Supporting Information

Electrochemical Nozaki–Hiyama–Kishi Coupling: Scope, Applications, and Mechanism

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General Experimental

Tetrahydrofuran (THF), dichloromethane (CH$_2$Cl$_2$), N,N-dimethylformamide (DMF), and acetonitrile (CH$_3$CN) were obtained by passing the previously degassed solvents through an activated alumina column. NiCl$_2$·glyme (98%) was purchased from Sigma-Aldrich. CrCl$_2$ was purchased from Strem and stored in the glovebox. Cp$_2$ZrCl$_2$ was purchased from Sigma-Aldrich. Cp$_2$ZrHCl was purchased from Strem and stored in the glovebox. Tetrabutylammonium bromide (TBAB) was purchased from Combi-Blocks. NiBr$_2$ was purchased from Sigma-Aldrich. CrCl$_3$ and TMSCl was purchased from Oakwood Chemical. Proton Sponge was purchased from Alfa Aesar. All the other reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Yields refer to chromatographically and spectroscopically (1H NMR) homogeneous material. TLC was performed on 0.25 mm E. Merck silica plates (60F-254), using short-wave UV light as the visualizing agent, and cerium ammonium molybdate (CAM) or KMnO$_4$ and heat as developing agents. NMR spectra were recorded on Bruker DRX-600, DRX-500, and AMX-400 instruments and are calibrated using residual undeuterated solvent (CHCl$_3$ at 7.26 ppm 1H NMR, 77.16 ppm 13C NMR; C$_6$H$_6$ at 7.16 ppm 1H NMR, 128.06 ppm 13C NMR). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Column chromatography was performed using E. Merck silica gel (60, particle size 0.043–0.063 mm). High-resolution mass spectra (HRMS) were recorded on Waters LC with G2-XS TOF mass spectrometer by electrospray ionization time-of-flight reflectron experiments. GCMS (EI) were recorded on Agilent 7820A GC systems and 5975 Series MSD. Melting points were recorded on a Fisher-Johns 12-144 melting point apparatus and are uncorrected.
Optimization Details

Evaluation of electrolytes

\[
\text{entry} \quad \begin{array}{c|c|c}
\text{electrolytes} & \text{yield (\%)} \\
1 & \text{TBAPF}_6 \quad 37 \\
2 & \text{TBABF}_4 \quad 41 \\
3 & \text{TBAB} \quad 42 \\
4 & \text{TBACIO}_4 \quad 40 \\
5 & \text{LiClO}_4 \quad 41 \\
6 & \text{LiCl} \quad 16 \\
7 & \text{LiBr} \quad 38 \\
\end{array}
\]

Evaluation of ligands for Ni

\[
\text{entry} \quad \begin{array}{c|c|c}
\text{ligand} & \text{yield (\%)} \\
1 & \text{MeO} \quad 29 \\
2 & \text{OMe} \quad 40 \\
3 & \text{Ph} \quad 25 \\
4 & \text{Ph} \quad 33 \\
5 & \text{Ph} \quad 42 \\
6 & \text{Ph} \quad 37 \\
7 & \text{Ph} \quad 58 \\
8 & \text{Bu} \quad 64 \\
9 & \text{Bu} \quad 47 \\
10 & \text{Bu} \quad 60 \\
11 & \text{Bu} \quad 49 \\
12 & \text{Bu} \quad 70 \\
\end{array}
\]
Evaluation of nickel sources

\[
\begin{align*}
0.2 \text{ mmol} & \quad \text{Me} \\
0.4 \text{ mmol} & \quad \text{Br}
\end{align*}
\]

- \[\text{NiCl}_2\cdot\text{glyme} \quad \text{entry 1} \quad \text{yield (\%)} 64\]
- \[\text{NiBr}_2\cdot\text{glyme} \quad \text{entry 2} \quad \text{yield (\%)} 50\]
- \[\text{NiBr}_2 \quad \text{entry 3} \quad \text{yield (\%)} 51\]
- \[\text{NiCl}_2 \quad \text{entry 4} \quad \text{yield (\%)} 45\]
- \[\text{Nil}_2 \quad \text{entry 5} \quad \text{yield (\%)} 49\]

Nickel source (2 mol\%)
Neocuproine (3 mol\%)
CrCl\(_2\) (20 mol\%)
Cp\(_2\)ZrCl\(_2\) (0.5 equiv)
TBAB (0.1 M), DMF (2.5 mL)
Al(+)/Ni foam(−)
\(E_{\text{cell}} = 2 \text{ V, } 4 \text{ F/mol}\)

Electrochemical decarboxylative NHK coupling

- \[\text{Ph} \quad \text{NHPI} \quad 0.2 \text{ mmol} \quad \text{OR} \quad \text{R} = \text{SiR}_2 \text{ or H} \quad \text{entry 6} \quad \text{yield (\%)} 56\]
- \[\text{Ph} \quad \text{NHPI} \quad 0.2 \text{ mmol} \quad \text{OR} \quad \text{R} = \text{SiR}_2 \text{ or H} \quad \text{entry 7} \quad \text{yield (\%)} 40\]
- \[\text{Ph} \quad \text{NHPI} \quad 0.2 \text{ mmol} \quad \text{OR} \quad \text{R} = \text{SiR}_2 \text{ or H} \quad \text{entry 8} \quad \text{yield (\%)} 40\]
- \[\text{Ph} \quad \text{NHPI} \quad 0.2 \text{ mmol} \quad \text{OR} \quad \text{R} = \text{SiR}_2 \text{ or H} \quad \text{entry 9} \quad \text{yield (\%)} 59\]

Anode: Al, Fe, Zn, Mg
Cathode: Nickel foam, RVC, Graphite, Nickel plate, Stainless steel, Pt foil
Electrolyte: TBAB, TBAI, TBAPF\(_6\), TBABF\(_4\), TBACIO\(_4\), LiCl, LiBr, LiClO\(_4\)
Solvent: DMF, CH\(_3\)CN, THF

0.2 mmol RAE, 0.2 mmol aldehyde,
CrCl\(_2\) (20 mol\%), TMSCl (2.0 eq.),
TBACIO\(_4\) (0.1 M), DMF (2.5 mL),
Al(+)/Ni foam(−), 2.5 mA, 12 h

- SiCl \(54\%\)
- SiCl \(47\%\)
- SiCl \(37\%\)
- SiCl \(38\%\)
- SiCl \(29\%\)
- PhSiCl \(38\%\)
- PhSiCl \(21\%\)
- PhSiCl \(23\%\)
- PhSiCl \(13\%\)
- PhSiCl \(13\%\)
- SiCl \(31\%\)
- SiCl \(43\%\)
- SiCl \(40\%\)
- SiCl \(32\%\)
- SiCl \(38\%\)
Preparation of Alkenyl Bromides

General Procedure A1

Schwartz’s reagent (1.1 equiv) was added to a flame-dried round-bottom flask containing a magnetic stir bar in the glovebox. Note: Schwartz’s reagent was stored in a glovebox to ensure the quality of the reagent. The round-bottom flask was removed from the glovebox, placed under Ar atmosphere, and wrapped in aluminum foil to keep it from light. THF (0.5 M) was added via syringe, and the alkyne (1 equiv) was added dropwise to the stirring mixture. The reaction mixture was stirred for one hour, and N-bromosuccinimide was added in one portion (1.1 equiv). The reaction mixture was stirred for 30 min, then quenched with saturated aq. NaHCO₃ solution. The solution was extracted with ether, and the organic layer was dried with Na₂SO₄, filtered, and concentrated under reduced pressure. The crude residue was purified by column chromatography over silica gel.

The following alkenyl bromides were prepared following General Procedure A1. The NMR spectra of S1,¹ S2,² S3,² S4,³ and S5⁴ matched those reported in literature. The characterization data for S6 is reported below.

![Chemical Structures]

Compound S6

\( \text{t-BuO}_2 \text{C}-\text{Br} \)

Prepared from tert-butyl pent-4-ynoate⁵ following General Procedure A1 with 64% yield.

Physical State: yellowish oil.
$R_f = 0.6$ (hexanes/EtOAc 9:1, KMnO$_4$).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 6.20 – 6.11 (m, 1H), 6.11 – 6.04 (m, 1H), 2.33 – 2.27 (m, 4H), 1.43 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 171.8, 136.2, 105.7, 80.7, 34.5, 28.6, 28.2.

The desired mass for HRMS was not observed.
General Procedure A2

A flame-dried round-bottom flask equipped with a magnetic stir bar was charged with tetrabromomethane (2 equiv) and triphenylphosphine (4 equiv). DCM (0.5 M) was added, and the reaction was cooled to 0 °C. The aldehyde (1 equiv) was dissolved in DCM (0.5 M) and added dropwise to the reaction mixture. The reaction mixture was allowed to warm to room temperature and stirred until TLC showed aldehyde was fully consumed. Pentane was added, and triphenylphosphine oxide (TPPO) precipitated out. Filtration and evaporation of the solvent afforded the crude dibromide, which was directly used for the next step.

The dibromoalkene (1 equiv) and dimethyl phosphite (3 equiv) were added to a round-bottom flask with a magnetic stir bar and sealed under Ar. The solution was cooled to 0 °C, and triethylamine (3 equiv) was added dropwise. The reaction mixture was warmed to room temperature and stirred overnight. The reaction mixture was quenched with water and extracted with Et_2O. The organic layer was washed with brine, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by column chromatography (silica) to afford the alkenyl bromide.

The crude alkenyl bromide (1.0 equiv) was dissolved in i-PrOH (0.5 M), NaOH (1.0 equiv) was added, and the mixture was heated to reflux for 1.5 hours. The reaction mixture was cooled to room temperature and quenched with water. The organic layer was extracted with ether, washed with 1 M HCl, and dried over Na_2SO_4. After filtration and concentration, the crude product was purified by flash chromatography (silica).

The following alkenyl bromides were prepared following General Procedure A2. The NMR spectra of S7, S8, S9, and S10 matched those reported in literature.
General Procedure A3

A solution of boron tribromide (0.5 equiv) in DCM (1 M) was cooled to $-78 \, ^\circ\text{C}$ in an oven-dried round-bottom flask under Ar atmosphere. To this was added alkyne (1.0 equiv) dropwise. The reaction mixture was stirred for 1 hour at $-78 \, ^\circ\text{C}$, allowed to warm to room temperature, and stirred for an additional 2 hours. Subsequently, acetic acid (30 equiv) was carefully added, and this solution was stirred for another hour at room temperature. The reaction mixture was quenched with saturated aq. NaHCO$_3$ solution and extracted with DCM. The combined organic layers were washed with brine, dried with Na$_2$SO$_4$, filtered, and concentrated in vacuo. The crude mixture was purified by column chromatography.

The following alkenyl bromides were prepared following General Procedure A3. The NMR spectra of S11, S12, S13, S14, S15, and S16 matched those reported in literature.
Other Alkenyl Bromides

**Compound S17**

\[
\text{Br} \quad \text{SO}_2\text{Ph}
\]

\((E)-3\text{-bromobut}-2\text{-en}-1\text{-ol}^{14}\) (1.0 equiv), triethylamine (1.5 equiv), and DMAP (0.1 equiv) were dissolved in DCM (0.1 M). MsCl (1.2 equiv) was added dropwise to the solution at 0 \(^\circ\)C. The reaction mixture was stirred for 1 hour and quenched with saturated NaHCO\(_3\) (aq.) solution. The organic layer was separated, washed with 1 M HCl and brine, dried, and concentrated. The crude mixture was dissolved in DMF (0.2 M), and sodium benzenesulfinic acid (2.0 equiv) was added. The reaction mixture was stirred for 30 min. The solution was poured into water and extracted with ether. The organic layer was washed with brine, then dried with Na\(_2\)SO\(_4\), filtered, and concentrated. The crude product was purified by silica gel chromatography.

**Physical State:** colorless sticky oil.

\(R_f = 0.43\) (hexanes/EtOAc 2:1, UV, \(p\)-anisaldehyde).

\(^1\text{H NMR (500 MHz, CDCl}_3\)): \(\delta 7.92 – 7.86\) (m, 2H), \(7.72 – 7.65\) (m, 1H), \(7.59\) (dd, \(J = 8.4, 7.2\) Hz, 2H), \(5.87\) (tq, \(J = 8.4, 1.5\) Hz, 1H), \(3.75\) (d, \(J = 8.3\) Hz, 2H), \(1.93 – 1.90\) (m, 3H).

\(^{13}\text{C NMR (126 MHz, CDCl}_3\)): \(\delta 138.2, 134.2, 129.7, 129.5, 128.7, 118.4, 56.8, 23.4\).

**HRMS:** Calc’d for C\(_{10}\)H\(_{12}\)BrO\(_2\)S, [M+H]\(^+\) 274.9736; found 274.9683.

**Compound S18**

\[
\text{Br} \quad \text{O} \quad \text{S}
\]

5-bromohex-5-en-1-ol\(^{15}\) (1.0 equiv), 2-thiophenecarboxylic acid (1.5 equiv), and DMAP (0.1 equiv) were dissolved in DCM (0.1 M). EDCI (1.5 equiv) was added slowly to the solution, and the reaction mixture was stirred overnight. After TLC showed alcohol was fully consumed, the reaction mixture was quenched with saturated
NaHCO$_3$ (aq.) solution and extracted with DCM. The organic layer was washed with brine, then dried with Na$_2$SO$_4$, filtered, and concentrated. The crude product was purified by silica gel chromatography.

**Physical State:** yellow oil.

$R_f = 0.5$ (hexanes/EtOAc 9:1, UV, $p$-anisaldehyde).

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.80 (dd, $J = 3.7$, 1.3 Hz, 1H), 7.55 (dd, $J = 5.0$, 1.3 Hz, 1H), 7.10 (dd, $J = 5.0$, 3.7 Hz, 1H), 5.60 (q, $J = 1.3$ Hz, 1H), 5.42 (d, $J = 1.7$ Hz, 1H), 4.31 (t, $J = 6.4$ Hz, 2H), 2.50 (td, $J = 7.1$, 1.2 Hz, 2H), 1.81 – 1.69 (m, 4H).

$^{13}$C NMR (126 MHz, CDCl$_3$): δ 162.3, 134.1, 134.0, 133.4, 132.4, 127.8, 117.1, 64.8, 40.9, 27.5, 24.4.

**HRMS:** Calc’d for C$_{11}$H$_{14}$BrO$_2$S, [M+H]$^+$ 288.9892; found 288.9848.

Alkenyl bromide S19 was prepared according to a procedure reported by Breit and coworkers.$^{12}$

![S19](image)

Alkenyl bromides S20 and S21 were prepared according to a procedure reported by Reisman and coworkers.$^{16}$

![S20](image) ![S21](image)

Alkenyl bromide S22 was prepared according to a procedure reported by Pattenden and coworkers.$^{17}$

![S22](image)

Alkenyl bromide S23 was prepared according to a procedure reported by Chakraborty and coworkers.$^{18}$

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S13
2-Bromopropene was purchased from a commercial source (Combi-Blocks).

1-Bromoethene was purchased from a commercial source (Acros) as 1.0 M solution in THF.
Preparation of NHPI Redox-Active Esters (General Procedure B)

NHPI esters were prepared according to a previously reported procedure. A round-bottom flask or culture tube was charged with carboxylic acid (1.0 equiv), N-hydroxyphthalimide (1.0 – 1.1 equiv), and DMAP (0.1 equiv). DCM was added (0.1 – 0.2 M), and the mixture was stirred vigorously. DIC (1.1 equiv) was then added dropwise via syringe, and the reaction mixture was allowed to stir until the acid was consumed (determined by TLC). Typical reaction times were between 0.5 and 12 hours. The mixture was filtered (through a thin pad of Celite, SiO₂, or frit funnel) and rinsed with additional DCM and Et₂O. Solvents were removed under reduced pressure, and purification of the crude mixture by column chromatography afforded the desired NHPI redox-active ester. If necessary, the NHPI redox-active ester could be further recrystallized from DCM/MeOH.
Electrochemical Nozaki–Hiyama–Kishi (NHK) Coupling (Racemic, General Procedure C)

**Preparation of CrCl₂ solution in DMF (0.08 M):** A screw-capped culture tube was charged with CrCl₂ (30 mg, 0.24 mmol) in the glovebox. The tube was removed from the glovebox and placed under an argon balloon, whereupon degassed DMF (3 mL) was added via a syringe. The resulting mixture was sonicated until a homogeneous green solution was obtained.

**Procedure for the electrochemical Nozaki–Hiyama–Kishi reaction:** An ElectroSyn vial (5 mL) with a magnetic stir bar was charged with NiCl₂·glyme (0.9 mg, 0.004 mmol, 2 mol%), 2,9-dibutyl-1,10-phenanthroline (1.8 mg, 0.006 mmol, 3 mol%), aldehyde (0.2 mmol, 1.0 equiv), alkenyl bromide (0.4 mmol, 2.0 equiv), Cp₂ZrCl₂ (29 mg, 0.1 mmol, 0.5 equiv), and TBAB (0.1 M, 80 mg). The ElectroSyn vial cap equipped with anode (aluminum) and cathode (nickel foam) was inserted into the mixture. The vial was then evacuated, and backfilled with an argon balloon for three cycles. *[Note: volatile aldehyde and alkenyl bromide should be added after this step.]* CrCl₂ solution in DMF (0.5 mL, 0.04 mmol, 20 mol%) and additional DMF (2.0 mL) were added to the vial via syringe. The ElectraSyn was set up as follows: New exp. > Constant voltage > 2 V > No ref. electrode > Total charge > 0.2 mmol, 4 F/mol > No alternating polarity > Start. After the reaction stopped, the ElectroSyn vial cap was removed and electrodes were rinsed with EtOAc. Water was added, and the resulting mixture was extracted with EtOAc. The combined organic layer was washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo. The crude material was purified by flash column chromatography or preparative thin-layer chromatography to furnish the desired product.
Graphical Guide for Electrochemical Nozaki–Hiyama–Kishi Coupling (Racemic)

Left: all reagents for this reaction. Center: electrodes and parts needed. Right: connect the electrodes to the ElectraSyn cap.

Left: weigh all reagents into an ElectraSyn vial wrapped with Teflon tape. Center: fasten the ElectraSyn cap to the vial. Right: connect the reaction vial to a vacuum line through a needle.
Left: evacuate and backfill the reaction vial with an argon balloon for three cycles. Center: add degassed DMF (1.5 mL) to the vial and stir for 2 minutes. Right: add degassed DMF (7 mL) to the culture tube containing CrCl₂ (35 mg, 0.28 mmol).

Left: select "New Experiments". Center: select "Constant Voltage". Right: set the voltage to "2.00 V".

Left: no need to use reference electrode. Center: select "Total Charge". Right: select 0.2 mmol of substrate and 4.0 F/mol.
Left: no need to alternate the polarity. Center: start the reaction when ready. Right: add 1.0 mL CrCl$_2$ solution in DMF to the vial and start the reaction.

Left: after completion of reaction, transfer the reaction mixture and rinse the electrodes into a separatory funnel with EtOAc and water. Center: wash the organic layer with brine. Right: obtain crude product.
Electrochemical Nozaki–Hiyama–Kishi (NHK) Coupling (Asymmetric, General Procedure D)

Preparation of CrCl$_2$-Ligand complex solution in CH$_3$CN (0.08 M): A screw-capped culture tube with a magnetic stir bar was charged with CrCl$_2$ (30 mg, 0.24 mmol, 1.0 equiv), Proton Sponge (57 mg, 0.26 mmol, 1.1 equiv), and (S)-N-(2-(4-isopropyl-4,5-dihydrooxazol-2-yl)-6-methylphenyl)methanesulfonamide (78 mg, 0.26 mmol, 1.1 equiv) in the glovebox. The tube was removed from the glovebox and placed under an argon balloon, whereupon degassed CH$_3$CN (3 mL) was added via a syringe. The resulting mixture was stirred at room temperature for one hour until a homogeneous solution was obtained.

Procedure for the electrochemical Nozaki–Hiyama–Kishi reaction: An ElectroSyn vial (5 mL) with a magnetic stir bar was charged with NiCl$_2$·glyme (0.9 mg, 0.004 mmol, 2 mol%), 2,9-dibutyl-1,10-phenanthroline (1.8 mg, 0.006 mmol, 3 mol%), aldehyde (0.2 mmol, 1.0 equiv), alkenyl bromide (0.4 mmol, 2.0 equiv), Cp$_2$ZrCl$_2$ (29 mg, 0.1 mmol, 0.5 equiv), and TBAB (0.1 M, 80 mg). The ElectroSyn vial cap equipped with anode (stainless steel) and cathode (nickel foam) was inserted into the mixture. The vial was then evacuated and backfilled with an argon balloon for three cycles. [Note: volatile aldehyde and alkenyl bromide should be added after this step.] CrCl$_2$-Ligand complex solution in CH$_3$CN (0.5 mL, 0.04 mmol, 20 mol%) and additional CH$_3$CN (2.0 mL) were added to the vial via syringe. The ElectraSyn was set up as follows: New exp. > Constant voltage > 2 V > No ref. electrode > Total charge > 0.2 mmol, 4 F/mol > No alternating polarity > Start. After the reaction stopped, the ElectroSyn vial cap was removed and electrodes were rinsed with EtOAc. Water was added and the resulting mixture was extracted with EtOAc. The combined organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated in vacuo. The crude material was purified by flash column chromatography or preparative thin-layer chromatography to furnish the desired product.
**Enantiomeric ratio was determined by Mosher ester analysis using the following procedure:** The product from above step (50 µmol, 1.0 equiv) and (R)-Mosher acid (35 mg, 150 µmol, 3.0 equiv) were dissolved in 1 mL DCM (0.05 M) and stirred at room temperature until dissolved. Dicyclohexylcarbodiimide (DCC) (31 mg, 150 µmol, 3.0 equiv) and DMAP (18 mg, 150 µmol, 3.0 equiv) were then added, and the reaction progress was monitored by TLC until starting material was completely consumed. The reaction mixture was diluted with Et₂O, partitioned with water, extracted with Et₂O, and the combined extracts dried over anhydrous Na₂SO₄. The organic extracts were filtered, the solvent was evaporated in vacuo, and the residue was dissolved in CDCl₃ to determine er.
Graphical Guide for Electrochemical Nozaki–Hiyama–Kishi (NHK) Coupling
(Asymmetric)

Left: all reagents for Cr-complex formation reaction. Center: weigh all the reagents in a culture tube, and then evacuate and backfill with argon three times. Right: add degassed CH$_3$CN to the culture tube and stir vigorously for 1 hour.

Left: all reagents for this reaction. Center: all the electrodes and parts for this reaction. Right: connect the electrodes to the ElectraSyn cap.
**Left:** weigh all the materials into the vial and fasten the cap to the vial. **Center:** evacuate and backfill with argon three times. **Right:** add degassed CH$_3$CN to the culture tube and stir for 2 minutes.

**Left:** homogeneous solution after one hour. **Center:** add 1 mL solution to the ElectraSyn vial. **Right:** set up the same parameters with General Procedure D.
Electrochemical Decarboxylative Nozaki–Hiyama–Kishi (NHK) Coupling

(General Procedure E)

Procedure for the electrochemical decarboxylative Nozaki–Hiyama–Kishi (NHK) Coupling: An ElectroSyn vial (5 mL) with a magnetic stir bar was charged with aldehyde (0.2 mmol, 1.0 equiv), redox-active ester (0.2 mmol, 1.0 equiv), CrCl$_3$ (6.4 mg, 0.04 mmol, 0.2 equiv), and TBAClO$_4$ (0.1 M, 85 mg). The ElectroSyn vial cap equipped with anode (aluminum) and cathode (nickel foam) was inserted into the mixture. The vial was then evacuated and backfilled with an argon balloon for three cycles. [Note: volatile aldehyde should be added after this step.] Then DMF (2.0 mL), THF (0.5 mL), and TESCl (67 μL, 0.4 mmol, 2.0 equiv) were added to the vial via syringe. The ElectraSyn was set up as follows: New exp. > Constant current > 2.5 mA > No ref. electrode > Time > 12 h > No alternating polarity > Start. After the reaction was completed, the EletraSyn vial cap was removed, and the electrodes were rinsed with EtOAc. Water was added, and the resulting mixture was extracted with EtOAc. The combined organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated in vacuo. The crude material was then dissolved in THF (2 mL), and TBAF (1.0 M in THF, 0.3 mL) was added. After 2 h, the reaction was quenched with sat. NH$_4$Cl (aq.) and extracted with EtOAc twice. The combined organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated in vacuo. The crude mixture was then purified by flash column chromatography or preparative thin-layer chromatography to furnish the desired product.
Graphical Guide for Electrochemical Decarboxylative Nozaki–Hiyama–Kishi (NHK) Coupling

**Left:** all the electrodes and parts for this reaction. **Center:** all reagents for this reaction. **Right:** connect the electrodes to the ElectraSyn cap.

**Left:** weigh all the materials into the vial and fasten the cap to the vial; then evacuate and backfill with argon three times. **Center:** add 2.0 mL DMF and 0.5 mL THF. **Right:** add 67 μL TESCl via micro syringe.
Left: select "constant current". Center: select "2.5 mA". Right: no need to use a reference electrode.

Left: select "Time". Center: select "12:00:00". Right: select "0.2 mmol".

Left: no need to alternate the polarity. Center: start the reaction when ready. Right: reaction completed.
Troubleshooting: Frequently Asked Questions

Electrochemical NHK coupling of alkenyl bromide and aldehyde

Question 1:
Are there any precautions that need to be taken for running this reaction?

Answer:
We used all the reagents without any special handling, but the CrCl₂ was weighed into a culture tube in the glovebox and taken out for use. The reaction is not particularly air-sensitive as it proceeds without freeze-pump-thaw. However, evacuation-argon backfill cycle and degassed solvent are still required to ensure the yield.

Question 2:
What can I do if I cannot reproduce the yield?

Answer:
Based on our experiences, certain aldehyde substrates will gradually be oxidized to acid, even when stored in the refrigerator under argon. Therefore, purification of aldehyde via flash column chromatography before use is recommended. Also, certain alkenyl bromides (such as (E)-2-(2-bromoethenyl)furan) are extremely unstable and should be used immediately after preparation. If the substrates are unlikely to be the cause of irreproducibility, make sure the reaction is degassed and the cap is screwed on tightly. Wrapping enough Teflon tape around the rim of the vial is an easy and effective way to improve sealing.

Question 3:
How do I clean the electrodes after the reaction?

Answer:
First, wash the electrodes with 1 N HCl, distilled water, and acetone. Then dry them in an oven. Once dried, scrape the aluminum electrodes with a razor blade to make the surface smooth and shiny.

Question 4:
What is the byproduct of this reaction?

Answer:
The major side reactions are homocoupling and proto-dehalogenation of the alkenyl halides. Sometimes, reduction of aldehyde to corresponding alcohol may also be observed.

Question 5:
How can I monitor the reaction and determine the yield?

Answer:
We have evaluated the reaction time on the standard substrate, which indicates 4 F/mol is enough for full conversion on 0.2 mmol scale. We ran the reaction without monitoring after 4 F/mol passed. Then, the reaction mixture was transferred into a separation funnel with EtOAc. The organic layer was washed with brine twice, dried over anhydrous Na₂SO₄, filtered, and evaporated to dryness. The yield was determined by crude ¹H NMR using 1,3,5-trimethoxybenzene as internal standard.

Question 6:
Is stirring crucial for this reaction?

Answer:
Stirring is crucial, and low yields will be obtained without stirring. Our preferred stirring rate is from 500 to 1000 rpm.

Question 7:
Does a longer reaction time cause a decrease in yield?

Answer:
We left the reaction running for 6 F/mol during optimization, and no significant decrease of yield was observed. In addition, we tested the stability of the model product under this reaction condition, and it was fully recovered from the reaction mixture.

Question 8:
Where can I get the electrode materials?

Answer:
Everything required for setting up this reaction can be obtained from IKA. (https://www.ika.com/en/Products-Lab-Eq/Electrochemistry-Kit-csp-516/).

Question 9:
How long does these reactions typically proceed?
Answer:
Reaction time varies based on different substrates, and typically ranges from 4–8 hours.

**Electrochemical decarboxylative NHK coupling**

**Question 1:**
Do I need a glovebox to run the reaction?

**Answer:**
We do not need a glovebox for electrochemical decarboxylative NHK coupling because we use CrCl₃ instead of CrCl₂.

**Question 2:**
Are there any indicative color changes during the reaction?

**Answer:**
Yes, the color of the reaction mixture first turned to green, indicating the formation of a Cr(II) species, and ultimately became black or brown.

**Question 3:**
Why do you use TESCl? Have you tried other chlorosilanes?

**Answer:**
For extensive screening of chlorosilane, see the optimization part of SI.

**Question 4:**
Do I need to run this reaction under inert atmosphere?

**Answer:**
An inert atmosphere is required (N₂ or Ar) to ensure the full consumption of starting materials.

**Question 5:**
Since CrCl₃ is not soluble in DMF, did any soluble Cr source improve the yields?

**Answer:**
We tried several soluble Cr sources, such as CrCl₃·3THF, CrCl₃·6H₂O, and CrCl₃·dtbpy, and did not obtain higher yields.
Experimental Procedures and Characterization Data

Compound 3

Following General Procedure C on 0.2 mmol scale. Purification by PTLC (2:1 hexanes/EtOAc) afforded 34.1 mg (62%) of the title compound 3.

Physical State: colorless oil.

$R_f = 0.46$ (hexanes/EtOAc 2:1, UV, $p$-anisaldehyde).

$^1$H NMR (500 MHz, CDCl₃): $\delta$ 7.28 (dd, $J = 7.6$, 0.9 Hz, 2H), 7.22 – 7.16 (m, 3H), 5.59 (ddd, $J = 3.7$, 2.6, 1.1 Hz, 1H), 4.06 (t, $J = 6.6$ Hz, 1H), 4.00 – 3.96 (m, 4H), 2.73 (ddd, $J = 13.8$, 9.0, 6.7 Hz, 1H), 2.62 (ddd, $J = 13.8$, 8.8, 7.1 Hz, 1H), 2.35 – 2.16 (m, 4H), 1.92 – 1.84 (m, 2H), 1.76 (ddd, $J = 7.1$, 6.2, 1.0 Hz, 2H).

$^{13}$C NMR (126 MHz, CDCl₃): $\delta$ 142.2, 139.8, 128.6, 128.5, 125.9, 120.4, 108.2, 75.2, 64.5, 36.7, 35.7, 32.2, 31.1, 23.0.

HRMS: Calc’d for C₁₇H₂₁O₂, [M-OH]$^+$ 257.1536; found 257.1548.

Compound 4

Following General Procedure C on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 23.3 mg (66%) of the title compound 4.

Physical State: colorless oil.

$R_f = 0.50$ (hexanes/EtOAc 4:1, UV, $p$-anisaldehyde).

$^1$H NMR (500 MHz, CDCl₃): $\delta$ 7.30 (td, $J = 7.4$, 1.4 Hz, 2H), 7.25 – 7.17 (m, 3H), 4.99 (dt, $J = 1.9$, 0.9 Hz, 1H), 4.89 (t, $J = 1.7$ Hz, 1H), 4.10 (t, $J = 6.5$ Hz, 1H), 2.70 (dddd, $J = 44.1$, 13.9, 9.3, 6.7 Hz, 2H), 1.93 – 1.84 (m, 2H), 1.77 – 1.73 (m, 4H).

$^{13}$C NMR (126 MHz, CDCl₃): $\delta$ 147.5, 142.1, 128.6, 128.5, 125.9, 111.4, 75.4, 36.7,
Spectroscopic data are in accordance with that reported in the literature.  

**Compound 5**

Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (3:1 hexanes/EtOAc) afforded 20.4 mg (63%) of the title compound 5.

**Physical State**: colorless oil.

$R_f = 0.38$ (hexanes/EtOAc 4:1, UV, $p$-anisaldehyde).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.33 – 7.25 (m, 2H), 7.24 – 7.16 (m, 3H), 5.91 (ddd, $J = 17.3$, 10.4, 6.2 Hz, 1H), 5.25 (dt, $J = 17.2$, 1.4 Hz, 1H), 5.15 (dt, $J = 10.5$, 1.3 Hz, 1H), 4.14 (dtt, $J = 7.3$, 6.0, 1.3 Hz, 1H), 2.81 – 2.66 (m, 2H), 1.93 – 1.81 (m, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 142.0, 141.1, 128.6, 128.5, 126.0, 115.1, 72.6, 38.7, 31.8.

Spectroscopic data are in accordance with that reported in the literature.  

**Compound 6**

Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (3:1 hexanes/EtOAc) afforded 25.1 mg (54%) of the title compound 6.

Following **General Procedure D** on 0.2 mmol scale using (S)-N-(2-(4-isopropyl-4,5-dihydrooxazol-2-yl)-6-methylphenyl)methanesulfonamide. Purification by PTLC (4:1 hexanes/EtOAc) afforded 31.5 mg (68%) of the title compound 40 and ee was determined to be 4.5:1 by Mosher ester analysis.

**Physical State**: colorless oil.

$R_f = 0.60$ (hexanes/EtOAc 4:1, UV, $p$-anisaldehyde).
$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.31 – 7.27 (m, 2H), 7.23 – 7.17 (m, 3H), 5.05 (p, $J$ = 1.1 Hz, 1H), 4.89 (q, $J$ = 1.5 Hz, 1H), 4.11 (t, $J$ = 6.8 Hz, 1H), 2.76 (ddd, $J$ = 13.8, 10.0, 5.7 Hz, 1H), 2.66 (ddd, $J$ = 13.8, 9.9, 6.5 Hz, 1H), 2.13 – 2.03 (m, 1H), 2.02 – 1.95 (m, 1H), 1.95 – 1.82 (m, 2H), 1.53 (d, $J$ = 3.2 Hz, 1H), 1.51 – 1.43 (m, 2H), 1.32 (qt, $J$ = 6.9, 3.6 Hz, 4H), 0.90 (t, $J$ = 6.9 Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 152.2, 142.2, 128.6, 128.5, 125.9, 109.6, 74.9, 37.3, 32.1, 31.9, 31.6, 27.8, 22.7, 14.2.

HRMS: Calc’d for C$_{16}$H$_{23}$, [M-OH]$^+$ 215.1794; found 215.1793.

Compound 7

Following General Procedure C on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 37.0 mg (66%) of the title compound 7.

Following General Procedure D on 0.2 mmol scale using (S)-N-(2-(4-isopropyl-4,5-dihydrooxazol-2-yl)-6-methylphenyl)methanesulfonyamide. Purification by PTLC (4:1 hexanes/EtOAc) afforded 34.2 mg (61%) of the title compound 42 and er was determined to be 4.0:1 by Mosher ester analysis.

Physical State: colorless oil.

$R_f$ = 0.50 (hexanes/EtOAc 4:1, UV, $p$-anisaldehyde).

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.31 – 7.27 (m, 4H), 7.19 (ddt, $J$ = 8.7, 5.7, 1.7 Hz, 6H), 5.08 (p, $J$ = 1.0 Hz, 1H), 4.91 (q, $J$ = 1.5 Hz, 1H), 4.10 (dt, $J$ = 7.8, 3.7 Hz, 1H), 2.75 (ddd, $J$ = 13.7, 9.9, 5.7 Hz, 1H), 2.65 (qt, $J$ = 9.3, 4.6 Hz, 3H), 2.15 (dt, $J$ = 14.8, 8.3, 7.5, 1.2 Hz, 1H), 2.08 – 2.02 (m, 1H), 1.94 – 1.78 (m, 4H), 1.50 (d, $J$ = 3.6 Hz, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 151.7, 142.4, 142.1, 128.59, 128.55, 128.52, 128.47, 125.97, 125.92, 109.9, 74.9, 37.2, 35.9, 32.1, 31.1, 29.9.

HRMS: Calc’d for C$_{20}$H$_{23}$, [M-OH]$^+$ 263.1794; found 263.1793.
**Compound 8**

Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 31.4 mg (54%) of the title compound **8**.

**Physical State**: colorless oil.

\[ R_f = 0.50 \text{ (hexanes/EtOAc 4:1, UV, } p\text{-anisaldehyde).} \]

\[
^1H \text{ NMR (500 MHz, CDCl}_3): \delta 7.31 - 7.26 (m, 2H), 7.23 - 7.16 (m, 3H), 5.09 - 5.06 (m, 1H), 4.87 (d, } J = 1.4 \text{ Hz, 1H), 4.12 (td, } J = 6.6, 2.8 \text{ Hz, 1H), 2.74 (dt, } J = 13.8, 7.9 \text{ Hz, 1H), 2.64 (dt, } J = 13.8, 8.0 \text{ Hz, 1H), 2.48 - 2.38 (m, 3H), 2.32 - 2.22 (m, 1H), 2.00 (d, } J = 3.6 \text{ Hz, 1H), 1.89 (td, } J = 8.1, 6.6 \text{ Hz, 2H), 1.44 (s, 9H).}
\]

\[
^{13}C \text{ NMR (126 MHz, CDCl}_3): \delta 172.9, 150.5, 142.1, 128.6, 128.5, 126.0, 110.7, 80.7, 75.1, 37.2, 34.1, 32.1, 28.3, 26.1.
\]

**HRMS**: Calc’d for C\text{18}H\text{26}O\text{3}Na, [M+Na]^+ 313.1774; found 313.1784.

**Compound 9**

Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 36.0 mg (71%) of the title compound **9**.

**Physical State**: colorless oil.

\[ R_f = 0.43 \text{ (hexanes/EtOAc 4:1, UV, } p\text{-anisaldehyde).} \]

\[
^1H \text{ NMR (500 MHz, CDCl}_3): \delta 7.32 - 7.25 (m, 2H), 7.24 - 7.16 (m, 3H), 5.08 (p, } J = 1.0 \text{ Hz, 1H), 4.90 (q, } J = 1.5 \text{ Hz, 1H), 4.11 (dd, } J = 7.8, 5.0 \text{ Hz, 1H), 3.55 (t, } J = 6.6 \text{ Hz, 2H), 2.76 (ddd, } J = 13.7, 9.7, 5.9 \text{ Hz, 1H), 2.65 (ddd, } J = 13.8, 9.6, 6.6 \text{ Hz, 1H), 2.18 - 2.08 (m, 1H), 2.08 - 1.98 (m, 1H), 1.94 - 1.78 (m, 4H), 1.67 - 1.60 (m, 2H).}
\]

\[
^{13}C \text{ NMR (126 MHz, CDCl}_3): \delta 151.3, 142.0, 128.6, 128.5, 126.0, 110.2, 74.9, 45.0, 37.2, 32.5, 32.1, 30.7, 25.3.
\]
HRMS: Calc’d for C_{15}H_{20}Cl, [M-OH]^+ 235.1248; found 215.1288.

Compound 10

Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (2:1 hexanes/EtOAc) afforded 25.2 mg (40%) of the title compound 10.

**Physical State:** yellowish oil.

$R_f = 0.27$ (hexanes/EtOAc 4:1, UV, $p$-anisaldehyde).

$^1\text{H NMR (500 MHz, CDCl}_3\text{): } \delta$ 7.28 (td, $J = 7.3, 1.5$ Hz, 2H), 7.23 – 7.16 (m, 3H), 5.26 (q, $J = 1.6$ Hz, 1H), 5.15 (q, $J = 1.2$ Hz, 1H), 4.82 (t, $J = 3.5$ Hz, 1H), 4.35 – 4.16 (m, 3H), 3.84 (dd, $J = 11.5, 9.0, 3.0$ Hz, 1H), 3.53 (dtd, $J = 11.2, 4.4, 1.6$ Hz, 1H), 3.15 – 2.97 (m, 2H), 2.80 – 2.62 (m, 2H), 1.96 – 1.50 (m, 9H).

$^{13}\text{C NMR (126 MHz, CDCl}_3\text{): } \delta$ 146.2, 141.9, 128.6, 128.5, 126.0, 112.6, 96.9, 83.3, 78.9, 74.2, 62.2, 54.7, 36.8, 32.0, 30.4, 25.5, 21.9, 19.2.

**HRMS:** Calc’d for C_{20}H_{27}O_{3}, [M+H]^+ 315.1955; found 315.1953.

Compound 11

Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (3:1 hexanes/EtOAc) afforded 22.7 mg (33%) of the title compound 11.

**Physical State:** yellowish oil.

$R_f = 0.30$ (hexanes/EtOAc 4:1, UV, $p$-anisaldehyde).

$^1\text{H NMR (600 MHz, CDCl}_3\text{): } \delta$ 7.79 (dd, $J = 3.8, 1.3$ Hz, 1H), 7.54 (dd, $J = 5.0, 1.3$ Hz, 1H), 7.28 (d, $J = 7.6$ Hz, 2H), 7.22 – 7.17 (m, 3H), 7.09 (dd, $J = 5.0, 3.7$ Hz, 1H), 5.08 (s, 1H), 4.90 (d, $J = 1.6$ Hz, 1H), 4.31 (t, $J = 6.5$ Hz, 2H), 4.11 (dt, $J = 8.3, 4.4$ Hz, 1H), 2.76 (ddd, $J = 13.8, 9.9, 5.7$ Hz, 1H), 2.65 (ddd, $J = 13.8, 9.8, 6.5$ Hz, 1H), 2.17
(dt, J = 15.7, 7.9 Hz, 1H), 2.07 (dt, J = 15.5, 7.6 Hz, 1H), 1.94 – 1.84 (m, 2H), 1.79 (tt, J = 8.7, 6.7 Hz, 2H), 1.62 (p, J = 7.4, 7.0 Hz, 2H), 1.54 (d, J = 4.0 Hz, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 162.5, 151.4, 142.1, 134.1, 133.5, 132.4, 128.6, 128.5, 127.9, 126.0, 110.1, 65.1, 37.3, 32.2, 31.0, 28.7, 24.5.

HRMS: Calc’d for C$_{20}$H$_{23}$O$_2$S, [M-OH]$^+$ 327.1413; found 327.1418.

**Compound 12**

Following General Procedure C on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 40.8 mg (61%) of the title compound 12.

Following General Procedure D on 0.2 mmol scale using ($R$)-N-(2-(4-isopropyl-4,5-dihydrooxazol-2-yl)-6-methylphenyl)methanesulphonamide. Purification by PTLC (4:1 hexanes/EtOAc) afforded 34.8 mg (52%) of the title compound 41 and err was determined to be 4.2:1 by Mosher ester analysis.

**Physical State:** colorless oil.

$R_f$ = 0.34 (hexanes/EtOAc 4:1, UV, p-anisaldehyde).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.30 – 7.26 (m, 2H), 7.22 – 7.16 (m, 3H), 5.08 – 5.03 (m, 1H), 4.89 (q, J = 1.5 Hz, 1H), 4.14 – 4.08 (m, 1H), 3.65 (t, J = 6.2 Hz, 2H), 2.74 (ddd, J = 13.7, 9.6, 6.1 Hz, 1H), 2.64 (ddd, J = 13.8, 9.6, 6.7 Hz, 1H), 2.21 – 2.14 (m, 1H), 2.10 – 2.02 (m, 1H), 1.93 – 1.82 (m, 2H), 1.76 – 1.67 (m, 2H), 0.90 (s, 9H), 0.05 (s, 6H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 151.6, 142.2, 128.6, 128.5, 125.9, 110.2, 75.1, 63.0, 37.3, 32.2, 31.4, 27.9, 26.1, 18.5, −5.1.

HRMS: Calc’d for C$_{20}$H$_{35}$O$_2$Si, [M+H]$^+$ 335.2401; found 335.2395.

**Compound 13**
Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (3:1 hexanes/EtOAc) afforded 22.0 mg (39%) of the title compound 13.

Following **General Procedure D** on 0.2 mmol scale using (S)-N-(2-(4-isopropyl-4,5-dihydrooxazol-2-yl)-6-methylphenyl)methanesulfonamide. Purification by PTLC (3:1 hexanes/EtOAc) afforded 45.0 mg (80%) of the title compound 45 and er was determined to be 1.4:1 by Mosher ester analysis.

**Physical State**: colorless oil.

$R_f = 0.35$ (hexanes/EtOAc 4:1, UV, $p$-anisaldehyde).

$^1$H NMR (600 MHz, CDCl$_3$): \( \delta \) 7.32 – 7.25 (m, 4H), 7.23 – 7.15 (m, 6H), 5.68 (dtd, \( J = 15.4, 6.7, 1.0 \) Hz, 1H), 5.52 (dddt, \( J = 15.4, 7.0, 1.4 \) Hz, 1H), 4.08 (q, \( J = 6.7 \) Hz, 1H), 2.77 – 2.59 (m, 4H), 2.14 – 2.05 (m, 2H), 1.94 – 1.76 (m, 2H), 1.73 (tt, \( J = 7.6, 6.7 \) Hz, 2H), 1.43 (s, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$): \( \delta \) 142.4, 142.1, 133.4, 132.1, 128.6, 128.5, 128.4, 125.94, 125.88, 72.5, 39.0, 35.5, 31.94, 31.87, 31.0.

**HRMS**: Calc’d for C$_{20}$H$_{23}$, [M-OH]$^+$ 263.1794; found 263.1796.

**Compound 14**

Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 26.2 mg (55%) of the title compound 14.

**Physical State**: colorless oil.

$R_f = 0.40$ (hexanes/EtOAc 4:1, UV, $p$-anisaldehyde).

$^1$H NMR (600 MHz, CDCl$_3$): \( \delta \) 7.41 – 7.36 (m, 2H), 7.35 – 7.27 (m, 4H), 7.27 – 7.17 (m, 4H), 6.62 – 6.56 (m, 1H), 6.25 (dd, \( J = 15.9, 6.8 \) Hz, 1H), 4.31 (d, \( J = 6.7 \) Hz, 1H), 2.77 (dddd, \( J = 23.2, 13.9, 9.3, 6.5 \) Hz, 2H), 2.04 – 1.90 (m, 2H), 1.62 (d, \( J = 3.6 \) Hz, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$): \( \delta \) 141.9, 136.8, 132.3, 130.8, 128.8, 128.62, 128.57, 127.9, 126.6, 126.0, 72.5, 38.9, 31.9.
Spectroscopic data are in accordance with that reported in the literature.\textsuperscript{22}

**Compound 15**

Following General Procedure C on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 13.2 mg (27\%) of the title compound 15.

**Physical State**: colorless oil.

\( R_f = 0.48 \) (hexanes/EtOAc 4:1, UV, \( p \)-anisaldehyde).

\( ^1\text{H NMR (600 MHz, CDCl}_3 \)): \( \delta 7.31 – 7.25 \text{ (m, 2H), 7.23 – 7.15 \text{ (m, 3H), 5.60 \text{ (ddd, } J = 15.6, 6.6, 0.9 \text{ Hz, 1H), 5.45 \text{ (ddd, } J = 15.5, 7.1, 1.3 \text{ Hz, 1H), 4.06 \text{ (q, } J = 6.7 \text{ Hz, 1H), 2.76 – 2.61 \text{ (m, 2H), 2.00 – 1.62 \text{ (m, 8H), 1.33 – 1.03 \text{ (m, 6H)}} \).}

\( ^13\text{C NMR (126 MHz, CDCl}_3 \)): \( \delta 142.2, 138.5, 130.3, 128.6, 128.5, 125.9, 72.7, 40.4, 39.0, 33.1, 33.0, 32.0, 26.3, 26.1 \).

Spectroscopic data are in accordance with that reported in the literature.\textsuperscript{22}

**Compound 16**

Following General Procedure C on 0.2 mmol scale. Purification by PTLC (2:1 hexanes/EtOAc) afforded 33.4 mg (62\%) of the title compound 16.

**Physical State**: colorless oil.

\( R_f = 0.18 \) (hexanes/EtOAc 4:1, UV, \( p \)-anisaldehyde).

\( ^1\text{H NMR (500 MHz, CDCl}_3 \)): \( \delta 8.09 \text{ (d, } J = 2.5 \text{ Hz, 1H), 7.64 \text{ (dd, } J = 8.6, 2.5 \text{ Hz, 1H), 7.31 – 7.27 \text{ (m, 2H), 7.23 – 7.18 \text{ (m, 3H), 6.71 \text{ (dt, } J = 8.7, 0.6 \text{ Hz, 1H), 6.50 \text{ (dd, } J = 15.9, 1.1 \text{ Hz, 1H), 6.13 \text{ (dd, } J = 15.9, 6.7 \text{ Hz, 1H), 4.29 \text{ (tdd, } J = 6.9, 5.6, 1.2 \text{ Hz, 1H), 3.94 \text{ (s, 3H), 2.83 – 2.70 \text{ (m, 2H), 2.02 – 1.89 \text{ (m, 2H)}} \).}

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 163.8, 145.8, 141.8, 135.7, 131.7, 128.59, 128.56, 126.8, 126.04, 125.96, 111.1, 72.4, 53.7, 38.9, 31.9.

HRMS: Calc’d for C$_{17}$H$_{20}$NO$_2$, [M+H]$^+$ 270.1489; found 270.1488.

**Compound 17**

Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (3:1 hexanes/EtOAc) afforded 20.0 mg (44\%) of the title compound 17.

**Physical State**: yellowish oil.

$R_f$ = 0.34 (hexanes/EtOAc 4:1, UV, $p$-anisaldehyde).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.36 (d, $J = 1.8$ Hz, 1H), 7.29 (t, $J = 7.5$ Hz, 2H), 7.24 – 7.18 (m, 3H), 6.45 – 6.37 (m, 2H), 6.26 – 6.18 (m, 2H), 4.28 (q, $J = 6.5$, 5.9 Hz, 1H), 2.81 – 2.70 (m, 2H), 2.00 – 1.89 (m, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 152.5, 142.2, 141.9, 130.9, 128.60, 128.55, 126.0, 118.9, 111.5, 108.3, 72.0, 38.9, 31.8.

Spectroscopic data are in accordance with that reported in the literature.$^{22}$

**Compound 18**

Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (5:1 hexanes/EtOAc) afforded 20.0 mg (39\%) of the title compound 18.

**Physical State**: colorless oil.

$R_f$ = 0.66 (hexanes/EtOAc 4:1, UV, $p$-anisaldehyde).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.31 – 7.27 (m, 2H), 7.23 – 7.17 (m, 3H), 5.10 (d, $J = 1.4$ Hz, 1H), 4.86 (d, $J = 1.5$ Hz, 1H), 4.07 (t, $J = 6.3$ Hz, 1H), 2.76 (ddd, $J = 13.9$, 10.1,
Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (3:1 hexanes/EtOAc) afforded 25.3 mg (50%) of the title compound 19.

**Physical State**: colorless oil.

$R_f = 0.35$ (hexanes/EtOAc 4:1, UV, $p$-anisaldehyde).

**1H NMR (600 MHz, CDCl₃)**: $\delta$ 7.30 – 7.27 (m, 2H), 7.21 – 7.17 (m, 3H), 5.65 (dtd, $J = 15.4, 6.7, 1.0$ Hz, 1H), 5.55 – 5.50 (m, 1H), 4.08 (q, $J = 6.7$ Hz, 1H), 3.54 (t, $J = 6.6$ Hz, 2H), 2.74 – 2.63 (m, 2H), 2.11 – 2.05 (m, 2H), 1.91 – 1.76 (m, 4H), 1.58 (s, 1H), 1.57 – 1.51 (m, 2H).

**13C NMR (151 MHz, CDCl₃)**: $\delta$ 142.1, 133.6, 131.6, 128.6, 128.5, 126.0, 72.5, 45.0, 39.0, 32.2, 31.9, 31.5, 26.5.


### Compound 20

Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 24.0 mg (36%) of the title compound 20.

Following **General Procedure D** on 0.2 mmol scale using (S)-N-(2-(4-isopropyl-4,5-dihydrooxazol-2-yl)-6-methylphenyl)methanesulfonamide. Purification by PTLC (4:1
hexanes/EtOAc) afforded 54.0 mg (81%) of the title compound 43 and ee was determined to be 1.2:1 by Mosher ester analysis.

Physical State: colorless oil.

$R_f = 0.50$ (hexanes/EtOAc 4:1, UV, $p$-anisaldehyde).

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.31 – 7.25 (m, 2H), 7.22 – 7.15 (m, 3H), 5.67 (dtd, $J = 15.4$, 6.8, 1.0 Hz, 1H), 5.52 (ddt, $J = 15.4$, 7.1, 1.4 Hz, 1H), 4.08 (q, $J = 6.7$ Hz, 1H), 3.62 (t, $J = 6.4$ Hz, 2H), 2.74 – 2.64 (m, 2H), 2.14 – 2.07 (m, 2H), 1.92 – 1.76 (m, 2H), 1.64 – 1.57 (m, 2H), 0.90 (s, 9H), 0.05 (s, 6H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 142.1, 133.2, 132.1, 128.6, 128.5, 125.9, 72.5, 62.6, 38.9, 32.4, 31.9, 28.6, 26.1, 18.5, –5.1.

Spectroscopic data are in accordance with that reported in the literature.\textsuperscript{23}

**Compound 21**

Following General Procedure C on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 30.2 mg (52%) of the title compound 21.

Physical State: colorless oil.

$R_f = 0.55$ (hexanes/EtOAc 4:1, UV, $p$-anisaldehyde).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.30 – 7.26 (m, 2H), 7.18 (dd, $J = 8.9$, 7.3 Hz, 3H), 5.70 – 5.63 (m, 1H), 5.55 (ddt, $J = 15.5$, 7.0, 1.2 Hz, 1H), 4.07 (q, $J = 6.6$ Hz, 1H), 2.68 (qdd, $J = 13.9$, 9.3, 6.4 Hz, 2H), 2.37 – 2.27 (m, 4H), 1.91 – 1.75 (m, 2H), 1.60 – 1.53 (m, 1H), 1.44 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 172.5, 142.1, 133.9, 130.4, 128.6, 128.5, 125.9, 80.5, 72.3, 38.8, 35.2, 31.8, 28.3, 27.7.

The desired mass for HRMS was not observed.
Compound 22

Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (1:1 hexanes/EtOAc) afforded 40.3 mg (61%) of the title compound 22.

**Physical State**: colorless oil.

$R_f = 0.23$ (hexanes/EtOAc 2:1, UV, $p$-anisaldehyde).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.90 – 7.86 (m, 2H), 7.65 – 7.60 (m, 1H), 7.55 – 7.50 (m, 2H), 7.31 – 7.26 (m, 2H), 7.21 – 7.14 (m, 3H), 5.49 (tt, $J$ = 7.9, 1.3 Hz, 1H), 4.05 – 3.99 (m, 1H), 3.91 – 3.82 (m, 2H), 2.66 (ddd, $J$ = 13.9, 9.3, 6.2 Hz, 1H), 2.55 (ddd, $J$ = 13.8, 9.2, 7.0 Hz, 1H), 1.82 – 1.70 (m, 2H), 1.65 (d, $J$ = 3.6 Hz, 1H), 1.39 (d, $J$ = 1.4 Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 148.1, 141.7, 138.9, 133.9, 129.3, 128.6, 128.5, 126.1, 111.7, 76.2, 55.8, 36.6, 31.9, 12.2.

**HRMS**: Calc’d for C$_{19}$H$_{21}$O$_2$S, [M-OH]$^+$ 313.1257; found 313.1251.

Compound 23

Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (3:1 hexanes/EtOAc) afforded 32.0 mg (50%) of the title compound 23.

**Physical State**: colorless oil.

$R_f = 0.33$ (hexanes/EtOAc 4:1, UV, $p$-anisaldehyde).

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.30 – 7.26 (m, 2H), 7.21 – 7.17 (m, 3H), 5.56 (tt, $J$ = 6.0, 1.2 Hz, 1H), 4.29 – 4.18 (m, 2H), 4.11 – 3.99 (m, 1H), 2.71 (ddd, $J$ = 13.7, 9.5, 6.2 Hz, 1H), 2.61 (ddd, $J$ = 13.8, 9.4, 6.7 Hz, 1H), 1.91 – 1.81 (m, 2H), 1.63 (q, $J$ = 1.0 Hz, 3H), 1.50 (d, $J$ = 3.3 Hz, 1H), 0.91 (s, 9H), 0.08 (s, 6H).
Compound 24

Following General Procedure C on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 18.0 mg (41%) of the title compound 24.

Following General Procedure D on 0.2 mmol scale using (S)-N-(2-(4-isopropyl-4,5-dihydrooxazol-2-yl)-6-methylphenyl) methanesulfonamide. Purification by PTLC (4:1 hexanes/EtOAc) afforded 30.0 mg (69%) of the title compound 44 and er was determined to be 1.3:1 by Mosher ester analysis.

Physical State: colorless oil.

$R_f = 0.50$ (hexanes/EtOAc 4:1, UV, $p$-anisaldehyde).

$^1$H NMR (500 MHz, CDCl₃): δ 7.32 – 7.25 (m, 2H), 7.23 – 7.15 (m, 3H), 5.66 (dtd, $J = 15.4, 6.7, 0.9$ Hz, 1H), 5.50 (ddt, $J = 15.4, 7.1, 1.4$ Hz, 1H), 4.08 (q, $J = 6.7$ Hz, 1H), 2.69 (qddd, $J = 13.8, 9.5, 6.4$ Hz, 2H), 2.08 – 2.01 (m, 2H), 1.93 – 1.76 (m, 2H), 1.48 – 1.42 (m, 1H), 1.40 – 1.28 (m, 4H), 0.90 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl₃): δ 142.2, 132.9, 132.8, 128.6, 128.5, 125.9, 72.6, 39.0, 32.02, 31.95, 31.5, 22.3, 14.1.

Spectroscopic data are in accordance with that reported in the literature.²⁴

Compound 25

$^{13}$C NMR (151 MHz, CDCl₃): δ 142.1, 138.3, 128.6, 128.5, 126.6, 126.0, 76.8, 60.1, 36.5, 32.2, 26.1, 18.6, 11.9, −4.95, −4.97.

HRMS: Calc’d for $\text{C}_{19}\text{H}_{33}\text{O}_{2}\text{Si}$, [M+H]$^+$ 321.2244; found 321.2243.
Following General Procedure C on 0.2 mmol scale. Purification by PTLC (1:1 hexanes/EtOAc) afforded 40.5 mg (58%) of the title compound 25.

**Physical State**: colorless oil.

*R* = 0.17 (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

**1H NMR** (600 MHz, CDCl₃): δ 7.84 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.73 – 7.69 (m, 2H), 7.28 – 7.24 (m, 2H), 7.20 – 7.14 (m, 3H), 5.11 – 5.08 (m, 1H), 4.92 (q, *J* = 1.5 Hz, 1H), 4.13 – 4.08 (m, 1H), 3.72 (td, *J* = 7.0, 2.4 Hz, 2H), 2.74 (ddd, *J* = 13.8, 8.9, 6.8 Hz, 1H), 2.63 (ddd, *J* = 13.8, 9.0, 7.1 Hz, 1H), 2.23 – 2.16 (m, 1H), 2.11 – 2.03 (m, 1H), 1.94 – 1.84 (m, 4H), 1.82 (d, *J* = 3.6 Hz, 1H).

**13C NMR** (151 MHz, CDCl₃): δ 168.6, 150.3, 142.1, 134.1, 132.2, 128.6, 125.9, 123.4, 110.6, 75.0, 37.7, 37.1, 28.3, 26.6.

**HRMS**: Calc’d for C₂₂H₂₄NO₃, [M+H]⁺ 350.1751; found 350.1747.

**Compound 26**

Following General Procedure C on 0.2 mmol scale. Purification by PTLC (2:1 hexanes/EtOAc) afforded 11.2 mg (21%) of the title compound 26.

**Physical State**: colorless oil.

*R* = 0.24 (hexanes/EtOAc 4:1, UV, *p*-anisaldehyde).

**1H NMR** (600 MHz, CDCl₃): δ 7.41 – 7.39 (m, 2H), 7.34 – 7.28 (m, 4H), 7.25 – 7.18 (m, 4H), 6.78 (ddd, *J* = 15.7, 10.5, 0.8 Hz, 1H), 6.56 (d, *J* = 15.6 Hz, 1H), 6.40 (ddt, *J* = 15.2, 10.5, 1.0 Hz, 1H), 5.86 (dd, *J* = 15.2, 6.8 Hz, 1H), 4.24 (q, *J* = 6.6 Hz, 1H), 2.74 (dddd, *J* = 23.2, 13.9, 9.4, 6.4 Hz, 2H), 1.99 – 1.85 (m, 2H), 1.57 (s, 1H).

**13C NMR** (151 MHz, CDCl₃): δ 141.9, 137.3, 136.4, 133.0, 131.2, 128.8, 128.61, 128.56, 128.3, 127.8, 126.5, 126.0, 72.2, 38.9, 31.9.

Spectroscopic data are in accordance with that reported in the literature.²⁵
Compound 27

Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 35.7 mg (53%) of the title compound 27.

**Physical State**: colorless oil.

$R_f = 0.48$ (hexanes/EtOAc 4:1, UV, $p$-anisaldehyde).

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.31 – 7.27 (m, 2H), 7.22 – 7.17 (m, 3H), 5.98 (s, 0.37H), 5.94 (d, $J = 2.3$ Hz, 0.63H), 5.49 (dd, $J = 5.1$, 3.0 Hz, 1H), 4.75 (dp, $J = 4.9$, 1.5 Hz, 2H), 4.08 (dt, $J = 13.7$, 6.9 Hz, 1H), 2.75 – 2.57 (m, 2H), 2.48 – 2.41 (m, 1H), 2.29 – 2.17 (m, 1H), 2.01 – 1.82 (m, 5H), 1.78 – 1.72 (m, 4H), 1.52 (dq, $J = 11.2$, 6.7, 4.6 Hz, 2H), 1.18 (td, $J = 12.7$, 2.1 Hz, 1H), 0.94 – 0.88 (m, 6H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 150.4, 150.3, 142.2, 142.1, 141.9, 141.8, 138.6, 128.59, 128.56, 128.52, 128.51, 125.97, 125.95, 125.93, 124.1, 123.9, 123.5, 108.84, 108.81, 75.6, 75.0, 40.3, 40.2, 39.2, 39.0, 37.44, 37.40, 37.1, 36.6, 36.42, 36.36, 32.4, 32.0, 31.6, 31.37, 31.35, 29.9, 20.8, 17.58, 17.56, 14.97, 14.96.

**HRMS**: Calc’d for C$_{24}$H$_{31}$, [M-OH]$^+$ 319.2420; found 319.2417.

Compound 28

Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (9:1 hexanes/EtOAc) afforded 26.3 mg (51%) of the title compound 28.

**Physical State**: colorless oil.

$R_f = 0.32$ (hexanes/EtOAc 9:1, $p$-anisaldehyde).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.29 (t, $J = 7.5$ Hz, 2H), 7.23 – 7.17 (m, 3H), 5.12 (tdd,
$J = 5.8, 2.9, 1.5 \text{ Hz, 1H}), 5.05 \ (t, \ J = 1.1 \text{ Hz, 1H}), 4.88 \ (q, \ J = 1.5 \text{ Hz, 1H}), 4.10 \ (dd, \ J = 7.8, 5.0 \text{ Hz, 1H}), 2.81 – 2.72 \ (m, \ 1H), 2.65 \ (ddd, \ J = 13.8, 9.8, 6.5 \text{ Hz, 1H}), 2.09 \ (dq, \ J = 14.7, 7.3, 6.7 \text{ Hz, 1H}), 2.04 – 1.97 \ (m, \ 3H), 1.94 – 1.81 \ (m, \ 2H), 1.69 \ (d, \ J = 1.5 \text{ Hz, 3H}), 1.60 \ (s, \ 3H), 1.51 \ (p, \ J = 7.7 \text{ Hz, 3H}).$

$^{13}$C NMR (126 MHz, CDCl$_3$): δ 152.1, 142.2, 131.9, 128.6, 128.5, 126.0, 124.5, 109.7, 75.0, 37.3, 32.2, 31.2, 28.4, 28.0, 25.9, 17.9.

HRMS: Calc’d for C$_{18}$H$_{27}$O, [M+H]$^+$ 259.2056; found 259.2064.

**Compound 29**

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Ph
   OH
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Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (9:1 hexanes/EtOAc) afforded 25.6 mg (56%) of the title compound 29.

**Physical State**: yellowish oil.

$R_f = 0.48$ (hexanes/EtOAc 6:1, p-anisaldehyde).

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.28 (t, $J = 7.6$ Hz, 2H), 7.22 – 7.17 (m, 3H), 5.80 (t, $J = 6.4$ Hz, 1H), 4.01 (t, $J = 6.6$ Hz, 1H), 2.70 (ddd, $J = 13.8, 9.1, 6.9$ Hz, 1H), 2.64 – 2.57 (m, 1H), 2.14 (qd, $J = 10.0, 8.5, 3.7$ Hz, 4H), 1.86 – 1.72 (m, 4H), 1.55 – 1.45 (m, 5H).

$^{13}$C NMR (126 MHz, CDCl$_3$): δ 146.3, 142.3, 128.6, 128.5, 128.4, 125.9, 77.5, 36.7, 32.8, 32.4, 28.3, 27.9, 27.4, 27.2.

HRMS: Calc’d for C$_{16}$H$_{21}$, [M-OH]$^+$ 213.1638; found 213.1642.

**Compound 30**

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Me
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Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (4:1
hexanes/EtOAc) afforded 18.2 mg (59%) of the title compound 30.

Physical State: colorless oil.

$R_f = 0.55$ (hexanes/EtOAc 4:1, UV, $p$-anisaldehyde).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 4.91 – 4.84 (m, 2H), 3.74 (d, $J = 7.5$ Hz, 1H), 1.93 (dqd, $J = 13.9, 3.5, 1.7$ Hz, 1H), 1.81 – 1.61 (m, 6H), 1.56 – 1.38 (m, 3H), 1.28 – 1.10 (m, 4H), 1.02 – 0.91 (m, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 146.6, 112.5, 81.1, 40.7, 29.8, 28.5, 26.6, 26.4, 26.2, 17.6.

Spectroscopic data are in accordance with that reported in the literature.$^{26}$

**Compound 31**

![Compound 31](image)

Following General Procedure C on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 17.0 mg (56%) of the title compound 31.

Physical State: colorless oil.

$R_f = 0.50$ (hexanes/EtOAc 4:1, $p$-anisaldehyde).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 5.76 (ddt, $J = 5.0, 3.7, 1.8$ Hz, 1H), 5.04 (dt, $J = 2.1$, 1.0 Hz, 1H), 4.91 (q, $J = 1.4$ Hz, 1H), 4.38 (s, 1H), 2.05 (dt, $J = 6.9, 3.6, 1.7$ Hz, 2H), 1.96 – 1.89 (m, 1H), 1.85 – 1.77 (m, 1H), 1.64 – 1.52 (m, 8H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 145.7, 137.7, 124.2, 110.8, 79.8, 25.2, 23.8, 22.8, 22.7, 18.7.

Spectroscopic data are in accordance with that reported in the literature.$^{27}$

**Compound 32**

![Compound 32](image)
Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 22.4 mg (69%) of the title compound 32.

**Physical State**: colorless oil.

$R_f = 0.48$ (hexanes/EtOAc 4:1, $p$-anisaldehyde).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 4.95 (dt, $J = 1.9, 1.0$ Hz, 1H), 4.85 (p, $J = 1.6$ Hz, 1H), 4.07 (t, $J = 6.2$ Hz, 1H), 3.54 (t, $J = 6.7$ Hz, 2H), 1.81 (tt, $J = 7.3, 6.5$ Hz, 2H), 1.72 (t, $J = 1.2$ Hz, 3H), 1.61 – 1.50 (m, 5H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 147.5, 111.4, 75.9, 45.1, 34.2, 32.6, 23.1, 17.6.

The desired mass for HRMS was not observed.

**Compound 33**

Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (2:1 hexanes/EtOAc) afforded 38.3 mg (75%) of the title compound 33.

**Physical State**: colorless oil.

$R_f = 0.21$ (hexanes/EtOAc 4:1, UV, $p$-anisaldehyde).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 4.91 – 4.83 (m, 2H), 4.10 (s, 2H), 3.74 (dd, $J = 8.0, 2.6$ Hz, 1H), 2.64 (s, 2H), 1.88 (dq, $J = 13.2, 2.8$ Hz, 1H), 1.76 (s, 1H), 1.70 (q, $J = 1.5$ Hz, 3H), 1.55 (dtt, $J = 11.5, 7.6, 3.7$ Hz, 1H), 1.43 (d, $J = 1.9$ Hz, 10H), 1.15 (pd, $J = 13.0, 4.3$ Hz, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 155.0, 145.9, 113.1, 80.3, 79.4, 43.9, 39.1, 28.7, 28.6, 28.0, 17.3.

**HRMS**: Calc’d for C$_9$H$_{18}$NO, [M-Boc+2H]$^+$ 156.1383; found 156.1383.

**Compound 34**
Following General Procedure C on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 25.6 mg (66%) of the title compound 34.

**Physical State:** yellowish oil.

\( R_f = 0.48 \) (hexanes/EtOAc 4:1, UV, \( p \)-anisaldehyde).

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 5.90 – 5.81 (m, 2H), 4.94 (ddp, \( J = 2.9, 1.9, 0.9 \) Hz, 1H), 4.83 (dp, \( J = 13.7, 1.6 \) Hz, 1H), 4.12 (dd, \( J = 8.3, 5.1 \) Hz, 0.55H), 4.02 (dd, \( J = 8.9, 4.2 \) Hz, 0.48H), 3.04 – 2.85 (m, 1H), 2.25 (t, \( J = 1.3 \) Hz, 3H), 1.97 – 1.83 (m, 1H), 1.73 (dt, \( J = 10.2, 1.2 \) Hz, 3H), 1.71 – 1.62 (m, 1H), 1.56 (s, 1H), 1.26 (dd, \( J = 7.0, 5.9 \) Hz, 3H).

\(^{13}\)C NMR (151 MHz, CDCl\(_3\)): \( \delta \) 158.5, 158.2, 150.44, 150.40, 147.9, 147.6, 111.4, 110.8, 105.79, 105.76, 104.7, 104.4, 74.1, 74.0, 41.7, 41.4, 30.2, 20.4, 19.3, 17.9, 17.6, 13.69, 13.67.

**HRMS:** Calc’d for C\(_{12}\)H\(_{19}\)O\(_2\), [M+H]+ 195.1380; found 195.1367.

**Compound 35**

Following General Procedure C on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 24.7 mg (63%) of the title compound 35.

**Physical State:** colorless oil.

\( R_f = 0.58 \) (hexanes/EtOAc 4:1, \( p \)-anisaldehyde).

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 5.10 (ddt, \( J = 8.8, 7.1, 1.5 \) Hz, 1H), 4.94 (ddt, \( J = 8.0, 1.9, 0.9 \) Hz, 1H), 4.82 (dp, \( J = 5.0, 1.6 \) Hz, 1H), 4.16 (ddd, \( J = 10.7, 7.9, 4.8 \) Hz, 1H), 2.06 – 1.91 (m, 2H), 1.72 (dt, \( J = 5.9, 1.2 \) Hz, 3H), 1.68 (t, \( J = 1.4 \) Hz, 3H), 1.60 (s, 3H), 1.57 – 1.47 (m, 2H), 1.43 – 1.25 (m, 2H), 1.23 – 1.13 (m, 1H), 0.93 (dd, \( J = 6.6, 5.6 \) Hz, 3H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \( \delta \) 148.6, 147.9, 131.39, 131.36, 124.9, 111.5, 110.5, 74.6, 73.9, 42.9, 42.4, 37.8, 37.1, 29.5, 29.2, 25.9, 25.6, 25.5, 20.2, 19.4, 17.9, 17.8, 17.2.

**HRMS:** Calc’d for C\(_{13}\)H\(_{25}\)O, [M+H]+ 197.1900; found 197.1900.
Compound 36

Following General Procedure C on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 16.1 mg (59%) of the title compound 36.

Physical State: colorless oil.

\( R_f = 0.38 \) (hexanes/EtOAc 4:1, UV, \( p \)-anisaldehyde).

\( ^1H \) NMR (600 MHz, CDCl\(_3\)): \( \delta 7.41 – 7.33 \) (m, 4H), 7.32 – 7.27 (m, 1H), 6.06 (ddd, \( J = 17.2, 10.3, 6.0 \) Hz, 1H), 5.39 – 5.33 (m, 1H), 5.25 – 5.17 (m, 2H), 2.00 (s, 1H).

\( ^{13}C \) NMR (151 MHz, CDCl\(_3\)): \( \delta 142.7, 140.4, 128.7, 127.9, 126.5, 115.3, 75.5 \).

Spectroscopic data are in accordance with that reported in the literature.\(^{29}\)

Compound 37

Following General Procedure C on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 20.3 mg (66%) of the title compound 37.

Less polar isomer:

Physical State: colorless oil.

\( [\alpha]_D^{20} = +1.2 \) (c 0.5, CHCl\(_3\)).

\( R_f = 0.40 \) (hexanes/EtOAc 4:1, UV, \( p \)-anisaldehyde).

\( ^1H \) NMR (600 MHz, CDCl\(_3\)): \( \delta 7.29 – 7.24 \) (m, 2H), 7.18 – 7.13 (m, 1H), 7.11 – 7.07 (m, 2H), 5.01 (dt, \( J = 1.8, 0.9 \) Hz, 1H), 4.86 (p, \( J = 1.6 \) Hz, 1H), 3.64 (d, \( J = 7.8 \) Hz, 1H), 2.03 – 1.98 (m, 1H), 1.85 (t, \( J = 1.2 \) Hz, 3H), 1.64 (s, 1H), 1.38 – 1.32 (m, 1H), 1.03 – 0.97 (m, 2H).

\( ^{13}C \) NMR (151 MHz, CDCl\(_3\)): \( \delta 147.1, 142.6, 128.5, 126.0, 125.8, 111.1, 79.2, 28.4, 21.5, 18.5, 13.7 \).
HRMS: Calc’d for C_{13}H_{15}, [M-OH]^+ 171.1168; found 171.1164.

More polar isomer:

Physical State: colorless oil.

$[\alpha]D^{20} = -0.6$ (c 0.6, CHCl₃).

$R_f = 0.33$ (hexanes/EtOAc 4:1, UV, $p$-anisaldehyde).

$^1$H NMR (600 MHz, CDCl₃): δ 7.28 – 7.23 (m, 2H), 7.18 – 7.14 (m, 1H), 7.08 – 7.03 (m, 2H), 5.02 (dt, $J = 1.9$, 1.0 Hz, 1H), 4.85 (q, $J = 1.7$ Hz, 1H), 3.61 (d, $J = 8.0$ Hz, 1H), 1.88 (dt, $J = 8.8$, 5.0 Hz, 1H), 1.82 (t, $J = 1.2$ Hz, 3H), 1.65 (s, 1H), 1.34 (tdd, $J = 8.2$, 5.6, 4.5 Hz, 1H), 1.09 (dt, $J = 8.8$, 5.3 Hz, 1H), 1.03 (dt, $J = 8.4$, 5.2 Hz, 1H).

$^{13}$C NMR (151 MHz, CDCl₃): δ 147.2, 142.3, 128.5, 126.0, 125.8, 110.9, 79.1, 28.2, 21.5, 18.8, 13.8.

HRMS: Calc’d for C_{13}H_{15}, [M-OH]^+ 171.1168; found 171.1167.

**Compound 38**

Following **General Procedure C** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 34.0 mg (71%) of the title compound 38.

Physical State: colorless oil.

$R_f = 0.48$ (hexanes/EtOAc 4:1, UV, $p$-anisaldehyde).

$^1$H NMR (600 MHz, CDCl₃): δ 7.42 – 7.37 (m, 2H), 7.39 – 7.33 (m, 2H), 7.31 (dd, $J = 8.4$, 6.9 Hz, 2H), 7.27 – 7.21 (m, 1H), 6.94 – 6.88 (m, 2H), 6.68 (dd, $J = 15.9$, 1.3 Hz, 1H), 6.39 (dd, $J = 15.8$, 6.3 Hz, 1H), 5.37 – 5.33 (m, 1H), 3.81 (s, 3H), 2.10 (s, 1H).

$^{13}$C NMR (151 MHz, CDCl₃): δ 159.4, 136.7, 135.1, 131.8, 130.3, 128.7, 127.8, 126.7, 114.1, 74.8, 55.4.

Spectroscopic data are in accordance with that reported in the literature.²⁸
To a stirred solution of alcohol \textbf{S24 [generously provided by Eisai]} (667 mg, 2.0 mmol, 1.0 equiv) and NaHCO$_3$ (840 mg, 10.0 mmol, 5 equiv) in DCM (20 mL) was added Dess–Martin periodinane (1.27 g, 3.0 mmol, 1.5 equiv) at 0 °C. After 3 hours, the reaction mixture was quenched with saturated NaHCO$_3$ (10 mL) and aqueous Na$_2$SO$_3$ (40 mL). After extraction with DCM, the combined organic layers were washed with brine, dried over anhydrous Na$_2$SO$_4$, and filtered. The solvent was evaporated under vacuum, and the residue was purified by flash column chromatography with hexanes/EtOAc (4:1) to give aldehyde \textbf{46} (610 mg, 1.84 mmol, 92%).

**Physical State:** colorless oil.

$R_f = 0.67$ (hexanes/EtOAc 3:2, $p$-anisaldehyde).

$[\alpha]_D^{20} = +12.0$ (c 1.0, CHCl$_3$).

$^1$H NMR (600 MHz, CDCl$_3$): δ 9.77 (t, $J = 1.6$ Hz, 1H), 3.75 – 3.69 (m, 1H), 3.69 (s, 3H), 3.16 (s, 3H), 2.95 (s, 1H), 2.51 (dddd, $J = 8.1$, 6.4, 3.3, 1.5 Hz, 2H), 1.91 – 1.79 (m, 2H), 1.72 – 1.65 (m, 1H), 1.44 (dt, $J = 13.8$, 6.3 Hz, 1H), 1.12 (d, $J = 7.0$ Hz, 3H), 0.86 (s, 9H), 0.02 (d, $J = 1.2$ Hz, 6H).

$^{13}$C NMR (151 MHz, CDCl$_3$): δ 202.6, 177.7, 69.8, 61.5, 40.5, 39.4, 32.4, 32.2, 28.9, 26.0, 18.2, 18.1, −4.2, −4.5.

**HRMS:** Calc’d for C$_{16}$H$_{34}$NO$_4$Si, [M+H]$^+$ 332.2252; found 332.2256.

**Compound 47a**
Compound 47b

Following **General Procedure D** on 0.2 mmol scale using (S)-N-(2-(4-isopropyl-4,5-dihydrooxazol-2-yl)-6-methylphenyl)methanesulfonylamine with the following modifications: 4Å MS (150 mg), 6 F/mol. Purification by PTLC (3:2 hexanes/EtOAc) afforded 57.5 mg (67%) of 47a and 47b as a mixture of inseparable diastereoisomers (47a/47b = 4.4:1).

Following **General Procedure D** on 0.2 mmol scale using (R)-N-(2-(4-isopropyl-4,5-dihydrooxazol-2-yl)-6-methylphenyl)methanesulfonylamine with the following modifications: 4Å MS (150 mg), 6 F/mol. Purification by PTLC (3:2 hexanes/EtOAc) afforded 60.0 mg (71%) of 47a and 47b as a mixture of inseparable diastereoisomers (47a/47b = 1:4.5).

**Physical State:** colorless oil.

\( R_f = 0.67 \) (hexanes/EtOAc 3:2, \( p \)-anisaldehyde).

**47a:** \(^1\)H NMR (500 MHz, C\(_6\)D\(_6\)): \( \delta \) 5.15 (dq, \( J = 1.9, 0.9 \) Hz, 0.19H), 5.13 (dq, \( J = 1.9, 1.0 \) Hz, 0.84H), 4.88 (p, \( J = 1.6 \) Hz, 1H), 4.04 (dd, \( J = 7.4, 4.2 \) Hz, 1H), 3.90 (dd, \( J = 10.1, 8.0, 5.6 \) Hz, 1H), 3.20 (s, 3H), 3.11 (s, 1H), 2.92 (d, \( J = 2.2 \) Hz, 3H), 2.30 (tt, \( J = 8.6, 5.3 \) Hz, 1H), 2.18 – 2.08 (m, 1H), 2.00 (dt, \( J = 15.5, 7.8 \) Hz, 1H), 1.85 – 1.62 (m, 5H), 1.58 (dd, \( J = 13.7, 6.8, 5.2, 3.4 \) Hz, 1H), 1.52 – 1.45 (m, 2H), 1.36 – 1.23 (m, 5H), 1.18 (d, \( J = 6.9 \) Hz, 3H), 1.01 (d, \( J = 2.0 \) Hz, 9H), 0.93 – 0.86 (m, 3H), 0.16 – 0.09 (m, 6H).

**13C NMR (126 MHz, C\(_6\)D\(_6\)):** \( \delta \) 177.8, 153.0, 108.9, 75.3, 71.4, 60.9, 41.0, 33.6, 32.6, 32.4, 32.2, 32.0, 31.0, 28.2, 26.3, 23.0, 18.8, 18.4, 14.3, −3.9, −4.3.

**HRMS:** Calc’d for C\(_{23}\)H\(_{48}\)NO\(_4\), [M+H]+ 430.3347; found 430.3343.

**47b:** \(^1\)H NMR (600 MHz, C\(_6\)D\(_6\)): \( \delta \) 5.15 (s, 0.79H), 5.14 (s, 0.19H), 4.88 (q, \( J = 1.7 \) Hz, 1H), 4.05 (td, \( J = 9.4, 8.2, 4.3 \) Hz, 1H), 3.93 – 3.85 (m, 1H), 3.20 (d, \( J = 2.4 \) Hz, 3H), 3.12 (s, 1H), 2.92 (d, \( J = 2.8 \) Hz, 3H), 2.30 (ddd, \( J = 13.7, 8.8, 5.1 \) Hz, 1H), 2.18
- 2.09 (m, 1H), 2.00 (dt, $J = 15.5, 7.8$ Hz, 1H), 1.90 – 1.62 (m, 4H), 1.58 (ddd, $J = 13.5, 6.8, 4.9$ Hz, 1H), 1.49 (p, $J = 7.8$ Hz, 2H), 1.34 – 1.24 (m, 4H), 1.17 (d, $J = 7.0$ Hz, 3H), 1.01 (d, $J = 2.6$ Hz, 9H), 0.93 – 0.87 (m, 3H), 0.16 – 0.11 (m, 6H).

$^{13}$C NMR (151 MHz, C$_6$D$_6$): $\delta$ 177.8, 152.9, 108.9, 75.1, 71.5, 60.9, 41.1, 33.7, 32.5, 32.4, 32.2, 32.0, 31.4, 28.2, 26.3, 23.0, 18.9, 18.4, 14.3, –3.9, –4.3.

HRMS: Calc’d for C$_{23}$H$_{48}$NO$_4$, [M+H]$^+$ 430.3347; found 430.3348.

**Compound 49**

![Chemical Structure](image)

A 50 mL round-bottom flask equipped with a magnetic stir bar was charged with alkenyl bromide S25 [generously provided by Eisai] (3.0 g, 5.0 mmol, 1.0 equiv) and LiCl (636 mg, 15.0 mmol, 3 equiv). Anhydrous DMF (10 mL) was added, and the resulting solution was stirred at 90 °C in a preheated oil bath for 1 h. After cooling to room temperature, the mixture was poured into water and extracted with EtOAc three times. The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, and filtered. The solvent was evaporated under vacuum, and the residue was purified by flash column chromatography with hexanes/EtOAc (20:1) to give 49 (1.58 g, 3.4 mmol, 68%).

**Physical State:** colorless oil.

$[\alpha]_D^{20} = -4.0$ (c 1.0, CHCl$_3$).

$R_f = 0.50$ (hexanes/EtOAc 20:1, UV, $p$-anisaldehyde).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.70 – 7.65 (m, 4H), 7.46 – 7.37 (m, 6H), 5.71 (dt, $J = 1.9, 1.1$ Hz, 1H), 5.55 (d, $J = 1.8$ Hz, 1H), 4.23 (tdd, $J = 8.1, 5.8, 3.8$ Hz, 1H), 3.77 – 3.66 (m, 2H), 2.86 – 2.74 (m, 2H), 2.04 – 1.92 (m, 1H), 1.87 – 1.67 (m, 3H), 1.06 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 135.7, 134.0, 129.8, 129.7, 127.8, 120.1, 63.2, 60.0, 50.3, 34.1, 29.4, 27.0, 19.4.

HRMS: Calc’d for C$_{23}$H$_{31}$BrClOSi, [M+H]$^+$ 465.1011; found 465.1016.
Following **General Procedure D** on 0.2 mmol scale using (S)-N-(2-(4-isopropyl-4,5-
dihydrooxazol-2-yl)-6-methylphenyl)methanesulfonamide with the following modifications: NiCl₂·glyme (0.1 equiv), 2,9-dibutyl-1,10-phenanthroline (0.15 equiv), CrCl₂-complex (0.4 equiv), Cp₂ZrCl₂ (1.0 equiv), 4Å MS (150 mg), aluminum as sacrificial anode instead of stainless steel, 6 F/mol. Purification by PTLC (5:1 hexanes/EtOAc) afforded 63.7 mg (55%) of 50a and 50b as a mixture of inseparable diastereoisomers (50a/50b = 6.1:1).

Following **General Procedure D** on 0.2 mmol scale using (R)-N-(2-(4-isopropyl-4,5-
dihydrooxazol-2-yl)-6-methylphenyl)methanesulfonamide with the following modifications: NiCl₂·glyme (0.1 equiv), 2,9-dibutyl-1,10-phenanthroline (0.15 equiv), CrCl₂-complex (0.4 equiv), Cp₂ZrCl₂ (1.0 equiv), 4Å MS (150 mg), aluminum as sacrificial anode instead of stainless steel, 6 F/mol. Purification by PTLC (5:1 hexanes/EtOAc) afforded 60.0 mg (52%) of 50a and 50b as a mixture of inseparable diastereoisomers (50a/50b = 1:4.5).

**Physical State**: colorless oil.

\[ R_f = 0.30 \] (hexanes/EtOAc 6:1, UV, \( p \)-anisaldehyde).

**50a**: ¹H NMR (600 MHz, CDCl₃): \( \delta \) 8.06 – 8.02 (m, 2H), 7.69 – 7.65 (m, 4H), 7.57 – 7.53 (m, 1H), 7.45 – 7.37 (m, 8H), 5.22 (d, \( J = 1.1 \) Hz, 1H), 5.01 (d, \( J = 1.4 \) Hz, 1H),
4.40 – 4.33 (m, 2H), 4.17 (dddd, J = 14.1, 8.7, 5.3, 3.3 Hz, 2H), 3.75 – 3.66 (m, 2H),
2.63 – 2.56 (m, 1H), 2.46 (dd, J = 15.2, 5.3 Hz, 0.88H), 2.42 (ddd, J = 15.4, 8.9, 1.0 Hz, 0.14H), 2.00 (ddd, J = 13.5, 9.6, 5.5, 3.5 Hz, 1H), 1.91 (dtd, J = 13.8, 6.3, 3.1 Hz, 1H), 1.86 – 1.66 (m, 8H), 1.06 (s, 9H).

^13^C NMR (151 MHz, CDCl₃): δ 166.8, 147.5, 135.68, 135.67, 134.0, 133.9, 133.0, 130.4, 129.8, 129.7, 128.5, 127.8, 113.7, 74.7, 64.9, 63.3, 61.8, 41.0, 34.8, 31.9, 29.5, 27.0, 25.1, 19.4.

HRMS: Calc’d for C₃₄H₄₄ClO₄Si, [M+H]^+ 579.2692; found 579.2687.

50b: ^1^H NMR (600 MHz, CDCl₃): δ 8.04 (dt, J = 8.4, 1.4 Hz, 2H), 7.66 (dt, J = 6.7, 1.5 Hz, 4H), 7.56 – 7.53 (m, 1H), 7.45 – 7.37 (m, 8H), 5.21 (dd, J = 3.7, 1.0 Hz, 1H), 5.01 (d, J = 1.3 Hz, 1H), 4.40 – 4.33 (m, 2H), 4.23 – 4.13 (m, 2H), 3.73 – 3.66 (m, 2H), 2.59 (td, J = 15.0, 6.9 Hz, 1H), 2.46 (dd, J = 15.2, 5.4 Hz, 0.18H), 2.41 (ddd, J = 15.3, 9.0, 1.1 Hz, 0.82H), 1.98 (ddd, J = 13.6, 9.8, 5.3, 3.6 Hz, 1H), 1.93 – 1.86 (m, 1H), 1.86 – 1.62 (m, 8H), 1.05 (s, 9H).

^13^C NMR (151 MHz, CDCl₃): δ 166.8, 147.6, 135.7, 134.0, 133.0, 130.5, 129.8, 129.7, 128.5, 127.8, 113.8, 75.0, 64.9, 63.4, 62.1, 41.2, 35.1, 31.7, 29.5, 27.0, 25.2, 19.4.

HRMS: Calc’d for C₃₄H₄₄ClO₄Si, [M+H]^+ 579.2692; found 579.2090.

**Compound 51**

To a stirred solution of diol S26 [generously provided by Eisai] (773 mg, 2.0 mmol, 1.0 equiv) in THF/H₂O (10 mL/10 mL) was added NaIO₄ (642 mg, 3.0 mmol, 1.5 equiv) at 0 °C. The resulting mixture was then stirred at room temperature until TLC showed the diol was completely consumed. The solution was filtered through a pad of Celite and washed with EtOAc. The combined organic solution was washed with aq. Na₂SO₃
solution, dried over Na$_2$SO$_4$, and filtered. The solvent was evaporated under vacuum and the residue was used directly in the next step without further purification.

**Compound 52**

Following **General Procedure D** on 0.2 mmol scale using (S)-N-(2-(4-isopropyl-4,5-dihydrooxazol-2-yl)-6-methylphenyl) methanesulfonamide with the following modifications: 4Å MS (150 mg), 6 F/mol. Purification by PTLC (1:1 hexanes/EtOAc) afforded 79.0 mg (78%) of the title compound 52 as a mixture of inseparable diastereoisomers (dr > 20:1).

Following **General Procedure D** on 0.2 mmol scale using (R)-N-(2-(4-isopropyl-4,5-dihydrooxazol-2-yl)-6-methylphenyl) methanesulfonamide with the following modifications: 4Å MS (150 mg), 6 F/mol. Purification by PTLC (1:1 hexanes/EtOAc) afforded 60.0 mg (73%) of the title compound 52 as a mixture of inseparable diastereoisomers (dr = 14:1).

**Physical State**: colorless oil.

$R_f = 0.42$ (hexanes/EtOAc 1:1, $p$-anisaldehyde).

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 5.80 (ddt, $J = 15.5, 6.4, 1.4$ Hz, 1H), 5.57 (ddt, $J = 15.4, 5.9, 1.4$ Hz, 1H), 5.48 (dd, $J = 15.3, 7.1$ Hz, 0.05H), 4.56 – 4.48 (m, 2H), 4.31 – 4.21 (m, 1H), 3.89 (td, $J = 10.7, 4.7$ Hz, 1H), 3.81 (ddt, $J = 11.2, 6.5, 2.1$ Hz, 1H), 3.65 (s, 3H), 3.54 (dd, $J = 5.4, 1.6$ Hz, 1H), 3.45 (dd, $J = 10.2, 3.0$ Hz, 1H), 2.93 (s, 1H), 2.69 (dd, $J = 16.1, 7.0$ Hz, 1H), 2.41 (dd, $J = 16.2, 6.0$ Hz, 1H), 2.36 – 2.26 (m, 4H), 2.15 – 2.07 (m, 1H), 1.86 – 1.38 (m, 25H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 172.4, 171.6, 131.0, 130.5, 111.3, 80.4, 76.4, 75.3, 74.2, 73.0, 71.8, 71.4, 66.4, 51.8, 40.4, 35.6, 35.1, 33.4, 30.7, 30.1, 28.2, 27.9, 25.2,
24.2, 23.8.

**HRMS:** Calc’d for C_{27}H_{42}NaO_9, [M+Na]^+ 533.2721; found 533.2719.

**Compound 54**

To a solution of alcohol **S27** [generously provided by Eisai] (250 mg, 0.5 mmol, 1.0 equiv) in DCM (5 mL) was added successively DIPEA (260 μL, 1.5 mmol, 3.0 equiv) and TBSOTf (140 μL, 0.6 mmol, 1.2 equiv) at 0 °C. After 30 min, the reaction mixture was quenched with aq. NaHCO_3 solution. The organic layer was separated, and the aqueous layer was extracted with DCM three times. The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered. The solvent was evaporated under vacuum and the residue was purified by flash column chromatography with hexanes/EtOAc (10:1) to give 54 (295 mg, 0.48 mmol, 96%).

**Physical State:** colorless oil.

[α]_D^20 = −30.4 (c 1.0, CHCl_3).

R_f = 0.77 (hexanes/EtOAc 3:1, p-anisaldehyde).

**^1H NMR (500 MHz, CDCl_3):** δ 5.07 (d, J = 3.9 Hz, 1H), 4.96 (q, J = 2.2 Hz, 1H), 4.89 (d, J = 3.9 Hz, 1H), 4.82 (q, J = 2.2 Hz, 1H), 4.35 – 4.30 (m, 1H), 4.05 (td, J = 6.3, 3.4 Hz, 2H), 3.99 (q, J = 6.4 Hz, 1H), 3.78 – 3.72 (m, 1H), 2.65 (ddq, J = 15.4, 6.2, 2.0 Hz, 1H), 2.55 (p, J = 6.9 Hz, 1H), 2.27 – 2.19 (m, 1H), 1.77 – 1.39 (m, 11H), 1.17 (s, 9H), 1.14 (d, J = 6.9 Hz, 3H), 0.87 (s, 9H), 0.03 (d, J = 7.9 Hz, 6H).

**^13C NMR (126 MHz, CDCl_3):** δ 178.6, 160.6, 151.7, 118.5 (q, J_C-F = 319.6 Hz), 105.0, 102.3, 79.8, 76.9, 69.9, 64.3, 40.9, 39.0, 38.8, 35.6, 33.2, 31.7, 30.4, 27.3, 26.0, 25.4, 18.9, 18.2, −3.9, −4.5.

**HRMS:** Calc’d for C_{28}H_{50}F_3O_7SSi, [M+H]^+ 615.2999; found 615.3002.
Following General Procedure D on 0.2 mmol scale using (S)-N-(2-(4-isopropyl-4,5-dihydrooxazol-2-yl)-6-methylphenyl)methanesulfonamide with the following modifications: NiCl$_2$·glyme (0.1 equiv), 2,9-dibutyl-1,10-phenanthroline (0.15 equiv), CrCl$_2$-complex (0.4 equiv), Cp$_2$ZrCl$_2$ (1.0 equiv), 4Å MS (150 mg), 6 F/mol. Purification by PTLC (3:1 hexanes/EtOAc) afforded 65.0 mg (31%) of the title compound 55a.

55a: Physical State: colorless oil.

$[\alpha]_{D}^{20} = -23.5$ (c 1.0, CHCl$_3$).

$R_f = 0.57$ (hexanes/EtOAc 3:1, UV, $p$-anisaldehyde).

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.93 (dt, $J = 7.2$, 1.3 Hz, 2H), 7.70 – 7.66 (m, 1H), 7.59 (t, $J = 7.8$ Hz, 2H), 5.12 (s, 1H), 4.96 (q, $J = 2.1$ Hz, 1H), 4.86 (s, 1H), 4.83 (q, $J = 2.1$ Hz, 1H), 4.34 – 4.29 (m, 1H), 4.12 – 3.98 (m, 4H), 3.92 (td, $J = 6.5$, 3.4 Hz, 1H),
3.80 – 3.65 (m, 4H), 3.56 (dd, J = 10.3, 5.4 Hz, 1H), 3.47 (dd, J = 10.3, 5.4 Hz, 1H),
3.38 (s, 3H), 3.16 – 3.05 (m, 2H), 2.66 (ddt, J = 17.1, 6.0, 1.9 Hz, 1H), 2.56 (dt, J = 9.8,
5.1 Hz, 1H), 2.23 (ddd, J = 15.3, 6.0, 2.5 Hz, 1H), 2.11 (q, J = 6.9 Hz, 1H), 2.04 – 1.96
(m, 1H), 1.88 – 1.59 (m, 10H), 1.45 (dddd, J = 27.4, 13.4, 6.4, 2.5 Hz, 4H), 1.18 (d, J =
1.0 Hz, 9H), 1.04 (d, J = 6.8 Hz, 3H), 0.91 – 0.85 (m, 30H), 0.10 – 0.01 (m, 20H).

13C NMR (151 MHz, CDCl3): δ 178.7, 157.5, 151.8, 139.7, 134.1, 129.6, 128.0, 108.1,
105.0, 85.8, 83.5, 80.2, 79.0, 76.8, 73.4, 71.3, 71.1, 67.9, 64.4, 58.2, 57.6, 45.2, 44.6,
41.6, 38.94, 38.86, 33.5, 33.0, 32.9, 31.7, 31.0, 27.3, 26.12, 26.06, 25.4, 21.3, 18.5,
18.30, 18.27, –4.0, –4.05, –4.09, –4.6, –5.2.

HRMS: Calc’d for C56H102NaO11SSi3, [M+Na]+ 1089.6343; found 1089.6338.

Following General Procedure D on 0.2 mmol scale using (R)-N-(2-(4-isopropyl-4,5-
dihydrooxazol-2-yl)-6-methylphenyl)methanesulfonamide with the following
modifications: NiCl2·glyme (0.1 equiv), 2,9-dibutyl-1,10-phenanthroline (0.15 equiv),
CrCl2-complex (0.4 equiv), Cp2ZrCl2 (1.0 equiv), 4Å MS (150 mg), 6 F/mol.

Purification by PTLC (3:1 hexanes/EtOAc) afforded 67.0 mg (32%) of the title
compound 55b.

55b: Physical State: colorless oil.

[α]D20 = –32.5 (c 1.0, CHCl3).

Rf = 0.52 (hexanes/EtOAc 3:1, UV, p-anisaldehyde).

1H NMR (500 MHz, CDCl3): δ 7.95 – 7.89 (m, 2H), 7.70 – 7.64 (m, 1H), 7.61 – 7.55
(m, 2H), 5.00 (s, 1H), 4.96 (d, J = 2.1 Hz, 1H), 4.85 – 4.81 (m, 2H), 4.32 (d, J = 5.8 Hz,
1H), 4.25 – 4.17 (m, 1H), 4.11 – 3.97 (m, 3H), 3.89 – 3.74 (m, 4H), 3.64 (q, J = 5.8 Hz,
1H), 3.57 (dd, J = 10.3, 5.6 Hz, 1H), 3.48 (dd, J = 10.3, 5.1 Hz, 1H), 3.41 (s, 3H), 3.15
(dd, J = 14.2, 4.0 Hz, 1H), 3.05 (dd, J = 14.1, 10.1 Hz, 1H), 2.67 (ddq, J = 15.5, 6.3,
2.0 Hz, 1H), 2.53 (dt, J = 10.0, 4.9 Hz, 1H), 2.34 – 2.19 (m, 2H), 2.02 – 1.93 (m, 1H),
1.85 – 1.44 (m, 14H), 1.18 (s, 9H), 1.01 (d, J = 6.9 Hz, 3H), 0.91 – 0.83 (m, 27H), 0.10
– 0.01 (m, 18H).

13C NMR (126 MHz, CDCl3): δ 178.7, 158.0, 151.7, 139.8, 134.0, 129.6, 128.0, 109.2,
105.0, 85.8, 81.4, 80.0, 78.7, 76.9, 71.83, 71.80, 71.5, 68.0, 64.4, 58.1, 57.6, 44.4, 44.3,
41.5, 38.93, 38.86, 33.5, 32.4, 31.7, 31.4, 30.9, 27.3, 26.2, 26.13, 26.09, 25.4, 23.1, 18.5,
18.33, 18.31, −4.0, −4.2, −4.3, −4.6, −5.2.

**HRMS:** Calc’d for C_{56}H_{102}NaO_{11}SSi_3, [M+Na]^+ 1089.6343; found 1089.6348.

**Compound 57**

Following **General Procedure D** on 0.2 mmol scale using (S)-N-(2-(4-isopropyl-4,5-dihydrooxazol-2-yl)-6-methylphenyl)methanesulfonamide with the following modifications: NiCl₂·glyme (0.1 equiv), 2,9-dibutyl-1,10-phenanthroline (0.15 equiv), Cp₂ZrCl₂ (1.0 equiv), 4Å MS (400 mg), CH₃CN (10 mL, c = 20 mM), 6 F/mol. Purification by PTLC (4:1 hexanes/EtOAc) afforded 67.4 mg (31%) compound 57a and 67.0 mg (31%) compound 57b.

**Less polar isomer, 57a:**

**Physical State:** white foam.

[α]$_D^{20}$ = −37.1 (c 1.0, CHCl₃).

$R_f$ = 0.48 (hexanes/EtOAc 4:1, UV, p-anisaldehyde).

**1H NMR (500 MHz, CDCl₃):** δ 5.83 (dd, J = 15.6, 9.2 Hz, 1H), 5.63 (dd, J = 15.6, 8.5 Hz, 1H), 5.02 (dd, J = 9.2, 4.0 Hz, 1H), 4.96 (q, J = 2.2 Hz, 1H), 4.90 (s, 1H), 4.83 – 4.76 (m, 2H), 4.26 (d, J = 6.7 Hz, 1H), 4.09 – 4.03 (m, 2H), 3.98 (p, J = 6.2 Hz, 1H), 3.93 – 3.76 (m, 6H), 3.73 (ddd, J = 8.1, 5.1, 3.2 Hz, 1H), 3.57 (dt, J = 10.2, 4.7 Hz, 2H), 3.53 – 3.46 (m, 2H), 3.44 – 3.41 (m, 1H), 3.28 (s, 3H), 2.91 – 2.78 (m, 2H), 2.66 (ddq, J = 15.6, 6.3, 1.8 Hz, 1H), 2.60 – 2.47 (m, 3H), 2.43 – 2.34 (m, 1H), 2.33 – 2.21 (m, 2H), 2.08 – 1.91 (m, 3H), 1.79 (dddd, J = 27.6, 13.9, 5.7, 3.4 Hz, 4H), 1.71 – 1.60 (m,
2H), 1.58 – 1.48 (m, 6H), 1.45 – 1.36 (m, 2H), 1.33 – 1.22 (m, 2H), 1.08 (d, J = 6.5 Hz, 3H), 0.97 (s, 9H), 0.92 (s, 9H), 0.88 (d, J = 3.8 Hz, 18H), 0.84 (s, 9H), 0.14 – 0.09 (m, 12H), 0.06 (d, J = 4.6 Hz, 6H), 0.05 – 0.01 (m, 12H).

$^{13}$C NMR (126 MHz, CDCl$_3$): δ 207.8, 151.7, 151.1, 134.9, 133.7, 105.04, 104.96, 87.6, 81.7, 80.8, 79.5, 79.0, 77.6, 77.4, 77.1, 75.6, 73.9, 73.6, 73.2, 72.5, 71.6, 70.8, 68.0, 63.7, 57.1, 49.2, 47.2, 44.3, 42.6, 38.9, 36.5, 35.8, 33.7, 33.0, 32.6, 31.2, 30.6, 30.3, 28.8, 26.9, 26.5, 26.4, 26.2, 26.1, 19.3, 18.9, 18.6, 18.3, 18.2, –2.0, –3.0, –3.7, –3.9, –4.1, –4.4, –4.5, –4.6, –5.16, –5.18.

HRMS: Calc’d for C$_{70}$H$_{132}$NaO$_{13}$Si$_{5}$, [M+Na]$^+$ 1343.8406; found 1343.8406.

More polar isomer, 57b:

Physical State: white foam.

[$\alpha$]$_{D}^{20}$ = –33.0 (c 1.0, CHCl$_3$).

$R_f$ = 0.40 (hexanes/EtOAc 4:1, UV, p-anisaldehyde).

$^1$H NMR (500 MHz, CDCl$_3$): δ 6.07 (ddd, J = 15.8, 7.5, 1.6 Hz, 1H), 5.76 (dd, J = 15.7, 4.7 Hz, 1H), 4.96 (dq, J = 4.2, 1.9 Hz, 2H), 4.91 (s, 1H), 4.79 (t, J = 2.3 Hz, 2H), 4.31 – 4.21 (m, 2H), 4.12 – 4.00 (m, 2H), 3.94 – 3.75 (m, 7H), 3.72 (q, J = 5.6 Hz, 1H), 3.65 – 3.52 (m, 3H), 3.49 (dd, J = 10.3, 5.2 Hz, 1H), 3.42 (dd, J = 3.8, 1.2 Hz, 1H), 3.27 (s, 3H), 2.91 (dd, J = 9.6, 2.4 Hz, 1H), 2.81 (dd, J = 15.8, 6.2 Hz, 1H), 2.68 – 2.48 (m, 4H), 2.40 – 2.23 (m, 3H), 2.02 (t, J = 5.9 Hz, 2H), 1.95 (ddd, J = 13.8, 6.3, 5.2 Hz, 1H), 1.90 – 1.85 (m, 1H), 1.85 – 1.79 (m, 1H), 1.76 (dt, J = 13.9, 6.9 Hz, 2H), 1.72 – 1.62 (m, 4H), 1.55 (ddd, J = 19.8, 6.8, 3.7 Hz, 4H), 1.46 – 1.35 (m, 2H), 1.32 – 1.23 (m, 2H), 1.08 (d, J = 6.5 Hz, 3H), 0.96 (s, 9H), 0.93 (s, 9H), 0.88 (d, J = 3.7 Hz, 18H), 0.86 (s, 9H), 0.14 – 0.08 (m, 12H), 0.06 (d, J = 4.4 Hz, 6H), 0.06 – 0.02 (m, 12H).

$^{13}$C NMR (126 MHz, CDCl$_3$): δ 207.8, 151.8, 151.0, 134.4, 130.2, 105.0, 87.4, 81.8, 80.9, 79.5, 79.0, 77.6, 77.03, 76.99, 75.7, 73.6, 73.0, 71.8, 71.6, 71.5, 70.9, 68.0, 64.1, 57.1, 49.0, 47.6, 44.3, 42.4, 38.6, 36.5, 35.8, 33.7, 33.0, 32.6, 31.2, 30.6, 30.3, 28.8, 26.9, 26.5, 26.4, 26.2, 26.1, 19.3, 18.9, 18.6, 18.31, 18.28, 18.2, –2.7, –3.5, –3.7, –3.9, –4.2, –4.3, –4.5, –4.6, –5.16, –5.18.

HRMS: Calc’d for C$_{70}$H$_{132}$NaO$_{13}$Si$_{5}$, [M+Na]$^+$ 1343.8406; found 1343.8403.
Two culture tubes were separately charged with 57a (60 mg, 0.046 mmol, 1.0 equiv) and 57b (60 mg, 0.046 mmol, 1.0 equiv). Then DCM (1 mL), NaHCO$_3$ (12 mg, 0.14 mmol, 3.0 equiv), and DMP (24 mg, 0.055 mmol, 1.2 equiv) were successively added to each reaction mixture. After 4 h, the reaction mixtures were separately quenched with aq. Na$_2$SO$_3$ and aq. NaHCO$_3$. For each reaction mixture, the organic layer was separated, the aqueous layer was extracted with DCM, and the combined organic layers were concentrated in vacuo. The crude residues were purified by flash column chromatography with hexanes/EtOAc (4:1) to give S28 (47 mg, 78% yield from 57a and 49 mg, 81% yield from 57b).

**Physical State:** colorless oil.

$\[\alpha\]_D^{20} = -44.5$ (c 1.0, CHCl$_3$).

$R_f = 0.57$ (hexanes/EtOAc 4:1, UV, $p$-anisaldehyde).

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.26 (dd, $J = 16.4, 5.9$ Hz, 1H), 6.34 (dd, $J = 16.4, 1.3$ Hz, 1H), 5.02 – 4.98 (m, 2H), 4.88 (s, 1H), 4.83 (q, $J = 2.2$ Hz, 1H), 4.78 (d, $J = 1.9$ Hz, 1H), 4.26 – 4.20 (m, 1H), 4.09 – 4.01 (m, 3H), 3.92 – 3.76 (m, 5H), 3.72 – 3.67 (m, 1H), 3.55 (td, $J = 9.6, 8.9, 5.9$ Hz, 2H), 3.49 (dd, $J = 10.3, 5.1$ Hz, 1H), 3.44 – 3.38 (m, 2H), 3.30 (s, 3H), 2.94 (dd, $J = 9.6, 2.3$ Hz, 1H), 2.85 (dd, $J = 15.8, 7.1$ Hz, 1H), 2.76 – 2.61 (m, 4H), 2.54 – 2.42 (m, 3H), 2.27 (tdd, $J = 16.6, 7.5, 4.1$ Hz, 2H), 2.04 (ddd, $J = 14.4, 8.0, 2.2$ Hz, 1H), 1.93 (ddddd, $J = 16.7, 11.2, 7.8, 5.8$ Hz, 2H), 1.85 – 1.64 (m, 7H), 1.59 – 1.53 (m, 2H), 1.47 – 1.38 (m, 1H), 1.32 (td, $J = 9.7, 8.4, 4.0$ Hz, 2H), 1.07 (d, $J = 6.5$ Hz, 3H), 0.97 (s, 9H), 0.93 (s, 9H), 0.87 (d, $J = 6.0$ Hz, 27H), 0.19 (s, 3H), 0.14 (s, 3H), 0.12 (s, 6H), 0.06 (d, $J = 8.2$ Hz, 6H), 0.04 – 0.02 (m, 9H), -0.05 (s, 3H).
\(^{13}\)C NMR (151 MHz, CDCl\(_3\)): \(\delta\) 207.8, 200.2, 151.2, 151.1, 146.5, 131.3, 105.5, 104.9, 87.6, 83.8, 80.7, 79.3, 78.8, 77.6, 77.5, 76.7, 75.6, 73.8, 72.7, 71.6, 71.0, 70.6, 68.0, 66.0, 57.1, 48.9, 47.7, 43.7, 42.5, 38.8, 35.9, 35.8, 33.6, 32.2, 32.1, 31.0, 29.5, 28.6, 26.9, 26.4, 26.2, 26.14, 26.09, 19.3, 19.0, 18.5, 18.3, 18.2, 18.1, -3.1, -3.3, -4.0, -4.1, -4.2, -4.4, -4.61, -4.63, -5.17, -5.19.
Spectroscopic data are in accordance with that reported in the literature.\(^{30}\)

**Compound 60**

![Compound 60](image)

Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 30.0 mg (53%) of the title compound 60.

**Physical State:** colorless oil.

\(R_f = 0.24\) (hexanes/EtOAc 5:1, \(p\)-anisaldehyde).

\(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 7.29 – 7.25 (m, 2H), 7.20 – 7.14 (m, 3H), 6.85 (t, \(J = 1.1\) Hz, 1H), 6.76 (d, \(J = 1.1\) Hz, 2H), 5.94 (s, 2H), 4.56 (dd, \(J = 7.4, 6.0\) Hz, 1H), 2.60 (dd, \(J = 8.9, 6.7\) Hz, 2H), 1.89 (s, 1H), 1.84 – 1.77 (m, 1H), 1.72 – 1.61 (m, 3H), 1.45 (ddtd, \(J = 15.5, 10.4, 7.3, 5.3\) Hz, 1H), 1.31 (dtt, \(J = 11.0, 8.1, 5.6\) Hz, 1H).

\(^{13}\)C NMR (151 MHz, CDCl\(_3\)): \(\delta\) 147.9, 147.0, 142.7, 139.1, 128.5, 128.4, 125.8, 119.4, 108.1, 106.5, 101.1, 74.5, 39.0, 36.0, 31.5, 25.7.
Spectroscopic data are in accordance with that reported in the literature.\(^{31}\)

**Compound 61**

![Compound 61](image)

Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (1:1 hexanes/EtOAc) afforded 31.6 mg (51%) of the title compound 61.
Physical State: yellowish oil.

$R_f = 0.24$ (hexanes/EtOAc 2:1, $p$-anisaldehyde).

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 6.84 (d, $J = 1.5$ Hz, 1H), 6.78 – 6.72 (m, 2H), 5.93 (s, 2H), 4.65 – 4.56 (m, 2H), 3.19 – 3.08 (m, 2H), 1.80 – 1.72 (m, 1H), 1.66 (ddt, $J = 13.5$, 9.5, 5.7 Hz, 1H), 1.55 (dd, $J = 17.3$, 13.9, 7.4 Hz, 1H), 1.48 (d, $J = 13.8$ Hz, 1H), 1.42 (s, 9H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 156.2, 147.9, 147.0, 138.9, 119.3, 108.2, 106.4, 101.1, 79.3, 74.1, 40.4, 36.1, 28.5, 26.6.

HRMS: Calc’d for C$_{16}$H$_{23}$NO$_5$Na, [M+Na]$^+$ 332.1468; found 332.1474.

Compound 62

Following General Procedure E on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 36.6 mg (63%) of the title compound 62.

Physical State: colorless oil.

$R_f = 0.52$ (hexanes/EtOAc 4:1, $p$-anisaldehyde).

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 6.86 (d, $J = 1.4$ Hz, 1H), 6.80 – 6.74 (m, 2H), 5.94 (s, 2H), 5.80 (ddt, $J = 16.9$, 10.2, 6.7 Hz, 1H), 4.99 (dq, $J = 17.1$, 1.8 Hz, 1H), 4.92 (ddt, $J = 10.2$, 2.2, 1.2 Hz, 1H), 4.56 (dd, $J = 7.4$, 6.1 Hz, 1H), 2.06 – 2.00 (m, 2H), 1.82 (s, 1H), 1.80 – 1.73 (m, 1H), 1.64 (ddt, $J = 13.1$, 9.8, 5.5 Hz, 1H), 1.40 – 1.33 (m, 3H), 1.32 – 1.20 (m, 10H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 147.9, 147.0, 139.4, 139.2, 119.5, 114.3, 108.2, 106.5, 101.1, 74.7, 39.2, 33.9, 29.6, 29.5, 29.2, 29.0, 26.0.

HRMS: Calc’d for C$_{18}$H$_{25}$O$_2$, [M-OH]$^+$ 273.1849; found 273.1850.
Compound 63

Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (2:1 hexanes/EtOAc) afforded 19.7 mg (37%) of the title compound 63.

**Physical State:** colorless oil.

$R_f = 0.40$ (hexanes/EtOAc 2:1, $p$-anisaldehyde).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 6.84 (dt, $J = 1.2, 0.6$ Hz, 1H), 6.76 (t, $J = 1.0$ Hz, 2H), 5.94 (s, 2H), 4.57 (dd, $J = 7.4, 5.9$ Hz, 1H), 3.65 (s, 3H), 2.29 (t, $J = 7.5$ Hz, 2H), 1.82 – 1.74 (m, 1H), 1.69 – 1.60 (m, 3H), 1.46 – 1.37 (m, 1H), 1.32 – 1.24 (m, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 174.3, 147.9, 147.1, 138.9, 119.4, 108.2, 106.5, 101.1, 74.3, 51.6, 38.7, 34.1, 25.5, 24.9.

**HRMS:** Calc’d for C$_{14}$H$_{17}$O$_4$, [M-OH]$^+$ 249.1121; found 249.1116.

Compound 64

Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 27.5 mg (55%) of the title compound 64.

**Physical State:** colorless oil.

$R_f = 0.50$ (hexanes/EtOAc 4:1, $p$-anisaldehyde).

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 6.86 (d, $J = 1.5$ Hz, 1H), 6.80 – 6.74 (m, 2H), 5.95 (s, 2H), 4.57 (dd, $J = 7.4, 6.1$ Hz, 1H), 1.84 – 1.73 (m, 2H), 1.68 – 1.62 (m, 1H), 1.41 – 1.33 (m, 1H), 1.33 – 1.20 (m, 9H), 0.87 (t, $J = 7.0$ Hz, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 147.9, 147.0, 139.2, 119.5, 108.2, 106.5, 101.1, 74.7, 39.2, 32.0, 29.6, 29.4, 26.0, 22.8, 14.2.

**HRMS:** Calc’d for C$_{15}$H$_{21}$O$_2$, [M-OH]$^+$ 233.1536; found 233.1532.
Compound 65

Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 28.7 mg (52%) of the title compound 65.

**Physical State**: colorless oil.

\[ R_f = 0.35 \text{ (hexanes/EtOAc 4:1, } p\text{-anisaldehyde)}. \]

\[ ^1H \text{ NMR (500 MHz, CDCl}_3\text{): } \delta 7.10 \text{ (dd, } J = 5.1, 1.2 \text{ Hz, 1H), 6.90 (dd, } J = 5.1, 3.4 \text{ Hz, 1H), 6.87 – 6.83 (m, 1H), 6.76 (dt, } J = 3.6, 1.3 \text{ Hz, 3H), 5.95 (s, 2H), 4.60 (dd, } J = 7.3, 5.6 \text{ Hz, 1H), 2.84 (td, } J = 7.4, 0.9 \text{ Hz, 2H), 1.89 – 1.62 (m, 5H)}. \]

\[ ^{13}C \text{ NMR (126 MHz, CDCl}_3\text{): } \delta 148.0, 147.1, 145.2, 138.8, 126.8, 124.3, 123.1, 119.5, 108.2, 106.5, 101.1, 74.4, 38.4, 29.8, 28.1. \]

**HRMS**: Calc’d for C_{15}H_{15}O_2S, [M-OH]^+ 259.0787; found 259.0782.

Compound 66

Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 31.2 mg (63%) of the title compound 66.

**Physical State**: colorless oil.

\[ R_f = 0.48 \text{ (hexanes/EtOAc 4:1, } p\text{-anisaldehyde)}. \]

\[ ^1H \text{ NMR (500 MHz, CDCl}_3\text{): } \delta 6.86 \text{ (dt, } J = 1.3, 0.5 \text{ Hz, 1H), 6.81 – 6.73 (m, 2H), 5.94 (s, 2H), 4.58 – 4.52 (m, 1H), 1.86 (s, 1H), 1.82 – 1.64 (m, 5H), 1.62 – 1.53 (m, 2H), 1.53 – 1.46 (m, 2H), 1.43 – 1.36 (m, 1H), 1.27 – 1.18 (m, 1H), 1.10 – 1.00 (m, \]
$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 6.88 (d, $J = 1.6$ Hz, 1H), 6.82 – 6.74 (m, 2H), 6.39 (s, 2H), 5.95 (s, 2H), 4.61 (dd, $J = 7.7$, 5.5 Hz, 1H), 3.83 (s, 6H), 3.82 (s, 3H), 2.70 – 2.63 (m, 1H), 2.58 (ddd, $J = 13.8$, 9.7, 6.3 Hz, 1H), 2.10 (ddddd, $J = 13.5$, 9.7, 7.7, 5.8 Hz, 1H), 1.97 (ddddd, $J = 13.6$, 10.0, 6.3, 5.5 Hz, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 153.3, 148.0, 147.2, 138.7, 137.6, 136.2, 119.5, 108.2, 106.5, 105.4, 101.2, 73.9, 61.0, 56.2, 40.5, 32.6.

HRMS: Calc’d for C$_{10}$H$_{21}$O$_2$, [M-OH]$^+$ 329.1384; found 329.1383.

Compound 68

Following General Procedure E (without desilylation) on 0.2 mmol scale. Purification
by PTLC (2:1 hexanes/EtOAc) afforded 30.3 mg (28%) of the title compound 68.

**Physical State**: colorless oil.

$R_f = 0.36$ (hexanes/EtOAc 4:1, $p$-anisaldehyde).

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.67 (s, 1H), 6.78 (d, $J = 1.6$ Hz, 1H), 6.71 – 6.64 (m, 2H), 5.94 – 5.89 (m, 2H), 5.21 – 5.14 (m, 3H), 4.47 (dd, $J = 7.2$, 5.5 Hz, 1H), 3.76 (s, 3H), 3.38 (d, $J = 7.0$ Hz, 2H), 2.14 (s, 3H), 2.03 – 1.97 (m, 1H), 1.90 (ddd, $J = 14.5$, 10.2, 5.4 Hz, 1H), 1.79 – 1.73 (m, 4H), 1.64 (ddt, $J = 13.4$, 10.7, 5.4 Hz, 1H), 0.84 (t, $J = 7.9$ Hz, 9H), 0.47 (qd, $J = 7.9$, 4.3 Hz, 6H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 173.1, 163.8, 153.8, 147.5, 146.5, 144.0, 140.0, 135.7, 122.6, 121.9, 119.2, 116.8, 107.8, 106.6, 106.5, 100.9, 74.6, 70.2, 61.1, 39.2, 35.8, 22.7, 16.5, 11.7, 6.9, 4.9.

**HRMS**: Calc’d for C$_{24}$H$_{25}$O$_6$, [M-OH]$^+$ 409.1646; found 409.1648.

**Compound 69**

Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 22.5 mg (41%) of the title compound 69.

**Physical State**: yellowish oil.

$R_f = 0.28$ (hexanes/EtOAc 4:1, $p$-anisaldehyde).

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.16 – 7.10 (m, 2H), 6.99 – 6.93 (m, 2H), 6.88 – 6.85 (m, 1H), 6.77 (d, $J = 1.1$ Hz, 2H), 5.95 (s, 2H), 4.58 (dd, $J = 7.7$, 5.6 Hz, 1H), 2.69 (ddd, $J = 15.1$, 9.8, 5.7 Hz, 1H), 2.63 – 2.57 (m, 1H), 2.07 (ddddd, $J = 13.5$, 9.5, 7.7, 5.8 Hz, 1H), 1.94 (dddd, $J = 13.6$, 9.8, 6.4, 5.5 Hz, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 161.4 (d, $J = 243.3$ Hz), 148.0, 147.2, 138.7, 137.4 (d, $J = 3.3$ Hz), 129.9 (d, $J = 7.7$ Hz), 119.5, 115.2 (d, $J = 21.1$ Hz), 108.3, 106.5, 101.2, 73.8, 40.7, 31.4.

$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ –120.36.
HRMS: Calc’d for C_{16}H_{14}FO_{2}, [M-OH]^+ 257.0972; found 257.0969.

**Compound 70**

Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 47.1 mg (61%) of the title compound 70.

**Physical State**: colorless oil.

$R_f$ = 0.46 (hexanes/EtOAc 4:1, p-anisaldehyde).

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 6.86 (d, $J = 1.5$ Hz, 1H), 6.80 – 6.74 (m, 2H), 5.94 (s, 2H), 5.42 – 5.29 (m, 4H), 4.56 (dd, $J = 7.4$, 6.1 Hz, 1H), 2.77 (t, $J = 6.9$ Hz, 2H), 2.09 – 1.99 (m, 4H), 1.83 – 1.72 (m, 2H), 1.64 (ddt, $J = 13.3$, 10.1, 5.6 Hz, 1H), 1.41 – 1.20 (m, 16H), 0.89 (t, $J = 6.9$ Hz, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 147.9, 147.0, 139.2, 130.3, 130.2, 128.12, 128.06, 119.5, 108.1, 106.5, 101.1, 74.7, 39.2, 31.7, 29.8, 29.62, 29.58, 29.5, 29.4, 27.34, 27.33, 26.0, 25.8, 22.7, 14.2.

HRMS: Calc’d for C$_{25}$H$_{39}$O$_3$, [M+H]$^+$ 387.2889; found 387.2894.

**Compound 71**

Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 24.0 mg (36%) of the title compound 71.

**Physical State**: colorless oil.

$R_f$ = 0.32 (hexanes/EtOAc 4:1, p-anisaldehyde).

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.54 – 7.49 (m, 1H), 7.24 – 7.19 (m, 2H), 7.05 (dt, $J =$
7.8, 4.5 Hz, 1H), 6.90 (d, J = 1.7 Hz, 1H), 6.82 (dd, J = 7.9, 1.7 Hz, 1H), 6.78 (d, J = 7.9 Hz, 1H), 5.95 (d, J = 0.6 Hz, 2H), 4.64 (dd, J = 7.8, 5.4 Hz, 1H), 2.87 (ddd, J = 13.7, 10.3, 5.3 Hz, 1H), 2.74 (ddd, J = 13.7, 10.1, 6.2 Hz, 1H), 2.12 – 1.96 (m, 2H).

$^{13}$C NMR (151 MHz, CDCl$_3$): δ 148.0, 147.2, 141.2, 138.6, 133.0, 130.5, 127.8, 127.6, 124.6, 119.5, 108.3, 106.6, 101.2, 73.9, 39.0, 32.7.

Spectroscopic data are in accordance with that reported in the literature.$^{32}$

**Compound 72**

Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (1:2 hexanes/EtOAc) afforded 50.0 mg (49%) of the title compound 72.

**Physical State:** white foam.

$R_f$ = 0.18 (hexanes/EtOAc 1:1, p-anisaldehyde).

$^1$H NMR (600 MHz, CDCl$_3$): δ 6.86 – 6.82 (m, 1H), 6.76 (d, J = 2.0 Hz, 2H), 5.94 (d, J = 3.3 Hz, 2H), 4.53 (dd, J = 7.6, 5.5 Hz, 0.45H), 4.50 (t, J = 6.7 Hz, 0.60H), 2.93 – 2.79 (m, 3H), 2.35 – 2.16 (m, 6H), 2.14 – 2.07 (m, 2H), 2.05 – 1.52 (m, 10H), 1.38 (s, 3H), 1.29 – 1.19 (m, 4H), 1.04 (d, J = 3.9 Hz, 3H), 0.82 (t, J = 6.8 Hz, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$): δ 212.18, 212.16, 209.3, 208.9, 147.91, 147.86, 147.0, 146.9, 139.2, 139.0, 119.6, 119.4, 108.2, 108.1, 106.51, 106.47, 101.11, 101.09, 75.2, 74.8, 57.0, 51.89, 51.87, 49.1, 47.0, 45.8, 45.7, 45.6, 45.1, 42.9, 38.7, 36.6, 36.12, 36.06, 35.9, 35.4, 31.6, 31.4, 27.8, 25.3, 22.0, 19.13, 19.09, 12.0.

**HRMS:** Calc’d for C$_{31}$H$_{39}$O$_5$, [M-OH]$^+$ 491.2792; found 491.2807.
Compound 73

Following General Procedure E on 0.2 mmol scale. Purification by PTLC (1:1 hexanes/EtOAc) afforded 79.5 mg (62%) of the title compound 73.

**Physical State:** white foam.

\[ R_f = 0.53 \text{ (hexanes/EtOAc 1:1, } p\text{-anisaldehyde).} \]

\[ ^{1}H\text{ NMR (600 MHz, CDCl}_3\text{): } \delta \text{ 6.83 (s, 1H), 6.74 (s, 2H), 5.93 (d, } J = 2.7 \text{ Hz, 2H), 5.05 (d, } J = 3.4 \text{ Hz, 1H), 4.87 (q, } J = 3.2 \text{ Hz, 1H), 4.59 – 4.45 (m, 2H), 2.10 (d, } J = 5.2 \text{ Hz, 3H), 2.06 (d, } J = 5.6 \text{ Hz, 3H), 2.04 – 1.88 (m, 7H), 1.86 – 1.54 (m, 10H), 1.52 – 1.42 (m, 3H), 1.39 – 1.01 (m, 8H), 0.89 (s, 3H), 0.78 (d, } J = 6.6 \text{ Hz, 3H), 0.69 (s, 3H).} \]

\[ ^{13}C\text{ NMR (151 MHz, CDCl}_3\text{): } \delta \text{ 170.7, 170.52, 170.51, 147.86, 147.84, 147.0, 146.9, 139.2, 139.0, 119.5, 119.3, 108.1, 106.5, 106.4, 101.08, 101.07, 75.6, 75.2, 74.9, 74.2, 70.8, 47.59, 47.55, 45.1, 43.5, 43.4, 41.0, 37.8, 35.42, 35.36, 34.9, 34.83, 34.78, 34.7, 34.4, 31.9, 31.3, 28.98, 28.97, 27.3, 27.2, 27.0, 25.7, 22.9, 22.7, 21.7, 21.59, 21.57, 21.56, 18.00, 17.97, 12.4, 12.3.} \]

**HRMS:** Calc’d for C\text{37}H\text{51}O\text{8}, [M-OH]\text{+} 623.3578; found 623.3589.

Compound 74

Following General Procedure E on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 19.8 mg (31%) of the title compound 74.

**Physical State:** colorless oil.

\[ R_f = 0.52 \text{ (hexanes/EtOAc 4:1, } p\text{-anisaldehyde).} \]
1H NMR (600 MHz, CDCl₃): δ 7.55 (dd, J = 7.8, 1.8 Hz, 1H), 7.52 (dd, J = 7.9, 1.2 Hz, 1H), 7.34 (td, J = 7.5, 1.2 Hz, 1H), 7.30 – 7.25 (m, 2H), 7.18 (ddt, J = 7.5, 3.4, 1.9 Hz, 3H), 7.13 (td, J = 7.6, 1.7 Hz, 1H), 5.08 (dd, J = 8.4, 4.1 Hz, 1H), 2.63 (t, J = 7.8 Hz, 2H), 1.82 (d, J = 3.9 Hz, 1H), 1.70 (dddd, J = 24.5, 10.9, 8.6, 6.3 Hz, 3H), 1.62 – 1.54 (m, 1H), 1.52 – 1.45 (m, 1H).

13C NMR (151 MHz, CDCl₃): δ 144.0, 142.7, 132.8, 128.9, 128.6, 128.4, 127.9, 127.4, 125.8, 122.1, 73.0, 37.6, 36.0, 31.4, 25.6.

The desired mass for HRMS was not observed.

**Compound 75**

Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 20.2 mg (39%) of the title compound 75.

**Physical State**: yellow oil.

\[ R_f = 0.46 \] (hexanes/EtOAc 4:1, p-anisaldehyde).

1H NMR (500 MHz, CDCl₃): δ 7.33 – 7.23 (m, 4H), 7.21 – 7.12 (m, 3H), 7.06 – 6.99 (m, 2H), 4.65 (dd, J = 7.5, 5.8 Hz, 1H), 2.60 (dd, J = 8.6, 6.9 Hz, 2H), 1.86 – 1.78 (m, 1H), 1.74 – 1.62 (m, 3H), 1.51 – 1.42 (m, 1H), 1.36 – 1.28 (m, 1H).

13C NMR (126 MHz, CDCl₃): δ 162.3 (d, J = 245.4 Hz), 142.6, 140.7, 128.5, 128.4, 127.6 (d, J = 8.1 Hz), 125.8, 115.4 (d, J = 21.2 Hz), 74.1, 39.2, 36.0, 31.5, 25.6.

19F NMR (376 MHz, CDCl₃): δ –117.83.

Spectroscopic data are in accordance with that reported in the literature.33
Compound 76

Following General Procedure E on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 29.0 mg (51%) of the title compound 76.

Physical State: colorless oil.

\[ R_f = 0.42 \text{ (hexanes/EtOAc 6:1, } p\text{-anisaldehyde).} \]

\[ ^1H \text{ NMR (500 MHz, CDCl}_3\]): \delta 7.31 – 7.24 (m, 2H), 7.18 (dt, } J = 7.0, 3.0 \text{ Hz, 3H}), 5.11 (td, } J = 7.0, 3.5 \text{ Hz, 1H), 3.74 – 3.64 (m, 1H), 2.63 (t, } J = 7.7 \text{ Hz, 2H), 1.98 (ddt, } J = 22.8, 15.1, 7.2 \text{ Hz, 2H), 1.70 – 1.57 (m, 8H), 1.53 – 1.09 (m, 10H), 0.91 (dd, } J = 8.3, 6.6 \text{ Hz, 3H).} \]

\[ ^{13}C \text{ NMR (126 MHz, CDCl}_3\): } \delta 142.8, 131.41, 131.36, 128.5, 128.4, 125.8, 124.9, 70.0, 69.7, 45.4, 45.1, 38.4, 38.1, 37.7, 36.8, 36.10, 36.09, 31.7, 29.4, 29.1, 25.9, 25.6, 25.53, 25.51, 25.4, 20.5, 19.3, 17.8. \]

HRMS: Calc’d for C\textsubscript{20}H\textsubscript{31}, [M-OH]+ 271.2420; found 271.2423.

Compound 77

Following General Procedure E on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 26.5 mg (55%) of the title compound 77.

Physical State: colorless oil.

\[ R_f = 0.44 \text{ (hexanes/EtOAc 4:1, } p\text{-anisaldehyde).} \]

\[ ^1H \text{ NMR (500 MHz, CDCl}_3\]): \delta 7.39 – 7.31 (m, 4H), 7.32 – 7.24 (m, 3H), 7.22 – 7.13 (m, 3H), 4.67 (dd, } J = 7.6, 5.7 \text{ Hz, 1H), 2.64 – 2.55 (m, 2H), 1.85 (dddd, } J = 13.0, 10.4, 7.6, 5.2 \text{ Hz, 1H), 1.75 (ddt, } J = 13.5, 10.3, 5.6 \text{ Hz, 1H), 1.69 – 1.62 (m, 2H), 1.55 – 1.47} \]
(m, 1H), 1.41 – 1.32 (m, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 145.0, 142.7, 128.6, 128.5, 128.4, 127.7, 126.0, 125.8, 74.7, 39.1, 36.0, 31.5, 25.7.

Spectroscopic data are in accordance with that reported in the literature.$^{33}$

**Compound 78**

Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 25.8 mg (47%) of the title compound **78**.

**Physical State:** colorless oil.

$R_f = 0.48$ (hexanes/EtOAc 4:1, $p$-anisaldehyde).

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.34 (t, $J = 1.8$ Hz, 1H), 7.30 – 7.22 (m, 4H), 7.22 – 7.13 (m, 4H), 4.64 (dd, $J = 7.7$, 5.5 Hz, 1H), 2.60 (t, $J = 7.7$ Hz, 2H), 1.79 (ddd, $J = 10.4$, 7.8, 5.2 Hz, 1H), 1.74 – 1.62 (m, 3H), 1.52 – 1.44 (m, 1H), 1.40 – 1.32 (m, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 147.1, 142.6, 134.5, 129.9, 128.5, 128.4, 127.7, 126.2, 125.8, 124.2, 74.1, 39.1, 35.9, 31.4, 25.5.

The desired mass for HRMS was not observed.

**Compound 79**

Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 21.0 mg (45%) of the title compound **79**.

**Physical State:** colorless oil.

$R_f = 0.44$ (hexanes/EtOAc 4:1, $p$-anisaldehyde).
$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.30 – 7.25 (m, 2H), 7.20 – 7.15 (m, 3H), 3.61 (dt, $J$ = 8.3, 4.1 Hz, 1H), 2.69 – 2.58 (m, 2H), 1.68 – 1.61 (m, 2H), 1.56 – 1.26 (m, 9H), 1.20 – 1.16 (m, 1H), 0.90 (td, $J$ = 7.5, 1.3 Hz, 6H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 142.8, 128.6, 128.4, 125.8, 73.3, 47.0, 36.1, 34.1, 31.7, 26.2, 22.2, 21.3, 12.1, 12.0.

The desired mass for HRMS was not observed.

**Compound 80**

Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (4:1 hexanes/EtOAc) afforded 23.8 mg (42%) of the title compound 80.

**Physical State**: colorless oil.

$R_f$ = 0.46 (hexanes/EtOAc 4:1, $p$-anisaldehyde).

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.30 – 7.24 (m, 2H), 7.20 – 7.14 (m, 3H), 5.41 (dtq, $J$ = 4.4, 2.8, 1.3 Hz, 1H), 3.98 (q, $J$ = 6.8 Hz, 1H), 2.61 (td, $J$ = 7.7, 6.8, 1.9 Hz, 2H), 2.44 – 2.38 (m, 1H), 2.34 – 2.18 (m, 3H), 2.10 (ddq, $J$ = 6.1, 3.1, 1.5 Hz, 1H), 1.64 (p, $J$ = 7.6 Hz, 2H), 1.53 – 1.33 (m, 5H), 1.33 – 1.25 (m, 3H), 1.11 (dd, $J$ = 31.0, 8.6 Hz, 1H), 0.81 (d, $J$ = 25.1 Hz, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 150.8, 150.2, 142.8, 128.5, 128.4, 125.8, 118.3, 117.7, 75.1, 75.0, 42.2, 41.9, 41.2, 41.1, 37.90, 37.87, 36.1, 36.0, 34.7, 34.4, 32.01, 31.95, 31.6, 31.5, 31.3, 31.2, 26.4, 26.3, 25.7, 25.5, 21.5.

**HRMS**: Calc’d for C$_{20}$H$_{27}$, [M-OH]$^+$ 267.2107; found 267.2112.
**Compound 84**

Following **General Procedure E** on 0.2 mmol scale. Purification by PTLC (2:1 hexanes/EtOAc) afforded 16.0 mg (23%) of the title compound 84.

**Physical State:** colorless oil.

*Rf* = 0.36 (hexanes/EtOAc 2:1, *p*-anisaldehyde).

**1H NMR (600 MHz, CDCl3):** δ 6.86 (d, *J* = 1.4 Hz, 1H), 6.77 (d, *J* = 1.7 Hz, 2H), 5.95 (s, 2H), 4.70 (dd, *J* = 8.5, 5.1 Hz, 1H), 4.06 (s, 2H), 2.67 (s, 2H), 1.77 – 1.65 (m, 4H), 1.57 – 1.48 (m, 2H), 1.45 (s, 9H), 1.13 (ddd, *J* = 23.6, 12.0, 4.1 Hz, 2H).

**13C NMR (151 MHz, CDCl3):** δ 155.0, 148.1, 147.2, 139.1, 119.4, 108.3, 106.4, 101.2, 79.4, 71.9, 45.9, 32.8, 28.6.

**HRMS:** Calc’d for C\textsubscript{14}H\textsubscript{20}NO\textsubscript{3}, [M-Boc+2H]\textsuperscript{+} 250.1438; found 250.1438.
Reaction Progress Kinetic Analysis

Procedure for electrochemical NHK reaction

Preparation of nickel catalyst stock solution in DMF (0.008 M, solution A): A screw-capped culture tube equipped with a magnetic stir bar was charged with NiCl₂·glyme (9 mg, 0.04 mmol) and 2,9-dibutyl-1,10-phenanthroline (18 mg, 0.06 mmol). The atmosphere was exchanged by 3 cycles of vacuum/Ar. Degassed DMF (5 mL) was added via a syringe, and the mixture was stirred for 5 min to give a homogeneous pink solution.

Preparation of CrCl₂ stock solution in DMF (0.04 M, solution B): A screw-capped culture tube was charged with CrCl₂ (30 mg, 0.24 mmol) in the glovebox. The tube was removed from the glovebox and placed under an argon balloon, whereupon degassed DMF (6 mL) was added via a syringe. The resulting mixture was sonicated until a homogeneous green solution was obtained.

To a 5 mL ElectraSyn vial equipped with a magnetic stir bar was added 3-phenylpropionaldehyde (sub-2, 26.8 mg, 0.2 mmol), (4-bromopent-4-en-1-yl)benzene (sub-1, 90.0 mg, 0.4 mmol), Cp₂ZrCl₂ (29.0 mg, 0.1 mmol), TBAB (80.6 mg, 0.25 mmol), and 4,4’-di-tert-butylbiphenyl (26.6 mg, 0.1 mmol). The vial cap equipped with aluminum anode and nickel foam cathode was tightened and the atmosphere was exchanged by cycling vacuum then argon (via a balloon). Degassed DMF (1.0 mL), solution A (0.5 mL), and solution B (1.0 mL) were added to the vial sequentially. The mixture was subjected to 10 mA constant current condition at a stir speed of 1000 rpm for 100 minutes which signified time = 0. Aliquots (~ 20 μL) were removed from the reaction at the indicated times and directly injected into 0.4 mL CH₃CN in a filter vial without any further quench and subjected to analysis.
Analysis

The reaction mixtures were analyzed on a Waters I-Class LC equipped with a Waters BEH C18 column (1.7 µm, 2.1 × 105 mm). The analyses was performed under gradient conditions at 55 °C using a gradient based on (A) 0.1% NH₄OH in water and (B) CH₃CN (15–99% B over 3.5 minutes, held at 99% B for 0.2 minutes).

Retention times for relevant species: (4-bromopent-4-en-1-yl)benzene (S11) 3.239 minutes (detection wavelength 285 nm), 3-phenylpropionaldehyde (1) 1.382 minutes (detection wavelength 285 nm), product (7) 3.032 minutes (detection wavelength 285 nm), pent-4-en-1-ylbenzene 3.077 minutes (detection wavelength 285 nm), 4,4’-di-tert-butylbiphenyl 4.219 minutes (detection wavelength 222 nm). Analyte concentrations were calculated against 4,4’-di-tert-butylbiphenyl as internal standard, and all analytes were calibrated separately using a series of ten calibration solutions of different concentrations, with the highest concentration of the series being 10 mM.

HPLC trace
Results

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{[sub-2]} & = 0.08 \text{ M} \\
\text{Br} & \quad \text{Ph} \\
\text{[sub-1]} & = 0.16 \text{ M}
\end{align*}
\]

\[
\begin{align*}
\text{[NiCl}_2\text{-glyme]} & = 0.0016 \text{ M} \\
\text{[L1]} & = 0.0024 \text{ M} \\
\text{[CrCl}_2] & = 0.016 \text{ M} \\
\text{[Cp}_2\text{ZrCl}_2] & = 0.04 \text{ M} \\
\text{[TBAB]} & = 0.1 \text{ M} \\
\text{DMF (2.5 mL)} & \\
\text{Al(+)/Ni foam(–)} & \\
\text{constant current} & = 10 \text{ mA, 100 min}
\end{align*}
\]

\[
\begin{align*}
\text{Ph} & \quad \text{OH} \\
\text{67%}
\end{align*}
\]

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<th>[sub-2] (M)</th>
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<th>[L1] (M)</th>
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Procedure for classical NHK reaction

**Preparation of nickel catalyst stock solution in DMF:** In a glovebox, NiCl₂·glyme (17.6 mg, 0.08 mmol) and 2,9-dibutyl-1,10-phenanthroline (35 mg, 0.12 mmol) were added into a 3 mL volumetric flask with DMF to form a Ni catalyst stock solution A.

**Preparation of LiCl, CrCl₂, and Cp₂ZrCl₂ stock solution in DMF:** In glovebox, LiCl (43.4 mg, 1 mmol), CrCl₂ (24.6 mg, 0.2 mmol), and Cp₂ZrCl₂ (146.2 mg, 0.5 mmol) were added into a 5 mL volumetric flask with DMF as solvent to form a stock solution B.

**Preparation of sub-1 and sub-2 stock solution in DMF:** To a 1 mL volumetric flask were added (4-bromopent-4-en-1-yl)benzene (sub-1, 119.5 mg, 0.53 mmol), 3-phenylpropionaldehyde (sub-2, 35.7 mg, 0.266 mmol), and DMF as solvent to form stock solution C.

In the glovebox, to a 1 dram glass vial equipped with a magnetic stir bar, Mn (0.16 mmol, 8.8 mg) was added, then stock solution C (sub-1 and sub-2, 0.3 mL) and stock solution B (LiCl, CrCl₂, and Cp₂ZrCl₂, 0.4 mL) were added into the reaction vial. 4,4’-Di-tert-butylbiphenyl was added as internal standard. The reaction was started by adding stock solution A (Ni catalyst and Ligand). The aliquots were taken every 30 min and quenched with CH₃CN (0.1% TFA, 0.4 mL), then added to the filter vial (PTFE, 0.2 μm) and analyzed by RP-LC.

**Results**

![Chemical structure](image)

- [NiCl₂·glyme] = 0.0016 M
- [L₁] = 0.0024 M
- [CrCl₂] = 0.016 M
- [Cp₂ZrCl₂] = 0.04 M
- DMF (1.0 mL)
- [LiCl] = 0.16 M, [Mn] = 0.16 M

79%
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</table>
Procedure for electrochemical decarboxylative NHK reaction

To a 5 mL ElectraSyn vial equipped with a magnetic stir bar were added aldehyde (30 mg, 0.2 mmol), redox-active ester (32.3 mg, 0.2 mmol), CrCl$_3$ (6.4 mg, 0.04 mmol, 0.2 equiv), TBAClO$_4$ (85 mg, 0.25 mmol, 0.1 M), and 4,4’-di-tert-butylbiphenyl (26.6 mg, 0.1 mmol). The vial cap equipped with aluminum anode and nickel foam cathode was tightened and the atmosphere was exchanged by cycling vacuum then argon (via a balloon). Then DMF (2.0 mL), THF (0.5 mL), and TESCl (67 μL, 0.4 mmol, 2.0 equiv) were added to the vial sequentially. The mixture was subjected to 2.5 mA constant current condition at a stir speed of 1000 rpm for 300 minutes which signified time = 0. Aliquots (~20 μL) were removed from the reaction at the indicated times and directly injected into 0.4 mL CH$_3$CN in a filter vial without any further quench and subjected to analysis.

Procedure for classical decarboxylative NHK reaction

Preparation of RAE, aldehyde, and 4,4’-di-tert-butylbiphenyl (internal standard) stock solution in DMF/THF: To a 3 mL volumetric flask were added RAE (258.4 mg, 0.8 mmol), aldehyde (120 mg, 0.8 mmol), 4,4’-di-tert-butylbiphenyl (106.4 mg, 0.4 mmol), and DMF/THF (4:1) to form stock solution A.

Preparation of TESCl stock solution in DMF/THF: To a volumetric flask were added TESCl (241.1 mg, 1.6 mmol) and DMF/THF (4:1) to form stock solution B.

In the glovebox, to a 1 dram glass vial equipped with a magnetic stir bar, Mn (0.16 mmol, 8.8 mg) was added, then stock solution A (RAE, aldehyde, and internal standard, 0.3 mL) and CrCl$_3$ (2.53 mg, 0.016 mmol) were added into a reaction vial. The reaction was started by adding TESCl (stock solution B, 0.4 mL). The aliquots were taken every 30 min and quenched with CH$_3$CN (0.1% TFA, 0.4 mL), then added to the filter vial (PTFE, 0.2 μm) and analyzed by RP-LC.
Analysis

The reaction mixtures were analyzed on a Waters I-Class LC with a Waters UPLC BEH C18 column (1.7 µm, 2.1 × 105 mm) using a 0.1% aqueous formic acid/CH₃CN gradient (0.6 mL/min, 15–99% CH₃CN over 2.1 minutes, followed by an isocratic hold at 99% CH₃CN) at 55 °C.

Retention times for relevant species: compound 60 1.765 minutes (detection wavelength 286 nm), compound 85 2.535 minutes (detection wavelength 286 nm), 4,4’-di-tert-butylbiphenyl 2.440 minutes (detection wavelength 286 nm). Analyte concentrations were calculated against 4,4’-di-tert-butylbiphenyl as internal standard, and all analytes were calibrated separately using a series of ten calibration solutions of different concentrations with the highest concentration of the series being 10 mM.

HPLC trace

Compare LC traces at 90 min for both reactions, the trace of e-chem looks much cleaner and with less by product, while trace with Mn, the peak of RAE almost decompose.
Results

\[
\text{NHPI} + \text{PhCHO} \rightarrow \text{PhSiEt}_3 + \text{PhCHO} + \text{H}_2
\]

<table>
<thead>
<tr>
<th></th>
<th>[RAE] (M)</th>
<th>[ArCHO] (M)</th>
<th>[CrCl}_3 (M)</th>
<th>[TESCl] (M)</th>
<th>Current (mA)</th>
<th>Mn (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-Chem</td>
<td>0.08</td>
<td>0.08</td>
<td>0.016</td>
<td>0.16</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>Mn_RAE</td>
<td>0.08</td>
<td>0.08</td>
<td>0.016</td>
<td>0.16</td>
<td></td>
<td>0.16</td>
</tr>
</tbody>
</table>
**Effect of current:**
Reaction exhibits an induction period that is proportional to current. Rate is not influenced by current post-induction period.

**Kinetic with current:**
Induction period, CrCl$_3$ do not soluble at the first 30 min; Reaction with RAE show 0th order in current; Current at 7.5 mA decompose the RAE substrate.

**Time shift of 2.5 mA for induction period**

**Kinetic with [Cr]:**
Reaction show 0.5th order in [Cr]; Reaction with 0.008M of [Cr], reaction stop at 100 min, suggest the catalyst decompose.

**Remove the induction period**
Kinetic with [RAE]:
Reaction show 0th order in [RAE]

Kinetic with [ArCHO]:
Reaction show positive order in [ArCHO]
General Details for UV-vis Spectroscopy and Electroanalytical Studies

**UV-vis Spectroscopy**

UV–visible (UV-vis) spectra were collected with either a Cary 50 Bio UV-vis or Cary 500 UV-vis near-IR (NIR) spectrophotometer. Samples were prepared inside a nitrogen-filled glovebox using air-tight quartz cuvettes.

**Electrochemistry**

Electrochemical experiments were performed using a standard three-electrode cell with a glassy carbon (GC) working electrode (3 mm diameter) or Ni wire [10931 Nickel wire, 0.25 mm diameter, Puratronic, 99.994% (metals basis)] working electrode, a 0.01 M Ag⁺/0 (AgNO₃) in CH₃CN non-aqueous reference electrode, and a 3.175 mm diameter aluminum (Al) rod (K&S Precision Metals) counter electrode. Voltammograms were collected in a nitrogen-filled glovebox in DMF with TBAPF₆ (0.1–0.2 M) (TBA = tetrabutylammonium) supporting electrolyte. A Gamry Reference 600 potentiostat was used for all room temperature voltammetry. All voltammograms were electronically compensated using positive-feedback $iR$-compensation at 90% of the $R_u$, which was measured by potentiostatic electrochemical impedance spectroscopy. Ferrocene (Fc) or cobaltocenium hexafluorophosphate (Co) served as the internal potential standard, and all potentials were referenced relative to Fc⁺/0.

**UV-vis Spectroelectrochemistry**

In situ spectroelectrochemical measurements were performed in a nitrogen-filled glovebox with a quartz spectroelectrochemical cell with a 0.17 mm path length from Pine Research Instrumentation (AKSTCKIT3), a custom working electrode prepared from Ni mesh (Alfa Aesar, 44128 Nickel gauze, 100 mesh woven from 0.1 mm diameter wire) and Ni wire [10931 Nickel wire, 0.25 mm diameter, Puratronic, 99.994% (metals basis)], and an Al wire counter electrode [(Alfa Aesar, aluminum wire, 1.0 mm diameter, annealed, Puratronic, 99.9995% (metals basis)]. Measurements were recorded using either an Analytical Instrument Systems, Inc. DT2000 deuterium-tungsten light source.
coupled to Stellarnet Black Comet UV-vis and DWARF-Star NIR spectrometers or a Hamamatsu L1179 deuterium light source coupled to an Ocean Optics USB4000-UV-Vis-ES spectrometer. The cell was placed in an Ocean Optics CUV-UV cuvette holder connected to the spectrometer by 600 µm core optical fibers.

Assembly of the UV-vis Spectroelectrochemical Cell

Figure S1: (Left) Individual components of spectroelectrochemical cell from left to right: PTFE cap, spectroelectrochemical cuvette, custom Ni-mesh working electrode, aluminum wire counter electrode, reference electrode. (Middle) Assembled spectroelectrochemical cell side profile. (Middle) Assembled spectroelectrochemical cell front on profile. (Right) Assembled spectroelectrochemical cell placed inside cuvette holder connected to both optics and potentiostat cables inside a glovebox.
Cyclic Voltammetry

Identification of CV Waves

Figure S2: Full Cr(II) e-NHK: [S11] = 104 mM, [I] = 52 mM, [CrCl₂] = 2 mM, [Cp₂ZrCl₂] = 2 mM, [NiCl₂·DME] = 0.2 mM, [L₄] = 0.3 mM. Cr(II) e-NHK no aldehyde or alkenyl bromide: [CrCl₂] = 2 mM, [Cp₂ZrCl₂] = 2 mM, [NiCl₂·DME] = 0.2 mM, [L₄] = 0.3 mM. All CV experiments were run in DMF with [TBAPF₆] = 0.1 M and acquired with a scan rate of 100 mV/s, GC working electrode, and Al counter electrode. All potentials referenced to Fc⁺/0.

After multiple attempts to observe a catalytic current for the analytical cyclic voltammetry of the Cr(II) e-NHK, we could not correlate any changes in current to the catalytic wave of the e-NHK, which had an expected onset potential of −1.6 V vs a nonaqueous AgNO₃ reference electrode. However, upon cathodic scan near the potential limit of the solvent window, we observed a substantial current (Figure S2 green) near −3.2 V vs Fc⁺/0 for Cr(II) e-NHK no aldehyde or alkenyl bromide. Recent electrochemical benchmarking studies by Nicewicz and coworkers suggest strongly reducing potentials are needed for direct reduction of alkyl aldehyde functional groups.³⁴ Therefore, we suspect the substantial current detected near −3.2 V vs Fc⁺/0 for Cr(II) e-NHK no aldehyde or alkenyl bromide is likely the direct reduction of 1 at the working electrode.

Since we demonstrated that Cr(III) salts were productive catalysts for the e-NHK, we opted to try this source of Cr for our analytical voltammetry studies and were
gratified to observe a cathodic current (−2.0 V vs Fc+/0) that corresponded to the catalytic wave of the e-NHK (see Figures S6 and S3 below).

![Graph showing Cr(III) e-NHK and Cr(III) e-NHK no aldehyde or alkenyl bromide currents](image)

**Figure S3:** Cr(III) e-NHK: [S11] = 104 mM, [1] = 52 mM, [CrCl3·3THF] = 2 mM, [Cp2ZrCl2] = 2 mM, [NiCl2·DME] = 0.2 mM, [L4] = 0.3 mM. Cr(III) e-NHK no aldehyde or alkenyl bromide: [CrCl3·3THF] = 2 mM, [Cp2ZrCl2] = 2 mM, [NiCl2·DME] = 0.2 mM, [L4] = 0.3 mM. All CV experiments were run in DMF with [TBAPF6] = 0.1 M and acquired with a scan rate of 100 mV/s, Ni-wire working electrode, and Al counter electrode. All potentials are referenced against a 0.01 M Ag+/0 (AgNO3) non-aqueous (CH3CN) reference electrode.

During our optimization studies, we observed that utilizing a Ni-foam working electrode improved the bulk electrolysis yield; however, higher quality analytical CV data were obtained when a GC working electrode was used instead of a Ni-wire. We note that the general features of the CV (see Figure S6) data are comparable whether collected with a GC working electrode or a Ni-wire working electrode.
**Figure S4:** CrCl$_3$·3THF + Ni(II) catalyst: [CrCl$_3$·3THF] = 2 mM, [NiCl$_2$·DME] = 0.2 mM, [L4] = 0.3 mM. CrCl$_3$·3THF + Ni(II) catalyst + Cp$_2$ZrCl$_2$: [CrCl$_3$·3THF] = 2 mM, [NiCl$_2$·DME] = 0.2 mM, [L4] = 0.3 mM, [Cp$_2$ZrCl$_2$] = 2 mM. Cp$_2$ZrCl$_2$: [Cp$_2$ZrCl$_2$] = 2 mM. All CV experiments were run in DMF with [TBAPF$_6$] = 0.1 M and acquired with a scan rate of 100 mV/s, GC working electrode, and Al counter electrode. All potentials referenced to Fc$^{+/0}$.

**Figure S5:** Cr(III) e-NHK: [S11] = 104 mM, [1] = 52 mM, [CrCl$_3$·3THF] = 2 mM, [Cp$_2$ZrCl$_2$] = 2 mM, [NiCl$_2$·DME] = 0.2 mM, [L4] = 0.3 mM. Cr(III) e-NHK no aldehyde or alkenyl bromide: [CrCl$_3$·3THF] = 2 mM, [Cp$_2$ZrCl$_2$] = 2 mM, [NiCl$_2$·DME] = 0.2 mM, [L4] = 0.3 mM. All CV experiments were run in DMF with [TBAPF$_6$] = 0.1 M and acquired with a scan rate of 100 mV/s, GC working electrode, and Al counter electrode. All potentials referenced to Fc$^{+/0}$.

**Figure S6:** Cr(III) e-NHK: [S11] = 104 mM, [1] = 52 mM, [CrCl$_3$·3THF] = 2 mM, [Cp$_2$ZrCl$_2$] = 2 mM, [NiCl$_2$·DME] = 0.2 mM, [L4] = 0.3 mM. Cr(III) e-NHK no aldehyde or alkenyl bromide: [CrCl$_3$·3THF] = 2 mM, [Cp$_2$ZrCl$_2$] = 2 mM, [NiCl$_2$·DME] = 0.2 mM, [L4] = 0.3 mM. Cr(III) e-NHK without alkenyl bromide: [S11] = 104 mM, [1] = 0 mM, [CrCl$_3$·3THF] = 2 mM, [Cp$_2$ZrCl$_2$] = 2 mM, [NiCl$_2$·DME] = 0.2 mM, [L4] = 0.3 mM. Cr(III) e-NHK without alkyl aldehyde: [S11] = 104 mM, [1] = 52 mM, [CrCl$_3$·3THF] = 2 mM, [Cp$_2$ZrCl$_2$] = 2 mM, [NiCl$_2$·DME] = 0.2 mM, [L4] = 0.3 mM. All CV experiments were run in DMF with [TBAPF$_6$] = 0.1 M.
and acquired with a scan rate of 100 mV/s, GC working electrode, and Al counter electrode. All potentials referenced to Fc$^{+/0}$.

During the course of our e-NHK kinetics experiments for the bulk electrolysis, we believe a significant amount of alkenyl bromide dehalogenation occurs concomitantly with productive e-NHK catalysis. We suggest the catalytic current in the absence of alkyl aldehyde corresponds to this electrocatalytic dehalogenation process. Nédélec and coworkers have previously reported electrocatalytic low-valent Ni homocoupling of alkenyl bromides under similar electrolysis conditions.$^{35}$

**Figure S7:** Cr(III) e-NHK: $[S11] = 104$ mM, $[1] = 52$ mM, $[CrCl_3\cdot3THF] = 2$ mM, $[Cp_2ZrCl_2] = 2$ mM, $[NiCl_2\cdotDME] = 0.2$ mM, $[L4] = 0.3$ mM. Ni(II) catalyst: $[NiCl_2\cdotDME] = 0.5$ mM, $[L4] = 0.75$ mM. Cr(III) e-NHK without alkyl aldehyde: $[S11] = 104$ mM, $[1] = 0$ mM, $[CrCl_3\cdot3THF] = 2$ mM, $[Cp_2ZrCl_2] = 2$ mM, $[NiCl_2\cdotDME] = 0.2$ mM, $[L4] = 0.3$ mM. Ni(II)-catalyst + 100 equiv alkenyl bromide: $[S11] = 50$ mM, $[NiCl_2\cdotDME] = 0.5$ mM, $[L4] = 0.75$ mM. All CV experiments were run in DMF with [TBAPF$_6$] = 0.1 M and acquired with a scan rate of 100 mV/s, GC working electrode, and Al counter electrode. All potentials referenced to Fc$^{+/0}$. 

![Graph](image1.png)

![Graph](image2.png)
**Figure S8:** A mixture of ferrocene with cobaltocenium hexafluorophosphate (Co) in DMF with [TBAPF₆] = 0.1 M and acquired with a scan rate of 100 mV/s, GC working electrode, and Al counter electrode. All potentials are referenced against a 0.01 M Ag⁺/AgNO₃ non-aqueous (CH₃CN) reference electrode.

When acquiring voltammetry with the Ni-based working electrodes, we observe an OCP of −0.6 V vs Fe⁺/Fe⁺₀. Therefore, we relied upon Cp₂CoPF₆ as an external electrochemical reference when conducting voltammetry with the Ni-mesh in the spectroelectrochemical experiments. We then referenced the Cp₂CoPF₆ formal potential to ferrocene as shown above.

**Catalytic Current Dependence on Substrate/Catalyst Concentration**

**Figure S9:** (Left) Cyclic voltammograms of e-NHK with varied [CrCl₃·3THF]: 4 mM, 2 mM, 1 mM. All experiments have [S11] = 80 mM, [1] = 46 mM, [Cp₂ZrCl₂] = 2 mM, [NiCl₂·DME] = 0.2 mM, [L4] = 0.3 mM. All CV experiments were run in DMF with [TBAPF₆] = 0.1 M and acquired with a scan rate of 100 mV/s, GC working electrode, and Al counter electrode. All potentials referenced to Fe⁺/Fe⁺₀. (Right) [CrCl₃·3THF] vs current at −2.0 V (E vs. Fe⁺/Fe⁺₀).
Figure S10: (Left) CVs of e-NHK with varied [Ni(II)]: 0.5 mM, 0.25 mM, 0.125 mM. All experiments have [S11] = 80 mM, [I] = 46 mM, [Cp₂ZrCl₂] = 2 mM, [CrCl₃·3THF] = 2 mM, and Ni/L₄ as 1:1.5. All CV experiments were run in DMF with [TBAPF₆] = 0.1 M and acquired with a scan rate of 100 mV/s, GC working electrode, and Al counter electrode. All potentials referenced to Fc⁺⁻/⁻. (Right) [Ni(II)] vs current at −2.0 V (E vs. Fc⁺⁻/⁻).

Figure S11: (Left) Cyclic voltammograms of e-NHK with varied [S11]: 208 mM, 104 mM, 52 mM, 27 mM. All experiments have [I] = 53 mM, [Cp₂ZrCl₂] = 2 mM, [CrCl₃·3THF] = 2 mM, [NiCl₂·DME] = 0.2 mM, and [L₄] = 0.3 mM. All CV experiments were run in DMF with [TBAPF₆] = 0.1 M and acquired with a scan rate of 100 mV/s, GC working electrode, and Al counter electrode. All potentials referenced to Fc⁺⁻/⁻. (Right) [S11] vs current at −2.0 V (E vs. Fc⁺⁻/⁻).

Scan Rate Dependence

All scan rate dependency studies were conducted in DMF with [TBAPF₆] = 0.1 M. The voltammetry was acquired with a freshly polished GC working electrode and Al counter electrode. All potentials referenced to Fc⁺⁻/⁻.
A linear correlation between baseline-corrected current density and square root of the scan rate was observed for all CV mixtures illustrated below.

**Figure S12:** Scan rate dependence for \([\text{CrCl}_3 \cdot 3\text{THF}] = 2 \, \text{mM}\) with corresponding Randles-Sevcik plot.

**Figure S13:** Scan rate dependence for \([\text{CrCl}_3 \cdot 3\text{THF}] = 2 \, \text{mM}, [\text{NiCl}_2 \cdot \text{DME}] = 0.2 \, \text{mM}, \) and \([L_4] = 0.3 \, \text{mM}\) with corresponding Randles-Sevcik plot for wave near $-1.4 \, \text{V vs Fc}^{+/0}$.

**Figure S14:** Scan rate dependence for \([\text{CrCl}_3 \cdot 3\text{THF}] = 2 \, \text{mM}, [\text{NiCl}_2 \cdot \text{DME}] = 0.2 \, \text{mM}, \) and \([L_4] = 0.3 \, \text{mM}\) with truncated potential window along with corresponding Randles-Sevcik plot.
**Figure S15:** Scan rate dependence for $[\text{CrCl}_3\cdot3\text{THF}] = 2 \text{ mM}$, $[\text{NiCl}_2\cdot\text{DME}] = 0.2 \text{ mM}$, $[\text{L}_4] = 0.3 \text{ mM}$, and $[\text{Cp}_2\text{ZrCl}_2] = 2 \text{ mM}$ with corresponding Randles-Sevcik plot for wave near $-1.4 \text{ V vs } \text{Fc}^{+/0}$.

**Figure S16:** Scan rate dependence for $[\text{CrCl}_3\cdot3\text{THF}] = 2 \text{ mM}$, $[\text{NiCl}_2\cdot\text{DME}] = 0.2 \text{ mM}$, $[\text{L}_4] = 0.3 \text{ mM}$, and $[\text{Cp}_2\text{ZrCl}_2] = 2 \text{ mM}$ with truncated potential window along with corresponding Randles-Sevcik plot.

**Figure S17:** Scan rate dependence for $[\text{NiCl}_2\cdot\text{DME}] = 0.2 \text{ mM}$ and $[\text{L}_4] = 0.3 \text{ mM}$ with corresponding Randles-Sevcik plot.
Figure S18: Scan rate dependence for [NiCl₂·DME] = 0.2 mM and [L₄] = 0.3 mM with truncated potential window along with corresponding Randles-Sevcik plot.

Figure S19: Scan rate dependence for [CrCl₃·3THF] = 2 mM, [NiCl₂·DME] = 0.2 mM, [L₄] = 0.3 mM, [Cp₂ZrCl₂] = 2 mM, [I] = 70 mM, and [S11] = 140 mM with corresponding Randles-Sevcik plot for wave near −2.0 V vs Fc⁺/₀.

Figure S20: Scan rate dependence for [CrCl₃·3THF] = 2 mM, [NiCl₂·DME] = 0.2 mM, [L₄] = 0.3 mM, [Cp₂ZrCl₂] = 2 mM, [I] = 70 mM, and [S11] = 140 mM with truncated potential window along with corresponding Randles-Sevcik plot.
**UV-vis Studies**

All UV-vis studies were acquired in DMF with [TBAPF$_6$] = 0.1 M.

**Figure S21**: (Left) UV-vis absorbance of [CrCl$_2$] = 6.67 mM. (Right) Plot of [CrCl$_2$] versus absorbance at 850 nm.

**Figure S22**: (Left) UV-vis absorbance of [NiCl$_2$·DME] = 10 mM and [L$_4$] = 15 mM. (Right) Plot of [Ni(II)] versus absorbance at 500 nm.

**Figure S23**: UV-vis absorbance of [CrCl$_3$·3THF] = 17 mM.
Figure S24: (Left) Plot of \([\text{CrCl}_3 \cdot 3\text{THF}]\) versus absorbance at 494 nm. (Right) Plot of \([\text{CrCl}_3 \cdot 3\text{THF}]\) versus absorbance at 685 nm.

Figure S25: (Left) UV-vis absorbance of \([\text{CrCl}_2]\) = 2.86 mM, \([\text{NiCl}_2 \cdot \text{DME}]\) = 1.43 mM and \([\text{L4}]\) = 2.15 mM. (Right) Plot of \([\text{Ni(II)}]\) versus absorbance at 646 nm.

Figure S26: A UV-vis spectrum of relevant e-NHK components that has been normalized for the concentration of the reaction component as well as the path length for the spectroelectrochemical cell (0.17 cm). \(\text{CrCl}_2\): \([\text{CrCl}_2]\) = 16 mM, \([\text{CrCl}_3 \cdot 3\text{THF}]\):
[CrCl₃·3THF] = 16 mM, Ni(II)-catalyst: [NiCl₂·DME] = 0.2 mM, and [L₄] = 0.3 mM. Ni(II)-catalyst + CrCl₂: [CrCl₂] = 0.4 mM, [NiCl₂·DME] = 0.2 mM, and [L₄] = 0.3 mM. All UV-vis data were acquired in DMF with [TBAPF₆] = 0.1 M.

**Figure S27**: UV-vis of relevant e-NHK mixtures acquire with spectroelectrochemical setup. Zr + Ald + AlkB: [Cp₂ZrCl₂] = 40 mM, [I] = 80 mM, [S₁₁] = 160 mM. Cr(II) NHK Pre Ni(II)-cat addition: [S₁₁] = 160 mM, [I] = 80 mM, [CrCl₂] = 16 mM, [Cp₂ZrCl₂] = 40 mM, [NiCl₂·DME] = 0 mM, [L₄] = 0 mM. Cr(II) NHK post Ni(II)-cat addition: [S₁₁] = 160 mM, [I] = 80 mM, [CrCl₂] = 16 mM, [Cp₂ZrCl₂] = 40 mM, [NiCl₂·DME] = 1.6 mM, [L₄] = 2.4 mM. All UV-vis experiments were run in DMF with [TBAPF₆] = 0.1 M.

**UV-vis Spectroelectrochemical Studies**
**Figure S28:** Absorbance versus time for the bulk electrolysis of CrCl$_3$:3THF to Cr(II) at $-1.6$ V vs Ag$^{+/0}$, $[\text{CrCl}_3$:3THF$] = 0.016$ M, $[\text{TBAPF}_6] = 0.1$ M, DMF, a Ni-mesh working electrode, and aluminum wire counter electrode. Potentials are referenced against a 0.01 M Ag$^{+/0}$ non-aqueous reference electrode. * Indicates portions of the UV-vis absorbance data that have signal saturation inherent to the detector/lamp equipment used for these experiments.

A constant potential of $-1.6$ V vs Ag$^{+/0}$ was applied to a solution of CrCl$_3$:3THF to demonstrate the bulk electroreduction of Cr(III) to Cr(II) for the UV-vis spectroelectrochemical setup. At open circuit potential, the CrCl$_3$:3THF solution exhibits ligand field transitions typical for pseudo-octahedral Cr(III) ($^4A_{2g} \rightarrow ^4T_{2g}$ ($\lambda_{\text{max}} = 677$ nm) $^4T_{1g}$ ($\lambda_{\text{max}} = 487$ nm) in $O_h$ symmetry). Upon commencing the bulk electroreduction of Cr(III) at $-1.6$ V vs Ag$^{+/0}$, these Cr(III) ligand field transitions gradually disappear, and new absorbances associated with high-spin, pseudo-octahedral Cr(II) ($^5E_g \rightarrow ^5T_{2g}$ ($\lambda_{\text{max}} = 843$ nm) in $O_h$ symmetry) concomitantly appear.

These temporal spectroelectrochemical results confirm the successful one-electron bulk electroreduction of Cr(III) to Cr(II) by application of a potential of $-1.6$ V vs Ag$^{+/0}$.

**Figure S29:** Temporal monitoring of the bulk electrolysis for the Cr(III)-based e-NHK: $[\text{S11}] = 160$ mM, $[\text{I}] = 80$ mM, $[\text{CrCl}_3$:3THF$] = 16$ mM, $[\text{Cp}_2\text{ZrCl}_2] = 40$ mM, $[\text{NiCl}_2$:DME$] = 1.6$ mM, $[\text{L4}] = 2.4$ mM, Ni-mesh working electrode, and Al counter electrode. SEC cell has a path length of 0.17 cm. All potentials referenced with Co$^{+/0}$ and then referenced to Fc$^{+/0}$. Absorbance data were baseline-corrected by taking the absorbance at 900 nm to be zero. A potential of $-1.5$ V vs Fc$^{+/0}$ was applied for 15 minutes and then a potential $-2.0$ V vs Fc$^{+/0}$ was applied for 30 minutes. * Indicates
portions of the UV-vis absorbance data that have signal saturation inherent to the detector/lamp equipment used for these experiments.

Figure S30: Temporal monitoring of the bulk electrolysis for the Cr(III)-based e-NHK: 
[S11] = 160 mM, [I] = 80 mM, [CrCl3·3THF] = 16 mM, [Cp2ZrCl2] = 40 mM, 
[NiCl2·DME] = 1.6 mM, [L4] = 2.4 mM, Ni-mesh working electrode, and Al counter 
electrode. SEC cell has a path length of 0.17 cm. All potentials referenced with Co^{+/0} 
and then referenced to Fc^{+/0}. Absorbance data were baseline-corrected by taking the 
absorbance at 900 nm to be zero. A potential of −1.5 V vs Fc^{+/0} was applied for 15 
minutes and then a potential −2.0 V vs Fc^{+/0} was applied for 30 minutes. * Indicates 
portions of the UV-vis absorbance data that have signal saturation inherent to the 
detector/lamp equipment used for these experiments.

Figure S31: Temporal monitoring of the bulk electrolysis for the Cr(II)-based e-NHK: 
[S11] = 160 mM, [I] = 80 mM, [CrCl2] = 16 mM, [Cp2ZrCl2] = 40 mM, [NiCl2·DME]
= 1.6 mM, [L4] = 2.4 mM, Ni-mesh working electrode, and Al counter electrode. SEC cell has a path length of 0.17 cm. All potentials referenced to Co^{+0}. Absorbance data were baseline-corrected by taking the absorbance at 900 nm to be zero. A potential of −1.5 V vs Fe^{+0} was applied for 15 minutes and then a potential −2.0 V vs Fe^{+0} was applied for 30 minutes. * Indicates portions of the UV-vis absorbance data that have signal saturation inherent to the detector/lamp equipment used for these experiments.

Figure S32: Temporal monitoring of the bulk electrolysis for the Cr(II)-based e-NHK: [S11] = 160 mM, [I] = 80 mM, [CrCl2] = 16 mM, [Cp2ZrCl2] = 40 mM, [NiCl2·DME] = 1.6 mM, [L4] = 2.4 mM, Ni-mesh working electrode, and Al counter electrode. SEC cell has a path length of 0.17 cm. All potentials referenced to Co^{+0}. Absorbance data were baseline-corrected by taking the absorbance at 900 nm to be zero. A potential of −1.5 V vs Fe^{+0} was applied for 15 minutes and then a potential −2.0 V vs Fe^{+0} was applied for 30 minutes. * Indicates portions of the UV-vis absorbance data that have signal saturation inherent to the detector/lamp equipment used for these experiments.
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NMR Spectra: Compound 3 $^1$H NMR
Compound 3 $^{13}$C NMR
Compound 4 $^1$H NMR
Compound 4 $^{13}$C NMR
Compound 5 $^1$H NMR
Compound 5 $^{13}$C NMR
Compound 6 $^1$H NMR

[Image of a compound structure with labels Ph, OH, and Me]
Compound 6 $^{13}\text{C}$ NMR
Compound 7 $^1$H NMR
Compound 7 $^{13}$C NMR
Compound 8 $^1$H NMR
Compound 8 $^{13}$C NMR
Compound 9 $^1$H NMR

![Compound 9 $^1$H NMR spectrum]
Compound 9 $^{13}$C NMR
Compound 10 $^1$H NMR
Compound 10 $^{13}$C NMR
Compound 11 $^1$H NMR
Compound 11 $^{13}$C NMR
Compound 12 $^1$H NMR

Ph

OH

OTBS

S129
Compound 12 $^{13}$C NMR

![NMR spectrum of Compound 12](image)
Compound 13 $^1$H NMR
Compound 13 $^{13}$C NMR
Compound 14 $^1\text{H}$ NMR
Compound 14 $^{13}$C NMR
Compound 15 $^1$H NMR

[Image of a chemical structure and a NMR spectrum]
Compound 15 $^{13}$C NMR

![Compound 15 $^{13}$C NMR](image_url)
Compound 16 $^1$H NMR
Compound 16 $^{13}$C NMR
Compound 17 $^1$H NMR
Compound 17 $^{13}$C NMR
Compound 18 $^1$H NMR
Compound 18 $^{13}$C NMR
Compound 19 $^{13}$C NMR
Compound 20 $^1$H NMR

[Image of NMR spectrum]
Compound 20 $^{13}$C NMR

![NMR Spectrum]

- Data points range from -10 to 200 ppm.
- Peaks indicate the chemical shifts of different carbon atoms within the molecule.

Ph

OH

OTBS
Compound 21 $^1$H NMR
Compound 21 $^{13}$C NMR
Compound 22 $^1$H NMR
Compound 22 $^{13}$C NMR

[Diagram showing a molecule with labeled atoms and nuclei]
Compound 23 $^{13}$C NMR
Compound 24 $^1$H NMR
Compound 24 $^{13}$C NMR
Compound 25 $^1$H NMR

![NMR Spectrum](image)
Compound 25 $^{13}$C NMR
Compound 26 $^1$H NMR
Compound 26 $^{13}$C NMR

![Compound 26 $^{13}$C NMR Spectrum](image)
Compound 27 $^1$H NMR

- Compound structure with $^1$H NMR spectrum
- Chemical shift values indicated in ppm
Compound 27 $^{13}$C NMR
Compound 28 $^1$H NMR
Compound 28 $^{13}$C NMR

Ph

OH

Me

Me
Compound 29 $^{13}$C NMR
Compound 35 $^1$H NMR
Compound 35 $^{13}$C NMR
Compound 32 $^{13}$C NMR
Compound 30 $^1$H NMR
Compound 30 $^{13}$C NMR
Compound 33 $^1$H NMR

$\text{Boc} \quad \text{OH} \quad \text{Me}$
Compound 33 $^{13}$C NMR
Compound 31 \(^1\)H NMR

![NMR spectrum of Compound 31](image)
Compound 31 $^{13}$C NMR

OH
Me
Compound 34 $^1$H NMR
Compound 34 $^{13}$C NMR
Compound 38 $^1$H NMR
Compound 38 $^{13}$C NMR
Compound 36 $^1$H NMR
Compound 36 $^{13}$C NMR
Compound 37 (less polar isomer) $^1$H NMR
Compound 37 (less polar isomer) $^{13}$C NMR
Compound 37 (more polar isomer) $^1$H NMR
Compound 37 (more polar isomer) $^{13}$C NMR
Compound S6 $^1$H NMR

$\text{Br} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CO}_2\text{Bu}$
Compound S6 $^{13}$C NMR
Compound S17 $^1$H NMR
Compound S17 $^{13}$C NMR

![Compound S17 $^{13}$C NMR spectrum](image-url)

- Br
- SO$_2$Ph
Compound S18 \(^1\)H NMR
Compound S18 $^{13}$C NMR
Determination the er of Compound 40 (from racemic 40)
Determination the er of Compound 40
Determination the er of Compound 41
Determination of the er of Compound 42
Determination the er of Compound 43
Determination the er of Compound 44
Determination the er of Compound 45
Compound 46^{13}C NMR

\[ \text{MeO} \quad \text{N} \quad \text{Me} \quad \text{Me} \quad \text{OTBS} \]
Compound 47a $^1$H NMR
Compound 47\textsuperscript{a} \textsuperscript{13}C NMR
Compound 47b $^1$H NMR
Compound 47b $^{13}$C NMR
Compound 49 $^1$H NMR

[Diagram of the compound with chemical shifts]

S204
Compound 49 $^{13}$C NMR
Compound 50a $^{13}$C NMR

![Compound 50a $^{13}$C NMR spectrum](image)
Compound \textit{50b} \textsuperscript{1}H NMR
Compound 50b $^{13}$C NMR
Compound 52 $^1$H NMR (from (S)-ligand)
Compound 52 $^1$H NMR (from (R)-ligand)

![NMR Spectrogram](image_url)

_S211_
Compound 52 $^{13}$C NMR
Compound 54 $^1$H NMR
Compound 54 $^{13}$C NMR
Compound 55a $^1$H NMR

[Image of an NMR spectrum with labeled peaks and molecular structure]
Compound 55a $^{13}$C NMR
Compound 55b $^1$H NMR
Compound 55b $^{13}$C NMR
Compound 57a (less polar isomer) $^1$H NMR
Compound 57a (less polar isomer) $^{13}$C NMR
Compound 57b (more polar isomer) $^1$H NMR
Compound 57b (more polar isomer) $^{13}$C NMR
Compound 60 $^1$H NMR
Compound 61 $^1$H NMR
Compound 61 $^{13}$C NMR
Compound 62 $^1$H NMR

[Compound structure and NMR spectrum]
Compound 62 $^{13}$C NMR
Compound 63 $^1$H NMR
Compound 63 $^{13}$C NMR
Compound 64 $^1$H NMR
Compound 64 $^{13}$C NMR
Compound 65 $^1$H NMR

[Image of NMR spectrum for compound 65]
Compound 65 $^{13}$C NMR
Compound 66 $^1$H NMR
Compound 66 $^{13}$C NMR
Compound 67 $^1$H NMR
Compound 67 $^{13}$C NMR
Compound 68 $^1$H NMR
Compound 68 $^{13}$C NMR
Compound 69 $^1$H NMR
Compound 69 $^{13}$C NMR
Compound 69 $^{19}$F NMR

![Fluorine NMR Spectrum]
Compound 70 $^1$H NMR
Compound 70 $^{13}$C NMR

![Carbon-13 NMR spectrum of Compound 70](image)
Compound 71 $^1$H NMR
Compound 71 $^{13}$C NMR
Compound 72 $^1$H NMR
Compound 72 $^{13}$C NMR
Compound 73 $^{13}$C NMR

![Compound 73 $^{13}$C NMR spectrum](image-url)
Compound 74 \( ^1H \) NMR
Compound 74 $^{13}$C NMR

![Carbon-13 NMR Spectrum of Compound 74]
Compound 75 $^1$H NMR
Compound 75 $^{13}$C NMR
Compound 75 $^{19}$F NMR
Compound 76 $^1$H NMR

[Compound structure diagram]

OH Me Me
Ph

[Graph showing NMR spectrum]
Compound 76 $^{13}$C NMR

![Compound 76 $^{13}$C NMR](image)
Compound 77 $^1$H NMR

[Image of a H NMR spectrum with peaks at various ppm values and a structural diagram of the compound.]
Compound 77 $^{13}$C NMR
Compound 78 $^1$H NMR

[Image of a 1H NMR spectrum with peaks at various ppm values, indicating the presence of chemical groups such as OH, Ph, and Cl.]
Compound 78 $^{13}$C NMR
Compound 79 $^{13}$C NMR
Compound 80 $^1$H NMR
Compound 84 $^1$H NMR
Compound 84 $^{13}$C NMR