 1.48-1.42 (m, 2H), 1.29-1.24 (m, 2H), 1.23 (s, 12H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 139.9, 113.8, 83.0, 38.3, 35.4, 32.5, 25.4, 24.8, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 35.2 (br). IR (neat): 2977, 2946, 2867, 1640, 1454, 1409, 1302, 1141, 966, 906, 855, 671, 579 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{15}H_{28}BO_2$) m/z 251.2177, found m/z 251.2182.

13

Tert-butyl 3-((1-hydroxycyclohexyl)methyl)piperidine-1-carboxylate (13): Followed general procedure A with **13-sub** (0.5 mmol), **13-Br** (1.5 mmol), and $TBAClO_4$ (3 mmol) in THF (2.5 mL). The residue was purified using silica gel chromatography (Hexanes : Acetone = 20:1) to give a mixture of desire product and the primary alkyl bromides. Then treated the isolated product with a mixture of H_2O_2 (30%wt, 1 mL)/NaOH (3M, 1 mL)/EtOH (1 mL)/THF (2 mL) at room temperature for 4 hours. Then the corresponding alcohol product was purified by silica gel chromatography (Hexanes:EA = 2:1) to give 125.0 mg (84% yield) of **13** as a colorless oil. .^{1}H NMR: (500 MHz, $CDCl_3$) δ 3.99-3.91 (m, 1H), 3.82 (br, 1H), 2.83 (s, 1H), 2.60 (t, *J* = 10.5 Hz, 1H), 1.83 (d, *J* = 12.5 Hz, 1H), 1.70 (br, 1H), 1.62-1.53 (m, 6H), 1.50-1.39 (m, 15H), 1.37-1.32 (m, 1H), 1.31-1.25 (m, 2H), 1.25-1.13 (m, 2H). ^{13}C NMR: (126 MHz, $CDCl_3$) δ 155.1, 79.3, 71.8, 45.8, 38.2, 38.0, 33.4, 31.4, 28.64,

28.6, 25.9, 25.1, 22.4. IR (neat): 3452 (br), 2927, 2851, 1667, 1467, 1426, 1364, 1266, 1241, 1149, 976, 854, 768, 731 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{17}H_{32}NO_3$) m/z 298.2377, found m/z 298.2381.

14

Ethyl 2,2,6-trimethyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octanoate (14): Followed general procedure A with **14-sub** (0.5 mmol), primary alkyl bromide (1.5 mmol), and $TBAClO_4$ (3 mmol) in THF (2.5 mL). The residue was purified using silica gel chromatography (Hexanes : Et_2O = 10:1) to give 141.4 mg (82% yield) of **14** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 4.14-4.03 (m, 2H), 1.51-1.38 (m, 3H), 1.37-1.31 (m, 1H), 1.23 (t, *J* = 7.0 Hz, 3H), 1.22 (s, 12H), 1.13 (s, 6H), 1.20-1.07 (m, 4H), 0.86 (s, 3H), 0.82 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR: (126 MHz, $CDCl_3$) δ 178.2, 83.0, 60.2, 42.4, 41.8, 39.7, 31.7, 25.4, 25.2, 25.0, 24.9, 21.3, 20.9, 14.4, 10.2, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.7 (br). IR (neat): 2976, 2938, 1728, 1471, 1386, 1370, 1304, 1263, 1141, 1027, 966, 856, 692 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{19}H_{41}BNO_4$) m/z 358.3123, found m/z 358.3128.

15

2-(7-Chlorohept-1-en-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15): Followed general procedure A and purified using silica gel chromatography (Hexanes : Et_2O = 50:1) to give 103.1 mg (40% yield) of **15** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 5.84-5.73 (m, 1H), 5.05-4.98 (m, 1H), 4.97-4.92 (m, 1H), 3.51 (t, *J* = 7.0 Hz, 2H), 2.24-2.08 (m, 2H), 1.84-1.71 (m, 2H), 1.58-1.46 (m, 2H), 1.23 (s, 12H), 1.12-1.03 (m, 1H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 138.3, 115.3, 83.3, 45.4, 35.5, 32.3, 28.2, 24.99, 24.96, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.1 (br). IR (neat): 2978, 2928, 1639, 1409, 1381, 1371, 1318, 1270, 1240, 1142, 967, 910, 863, 726, 650 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{13}H_{28}BClNO_2$) m/z 276.1896, found m/z 276.1899.

16

2-(1-((*1R,5S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-6-phenylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (16): Followed general procedure A with **16-sub** (0.5 mmol), primary alkyl bromide (1.5 mmol), and $TBAClO_4$ (3 mmol) in THF (2.5 mL). The residue was purified using silica gel chromatography (Hexanes : Et_2O = 33:1) to give 132.8 mg (63% yield, dr = 1:1) of **16** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.29-7.23 (m, 2H), 7.19-7.13 (m, 3H), 5.19-5.11 (m, 1H), 2.65-2.55

(m, 2H), 2.33 (dt, J = 8.5 Hz, 5.5 Hz,1H), 2.27-2.12 (m, 2H), 2.08-2.03 (m, 1H), 2.02-1.97 (m, 1H), 1.96-1.85 (m, 2H), 1.66-1.57 (m, 2H), 1.53-1.31 (m, 4H), 1.26 (s, 3H), 1.24 (s, 12H), 1.13 (dd, J = 8.5 Hz, 1.0 Hz, 1H), 1.05-0.97 (m, 1H), 0.81 (s, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 148.9/148.8, 143.0, 128.5/128.3, 125.6, 115.7/115.6, 83.0, 46.0/45.9, 41.0, 38.09/38.07, 36.77/36.75, 36.4, 31.84/31.81, 31.4, 31.24/31.22, 31.19/31.18, 29.3/29.1, 26.52/26.51, 24.99/24.97, 24.97/24.95, 21.40/21.26, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.3 (br). IR (neat): 2978, 2915, 2832, 1496, 1454, 1380, 1313, 1164, 1143, 966, 747 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{27}H_{45}BNO_2$) m/z 426.3538, found m/z 426.3543.

17

2-(1-(2,2-Dimethyl-1,3-dioxolan-4-yl)-5-(5-methylfuran-2-yl)pentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (17): Followed general procedure A with **17-sub** (0.5 mmol), primary alkyl bromide (1.5 mmol), and $TBAClO_4$ (3 mmol) in THF (2.5 mL). The reaction was electrolyzed at constant current of 5 mA until passing 2.2 F/mol of charge. The residue was purified using silica gel chromatography (Hexanes : Et_2O = 10:1) to give 134.0 mg (71% yield, dr = 1.3:1) of **17** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 5.82 (s, 2H), 4.13-3.97 (m, 2H), 3.40-3.43 (m, 1H), 2.54 (t, J = 7.5 Hz, 2H), 2.23 (s, 3H), 1.83-1.75 (m, 0.4H), 1.71-1.56 (m, 3.6H), 1.55-1.40 (m, 2H), 1.391/1.388 (s, 3H), 1.334/1.330 (s, 3H), 1.244/1.237 (s, 12H), 1.17-1.11 (m, 0.6H), 1.04-0.95 (m, 0.4H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 154.65/154.58, 150.17/150.15, 108.73/108.72, 105.84, 105.32/105.28, 83.2, 76.06/75.94, 69.92/69.86, 35.4/34.8, 31.4/31.2, 28.38/28.36, 27.62/27.60, 27.18/27.16, 26.1/26.0, 25.04/25.02, 24.9, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.2 (br). IR (neat): 2980, 2930, 2863, 1570, 1378, 1370, 1316, 1245, 1215, 1143, 1058, 1020, 855, 829, 778 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{21}H_{39}BNO_5$) m/z 396.2916, found m/z 396.2921.

18

1-(8-Fluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl)cyclohexane-1-carbonitrile (18): Followed general procedure A with **18-sub** (0.5 mmol), primary alkyl bromide (1.5 mmol), and $TBAClO_4$ (3 mmol) in THF (2.5 mL).The residue was purified using silica gel chromatography (Hexanes : Et_2O = 10:1) to give 133.1 mg (73% yield) of **18** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 4.42 (dt, J = 47.5 Hz, 6.0 Hz, 2H), 2.00-1.90 (m, 2H), 1.78-1.57 (m, 7H), 1.54-1.31 (m, 10H), 1.24 (s, 12H), 1.22-1.13 (m, 3H), 1.04-0.96 (m, 1H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 123.9, 84.2 (d, J = 163.1 Hz), 83.2, 40.9, 39.1, 35.9 (d, J = 14.2 Hz), 31.5, 31.0, 30.8 (d, J = 30.8 Hz), 25.6, 24.96 (d, J = 6.6 Hz), 24.87 (d, J = 5.5 Hz), 24.1, 23.2, *carbon*

attached to boron not observed. ^{19}F NMR (CDCl3, 470 MHz) δ -218.1 (tt, *J* = 47.0 Hz, 24.9 Hz). ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.1 (br). IR (neat): 2932, 2859, 2230, 1451, 1387, 1372, 1316, 1143, 1005, 966, 852, 736, 670 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{21}H_{41}BFN_2O_2$) m/z 383.3240, found m/z 383.3247.

19

Ethyl 9-methoxy-2,2-dimethyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonanoate (19): Followed general procedure A with **19-sub** (0.5 mmol), primary alkyl bromide (1.5 mmol), and $TBAClO_4$ (3 mmol) in THF (2.5 mL). The reaction was electrolyzed at constant current of 2.5 mA until passing 2.0 F/mol of charge. The residue was purified using silica gel chromatography (Hexanes : Et_2O = 10:1) to give 138.9 mg (75% yield) of **19** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 4.09 (q, *J* = 7.0 Hz, 2H), 3.34 (t, *J* = 7.0 Hz, 2H), 3.31 (s, 3H), 1.65-1.52 (m, 2H), 1.51-1.46 (m, 2H), 1.45-1.26 (m, 4H), 1.22 (s, 12H), 1.25-1.17 (m, 5H), 1.13 (s, 6H), 1.00-0.91 (m, 1H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 178.2, 83.0, 73.3, 60.2, 58.6, 42.3, 41.1, 32.0, 29.3, 27.8, 25.3, 25.2, 24.95, 24.94, 24.6, 14.4, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 35.7 (br). IR (neat): 2977, 2931, 2858, 1727, 1460, 1386, 1371, 1314, 1255, 1142, 1118, 1026, 967, 858, 717, 671 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{20}H_{43}BNO_5$) m/z 388.3229, found m/z 388.3235.

20

9-(7-Methoxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptyl)-9*H*-carbazole (20): Followed general procedure A and purified using silica gel chromatography (Hexanes : EA = 10:1) to give 223.5 mg (53% yield) of **20** as a white solid.^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.5 Hz, 2H), 7.48-7.40 (m, 4H), 7.24-7.19 (m, 2H), 4.35-4.22 (m, 2H), 3.35-3.31 (m, 2H), 3.30 (s, 3H), 1.96-1.80 (m, 2H), 1.60-1.48 (m, 4H), 1.46-1.34 (m, 2H), 1.18 (d, *J* = 4.0 Hz, 12H), 1.07-1.01 (m, 1H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 140.5, 125.6, 122.9, 120.4, 118.8, 108.8, 83.2, 73.2, 58.6, 43.4, 29.2, 29.1, 28.5, 27.9, 25.0, 24.9, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 33.9 (br). IR (neat): 3051, 2976, 2927, 2859, 1597, 1484, 1371, 1347, 1241, 1142, 1119, 1065, 967, 858, 749, 723 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{26}H_{37}BNO_3$) m/z 422.2861, found m/z 422.2856.

21

2-(1-(4,4-Difluorocyclohexyl)-5-(5-methylfuran-2-yl)pentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (21): Followed general procedure A with **21-sub** (0.5 mmol), primary alkyl bromide (1.5 mmol), and $TBAClO_4$ (3 mmol) in THF (2.5 mL). The residue was purified using silica gel chromatography (Hexanes : Et_2O = 30:1) to give 132.9 mg (67% yield) of **21** as a colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 5.82 (s, 2H), 2.60-2.49 (m, 2H), 2.24 (s, 3H), 2.09-2.00 (m, 2H), 1.83-1.77 (m, 1H), 1.76-1.66 (m, 2H), 1.65-1.57 (m, 3H), 1.49-1.35 (m, 3H), 1.34-1.27 (m, 2H), 1.24 (d, *J* = 1.0 Hz, 12H), 1.22-1.15 (m, 2H), 1.13-1.01 (m, 1H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 154.7, 150.2, 124.1 (t, *J* = 238.4 Hz), 105.8, 105.3, 83.1, 37.3, 35.3, 33.9-33.5 (m, 2C), 31.3, 29.5 (d, *J* = 9.4 Hz), 29.0 (d, *J* = 9.4 Hz), 28.4, 27.7, 25.0 (d, *J* = 9.9 Hz), 13.7, *carbon attached to boron not observed*. ^{19}F NMR ($CDCl_3$, 470 MHz) δ -91.5 (d, *J* = 234.1 Hz), -101.6 (d, *J* = 231.7 Hz). ^{11}B NMR ($CDCl_3$, 160 MHz): δ 33.8 (br). IR (neat): 2977, 2930, 2862, 1570, 1449, 1379, 1317, 1166, 1143, 1114, 964, 863, 778, 671 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{22}H_{39}BF_2NO_3$) m/z 414.2986, found m/z 414.2987.

22

4,4,5,5-Tetramethyl-2-(6-(phenylthio)-1-(thiophen-3-yl)hexan-3-yl)-1,3,2-dioxaborolane (22): Followed general procedure A with **22-sub** (0.5 mmol), primary alkyl bromide (1.5 mmol), and $TBAClO_4$ (3 mmol) in THF (2.5 mL). The reaction was electrolyzed at constant current of 2.5 mA until passing 2.3 F/mol of charge. The residue was purified using silica gel chromatography (Hexanes : Et_2O = 33:1) to give 140.8 mg (70% yield) of **22** as a colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.34-7.29 (m, 2H), 7.28-7.24 (m, 2H), 7.22 (dd, *J* = 5.0 Hz, 2.5 Hz, 1H), 7.15 (tt, *J* = 7.5 Hz, 1.5 Hz, 1H), 6.92 (dd, *J* = 5.0 Hz, 1.0 Hz, 1H), 6.92-6.90 (m, 1H), 2.95-2.85 (m, 2H), 2.68-2.55 (m, 2H), 1.81-1.71 (m, 1H), 1.70-1.60 (m, 3H), 1.59-1.48 (m, 2H), 1.22 (s, 12H), 1.08-0.99 (m, 1H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 143.2, , 128.9, 128.4, 125.7, 125.2, 120.0, 83.2, 33.9, 32.3, 30.5, 29.9, 28.9, 24.9, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.4 (br). IR (neat): 2976, 2923, 2854, 1584, 1480, 1438, 1379, 1316, 1213, 1141, 966, 776, 737, 689, 634 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{22}H_{35}BNO_2S_2$) m/z 420.2197, found m/z 420.2205.

23

7-(1*H*-Pyrrol-1-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptyl 4-methoxybenzoate (23): Followed general procedure A with **23-sub** (0.5 mmol), primary alkyl bromide (1.5 mmol), and $TBAClO_4$ (3 mmol) in THF (2.5 mL). The reaction was electrolyzed at constant current of 2.5 mA until passing 2.2 F/mol of

charge. The residue was purified using silica gel chromatography (Hexanes : Et_2O = 5:1) to give 167.9 mg (76% yield) of **23** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.02-7.96 (m, 2H), 6.94-6.88 (m, 2H), 6.63 (t, *J* = 2.0 Hz, 2H), 6.12 (t, *J* = 2.0 Hz, 2H), 4.25 (t, *J* = 6.5Hz, 2H), 3.86 (s, 3H), 3.85 (t, *J* = 7.5 Hz, 2H), 1.87-1.67 (m, 4H), 1.61-1.53 (m, 1H), 1.52-1.42 (m, 2H), 1.41-1.33 (m, 1H), 1.23 (s, 12H), 1.08-1.00 (s, 1H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 166.5, 163.4, 131.7, 123.1, 120.6, 113.7, 107.9, 83.3, 65.0, 55.6, 49.9, 31.2, 28.4, 27.8, 25.0, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 33.7 (br). IR (neat): 2976, 2931, 2859, 1710, 1606, 1510, 1418, 1274, 1254, 1166, 1142, 1029, 968, 771, 722, 696, 634 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{25}H_{37}BNO_5$) m/z 442.2759, found m/z 442.2762.

24

Methyl 4-(5-(5-methylfuran-2-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)bicyclo[2.2.2]octane-1-carboxylate (24): Followed general procedure C with **24-sub** (0.5 mmol) and primary alkyl bromide (1.5 mmol), but without TBAB. The residue was purified using silica gel chromatography (Hexanes : Et_2O = 10:1) to give 166.8 mg (75% yield) of **24** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 5.81 (s, 2H), 3.62 (s, 3H), 2.59-2.46 (m, 2H), 2.23 (s, 3H), 1.73 (t, *J* = 8.0 Hz, 6H), 1.66-1.54 (m, 2H), 1.47-1.38 (m, 5H), 1.37-1.25 (m, 4H), 1.23 (d, *J* = 5.0 Hz, 12H), 1.06 (dd, *J* = 13.5 Hz, 2.0 Hz, 1H), 0.99-0.90 (m, 1H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 178.8, 154.7, 150.1, 105.8, 105.3, 83.1, 51.7, 43.3, 39.1, 33.2, 31.2, 30.7, 28.7, 28.4, 27.6, 25.0 (d, *J* = 6.5 Hz), 13.6, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 33.8 (br). IR (neat): 2977, 2919, 2860, 1727, 1569, 1387, 1370, 1312, 1234, 1142, 1066, 967, 860, 827, 754, 685, 577 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{26}H_{42}BO_5$) m/z 445.3120, found m/z 445.3127.

25

2-(1-((*1S,2S,5R*)-2-Isopropyl-5-methylcyclohexyl)-4-methoxybutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (25): Followed general procedure A and purified using silica gel chromatography (Hexanes : Et_2O = 10:1) to give 158.5 mg (45% yield, dr = 2:1) of **25** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 3.41-3.34 (m, 2H), 3.32 (s, 3H), 2.18-2.08 (m, 0.3H), 1.96-1.85 (m, 0.7H), 1.83-1.64 (m, 2H), 1.63-1.46 (m, 3H), 1.45-1.27 (m, 3H), 1.25-1.19 (m, 13H), 1.18-1.08 (m, 1H), 1.03-0.65 (m, 13H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 82.91/82.83, 73.44/73.41, 58.65/58.53, 46.9/44.1,

42.0/40.9, 40.3/38.6, 35.73/35.71, 33.6/33.3, 30.4/29.9, 26.5, 26.3/26.2, 25.3/25.2, 24.9/24.6, 24.68/24.66, 23.1/23.0, 21.8/21.6, 21.1, 15.6/15.1, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 35.5 (br). IR (neat): 2916, 2867, 1455, 1378, 1371, 1311, 1262, 1144, 1119, 970, 912, 861, 759, 701, 672 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{21}H_{45}BNO_3$) m/z 370.3487, found m/z 370.3490.

26

Ethyl 11-(2,5-dimethylphenoxy)-2,2,8,8-tetramethyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undecanoate (26): Followed general procedure with **26-sub** (0.5 mmol), primary alkyl bromide (1.5 mmol), and $TBAClO_4$ (3 mmol) in THF (2.5 mL). The reaction was electrolyzed at constant current of 2.5 mA until passing 2.2 F/mol of charge. The residue was purified using silica gel chromatography (Hexanes : Et_2O = 10:1) to give 134.0 mg (52% yield) of **26** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 6.99 (d, *J* = 7.5 Hz, 1H), 6.64 (d, *J* = 7.5 Hz, 1H), 6.61 (s, 1H), 4.14-4.04 (m, 2H), 3.89 (t, *J* = 6.5 Hz, 2H), 2.30 (s, 3H), 2.17 (s, 3H), 1.80-1.67 (m, 2H), 1.58-1.53 (m, 1H), 1.52-1.47 (m, 2H), 1.42-1.30 (m, 3H), 1.29-1.13 (m, 19H), 1.14 (s, 6H), 1.00-0.92 (m, 1H), 0.86 (d, *J* = 1.0 Hz, 6H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 178.2, 157.2, 136.5, 130.4, 123.7, 120.6, 112.1, 83.0, 68.9, 60.3, 44.3, 42.3, 41.2, 38.8, 34.4, 33.4, 27.2, 25.3, 25.2, 25.05, 24.98, 24.54, 24.48, 21.6, 16.0, 14.4, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 35.0 (br). IR (neat): 2933, 1727, 1614, 1585, 1509, 1471, 1412, 1370, 1311, 1284, 1142, 1130, 1035, 862, 802, 771, 688 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{31}H_{57}BNO_5$) m/z 534.4324, found m/z 534.4330.

27

2-(1-((*1S,4aS,10aS*)-7-Isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)-5-methoxypentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (27): Followed general procedure A with **27-sub** (0.5 mmol), primary alkyl bromide (1.5 mmol), and $TBAClO_4$ (3 mmol) in THF (2.5 mL). The reaction was electrolyzed at constant current of 5 mA until passing 2.2 F/mol of charge. The residue was purified using silica gel chromatography (Hexanes : Et_2O = 10:1) to give 103.8 mg (43% yield, dr = 3:1) of **27** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.88 (s, 1H), 3.38-3.33 (m, 2H), 3.32/3.31 (s, 3H), 2.95-2.76 (m, 3H), 2.26 (d, *J* = 12.5 Hz, 1H), 1.95-1.82 (m, 1H), 1.74-1.53 (m, 5H), 1.49-1.28 (m, 6H), 1.27-1.15 (m, 23H), 0.99-0.91 (m, 1H), 0.90/0.89 (s, 3H); ^{13}C

NMR: (126 MHz, $CDCl_3$) δ 148.0/147.9, 145.50/145.46, 135.15/135.10, 126.94/126.92, 124.32/124.28, 123.83/123.82, 83.0, 73.3/73.2, 58.64/58.61, 50.2/47.5, 46.4/46.2, 38.9/38.8, 38.3/37.80, 37.77/37.70, 36.6/36.5, 33.6, 30.47/30.54, 30.48/30.1, 29.3/29.2, 25.6/25.4, 25.06/25.01, 24.98/24.92, 24.15/24.14, 21.2/18.96, 19.2/19.1, 19.0/18.9, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.5 (br). IR (neat): 2924, 2865, 1497, 1457, 1374, 1315, 1143, 1119, 951, 903, 884, 861, 820, 678, 628 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{31}H_{55}BNO_3$) m/z 500.4270, found m/z 500.4275.

28

4,4,5,5-Tetramethyl-2-(4-phenylbutyl)-1,3,2-dioxaborolane (28): Followed general procedure A. The reaction was electrolyzed at constant current of 2.5 mA until passing 2.0 F/mol of charge. and purified using silica gel chromatography (Hexanes:Et_2O = 30 : 1) to give 103.8 mg (40% yield) of **28** as a colorless oil.^1H NMR: (500 MHz, $CDCl_3$) δ 7.29-7.22 (m, 2H), 7.20-7.12 (m, 3H), 2.64-2.57 (m, 2H), 1.68-1.59 (m, 2H), 1.52-1.43 (m, 2H), 1.24 (s, 12H), 0.82 (t, *J* = 8.0 Hz, 2H).; ^{13}C NMR: (126 MHz, $CDCl_3$) δ 143.1, 128.5, 128.3, 125.6, 83.0, 35.9, 34.3, 25.0, 23.9, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.0 (br). Data are consistent with those reported in the literature[43].

29

2-(Cyclopentylmethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (29): Followed general procedure A **29-sub** (0.5 mmol), primary alkyl bromide (2.0 mmol), and $TBAClO_4$ (3 mmol) in THF (2.5 mL). The residue was purified using silica gel chromatography (Hexanes : Et_2O = 30:1) to give 80.1 mg (38% yield) of **29** as a colorless oil.^1H NMR: (500 MHz, $CDCl_3$) δ 2.01-1.89 (m, 1H), 1.82-1.73 (m, 2H), 1.66-1.55 (m, 2H), 1.54-1.45 (m, 2H), 1.24 (s, 12H), 1.10-1.00 (m, 2H), 0.83 (d, *J* = 7.0 Hz, 2H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 83.0, 36.3, 35.2, 25.3, 25.0, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 33.8 (br). Data are consistent with those reported in the literature[44].

36

1-(3-((*1r,3r,5r,7r*)-2-phenyladamantan-2-yl)propyl)-1H-pyrrole (36): Followed general procedure A and purified using silica gel chromatography (Hexanes:Et_2O = 25 : 1) to give 230.1 mg (72% yield) of **36** as a white solid.^1H NMR: (500 MHz, $CDCl_3$) δ 7.34-7.28 (m, 2H), 7.27-7.23 (m, 2H),7.17 (t, *J* = 7.5 Hz, 1H), 6.48 (s, 2H),

6.07 (s, 2H), 3.60 (t, J = 7.5 Hz, 2H), 2.34 (s, 2H), 2.10 (d, J = 12.5 Hz, 2H), 1.90 (s, 1H), 1.84 (d, J = 12.0 Hz, 2H), 1.76-1.67 (m, 5H), 1.66-1.60 (m, 2H), 1.54 (d, J = 12.0 Hz, 2H), 1.42-1.32 (m, 2H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 147.1, 128.1, 126.9, 125.2, 120.4, 107.8, 50.2, 45.8, 38.9, 37.0, 33.9, 32.9, 32.7, 28.4, 27.4, 25.0. IR (neat): 2903, 2855, 1546, 1498, 145, 1361, 1270, 1241, 1087, 967, 719, 702, 615 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{23}H_{30}N$) m/z 320.2373, found m/z 320.2381.

37

4-(4-Fluorobutyl)-4-phenyltetrahydro-2*H*-thiopyran (37): Followed general procedure A and purified using silica gel chromatography (Hexanes) to give 214.8 mg (85% yield) of **37** as a colorless oli.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.34 (t, J = 7.5 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.20 (t, J = 7.5 Hz, 1H), 4.31 (dt, J = 47.5 Hz, 6.0 Hz, 2H), 2.71 (t, J = 12.0 Hz, 2H), 2.60-2.42 (m, 4H), 2.02-1.88 (m, 2H), 1.61-1.43 (m, 4H), 1.12-0.99 (m, 2H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 144.9, 128.7, 127.0, 126.0, 84.1 (d, J = 163.4 Hz), 44.1, 40.6, 37.2, 31.0 (d, J = 19.4 Hz), 24.3, 19.0 (d, J = 5.2 Hz). ^{19}F NMR ($CDCl_3$, 470 MHz) δ -218.1 (hept, J = 25.4 Hz). IR (neat): 2925, 1599, 1495, 1445, 1428, 1273, 1057, 1034, 786, 700 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{15}H_{22}FS$) m/z 253.1421, found m/z 253.1426.

38

2-(4-Phenylbutan-2-yl)biphenylene (38): Followed general procedure A under constant current of 2.5 mA until passing 2.0 F/mol of charge and purified using silica gel chromatography (Hexanes : EA=200:1) to give 142.4 mg (50% yield) of **38** as a yellow solid.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.27 (t, J = 7.5 Hz, 2H), 7.20-7.13 (m, 3H), 6.76-6.69 (m, 2H), 6.65-6.60 (m, 2H), 6.59-6.53 (m, 3H), 2.61-2.47 (m, 3H), 1.91-1.78 (m, 2H), 1.21 (d, J = 6.5 Hz, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 151.7, 151.5, 151.2, 149.0, 147.9, 142.6, 128.5, 128.4, 128.3, 128.0, 126.6, 125.8, 117.4, 117.3, 117.1, 116.8, 40.2, 39.7, 34.0, 22.3. IR (neat): 2962, 2901, 2856, 1600, 1583, 1492, 1465, 1434, 1372, 1268, 1125, 987, 876, 740, 698, 629 cm^{-1}. HRMS (DART) calculated for $[M]^+$ ($C_{22}H_{20}$) m/z 284.1565, found m/z 284.1565.

39

4-Fluoro-5-isopropyl-2-methoxy-2'-(4-methoxybutyl)-4'-(trifluoromethyl)-1,1'-bi phenyl (39): Followed general procedure A and purified using silica gel

chromatography (Hexanes : DCM=5:1) to give 141.4 mg (45% yield) of **39** as a colorless oli.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.20-7.14 (m, 2H), 7.02 (d, *J* = 8.5 Hz, 1H), 6.61 (t, *J* = 2.0 Hz, 2H), 6.44 (t, *J* = 74.0 Hz, 1H), 6.13 (t, *J* = 2.0 Hz, 2H), 3.84 (t, *J* = 7.0 Hz, 2H), 3.22-3.12 (m, 1H), 1.80-1.68 (m, 1H), 1.67-1.58 (m, 1H), 1.57-1.50 (m, 2H), 1.20 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 147.5, 140.6, 131.4, 127.9, 127.2, 120.58, 120.54, 116.3 (t, *J* = 258.7 Hz), 108.1, 49.5, 34.2, 32.0, 29.5, 21.3. ^{19}F NMR ($CDCl_3$, 470 MHz) δ -80.0 (d, *J* = 73.8 Hz). IR (neat): 2932, 2872, 1489, 1382, 1354, 1280, 1229, 1118, 1039, 882, 815, 721, 616 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{16}H_{19}ClF_2NO$) m/z 314.1118, found m/z 314.1119.

40

2-(4-(6-(Tert-butyl)-1,1-dimethyl-2,3-dihydro-1H-inden-4-yl)pentyl)-5-methylfuran (40): Followed general procedure A with **40-sub** (0.5 mmol), primary alkyl bromide (1.5 mmol), and $TBAClO_4$ (3 mmol) in THF (2.5 mL). The reaction was electrolyzed at constant current of 2.5 mA until passing 2.0 F/mol of charge. The residue was purified using silica gel chromatography (Hexanes) to give 128.7 mg (62% yield) of **40** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.04 (s, 1H), 7.00 (s, 1H), 5.81 (dd, *J* = 9.5 Hz, 3.0 Hz, 2H), 2.87-2.75 (m, 3H), 2.55 (t, *J* = 6.5 Hz, 2H), 2.24 (s, 3H), 1.90 (t, *J* = 7.0 Hz, 2H), 1.74-1.51 (m, 4H), 1.32 (s, 9H), 1.25 (d, *J* = 5.0 Hz, 6H), 1.23 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 154.7, 152.2, 150.2, 149.8, 142.6, 137.8, 120.4, 116.3, 105.8, 105.3, 44.2, 41.5, 37.2, 36.6, 34.9, 31.8, 29.0, 28.9, 28.3, 28.1, 26.5, 21.2, 13.7. IR (neat): 2952, 2862, 1570, 1478, 1458, 1361, 1219, 1102, 936, 874, 775. HRMS (DART) calculated for $[M+H]^+$ ($C_{25}H_{40}NO$) m/z 370.3104, found m/z 370.3104.

41

1-Methyl-4-(4-phenoxy-1-phenylbutyl)piperidine (41): Followed general procedure with **41-sub** (0.5 mmol), primary alkyl bromide (1.5 mmol), and $TBAClO_4$ (3 mmol) in THF (2.5 mL). The residue was purified using silica gel chromatography (Hexanes : EA : Et_3N = 8:1:0.5) to give 100.4 mg (62% yield) of **41** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.31-7.22 (m, 4H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 2H), 6.91 (t, *J* = 7.5 Hz, 2H), 6.83 (d, *J* = 8.0 Hz, 2H), 3.90-3.80 (m, 2H), 2.99 (d, *J* = 11.0 Hz, 1H), 2.84 (d, *J* = 11.0 Hz, 1H), 2.39-2.33 (m, 1H), 2.30 (s, 3H), 2.08-1.98 (m, 2H), 1.98-1.85 (m, 2H), 1.73-1.63 (m, 1H), 1.58-1.49 (m, 2H), 1.48-1.42 (m, 2H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 159.1, 143.6, 129.5, 128.47, 128.45, 126.3, 120.6, 114.6, 67.9, 56.0, 51.4, 46.0, 40.9, 30.3, 29.1, 27.6. IR (neat): 2939, 2780, 1600, 1495, 1471, 1452, 1276, 1243, 1101, 1078, 753, 701, 691 cm^{-1}. HRMS (DART) calculated for

$[M+H]^+$ ($C_{22}H_{30}NO$) m/z 324.2322, found m/z 324.2325.

42

4-(2-(1,3-Dioxan-2-yl)ethyl)chromane (42): Followed general procedure A under constant current of 1.5 mA until passing 1.3 F/mol of charge (The cell voltage is too high, so we stop the reaction). The residue was purified using silica gel chromatography (Hexanes : EA = 5:1) to give 114.5 mg (46% yield) of **42** as a white solid.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.14 (d, *J* = 7.5 Hz, 1H), 7.09-7.04 (m, 1H), 6.84 (td, *J* = 7.5 Hz, 1.0 Hz, 1H), 6.78 (dd, *J* = 8.0 Hz, 1.0 Hz, 1H), 4.55 (t, *J* = 5.0 Hz, 1H), 4.23-4.14 (m, 2H), 4.13-4.08 (m, 2H), 3.81-3.71 (m, 2H), 2.83-2.74 (m, 1H), 2.14-2.00 (m, 2H), 1.97-1.88 (m, 1H), 1.84-1.58 (m, 4H), 1.38-1.30 (m, 1H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 154.6, 129.3, 127.4, 126.4, 120.2, 116.9, 102.4, 67.1, 63.6, 33.5, 32.8, 30.6, 26.9, 26.0. IR (neat): 2952, 2856, 1604, 1577, 1487, 1450, 1357, 1261, 1223, 1109, 1053, 1042, 758, 645 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{15}H_{24}NO_3$) m/z 266.1751, found m/z 266.1754.

43

Tert-butyl 5-(3-methoxypropyl)-1,3,4,5-tetrahydro-2H-benzo[c]azepine-2-carboxylate (43): Followed general procedure A with **43-sub** (0.5 mmol), primary alkyl bromide (1.5 mmol), and $TBAClO_4$ (3 mmol) in THF (2.5 mL). The residue was purified using silica gel chromatography (Hexanes : EA = 8:1) to give 89.5 mg (56% yield, a mixture of rotamers (2.3:1)) of **43** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.2-7.09 (m, 4H), 4.60 (d, *J* = 15.0 Hz, 0.4H), 4.51-4.33 (m, 1.6H), 3.85-3.62 (m, 1H), 3.60-3.48 (m, 0.6H), 3.39 (t, *J* = 6.5 Hz, 2H), 3.44-3.33 (m, 0.4H), 3.32 (s, 3H), 3.00-2.87 (m, 1H), 2.05-1.83 (m, 2H), 1.78-1.43 (m, 4H), 1.42 (s, 3.3H), 1.39 (s, 5.7H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 155.1/154.9, 144.0/143.3, 137.8/137.2, 130.1/129.9, 127.6/127.5, 126.3/125.8, 79.6/79.5, 72.9, 58.8, 52.0/51.6, 45.6/44.9, 43.9/42.7, 33.4/32.7, 29.6/29.5, 28.63/28.58, 28.4/28.3. IR (neat): 2974, 2929, 2865, 1690, 1460, 1410, 1364, 1237, 1161, 1118, 960, 936, 876, 754, 668 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{19}H_{30}NO_3$) m/z 320.2220, found m/z 320.2224.

44

3-(6-Phenylhexan-3-yl)benzo[b]thiophene (44): Followed general procedure A with

44-sub (1 mmol), primary alkyl bromide (1.5 mmol) and purified using silica gel chromatography (Hexanes:DCM = 50:1) to give 176.9 mg (60% yield) of **44** as a colorless oil. The product could also be afforded by the reaction of **44-sub** (0.5 mmol) with 3-phenylpropyl 4-methylbenzenesulfonate (1.5 mmol) following the protocol in general procedure E. The residue was purified using silica gel chromatography (Hexanes : DCM = 50:1) to give 76.8 mg (52% yield) of **44** as a colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.88-7.84 (m, 1H), 7.79-7.76 (m, 1H), 7.38-7.30 (m, 2H), 7.25-7.21 (m, 2H), 7.18-7.13 (m, 1H), 7.10 (d, *J* = 7.0 Hz, 2H), 7.02 (s, 1H), 3.07-2.97 (m, 1H), 2.63-2.52 (m, 2H), 1.85-1.70 (m, 4H), 1.64-1.55 (m, 2H), 0.82 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 142.6, 140.8, 140.6, 139.4, 128.5, 128.4, 125.8, 124.1, 123.8, 123.0, 122.1, 120.5, 40.6, 36.2, 34.7, 29.3, 28.4, 12.1. IR (neat): 3024, 2958, 2928, 2856, 1602, 1495, 1454, 1426, 1070, 1022, 761, 730, 697, 571 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{20}H_{23}S$) m/z 295.1515, found m/z 295.1521.

45

2-(5-Chloro-2-phenylpentyl)pyrazine (45): Followed general procedure A with **45-sub** (0.5 mmol), primary alkyl bromide (1.5 mmol), and $TBAClO_4$ (3 mmol) in THF (2.5 mL). The reaction was electrolyzed at constant current of 2.5 mA until passing 2.0 F/mol of charge. The residue was purified using silica gel chromatography (Hexanes : EA = 8:1) to give 26.2 mg (20% yield) of **45** as a yellow solid.^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.34 (s, 1H), 8.12 (s, 1H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.13-7.04 (m, 2H), 3.45 (t, *J* = 7.0 Hz, 2H), 3.18-3.09 (m, 2H), 3.08-3.00 (m, 1H), 1.94-1.78 (m, 2H), 1.73-1.59 (m, 2H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 156.0, 143.2, 142.4, 128.8, 127.6, 126.8, 45.7, 45.1, 43.2, 33.2, 30.6. IR (neat): 2927, 2854, 1526, 1494, 1474, 1453, 1403, 1121, 1057, 1018, 761, 702 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{15}H_{18}ClN_2$) m/z 261.1153, found m/z 261.1155.

46

2-Methoxy-5-(2-methyl-6-(1H-pyrrol-1-yl)hexan-3-yl)pyridine (46): Followed general procedure A under constant current of 2.5 mA until passing 2.0 F/mol of charge. The residue was purified using silica gel chromatography (Hexanes : EA = 50:3) to give 168.5 mg (62% yield) of **1** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 1.5 Hz, 1H), 7.29 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H), 6.69 (d, *J* = 8.5 Hz, 1H), 6.57 (s, 2H), 6.11 (s, 2H), 3.93 (s, 3H), 3.86-3.73 (m, 2H), 2.25-2.18 (m, 1H), 1.80-1.68 (m, 2H), 1.59-1.45 (m, 3H), 0.90 (d, *J* = 7.0 Hz, 3H), 0.70 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 163.0, 146.7, 138.2, 131.5, 120.5, 110.6, 108.0,

53.4, 49.6, 49.2, 33.4, 29.94, 29.88, 21.1, 20.3. IR (neat): 2954, 2870, 1604, 1571, 1489, 1462, 1396, 1283, 1088, 1027, 922, 762, 617 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{17}H_{25}N_2O$) m/z 273.1961, found m/z 273.1965.

47

2-Methoxy-5-(4-methoxy-1-phenylbutyl)pyridine (47): Followed general procedure with **47-sub** (0.5 mmol), primary alkyl bromide (1.5 mmol), and $TBAClO_4$ (3 mmol) in THF (2.5 mL). The residue was purified using silica gel chromatography (Hexanes : EA = 10:1) to give 54.4 mg (40% yield) of **47** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 2.5 Hz, 1H), 7.42 (dd, *J* = 8.5 Hz, 2.5 Hz, 1H), 7.32-7.24 (m, 2H), 7.23-7.20 (m, 2H), 7.20-7.15 (m, 1H), 6.65 (d, *J* = 8.5 Hz, 1H), 3.90 (s, 3H), 3.85 (t, *J* = 8.0 Hz, 1H), 3.38 (t, *J* = 6.0 Hz, 2H), 3.30 (s, 3H), 2.16-2.01 (m, 2H), 1.58-1.48 (m, 2H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 162.9, 145.8, 144.5, 138.3, 133.2, 128.7, 127.8, 126.5, 110.9, 72.6, 58.7, 53.5, 48.0, 32.2, 28.2. IR (neat): 2943, 2867, 1604, 1490, 1391, 1287, 1117, 1028, 804, 787, 700 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{17}H_{22}NO_2$) m/z 272.1645, found m/z 272.1648.

48

2-(1-(But-3-en-1-yl)cyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (48): Followed general procedure A and purified using silica gel chromatography (Hexanes : DCM = 5:2) to give 122.1 mg (80% yield) of **48** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.5 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.40-7.32 (m, 2H), 7.05 (s, 1H), 6.65 (t, *J* = 2.0 Hz, 2H), 6.14 (t, *J* = 2.0 Hz, 2H), 1.93-1.84 (m, 2H), 1.80-1.72 (m, 2H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 140.6, 139.0, 136.4, 124.3, 124.0, 123.1, 121.7, 121.4, 120.6, 108.1, 49.6, 31.5, 28.2, 26.4. IR (neat): 3099, 2932, 1498, 1427, 1360, 1270, 1211, 1088, 1000, 719, 664, 615 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{16}H_{18}NS$) m/z 256.1154, found m/z 256.1159.

49

4-Fluoro-5-isopropyl-2-methoxy-2'-(4-methoxybutyl)-4'-(trifluoromethyl)-1,1'-bi phenyl (49): Followed general procedure A with **49-sub** (0.5 mmol), primary alkyl bromide (1.5 mmol), and $TBAClO_4$ (3 mmol) in THF (2.5 mL). The residue was purified using silica gel chromatography (Hexane : EA=25:1) to give 61.5 mg (31%

yield) of **49** as a white solid.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.47 (dd, *J* = 8.0 Hz, 1.0 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 9.0 Hz, 1H), 6.66 (d, *J* = 12.0 Hz, 1H), 3.71 (s, 3H), 3.25 (s, 3H), 3.24-3.18 (m, 3H), 2.57-2.38 (m, 2H), 1.60-1.40 (m, 4H), 1.24 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 160.7 (d, *J* = 243.9 Hz), 155.4 (d, *J* = 9.9 Hz), 142.3, 141.7, 131.1, 129.7 (q, *J* = 31.9 Hz), 129.2 (d, *J* = 7.1 Hz), 126.8 (d, *J* = 15.2 Hz), 125.6 (m), 124.9 (d, *J* = 3.5 Hz), 124.5 (q, *J* = 270.8 Hz), 122.4 (q, *J* = 3.8 Hz), 99.2 (d, *J* = 27.4 Hz), 72.6, 58.6, 55.8, 33.0, 29.5, 27.3, 26.7 (d, *J* = 1.6 Hz), 23.0 (d, *J* = 7 Hz). ^{19}F NMR ($CDCl_3$, 470 MHz) δ -62.4, -117.3 (q, *J* = 8.5 Hz). IR (neat): 2962, 2934, 2868, 1620, 1589, 1512, 1493, 1328, 1310, 1271, 1086, 891, 835 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{22}H_{30}F_4NO_2$) m/z 416.2207, found m/z 416.2210.

50

Methyl 2-(10-(3-chloropropyl)-10,11-dihydrodibenzo[b,f]thiepin-2-yl)propanoate (50): Followed general procedure A with **50-sub** (0.5 mmol), primary alkyl bromide (1.5 mmol), and $TBAClO_4$ (3 mmol) in THF (2.5 mL). The residue was purified using silica gel chromatography (Hexanes : EA = 25:1) to give 86.4 mg (46% yield, dr = 1:1) of **50** as a colorless oli.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 8.0 Hz, 1.0 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.25-7.20 (m, 1H), 7.16 (d, *J* = 6.5 Hz, 1H), 7.12-7.05 (m, 2H), 7.02 (dd, *J* = 8.0 Hz, 1.0 Hz, 1H), 3.75-3.67 (m, 1H), 3.642 (s, 3H), 3.639 (q, *J* = 7.0 Hz, 1H), 3.53 (t, *J* = 6.0 Hz, 2H), 3.34 (dd, *J* = 15.5 Hz, 3.5 Hz, 1H), 3.15 (dd, *J* = 15.0 Hz, 10.0 Hz, 1H), 1.96-1.83 (m, 3H), 1.82-1.72 (m, 1H), 1.45 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 174.9, 144.97/144.95, 140.59/140.56, 139.90/130.84, 134.9, 134.0, 131.7, 131.4, 130.2/130.1, 129.20/129.16, 128.0, 126.4, 125.61/125.59, 52.2, 45.25/45.22, 45.09/45.02, 40.79/40.77, 39.4, 33.7, 30.38/30.36, 18.7/18.6. IR (neat): 2948, 1734, 1474, 1434, 1195, 1161, 1070, 975, 790, 649 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{21}H_{27}ClNO_2S$) m/z 392.1446, found m/z 392.1441.

51

Hex-5-en-1-ylbenzene (51): Followed general procedure A and purified using silica gel chromatography (Hexanes) to give 88.0 mg (55% yield) of **51** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.33-7.24 (m, 2H), 7.22-7.15 (m, 3H), 5.89-5.74 (m, 1H), 5.01 (d, *J* = 17.0 Hz, 1H), 4.95 (d, *J* = 10.0 Hz, 1H), 2.62 (t, *J* = 7.5 Hz, 2H), 2.09 (q, *J* = 6.5 Hz, 2H), 1.71-1.59 (m, 2H), 1.72-1.59 (m, 2H), 1.51-1.38 (m, 2H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 142.8, 139.0, 128.5, 128.4, 125.8, 114.5, 36.0, 33.8, 31.1, 28.7. Data are consistent with those reported in the literature[45].

52

((5-Methylhex-5-en-1-yl)oxy)benzene (52): Followed general procedure A under constant current of 1.5 mA until passing 1.4 F/mol of charge (The cell voltage is too high, so we stop the reaction). The residue was purified using silica gel chromatography (Hexanes : EA = 30:1) to give 114.0 mg (60% yield) of **52** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.31-7.27 (m, 2H), 6.96-6.92 (m, 1H), 6.92-6.88 (m, 2H), 4.73 (s, 1H), 4.70 (s, 1H), 3.97 (t, *J* = 6.5 Hz, 2H), 2.09 (t, *J* = 8.0 Hz, 2H), 1.83-1.76 (m, 2H) 1.74 (s, 3H), 1.67-1.58 (m, 2H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 159.2, 145.8, 129.5, 120.6, 114.6, 110.2, 67.8, 37.6, 29.0, 24.2, 22.5. IR (neat): 2938, 2870, 1649, 1600, 1586, 1496, 1470, 1241, 1171, 1033, 973, 882, 751, 690, 510 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{13}H_{19}O$) m/z 191.1430, found m/z 191.1432.

53

(6-Chlorohex-1-en-2-yl)benzene (53): Followed general procedure A with **53-sub** (1 mmol), primary alkyl bromide (3 mmol), and $TBAClO_4$ (2 mmol) in THF/DME (2.5 mL/0.5 mL). The residue was purified using silica gel chromatography (Hexanes) to give 103.3 mg (52% yield) of **53** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.42-7.37 (m, 2H), 7.36-7.31 (m, 2H), 7.30-7.27 (m, 1H), 5.29 (s, 1H), 5.07 (d, *J* = 1.5 Hz, 1H), 3.52 (t, *J* = 6.5 Hz, 2H), 2.54 (t, *J* = 7.5 Hz, 2H), 1.84-1.77 (m, 2H), 1.65-1.57 (m, 2H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 148.0, 141.2, 128.5, 127.6, 126.2, 112.8, 45.0, 34.7, 32.3, 25.5. Data are consistent with those reported in the literature[46].

56 **57**

Hept-5-en-1-ylbenzene (56) and (4-methylhex-5-en-1-yl)benzene (57): Followed general procedure A with **54** or **55** (1 mmol), primary alkyl bromide (3 mmol), and $TBAClO_4$ (2 mmol) in THF/DME (2.5 mL/0.5 mL). The residue was purified using silica gel chromatography (pentane) to give a mixture of **56** and **57** (109.8 mg, 63% yield) as a colorless oil. The yield of **56** (33%) and **57** (30%) was determined by ^{1}H-NMR. **4-Methylhex-5-en-1-yl)benzene (57):** ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.34-7.29 (m, 2H), 7.24-7.18 (m, 3H), 5.77-5.67 (m, 1H), 4.99 (d, *J* = 17.0 Hz, 1H), 4.94 (d, *J* = 10.0 Hz, 1H), 2.69-2.58 (m, 2H), 2.24-2.15 (m, 1H), 1.73-1.59 (m, 2H), 1.40-1.34 (m, 2H), 1.02 (d, *J* = 7.0 Hz, 3H); **Hept-5-en-1-ylbenzene (56) :** ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.34-7.29 (m, 2H), 7.24-7.18 (m, 3H), 5.53-5.37 (m, 2H), 2.69-2.58 (m, 2H), 2.14-2.01 (m, 2H), 1.73-1.59 (m, 5H), 1.49-1.41 (m, 2H). ^{13}C NMR (a mixture of **56** and **57**): (126 MHz, $CDCl_3$) δ 144.8, 143.0, 142.9, 131.5, 130.7, 128.55, 128.54, 128.4, 125.74, 125.72, 125.0, 124.0 112.6, 37.9, 36.4, 36.2, 36.03, 36.01, 32.6, 31.24, 31.17, 29.4, 29.3, 26.8, 20.4, 18.1, 12.9. IR (neat): 2929,

2856, 1639, 1603, 1496, 1453, 1030, 995, 965, 909, 745, 696 cm^{-1}. LRMS (EI) calculated for $[M]^+$ ($C_{13}H_{18}$) m/z 174.1, found m/z 174.1.

58

Tert-butyl(6-methoxyhex-1-yn-1-yl)dimethylsilane (58): Followed general procedure A and purified using silica gel chromatography (Hexanes : EA = 100:3) to give 95.3 mg (42% yield) of **58** as a colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 3.40 (t, *J* = 6.0 Hz, 2H), 3.33 (s, 3H), 2.60 (t, *J* = 7.0 Hz, 2H), 1.72-1.65 (m, 2H), 1.62-1.56 (m, 2H), 0.92 (s, 3H), 0.07 (s, 6H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 107.8, 82.8, 72.4, 58.6, 28.8, 26.2, 25.5, 19.8, 16.7, -4.3. IR (neat): 2952, 2929, 2857, 2174, 1462, 1388, 1249, 1121, 836, 824, 808, 773, 679, 598 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{13}H_{27}OSi$) m/z 227.1826, found m/z 227.1831.

(3-Ethyl-6-(phenylthio)hex-1-yn-1-yl)triisopropylsilane (59) and **triisopropyl(1-(phenylthio)octa-4,5-dien-4-yl)silane (59'):** Followed general procedure A under constant current of 4 mA until passing 2.0 F/mol. The residue was purified using silica gel chromatography (Hexanes) to give part of pure **59** (102.3 mg, colorless oil), a mixture of **59** and **59'** (132.4 mg, colorless oil), and pure **59'** (31.5 mg, colorless, oil). The yield of **59** (53%) and **59'** (18%) was determined by ^{1}H-NMR with CH_3NO_2 as internal standard after column chromatography purification. **(3-Ethyl-6-(phenylthio)hex-1-yn-1-yl)triisopropylsilane (59):** ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.36-7.30 (d, *J* = 7.5 Hz, 2H), 7.29-7.24 (t, *J* = 7.5 Hz, 2H), 7.16 (t, *J* = 7.5 Hz, 1H), 2.95 (t, *J* = 7.0 Hz, 2H), 2.37-2.27 (m, 1H), 1.96-1.85 (m, 1H), 1.83-1.73 (m, 1H), 1.66-1.57 (m, 1H), 1.56-1.39 (m, 3H), 1.07-0.97 (m, 24H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 137.0, 129.1, 129.0, 125.8, 111.9, 81.6, 34.2, 34.1, 33.7, 28.5, 27.2, 18.8, 11.9, 11.4. IR (neat): 2939, 2863, 2163, 1585, 1480, 1461, 1438, 1341, 1091, 995, 736, 675, 660 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{23}H_{39}SSi$) m/z 375.2536, found m/z 375.2543.

Triisopropyl(1-(phenylthio)octa-4,5-dien-4-yl)silane (59'): ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.0 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 2H), 7.16 (t, *J* = 7.5 Hz, 1H), 4.87-4.76 (m, 1H), 3.02-2.90 (m, 2H), 2.09-2.02 (m, 2H), 2.01-1.92 (m, 2H), 1.89-1.81 (m, 2H), 1.18-1.09 (m, 4H), 1.08-1.04 (m, 17H), 0.98 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 206.6, 137.1, 129.2, 128.9, 125.8, 91.6, 88.4, 33.6, 29.0, 28.3, 22.2, 18.85, 18.83, 14.5, 11.5. IR (neat): 2932, 2873, 1366, 1179, 1060, 921, 765 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{23}H_{39}SSi$) m/z 375.2536, found m/z 375.2543.

(5-Butyl-8-methylnona-3,4-dien-1-yl)benzene (60) and **(3-isopentylnon-4-yn-1-yl)benzene (60'):** Followed general procedure A under constant current of 2.5 mA until passing 2.0 F/mol of charge. The residue was purified using silica gel chromatography (Hexanes) to give part of pure **60** (121.2 mg, colorless oil), a mixture of **60** and **60'** (52.3 mg, colorless oil), and majorly **60'** with small amount of unknown side product (17.8 mg, colorless, oil). The yield of **60** (60%) and **60'** (10%) was determined by ^{1}H-NMR with CH_3NO_2 as internal standard after column chromatography purification. **(5-butyl-8-methylnona-3,4-dien-1-yl)benzene (60):** ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.5 Hz, 2H), 7.23-7.15 (m, 3H), 5.15-5.07 (m, 1H), 2.71 (t, *J* = 8.0 Hz, 2H), 2.32-2.26 (m, 2H), 1.95-1.85 (m, 4H), 1.61-1.49 (m, 1H), 1.40-1.28 (m, 4H), 1.28-1.21 (m, 2H), 0.894 (t, *J* = 7.0 Hz, 3H), 0.885 (s, 3H), 0.87 (s, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 200.9, 142.3, 128.6, 128.4, 125.8, 105.1, 91.1, 37.0, 35.9, 32.6, 31.4, 30.7, 30.0, 27.8, 22.78, 22.74, 22.6, 14.2. IR (neat): 2954, 2928, 2869, 1720, 1603, 1496, 1466, 1454, 1383, 1366, 1076, 1030, 744, 697 cm^{-1}. LRMS (EI) calculated for $[M]^+$ ($C_{20}H_{30}$) m/z 270.2, found m/z 270.3.

(3-Isopentylnon-4-yn-1-yl)benzene (60'): ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.5 Hz, 2H), 7.21 (d, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 7.5 Hz, 1H), 2.90-2.79 (m, 1H), 2.74-2.64 (m, 1H), 2.30-2.24 (m, 1H), 2.22 (td, *J* = 6.5 Hz, 1.5 Hz, 2H), 1.77-1.64 (m, 2H), 1.57-1.48 (m, 4H), 1.47-1.33 (m, 4H), 1.29-1.19 (m, 1H), 0.93 (t, *J* = 7.5 Hz, 3H), 0.89 (d, *J* = 2.5 Hz, 3H), 0.87 (d, *J* = 2.5 Hz, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 142.7, 128.6, 128.4, 125.8, 83.5, 82.0, 37.5, 36.7, 33.9, 33.5, 31.8, 31.5, 28.2, 22.9, 22.7, 22.1, 18.6, 13.8. IR (neat): 2954, 2928, 2867, 1603, 1495, 1454, 1383, 1366, 744, 698 cm^{-1}. LRMS (EI) calculated for $[M]^+$ ($C_{20}H_{30}$) m/z 270.2, found m/z 270.3.

1-Methoxy-4-(2-methoxyethyl)-8-methylnona-4,5-diene (61) and 5-isobutyl-1,8-dimethoxyoct-3-yne (61'): Followed general procedure A and purified using silica gel chromatography (Hexanes : EA=20:1) to give colorless oil product (131.3 mg, 58% yield). The obtained product is a mixture of **61** and **61'**. The yield of **61** (50%) and **61'** (8%) was determined by ^{1}H-NMR with CH_3NO_2 as internal standard after column chromatography purification. Only the major product was characterized in here. ^{1}H NMR ^{1}H NMR: (500 MHz, $CDCl_3$) δ 5.11-5.04 (m, 1H), 3.46 (t, *J* = 7.0 Hz, 2H), 3.38 (t, *J* = 6.5 Hz, 2H), 3.33 (s, 3H), 3.32 (s, 3H), 2.21 (td, *J* = 7.0 Hz, 2.5 Hz, 2H), 2.00 (td, *J* = 7.0 Hz, 3.0 Hz, 2H), 1.86 (t, *J* = 7.0 Hz, 2H), 1.73-1.67 (m, 2H), 1.66-1.59 (m, 1H), 0.91 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR: (126 MHz,

$CDCl_3$) δ 201.3, 99.8, 91.5, 72.5, 71.4, 58.71, 58.69, 39.1, 32.9, 29.5, 28.8, 27.8, 22.50, 22.48. IR (neat): 2956, 2930, 2871, 1721, 1452, 1386, 1368, 1191, 1114, 960, 642 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{14}H_{27}O_2$) m/z 227.2006, found m/z 227.2009.

62

1-Chloro-4-isopropyl-7-methylnona-4,5-diene (62): Followed general procedure A under constant current of 5 mA until passing 2.1 F/mol of charge. The residue was purified using silica gel chromatography (Hexanes) to give 49.5 mg (23% yield, dr = 1:1) of **62** as a colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 5.17-5.11 (m, 1H), 3.61-3.53 (m, 2H), 2.13-2.05 (m, 3H), 2.04-1.97 (m, 1H), 1.94-1.85 (m, 2H), 1.03-1.00 (m, 6H), 0.97 (dd, *J* = 7.0 Hz, 1.0 Hz, 3H), 0.91 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 198.4/198.3, 110.34/110.32, 100.20/100.18, 45.15/45.12, 35.8/35.7, 31.5/31.4, 31.08/31.07, 30.25/30.22, 28.1/28.0, 22.13/22.09, 21.91/21.87, 20.3/20.1, 12.04/11.96. IR (neat): 2961, 2929, 2873, 1714, 1460, 1380, 1289, 1150, 961, 810, 652 cm^{-1}. LRMS (EI) calculated for $[M]^+$ ($C_{13}H_{23}Cl$) m/z 214.1, found m/z 214.2.

63

(4-Chloro-1-phenylbutyl)trimethylsilane (63): Followed general procedure A under constant current of 10 mA until passing 2.0 F/mol of charge. The residue was purified using silica gel chromatography (Hexanes) to give 204.9 mg (85% yield) of **63** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.24 (t, *J* = 7.5 Hz, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 2H), 3.52-3.44 (m, 2H), 2.04-1.97 (m, 1H), 1.94-1.86 (m, 2H), 1.82-1.72 (m, 1H), 1.68-1.58 (m, 1H), -0.05 (s, 9H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 143.1, 128.3, 127.8, 124.6, 45.2, 36.2, 32.1, 26.4, -2.9. IR (neat): 2953, 2860, 1600, 1491, 1450, 1247, 832, 741, 699, 649, 614 cm^{-1}. HRMS (DART) calculated for $[M-CH_3]^+$ ($C_{12}H_{18}ClSi$) m/z 225.0861, found m/z 225.0861.

64

(Cyclopentyl(phenyl)methyl)trimethylsilane (64): Followed general procedure A and purified using silica gel chromatography (Pentane) to give 116.4 mg (50% yield) of **64** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.20 (t, *J* = 7.5 Hz, 2H), 7.07 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 7.0 Hz, 2H), 2.38-2.23 (m, 1H), 1.99-1.89 (m, 1H), 1.84 (d, *J* = 11.0 Hz, 1H), 1.77-1.66 (m, 1H), 1.65-1.48 (m, 3H), 1.47-1.36 (m, 1H), 1.25-1.14 (m, 1H), 1.01-0.90 (m, 1H), -0.06 (s, 9H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 145.6, 128.2, 128.0, 124.3, 44.0, 42.8, 34.4, 33.5, 25.7, 24.3, -1.2. Data are consistent

with those reported in the literature[47].

65

Methyl(2-methyl-5-phenylpentan-2-yl)diphenylsilane (65): Followed general procedure A with **65-sub** (0.5 mmol), primary alkyl bromide (1.5 mmol), and $TBAClO_4$ (2 mmol) in THF/DME (2.5 mL/0.5 mL). The reaction was electrolyzed under constant current of 2 mA until passing 2.2 F/mol of charge. The residue was purified using silica gel chromatography (Hexanes : EA = 200:1) to give 93.3 mg (52% yield) of **65** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 6.5 Hz, 4H), 7.42-7.31 (m, 6H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 2H), 2.47 (t, *J* = 7.5 Hz, 2H), 1.59-1.51 (m, 2H), 1.50-1.44 (m, 2H), 1.03 (s, 6H), 0.57 (s, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 142.9, 136.5, 135.6, 129.0, 128.5, 128.3, 127.7, 125.7, 39.2, 36.9, 25.6, 24.2, 21.1, -5.6. ^{29}Si NMR (99 MHz, $CDCl_3$) δ -4.2. IR (neat): 2940, 2858, 1495, 1453, 1383, 1156, 784, 697, 596 cm^{-1}. HRMS (DART) calculated for $[M-CH_3]^+$ ($C_{24}H_{27}Si$) m/z 343.1877, found m/z 343.1882.

66

5-(4-((Tert-butyldimethylsilyl)oxy)-1-(dimethyl(phenyl)silyl)butyl)-2-methoxypyridine (66): Followed general procedure A under constant current of 2 mA until passing 2.0 F/mol of charge. The residue was purified using silica gel chromatography (Hexanes : EA = 50:1) to give 279.0 mg (65% yield) of **66** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 2.5 Hz, 1H), 7.39-7.30 (m, 5H), 7.06 (dd, *J* = 8.5 Hz, 2.5 Hz, 1H), 6.58 (d, *J* = 8.5 Hz, 1H), 3.90 (s, 3H), 3.52-3.44 (m, 2H), 2.12 (dd, *J* = 12.5 Hz, 3.5 Hz, 1H), 1.89-1.80 (m, 1H), 1.71-1.62 (m, 1H), 1.48-1.39 (m, 1H), 1.32-1.21 (m, 1H), 0.85 (s, 9H), 0.24 (s, 3H), 0.21 (s, 3H), -0.02 (d, *J* = 2.0 Hz, 6H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 162.0, 145.8, 138.1, 137.1, 134.2, 130.9, 129.3, 127.8, 110.2, 62.7, 53.4, 32.2, 32.1, 26.1, 25.5, 18.4, -4.5 (d, *J* = 129.3 Hz), -5.2. IR (neat): 2952, 2856, 1603, 1489, 1387, 1099, 832, 814, 774, 734, 700, 661 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{24}H_{40}NO_2Si_2$) m/z 430.2592, found m/z 430.2596.

67

(1-Chlorononan-4-yl)(methyl)diphenylsilane (67): Followed general procedure A under constant current of 3 mA until passing 2.0 F/mol of charge. The residue was purified using silica gel chromatography (Hexanes) to give 161.6 mg (45% yield) of **67** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.56-7.50 (m, 4H), 7.41-7.31 (m, 6H), 3.46-3.34 (m, 2H), 1.84-1.72 (m, 1H), 1.71-1.60 (m, 2H), 1.59-1.44 (m, 2H), 1.39-1.28 (m, 2H), 1.27-1.10 (m, 6H), 0.82 (t, *J* = 7.0 Hz, 3H), 0.58 (s, 3H); ^{13}C NMR:

(126 MHz, $CDCl_3$) δ 136.98, 136.97, 134.852, 134.846, 129.23, 129.21, 127.94, 127.91, 45.4, 32.6, 32.2, 29.9, 29.2, 27.4, 23.4, 22.6, 14.2, -5.2. IR (neat): 2954, 2923, 2854, 1458, 1426, 1252, 1107, 785, 734, 719, 697, 651 cm^{-1}. HRMS (DART) calculated for $[M-CH_3]^+$ ($C_{21}H_{28}ClSi$) m/z 343.1643, found m/z 343.1649.

68

Dimethyl(phenyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)silane (68): Followed general procedure B and purified using silica gel chromatography (Hexanes : Et_2O = 50:1) to give 203.9 mg (67% yield) of **68** as a white solid.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.57-7.51 (m, 2H), 7.37-7.29 (m, 3H), 1.18 (s, 12H), 1.01 (s, 6H), 0.32 (s, 6H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 137.8, 134.8, 128.8, 127.4, 82.8, 25.0, 19.9, -4.75, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 35.1 (br). ^{29}Si NMR (99 MHz, $CDCl_3$) δ 1.30. IR (neat): 2977, 2958, 2861, 1461, 1387, 1358, 1325, 1110, 1013, 911, 826, 814, 771, 671 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{17}H_{33}BNO_2Si$) m/z 322.2368, found m/z 322.2373.

69

1,1,1,2,2-Pentamethyl-2-(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)disilane (69): Followed general procedure C and purified using silica gel chromatography (Hexanes : Et_2O = 33:1) to give 126.7 mg (67% yield) of **69** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.29-7.23 (m, 2H), 7.19-7.12 (m, 3H), 2.78-2.67 (m, 1H), 2.55-2.43 (m, 1H), 1.96-1.83 (m, 1H), 1.70-1.58 (m, 1H), 1.26 (s, 12H), 0.53 (dd, *J* = 12.5 Hz, 2.5 Hz, 1H), 0.06 (s, 6H), 0.04 (s, 9H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 142.9, 128.7, 128.4, 125.7, 82.9, 39.9, 29.3, 25.5, 25.0, -1.4, -3.1, -4.3, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.8 (br). ^{29}Si NMR (99 MHz, $CDCl_3$) δ -15.1, -18.8. IR (neat): 2977, 2947, 2893, 1496, 1453, 1349, 1304, 1244, 1143, 831, 796, 744, 723, 697, 578 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{20}H_{41}BNO_2Si_2$) m/z 394.2763, found m/z 394.2766.

70

Allyldimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)silane (70): Followed general procedure B under constant current of 3 mA until passing 2.0 F/mol of charge. The residue was purified using silica gel chromatography (Hexanes : Et_2O = 50:1) to give 129.5 mg (46% yield) of **70** as a white solid.^{1}H NMR: (500 MHz, $CDCl_3$) δ 5.85-5.74 (m, 1H), 4.86-4.77 (m, 2H), 1.81-1.71 (m, 1H), 1.63-1.56 (m, 2H), 1.23 (d, *J* = 1.0 Hz, 12H), 1.21-1.14 (m, 1H), 1.00 (s, 3H), 0.90 (t, *J* = 7.0 Hz, 3H), -0.02 (s, 6H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 135.9, 112.8, 82.9, 25.9, 25.3, 25.1,

21.4, 14.8, 11.9, -5.6, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 35.0 (br). ^{29}Si NMR (99 MHz, $CDCl_3$) δ -5.4. IR (neat): 3077, 2961, 2929, 2870, 1630, 1454, 1370, 1340, 1295, 1135, 890, 854, 836, 568 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{15}H_{35}BNO_2Si$) m/z 300.2525, found m/z 300.2527.

71

Dimethyl(4-phenyltetrahydro-2H-thiopyran-4-yl)silane (71): Followed general procedure C and purified using silica gel chromatography (Hexanes) to give 61.5 mg (52% yield) of **71** as a light yellow oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.35-7.31 (m, 2H), 7.17-7.10 (m, 3H), 3.67-3.59 (m, 1H), 2.98-2.86 (m, 2H), 2.72-2.61 (m, 2H), 2.32-2.23 (m, 2H), 2.21-2.11 (m, 2H), -0.09 (d, *J* = 3.5 Hz, 6H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 142.2, 128.7, 127.2, 124.5, 31.9, 31.5, 22.5, -7.3; ^{29}Si NMR (99 MHz, $CDCl_3$) δ -0.12. IR (neat): 2920, 2851, 2106, 1597, 1492, 1445, 1426, 1012, 978, 874, 837, 756, 697, 657, 518 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{13}H_{21}SSi$) m/z 237.1128, found m/z 237.1126.

72

((Dimethylsilyl)(phenyl)methyl)dimethyl(phenyl)silane (72): Followed general procedure A with **72-sub** (1 mmol) and purified using silica gel chromatography (Hexanes) to give 256.0 mg (90% yield) of **72** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.48-7.43 (m, 2H), 7.37-7.28 (m, 3H), 7.20-7.13 (m, 2H), 7.06-7.00 (m, 1H), 6.94-6.88 (m, 2H), 4.15-4.07 (m, 1H), 1.78-1.74 (m, 1H), 0.39 (s, 3H), 0.25 (s, 3H), -0.08 (d, *J* = 3.5 Hz, 3H), -0.10 (d, *J* = 3.5 Hz, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 142.0, 139.0, 134.1, 129.1, 129.0, 128.3, 127.7, 123.7, 26.5, -2.3 (d, *J* = 141.6 Hz), -3.0 (d, *J* = 116.8 Hz); ^{29}Si NMR (99 MHz, $CDCl_3$) δ -3.69, -13.58. IR (neat): 2955, 2899, 2110, 1595, 1492, 1427, 1248, 1200, 1112, 1030, 908, 884, 829, 801, 732, 696, 643, 503 cm^{-1}. HRMS (DART) calculated for $[M-CH_3]^+$ ($C_{16}H_{21}Si_2$) m/z 269.1176, found m/z 269.1185.

73

5-(1-(Dimethyl(phenyl)silyl)-2-methylpropyl)-2-methoxypyridine (73): Followed general procedure B with **46-sub** (1 mmol) under constant current of 5 mA until passing 2.2 F/mol of charge. The residue was purified using silica gel chromatography (Hexanes : EA = 20:1) to give 248.4 mg (83% yield) of **73** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 2.0 Hz, 1H), 7.46-7.39 (m, 2H), 7.37-7.28 (m, 3H), 7.18 (dd, *J* = 8.5 Hz, 2.5 Hz, 1H), 6.61 (d, *J* = 8.5 Hz, 1H), 3.91 (s, 3H), 2.16-2.05 (m,

1H), 1.96 (d, J = 9.0 Hz, 1H), 0.93 (d, J = 7.0 Hz, 3H), 0.76 (d, J = 6.5 Hz, 3H), 0.31 (s, 3H), 0.17 (s, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 162.0, 146.3, 139.3, 138.7, 134.0, 131.7, 129.0, 127.8, 110.1, 53.4, 41.4, 30.2, 24.1, 23.1, -1.5, -3.3; ^{29}Si NMR (99 MHz, $CDCl_3$) δ -2.7 (s). IR (neat): 2954, 2870, 1600, 1568, 1427, 1306, 1255, 1110, 1028, 814, 790, 700, 551 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{18}H_{26}NOSi$) m/z 300.1778, found m/z 300.1782.

74

2-Phenyladamantane-2-carboxylic acid (74): Followed general procedure D and purified using silica gel chromatography (Hexanes : EA : HOAc = 10:1:0.2) to give 106.1 mg (83% yield) of **74** as a white solid.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.49 (d, J = 7.5 Hz, 2H), 7.34 (t, J = 7.5 Hz, 2H), 7.23 (t, J = 7.5 Hz, 1H), 2.95 (s, 2H), 2.04 (d, J = 12.5 Hz, 2H), 1.93-1.83 (m, 3H), 1.77 (d, J = 13.0 Hz, 2H), 1.69 (s, 3H), 1.58 (d, J = 12.5 Hz, 2H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 181.0, 140.9, 128.7, 127.6, 126.9, 55.8, 37.6, 35.3, 32.6, 31.6, 27.3, 26.7. IR (neat): 2902, 2862, 1687, 1495, 1452, 1354, 1228, 967, 734, 720 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{17}H_{21}O_2$) m/z 257.1536, found m/z 257.1537.

75

Trimethyl(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexyl)germane (75): Followed general procedure A with **13-sub** (0.5 mmol), trimethylgermanium chloride (1.5 mmol), and $TBAClO_4$ (3 mol) in THF (2.5 mL). The reaction was electrolyzed under constant current of 5 mA until passing 2.1 F/mol of charge. The residue was purified using silica gel chromatography (Hexanes : Et_2O = 30:1) to give 138.7 mg (85% yield) of **75** as a white solid.^{1}H NMR: (500 MHz, $CDCl_3$) δ 1.91 (d, J = 11.5 Hz, 2H), 1.70-1.61 (m, 3H), 1.31-1.26 (m, 1H), 1.24 (s, 12H), 1.23-1.10 (m, 4H), 0.10 (s, 9H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 82.8, 29.8, 27.4, 27.1, 25.2, -4.3, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.8 (br). IR (neat): 2972, 2916, 2837, 1633, 1445, 1412, 1359, 1330, 1147, 1132, 1015, 969, 859, 594 cm^{-1}. HRMS (DART) calculated for $[M-CH_3]^+$ ($C_{14}H_{28}BGeO$) m/z 313.1389, found m/z 313.1391.

89

4,4,5,5-Tetramethyl-2-(2-methyl-6-phenoxyhexan-2-yl)-1,3,2-dioxaborolane (89): Followed general procedure A under constant current of 3 mA until passing 2.0 F/mol of charge. The residue was purified using silica gel chromatography (Hexanes : Et_2O = 30:1) to give 254.6 mg (80% yield) of **89** as a white solid.^{1}H NMR: (500 MHz,

$CDCl_3$) δ 7.30-7.23 (m, 2H), 6.94-6.86 (m, 3H), 3.93 (t, *J* = 6.5 Hz, 2H), 1.80-1.71 (m, 2H), 1.44-1.36 (m, 2H), 1.22 (s, 12H), 0.96 (s, 6H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 159.2, 129.5, 120.5, 114.6, 83.1, 68.8, 37.2, 26.4, 24.94, 24.85, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.8 (br). IR (neat): 2940, 2860, 1601, 1584, 1493, 1470, 1390, 1308, 1260, 1208, 1138, 1059, 829, 756, 692 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{19}H_{32}BO_3$) m/z 319.2439, found m/z 319.2437.

90

2-(6-chloro-3-methylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (90): Followed general procedure A and purified using silica gel chromatography (Hexanes : Et_2O = 50:1) to give 229.1 mg (88% yield) of **90** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 3.55-3.45 (m, 2H), 1.82-1.64 (m, 2H), 1.53-1.39 (m, 2H), 1.32-1.23 (m, 2H), 1.23 (s, 12H), 0.90 (s, 3H), 0.84 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 83.2, 46.1, 36.1, 31.5, 29.4, 25.0, 24.9, 21.0, 10.2, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.6 (br). IR (neat): 2976, 2959, 2875, 1462, 1387, 1370, 1305, 1262, 1138, 966, 883, 669 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{13}H_{30}BClNO_2$) m/z 278.2053, found m/z 278.2053.

91

4,4,5,5-Tetramethyl-2-(1-(3-(5-methylfuran-2-yl)propyl)cyclohexyl)-1,3,2-dioxaborolane(91): Followed general procedure A with **13-sub** (0.5 mmol), primary alkyl bromide (1.5 mmol), and $TBAClO_4$ (3 mmol) in THF (2.5 mL). The residue was purified using silica gel chromatography (Hexanes : Et_2O = 50:1) to give 146.0 mg (88% yield) of **91** as a white solid.^{1}H NMR: (500 MHz, $CDCl_3$) δ 5.82-5.80 (m, 2H), 2.50 (t, *J* = 7.5 Hz, 2H), 2.23 (s, 3H), 1.88 (d, *J* = 13.0 Hz, 2H), 1.66-1.53 (m, 6H), 1.33-1.26 (m, 4H), 1.24 (s, 12H), 0.90 (td, *J* = 12.5 Hz, 3.0 Hz, 2H). ^{13}C NMR: (126 MHz, $CDCl_3$) δ 154.8, 150.0, 105.8, 105.2, 83.0, 35.5, 29.1, 26.9, 25.4, 25.0, 24.3, 13.6, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 35.6 (br). IR (neat): 2974, 2919, 2848, 1567, 1450, 1390, 1367, 1298, 1270, 1183, 1162, 970, 897, 793, 708, 670 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{20}H_{34}BO_3$) m/z 333.2596, found m/z 333.2600.

92

2-(1-(2-(1,3-Dioxan-2-yl)ethyl)cycloheptyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (92): Followed general procedure A under constant current of 3 mA until passing 2.0 F/mol of charge. The residue was purified using silica gel chromatography

(Hexanes : Et_2O = 10:1) to give 220.1 mg (65% yield) of **92** as a white solid. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 4.43 (t, *J* = 5.0 Hz, 1H), 4.08 (dd, *J* = 11.0 Hz, 4.5 Hz, 2H), 3.73 (td, *J* = 12.0 Hz, 2.0 Hz, 2H), 2.06 (qt, *J* = 12.5 Hz, *J* = 5.0 Hz, 1H), 1.79 (dd, *J* = 14.0 Hz, 8.0 Hz, 2H), 1.59-1.38 (m, 10H), 1.37-1.23 (m, 5H), 1.22 (s, 12H). ^{13}C NMR: (126 MHz, $CDCl_3$) δ 103.5, 83.0, 67.0, 36.2, 34.3, 32.1, 30.0, 26.0, 25.0, 24.6, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 35.3 (br). IR (neat): 2961, 2920, 2853, 1465, 1378, 1262, 1138, 1091, 1083, 1008, 964, 841, 695, 578 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{19}H_{39}BNO_4$) m/z 356.2967, found m/z 356.2969.

93

2-(1-(3-methoxypropyl)cycloheptyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (93): Followed general procedure A with **92-sub** (0.5 mmol), primary alkyl bromide (1.5 mmol), and $TBAClO_4$ (2 mmol) in a mixture solvent of THF (2.5 mL) and DME (0.5 mL). The residue was purified using silica gel chromatography (Hexanes : Et_2O = 10:1) to give 133.2 mg (90% yield) of **93** as a colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 3.32 (t, *J* = 6.5 Hz, 2H), 3.31 (s, 3H), 1.85-1.75 (m, 2H), 1.60-1.38 (m, 10H), 1.33-1.24 (m, 4H), 1.23 (s, 12H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 83.0, 74.0, 58.6, 36.5, 36.3, 29.9, 26.5, 25.0, 24.6, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.8 (br). HRMS (DART) calculated for $[M+H]^+$ ($C_{17}H_{34}BO_3$) m/z 297.2596, found m/z 297.2600.

94

2-(4-methoxy-2-methylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (94): Followed general procedure A with **1** (0.5 mmol), primary alkyl bromide (1.5 mmol), and $TBAClO_4$ (2 mmol) in a mixture solvent of THF (2.5 mL) and DME (0.5 mL). The residue was purified using silica gel chromatography (Hexanes : Et_2O = 15:1) to give 99.3 mg (87% yield) of **94** as a colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 3.37 (t, *J* = 7.0 Hz, 2H), 3.29 (s, 3H), 1.56 (s, 2H), 1.22 (s, 12H), 0.93 (s, 6H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 83.0, 70.7, 58.6, 40.6, 25.2, 24.8, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.7 (br). HRMS (DART) calculated for $[M+H]^+$ ($C_{12}H_{26}BO_3$) m/z 229.1970, found m/z 229.1973.

95

tert-butyldimethyl(3-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butoxy)silane (95): Followed general procedure A with **1** (0.5 mmol), primary alkyl bromide (1.5 mmol), and $TBAClO_4$ (2 mmol) in a mixture solvent of THF (2.5 mL) and DME (0.5 mL). The residue was purified using silica gel chromatography (Hexanes : Et_2O = 30:1) to give 116.7 mg (71% yield) of **95** as a colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 3.66-3.59 (m, 2H), 1.58-1.52 (m, 2H), 1.22 (s, 12H), 0.93

(s, 6H), 0.89 (s, 9H), 0.05 (s, 6H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 83.1, 61.8, 44.0, 26.2, 25.4, 24.8, 18.6, -5.0, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.7 (br). HRMS (DART) calculated for $[M+H]^+$ ($C_{17}H_{38}BO_3Si$) m/z 329.2678, found m/z 329.2684.

96

2-(9-Chloro-1-methoxynonan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (96): Followed general procedure A and purified using silica gel chromatography (Hexanes : Et_2O = 10:1) to give 176.5 mg (55% yield) of **96** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 3.51 (t, *J* = 7.0 Hz, 2H), 3.35 (td, *J* = 6.5 Hz, 1.0 Hz, 2H), 3.31 (s, 3H), 1.76 (dt, *J* = 14.5 Hz, 7.0 Hz, 2H), 1.62-1.52 (m, 2H), 1.48-1.27 (m, 8H), 1.24 (s, 12H), 1.00-0.92 (m, 1H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 83.1, 73.3, 58.6, 45.2, 32.7, 31.2, 29.3, 28.5, 27.8, 27.3, 25.0, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.6 (br). IR (neat): 2978, 2927, 2855, 1460, 1386, 1314, 1243, 1143, 1118, 966, 859, 709, 687, 670, 651 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{16}H_{33}BClO_3$) m/z 319.2206, found m/z 319.2208.

97

4,4,5,5-Tetramethyl-2-(1-phenylhept-6-en-3-yl)-1,3,2-dioxaborolane (97): Followed general procedure A and purified using silica gel chromatography (Hexanes : Et_2O = 50:1) to give 195.4 mg (65% yield) of **97** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.29-7.23 (m, 2H), 7.20-7.13 (m, 3H), 5.87-5.77 (m, 1H), 5.02-4.96 (m, 1H), 4.95-4.90 (m, 1H), 2.67-2.53 (m, 2H), 2.14-2.00 (m, 2H), 1.80-1.71 (m, 1H), 1.70-1.63 (m, 1H), 1.62-1.53 (m, 1H), 1.52-1.44 (m, 1H), 1.27 (s, 12H), 1.13-1.03 (m, 1H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 143.2, 139.3, 128.5, 128.4, 125.7, 114.4, 83.1, 35.7, 33.54, 33.53, 30.7, 25.02, 24.99, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.7 (br). IR (neat): 2977, 2923, 2856, 1640, 1455, 1379, 1370, 1315, 1142, 995, 966, 907, 851, 698, 578 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{19}H_{33}BNO_2$) m/z 318.2599, found m/z 318.2600.

98

2-(4-Chloro-1-cyclopropylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (98): Followed general procedure A and purified using silica gel chromatography (Hexanes : Et_2O = 50:1) to give 163.1 mg (63% yield) of **98** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 3.52 (t, *J* = 7.0 Hz, 2H), 1.89-1.72 (m, 2H), 1.62 (q, *J* = 8.0 Hz, 2H), 1.25 (s, 12H), 0.70-0.61 (m, 1H), 0.47-0.37 (m, 2H), 0.36-0.31 (m, 1H), 0.13-0.07 (m, 1H), 0.06--0.01 (m, 1H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 83.2, 45.5, 32.6, 29.1, 24.9, 24.8, 12.5, 5.5, 3.7, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.6 (br). IR (neat): 3075, 2978, 2930, 2867, 1460, 1371, 1317, 1270, 1214,

1142, 968, 876774, 670 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{13}H_{28}BClNO_2$) m/z 276.1896, found m/z 276.1897.

99

1-(4-(Tetrahydro-2*H*-pyran-4-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) butyl)-1*H*-pyrrole (99): Followed general procedure A under constant current of 2.5 mA until passing 2.0 F/mol of charge. The residue was purified using silica gel chromatography (DCM : EA = 50:1) to give 186.8 mg (56% yield) of **99** as a white solid.^{1}H NMR: (500 MHz, $CDCl_3$) δ 6.63 (t, *J* = 2.0 Hz, 2H), 6.12 (t, *J* = 2.0 Hz, 2H), 3.97-3.90 (m, 2H), 3.86 (t, *J* = 7.5 Hz, 2H), 3.38-3.30 (m, 2H), 1.84-1.76 (m, 1H), 1.74-1.66 (m, 1H), 1.64-1.50 (m, 3H), 1.49-1.30 (m, 5H), 1.25 (s, 12H), 0.96-0.85 (m, 1H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 120.5, 107.9, 83.3, 68.6, 68.5, 49.8, 37.0, 32.8, 32.4, 31.4, 25.6, 25.2, 25.0, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.1 (br). IR (neat): 2975, 2956, 2923, 2836, 1504, 1416, 1260, 1207, 909, 734, 670 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{19}H_{33}BNO_3$) m/z 334.2548, found m/z 334.2545.

100

1-(4-(2,3-Dihydro-1*H*-inden-2-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) butyl)-1*H*-pyrrole (100): Followed general procedure A under constant current of 2.5 mA until passing 2.0 F/mol of charge. The residue was purified using silica gel chromatography (Hexanes : Et_2O = 50:3) to give 186.5 mg (51% yield) of **100** as a white solid.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.19-7.14 (m, 2H), 7.13-7.07 (m, 2H), 6.65 (s, 1H), 6.14 (s, 2H), 3.95-3.83 (m, 2H), 3.03 (dd, *J* = 15.0 Hz, 7.5 Hz, 1H), 2.98 (dd, *J* = 15.0 Hz, 7.5 Hz, 1H), 2.72-2.57 (m, 2H), 2.56-2.43 (m, 1H), 1.92-1.70 (m, 2H), 1.59-1.41 (m, 2H), 1.27-1.15 (m, 13H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 143.6 (d, *J* = 25.9 Hz), 126.1 (d, *J* = 2.5 Hz), 124.4 (d, *J* = 2.9 Hz), 120.6, 107.9, 83.3, 49.9, 42.1, 39.2, 38.7, 31.4, 27.6, 25.0 (d, *J* = 7.6 Hz), *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.1 (br). IR (neat): 2977, 2930, 1501, 1465, 1405, 1379, 1319, 1281, 1111, 1088, 852, 780, 719, 696 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{23}H_{33}BNO_2$) m/z 366.2599, found m/z 366.2606.

101

(*3aR,4R,6R,7aS*)-2-(6-Methoxy-1-phenylhexan-3-yl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (101): Followed general procedure A with **98-sub** (0.5 mmol), primary alkyl bromide (1.5 mmol), and $TBAClO_4$ (3 mol) in THF (2.5 mL). The residue was purified using silica gel chromatography (Hexanes : Et_2O = 8:1) to give 127.5 mg (69% yield, dr = 1:1) of **101** as a colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.31-7.23 (m, 2H), 7.21-7.13 (m, 3H), 4.28 (d, *J* = 8.5 Hz, 1H), 3.36 (t, *J* = 7.0 Hz, 2H), 3.32 (s, 3H), 2.72-2.54 (m, 2H), 2.41-2.31 (m, 1H), 2.28-2.19 (m, 1H), 2.07 (t, *J* = 5.5 Hz, 1H), 1.96-1.89 (m, 1H), 1.85 (d, *J* = 14.5 Hz, 1H), 1.82-1.74 (m, 1H), 1.73-1.66 (m, 1H), 1.65-1.45 (m, 4H), 1.38 (s, 3H), 1.29 (s, 3H), 1.16 (d, *J* = 11.0 Hz, 1H), 1.13-1.07 (m, 1H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 143.14/143.12, 128.6, 128.4, 125.7, 85.5, 77.7, 73.3, 58.6, 51.4, 39.7, 38.3, 35.9, 35.7/35.2, 33.6, 29.26/29.22, 29.0, 27.8/27.7, 27.2, 26.8, 24.2, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.4 (br). IR (neat): 2917, 2865, 1603, 1495, 1475, 1366, 1235, 1154, 1077, 1029, 990, 698, 625 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{23}H_{39}BNO_3$) m/z 388.3018, found m/z 388.3027.

102

1-Methoxy-3-(5-methoxy-2-methylpentan-2-yl)benzene (102): Followed general procedure A under constant current of 2.5 mA until passing 2.0 F/mol of charge. The residue was purified using silica gel chromatography (Hexanes : EA = 25:1) to give 140.3 mg (63% yield) of **102** as a colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.22 (t, *J* = 8.0 Hz, 1H), 6.96-6.91 (m, 1H), 6.89 (t, *J* = 2.0 Hz, 1H), 6.72 (dd, *J* = 8.0 Hz, 2.5 Hz, 1H), 3.81 (s, 3H), 3.30-3.24 (m, 5H), 1.68-1.60 (m, 2H), 1.39-1.32 (m, 2H), 1.30 (s, 6H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 159.5, 151.2, 129.1, 118.6, 112.8, 110.0, 58.6, 55.3, 40.9, 37.7, 29.0, 25.2. IR (neat): 2946, 2861, 2831, 1600, 1581, 1487, 1451, 1429, 1365, 1318, 1290, 1048, 996, 873, 777, 701 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{14}H_{26}NO_2$) m/z 240.1958, found m/z 240.1962.

103

Tert-butyl 4-(2-(1,3-dioxolan-2-yl)ethyl)-4-phenylpiperidine-1-carboxylate (103): Followed general procedure A with **103-sub** (0.5 mmol), primary alkyl bromide (1.5 mmol), and $TBAClO_4$ (3 mol) in THF/DME (2.5 mL/0.5 mL). The reaction was electrolyzed under constant current of 5 mA until passing 2.2 F/mol of charge. The residue was purified using silica gel chromatography (Hexanes : EA = 5:1) to give 99.4 mg (55% yield) of **103** as a colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.35-7.29 (m, 2H), 7.28-7.24 (m, 2H), 7.21-7.16 (m, 1H), 4.66 (t, *J* = 5.0 Hz, 1H), 3.90-3.83 (m, 2H), 3.81-3.74 (m, 2H), 3.73-3.57 (br, 2H), 3.17-3.07 (m, 2H), 2.14 (d,

J = 13.0 Hz, 2H), 1.76-1.64 (m, 4H), 1.43 (s, 9H), 1.34-1.27 (m, 2H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 155.2, 144.4, 128.6, 126.9, 126.1, 104.8, 79.4, 64.9, 40.8, 39.6, 37.0, 35.3, 28.6, 28.2. Data are consistent with those reported in the literature[48].

104

6-Chloro-N,N-dimethyl-3-phenylhexan-1-amine (104): Followed general procedure A and purified using silica gel chromatography (Hexanes : EA : Et_3N = 10:1:0.3) to give 127.2 mg (53% yield) of **104** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.29 (t, J = 7.5 Hz, 2H), 7.22-7.17 (m, 1H), 7.16-7.12 (m, 2H), 3.50-3.41 (m, 2H), 2.62-2.54 (m, 1H), 2.17 (s, 6H), 2.22-2.13 (m, 1H), 2.09-2.01 (m, 1H), 1.88-1.79 (m, 2H), 1.78-1.52 (m, 4H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 144.8, 128.6, 127.7, 126.4, 57.9, 45.6, 45.3, 43.6, 35.0, 34.3, 30.7. IR (neat): 2939, 2856, 2814, 2763, 1602, 1493, 1452, 1306, 1265, 1040, 756, 700, 650 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{14}H_{23}ClN$) m/z 240.1514, found m/z 240.1515.

105

(4-Cyclohexyl-4-phenylbutyl)(phenyl)sulfane (105): Followed general procedure A under constant current of 3 mA until passing 2.0 F/mol of charge. The residue was purified using silica gel chromatography (Pentane) to give 263.1 mg (81% yield) of **105** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.28-7.21 (m, 6H), 7.20-7.16 (m, 1H), 7.15-7.11 (m, 1H), 7.08 (d, J = 7.5 Hz, 2H), 2.90-2.76 (m, 2H), 2.33-2.24 (m, 1H), 2.00-1.92 (m, 1H), 1.91-1.86 (m, 1H), 1.77-1.65 (m, 2H), 1.64-1.56 (m, 2H), 1.48-1.37 (m, 4H), 1.28-1.17 (m, 1H), 1.15-1.01 (m, 2H), 0.91 (qd, J = 12.5 Hz, 3.5 Hz, 1H), 0.83-0.72 (m, 1H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 144.3, 137.1, 128.93, 128.89, 128.6, 128.2, 126.0, 125.7, 51.9, 43.4, 33.8, 31.7, 31.5, 31.2, 27.3, 26.73, 26.72, 26.66. IR (neat): 2954, 2847, 1585, 1493, 1479, 1361, 1185, 729, 696, 686 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{22}H_{29}S$) m/z 325.1984, found m/z 325.1988.

106

1,2-Dimethoxy-4-(1-(4-(trifluoromethyl)phenyl)heptan-3-yl)benzene (106): Followed general procedure A with **106-sub** (0.5 mmol), primary alkyl bromide (1.5 mmol), and $TBAClO_4$ (3 mol) in THF (2.5 mL). The reaction was electrolyzed under constant current of 3 mA until passing 2.0 F/mol of charge. The residue was purified using silica gel chromatography (Hexane : EA=10:1) to give 95.3 mg (50% yield) of **106** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.50 (d, J = 8.0 Hz, 2H), 7.20 (d,

J = 8.0 Hz, 2H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.70 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 6.66 (d, *J* = 2.0 Hz, 1H), 3.88 (d, *J* = 1.0 Hz, 6H), 2.55-2.40 (m, 3H), 2.00-1.91 (m, 1H), 1.89-1.78 (m, 1H), 1.67-1.58 (m, 1H), 1.57-1.49 (m, 1H), 1.31-1.04 (m, 4H), 0.83 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 149.0, 147.4, 147.0, 138.1 128.8, 128.1 (q, *J* = 32.0 Hz), 125.3 (q, *J* = 3.8 Hz), 124.5 (q, *J* = 270.2 Hz), 119.8, 111.2, 110.8, 56.03, 56.00, 45.3, 38.5, 37.1, 33.9, 29.9, 22.9, 14.2; ^{19}F NMR ($CDCl_3$, 470 MHz) δ -62.3 (s). IR (neat): 2929, 2858, 1617, 1591, 1516, 1464, 1323, 1255, 1233, 1159, 1116, 1066, 1028, 1018, 843, 821, 807, 762, 653 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{22}H_{31}F_3NO_2$) m/z 398.2301, found m/z 398.2303.

107

Tert-butyl 4-((4S)-9-fluoro-5-(4-methoxyphenyl)nonan-4-yl)benzoate (107): Followed general procedure A with **107-sub** (0.5 mmol), primary alkyl bromide (1.5 mmol), and $TBAClO_4$ (3 mol) in THF (2.5 mL). The reaction was electrolyzed under constant current of 2.5 mA until passing 2.0 F/mol of charge. The residue was purified using silica gel chromatography (Hexane : EA = 10:1) to give 66.5 mg (31% yield, dr = 3:1) of **107** as a white solid. Major isomer: ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.75 (d, *J* = 9.0 Hz, 2H), 6.67 (d, *J* = 8.5 Hz, 2H), 4.44-4.27 (m, 2H), 3.74 (s, 3H), 2.87-2.80 (m, 1H), 2.79-2.73 (m, 1H), 1.90-1.74 (m, 2H), 1.57 (s, 9H), 1.69-1.52 (m, 3H), 1.39-1.28 (m, 1H), 1.23-1.15 (m, 2H), 1.11-1.02 (m, 2H), 0.82 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 166.1, 157.8, 148.5, 134.4, 129.8, 129.6, 129.0, 128.9, 84.2 (d, *J* = 163.4 Hz), 80.8, 55.2, 51.7, 50.6, 35.6, 33.2, 30.6 (d, *J* = 19.2 Hz), 28.3, 23.5 (d, *J* = 5.5 Hz), 20.9, 14.2. ^{19}F NMR ($CDCl_3$, 470 MHz) δ -217.7 (m); Minor isomer: ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.07 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 4.27-4.11 (m, 2H), 3.82 (s, 3H), 2.70 (td, *J* = 10.0 Hz, 5.0 Hz, 1H), 2.62 (td, *J* = 10.5 Hz, 3.5 Hz, 1H), 1.61 (s, 9H), 1.69-1.52 (m, 4H), 1.38-1.28 (m, 2H), 1.02-0.95 (m, 2H), 0.92-0.86 (m, 2H), 0.64 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 166.0, 158.1, 150.1, 135.9, 130.1, 129.8, 129.2, 128.3, 113.9, 84.1 (d, *J* = 163.4 Hz), 80.9, 55.3, 52.5, 51.4, 36.6, 34.2, 30.3 (d, *J* = 19.1 Hz), 28.4, 23.2 (d, *J* = 5.9 Hz), 20.7, 14.0; ^{19}F NMR ($CDCl_3$, 470 MHz) δ -217.7 (m). IR (neat): 2957, 2933, 2871, 1709, 1609, 1511, 1458, 1291, 1248, 1165, 1036, 1019, 849, 829, 803, 744, 709 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{27}H_{41}FNO_3$) m/z 446.3065, found m/z 446.3073.

108

1-(3-Methoxypropyl)-2,3-dihydro-1*H*-indene (108): Followed general procedure A and purified using silica gel chromatography (Hexanes : EA = 30:1) to give 106.2 mg (56% yield) of **108** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.24-7.19 (m, 2H), 7.18-7.12 (m, 2H), 3.43 (t, *J* = 6.5 Hz, 2H), 3.36 (s, 3H), 3.16-3.08 (m, 1H), 2.97-2.89 (m, 1H), 2.87-2.79 (m, 1H), 2.34-2.25 (m, 1H), 1.97-1.89 (m, 1H), 1.78-1.64 (m, 3H), 1.51-1.41 (m, 1H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 147.5, 144.1, 126.4, 126.1, 124.5, 123.7, 73.2, 58.8, 44.8, 32.2, 31.6, 31.5, 27.9. IR (neat): 2935, 2850, 1477, 1457, 1386, 1117, 1024, 742, 717, 626 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{13}H_{22}NO$) m/z 208.1696, found m/z 208.1699.

109

4-(2-((*1R,5S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl)thiochromane (109): Followed general procedure A under constant current of 2.5 mA until passing 2.0 F/mol of charge. The residue was purified using silica gel chromatography (Hexanes) to give 125.6 mg (42% yield, dr = 1:1) of **109** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.11-7.08 (m, 1H), 7.08-7.01 (m, 2H), 7.01-6.96 (m, 1H), 5.27-5.20 (m, 1H), 3.16 (td, *J* = 12.5 Hz, 4.0 Hz, 1H), 2.91 (dq, *J* = 12.0 Hz, 4.0 Hz, 1H), 2.86-2.78 (m, 1H), 2.42-2.33 (m, 1H), 2.30-2.14 (m, 3H), 2.12-2.07 (m, 1H), 2.06-1.90 (m, 4H), 1.73-1.50 (m, 2H), 1.28 (d, *J* = 1.0 Hz, 3H), 1.16 (dd, *J* = 13.0 Hz, 3.5 Hz, 1H), 0.84 (d, *J* = 3.0 Hz, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 148.1/147.9, 138.0/137.9, 132.34/132.30, 130.1, 126.68/126.66, 126.60/126.56, 123.8/123.7, 116.6/116.4, 46.0/45.8, 41.03/41.00, 38.12/38.10, 37.5/37.2, 34.5/34.4, 31.89/31.87, 31.81/31.76, 31.45/31.43, 26.49/26.48, 26.0/25.7, 22.94/22.92, 21.4/21.3. IR (neat): 2913, 2831, 1588, 1566, 1472, 1436, 1330, 1203, 1069, 957, 886, 745 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{20}H_{27}S$) m/z 299.1828, found m/z 299.1833.

110

Pent-4-ene-1,1-diyldibenzene (110): Followed general procedure A and purified using silica gel chromatography (Hexanes) to give 160.1 mg (72% yield) of **110** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.31-7.22 (m, 8H), 7.20-7.15 (m, 2H), 5.90-5.78 (m, 1H), 5.02-4.98 (m, 1H), 4.98-4.95 (m, 1H), 3.94 (t, *J* = 8.0 Hz, 1H), 2.19-2.11 (m, 2H), 2.08-1.98 (m, 2H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 145.0, 138.5, 128.6, 128.0, 126.2, 115.0, 50.7, 34.9, 32.1. Data are consistent with those reported in

the literature[49].

111

5-(1-(Benzo[b]thiophen-5-yl)-4-chlorobutyl)-2-methoxypyridine (111): Followed general procedure A with **111-sub** (0.5 mmol), primary alkyl bromide (1.5 mmol), and $TBAClO_4$ (3 mol) in THF (2.5 mL). The residue was purified using silica gel chromatography (Hexanes : EA = 20:1) to give 56.7 mg (34% yield) of **111** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 2.5 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.68 (d, *J* = 1.5 Hz, 1H), 7.45-7.42 (m, 2H), 7.29 (dd, *J* = 5.5 Hz, 0.5 Hz, 1H), 7.20 (dd, *J* = 8.5 Hz, 1.5 Hz, 1H), 6.67 (d, *J* = 8.5 Hz, 1H), 3.99 (t, *J* = 8.0 Hz, 1H), 3.90 (s, 3H), 3.56 (t, *J* = 6.5 Hz, 2H), 2.32-2.18 (m, 2H), 1.83-1.73 (m, 2H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 163.0, 145.7, 140.3, 140.1, 138.3, 138.1, 132.9, 127.1, 124.6, 123.9, 122.9, 122.4, 111.0, 53.5, 47.4, 45.0, 32.9, 31.0. IR (neat): 2943, 2867, 1604, 1571, 1490, 1459, 1437, 1287, 1260, 1026, 817, 783, 755, 702 648 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{18}H_{19}ClNOS$) m/z 332.0870, found m/z 332.0876.

112

Isopropyl 2-(4-(1-(4-chlorophenyl)-5-fluoropentyl)phenoxy)-2-methylpropanoate (109): Followed general procedure A with **112-sub** (0.5 mmol), primary alkyl bromide (1.5 mmol), and $TBAClO_4$ (3 mol) in THF (2.5 mL). The residue was purified using silica gel chromatography (Hexanes : EA = 10:1) to give 88.5 mg (42% yield) of **112** as a colorless oli.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.25-7.20 (m, 2H), 7.14-7.09 (m, 2H), 7.06-7.00 (m, 2H), 6.79-6.73 (m, 2H), 5.06 (hept, *J* = 6.0 Hz, 1H), 4.39 (dt, *J* = 47.0 Hz, 6.0 Hz, 2H), 3.80 (t, *J* = 8.0 Hz, 1H), 2.06-1.92 (m, 2H), 1.77-1.62 (m, 2H), 1.56 (s, 6H), 1.38-1.28 (m, 2H), 1.19 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 173.9, 154.1, 143.8, 137.9, 131.9, 129.3, 128.6, 128.4, 119.2, 84.1 (d, *J* = 163.6 Hz), 79.2, 69.0, 50.0, 35.5, 30.5 (d, *J* = 19.4 Hz), 25.6 (d, *J* = 1.6 Hz), 23.9 (d, *J* = 5.4 Hz), 21.7. ^{19}F NMR ($CDCl_3$, 470 MHz) δ -218.1 (hept, *J* = 25.4 Hz). IR (neat): 2981, 2938, 1726, 1507, 1489, 1465, 1383, 1285, 1236, 1177, 1147, 1102, 1013, 821, 770 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{24}H_{34}ClFNO_3$) m/z 438.2206, found m/z 438.2212.

113

(4-(1,3-Dioxan-2-yl)-1-phenylbutyl)dimethyl(phenyl)silane (113): Followed general procedure A under constant current of 2.5 mA until passing 2.0 F/mol of charge. The residue was purified using silica gel chromatography (Hexanes : EA = 9:1) to give 255.4 mg (72% yield) of **113** as a colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.41-7.28 (m, 5H), 7.16 (t, *J* = 7.5 Hz, 2H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 4.38 (t, *J* = 5.0 Hz, 1H), 4.03 (dd, *J* = 11.0 Hz, 5.0 Hz), 3.66 (qdd, *J* = 12.0 Hz, 7.5 Hz, 2.5 Hz, 2H), 2.18 (dd, *J* = 11.5 Hz, 4.5 Hz, 1H), 2.08-1.94 (m, 1H), 1.90-1.76 (m, 2H), 1.60-1.51 (m, 1H), 1.44-1.35 (m, 1H), 1.31-1.23 (m, 1H), 0.25 (s, 3H), 0.16 (s, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 142.7, 137.8, 134.3, 129.1, 128.2, 128.1, 127.7, 124.6, 102.4, 67.0, 36.7, 35.1, 26.0, 23.8, -4.4 (d, *J* = 158.0 Hz). IR (neat): 2954, 2848, 1599, 1490, 1450, 1378, 1246, 1142, 1112, 985, 925, 819, 699 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{21}H_{32}NO_2Si$) m/z 358.2197, found m/z 358.2199.

114

Dimethyl(phenyl)(4-phenyl-1-(4-vinylphenyl)butyl)silane (114): Followed general procedure A and purified using silica gel chromatography (Hexanes) to give 141.0 mg (38% yield) of **114** as a colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.42-7.31 (m, 5H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 7.0 Hz, 2H), 7.13 (t, *J* = 7.0 Hz, 1H), 7.03 (d, *J* = 7.0 Hz, 2H), 6.88 (d, *J* = 8.0 Hz, 2H), 6.69 (dd, *J* = 18.0 Hz, 11.0 Hz, 1H), 5.69 (dd, *J* = 17.5 Hz, 1.0 Hz, 1H), 5.17 (dd, *J* = 11.0 Hz, 1.0 Hz, 1H), 2.60-2.52 (m, 1H), 2.49-2.41 (m, 1H), 2.28 (dd, *J* = 12.0 Hz, 4.0 Hz, 1H), 1.87-1.78 (m, 1H), 1.77-1.70 (m, 1H), 1.64-1.54 (m, 1H), 1.47-1.36 (m, 1H), 0.23 (s, 3H), 0.17 (s, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 142.9, 142.6, 137.7, 137.0, 134.3, 134.0, 129.1, 128.4, 128.3, 128.2, 127.7, 126.1, 125.6, 112.3, 36.4, 35.7, 30.9, 29.0, -4.5 (d, *J* = 185.2 Hz). IR (neat): 3023, 2927, 2855, 1627, 1604, 1507, 1495, 1453, 1426, 1406, 1247, 1112, 810, 782, 733, 697, 648 cm^{-1}. HRMS (DART) calculated for $[M]^+$ ($C_{26}H_{30}Si$) m/z 370.2117, found m/z 370.2120.

115

Trimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)silane (115): Followed general procedure B and purified using silica gel chromatography (Hexanes : Et_2O = 50:1) to give 172.2 mg (71% yield) of **115** as a white solid. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 1.21 (s, 12H), 1.00 (s, 6H), -0.01 (s, 9H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 82.8, 25.0, 19.4, -3.6, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 35.2 (br). ^{29}Si NMR (99 MHz, $CDCl_3$) δ -18.2. IR (neat): 2982, 2956, 2931, 2861, 1459, 1386, 1370, 1325, 1297, 1254, 832, 718, 686, 647 cm^{-1}. HRMS (DART) calculated for $[M-CH_3]^+$ ($C_{11}H_{24}BO_2Si$) m/z 227.1633, found m/z 227.1634.

116

Dimethyl(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexyl)silane (116): Followed general procedure B and purified using silica gel chromatography (Hexanes : Et_2O = 50:1) to give 206.3 mg (77% yield) of **116** as a white solid.^{1}H NMR: (500 MHz, $CDCl_3$) δ 3.64 (hept, *J* = 3.5 Hz, 1H), 1.93 (d, *J* = 12.5 Hz, 2H), 1.71-1.61 (m, 3H), 1.32-1.22 (m, 2H), 1.24 (s, 12H), 1.21-1.13 (m, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 82.9, 29.8, 27.02, 26.98, 25.1, -6.1, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.8 (br). ^{29}Si NMR (99 MHz, $CDCl_3$) δ -4.7. IR (neat): 2978, 2921, 2849, 2101, 1381, 1330, 1258, 1214, 1145, 1006, 880, 858, 758 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{14}H_{33}BNO_2Si$) m/z 286.2368, found m/z 286.2375.

117

Methyldiphenyl(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cycloheptyl)silane (117): Followed general procedure B under constant current of 3 mA until passing 2.0 F/mol of charge. The residue was purified using silica gel chromatography (Hexanes : Et_2O = 50:1) to give 214.3 mg (51% yield) of **117** as a white solid.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.70-7.61 (m, 4H), 7.41-7.30 (m, 6H), 2.34-2.24 (m, 2H), 1.63-1.46 (m, 8H), 1.43-1.34 (m, 2H), 1.17 (s, 12H), 0.63 (s, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 137.0, 136.0, 128.9, 127.4, 83.0, 32.2, 29.0, 28.4, 25.2, -3.8, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 35.8 (br). ^{29}Si NMR (99 MHz, $CDCl_3$) δ -4.9. IR (neat): 2977, 2917, 2849, 1629, 1378, 1327, 1298, 1260, 1142, 1109, 852, 788, 734, 698 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{26}H_{41}BNO_2Si$) m/z 438.2994, found m/z 438.3000.

118

9-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(triethylsilyl)butyl)-9H-carbazole (118): Followed general procedure C and purified using silica gel chromatography (Hexanes : Et_2O = 20:1) to give 81.0 mg (35% yield) of **118** as a white solid.^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.0 Hz, 2H), 7.49-7.39 (m, 4H), 7.24-7.16 (m, 2H), 4.36-4.15 (m, 2H), 2.06-1.92 (m, 1H), 1.82-1.67 (m, 2H), 1.55-1.45 (m, 1H), 1.20 (d, *J* = 16.0 Hz, 12H), 0.93 (t, *J* = 8.0 Hz, 9H), 0.56 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 140.5, 125.6, 122.9, 120.4, 118.7, 108.8, 82.9, 43.2, 32.5, 25.4, 24.8, 23.7, 7.7, 3.6, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.6 (br). ^{29}Si NMR (99 MHz, $CDCl_3$) δ 8.0. IR (neat):

2976, 2875, 1597, 1485, 1453, 1414, 1303, 1241, 969, 850, 721, 666 cm^{-1}. HRMS (DART) calculated for $[M+H]^+$ ($C_{28}H_{43}BNO_2Si$) m/z 464.3151, found m/z 464.3151.

119

dimethyl(phenyl)(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)silane (119): Followed general procedure C and purified using silica gel chromatography (Hexanes : Et_2O = 20:1) to give 11.5 mg (58% yield) of **119** as a colorless oil. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.51-7.46 (m, 2H), 7.34-7.28 (m, 3H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 7.0 Hz, 2H), 2.76-2.62 (m, 1H), 2.53-2.38 (m, 1H), 1.95-1.81 (m, 1H), 1.71-1.57 (m, 1H), 1.21 (d, *J* = 15.5 Hz, 12H), 0.71 (dd, *J* = 12.0 Hz, 3.0 Hz, 1H), 0.31 (s, 3H), 0.30 (s, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 142.7, 139.0, 134.0, 128.9, 128.7, 128.3, 127.7, 125.7, 83.0, 39.6, 28.2, 25.4, 24.9, -2.1, -3.2, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.5 (br). ^{29}Si NMR (99 MHz, $CDCl_3$) δ -1.89. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{23}H_{37}BNO_2Si$) m/z 398.2681, found m/z 398.2688.

120

Trimethyl(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(thiophen-3-yl)propyl)silane (120): Followed general procedure C under constant current of 2.5 mA until passing 2.2 F/mol of charge. The residue was purified using silica gel chromatography (Hexanes : Et_2O = 25:1) to give 99.1 mg (61% yield) of **120** as a white solid.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 5.0 Hz, 3.0 Hz, 1H), 6.94 (dd, *J* = 5.0 Hz, 1.0 Hz, 1H), 6.93-6.90 (m, 1H), 2.78-2.67 (m, 1H), 2.58-2.49 (m, 1H), 1.92-1.80 (m, 1H), 1.71-1.60 (m, 1H), 1.25 (d, *J* = 2.5 Hz, 12H), 0.41 (dd, *J* = 12.0 Hz, 3.0 Hz, 1H), -0.03 (s, 9H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 143.3, 128.5, 125.1, 120.1, 82.9, 33.9, 27.2, 25.4, 24.9, -1.4, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.5 (br). ^{29}Si NMR (99 MHz, $CDCl_3$) δ -2.7. IR (neat): 2972, 2931, 2857, 1536, 1409, 1379, 1349, 1306, 1272, 1245, 1106, 884, 800, 755 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{16}H_{33}BNO_2SSi$) m/z 342.2089, found m/z 342.2094.

121

(2-(4,4-Difluorocyclohexyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)dimethylsilane (121): Followed general procedure C under constant current of 5 mA until passing 2.2 F/mol of charge. The residue was purified using silica gel chromatography (Hexanes : Et_2O = 33:1) to give 100.0 mg (60% yield) of **121** as a white solid.^{1}H NMR: (500 MHz, $CDCl_3$) δ 3.93-3.82 (m, 1H), 2.11-1.99 (m, 2H),

1.87-1.73 (m, 2H), 1.72-1.54 (m, 3H), 1.32-1.26 (m, 2H), 1.23 (d, J = 5.0 Hz, 12H), 1.24-1.09 (m, 2H), ;0.55-0.44 (m, 1H), 0.11 (t, J = 3.5 Hz, 6H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 124.1 (t, J = 238.4 Hz), 83.0, 38.2, 33.9-33.4 (m, 2C), 32.0 (d, J = 2.4 Hz), 29.3 (d, J = 9.2 Hz), 28.2 (d, J = 9.4 Hz), 25.0 (d, J = 50.8 Hz), -4.30 (d, J = 23.5 Hz), *carbon attached to boron not observed*. ^{19}F NMR ($CDCl_3$, 470 MHz) δ -91.7 (d, J = 233.6 Hz), -101.7 (d, J = 232.6 Hz). ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.7 (br). ^{29}Si NMR (99 MHz, $CDCl_3$) δ -9.9. IR (neat): 2975, 2939, 2115, 1447, 1353, 1308, 1249, 1192, 1065, 1006, 939, 878, 809, 700, 577 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{16}H_{35}BF_2NO_2Si$) m/z 350.2493, found m/z 350.2493.

122

2-Cyclohexyl-2-phenylacetic acid (122): Followed general procedure D and purified using silica gel chromatography (Hexanes : EA : HOAc = 10:1:0.3) to give 96.1 mg (88% yield) of **122** as a white solid.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.36-7.28 (m, 4H), 7.28-7.23 (m, 1H), 3.22 (d, J = 10.5 Hz, 1H), 2.00 (qt, J = 12.5 Hz, 3.0 Hz, 1H), 1.90 (d, J = 12.5 Hz, 1H), 1.75 (d, J = 11.5 Hz, 1H), 1.68-1.56 (m, 2H), 1.39-1.22 (m, 2H), 1.21-1.01 (m, 3H), 0.74 (qd, J = 12.0 Hz, 3.0 Hz, 1H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 179.8, 137.4, 128.8, 128.6, 127.5, 58.9, 40.8, 32.1, 30.4, 26.4, 26.10, 26.06. Data are consistent with those reported in the literature[50].

123

2-(4-((*1R*,*5S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)butan-2-yl-1,1,1-*d*$_3$)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (123): Followed general procedure E and purified using silica gel chromatography (Hexanes : Et_2O = 33:1) to give 132.8 mg (64% yield, dr = 1:1) of **123** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 5.18-5.12 (m, 1H), 2.33 (dt, J = 8.5 Hz, 5.5 Hz, 1H), 2.26-2,11 (m, 2H), 2.09-1.98 (m, 1H), 2.01 (t, J = 5.5Hz, 1H), 1.97-1.89 (m, 2H), 1.54-1.42 (m, 1H), 1.38-1.27 (m, 1H), 1.26 (s, 3H), 1.23 (s, 12H), 1.13 (dd, J = 8.5 Hz, 1.5 Hz, 1H), 0.99 (t, J = 6.5 Hz, 1H), 0.81 (s, 3H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 148.95/148.94, 115.62/115.6, 82.9, 46.02/45.96, 41.0, 38.08/38.07, 36.52/36.50, 31.84/31.83, 31.4, 30.95/30.93, 26.5, 24.93/24.92, 24.88/24.86, 21.37/21.35, *carbon attached to boron and deuterium not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.6 (br). IR (neat): 2979, 2913, 2833, 1468, 1370, 1313, 1213, 1143, 969, 885, 799, 670 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{19}H_{34}D_3BNO_2$) m/z 325.3100, found m/z 325.3103.

124

Isopropyl 2-(4-(1-(4-chlorophenyl)ethyl-2,2,2-*d*$_3$)phenoxy)-2-methylpropanoate (124): Followed general procedure E and purified using silica gel chromatography (Hexanes : EA = 30:1) to give 109.0 mg (60% yield) of **124** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.24-7.21 (m, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 7.03 (d, *J* = 8.5 Hz, 2H), 6.80-6.73 (m, 2H), 5.07 (hept, *J* = 6.5 Hz, 1H), 4.03 (s, 1H), 1.56 (s, 6H), 1.20 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 173.9, 154.0, 145.3, 139.3, 131.8, 129.1, 128.5, 128.2, 119.1, 79.2, 69.0, 43.3, 25.5, 21.7, *the carbon attached to deuterium not observed*. IR (neat): 2981, 1726, 1609, 1506, 1489, 1382, 1176, 1145, 1101, 1013, 816, 732, 696, 645 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{21}H_{26}D_3ClNO_3$) m/z 381.2019, found m/z 381.2024.

125

2-(5-chloro-2-methylpentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (125): Followed general procedure A and purified using silica gel chromatography (Hexanes:Et_2O = 50:1) to give 212.0 mg (86% yield) of **125** as a colorless oil.^{1}H NMR: (500 MHz, $CDCl_3$) δ 3.50 (t, *J* = 7.0 Hz, 2H), 1.78-1.70 (m, 2H), 1.40-1.33 (m, 2H), 1.22 (s, 12H), 0.93 (s, 6H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 83.2, 46.0, 38.4, 30.0, 24.9, 24.8, *carbon attached to boron not observed*. ^{11}B NMR ($CDCl_3$, 160 MHz): δ 34.6 (br). IR (neat): 2978, 2937, 2863, 1475, 1390, 1369, 1270, 1134, 966, 894, 719, 669 cm^{-1}. HRMS (DART) calculated for $[M+NH_4]^+$ ($C_{12}H_{28}BClNO_2$) m/z 264.1896, found m/z 264.1896.

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20. NMR Spectra of Starting Materials and Products

1

31.334
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

Br
Bpin

11-sub

7.260
2.676
2.670
2.664
2.660
2.651
2.644
2.641
2.635
2.628
2.598
2.593
2.579
2.573
2.559
2.554
2.539
2.534
2.108
2.086
1.779
1.760
1.758
1.352
2.01
2.01
1.18
1.12
12.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

84.550
77.414
77.160
76.905
37.380
24.574
19.216
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

32.005
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

Br
Bpin

12-sub

7.260
2.220
2.208
2.195
2.026
2.014
2.009
2.002
1.995
1.980
1.690
1.278
2.00
4.17
2.23
12.52
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

84.261
77.414
77.160
76.906
40.081
24.553
23.813
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

31.340
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

Br
Bpin

13-sub

7.260
2.249
2.232
1.944
1.937
1.919
1.900
1.790
1.780
1.770
1.760
1.749
1.662
1.641
1.583
1.565
1.559
1.553
1.542
1.534
1.346
1.331
1.313
1.289
This peak belongs to staring material
1.346
1.331
1.313
1.289
2.23
12.60
1.35
1.25
1.15
f1 (ppm)
2.00
2.10
2.13
2.19
2.23
12.60
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

84.149
77.414
77.160
76.906
38.890
25.409
24.898
24.533
These peaks belongs to staring material
f1 (ppm)

31.169
f1 (ppm)

Br
Me
Bpin
Me

14-sub

7.260
2.042
2.027
2.013
1.999
1.992
1.984
1.977
1.970
1.962
1.948
1.934
1.920
1.727
1.277
0.989
0.975
0.960
2.00
3.00
12.22
3.00
f1 (ppm)

84.288
77.414
77.160
76.906
35.556
26.766
24.616
24.513
11.353
f1 (ppm)

Br
Bpin

92-sub

7.260
2.388
2.384
2.372
2.368
2.360
2.355
2.344
2.339
2.181
2.176
2.161
2.156
2.153
2.147
2.132
2.127
1.710
1.705
1.593
1.583
1.576
1.573
1.563
1.560
1.557
1.548
1.540
1.412
2.00
1.93
2.28
4.34
2.20
12.74
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

84.142
77.414
77.160
76.905
41.363
27.954
25.058
24.516
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

31.175
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

Cl
nBu
Bpin

7-Cl

7.260
3.418
3.405
3.402
3.389
1.822
1.816
1.804
1.361
1.359
1.349
1.344
1.329
0.901
0.887
1.00
1.97
0.95
3.03
12.49
3.20
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

84.483
77.415
77.160
76.906
33.893
29.626
24.739
24.714
22.360
14.102
f1 (ppm)

31.378
f1 (ppm)

Cl
Bpin

15-sub

7.260
5.861
5.855
5.848
5.841
5.827
5.820
5.813
5.807
5.793
5.159
5.156
5.125
5.121
5.106
5.105
5.103
5.086
5.084
3.451
3.436
3.421
2.639
2.625
2.610
2.596
2.582
2.568
2.554
2.540
2.525
1.277
1.00
1.00
0.97
0.98
1.97
12.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

134.854
117.790
84.644
77.414
77.160
76.906
38.461
24.772
24.720
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

31.460
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

Me
Me
Bpin
S2
7.260
5.155
5.151
5.148
5.144
5.140
5.137
2.344
2.329
2.323
2.316
2.308
2.294
2.244
2.201
2.195
2.173
2.167
2.161
2.155
2.124
2.118
2.072
2.067
2.062
2.050
2.047
2.039
2.033
2.029
2.018
2.012
2.008
2.004
1.994
1.991
1.980
1.976
1.255
1.248
1.243
1.237
1.228
1.217
1.210
1.204
1.137
1.116
0.871
0.858
0.850
0.838
0.831
0.824
0.819
0.803
0.786
0.780
1.00
0.94
1.97
4.05
15.25
1.25
5.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

150.298
114.366
83.040
77.477
77.160
76.842
46.110
41.110
38.054
31.716
31.319
30.940
26.491
25.012
24.946
21.274
f1 (ppm)

Me
Me
Bpin
Cl

16-sub

7.260
5.230
5.227
5.224
5.222
5.220
5.217
5.214
3.430
3.417
3.401
2.364
2.358
2.353
2.347
2.341
2.336
2.330
2.325
2.260
2.227
2.225
2.191
2.188
2.186
2.156
2.153
2.151
2.107
2.104
2.095
2.081
2.068
2.019
2.015
2.008
2.004
1.994
1.892
1.879
1.874
1.866
1.861
1.858
1.852
1.845
1.842
1.835
1.831
1.826
1.823
1.281
1.262
1.151
1.134
1.118
0.823
0.805
1.00
0.93
1.08
2.30
4.21
1.97
12.06
3.04
1.17
3.16
f1 (ppm)

147.217
147.100
117.000
116.936
84.502
84.496
77.414
77.160
76.906
45.966
45.876
40.957
38.132
38.081
34.626
34.578
31.921
31.864
31.824
31.808
31.415
26.450
24.754
24.743
24.723
21.368
21.286
f1 (ppm)

31.233
f1 (ppm)

CN
Bpin

S8

7.260
1.981
1.949
1.715
1.707
1.698
1.689
1.680
1.671
1.664
1.654
1.644
1.623
1.611
1.601
1.591
1.584
1.571
1.566
1.555
1.541
1.530
1.523
1.513
1.503
1.492
1.487
1.239
1.214
1.206
1.192
1.182
1.173
1.161
1.151
1.141
1.130
1.119
0.808
0.789
0.770
2.00
10.08
12.37
2.16
1.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

124.035
83.209
77.478
77.160
76.842
43.334
39.156
35.811
25.638
24.979
23.201
19.096
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

CN
Cl
Bpin

18-sub

7.260
3.434
3.421
3.419
3.405
1.977
1.952
1.723
1.718
1.709
1.704
1.695
1.688
1.622
1.615
1.597
1.534
1.532
1.523
1.284
1.236
1.218
1.211
1.00
2.42
1.95
4.69
4.15
2.45
12.15
2.09
f1 (ppm)

123.675
84.657
77.414
77.160
76.905
40.051
39.081
35.803
35.735
34.104
25.555
24.950
24.755
24.708
23.172
22.351
f1 (ppm)

Me
Me
Cl
EtO2C
Bpin

19-sub

7.260
4.130
4.112
4.095
4.077
3.419
3.400
3.382
1.824
1.821
1.804
1.785
1.778
1.764
1.567
1.554
1.538
1.534
1.523
1.505
1.494
1.276
1.258
1.253
1.241
1.236
1.223
2.34
1.00
1.96
3.03
12.54
4.12
6.15
f1 (ppm)

177.971
84.541
77.477
77.160
76.842
60.395
42.257
40.130
34.565
25.252
25.205
24.752
14.391
f1 (ppm)

O
O
Bpin
MeO

S19

8.010
8.003
7.998
7.986
7.981
7.974
7.260
6.916
6.910
6.904
6.892
6.887
6.880
4.271
4.254
4.237
3.851
1.899
1.882
1.870
1.863
1.860
1.854
1.842
1.825
1.243
0.923
0.903
0.883
1.91
1.97
2.00
2.97
2.01
12.11
2.01
f1 (ppm)

166.571
163.342
131.706
123.182
113.640
83.295
77.478
77.160
76.842
66.541
55.540
24.962
23.493
f1 (ppm)

Cl
N
Bpin

20-sub

8.113
8.098
7.481
7.479
7.465
7.451
7.449
7.423
7.406
7.260
7.250
7.248
7.234
7.220
7.219
4.362
4.347
4.332
3.465
3.452
3.450
3.437
2.092
2.079
2.032
1.985
1.972
1.967
1.962
1.953
1.941
1.232
2.02
2.08
2.03
2.01
2.05
1.00
4.13
12.29
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

140.430
125.767
123.013
120.488
118.964
108.712
84.673
77.414
77.160
76.905
42.671
31.717
26.824
24.700
24.673
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

31.107
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

Bpin
F
F
Cl

21-sub

7.260
3.482
3.472
3.460
3.451
2.075
2.069
2.062
2.055
1.846
1.826
1.748
1.743
1.733
1.725
1.719
1.697
1.688
1.680
1.673
1.663
1.653
1.281
1.268
1.00
2.21
1.95
5.35
13.22
1.25
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

125.653
123.747
123.728
121.822
84.650
77.414
77.160
76.905
39.420
39.401
33.791
33.611
33.587
33.408
33.383
33.202
33.107
29.491
29.415
27.589
27.512
24.712
24.699
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

-91.462
-91.961
-101.869
-102.369
-55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130
f1 (ppm)

31.263
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

Bpin
S

S17

7.260
7.218
7.210
7.205
7.198
6.966
6.964
6.951
6.945
6.942
6.938
6.935
2.783
2.763
2.743
1.217
1.172
1.152
1.132
1.00
2.04
2.06
12.12
2.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

145.005
128.328
125.102
119.546
83.239
77.478
77.160
76.842
24.925
24.667
f1 (ppm)

Cl
Bpin
S

22-sub

7.260
7.255
7.249
7.246
7.240
6.985
6.984
6.982
6.959
6.957
6.950
6.947
3.427
3.415
3.411
3.398
2.843
2.830
2.816
2.137
2.122
2.118
2.109
2.105
1.02
1.09
1.12
1.00
2.05
1.95
12.26
f1 (ppm)

141.366
128.410
125.566
120.867
84.617
77.414
77.160
76.906
34.865
27.792
24.756
24.748
f1 (ppm)

31.675
f1 (ppm)

Me
Bpin
H
Cl
Me
Me

25-sub

The small peaks belong to the minor diastereomer and starting material

CO2Me
Bpin

S23

7.260
3.612
1.758
1.743
1.727
1.489
1.473
1.458
1.223
0.660
3.00
6.15
6.02
12.13
1.98
f1 (ppm)

178.928
82.949
77.414
77.160
76.906
51.666
38.727
32.771
29.587
28.988
25.019
f1 (ppm)

Me
Me
O
Bpin
Me
Me
Cl

26-sub

7.260
7.007
6.992
6.660
6.645
6.609
3.939
3.920
3.908
3.906
3.895
3.874
3.494
3.483
3.476
3.465
2.306
2.178
1.978
1.959
1.853
1.842
1.777
1.764
1.751
1.435
1.429
1.421
1.409
1.402
1.395
1.277
1.274
1.06
1.09
1.02
2.12
0.98
3.20
3.17
0.99
1.07
2.10
2.11
11.94
6.93
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

157.162
136.562
130.400
123.734
120.735
112.076
84.366
77.414
77.160
76.905
68.523
46.228
38.813
33.731
27.238
24.643
24.600
24.403
21.558
15.957
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

30.879
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

Me
Me
O
Bpin
Me Me

S27

7.260
7.012
6.997
6.661
6.646
6.634
3.934
3.920
3.907
2.315
2.186
1.799
1.785
1.779
1.775
1.766
1.753
1.449
1.440
1.431
1.424
1.415
1.251
1.010
1.00
1.03
0.95
1.99
2.99
3.01
1.99
1.95
12.06
5.93
1.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

157.295
136.512
130.340
123.737
120.600
112.110
82.889
77.414
77.160
76.905
68.874
40.995
32.183
29.544
25.020
24.928
21.560
15.938
f1 (ppm)

Ph
Bpin
Cl

80

7.268
7.260
7.253
7.238
7.170
7.156
7.146
7.131
7.123
7.121
7.107
3.144
3.128
3.108
2.022
2.012
2.004
1.996
1.986
1.579
1.571
1.562
1.312
1.273
1.263
1.145
1.138
1.093
1.082
1.075
2.25
3.14
1.00
1.09
1.18
5.98
6.61
1.08
1.07
f1 (ppm)

141.909
141.779
128.349
126.502
125.909
125.891
84.635
84.616
77.414
77.160
76.906
26.255
26.081
24.708
24.685
24.660
24.145
16.212
15.975
f1 (ppm)

30.863
f1 (ppm)

Cl
MeO
Bpin

96-sub

7.260
3.446
3.429
3.409
3.396
3.384
3.317
1.908
1.853
1.834
1.824
1.814
1.808
1.795
1.695
1.217
1.03
1.98
3.00
0.98
2.13
1.16
12.20
f1 (ppm)

84.533
77.415
77.160
76.906
72.221
58.622
30.889
27.445
24.757
24.719
f1 (ppm)

Cl
Ph
Bpin

97-sub

7.303
7.288
7.273
7.260
7.217
7.212
7.203
7.196
7.181
3.433
3.418
3.403
2.846
2.832
2.129
2.114
2.099
1.287
2.00
2.95
1.00
1.04
1.01
1.98
11.82
f1 (ppm)

141.233
128.772
128.549
126.140
84.595
77.414
77.160
76.906
35.836
33.443
24.757
24.744
f1 (ppm)

31.566
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

Cl
Bpin

98-sub

7.260
2.910
2.890
1.289
1.270
1.262
1.248
1.235
0.681
0.665
0.651
0.396
0.394
0.387
0.384
1.00
12.00
1.19
1.99
2.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

84.501
77.414
77.160
76.906
24.696
24.690
15.174
6.483
6.134
f1 (ppm)

30.638
f1 (ppm)

Cl
Bpin
O

99-sub

7.260
4.014
4.006
3.989
3.985
3.981
3.964
3.957
3.386
3.381
3.377
3.230
3.214
1.984
1.968
1.869
1.866
1.842
1.608
1.605
1.582
1.579
1.489
1.479
1.463
1.454
1.445
1.437
1.411
2.00
1.99
1.00
1.05
1.03
1.21
2.17
12.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

84.588
77.414
77.160
76.906
68.015
67.755
38.899
30.789
30.686
24.764
24.726
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Ph
B
O
O
Me
Me
Me

S37

7.277
7.260
7.247
7.230
7.216
7.168
7.154
7.140
4.264
4.260
4.246
4.243
2.786
2.770
2.753
2.350
2.346
2.341
2.333
2.328
2.322
2.316
2.312
2.304
2.299
2.294
2.176
2.172
2.163
2.154
2.150
2.142
2.137
2.044
2.034
2.022
1.905
1.899
1.893
1.888
1.883
1.877
1.871
1.841
1.837
1.831
1.812
1.808
1.801
1.552
1.364
1.281
1.207
1.190
1.174
1.019
0.997
0.837
4.56
1.04
1.00
2.00
1.00
1.01
1.01
1.00
1.02
2.97
3.02
2.01
1.01
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

144.551
128.349
128.144
125.656
85.684
77.827
77.414
77.160
76.905
51.392
39.643
38.261
35.594
30.247
28.803
27.222
26.519
24.145
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Cl
Ph
B
O
O
Me
Me
Me

101-sub

36-sub

7.579
7.565
7.408
7.393
7.380
7.378
7.299
7.284
7.270
7.260
2.918
2.671
2.646
1.997
1.887
1.862
1.794
1.771
2.00
1.99
0.99
1.96
1.96
1.00
3.97
1.43
5.04
f1 (ppm)

144.250
128.838
127.564
125.176
79.723
77.414
77.160
76.905
38.254
37.301
35.155
33.979
27.279
26.896
f1 (ppm)

Cl
Me

38-sub

7.260
6.782
6.774
6.770
6.763
6.666
6.664
6.573
6.572
6.556
4.889
4.872
4.855
1.789
1.772
3.03
1.03
2.05
1.01
1.00
2.96
f1 (ppm)

152.065
151.410
150.706
150.610
142.950
128.707
126.329
117.850
117.795
116.955
115.953
77.477
77.160
76.842
59.679
26.196
f1 (ppm)

Me
Me
Cl
Me
tBu

40--sub

7.338
7.334
7.260
7.126
7.122
5.245
5.228
5.211
5.194
3.015
2.998
2.976
2.958
2.939
2.924
2.907
2.905
2.888
2.868
2.865
2.849
1.961
1.957
1.956
1.889
1.268
1.00
1.01
1.02
2.07
2.00
3.01
9.06
6.10
f1 (ppm)

153.096
150.541
137.672
137.409
120.747
119.080
77.477
77.160
76.842
57.208
44.155
41.439
35.015
31.748
28.886
28.857
27.875
25.471
f1 (ppm)

Cl
O

42-sub

7.307
7.303
7.287
7.283
7.260
7.229
7.225
7.211
7.208
7.205
7.190
7.186
6.939
6.936
6.920
6.917
6.901
6.898
6.848
6.828
5.251
5.243
5.235
4.508
4.503
4.480
4.475
4.450
4.445
4.363
4.360
4.355
4.353
4.345
4.342
4.335
4.332
4.327
4.324
4.317
2.527
2.517
2.507
2.500
2.497
2.490
2.487
2.480
2.470
2.460
2.450
2.331
2.323
2.318
2.310
2.294
2.286
2.281
1.00
1.01
1.00
1.01
1.00
1.02
1.03
1.02
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

154.284
130.839
130.357
122.234
120.831
117.478
77.478
77.160
76.843
61.791
53.131
32.149
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Cl
NBoc

43-sub

7.282
7.278
7.260
7.248
7.241
7.231
7.226
7.220
7.206
7.190
5.346
5.335
4.722
4.685
4.609
4.572
4.549
4.511
4.500
4.462
4.386
4.368
4.330
4.237
4.201
3.833
3.797
3.778
3.773
3.743
3.713
3.709
3.693
1.359
4.16
1.00
2.08
1.28
1.03
2.03
9.45
f1 (ppm)

155.113
139.916
139.510
131.004
130.568
129.748
129.662
128.917
128.436
127.632
127.566
79.925
79.877
77.478
77.160
76.842
65.272
65.089
51.688
51.191
44.883
44.509
36.511
35.799
28.536
28.481
f1 (ppm)

Cl
Me
S

44-sub

7.952
7.936
7.883
7.867
7.460
7.452
7.450
7.437
7.436
7.421
7.419
7.403
7.402
7.387
7.373
7.260
5.224
5.210
5.196
2.364
2.349
2.334
2.322
2.319
2.307
2.304
2.290
1.148
1.133
1.119
1.01
1.02
1.01
1.03
1.02
1.00
2.00
3.01
f1 (ppm)

140.795
137.103
136.333
124.808
124.341
124.142
123.124
122.415
77.414
77.160
76.906
59.303
31.370
12.020
f1 (ppm)

Cl
Me
Me
MeO
N

46-sub

8.058
8.052
7.627
7.620
7.605
7.599
7.260
6.752
6.731
4.610
4.591
3.930
2.261
2.244
2.228
2.211
2.209
2.194
2.192
2.175
2.158
2.142
1.115
1.099
0.871
0.854
1.00
1.01
1.01
1.01
3.04
1.02
2.99
2.98
f1 (ppm)

164.026
145.670
137.897
129.669
111.107
77.478
77.160
76.843
67.922
53.659
36.725
20.040
19.865
f1 (ppm)

Cl
Ph
N
OMe

47-sub

8.156
8.150
7.408
7.406
7.365
7.346
6.745
6.109
3.953
1.00
1.03
2.02
2.32
1.35
1.04
1.01
3.07
f1 (ppm)

163.808
145.544
140.305
138.915
130.245
128.837
128.468
127.679
111.367
77.478
77.160
76.842
61.687
54.048
f1 (ppm)

Cl
Me
CO2Me
S

50-sub

7.542
7.527
7.500
7.493
7.484
7.477
7.438
7.436
7.422
7.420
7.260
7.252
7.249
7.245
7.241
7.237
7.222
7.160
7.158
7.145
5.832
5.820
5.813
3.980
3.974
3.951
3.945
3.750
3.745
3.731
3.726
3.721
3.716
3.703
3.690
3.686
3.676
3.649
3.647
1.485
1.484
1.471
1.470
1.03
1.01
1.01
2.03
2.01
1.00
0.99
2.09
3.10
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

174.742
174.718
141.093
141.033
140.081
139.436
139.406
134.604
133.808
133.258
133.224
132.040
131.989
131.892
130.480
130.295
128.330
127.859
127.849
126.600
126.396
77.414
77.160
76.906
60.340
60.311
52.285
45.182
45.108
42.309
42.270
18.649
18.606
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Me
Me
MeO
Cl

102-sub

7.293
7.277
7.260
7.169
7.168
7.156
7.153
6.837
6.836
6.833
6.821
6.818
6.815
3.834
1.987
0.97
2.00
1.05
3.14
5.90
f1 (ppm)

159.516
148.014
129.340
117.892
112.612
112.197
77.414
77.160
76.906
69.586
55.427
34.393
f1 (ppm)

Cl
Ph
Cy

105-sub

7.365
7.344
7.333
7.322
7.306
7.299
7.295
7.285
7.273
7.260
4.626
4.605
2.217
2.185
1.922
1.901
1.893
1.884
1.873
1.865
1.856
1.844
1.835
1.822
1.814
1.805
1.781
1.664
1.656
1.652
1.464
1.432
1.288
1.280
1.272
1.256
1.248
1.240
1.225
1.217
1.195
1.188
1.180
1.157
1.145
1.136
1.115
1.106
1.094
1.085
1.064
1.055
0.964
0.956
0.934
0.926
0.904
0.895
4.96
1.00
1.01
2.06
2.04
1.03
4.08
1.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

141.079
128.470
128.064
127.690
77.478
77.160
76.843
69.976
45.818
30.600
30.435
26.277
26.086
26.026
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Cl

108-sub

7.459
7.454
7.444
7.294
7.282
7.273
7.272
7.263
7.260
7.254
7.241
5.463
5.454
5.446
5.438
3.250
3.231
3.211
3.192
3.173
2.950
2.940
2.930
2.920
2.910
2.900
2.890
2.880
2.666
2.648
2.630
2.613
2.612
2.594
2.576
2.439
2.430
2.420
2.411
2.403
2.395
2.385
2.376
2.366
1.02
3.20
1.00
1.02
1.02
1.02
1.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

143.473
143.226
128.985
127.174
125.108
124.930
77.477
77.160
76.842
63.321
37.060
30.445
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Cl
S

109-sub

7.292
7.288
7.273
7.269
7.260
7.172
7.168
7.154
7.152
7.149
7.135
7.131
7.118
7.114
7.098
7.094
7.063
7.059
7.043
7.041
7.040
7.026
7.022
5.333
5.325
5.317
3.656
3.649
3.624
3.617
3.592
3.585
2.909
2.906
2.898
2.889
2.887
2.866
2.857
2.638
2.636
2.629
2.628
2.609
2.602
2.599
2.592
2.591
2.589
2.412
2.404
2.396
2.380
2.375
2.372
2.367
2.364
2.335
0.99
2.05
0.99
0.97
1.00
1.01
1.01
1.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

132.939
132.315
131.714
129.044
126.855
124.364
77.478
77.160
76.842
57.034
31.298
21.592
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Cl
Cl
Me
Me
O
O
O
iPr

112-sub

7.340
7.332
7.325
7.317
7.312
7.305
7.297
7.292
7.290
7.260
7.242
7.235
7.230
7.218
7.213
7.206
6.809
6.804
6.793
5.116
5.100
5.085
5.069
5.053
5.038
5.022
1.587
1.210
1.194
4.03
2.06
2.09
1.00
1.04
6.47
6.09
f1 (ppm)

173.614
155.682
139.874
134.004
133.944
129.270
128.774
128.762
118.720
79.321
77.478
77.160
76.842
69.164
63.340
25.509
25.495
21.669
f1 (ppm)

Ph
Cl

53-sub

7.507
7.503
7.497
7.490
7.486
7.483
7.476
7.409
7.405
7.400
7.388
7.384
7.373
7.369
7.363
7.359
7.355
7.351
7.344
7.337
7.319
5.579
5.475
5.473
4.489
4.487
2.05
3.24
1.00
1.01
2.06
f1 (ppm)

144.119
137.825
128.671
128.386
126.282
116.927
77.477
77.160
76.842
46.699
f1 (ppm)

Cl
Me
TIPS

59-sub

7.260
4.547
4.531
4.515
2.010
1.991
1.975
1.973
1.957
1.939
1.130
1.111
1.093
1.077
1.074
1.00
1.98
3.71
21.34
f1 (ppm)

105.320
87.820
77.478
77.160
76.842
50.505
32.816
18.699
11.270
10.611
f1 (ppm)

Cl
Ph
nBu

60-sub

7.322
7.318
7.314
7.303
7.295
7.285
7.260
7.229
7.221
7.219
7.213
7.202
7.200
7.199
4.535
4.530
4.524
4.518
4.513
4.508
4.501
4.496
4.491
2.875
2.857
2.837
2.268
2.263
2.245
1.548
1.521
1.503
0.928
0.910
2.05
3.05
1.00
2.00
4.03
2.17
1.96
3.09
f1 (ppm)

140.594
128.690
128.666
126.345
87.931
78.521
77.477
77.160
76.842
48.988
41.294
32.533
30.663
22.072
18.643
13.711
f1 (ppm)

Cl
Me
Me
MeO

61-sub

7.260
4.579
4.573
4.568
4.560
4.555
4.549
4.542
4.536
4.531
3.515
3.498
3.480
3.368
2.537
2.531
2.519
2.514
1.833
1.825
1.818
1.814
0.918
0.916
1.00
2.03
3.02
1.99
1.02
2.04
6.06
f1 (ppm)

83.707
79.974
77.478
77.160
76.842
70.716
58.843
48.529
48.000
25.810
22.229
22.036
20.211
f1 (ppm)

Cl
Ph
SiMe3

63-sub

7.320
7.317
7.305
7.294
7.290
7.260
7.255
7.252
7.239
7.238
7.224
7.221
7.219
7.207
7.195
7.193
7.190
4.338
0.091
2.03
3.06
1.00
9.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

140.348
128.330
127.041
126.680
77.414
77.160
76.906
53.142
3.387
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

5.678
36 32 28 24 20 16 12 8 6 4 2 0 -4 -8 -14 -20 -26
f1 (ppm)

Br
Me
Me
SiMePh2

65-sub

7.749
7.745
7.741
7.734
7.729
7.725
7.433
7.429
7.426
7.420
7.416
7.411
7.402
7.387
7.384
7.371
7.367
7.362
7.260
1.853
0.777
3.99
6.69
6.00
2.92
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

135.765
134.115
129.812
127.915
77.478
77.160
76.843
53.947
31.495
4.813
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Cl
SiMe2Ph
MeO
N

66-sub

7.884
7.877
7.431
7.415
7.411
7.354
6.603
4.428
3.907
0.444
0.393
1.00
3.11
2.13
1.15
1.01
1.01
3.04
2.99
2.92
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

163.287
145.138
138.154
134.544
134.505
130.069
128.465
127.965
110.561
77.478
77.160
76.842
53.590
49.353
-4.928
-5.084
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Br
nBu
SiMePh2

67-sub

7.632 7.628 7.618 7.612 7.608 7.587 7.583 7.573 7.568 7.563 7.440 7.437 7.432 7.422 7.414 7.409 7.405 7.397 7.379 7.366 7.363 7.357 7.260
3.782 3.773 3.754 3.745 1.842 1.825 1.819 1.814 1.810 1.802 1.792 1.785 1.780 1.775 1.752 1.725 1.704 1.682 1.296 1.286 1.280 1.273 1.267 1.256 1.250 1.238 1.234 1.218 1.187 1.172 1.167 0.880 0.862 0.845 0.735
2.03 2.04 6.19
1.00
3.04 0.99 3.17 0.95 3.05 3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

135.160
135.135
134.715
134.541
129.857
129.833
128.090
128.021
77.478
77.160
76.842
41.965
33.427
30.988
28.978
22.616
14.155
-5.389
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Cl
Ph
SiMe2Ph

72-sub

7.407
7.393
7.392
7.380
7.368
7.338
7.324
7.309
7.260
7.240
7.225
7.210
7.193
7.178
7.173
7.164
7.091
7.076
4.481
0.445
0.344
3.09
2.08
2.06
1.08
2.05
1.00
3.00
3.29
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

139.731
135.098
134.542
129.837
128.157
127.789
127.336
126.771
77.415
77.160
76.906
52.428
-5.050
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Cl
SiMe2Ph

114-sub

7.429
7.422
7.413
7.410
7.403
7.398
7.389
7.385
7.381
7.350
7.332
7.315
7.312
7.288
7.267
7.260
7.055
7.034
6.719
6.692
6.675
6.648
5.745
5.701
5.242
5.215
4.480
0.446
0.354
3.07
2.05
1.92
1.97
1.00
1.00
1.00
1.00
2.95
3.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

139.414
136.550
136.150
135.043
134.567
129.867
127.818
127.535
126.035
113.691
77.478
77.160
76.842
52.325
-5.011
-5.026
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Br
N
Boc

13-Br

7.260
4.024
3.847
3.821
3.287
3.276
3.273
2.834
1.897
1.871
1.848
1.840
1.835
1.828
1.821
1.815
1.667
1.659
1.651
1.640
1.632
1.624
1.473
1.465
1.449
0.96
1.00
1.97
1.08
0.82
1.95
0.98
9.91
1.06
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

154.912
79.715
77.414
77.160
76.905
48.438
44.296
38.078
36.064
29.729
28.544
24.362
f1 (ppm)

Br
Ph
Me

82

7.314
7.299
7.290
7.284
7.260
7.223
7.209
7.197
7.195
4.106
4.097
4.093
4.088
4.084
4.079
4.075
4.066
2.900
2.889
2.882
2.872
2.862
2.854
2.844
2.783
2.769
2.766
2.755
2.751
2.741
2.738
2.724
2.173
2.165
2.155
2.147
2.144
2.136
2.126
2.119
2.108
2.087
2.078
2.072
2.069
2.064
2.060
2.058
2.055
2.049
2.046
2.044
2.040
2.035
2.031
2.026
1.744
1.731
2.05
2.98
1.00
1.00
1.01
1.00
1.00
2.97
f1 (ppm)

Bpin
Me
Me
SPh

3

7.32 7.32 7.31 7.30 7.27 7.27 7.26 7.26 7.24 7.15 7.14 7.13
2.90 2.88 2.87
1.64 1.63 1.62 1.61 1.61 1.60 1.59 1.59 1.59 1.58 1.40 1.40 1.39 1.38 1.37
2.03 2.41 1.02 1.99 1.96
7.35 7.30 7.25 7.20 7.15 1.60 1.50 1.40
f1 (ppm)
2.03 2.41 1.02 2.00 1.99 1.96 12.10 6.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

137.19
128.95
128.91
125.67
83.09
77.41
77.16
76.91
40.61
34.43
26.52
24.98
24.80
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

35.010
f1 (ppm)

Bpin
nBu
SPh
8
f1 (ppm)

137.15
128.99
128.90
125.69
83.03
77.41
77.16
76.91
33.89
31.56
31.10
30.81
29.03
24.93
24.90
23.09
14.23
f1 (ppm)

34.300
f1 (ppm)

Bpin
OPh

11

7.28 7.28 7.27 7.26 7.25 7.25 7.24 6.93 6.91 6.90 6.88
3.94 3.94 3.93 3.92 3.92
2.15 2.14 1.93 1.73 1.72 1.71 1.70 1.69 1.69 1.68 1.67
2.59
3.00
1.99
2.05
5.96
12.03
f1 (ppm)

159.22
129.49
120.50
114.67
83.18
77.41
77.16
76.91
68.42
36.11
30.40
26.79
24.85
18.28
f1 (ppm)

34.947
46
44
42
40
38
36
34
32
30
28
26
24
22
f1 (ppm)

Bpin
12
7.26
5.85
5.83
5.82
5.80
5.00
4.99
4.99
4.96
4.96
4.90
4.90
4.90
4.88
4.88
4.88
2.03
2.01
2.01
2.01
2.00
2.00
1.99
1.99
1.99
1.98
1.82
1.81
1.79
1.78
1.62
1.61
1.60
1.60
1.59
1.58
1.57
1.56
1.55
1.54
1.54
1.53
1.53
1.53
1.52
1.51
1.51
1.51
1.47
1.46
1.45
1.44
1.43
1.28
1.27
1.26
1.24
1.24
1.23
1.9
1.7
1.5
1.3
f1 (ppm)
1.00
1.02
0.99
1.99
2.03
1.94
2.26
2.09
1.94
12.15
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

139.93
113.83
83.04
77.41
77.16
76.91
38.31
35.45
32.52
25.41
24.85
f1 (ppm)

35.157
f1 (ppm)

OH
N
Boc

13

7.260
3.961
3.958
3.954
3.935
3.928
3.821
2.829
2.622
2.600
2.580
1.589
1.583
1.573
1.566
1.549
1.533
1.484
1.480
1.470
1.450
1.425
1.298
1.289
1.269
1.14
1.00
0.95
1.00
1.07
1.29
6.05
15.22
1.06
2.16
1.94
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

155.081
79.324
77.414
77.160
76.906
71.858
45.793
38.250
37.976
33.435
31.354
28.637
28.601
25.920
25.079
22.396
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Bpin
Me
Me
Me
Me
CO2Et

14

7.260
4.135
4.121
4.114
4.109
4.100
4.095
4.085
4.081
4.071
4.067
4.059
4.045
1.487
1.473
1.469
1.455
1.341
1.246
1.232
1.216
1.202
1.187
1.174
1.159
1.135
1.111
1.103
0.863
0.832
0.817
1.487
1.473
1.469
1.455
1.436
1.424
1.409
1.341
1.246
1.232
1.216
1.202
1.194
1.187
1.174
1.159
1.135
1.111
1.103
3.06
1.06
3.09
11.94
10.04
6.10
1.5
1.4
1.3
1.2
1.1
f1 (ppm)
2.00
3.06
1.06
3.09
11.94
10.04
6.10
2.98
2.98
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

178.24
83.02
77.41
77.16
76.91
60.23
42.37
41.84
39.68
31.73
25.38
25.17
24.98
24.94
21.32
20.94
14.41
10.19
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

34.764
f1 (ppm)

Bpin
Cl
15
f1 (ppm)

138.344
115.289
83.295
77.414
77.160
76.906
45.391
35.481
32.317
28.188
24.987
24.963
f1 (ppm)

34.139
f1 (ppm)

Me
Me
Bpin
Ph

16

7.276
7.260
7.251
7.246
7.174
7.159
7.145
5.148
5.146
2.611
2.608
2.596
2.593
2.580
2.348
2.337
2.332
2.326
2.320
2.309
2.218
2.215
2.176
2.173
2.056
2.005
1.997
1.987
1.922
1.908
1.890
1.631
1.614
1.599
1.584
1.481
1.472
1.468
1.455
1.449
1.437
1.429
1.419
1.412
1.406
1.399
1.393
1.387
1.379
1.373
1.361
1.256
1.236
1.141
1.139
1.124
1.122
0.809
2.58
2.93
1.00
1.93
1.06
2.14
1.09
1.05
2.01
1.99
4.28
3.16
11.90
1.02
0.97
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

148.91
148.83
143.03
128.52
128.33
125.64
115.69
115.63
83.00
77.41
77.16
76.91
46.03
45.89
41.04
38.07
36.77
36.75
36.35
31.84
31.81
31.41
31.24
31.22
31.19
31.18
29.30
26.52
26.51
24.99
24.97
24.95
21.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

34.322
f1 (ppm)

O
O
Me
Me
Bpin
O
Me

17

7.260
5.821
4.112
4.098
4.097
4.083
4.077
4.071
4.063
4.050
4.034
4.023
4.018
4.007
4.003
3.991
3.480
3.475
3.465
3.460
3.449
3.445
2.563
2.548
2.533
2.234
1.791
1.771
1.665
1.661
1.653
1.648
1.635
1.620
1.604
1.589
1.578
1.544
1.533
1.521
1.517
1.506
1.499
1.494
1.488
1.477
1.443
1.391
1.388
1.334
1.330
1.244
1.237
1.163
1.159
1.146
1.134
1.130
2.00
1.99
0.99
1.96
2.99
0.39
3.63
2.30
3.05
2.99
12.33
0.69
0.40
f1 (ppm)

154.65
154.58
150.17
150.15
108.73
108.72
105.84
105.32
105.28
83.22
77.41
77.16
76.91
76.06
75.95
69.92
69.86
34.79
31.22
28.39
28.36
27.62
27.60
27.18
27.16
26.07
26.00
25.04
25.03
14.99
13.85
f1 (ppm)

34.243
f1 (ppm)

CN
Bpin
F

18

7.260
4.485
4.472
4.460
4.390
4.377
4.365
1.965
1.950
1.938
1.742
1.735
1.731
1.714
1.702
1.694
1.686
1.680
1.674
1.660
1.652
1.647
1.640
1.621
1.618
1.596
1.593
1.590
1.499
1.495
1.484
1.472
1.464
1.459
1.455
1.451
1.435
1.431
1.424
1.417
1.407
1.392
1.380
1.369
1.360
1.244
1.216
1.204
1.197
1.190
1.183
1.176
1.171
1.159
1.152
1.011
1.001
0.990
1.99
2.09
7.29
10.29
12.49
3.02
0.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

123.921
84.902
83.597
83.197
77.414
77.160
76.906
40.920
39.142
35.923
35.809
31.508
31.016
30.863
30.708
25.642
24.989
24.936
24.890
24.846
24.110
23.227
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

-217.951
-218.004
-218.052
-218.104
-218.157
-218.205
-218.258
-212.5
-214.0
-215.5
-217.0
-218.5
-220.0
-221.5
-223.0
f1 (ppm)

34.094
47
45
43
41
39
37
35
33
31
29
27
25
23
21
19
f1 (ppm)

Me
Me
Bpin
OMe
EtO2C

19

7.260
4.108
4.094
4.079
4.065
3.354
3.340
3.327
3.309
1.565
1.558
1.553
1.545
1.534
1.501
1.485
1.477
1.469
1.427
1.409
1.397
1.383
1.369
1.363
1.350
1.225
1.131
0.959
2.46
2.00
4.37
17.33
5.98
0.99
1.6
1.4
1.2
1.0
f1 (ppm)
2.00
2.01
2.88
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

178.204
83.032
77.414
77.160
76.906
73.288
60.253
58.597
42.285
41.122
29.293
27.776
25.303
25.184
24.953
24.938
14.393
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

35.748
f1 (ppm)

Bpin
N
OMe
20
f1 (ppm)

140.52
125.63
122.92
120.41
118.76
108.84
83.19
77.41
77.16
76.91
73.16
58.59
43.38
29.22
29.10
28.53
27.87
24.97
24.87
f1 (ppm)

33.920
f1 (ppm)

F
F
Bpin
O
Me

21

7.260
5.823
2.564
2.559
2.549
2.544
2.534
2.529
2.237
2.068
2.060
2.054
2.047
2.040
2.034
2.027
2.020
2.013
1.806
1.780
1.773
1.745
1.740
1.714
1.707
1.681
1.671
1.655
1.642
1.633
1.630
1.626
1.620
1.615
1.606
1.593
1.589
1.579
1.573
1.438
1.425
1.413
1.407
1.395
1.387
1.381
1.375
1.369
1.363
1.239
1.237
1.201
1.179
1.084
1.079
1.072
1.066
1.054
2.00
2.00
2.99
2.31
1.22
2.35
3.30
3.20
1.92
12.00
2.04
1.14
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

154.672
150.156
125.968
124.061
122.139
105.849
105.292
83.142
77.414
77.160
76.906
37.302
35.270
33.709
33.687
33.669
33.508
33.491
31.274
29.512
29.437
29.008
28.933
28.431
27.748
24.986
13.852
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

-91.198
-91.696
-101.531
-102.024
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170
f1 (ppm)

-33.779
70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -20 -30 -40
f1 (ppm)

Bpin
SPh
S

22

2.06
2.55
1.00
1.02
1.01
1.00
7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)
1.10
3.19
2.12
1.85 1.75 1.65 1.55
f1 (ppm)
2.06
2.55
1.00
1.02
1.01
1.00
2.02
2.00
1.10
3.19
2.12
2.10
1.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
143.24
137.05
129.04
128.93
128.46
125.75
125.18
120.03
83.19
77.41
77.16
76.91
33.87
32.34
30.54
29.90
28.88
24.95
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

34.436
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

O
O
MeO
Bpin
N

23

8.000 7.996 7.986 7.982 7.260 6.920 6.916 6.907 6.903 6.638 6.634 6.630 6.124 6.120 6.116 4.265 4.252 4.239 3.869 3.862 3.855 3.840 1.810 1.795 1.790 1.782 1.778 1.776 1.768 1.763 1.756 1.748 1.744 1.735 1.732 1.726 1.723 1.713 1.554 1.543 1.504 1.492 1.484 1.477 1.472 1.466 1.458 1.447 1.434 1.397 1.385 1.377 1.359 1.234 1.058 1.052 1.040 1.028
2.03 2.03 2.04 2.05 2.00 5.05 4.01 1.40 2.07 1.08 12.62 1.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

166.53
163.37
131.70
123.12
120.56
113.68
107.88
83.27
77.41
77.16
76.91
65.06
55.56
49.92
31.19
28.43
27.79
24.97
f1 (ppm)

33.662
f1 (ppm)

MeO2C
O
Me
Bpin

24

7.260
5.811
3.618
2.541
2.526
2.511
2.229
1.746
1.730
1.714
1.645
1.630
1.624
1.620
1.610
1.595
1.590
1.577
1.563
1.559
1.466
1.456
1.445
1.439
1.435
1.429
1.424
1.420
1.413
1.407
1.402
1.388
1.383
1.359
1.354
1.345
1.340
1.334
1.327
1.320
1.311
1.301
1.296
1.289
1.284
1.276
1.262
1.251
1.236
1.226
1.071
1.067
1.044
1.039
0.970
0.965
0.950
0.935
2.00
3.10
1.99
3.00
6.24
2.63
0.52
5.10
4.43
12.66
1.01
1.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

178.844
154.662
150.124
105.824
105.278
83.080
77.414
77.160
76.905
51.690
39.063
33.176
31.163
30.732
28.721
28.396
27.658
25.034
13.849
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

25

82.91
82.83
77.41
77.16
76.91
73.44
73.41
58.65
58.53
44.11
40.87
40.32
35.71
33.56
30.45
26.54
25.30
25.23
24.90
24.68
24.67
24.60
23.03
21.80
21.13
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

35.499
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

Me
Me
O
Me
Me
Bpin
Me
Me
CO2Et

26

7.260
7.001
6.986
6.652
6.637
6.607
4.120
4.113
4.109
4.098
4.095
4.084
4.081
4.070
4.066
4.059
3.901
3.888
3.875
2.304
2.174
1.766
1.753
1.747
1.734
1.720
1.706
1.701
1.568
1.562
1.548
1.541
1.521
1.508
1.493
1.392
1.387
1.375
1.370
1.363
1.347
1.342
1.328
1.314
1.308
1.294
1.230
1.217
1.141
0.982
0.970
0.966
0.958
0.955
0.939
0.934
0.866
0.864
1.747
1.734
1.720
1.568
1.562
1.548
1.541
1.521
1.508
1.493
1.363
1.347
1.342
1.328
1.314
1.308
1.230
1.217
1.141
1.97
1.13
2.13
3.05
19.13
5.91
1.8
1.6
1.4
1.2
f1 (ppm)
1.01
1.02
1.01
2.00
2.03
3.09
3.06
1.97
1.13
2.13
3.05
19.13
5.91
1.10
5.95
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

178.184
157.259
136.529
130.359
123.739
120.637
112.096
83.006
77.414
77.160
76.906
68.877
60.266
44.320
42.297
41.172
38.750
34.415
33.368
27.217
25.335
25.198
25.052
24.984
24.539
24.481
21.568
15.965
14.398
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

35.028
57
54
51
48
45
42
39
36
33
30
27
24
f1 (ppm)

OMe
Bpin
H
Me
Me
Me
Me

27

7.260
7.169
7.153
6.985
6.969
6.880
3.370
3.358
3.345
3.331
3.325
3.308
2.883
2.870
2.848
2.833
2.824
2.819
2.806
2.269
2.244
1.701
1.696
1.680
1.673
1.656
1.649
1.634
1.629
1.621
1.607
1.596
1.583
1.577
1.570
1.450
1.439
1.425
1.396
1.374
1.371
1.352
1.340
1.271
1.261
1.245
1.237
1.230
1.227
1.222
1.216
1.204
1.196
1.183
1.167
1.155
0.895
0.885
0.96
1.03
1.00
1.98
2.91
3.03
1.02
0.98
5.59
6.22
22.98
1.11
3.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

148.019
147.932
145.498
145.463
135.147
135.102
126.936
126.921
124.315
124.285
123.829
123.816
83.003
77.415
77.160
76.906
73.287
73.207
58.641
58.614
50.212
47.524
46.187
37.773
36.491
33.596
30.479
29.272
25.355
25.061
25.010
24.981
24.925
24.154
24.137
f1 (ppm)

34.484
f1 (ppm)

Bpin
Ph

28

7.279
7.276
7.263
7.260
7.253
7.249
7.182
7.178
7.168
7.167
7.161
7.146
2.622
2.607
2.591
1.647
1.631
1.616
1.491
1.475
1.460
0.816
0.801
2.42
3.10
2.00
2.02
2.01
12.24
1.97
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

143.07
128.53
128.33
125.63
83.04
77.41
77.16
76.91
35.93
34.35
24.97
23.93
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

34.054
f1 (ppm)

Bpin
29
f1 (ppm)

82.96
77.41
77.16
76.91
36.29
35.21
25.27
24.96
f1 (ppm)

33.819
f1 (ppm)

Bpin
nBu
Cl

32

7.260
3.527
3.514
3.500
1.814
1.801
1.797
1.787
1.783
1.774
1.769
1.760
1.755
1.752
1.741
1.739
1.550
1.539
1.529
1.525
1.511
1.497
1.482
1.478
1.464
1.446
1.430
1.419
1.403
1.389
1.379
1.365
1.351
1.336
1.324
1.318
1.310
1.298
1.294
1.286
1.283
1.278
1.275
1.270
1.264
1.258
1.253
1.241
0.997
0.984
0.979
0.967
0.955
0.950
0.938
0.889
0.875
0.861
1.783
1.774
1.769
1.755
1.752
1.511
1.497
1.482
1.298
1.294
1.286
1.283
1.278
1.275
1.270
1.264
1.258
1.253
1.241
2.04
2.03
1.46
1.38
4.02
12.75
1.8
1.6
1.4
1.2
f1 (ppm)
2.00
2.04
2.03
1.46
1.38
4.02
12.75
1.09
3.31
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

83.12
77.41
77.16
76.91
45.52
32.49
31.52
31.05
28.74
24.97
24.93
23.09
14.23
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

34.381
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

Bpin
Cl
OPh
nBu

35

7.26 7.26 7.24 7.24 7.24 7.23 7.23 6.91 6.90 6.88 6.87 6.85
3.92 3.90 3.89 3.50 3.48 3.47
1.70 1.69 1.69 1.68 1.67 1.67 1.48 1.46 1.46 1.44 1.36 1.32 1.27 1.25 1.24 1.22 1.21 0.88 0.87
2.40 1.05 2.01 2.00 2.01 4.02 3.99 2.12 2.27 12.14 2.17 3.16
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

159.15
129.51
120.54
114.60
83.28
77.41
77.16
76.91
68.62
46.09
34.39
31.61
30.26
29.42
27.25
25.03
24.63
23.71
14.30
f1 (ppm)

34.857
f1 (ppm)

Ph
N

36

7.326
7.310
7.296
7.274
7.260
7.182
7.168
7.153
6.482
6.074
3.619
3.605
3.590
2.344
2.120
2.095
1.898
1.855
1.831
1.728
1.703
1.679
1.656
1.646
1.640
1.632
1.623
1.552
1.528
1.384
1.376
1.368
1.361
2.09
2.37
1.05
1.98
2.00
1.96
2.00
2.04
1.07
2.09
5.17
2.18
2.23
2.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

147.076
128.106
126.918
125.248
120.420
107.786
77.415
77.160
76.906
50.199
45.820
38.943
36.991
33.918
32.890
32.697
28.394
27.358
25.057
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

S
Ph
F

37

7.360
7.344
7.329
7.260
7.255
7.239
7.217
7.202
7.188
4.372
4.360
4.348
4.277
4.265
4.253
2.707
2.684
2.567
2.558
2.529
2.512
2.483
2.472
1.954
1.949
1.542
1.087
1.081
1.072
1.064
1.055
1.039
2.05
1.92
0.98
2.00
2.02
4.15
2.08
4.36
2.07
f1 (ppm)

144.878
128.682
126.966
125.958
84.742
83.435
77.414
77.160
76.905
44.137
40.603
37.196
31.063
30.908
24.271
19.007
18.965
f1 (ppm)

-217.930
-217.984
-218.031
-218.084
-218.138
-218.185
-218.239
-215.5 -216.0 -216.5 -217.0 -217.5 -218.0 -218.5 -219.0 -219.5 -220.0 -220.5 -221.0 -221.5 -222.0
f1 (ppm)

Me
Ph

38

7.289 7.274 7.260 7.191 7.189 7.176 7.164 7.150
6.749 6.734 6.728 6.721 6.719 6.706 6.634 6.626 6.619 6.612 6.603 6.581 6.567 6.546
2.596 2.580 2.565 2.548 2.538 2.533 2.528 2.512 2.498 2.484
1.852 1.843 1.838 1.206
2.46 3.06 2.08 2.04 3.05 3.02 2.00 3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

151.700
151.479
151.220
149.023
147.862
142.625
128.522
128.415
127.988
117.283
117.087
116.760
77.414
77.160
76.906
40.151
39.665
34.023
22.270
f1 (ppm)

Me
Cl
N
OCF2H

39

7.260
7.184
7.179
7.173
7.168
7.156
7.151
7.031
7.014
6.615
6.611
6.607
6.588
6.441
6.293
6.138
6.133
6.129
3.857
3.843
3.829
3.199
3.185
3.171
3.156
3.142
3.128
1.743
1.731
1.728
1.714
1.700
1.653
1.639
1.624
1.610
1.597
1.563
1.547
1.533
1.517
1.203
2.03
1.00
1.99
1.12
1.99
2.03
1.03
1.10
1.15
2.25
3.12
f1 (ppm)

147.487
140.586
131.386
127.863
127.195
120.575
120.545
118.377
116.307
114.237
108.069
77.414
77.160
76.906
49.495
34.248
31.952
29.521
21.322
f1 (ppm)

-79.931
-80.088
f1 (ppm)

Me
Me
Me
Me
O
tBu

40

7.260
7.039
6.998
5.819
5.800
5.794
2.857
2.844
2.830
2.819
2.805
2.791
2.561
2.547
2.534
2.240
1.917
1.903
1.889
1.721
1.707
1.700
1.688
1.677
1.663
1.648
1.628
1.624
1.610
1.588
1.571
1.560
1.550
1.321
1.259
1.249
1.242
1.228
0.98
1.02
2.00
2.98
1.97
3.02
1.99
4.30
9.08
6.09
2.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

154.722
152.181
150.173
149.856
142.641
137.852
120.412
116.340
105.858
105.312
77.414
77.160
76.906
44.197
41.497
37.234
36.567
34.929
31.859
28.993
28.932
28.287
28.108
26.528
21.173
13.661
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Ph
OPh
Me
N

41

7.296 7.281 7.266 7.260 7.248 7.231 7.204 7.189 7.174 7.123 7.108 6.924 6.910 6.895 6.836 6.820 3.861 3.848 3.835 3.008 2.986 2.854 2.832 2.365 2.358 2.351 2.343 2.300 2.047 2.041 2.036 2.028 2.022 2.016 2.008 2.001 1.996 1.988 1.964 1.949 1.945 1.893 1.668 1.656 1.548 1.543 1.535 1.530 1.523 1.517 1.511 1.458 1.452 1.353 1.332 1.326 1.306 1.284
4.76 1.01 2.01 1.02 2.01 2.00 1.06 1.07 0.97 3.01 2.03 2.12 1.13 2.15 2.27 2.27
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

159.127 143.606 129.512 128.474 128.450 126.342 120.617 114.569 77.415 77.160 76.906 67.879 56.032 51.365 45.987 40.889 30.286 29.126 27.583
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

42

43

7.260
7.250
7.209
7.195
7.181
7.161
7.145
7.124
4.614
4.584
4.471
4.441
4.416
4.387
3.400
3.387
3.375
3.369
2.932
1.987
1.981
1.891
1.743
1.735
1.731
1.721
1.691
1.677
1.664
1.654
1.643
1.632
1.620
1.561
1.550
1.421
0.81
4.77
0.39
1.61
0.98
0.57
1.93
5.37
3.08
0.98
2.00
4.38
3.29
5.86
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

155.093
154.957
144.031
143.286
137.854
137.202
130.109
129.906
127.598
127.530
126.303
125.836
79.643
79.546
77.415
77.160
76.906
72.927
58.752
52.043
51.562
45.601
44.938
43.908
42.749
33.375
32.748
29.616
29.500
28.626
28.575
28.389
28.327
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Et
Ph
S

44

7.871
7.868
7.857
7.855
7.786
7.783
7.769
7.375
7.372
7.361
7.358
7.346
7.343
7.331
7.328
7.317
7.314
7.260
7.255
7.240
7.225
7.179
7.168
7.154
7.139
7.111
7.097
7.022
3.031
3.017
3.003
2.989
2.612
2.599
2.585
2.571
2.556
2.544
1.822
1.807
1.791
1.776
1.763
1.759
1.751
1.744
1.736
1.730
1.614
1.599
1.581
1.569
1.565
1.554
1.550
0.839
0.825
0.810
1.03
1.02
2.11
2.18
1.29
2.04
1.00
1.00
2.21
4.11
2.19
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

142.590
140.825
140.657
139.392
128.503
128.360
125.771
124.145
123.751
123.057
122.064
120.528
77.414
77.160
76.906
40.599
36.158
34.714
29.345
28.453
12.067
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

N
N
Cl
Ph

45

8.476
8.337
8.120
7.260
7.244
7.229
7.181
7.166
7.152
7.097
7.094
7.080
3.463
3.450
3.436
3.157
3.144
3.139
3.126
3.111
3.099
3.068
3.058
3.047
3.038
3.028
3.016
1.885
1.875
1.868
1.865
1.855
1.843
1.835
1.825
1.674
1.667
1.662
1.654
1.643
1.634
1.630
1.00
0.91
0.91
2.42
1.07
2.04
2.00
2.00
1.04
2.03
2.32
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

155.989
143.225
142.353
128.763
127.651
126.852
77.414
77.160
76.905
45.722
45.061
43.175
33.212
30.657
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Me
Me
N
MeO
N

46

47

8.060
8.055
7.277
7.260
7.221
7.207
7.174
6.665
6.648
3.897
3.864
3.848
3.833
3.387
3.375
3.362
3.298
2.104
2.097
2.088
2.081
2.072
2.066
1.548
1.533
1.520
1.518
1.505
1.00
1.01
2.64
2.01
1.07
1.01
3.09
1.01
2.05
3.03
2.02
2.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

162.905
145.824
144.495
138.309
133.175
128.697
127.825
126.477
110.866
77.414
77.166
76.906
72.624
58.715
53.465
48.000
32.180
28.226
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

N
S

48

7.87
7.85
7.72
7.70
7.39
7.38
7.38
7.37
7.36
7.36
7.36
7.34
7.34
7.33
7.33
7.26
7.05
6.65
6.65
6.15
6.14
6.14
3.93
3.91
3.90
2.87
2.86
2.84
1.90
1.89
1.87
1.79
1.78
1.77
1.76
1.75
1.75
1.73
1.10
1.07
2.32
1.04
1.95
1.94
2.00
2.06
2.15
2.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

140.65
139.04
136.37
124.32
123.97
123.06
121.73
121.41
120.62
108.11
77.41
77.16
76.91
49.56
31.50
28.24
26.41
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

MeO
F
iPr
F3C
OMe

49

7.525
7.475
7.459
7.457
7.260
7.253
7.237
6.960
6.942
6.670
6.646
3.712
3.253
3.243
3.230
3.218
2.516
2.503
2.453
2.441
1.565
1.549
1.534
1.518
1.504
1.489
1.468
1.456
1.444
1.429
1.413
1.246
0.98
1.02
1.01
1.00
1.00
3.00
2.95
3.11
2.00
4.15
6.31
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

161.653
159.702
155.390
155.311
142.283
141.712
131.090
129.201
129.144
126.861
126.739
125.603
125.590
125.560
122.482
99.080
77.414
77.160
76.906
72.562
58.645
55.831
33.023
29.485
27.309
26.688
26.675
23.031
22.975
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

-62.369
-117.268
-117.286
-117.293
-117.312
40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180
f1 (ppm)

Cl
Me
S
CO2Me

50

7.476 7.474 7.461 7.458 7.397 7.381 7.260 7.236 7.234 7.220 7.206 7.204 7.170 7.157 7.105 7.102 7.090 7.087 7.072 7.029 7.027 7.013 7.011
3.715 3.710 3.704 3.690 3.660 3.642 3.632 3.618 3.547 3.534 3.523 3.366 3.359 3.335 3.328 3.177 3.157 3.147 3.126
1.907 1.903 1.895 1.892 1.889 1.886 1.876 1.873 1.860 1.796 1.779 1.775 1.764 1.760 1.457 1.443
0.99 1.00 1.05 1.05 2.02 1.02
1.03 4.12 1.94 1.03 0.98
2.93 0.98 3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

174.862
144.971
144.953
140.590
140.562
139.901
139.842
134.874
134.044
131.749
131.397
130.170
130.119
129.202
129.164
128.025
126.389
125.606
125.588
77.414
77.160
76.906
52.246
45.222
45.087
45.025
40.769
39.378
33.735
30.375
18.582
f1 (ppm)

Ph

51

7.297
7.283
7.270
7.194
7.180
5.842
5.836
5.822
5.808
5.796
5.788
5.025
4.991
4.958
4.938
2.640
2.624
2.610
2.099
1.662
1.648
1.633
1.618
1.479
1.464
1.449
1.434
1.420
2.30
3.00
1.00
1.02
0.97
2.01
2.01
2.05
1.98
f1 (ppm)

142.84
139.02
128.54
128.39
125.76
114.54
77.41
77.16
76.91
35.96
33.79
31.11
28.70
f1 (ppm)

Me
OPh

52

7.30
7.29
7.28
7.28
7.26
7.26
6.95
6.93
6.92
6.92
6.91
6.91
6.89
4.73
4.70
3.99
3.97
3.96
2.11
2.09
2.08
1.82
1.81
1.79
1.78
1.76
1.74
1.65
1.64
1.63
1.62
1.61
1.61
1.59
f1 (ppm)

159.22
145.77
129.55
120.62
114.62
110.22
77.41
77.16
76.91
67.80
37.60
29.04
24.16
22.48
f1 (ppm)

Ph
Cl

53

7.407
7.405
7.401
7.390
7.348
7.344
7.333
7.330
7.318
7.290
7.288
7.274
7.260
5.290
5.076
5.073
3.537
3.524
3.510
2.560
2.545
2.530
1.835
1.822
1.807
1.791
1.778
1.635
1.619
1.610
1.604
1.589
1.574
2.25
2.25
1.02
1.09
1.00
2.01
2.01
2.03
2.09
f1 (ppm)

148.052
141.157
128.464
127.566
126.248
112.828
77.414
77.160
76.906
45.003
34.668
32.266
25.527
f1 (ppm)

Me
Ph
+
Me
Ph

56 57

4.77
7.15
1.00
2.75
1.00
0.99
4.76
0.99
2.77
8.89
2.69
2.10
3.00
f1 (ppm)

144.828
142.953
142.912
130.692
128.547
128.536
128.376
125.738
77.414
77.160
76.906
37.877
36.413
36.200
36.027
36.007
32.598
31.241
31.170
29.392
29.340
26.812
20.365
18.075
12.930
f1 (ppm)

OMe
TBS

58

7.260
3.408
3.396
3.383
3.328
2.274
2.260
2.246
1.686
1.601
1.587
1.584
0.073
2.09
3.12
1.95
2.05
2.17
9.32
6.17
f1 (ppm)

107.840
82.822
77.414
77.160
76.906
72.368
58.659
28.807
26.235
25.503
19.806
16.668
-4.277
f1 (ppm)

Et
SPh
(iPr)3Si

59

f1 (ppm)

136.99
129.09
128.96
125.84
111.94
81.55
77.41
77.16
76.91
34.20
34.08
33.67
28.51
27.23
18.80
11.87
11.41
f1 (ppm)

PhS
C
Et
(iPr)3Si

59'

7.338
7.322
7.282
7.267
7.260
7.252
7.172
7.158
7.143
4.831
4.824
4.818
4.811
4.804
4.798
4.791
3.011
2.997
2.986
2.972
2.959
2.945
2.934
2.920
2.054
1.976
1.962
1.862
1.848
1.158
1.144
1.134
1.128
1.115
1.103
1.062
1.048
0.990
0.975
2.05
3.18
1.06
1.04
1.00
2.04
2.01
2.10
1.97
4.30
17.19
3.26
f1 (ppm)

206.598
137.111
129.209
128.918
125.812
91.649
88.427
77.414
77.160
76.906
33.616
28.985
28.301
22.219
18.848
18.832
14.486
11.499
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

iBu
C
Ph
nBu

60

7.291
7.276
7.260
7.207
7.192
7.175
7.160
5.127
5.121
5.114
5.108
5.102
5.096
5.090
2.723
2.708
2.691
2.312
2.299
2.296
2.281
2.268
1.910
1.904
1.894
1.879
1.874
1.579
1.566
1.553
1.539
1.533
1.526
1.379
1.367
1.353
1.337
1.330
1.324
1.316
1.309
1.292
1.278
1.274
1.270
1.264
1.256
1.253
1.250
1.247
1.239
1.234
1.225
0.908
0.894
0.885
0.880
0.872
1.94
3.05
1.00
2.01
1.90
3.94
1.25
4.28
1.99
9.22
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

200.913
142.347
128.622
128.360
125.846
105.064
91.119
77.414
77.160
76.906
36.981
35.917
32.593
31.447
30.731
30.037
27.846
22.767
22.740
22.604
14.180
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

iBu
Ph
nBu

60'

7.297 7.282 7.267 7.260 7.218 7.203 7.195 7.180 7.166 2.846 2.836 2.829 2.702 2.687 2.278 2.271 2.266 2.255 2.231 2.229 2.218 2.215 2.205 2.201 1.732 1.721 1.718 1.714 1.708 1.703 1.692 1.550 1.537 1.524 1.511 1.498 1.485 1.475 1.461 1.446 1.438 1.429 1.415 1.403 1.395 1.380 1.367 1.260 1.248 1.242 1.228 0.949 0.934 0.920 0.887 0.882 0.874 0.869
1.95 2.01 1.22 1.00 0.99 1.09 1.97 2.12 4.05 0.85 5.09 1.34 3.32 3.04 3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

142.682
128.648
128.418
125.801
83.461
82.041
77.414
77.160
76.906
37.536
36.747
33.941
33.516
31.774
31.526
28.156
22.934
22.666
22.072
18.638
13.800
f1 (ppm)

MeO
MeO
C
iBu
61
+
iBu
OMe
MeO
61'

7.260
5.107
5.101
5.095
5.087
5.081
5.074
5.066
5.060
5.054
3.472
3.458
3.443
3.398
3.385
3.372
3.328
3.322
2.213
2.208
1.999
1.878
1.865
1.850
1.711
1.698
0.908
The minor peaks belongs to the alkyne product
1.00
2.12
2.24
3.16
3.25
0.25
1.93
1.95
1.99
1.99
1.31
6.27
f1 (ppm)

201.297
99.831
91.526
77.415
77.160
76.906
72.542
71.414
58.711
58.691
39.120
32.942
29.491
28.779
27.808
22.501
22.479
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Cl
C
Me
Me
iPr

62

7.260
5.151
5.146
5.139
5.133
5.128
3.587
3.584
3.582
3.574
3.571
3.568
3.561
3.558
3.555
2.107
2.099
2.093
2.085
2.080
2.078
2.067
2.063
2.029
2.027
2.016
2.014
2.002
2.000
1.924
1.914
1.910
1.899
1.896
1.886
1.883
1.881
1.367
1.357
1.352
1.343
1.338
1.329
1.315
1.302
1.288
1.027
1.017
1.015
1.004
1.002
0.975
0.973
0.961
0.959
0.924
0.910
0.895
1.00
1.96
3.00
1.10
1.96
2.18
6.31
3.02
3.51
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

198.367
198.310
110.344
110.316
100.198
100.178
77.414
77.160
76.905
45.149
45.122
31.066
30.220
28.031
22.094
21.910
20.255
12.039
11.963
f1 (ppm)

TMS
Ph
Cl

63

7.26
7.25
7.24
7.22
7.11
7.09
7.08
7.02
7.00
3.51
3.50
3.49
3.48
3.47
2.03
2.02
2.01
2.00
1.93
1.92
1.90
1.89
1.88
1.79
1.77
1.76
1.64
1.63
1.62
0.05
2.06
1.04
2.03
2.00
1.05
9.24
f1 (ppm)

143.10
128.33
127.76
124.66
77.41
77.16
76.91
45.20
36.21
32.07
26.41
2.88
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

TMS
Ph

64

7.260 7.220 7.204 7.189 7.081 7.067 7.052 7.018 7.004 2.338 2.324 2.303 2.289 2.283 1.959 1.944 1.937 1.928 1.908 1.847 1.825 1.719 1.712 1.701 1.695 1.689 1.684 1.678 1.618 1.613 1.601 1.596 1.585 1.567 1.560 1.544 1.537 1.529 1.525 1.520 1.513 1.508 1.502 1.491 1.443 1.430 1.427 1.416 1.409 1.213 1.193 1.189 1.169 0.972 0.953 0.948 0.929 0.060
2.04 1.05 1.99
1.00 1.00 1.02 1.04 3.23 1.09 1.05 1.03
8.95
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

145.626
128.221
128.050
124.309
77.414
77.160
76.905
43.993
42.768
34.428
33.472
25.695
24.274
1.167
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

SiMePh2
Ph
Me
Me

65

7.611
7.598
7.392
7.389
7.385
7.377
7.366
7.363
7.356
7.342
7.329
7.325
7.260
7.247
7.232
7.178
7.163
7.148
7.088
7.073
2.487
2.473
2.457
1.552
1.546
1.535
1.522
1.491
1.479
1.433
0.570
4.02
6.25
2.63
1.04
1.99
2.00
2.68
1.98
6.03
2.95
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

142.903
136.475
135.566
129.041
128.483
128.329
127.731
125.698
77.415
77.160
76.906
39.256
36.918
25.638
24.214
21.115
f1 (ppm)

-4.179
f1 (ppm)

SiMe2Ph
OTBS
MeO
N

66

7.754
7.749
7.384
7.381
7.378
7.368
7.365
7.357
7.352
7.346
7.343
7.340
7.329
7.314
7.301
7.298
7.260
7.067
7.062
7.050
7.045
6.592
6.575
3.898
3.506
3.497
3.493
3.485
3.480
3.473
3.465
2.142
2.135
2.117
2.110
1.685
1.676
1.670
1.659
1.657
1.651
1.439
1.433
1.426
1.419
1.414
1.295
1.282
1.275
1.268
1.263
1.255
1.248
0.848
0.244
0.211
-0.020
-0.024
0.98
5.17
0.98
1.03
2.99
2.01
1.01
1.03
1.09
1.09
1.09
9.00
3.04
3.03
6.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

162.02
145.78
138.13
137.12
134.23
130.90
129.30
127.84
110.22
77.41
77.16
76.91
62.70
53.36
32.25
32.08
26.08
25.50
18.43
-4.02
-5.05
-5.19
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (ppm)

SiMePh2
nPent
Cl

67

68

7.55
7.54
7.54
7.54
7.53
7.36
7.35
7.34
7.34
7.33
7.33
7.32
7.31
7.31
7.30
7.26
1.18
1.01
0.32
2.06
3.08
12.09
6.00
6.04
f1 (ppm)

137.83
134.81
128.85
127.44
82.84
77.41
77.16
76.91
25.03
19.92
-4.75
f1 (ppm)

35.102
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

1.303
40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35
f1 (ppm)

Bpin
Ph
Si
SiMe3
Me
Me

69

7.277
7.260
7.247
7.168
7.159
7.152
2.751
2.742
2.732
2.724
2.715
2.705
2.696
2.507
2.493
2.488
2.480
2.474
2.466
2.461
2.447
1.907
1.882
1.879
1.646
1.640
1.261
0.548
0.543
0.041
2.94
2.99
1.00
1.00
1.00
0.99
12.22
1.00
6.00
9.04
f1 (ppm)

142.88
128.67
128.36
125.72
82.90
77.41
77.16
76.91
39.88
29.31
25.48
25.05
1.43
-3.07
-4.28
f1 (ppm)

34.850
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)
15.144
18.822
15 10 5 0 -5 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

Bpin
Me
Me
Si
Me2

70

7.26
5.82
5.82
5.81
5.80
5.79
5.79
5.77
5.77
5.75
4.85
4.84
4.81
4.81
4.81
4.79
4.79
4.79
1.79
1.77
1.76
1.74
1.73
1.60
1.59
1.58
1.57
1.56
1.23
1.23
1.20
1.19
1.17
1.00
0.91
0.90
0.88
0.02
1.80
1.79
1.77
1.76
1.74
1.73
1.63
1.61
1.60
1.59
1.58
1.57
1.56
1.11
1.97
1.75
1.65
1.55
f1 (ppm)
1.03
2.00
1.11
1.97
12.28
1.19
3.03
3.16
6.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

135.94
112.77
82.94
77.41
77.16
76.91
25.94
25.29
25.07
21.42
14.83
11.91
-5.57
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

35.009
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

5.374
0 25 20 15 10 5 0 -5 -10 -15 -20 -25
f1 (ppm)

S
Ph
SiMe2H

71

7.347
7.332
7.330
7.315
7.260
7.151
7.136
7.122
7.108
3.649
3.642
3.635
3.628
3.620
2.946
2.943
2.919
2.894
2.891
2.686
2.682
2.661
2.657
2.293
2.271
2.266
2.185
2.180
2.156
0.084
-0.091
2.07
3.08
1.00
2.12
2.15
2.17
2.07
5.96
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

142.168
128.747
127.243
124.510
77.414
77.160
76.906
31.868
31.524
22.488
-7.289
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

72

142.01
139.00
134.10
129.08
128.98
128.31
127.70
123.72
77.41
77.16
76.91
26.55
-1.77
-2.53
-2.89
-3.46
f1 (ppm)

-3.690
-13.575
f1 (ppm)

SiMe2Ph
Me
Me
MeO
N

73

7.802
7.798
7.436
7.420
7.326
6.616
6.599
3.909
2.138
2.125
2.120
2.111
2.107
2.098
2.093
2.085
2.080
2.067
1.971
1.953
0.934
0.920
0.767
0.754
0.312
0.166
0.99
2.02
3.02
1.00
1.00
2.98
0.92
0.92
3.07
2.98
2.99
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

161.969
146.339
139.332
138.727
134.019
131.674
129.050
127.842
110.140
77.414
77.160
76.906
53.453
41.363
30.203
24.092
23.146
1.542
3.314
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

2.711
20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85
f1 (ppm)

Ph
CO2H

74

7.494
7.479
7.350
7.335
7.319
7.260
7.245
7.230
7.215
2.954
2.058
2.033
1.898
1.881
1.852
1.784
1.758
1.688
1.590
1.565
2.03
2.03
0.99
2.00
2.07
3.07
2.09
3.05
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

181.01
140.94
128.67
127.58
126.95
77.41
77.16
76.91
55.76
37.64
35.29
32.57
31.65
27.31
26.75
f1 (ppm)

Bpin
GeMe3

75

7.260
1.919
1.896
1.676
1.656
1.634
1.292
1.287
1.267
1.256
1.243
1.209
1.186
1.167
1.162
1.143
1.115
0.102
2.00
3.08
1.14
12.06
4.02
9.03
f1 (ppm)

82.79
77.41
77.16
76.91
29.80
27.45
27.12
25.19
4.28
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

34.797
80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10
f1 (ppm)

Me
Me
Me
Me
Me
H
CO2Me

77

78-Cl

7.305
7.288
7.271
7.260
7.254
4.629
4.614
3.744
3.730
3.716
3.701
3.664
2.271
2.258
2.244
2.231
2.216
2.203
2.189
2.176
1.500
1.486
1.104
1.091
0.875
0.862
4.31
1.00
1.09
3.04
1.06
3.12
2.93
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

175.000
174.986
140.308
140.290
140.050
127.860
127.574
77.414
77.160
76.906
70.625
52.210
45.221
36.706
20.341
19.687
18.703
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

CD3
Me
Me
Me
CO2Me

78

7.260
7.203
7.187
7.105
7.088
3.720
3.705
3.691
3.677
3.663
2.399
2.384
1.764
1.751
1.737
1.495
0.905
0.757
0.744
2.04
2.49
1.07
2.95
1.00
0.99
3.04
3.31
2.94
f1 (ppm)

175.419
146.025
137.836
128.020
127.173
77.414
77.160
76.906
52.117
46.297
45.151
34.492
21.348
20.190
18.766
f1 (ppm)

Cl
nBu
MeO2C

79-Cl

8.116
8.113
8.099
8.096
7.664
7.660
7.647
7.620
7.603
7.483
7.467
7.260
4.917
4.904
4.888
3.944
2.171
2.161
2.154
2.144
2.125
2.078
2.068
2.066
2.056
2.051
2.040
1.518
1.323
0.888
0.874
2.28
2.38
2.25
1.98
1.00
3.14
0.99
1.07
1.30
5.29
3.42
f1 (ppm)

167.079
145.082
142.116
139.997
130.276
129.204
127.698
127.635
127.135
77.414
77.160
76.905
63.559
52.300
40.024
31.340
26.908
22.608
14.131
f1 (ppm)

CD3
nBu
MeO2C

79

8.100
8.083
7.669
7.665
7.652
7.568
7.555
7.552
7.287
7.271
7.260
3.938
2.731
2.717
2.702
1.612
1.603
1.596
1.593
1.587
1.577
1.328
1.323
1.315
1.307
1.297
1.267
1.264
0.875
0.861
2.40
2.23
2.30
2.48
3.26
1.00
2.44
6.18
3.22
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

167.219
148.385
145.746
137.516
130.200
129.142
127.735
127.279
126.950
77.414
77.160
76.906
52.237
39.584
38.428
32.097
27.542
22.740
14.242
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Cl
Ph
Bpin

81

These peaks belongs to ring opened protonation product
f1 (ppm)

f1 (ppm)

29.738
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

Me
Me
O
Me
Me
B
Me
O
Me
Ph
Me

83

7.282
7.267
7.260
7.252
7.185
7.180
7.171
7.163
2.761
2.751
2.738
2.734
2.728
2.724
2.711
2.701
2.504
2.493
2.483
2.477
2.471
2.466
2.456
2.444
1.721
1.714
1.709
1.699
1.695
1.687
1.677
1.672
1.665
1.660
1.539
1.534
1.526
1.518
1.513
1.504
1.500
1.491
1.486
1.359
1.348
1.337
1.332
1.327
1.323
1.316
1.311
1.306
1.301
1.222
0.925
0.912
0.875
0.867
2.87
3.25
1.02
1.06
1.07
1.04
1.11
12.00
3.09
5.91
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

143.509
128.496
128.363
125.613
82.939
77.414
77.160
76.906
39.697
35.717
35.121
24.896
24.794
21.807
20.841
14.742
f1 (ppm)

34.890
f1 (ppm)

Me
OH
Me
Ph
Me

83-ol

7.297
7.282
7.267
7.260
7.207
7.193
7.181
7.166
2.813
2.803
2.792
2.785
2.776
2.764
2.755
2.534
2.521
2.514
2.507
2.500
2.493
2.487
2.473
1.968
1.961
1.956
1.953
1.948
1.942
1.935
1.926
1.922
1.482
1.477
1.469
1.463
1.461
1.456
1.447
1.442
1.434
1.429
1.391
1.339
1.329
1.318
1.313
1.308
1.303
1.297
1.292
1.288
1.282
1.271
1.164
1.146
1.000
0.986
2.23
3.00
1.11
1.12
1.13
1.31
1.04
1.38
6.57
3.29
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

142.870
128.525
128.463
125.849
77.415
77.160
76.906
73.555
44.004
34.676
33.759
27.270
26.333
14.570
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Bpin
OMe

86

7.260
3.326
3.312
3.303
1.878
1.853
1.635
1.632
1.627
1.605
1.549
1.535
1.531
1.529
1.524
1.515
1.276
1.267
1.258
1.252
1.239
0.903
5.00
1.98
3.25
2.45
16.04
1.16
2.01
3.35
3.30
3.25
f1 (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

83.07
77.41
77.16
76.91
73.98
58.56
37.25
35.44
26.86
25.74
25.38
25.02
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

34.654
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

Me
Cl

88

7.317
7.302
7.287
7.260
7.212
7.210
7.195
7.179
3.521
3.508
3.499
3.495
3.487
3.482
3.475
3.470
3.461
3.448
2.734
2.720
2.706
2.693
1.747
1.735
1.730
1.724
1.715
1.708
1.706
1.697
1.670
1.657
1.644
1.640
1.636
1.280
2.05
3.08
2.00
1.01
4.05
3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

146.99
128.58
127.07
126.23
77.41
77.16
76.91
45.35
39.60
35.60
30.95
22.58
f1 (ppm)

Bpin
Me
Me
OPh

89

7.281
7.266
7.260
7.250
6.930
6.916
6.900
6.883
3.944
3.931
3.917
1.787
1.773
1.759
1.755
1.750
1.740
1.726
1.420
1.411
1.403
1.395
1.386
1.225
0.962
2.55
3.02
2.00
2.00
2.01
12.27
6.03
f1 (ppm)

159.24
129.50
120.50
114.66
83.12
77.41
77.16
76.91
68.80
37.16
26.37
24.93
24.85
f1 (ppm)

34.787
f1 (ppm)

Bpin
Me
Me
Cl

90

7.260
3.522
3.515
3.511
3.501
3.497
3.487
3.483
3.476
3.462
1.797
1.793
1.783
1.780
1.770
1.766
1.756
1.746
1.743
1.737
1.733
1.729
1.723
1.719
1.713
1.709
1.700
1.696
1.686
1.682
1.673
1.668
1.659
1.514
1.505
1.488
1.478
1.463
1.460
1.454
1.445
1.433
1.418
1.403
1.312
1.302
1.288
1.276
1.270
1.261
1.257
1.252
1.245
1.229
0.898
0.856
0.841
0.826
2.00
2.16
2.16
2.14
12.22
3.18
3.09
f1 (ppm)

83.19
77.41
77.16
76.91
46.14
36.06
31.49
29.37
24.98
24.95
21.05
10.17
f1 (ppm)

34.563
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

Bpin
Me
O

91

7.260
5.821
5.814
5.808
2.518
2.503
2.488
2.229
1.886
1.860
1.641
1.634
1.626
1.609
1.607
1.601
1.595
1.586
1.580
1.577
1.569
1.561
1.554
1.548
1.312
1.303
1.295
1.293
1.286
1.277
1.241
0.929
0.924
0.904
0.898
0.879
0.873
2.00
2.00
3.01
2.07
6.09
4.32
12.41
2.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

154.85
150.05
105.82
105.20
83.06
77.41
77.16
76.91
35.49
29.11
26.88
25.44
25.01
24.26
13.65
f1 (ppm)

35.575
f1 (ppm)

Bpin
O
O

92

7.260
4.443
4.432
4.422
4.097
4.088
4.075
4.066
3.757
3.753
3.732
3.728
3.708
3.704
1.764
1.567
1.557
1.549
1.541
1.533
1.523
1.493
1.482
1.474
1.465
1.458
1.352
1.345
1.335
1.268
1.250
1.241
1.00
2.05
2.05
1.05
2.05
10.52
5.18
12.18
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

103.49
82.99
77.41
77.16
76.91
67.05
36.17
34.26
32.13
29.99
26.03
24.96
24.60
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

35.265
f1 (ppm)

Bpin
OMe

93

7.260
3.333
3.320
3.308
1.797
1.551
1.537
1.523
1.518
1.512
1.504
1.498
1.490
1.479
1.474
1.304
1.287
1.286
1.279
1.270
1.254
1.246
5.04
2.00
10.18
3.98
12.26
f1 (ppm)

82.989
77.414
77.160
76.905
74.001
58.557
36.473
36.302
29.940
26.496
24.960
24.639
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

34.753
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

Bpin
Me
Me
OMe

94

7.260
3.384
3.370
3.357
3.286
1.569
1.556
1.542
1.215
0.930
1.99
2.97
1.98
12.06
6.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

82.954
77.414
77.160
76.905
70.668
58.606
40.632
25.151
24.782
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

34.676
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

Bpin
Me
Me
OTBS

95

7.260
3.641
3.634
3.627
3.625
3.622
3.616
3.609
1.569
1.562
1.553
1.544
1.537
1.218
0.933
0.889
0.048
2.00
4.97
12.12
6.06
9.07
6.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

83.080
77.414
77.160
76.905
61.842
44.027
26.203
25.384
24.846
18.561
-5.006
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

34.722
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

Bpin
MeO
Cl

96

7.260
3.529
3.515
3.502
3.364
3.361
3.350
3.348
3.337
3.335
3.315
1.785
1.771
1.757
1.742
1.728
1.600
1.587
1.577
1.574
1.567
1.564
1.559
1.554
1.546
1.541
1.533
1.471
1.457
1.453
1.445
1.440
1.427
1.423
1.414
1.411
1.402
1.396
1.390
1.381
1.374
1.369
1.360
1.347
1.330
1.320
1.305
1.291
1.286
1.235
0.992
0.980
0.975
0.969
0.963
0.951
0.946
0.934
1.96
2.02
3.07
1.97
2.43
8.23
12.50
4.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

83.07
77.41
77.16
76.91
73.29
58.62
45.26
32.69
31.24
29.30
28.50
27.79
27.26
24.96
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

34.581
f1 (ppm)

Bpin
Ph
97
f1 (ppm)

143.173
139.281
128.529
128.373
125.705
114.439
83.137
77.414
77.160
76.906
35.724
33.541
33.528
30.681
25.022
24.993
f1 (ppm)

34.698
f1 (ppm)

Bpin
Cl

98

7.26
3.53
3.52
3.50
1.86
1.84
1.83
1.81
1.80
1.78
1.77
1.64
1.62
1.61
1.59
1.25
0.43
0.41
0.40
0.39
0.36
0.34
0.09
0.08
0.05
0.04
2.19
2.03
12.23
1.08
2.21
0.97
1.02
1.20
2.00
f1 (ppm)

83.19
77.41
77.16
76.91
45.52
32.58
29.10
24.94
24.82
12.55
5.48
3.67
f1 (ppm)

Bpin
N
O

99

f1 (ppm)

f1 (ppm)

34.101
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

N
Bpin

100

7.260 7.160 7.153 7.110 7.101 7.093 6.653 6.138 3.906 3.891 3.884 3.870 3.857 3.054 3.039 3.024 3.008 3.002 2.985 2.970 2.955 2.686 2.668 2.655 2.648 2.636 2.630 2.617 2.598 2.536 2.519 2.502 2.485 1.886 1.856 1.844 1.832 1.794 1.780 1.762 1.749 1.735 1.542 1.532 1.521 1.512 1.502 1.491 1.482 1.471 1.269 1.247 1.225 1.205 1.194 1.183 1.175 1.157
2.05 2.02 1.99 1.98 2.10 0.96 1.05 1.99 4.02 2.00 2.18 13.52
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

143.75
143.54
126.11
126.09
124.42
124.39
120.57
107.91
83.28
77.41
77.16
76.91
49.91
42.11
39.22
38.68
31.45
27.65
25.06
24.99
f1 (ppm)

34.117
f1 (ppm)

OMe
Ph
B
O
O
Me
Me
Me

101

7.277
7.260
7.247
7.188
7.174
7.160
4.289
4.272
3.376
3.363
3.349
3.319
2.660
2.654
2.649
2.644
2.638
2.629
2.617
2.608
2.605
2.364
2.359
2.354
2.336
2.246
2.242
2.233
2.224
2.220
2.080
2.070
2.058
1.917
1.863
1.834
1.781
1.776
1.696
1.684
1.644
1.638
1.626
1.614
1.597
1.584
1.517
1.502
1.488
1.481
1.385
1.293
1.167
1.145
1.116
1.103
1.091
0.853
2.44
3.00
1.00
2.02
2.99
2.00
1.03
1.02
1.00
1.01
1.01
1.04
1.12
4.53
3.07
3.16
1.05
1.04
3.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

143.142
143.121
128.556
128.365
125.701
85.545
77.744
77.414
77.160
76.906
73.264
58.614
51.389
39.723
38.313
35.862
35.729
35.621
33.616
29.264
29.223
29.013
27.813
27.707
27.239
26.808
24.186
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

34.441
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

Me
Me
MeO
OMe

102

7.260
7.237
7.221
7.205
6.940
6.938
6.926
6.925
6.923
6.891
6.887
6.883
6.725
6.720
6.709
6.704
3.806
3.283
3.269
3.257
1.657
1.648
1.642
1.632
1.624
1.380
1.372
1.367
1.362
1.359
1.354
1.351
1.348
1.347
1.343
1.334
1.330
1.320
1.299
0.99
1.04
0.98
1.00
3.06
5.02
2.00
2.09
6.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

159.538
151.258
129.064
118.567
112.750
110.029
77.414
77.160
76.906
73.482
58.591
55.265
40.943
37.671
29.009
25.185
f1 (ppm)

Boc
N
Ph
O
O

103

7.340
7.324
7.309
7.265
7.260
7.251
7.204
7.189
7.175
4.666
4.656
4.647
3.876
3.873
3.781
3.774
3.767
3.743
3.138
3.117
3.097
3.092
2.155
2.129
1.720
1.693
1.684
1.677
1.668
1.659
1.432
1.331
1.321
1.313
1.305
1.296
1.287
2.11
2.57
0.98
1.00
2.05
2.02
1.94
2.00
1.97
4.07
9.27
2.13
f1 (ppm)

155.15
144.37
128.65
126.90
126.12
104.75
79.39
77.41
77.16
76.91
64.92
40.85
39.56
37.06
35.28
28.60
28.20
f1 (ppm)

Ph
Me
N
Me
Cl

104

7.306
7.291
7.276
7.260
7.211
7.209
7.197
7.184
7.182
7.156
7.153
7.139
3.465
3.460
3.452
3.447
3.439
3.435
2.602
2.593
2.583
2.573
2.183
2.169
2.152
2.140
2.070
2.060
2.051
2.046
2.041
2.036
2.027
1.856
1.845
1.841
1.835
1.830
1.819
1.810
1.799
1.777
1.757
1.747
1.738
1.730
1.728
1.706
1.697
1.686
1.679
1.674
1.663
1.650
1.639
1.589
1.577
1.565
2.06
1.11
2.00
2.00
1.03
7.00
1.02
1.97
4.05
f1 (ppm)

144.842
128.613
127.685
126.404
77.414
77.160
76.906
57.925
45.639
45.314
43.576
35.012
34.265
30.736
f1 (ppm)

Ph
SPh

105

f1 (ppm)

144.261
137.067
128.934
128.893
128.630
128.154
125.982
125.701
77.414
77.160
76.906
51.864
43.425
33.842
31.723
31.508
31.184
27.304
26.730
26.717
26.664
f1 (ppm)

nBu
MeO
MeO
CF3

106

7.506
7.490
7.260
7.207
7.191
6.835
6.819
6.705
6.701
6.689
6.685
6.659
6.655
3.886
3.884
2.518
2.510
2.507
2.497
2.488
2.479
2.448
2.439
2.429
2.420
1.967
1.952
1.853
1.841
1.834
1.826
1.623
1.616
1.606
1.596
1.554
1.544
1.535
1.526
1.282
1.268
1.264
1.255
1.253
1.239
1.225
1.210
1.197
1.185
1.161
1.143
1.141
1.123
1.111
1.102
0.841
0.826
0.812
2.00
2.01
0.99
0.99
1.00
5.95
2.99
1.01
0.99
1.03
1.20
4.33
3.06
f1 (ppm)

149.036
147.410
146.951
138.065
128.798
125.321
125.291
125.261
125.231
110.790
77.415
77.160
76.906
56.032
55.999
45.345
38.493
37.078
33.873
29.926
22.900
14.167
f1 (ppm)

-62.261
f1 (ppm)

nPr
F
tBuO2C
OMe

107

7.947
7.930
7.762
7.746
7.260
7.219
7.202
7.076
7.059
6.903
6.887
6.875
6.858
6.755
6.737
6.682
6.665
4.398
4.390
4.386
4.378
4.304
4.295
4.291
4.283
4.279
3.822
3.741
2.838
2.824
2.773
2.759
1.624
1.617
1.606
1.591
1.582
1.569
1.541
1.256
1.211
1.205
1.199
1.192
1.180
1.173
1.161
1.087
1.072
1.057
1.041
0.831
0.816
0.801
0.658
0.643
0.629
0.62
2.02
0.61
0.61
2.02
0.61
2.05
2.04
2.00
0.67
0.92
2.99
1.07
1.02
0.32
0.31
2.00
16.40
1.60
2.09
2.23
0.59
0.63
3.23
0.91
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

166.112
166.025
158.129
157.815
150.129
148.496
135.893
134.426
130.096
129.808
129.623
129.178
128.985
113.214
84.847
84.777
83.540
83.470
80.908
77.414
77.160
76.906
55.343
55.224
52.529
51.716
51.429
50.635
36.572
35.645
33.250
30.653
30.499
28.385
28.355
23.538
23.494
20.916
20.686
14.252
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

-217.621
-217.674
-217.723
-217.775
-217.827
-217.876
-217.929
-217.983
15.0
-215.8
-216.6
-217.4
-218.2
-219.0
-219.8
-220.6
f1 (ppm)

OMe

108

7.25
7.20
7.15
7.10
f1 (ppm)
2.8
2.4
2.0
1.6
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

147.53
144.15
126.39
126.13
124.55
123.74
77.41
77.16
76.91
73.18
58.75
44.80
32.24
31.59
31.54
27.94
f1 (ppm)

Me
Me
S

109

7.260
7.104
7.089
7.071
7.057
7.042
7.030
7.018
6.999
6.997
6.984
5.239
5.236
5.233
5.230
3.165
3.157
3.140
2.927
2.919
2.903
2.895
2.824
2.817
2.370
2.366
2.245
2.213
2.208
2.188
2.181
2.179
2.169
2.162
2.092
2.086
2.039
2.027
2.015
2.013
2.005
2.002
1.993
1.984
1.980
1.960
1.956
1.953
1.672
1.601
1.279
1.277
1.175
1.158
1.149
1.132
0.844
0.838
1.02
2.03
0.99
1.00
1.00
1.00
1.00
1.03
3.09
1.18
3.93
2.67
3.14
1.05
3.05
f1 (ppm)

148.058
147.885
130.083
126.676
126.657
126.599
126.564
123.792
116.395
77.414
77.160
76.905
46.002
45.802
41.028
40.996
37.488
37.222
34.462
34.388
31.887
31.867
31.757
31.447
31.428
26.494
26.483
26.002
25.678
22.939
22.922
21.441
f1 (ppm)

Ph
Ph

110

7.300
7.297
7.284
7.274
7.270
7.260
7.258
7.255
7.241
7.194
7.191
7.188
7.177
7.166
7.163
7.160
5.862
5.842
5.828
5.821
5.815
5.808
5.010
5.007
4.991
4.989
4.972
3.938
3.922
2.180
2.166
2.150
2.134
2.049
2.035
2.026
2.020
2.006
8.56
2.02
1.00
1.03
0.97
1.00
2.00
2.00
f1 (ppm)

145.056
138.492
128.561
128.034
126.244
115.014
77.414
77.160
76.906
50.688
34.889
32.137
f1 (ppm)

Cl
S
N
OMe

111

8.109
8.104
7.801
7.784
7.681
7.678
7.450
7.445
7.439
7.433
7.428
7.291
7.290
7.280
7.279
7.260
7.203
6.679
6.662
4.010
3.994
3.978
3.905
3.571
3.558
3.545
2.280
2.264
2.246
2.231
2.219
1.793
1.778
1.763
1.750
1.03
1.04
1.01
2.04
1.06
1.00
1.02
1.00
3.05
2.02
2.02
2.00
f1 (ppm)

163.041
145.692
140.264
140.127
138.295
138.116
132.886
127.123
124.583
123.878
122.863
122.357
111.047
77.414
77.160
76.906
53.513
47.427
45.031
32.906
31.050
f1 (ppm)

F
Cl
Me
Me
O
O
O
Me
Me

112

7.260
7.242
7.237
7.233
7.224
7.220
7.215
7.132
7.127
7.114
7.110
7.045
7.028
6.773
6.767
6.763
6.754
6.750
6.744
5.084
5.071
5.059
5.046
5.033
4.445
4.433
4.421
4.351
4.339
4.326
3.811
3.796
3.780
2.016
2.007
1.999
1.991
1.984
1.974
1.969
1.737
1.722
1.719
1.706
1.686
1.672
1.669
1.656
1.555
1.361
1.348
1.343
1.330
1.327
1.318
1.312
1.196
1.184
1.99
1.94
1.94
1.99
1.00
1.94
0.96
1.92
1.98
6.55
1.94
6.00
f1 (ppm)

173.870
154.129
143.834
137.919
131.896
129.260
128.642
128.369
119.158
84.722
83.413
79.214
77.414
77.160
76.905
68.983
49.976
35.545
30.545
30.390
25.560
25.547
23.905
23.862
21.681
f1 (ppm)

-217.944
-217.998
-218.045
-218.098
-218.151
-218.199
-218.252
f1 (ppm)

SiMe2Ph
Ph
O
O

113

114

115

7.260
1.210
0.998
0.014
12.00
6.00
9.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

82.76
77.41
77.16
76.91
25.05
19.41
3.56
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

35.224
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

-18.164
20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70
f1 (ppm)

Bpin
SiMe2H

116

7.26
3.66
3.65
3.64
3.63
3.63
3.62
3.61
1.92
1.66
1.66
1.24
1.17
0.06
0.05
1.95
1.92
1.66
1.66
1.65
1.64
1.28
1.27
1.24
1.23
1.20
1.17
1.17
1.15
2.10
3.22
2.29
12.77
3.05
2.0
1.8
1.6
1.4
1.2
f1 (ppm)
1.00
2.10
3.22
2.29
12.77
3.05
6.19
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

82.937
77.414
77.160
76.906
29.821
27.019
26.976
25.091
-6.136
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

34.776
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

-4.701
40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35
f1 (ppm)

Bpin
SiPh2Me

117

7.668
7.665
7.653
7.650
7.373
7.367
7.362
7.359
7.355
7.348
7.334
7.321
7.317
7.284
2.314
2.308
2.294
2.285
2.269
2.255
1.575
1.552
1.545
1.527
1.509
1.166
0.633
4.00
6.02
2.01
8.53
2.18
12.44
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

137.04
136.03
128.93
127.42
83.05
77.41
77.16
76.91
32.23
28.95
28.38
25.21
-3.84
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

35.845
70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -20 -30 -40
f1 (ppm)

-4.939
8 6 4 2 0 -3 -6 -9 -12 -16 -20 -24
f1 (ppm)

Bpin
N
SiEt3

118

8.100
8.084
7.462
7.446
7.431
7.413
7.260
7.226
7.223
7.211
7.198
7.195
4.335
4.324
4.316
4.305
4.295
4.287
4.275
4.264
4.252
4.247
4.235
4.223
4.218
4.205
2.021
2.009
2.003
1.990
1.986
1.974
1.955
1.773
1.762
1.750
1.730
1.713
1.706
1.695
1.686
1.530
1.514
1.508
1.500
1.496
1.481
1.476
1.465
1.208
1.176
0.946
0.930
0.914
0.581
0.565
0.549
0.534
1.96
4.03
1.96
2.00
0.96
1.94
1.02
11.76
9.08
6.36
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

140.49
125.61
122.92
120.40
118.73
108.83
82.88
77.41
77.16
76.91
43.20
32.49
25.45
24.84
23.75
7.70
3.60
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

34.596
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -15 -25 -35
f1 (ppm)

8.037
25 15 5 0 -5 -15 -25 -35 -45 -55 -65 -75 -85 -95 -105
f1 (ppm)

Bpin
Ph
SiMe2Ph

119

7.495 7.491 7.485 7.482 7.476 7.333 7.327 7.324 7.316 7.313 7.260 7.255 7.240 7.225 7.166 7.151 7.136 7.112 7.098 2.718 2.709 2.699 2.690 2.682 2.672 2.662 2.482 2.468 2.462 2.455 2.449 2.441 2.436 2.422 1.899 1.893 1.884 1.874 1.865 1.859 1.849 1.839 1.655 1.647 1.642 1.635 1.628 1.622 1.615 1.609 1.225 1.194 0.723 0.717 0.699 0.693 0.313 0.299
7.491 7.485 7.482 7.476 7.327 7.324 7.316 7.313 7.260 7.240 7.166 7.151 7.136 7.112 7.098
1.98 3.04 2.17 1.02 1.97
7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
1.98 3.04 2.17 1.02 1.97 1.00 0.99 0.99 0.99 12.02 0.99 2.95 2.97
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

142.737 138.965 133.964 128.914 128.673 128.311 127.726 125.714
82.966 77.414 77.160 76.906
39.603
28.194 25.352 24.873
2.120 3.199
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

34.507
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

1.888
35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65
f1 (ppm)

Bpin
SiMe3
S

120

7.260
7.228
7.222
7.218
7.212
6.947
6.945
6.937
6.935
6.922
6.921
6.918
6.917
2.755
2.745
2.736
2.726
2.717
2.708
2.698
2.566
2.553
2.547
2.538
2.534
2.525
2.519
2.505
1.903
1.893
1.883
1.877
1.874
1.869
1.867
1.857
1.852
1.849
1.847
1.843
1.833
1.823
1.689
1.683
1.676
1.670
1.663
1.657
1.650
1.643
1.637
1.254
1.249
0.425
0.419
0.401
0.395
0.029
0.99
1.00
0.98
1.00
1.00
0.98
0.98
12.54
1.00
9.29
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

143.34
128.53
125.11
120.15
82.87
77.41
77.16
76.91
33.93
27.19
25.38
24.91
-1.36
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

34.516
65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20
f1 (ppm)

2.691
15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40
f1 (ppm)

SiMe2H
F
F
Bpin

121

7.260
3.894
3.887
3.879
3.874
3.867
3.859
2.055
2.047
2.040
1.627
1.612
1.604
1.589
1.293
1.287
1.280
1.270
1.262
1.234
1.224
0.512
0.111
0.104
1.00
2.09
2.11
3.27
2.08
12.57
14.38
1.03
6.31
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

126.01
124.10
122.18
83.04
77.41
77.16
76.91
38.25
33.84
33.81
33.67
33.63
33.60
33.47
33.43
32.02
32.00
29.40
29.32
28.28
28.21
25.20
24.79
-4.20
-4.39
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

-91.422
-91.919
-101.400
-101.895
15
-25
-35
-45
-55
-65
-75
-85
-95
-105
-120
-135
-150
f1 (ppm)

34.735
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-20
-30
f1 (ppm)

-9.860
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120
f1 (ppm)

CO2H
Ph

122

7.338 7.334 7.321 7.306 7.291 7.274 7.270 7.265 7.260 7.251 7.248 7.245 7.240 7.228 3.207 2.034 2.018 2.012 2.005 1.996 1.989 1.983 1.967 1.912 1.887 1.757 1.734 1.640 1.631 1.624 1.619 1.608 1.602 1.337 1.318 1.312 1.294 1.287 1.275 1.268 1.261 1.180 1.156 1.137 1.116 1.091 1.087 1.068 1.062 1.043 1.036 0.777 0.770 0.753 0.747 0.728 0.722 0.704
4.05
1.24
1.00
1.00
1.02
1.03
2.03
2.18
3.10
1.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

179.825
137.398
128.836
128.655
127.544
77.414
77.160
76.906
58.924
40.823
32.079
30.439
26.388
26.101
26.064
f1 (ppm)

Me
Me
CD3
Bpin

123

7.260
5.158
5.156
2.350
2.339
2.334
2.328
2.322
2.311
2.214
2.177
2.175
2.143
2.140
2.055
2.018
2.007
1.995
1.948
1.933
1.918
1.487
1.472
1.461
1.431
1.257
1.234
1.145
1.142
1.128
1.125
0.987
0.96
1.00
2.08
1.07
1.05
1.91
1.05
0.98
3.13
11.82
1.13
0.97
3.07
f1 (ppm)

148.95
148.94
115.62
115.61
82.92
77.41
77.16
76.91
46.02
45.96
41.06
38.08
38.07
36.52
36.50
31.84
31.83
31.43
30.95
30.93
26.53
24.93
24.92
24.87
24.86
21.37
21.35
f1 (ppm)

-34.610
f1 (ppm)

CD3
Me
Me
Cl
O
O
O
Me
Me

124

7.260
7.236
7.233
7.223
7.219
7.110
7.093
7.035
7.018
6.779
6.773
6.759
6.755
5.104
5.092
5.079
5.066
5.054
5.041
5.029
4.031
1.560
1.211
1.199
1.99
2.01
2.01
2.01
1.00
1.00
6.21
6.02
f1 (ppm)

173.90
154.00
145.32
139.32
131.76
129.08
128.52
128.20
119.13
79.21
77.41
77.16
76.91
68.99
43.29
25.54
21.70
f1 (ppm)

Bpin
Me
Me
Cl

125

7.260
3.514
3.500
3.486
1.772
1.763
1.758
1.749
1.743
1.741
1.734
1.725
1.720
1.711
1.381
1.372
1.364
1.357
1.348
1.223
0.931
2.00
1.98
2.04
12.47
6.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

83.17
77.41
77.16
76.91
46.04
38.42
30.01
24.89
24.83
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

34.619
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)