Merging Photoredox and Nickel Catalysis: The Decarboxylative Cross-Coupling of Carboxylic Acids with Vinyl Halides

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Supporting Information
Table of Contents

1) General Information......................................................................................................................... S3

2) Cyclic Voltammetry of Tetrahydrofuran-2-carboxylic acid...................................................... S3

3) Preparation of Vinyl Halides ........................................................................................................ S4

4) Preparation of Carboxylic Acids .................................................................................................. S5

5) General Decarboxylative Vinylation Procedure........................................................................ S6

6) Experimental Data for Vinylation Products .............................................................................. S7

7) Experimental Data for Additional Examples............................................................................. S21

8) Spectral Data.................................................................................................................................. S22

9) References Cited ............................................................................................................................. S51
1) General Information

Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego.\textsuperscript{1} \(\text{Ir}[(\text{dF(CF}_3\text{))ppy})_2(\text{dtbbpy})\text{PF}_6\) and \(\text{Ir}[(\text{dF(Me)ppy})_2(\text{dtbbpy})\text{PF}_6\) were prepared according to the literature procedures.\textsuperscript{2} All solvents were purified according to the method of Grubbs.\textsuperscript{3} Non-aqueous reagents were transferred under nitrogen or argon via syringe or cannula. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator using a water bath. Chromatographic purification of products was accomplished using forced-flow chromatography on ICN 60 32–64 mesh silica gel 63 or Davisil Grade 643 silica gel according to the method of Still.\textsuperscript{4} Thin-layer chromatography (TLC) was performed on Silicycle 0.25 mm silica gel F-254 plates. Visualization of the developed chromatogram was performed by fluorescence quenching or KMnO\textsubscript{4} stain. \(^1\text{H} \) NMR spectra were recorded on a Bruker UltraShield Plus 500 MHz unless otherwise noted and are internally referenced to residual protio CDCl\textsubscript{3} signals (7.27 ppm). Data for \(^1\text{H} \) NMR are reported as follows: chemical shift (\(\delta \) ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, br = broad), coupling constant (Hz), and assignment. \(^{13}\text{C} \) NMR spectra were recorded on a Bruker UltraShield Plus 500 MHz and data are reported in terms of chemical shift relative to CDCl\textsubscript{3} (77.0 ppm). IR spectra were recorded on a Perkin Elmer Spectrum 100 FTIR spectrometer and are reported in wavenumbers (cm\textsuperscript{-1}). High Resolution Mass Spectra were obtained from the Princeton University Mass Spectral Facility.

2) Cyclic Voltammetry of Tetrahydrofuran-2-carboxylic acid

Cyclic voltammetry was performed using a CH Instruments Electrochemical Workstation model CHI600E with a scan rate of 0.5 V/s, 4 sweep segments, a sample interval of 0.001 V, and a sensitivity of 0.001 A/V. Tetrahydrofuran-2-carboxylic acid (23 mg, 0.2 mmol) and NBu\textsubscript{4}PF\textsubscript{6} (774 mg, 2 mmol) were dissolved in MeCN (20 mL) and CsOH (50 wt% in H\textsubscript{2}O, 35 µL, 0.2 mmol) was added. The solution was degassed by sparging with N\textsubscript{2} for 15 minutes before the electrochemical measurement. An irreversible oxidation peak was observed at +1.08 V vs. SCE.
3) Preparation of Vinyl Halides

The following vinyl halides were prepared according to literature procedures: (E)-(3-iodoallyl)benzene, (E)-1-iodo-3,3-dimethylbut-1-ene, (E)-(4-iodobut-3-en-1-yl)oxy)methyl)benzene, (E)-5-chloro-1-iodopent-1-ene, (Z)-1-iodo-hept-1-ene, (E)-(2-iodovinyl)cyclohexane, 1-bromocyclohept-1-ene, and (E)-1-bromoocct-1-ene. The following vinyl halides are commercially available: (E)-1-iodooct-1-ene, 1-bromo-2-methylprop-1-ene, and (2-bromoallyl)trimethylsilane.

(E)-2-(2-Iodoallyl)isoindoline-1, 3-dione

In a glovebox zirconocene chloride hydride (2.90 g, 11 mmol, 1.1 equiv.) was added to 2-(prop-2-yn-1-yl)isoindoline-1,3-dione (1.85 g, 10 mmol, prepared according to a literature procedure). After removal from glovebox dry THF (20 mL, 0.25 M) was added through a septum and the reaction stirred for 2 hours at room temperature. The solution was then cooled to...
0 °C and I₂ (1.90 g, 15 mmol, 1.50 equiv.) was added against a positive pressure of N₂. The solution was allowed to warm to room temperature over 1 hour. The reaction was quenched with saturated Na₂SO₃ (5 mL), diluted with EtOAc, and filtered through celite. The filtrate was washed with brine, dried (MgSO₄), filtered, and concentrated. The crude product was purified by flash column chromatography (10-30% EtOAc/hexanes) to yield the product (1.4 g, 46%) as a white solid. IR (film) ν\text{max} 1765, 1710, 1429, 1395, 1305, 1206, 1036, 929, 716 cm⁻¹; \textsuperscript{1}H NMR (500 MHz, CDCl₃) δ 4.24 (2H, dt, J = 6.6, 1.3, CH=CHCH₂), 6.50 (1H, dt, J = 14.5, 1.3, ICH=CH), 6.61 (1H, dtd, J = 14.1, 6.4, 1.3, ICH=CH), 7.74 (2H, ddd, J = 5.6, 3.0, 1.2, ArH), 7.87 (2H, ddd, J = 5.5, 3.1, 1.2, ArH); \textsuperscript{13}C NMR (126 MHz, CDCl₃) δ 41.4, 81.1, 123.5, 131.9, 134.2, 138.6, 167.6; HRMS (ESI-TOF) m/z calcd. for C₁₁H₂₉INO₂ ([M+H]+) 313.9673, found 313.9669.

4) Preparation of Carboxylic Acids

(R)-2-(benzylxoy)-2-((R)-2, 2-dimethyl-1, 3-dioxolan-4-yl)acetic acid was prepared according to a literature procedure.\textsuperscript{14} The following carboxylic acids are commercially available: tetrahydrofurane-2-carboxylic acid, tetrahydropyran-2-carboxylic acid, (3aS,4S,6R,6aR)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole-4-carboxylic acid, 2-(benzylxox)propanoic acid, 2-(benzylxox)acetic acid, N-Boc-proline, N-Me-Boc-leucine, N-Boc-phenylalanine, N-Boc-tryptophan, phenylacetic acid, cyclohexanecarboxylic acid, 5-phenylvaleric acid, 4-methoxyphenylacetic acid, and 3-chlorophenylacetic acid.

\[\text{(cis)-4-Methyltetrahydro-2H-pyran-2-carboxylic acid (35)}\]

To a solution of 4-methyl-3, 6-dihydro-2H-pyran-2-carboxylic acid (0.45 g, 3.17 mmol, prepared according to a literature procedure)\textsuperscript{15} in EtOAc (15.8 mL, 0.2 M) was added palladium on carbon (0.168 g, 10 wt%). The atmosphere was replaced with hydrogen and the reaction stirred overnight. Filtration of the reaction mixture through celite and concentration provided the product (0.44 g, 97%, 4.8:1 dr). The inseparable diastereomers were characterized as a mixture.
IR (film) \( \nu_{\text{max}} \): 2954, 2927, 1732, 1458, 1258, 1174, 1102, 1043, 885 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\) \( \delta \): 1.01 (3H, d, \( J = 6.5 \)), 1.05 (0.6 H, d, \( J = 6.8 \)), 1.14–1.39 (2.4 H, m), 1.56–1.65 (1.2 H, m), 1.65–1.80 (1.4 H, m), 1.88 (0.2 H, dq, \( J = 7.3, 3.7 \)), 1.97–2.06 (0.2 H, m), 2.11 (1H, ddt, \( J = 13.3, 4.0, 2.3 \)), 3.54 (1H, ddd, \( J = 12.4, 11.5, 2.3 \)), 3.82–3.89 (0.4 H, m), 3.97 (1H, dd, \( J = 12.0, 2.5 \)), 4.15 (1H, ddd, \( J = 11.6, 4.7, 1.5 \)), 4.38 (0.2 H, dd, \( J = 6.4, 4.7 \)); \(^1\)C NMR (126 MHz, CDCl\(_3\) \( \delta \): 19.7, 21.9, 25.6, 30.0, 32.3, 33.6, 34.2, 36.7, 64.0, 68.1, 71.7, 75.3, 173.4; HRMS (ESI-TOF) \( m/z \) calcd. for \( \text{C}_7\text{H}_{12}\text{O} ([\text{M}+\text{H}]^+) \): 145.08592, found 145.08606.

\((\text{trans})\)-4-Methyltetrahydro-2H-pyran-2-carboxylic acid (36)

In order to selectively access the trans isomer a literature procedure was followed starting from methyl-4-methyl-3,6-dihydro-2H-pyran-2-carboxylate (0.80 g, 5.12 mmol).\(^{17}\) The product was purified by flash column chromatography (20% EtOAc/hexanes) to afford \((\text{trans})\)-methyl-4-methyltetrahydro-2H-pyran-2-carboxylate (0.50 g, 3.16 mmol, 62%, 20:1 dr). The methyl ester was hydrolyzed using LiOH (0.098 g, 1.3 equiv., 4.11 mmol) in 1:1 THF:H\(_2\)O (31 mL, 0.1 M). After stirring 1 hour the pH was adjusted to 3 and 30 mL saturated NH\(_4\)Cl solution was added. The solution was extracted with CH\(_2\)Cl\(_2\) (3x30 mL), dried (Na\(_2\)SO\(_4\)), filtered and concentrated. The carboxylic acid was used without further purification.

5) General Decarboxylative Vinlylation Procedure

**General procedure for the decarboxylative vinylation of \( \alpha \)-oxy and \( \alpha \)-amino acids:**

To an oven dried 8 mL vial equipped with a stir bar was added Ir[\(\text{dF(Me)ppy}\)]\(_2\)(dtbbpy)PF\(_6\) (5.1 mg, 5.0 \( \mu \)mol, 0.01 equiv.), the carboxylic acid (if solid, 0.80 mmol, 1.6 equiv.), and the vinyl halide (if solid, 0.50 mmol, 1.0 equiv.). The vial was sealed and evacuated then backfilled with nitrogen three times. DMSO (4.0 mL) was added to the vial, followed by the carboxylic acid (if liquid, 0.80 mmol, 1.6 equiv.), 1,8-diazabicycloundec-7-ene (DBU) (0.12 mL, 0.80 mmol, 1.6 equiv.), and the vinyl halide (if liquid, 0.50 mmol, 1.0 equiv.). NiCl\(_2\)-glyme (2.2 mg, 10 \( \mu \)mol, 0.02 equiv.) and dtbbpy (2.7 mg, 10 \( \mu \)mol, 0.02 equiv.) were added as a 0.01 M solution in DMSO (1.0 mL). The reaction mixture was degassed by sparging with \( \text{N}_2 \) while stirring for 15 min before sealing the vial with Parafilm. The reaction was stirred and irradiated with a 34 W blue LED lamp until complete consumption of the vinyl halide. The reaction was diluted with
water (15 mL) and brine (5 mL) and the product extracted into Et₂O (3 x 20 mL). The combined organic extracts were combined and washed with water (2 x 15 mL), brine (10 mL), dried (MgSO₄), and concentrated in vacuo. Purification by flash column chromatography yielded the vinylation product.

6) Experimental Data for Vinylation Products

(E)-2-(2-Cyclohexylvinyl)tetrahydrofuran (13)
Prepared following the general procedure outlined above using (E)-(2-iodovinyl)cyclohexane (118 mg, 0.50 mmol, 1.0 equiv.), tetrahydrofuran-2-carboxylic acid (99 mg, 0.85 mmol, 1.70 equiv.), Ir[dF(Me)ppy]₂(dtbbpy)PF₆ (5.1 mg, 5.0 µmol, 0.01 equiv.), NiCl₂·glyme (2.2 mg, 10 µmol, 0.02 equiv.), dtbbpy (2.7 mg, 10 µmol, 0.02 equiv.), DBU (129 mg, 0.85 mmol, 1.70 equiv.), and DMSO (5.0 mL). After 18 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by flash column chromatography (5% Et₂O/pentane) provided the title compound (81 mg, 0.45 mmol, 90%) as a colorless oil. IR (film) νₘₐₓ 2970, 2923, 2851, 1449, 1056, 967 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.03–1.11 (2H, m, CyC₆H₁₂), 1.16 (1H, tt, J = 12.5, 3.1, CyC₆H₁₂), 1.22–1.30 (2H, m, CyC₆H₁₂), 1.54–1.66 (2H, m, OCH₂(C₆H₁₂)₂ + CyC₆H₁₂), 1.70–1.74 (4H, m, CyC₆H₁₂), 1.84–2.05 (4H, m, OCH₂(C₆H₁₂)₂ + OCHCH=CHC₆H₁₂), 3.76 (1H, td, J = 8.0, 6.0, OCH₂), 3.90 (1H, td, J = 7.9, 6.5, OCH₂), 4.21 (1H, app. q, J = 7.2, OCHCH=CH), 5.40 (1H, dd, J = 15.5, 7.2, OCHCH=CH), 5.63 (1H, dd, J = 15.5, 6.6, OCHCH=CH); ¹³C NMR (126 MHz, CDCl₃) δ 26.0, 26.0, 26.2, 32.3, 32.7, 32.8, 40.3, 67.9, 80.2, 128.0, 138.7; HRMS (ESI-TOF) m/z calcd. for C₁₂H₂₁O ([M+H]⁺) 181.1587, found 181.1587.

(E)-2-(3, 3-dimethylbut-1-en-1-yl)tetrahydrofuran (14)
Prepared following the general procedure outlined above using (E)-1-iodo-3, 3-dimethyl-but-1-ene (105 mg, 0.50 mmol, 1.0 equiv.), tetrahydrofuran-2-carboxylic acid (99 mg, 0.85 mmol, 1.70 equiv.), Ir[Me(ppy)]_2(dtbbpy)PF_6 (5.1 mg, 5.0 µmol, 0.01 equiv.), NiCl_2-glyme (2.2 mg, 10 µmol, 0.02 equiv.), dtbbpy (2.7 mg, 10 µmol, 0.02 equiv.), DBU (129 mg, 0.85 mmol, 1.70 equiv.), and DMSO (5.0 mL). After 18 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by flash column chromatography (5% Et_2O/pentane) provided the title compound (60 mg, 0.39 mmol, 78%) as a colorless oil. IR (film) ν max 2957, 2905, 2866, 1461, 1362, 1056, 970 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.02 (9H, s, C(CH₃)₃), 1.55–1.62 (1H, m, OCH₂(CH₂)₂), 1.92 (2H, m, OCH₂(CH₂)₂), 2.02 (1H, m, OCH₂(CH₂)₂), 3.77 (1H, td, J = 8.0, 6.2, OCH₂), 3.91 (1H, td, J = 8.0, 6.2, OCH₂), 4.21 (1H, app. q, J = 7.3, OCHCH=CH), 5.36 (1H, dd, J = 15.4, 7.3, OCHCH=CH), 5.70 (1H, d, J = 15.4, OCHCH=CH); ¹³C NMR (126 MHz, CDCl₃) δ 26.0, 29.5, 32.4, 32.8, 67.9, 80.4, 125.3, 143.8; HRMS (ESI-TOF) m/z calcd. for C₁₀H₁₉O ([M+H]^+) 155.1430, found 155.1434.

(E)-2-(3-phenylprop-1-en-1-yl)tetrahydrofuran (15)

Prepared following the general procedure outlined above using (E)-(3-iodoallyl)benzene (78 µL, 0.50 mmol, 1.0 equiv.), tetrahydrofuran-2-carboxylic acid (87 mg, 0.75 mmol, 1.50 equiv.), Ir[CF₃ppy]_2(dtbbpy)PF_6 (5.6 mg, 5.0 µmol, 0.01 equiv.), NiCl₂-glyme (11 mg, 50 µmol, 0.10 equiv.), dtbbpy (20 mg, 75 µmol, 0.15 equiv.), Cs₂CO₃ (277 mg, 0.850 mmol, 1.70 equiv.), and DMF (25.0 mL). After 72 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by flash column chromatography (10% EtOAc/hexanes) provided the title compound (70 mg, 0.37 mmol, 74%) as a colorless oil. IR (film) ν max 3062, 2867, 1051, 969, 699 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.56–1.66 (1H, m, OCH₂(CH₂)₂), 1.85–1.99 (2H, m, OCH₂(CH₂)₂), 2.00–2.08 (1H, m, OCH₂(CH₂)₂), 3.39 (2H, d, J = 7.1, CH=CHCH₂), 3.78 (1H, td, J = 7.8, 6.2, OCH₂), 3.91 (1H, td, J = 7.8, 6.2, OCH₂), 4.28 (1H, q, J = 7.1, OCHCH=CH), 5.55 (1H, dd, J = 15.5, 7.1, OCHCH=CH), 5.84 (1H, dt, J = 15.5, 6.8, OCHCH=CH), 7.17–7.24 (3H, m, ArH), 7.29 (2H, t, J = 7.5, ArH); ¹³C NMR (126 MHz, CDCl₃) δ 25.9, 32.2, 38.6, 68.0, 79.6, 126.0, 128.4, 128.6, 130.9, 132.2, 140.1; HRMS (ESI-TOF) m/z calcd. for C₁₃H₁₅O ([M+H]^+) 189.1274, found 189.1274.
(E)-2-(4-(benzyloxy)but-1-en-1-yl)tetrahydrofuran (16)
Prepared following the general procedure outlined above using (E)-((4-iodobutyl-3-en-1-yl)oxy)methyl)benzene (144 mg, 0.50 mmol, 1.0 equiv.), tetrahydrofuran-2-carboxylic acid (99 mg, 0.85 mmol, 1.70 equiv.), Ir[dF(Me)ppy]2(dtbbpy)PF6 (5.1 mg, 5.0 μmol, 0.01 equiv.), NiCl2·glyme (2.2 mg, 10 μmol, 0.02 equiv.), dtbbpy (2.7 mg, 10 μmol, 0.02 equiv.), DBU (129 mg, 0.85 mmol, 1.70 equiv.), and DMSO (5.0 mL). After 18 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by flash column chromatography (5–20% Et2O/pentane) provided the title compound (89 mg, 0.39 mmol, 77%) as a colorless oil. IR (film) νmax 2858, 1361, 1098, 1051, 967, 912, 731, 697 cm⁻¹; ¹H NMR (500 MHz, CDCl3) δ 1.56–1.63 (1H, m, OCH2(C6H5)2), 1.82–2.10 (3H, m, OCH2(C6H5)2), 2.38 (2H, q, J = 6.9, CH=CHC6H5C6H5), 3.52 (2H, td, J = 6.9, 1.8, CH=CHCH2CH3), 3.77 (1H, q, J = 7.5, OCH2(CH2)2), 3.90 (1H, q, J = 7.3, OCH2(CH2)2), 4.25 (1H, q, J = 7.1, OCHCH=CH), 4.52 (2H, s, OCH3Ph), 5.55 (1H, dd, J = 15.4, 7.1, OCHCH=CH), 7.28–7.38 (5H, m, ArH); ¹³C NMR (126 MHz, CDCl3) δ 25.9, 32.1, 67.9, 69.7, 72.9, 79.7, 127.5, 127.5, 127.6, 128.3, 128.6, 132.7, 138.4; HRMS (ESI-TOF) m/z calcd. for C15H21O2 ([M+H]+) 233.1536, found 233.1541.

(E)-2-(5-chloropent-1-en-1-yl)tetrahydrofuran (17)
Prepared following the general procedure outlined above using (E)-5-chloro-1-iodopent-1-ene (115 mg, 0.50 mmol, 1.0 equiv.), tetrahydrofuran-2-carboxylic acid (99 mg, 0.85 mmol, 1.70 equiv.), Ir[dF(Me)ppy]2(dtbbpy)PF6 (5.1 mg, 5.0 μmol, 0.010 equiv.), NiCl2·glyme (2.2 mg, 10 μmol, 0.02 equiv.), dtbbpy (2.7 mg, 10 μmol, 0.02 equiv.), DBU (129 mg, 0.850 mmol, 1.7 equiv.), and DMSO (5.0 mL). After 18 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by flash column chromatography (5–20% Et2O/pentane) provided the title compound (59 mg, 0.34 mmol, 68%) as a colorless oil. IR (film)
$\nu_{\text{max}}$ 2957, 2868, 1444, 1052, 969, 725 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.54–1.64 (1H, m, OCH$_3$(CH$_2$)$_2$), 1.82–2.08 (5H, m, OCH$_3$(CH$_2$)$_2$ + CH$_2$CH$_2$Cl), 2.16–2.24 (2H, m, ), 3.54 (2H, t, J = 6.6, CH$_2$Cl), 3.77 (1H, td, J = 7.9, 6.3, OCH$_2$), 3.90 (1H, td, J = 7.9, 6.3, OCH$_2$), 4.24 (1H, q, J = 6.9, OCHCH=CH), 5.53 (1H, ddt, J = 15.4, 7.0, 1.4, OCHC=CH), 5.65 (1H, dt, J = 15.4, 6.9, OCHCH=CH); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 25.9, 29.3, 32.2, 44.4, 68.0, 79.7, 130.3, 132.2; HRMS (ESI-TOF) m/z calcd. for C$_9$H$_{16}$ClO ([M+H$^+$]) 175.0884, found 175.0882.

$^{(E)}$-2-(3-(tetrahydrofuran-2-yl)allyl)isoindoline-1, 3-dione (18)

Prepared following the general procedure outlined above using $^{(E)}$-2-(3-iodoallyl)isoindoline-1, 3-dione (157 mg, 0.50 mmol, 1.0 equiv.), tetrahydrofuran-2-carboxylic acid (87 mg, 0.75 mmol, 1.50 equiv.), Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (5.6 mg, 5.0 µmol, 0.01 equiv.), NiCl$_2$-glyme (22.0 mg, 100 µmol, 0.20 equiv.), dtbbpy (27.0 mg, 100 µmol, 0.20 equiv.), Cs$_2$CO$_3$ (277 mg, 0.85 mmol, 1.70 equiv.), and DMF (25.0 mL). After 72 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by flash column chromatography (10-30% EtOAc/hexanes) provided the title compound (86 mg, 0.34 mmol, 67%) as a clear oil. IR (film) $\nu_{\text{max}}$ 2973–2870, 1771, 1712, 1429, 1393, 1054, 721 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.55–1.65 (1H, m, OCH$_2$(CH$_2$)$_2$), 1.82–1.96 (2H, m, OCH$_2$(CH$_2$)$_2$), 1.99–2.05 (1H, m, OCH$_2$(CH$_2$)$_2$), 3.76 (1H, td, J = 7.9, 6.1, OCH$_2$), 3.84–3.91 (1H, m, OCH$_2$), 4.25–4.32 (3H, m, OCHCH=CH + CH=CHCH$_2$N), 5.71–5.84 (2H, m, OCHCH=CH + OCHCH=CH), 7.72 (2H, dd, J = 5.5, 3.0, ArH), 7.85 (2H, dd, J = 5.5, 3.0, ArH); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 25.69, 31.95, 38.99, 68.07, 78.57, 123.25, 124.09, 132.13, 133.91, 135.01, 167.86; HRMS (ESI-TOF) m/z calcd. for C$_{15}$H$_{16}$NO$_3$ ([M+H$^+$]) 258.1125, found 258.1121.

$^{(Z)}$-2-(Hept-1-en-1-yl)tetrahydrofuran (19)

Prepared following the general procedure outlined above using $^{(Z)}$-1-iodohept-1-ene (112 mg, 0.50 mmol, 1.0 equiv., 97:3 Z:E), tetrahydrofuran-2-carboxylic acid (87 mg, 0.75 mmol, 1.50
equiv.), Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (5.6 mg, 5.0 µmol, 0.01 equiv.), NiCl$_2$-glyme (11 mg, 50 µmol, 0.10 equiv.), dtbbpy (20 mg, 75 µmol, 0.15 equiv.), Cs$_2$CO$_3$ (277 mg, 0.85 mmol, 1.70 equiv.), and DMF (25.0 mL). After 70 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by flash column chromatography (0–20% EtOAc/hexanes) provided the title compound (71 mg, 0.42 mmol, 84%, 95:5 Z:E) as a colorless oil. IR (film) $\nu_{\text{max}}$ 3015–2858, 1461, 1056 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 0.89 (3H, t, $J$ = 6.8, (CH$_2$)$_3$CH$_3$), 1.25–1.44 (6H, m, (CH$_2$)$_3$CH$_3$), 1.50–1.58 (1H, m, OCH$_2$(CH$_2$)$_2$), 1.86–2.16 (5H, m, OCH$_2$(CH$_2$)$_2$ + CH=CHCH$_2$), 3.76 (1H, td, $J$ = 8.0, 5.9, OCH$_2$), 3.89–3.94 (1H, m, OCH$_2$), 4.58 (1H, td, $J$ = 8.3, 6.5, OCHCH=CH), 5.40–5.44 (1H, m, OCHCH=CH), 5.51 (1H, dt, $J$ = 10.9, 7.4, OCHCH=CH); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 14.1, 22.5, 26.2, 27.7, 29.4, 31.5, 32.7, 67.9, 74.8, 130.6, 132.6; HRMS (ESI-TOF) m/z calcd. for C$_{11}$H$_{21}$O ([M+H]$^+$) 167.1430, found 167.1430.

2-(2-Methylprop-1-en-1-yl)tetrahydrofuran (20)

Prepared following the general procedure outlined above using 1-bromo-2-methylprop-1-ene (68 mg, 0.50 mmol, 1.0 equiv.), tetrahydrofuran-2-carboxylic acid (105 mg, 0.90 mmol, 1.80 equiv.), Ir[dF(Me)ppy]$_2$(dtbbpy)PF$_6$ (5.1 mg, 5.0 µmol, 0.01 equiv.), NiCl$_2$-glyme (2.2 mg, 10 µmol, 0.02 equiv.), dtbbpy (2.7 mg, 10 µmol, 0.02 equiv.), Cs$_2$CO$_3$ (293 mg, 0.90 mmol, 1.80 equiv.), N-Boc-benzylamine (6.2 mg, 30 µmol, 0.06 equiv.), and DMA (5.0 mL). After 24 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by flash column chromatography (10% Et$_2$O/pentane) provided the title compound (45 mg, 71%) as a colorless oil. IR (film) $\nu_{\text{max}}$ 2970, 2930, 2870, 1445, 1377, 1050 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.52 (1H, dq, $J$ = 11.8, 8.2, OCH$_2$(CH$_2$)$_2$), 1.71 (3H, s, CH$_3$), 1.73 (3H, s, CH$_3$), 1.85–2.06 (3H, m, OCH$_2$(CH$_2$)$_2$), 3.75 (1H, td, $J$ = 8.0, 5.8, OCH$_2$), 3.90 (1H, q, $J$ = 7.3, OCH$_2$), 4.50 (1H, td, $J$ = 8.4, 6.1, OCHCH=CM$_2$), 5.21 (1H, d, $J$ = 8.4, CH=CM$_2$); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 18.2, 25.9, 26.3, 32.5, 67.7, 75.8, 125.9, 135.9; HRMS (ESI-TOF) m/z calcd. for C$_8$H$_{15}$O ([M+H]$^+$) 127.1117, found 127.1117.
2-(Cyclohept-1-en-1-yl)tetrahydrofuran (21)

Prepared following the general procedure outlined above using 1-bromocyclohept-1-ene (88 mg, 0.50 mmol, 1.0 equiv.), tetrahydrofuran-2-carboxylic acid (105 mg, 0.90 mmol, 1.80 equiv.), Ir[dF(Me)ppy]₂(dtbbpy)PF₆ (5.1 mg, 5.0 µmol, 0.01 equiv.), NiCl₂·glyme (2.2 mg, 10 µmol, 0.02 equiv.), dtbbpy (2.7 mg, 10 µmol, 0.02 equiv.), Cs₂CO₃ (293 mg, 0.90 mmol, 1.80 equiv.), N-Boc-benzylamine (6.2 mg, 30 µmol, 0.06 equiv.), and DMA (5.0 mL). After 24 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by flash column chromatography (10% Et₂O/pentane) provided the title compound (61 mg, 0.37 mmol, 73%) as a colorless oil. IR (film) νₘₐₓ 2969, 2919, 2849, 1446, 1081, 1054 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.43–1.55 (4H, m, CH₂), 1.59–1.66 (1H, m, OCH₂(C₂H₅)₂), 1.71–1.78 (2H, m, CH₂), 1.84–1.96 (3H, m, OCH₂(C₂H₅)₂), 2.04–2.18 (4H, m, CH₂C=CHCH₂), 3.77–3.81 (1H, m, OCH₂(C₂H₅)₂), 3.90–3.95 (1H, m, OCH₂(C₂H₅)₂), 4.18 (1H, dd, J = 8.1, 6.1, OCHC=CH), 5.83 (1H, t, J = 6.1, OCHC=CH); ¹³C NMR (126 MHz, CDCl₃) δ 26.0, 27.0, 27.3, 28.2, 28.3, 30.3, 32.7, 68.4, 84.2, 127.5, 144.2; HRMS (ESI-TOF) m/z calcd. for C₁₁H₁₉O ([M+H]⁺) 167.1434, found 167.1430.

Trimethyl(2-(tetrahydrofuran-2-yl)allyl)silane (22)

Prepared following the general procedure outlined above using (2-bromoallyl)trimethylsilane (97 mg, 0.50 mmol, 1.0 equiv.), tetrahydrofuran-2-carboxylic acid (87 mg, 0.75 mmol, 1.50 equiv.), Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (5.6 mg, 5.0 µmol, 0.01 equiv.), NiCl₂·glyme (11 mg, 50 µmol, 0.10 equiv.), dtbbpy (20 mg, 75 µmol, 0.15 equiv.), Cs₂CO₃ (277 mg, 0.850 mmol, 1.70 equiv.), and DMF (25.0 mL). After 72 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by flash column chromatography (0–20% EtOAc/hexanes) provided the title compound (55 mg, 0.30 mmol, 60%) as a colorless oil. IR (film) νₘₐₓ 3078, 2954, 2872, 1248, 1161, 1067, 882, 849 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.04 (9H, s, Si(CH₃)₃), 1.38 (1H, d, J = 13.9, CH₂SiMe₃), 1.61 (1H, d, J = 14.0, CH₂SiMe₃), 1.63–1.70 (1H,
m, OCH$_2$(CH$_2$)$_2$, 1.83–1.96 (2H, m, OCH$_2$(CH$_2$)$_2$), 2.01–2.08 (1H, m, OCH$_2$(CH$_2$)$_2$), 3.81 (1H, dd, $J = 7.9, 6.5$, OCH$_3$), 3.95 (1H, dd, $J = 8.2, 7.2$, OCH$_3$), 4.20 (1H, s, OHC=CH$_2$), 4.61 (1H, s, OHC=CH$_2$), 4.91 (1H, t, $J = 1.6$, OCHC=CH$_2$); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 0.0, 24.0, 26.8, 32.4, 69.5, 83.1, 107.4, 149.1; HRMS (ESI-TOF) $m/z$ calcd. for C$_{10}$H$_2$IOSi ([M+H]$^+$) 185.1351, found 185.1356.

(E)-2-(Oct-1-en-1-yl)tetrahydrofuran (23)

Prepared following the general procedure outlined above using (E)-1-iodooct-1-ene (87 µL, 0.50 mmol, 1.0 equiv.), tetrahydrofuran-2-carboxylic acid (99 mg, 0.85 mmol, 1.70 equiv.), Ir[dF(Me)ppy]$_2$(dtbbpy)PF$_6$ (5.1 mg, 5.0 µmol, 0.01 equiv.), NiCl$_2$·glyme (2.2 mg, 10 µmol, 0.02 equiv.), dtbbpy (2.7 mg, 10 µmol, 0.02 equiv.), DBU (129 mg, 0.85 mmol, 1.70 equiv.), and DMSO (5.0 mL). After 18 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by flash column chromatography (5% Et$_2$O/pentanes) provided the title compound (84 mg, 0.46 mmol, 92%) as a colorless oil. IR (film) $\nu$ max 2957–2855, 1461, 1056, 965 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 0.88 (3H, t, $J = 6.9$, CH$_3$), 1.23–1.40 (8H, m, (CH$_2$)$_4$CH$_3$), 1.57–1.62 (1H, m, OCH$_2$(CH$_2$)$_2$), 1.85–2.05 (5H, m, CH=CHCH$_2$ + OCH$_2$(CH$_2$)$_2$), 3.76 (1H, td, $J = 7.9, 6.2$, OCH$_3$), 3.90 (1H, td, $J = 7.9, 6.2$, OCH$_3$), 4.23 (1H, q, $J = 7.1$, OCHCH=CH), 5.45 (1H, dd, $J = 15.3, 7.2$, OCHCH=CH), 5.68 (1H, dt, $J = 15.3, 6.7$, OCHCH=CH); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 14.1, 22.6, 26.0, 28.9, 29.1, 31.7, 32.3, 32.3, 67.9, 80.0, 130.5, 133.0; HRMS (ESI-TOF) $m/z$ calcd. for C$_{12}$H$_{25}$O ([M+H]$^+$) 183.1742, found 183.1743.

(E)-2-(Oct-1-en-1-yl)tetrahydro-2H-pyran (24)

Prepared following the general procedure outlined above using (E)-1-iodooct-1-ene (87 µL, 0.50 mmol, 1.0 equiv.), tetrahydro-2H-pyran-2-carboxylic acid (195 mg, 1.50 mmol, 3.0 equiv.), Ir[dF(Me)ppy]$_2$(dtbbpy)PF$_6$ (5.1 mg, 5.0 µmol, 0.010 equiv.), NiCl$_2$·glyme (5.5 mg, 25 µmol, 0.05 equiv.), dtbbpy (6.7 mg, 25 µmol, 0.05 equiv.), Cs$_2$CO$_3$ (489 mg, 1.50 mmol, 3.0 equiv.),
and DMSO (20.0 mL). After 24 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by flash column chromatography (5% Et$_2$O/pentane) provided the title compound (73 mg, 0.37 mmol, 74%) as a colorless oil. IR (film) $\nu_{\text{max}}$ 2928, 2854, 1463, 1440, 1204, 1087, 1050, 1036 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 0.88 (3H, t, $J = 6.8$, CH$_3$), 1.23–1.65 (13H, m, CH$_2$), 1.82–1.86 (1H, m, CH$_2$), 2.00–2.04 (2H, m, CH$_2$), 3.48 (1H, td, $J = 11.6$, 2.3, OCH$_2$), 3.72–3.76 (1H, m, OCH$_2$), 3.99–4.03 (1H, m, OCHCH=CH), 5.47 (1H, dd, $J = 15.5$, 6.3, OCH=OCH), 5.64–5.70 (1H, m, OCHCH=CH); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 14.1, 22.6, 23.5, 25.9, 28.9, 31.7, 32.2, 32.4, 68.4, 78.3, 131.1, 132.0; HRMS (ESI-TOF) $m/z$ calcd. for C$_{13}$H$_{25}$O ([M+H]$^+$) 197.1896, found 197.1900.

![Chemical Structure](image)

4-Methoxy-2,2-dimethyl-6-((E)-oct-1-en-1-yl)tetrahydrofuro[3,4-d][1,3]dioxole (25)

Prepared following the general procedure outlined above using (E)-1-iodooct-1-ene (87 µL, 0.50 mmol, 1.0 equiv.), 2, 3-O-isopropylidene-1-O-methyl-D-ribose (164 mg, 0.75 mmol, 1.5 equiv.), Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (5.6 mg, 5.0 µmol, 0.010 equiv.), NiCl$_2$·glyme (11 mg, 50 µmol, 0.10 equiv.), dtbbpy (20 mg, 75 µmol, 0.15 equiv.), Cs$_2$CO$_3$ (277 mg, 0.850 mmol, 1.70 equiv.), and DMF (25.0 mL). After 72 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by flash column chromatography (0–20% EtOAc/hexanes) provided the title compound (126 mg, 0.45 mmol, 89%, 18:1 dr) as a colorless oil. IR (film) $\nu_{\text{max}}$ 2926, 2856, 1462, 1372, 1271, 1209, 1161, 1089, 1104, 1055, 1028, 964, 869, 829, 774 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 0.89 (3H, t, $J = 6.6$, CH$_3$), 1.22–1.42 (11H, m, ((CH$_2$)$_4$CH$_3$) + OC(CH$_3$)$_2$), 1.50 (3H, s, OC(CH$_3$)$_2$), 2.02 (2H, q, $J = 6.9$, CH=CHCH$_2$), 3.34 (3H, s, OCH$_3$), 4.56–4.65 (3H, m, CH + CH + CH), 4.97 (1H, s, CH), 5.49 (1H, dd, $J = 15.4$, 8.9, OCHCH=CH), 5.69 (1H, dt, $J = 15.4$, 6.7, OCHCH=CH); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 14.1, 22.6, 25.0, 26.5, 28.8, 28.9, 31.7, 32.1, 54.5, 84.8, 85.7, 88.4, 109.0, 112.2, 129.3, 134.9; HRMS (ESI-TOF) $m/z$ calcd. for C$_{16}$H$_{29}$O$_4$ ([M+H]$^+$) 285.2060, found 285.2062.
(E)-((Dec-3-en-2-yloxy)methyl)benzene (26)
Prepared following the general procedure outlined above using (E)-1-iodooct-1-ene (87 µL, 0.50 mmol, 1.0 equiv.), 2-(benzylxyloxy)propanoic acid (162 mg, 0.90 mmol, 1.80 equiv.), Ir[dF(Me)ppy]₂(dtbbpy)PF₆ (5.1 mg, 5.0 µmol, 0.01 equiv.), NiCl₂·glyme (11 mg, 50 µmol, 0.10 equiv.), dtbbpy (20 mg, 75 µmol, 0.15 equiv.), Cs₂CO₃ (277 mg, 0.850 mmol, 1.70 equiv.), and DMF (25.0 mL). After 72 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by flash column chromatography (0–20% EtOAc/hexanes) provided the title compound (90 mg, 0.39 mmol, 77%) as a colorless oil. IR (film) νₓ 3029, 2956, 2926, 2854, 1455, 1105, 1070 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.89 (3H, t, J = 6.9, CH₃), 1.26–1.42 (8H, m, (CH₂)₄CH₂), 2.06 (2H, q, J = 6.9, CH=CHCH₃), 3.98 (2H, s, OCH₂Ph), 5.98–6.04 (1H, m, OCH₂CH=CH), 7.25–7.35 (5H, m, ArH); ¹³C NMR (126 MHz, CDCl₃) δ 14.1, 14.7, 69.6, 75.9, 127.3, 127.7, 128.3, 131.8, 133.5, 135.9, 139.0; HRMS (ESI-TOF) m/z calcd. for C₁₇H₂₆ONa ([M+Na]⁺) 269.1875, found 269.1876.

(E)-((Non-2-en-1-yloxy)methyl)benzene (27)
Prepared following the general procedure outlined above using (E)-1-iodooct-1-ene (87 µL, 0.50 mmol, 1.0 equiv.), 2-(benzylxyloxy)acetic acid (107 µL, 0.75 mmol, 1.50 equiv.), Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (5.6 mg, 5.0 µmol, 0.01 equiv.), NiCl₂·glyme (11 mg, 50 µmol, 0.10 equiv.), dtbbpy (20 mg, 75 µmol, 0.15 equiv.), Cs₂CO₃ (277 mg, 0.850 mmol, 1.70 equiv.), and DMF (25.0 mL). After 72 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by flash column chromatography (0–20% EtOAc/hexanes) provided the title compound (90 mg, 0.39 mmol, 77%) as a colorless oil. IR (film) νₓ 3029, 2956, 2926, 2854, 1455, 1105, 1070 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.89 (3H, t, J = 6.9, CH₃), 1.26–1.42 (8H, m, (CH₂)₄CH₂), 2.06 (2H, q, J = 6.9, CH=CHCH₂), 3.98 (2H, d, J = 6.2, OCH₂CH=CH), 4.51 (2H, s, OCH₂Ph), 5.57–5.63 (1H, m, OCH₂CH=CH), 5.70–5.76 (1H,
(4R)-4-(E)-1-(benzylxylo)non-2-en-yl-2,2-dimethyl-1,3-dioxolane (28)

Prepared following the general procedure outlined above using (E)-1-bromooc-1-ene (87 μL, 0.50 mmol, 1.0 equiv.), (R)-2-(benzylxylo)-2-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)acetic acid (240 mg, 0.90 mmol, 1.80 equiv.), Ir[dF(Me)ppy]2(dtbbpy)PF6 (5.1 mg, 5.0 μmol, 0.01 equiv.), NiCl2-glyme (2.2 mg, 10 μmol, 0.02 equiv.), dtbbpy (2.7 mg, 10 μmol, 0.02 equiv.), Cs2CO3 (293 mg, 0.90 mmol, 1.80 equiv.), N-Boc benzylamine (6.2 mg, 30 μmol, 0.06 equiv.), and DMA (5.0 mL). After 18 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by flash column chromatography (0–10% Et2O/pentane) provided the title compound (132 mg, 0.40 mmol, 79%, 1.4:1.0 dr) as a colorless oil. The inseparable diastereomers were characterized as a mixture. IR (film) νmax 2927, 2857, 1455, 1370, 1211, 1068, 969, 851, 732, 697 cm⁻¹; ¹H NMR (500 MHz, CDCl3) For major isomer δ 0.90 (3H, t, J = 6.7, (CH2)2CH3), 1.25–1.47 (14H, m, CH=CH(CH2)3CH3 + C(CH3)2), 2.04–2.20 (2H, m, CH=CHCH2), 3.69–4.22 (4H, m, CH2OCHOCCH=CH), 4.39 (1H, d, J = 11.9, OCH2Ph), 4.64 (1H, d, J = 11.9, OCH2Ph), 5.42 (dd, J = 15.5, 8.2, CH=CHCH2), 5.72 (dt, J = 15.5, 6.8, CH=CHCH2), 7.28–7.38 (5H, m, ArH). For minor isomer δ 0.90 (3H, t, J = 6.7, (CH2)2CH3), 1.25–1.47 (14H, m, CH=CH(CH2)3CH3 + C(CH3)2), 2.04–2.20 (2H, m, CH=CHCH2), 3.69–4.22 (4H, m, CH2OCHOCCH=CH), 4.47 (1H, d, J = 12.4, OCH2Ph), 4.68 (1H, d, J = 12.4, OCH2Ph), 5.31 (1H, dd, J = 15.5, 8.6, CH=CHCH2), 5.72 (dt, J = 15.5, 6.8, CH=CHCH2), 7.28–7.38 (5H, m, ArH); ¹³C NMR (126 MHz, CDCl3) δ 14.1, 22.6, 25.4, 25.4, 26.5, 28.8, 29.0, 29.1, 31.6, 31.7, 32.3, 32.4, 66.0, 66.8, 69.6, 70.0, 77.8, 77.9, 80.5, 80.9, 109.4, 109.7, 125.7, 126.4, 127.4, 127.5, 127.7, 127.8, 128.2, 128.3, 137.3, 137.7, 138.4, 138.5; HRMS (ESI-TOF) m/z calcd. for C23H33O3 ([M+H]+) 333.2424, found 333.2432.
tert-Butyl (E)-2-(oct-1-en-1-yl)pyrrolidine-1-carboxylate (29)

Prepared following the general procedure outlined above using (E)-1-iodooct-1-ene (87 µL, 0.50 mmol, 1.0 equiv.), Boc-Pro-OH (183 mg, 0.85 mmol, 1.70 equiv.), Ir[dF(Me)ppy]₂(dtbbpy)PF₆ (5.1 mg, 5.0 µmol, 0.01 equiv.), NiCl₂·glyme (2.2 mg, 10 µmol, 0.02 equiv.), dtbbpy (2.7 mg, 10 µmol, 0.02 equiv.), DBU (129 mg, 0.850 mmol, 1.70 equiv.), and DMSO (5.0 mL). After 18 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by flash column chromatography (10% Et₂O/pentane) provided the title compound (127 mg, 0.45 mmol, 90%) as a colorless oil. IR (film) ν max 2961, 2956, 2856, 1694, 1390, 1364, 1170, 1116 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.88 (3H, t, J = 6.7, CH₂CH₃), 1.27–1.37 (8H, m, CH₂), 1.44 (9H, s, OC(CH₃)₃), 1.64–1.69 (1H, m, CH₂), 1.75–1.89 (2H, m, CH₂), 1.94–2.02 (3H, m, CH₂), 3.32–3.41 (2H, m, NC₃H₂), 4.22 (1H, br s, NC₃HCH=CH), 5.31 (1H, dd, J = 15.3, 6.4, NCHCH=CH), 5.46 (1H, dt, J = 14.1, 6.8, NCHCH=CH); ¹³C NMR (126 MHz, CDCl₃) δ 14.1, 22.6, 23.0, 28.5, 28.8, 29.4, 31.7, 32.1, 32.3, 46.1, 58.5, 78.9, 130.4, 130.4, 154.6; HRMS (ESI-TOF) m/z calcd. for C₁₇H₃₁NO₂Na ([M+Na⁺) 304.2247, found 304.2249.

tert-Butyl (E)-methyl(2-methyldodec-5-en-4-yl)carbamate (30)

Prepared following the general procedure outlined above using (E)-1-iodooct-1-ene (87 µL, 0.50 mmol, 1.0 equiv.), N-Me-Boc-Leu-OH (184 mg, 0.75 mmol, 1.50 equiv.), Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (5.6 mg, 5.0 µmol, 0.01 equiv.), NiCl₂·glyme (11 mg, 50 µmol, 0.10 equiv.), dtbbpy (20 mg, 75 µmol, 0.15 equiv.), Cs₂CO₃ (277 mg, 0.850 mmol, 1.70 equiv.), and DMF (25.0 mL). After 38 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by flash column chromatography (0–20% EtOAc/hexanes) provided the title compound (139 mg, 0.45 mmol, 89%) as a colorless oil. IR (film) ν max 2957-2856, 1692, 1468, 1455, 1390, 1365, 1321, 1253, 1143 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.87–0.93 (9H, m, 3 × CH₃), 1.26–1.37 (9H, m, 4 × CH₂ + CH(CH₃)₂), 1.47 (9H, s, OC(CH₃)₃), 1.46–1.50 (2H, m, CH₂), 2.01 (2H, q, J = 7.0, CH=CHCH₂), 2.64 (3H, s, NCH₃), 4.55–4.72 (1H,
br m, NCHCH=CH), 5.34 (1H, dd, J = 15.5, 5.6, NCHCH=CH), 5.49–5.53 (1H, br m, NCHCH=CH); \(^{13}\text{C}\) NMR (126 MHz, CDCl\(_3\)) \(\delta\) 14.1, 22.1, 22.6, 23.2, 24.6, 28.5, 28.8, 29.3, 31.7, 32.5, 40.8, 54.5, 79.1, 129.1, 132.2, 156.0; HRMS (ESI-TOF) \(m/z\) calcd. for C\(_{19}\)H\(_{37}\)NO\(_2\)Na ([M+Na]') 334.2714, found 334.2717.

(E)-tert-butyl (1-phenyldec-3-en-2-yl)carbamate (31)

Prepared following the general procedure outlined above using (E)-1-bromooc-1-ene (87 \(\mu\)L, 0.50 mmol, 1.0 equiv.), N-Boc-Phe-OH (212 mg, 0.8 mmol, 1.6 equiv.), Ir[dF(Me)ppy]\(_2\)(dtbbpy)PF\(_6\) (5.1 mg, 5.0 \(\mu\)mol, 0.01 equiv.), NiCl\(_2\)·glyme (1.1 mg, 5 \(\mu\)mol, 0.01 equiv.), dtbbpy (1.3 mg, 5 \(\mu\)mol, 0.01 equiv.), Cs\(_2\)CO\(_3\) (261 mg, 0.80 mmol, 1.6 equiv.), and DMA (5.0 mL). After 4 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by flash column chromatography (5% Et\(_2\)O/pentanes) provided the title compound (159 mg, 0.48 mmol, 96%) as a colorless oil. IR (film) \(\nu_{\text{max}}\) 2958, 2927, 2856, 1697, 1658, 1494, 1366, 1248, 1166, 699 cm\(^{-1}\); \(^1\text{H}\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 0.89 (3H, t, \(J = 7.0\), CH\(_3\)), 1.20–1.34 (8H, m, (CH\(_2\))\(_4\)CH\(_3\)), 1.41 (9H, s, C(CH\(_3\))\(_3\)), 1.98 (2H, q, \(J = 7.0\), CH=CHC\(_2\)H), 2.79–2.88 (2H, m, CH\(_2\)Ph), 4.35 (1H, br s, CHNH), 4.44 (1H, br s, CHNH), 5.32–5.39 (1H, m, NHCHCH=CH), 5.45–5.53 (1H, m, NHCHCH=CH), 7.16–7.24 (3H, m, ArH), 7.26–7.30 (2H, m, ArH); \(^{13}\text{C}\) NMR (126 MHz, CDCl\(_3\)) \(\delta\) 14.1, 22.6, 28.4, 28.7, 29.1, 31.7, 32.2, 42.0, 53.1, 125.1, 126.3, 128.2, 128.6, 129.6, 131.7, 137.8, 155.1; HRMS (ESI-TOF) \(m/z\) calcd. for C\(_{21}\)H\(_{34}\)NO\(_2\) ([M+H]') 332.2584, found 332.2578.

(E)-tert-butyl (1-([1H-indol-3-yl]dec-3-en-2-yl)carbamate (32)

Prepared following the general procedure outlined above using (E)-1-bromooc-1-ene (87 \(\mu\)L, 0.50 mmol, 1.0 equiv.), N-Boc-Trp-OH (243 mg, 0.80 mmol, 1.60 equiv.), Ir[dF(Me)ppy]\(_2\)(dtbbpy)PF\(_6\) (5.1 mg, 5.0 \(\mu\)mol, 0.01 equiv.), NiCl\(_2\)·glyme (1.1 mg, 5 \(\mu\)mol, 0.01 equiv.), dtbbpy (1.3 mg, 5 \(\mu\)mol, 0.01 equiv.), Cs\(_2\)CO\(_3\) (261 mg, 0.80 mmol, 1.60 equiv.), and
DMA (5.0 mL). After 4 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by flash column chromatography (20% Et₂O/pentanes) provided the title compound (146 mg, 0.40 mmol, 79%) as a colorless oil. IR (film) ν<sub>max</sub> 3330, 2957, 2925, 2854, 1691, 1497, 1366, 1247, 1167, 1011, 968, 740 cm<sup>-1</sup>; <sup>1</sup> H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.89 (3H, t, J = 7.0, CH₃), 1.22–1.31 (8H, m, (CH₂)₄CH₃), 1.42 (9H, s, C(CH₃)₃), 1.97 (2H, q, J = 6.9, CH=CHCH₂), 2.99 (2H, d, J = 6.1, CH₂CHNH), 4.46 (1H, br s, CH₂CHNH), 4.56 (1H, br s, CH₂CHNH), 5.43 (1H, dd, J = 15.5, 5.7, NHCHCH=CH), 5.55 (1H, dt, J = 15.5, 6.9, NHCHCH=CH), 7.02 (1H, d, J = 2.4, C=CHNH), 7.13 (1H, app. t, J = 7.5, ArH), 7.20 (1H, app. t, J = 7.5, ArH), 7.36 (1H, d, J = 8.0, ArH), 7.63 (1H, d, J = 8.0, ArH), 8.08 (1H, br s, ArNH).<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 14.1, 22.6, 28.4, 28.8, 29.1, 31.4, 31.7, 32.2, 52.4, 79.1, 111.0, 111.9, 119.2, 119.3, 121.9, 122.7, 128.0, 130.3, 131.2, 136.1, 155.3; HRMS (ESI-TOF) m/z calcd. for C<sub>23</sub>H₃₅N₂O₂ ([M+H]⁺) 371.2693, found 371.2692.

(E)-non-2-en-1-ylbenzene (33)

Prepared following the general procedure outlined above using (E)-1-iodooct-1-ene (87 µL, 0.50 mmol, 1.0 equiv.), phenylacetic acid (102 mg, 0.75 mmol, 1.50 equiv.), Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (5.6 mg, 5.0 µmol, 0.01 equiv.), NiCl₂·glyme (11 mg, 50 µmol, 0.10 equiv.), dtbbpy (20 mg, 75 µmol, 0.15 equiv.), Cs₂CO₃ (277 mg, 0.850 mmol, 1.70 equiv.), and DMF (25.0 mL). After 72 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by flash column chromatography (pentane) provided the title compound (85 mg, 0.42 mmol, 84%) as a colorless oil. IR (film) ν<sub>max</sub> 2924, 2854, 1494, 1454, 956, 737, 696 cm<sup>-1</sup>; <sup>1</sup> H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.90 (3H, t, J = 6.7, (CH₂)₄CH₃), 1.26–1.44 (8H, m, (CH₂)₂CH₃), 2.04 (2H, q, J = 6.9, PhCH₂CH=CHCH₂), 3.35 (2H, d, J = 6.0, PhCH₂), 5.55 (2H, m, CH=CH), 7.19–7.22 (3H, m, ArH), 7.31 (2H, d, J = 7.5, ArH); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 14.1, 22.7, 28.9, 29.5, 31.8, 32.5, 39.1, 125.9, 128.3, 128.5, 128.7, 132.2, 141.2; HRMS (ESI-TOF) m/z calcd. for C<sub>15</sub>H<sub>22</sub> ([M•]⁺) 201.1638, found 201.1625.
(E)-oct-1-en-1-ylcyclohexane (34)

Prepared following the general procedure outlined above using (E)-1-iodooct-1-ene (87 µL, 0.50 mmol, 1.0 equiv.), cyclohexanecarboxylic acid (192 mg, 1.50 mmol, 3.0 equiv.), Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (5.6 mg, 5.0 µmol, 0.01 equiv.), NiCl₂-glyme (5.5 mg, 25 µmol, 0.05 equiv.), dtbbpy (6.7 mg, 25 µmol, 0.05 equiv.), Cs₂CO₃ (489 mg, 1.5 mmol, 3.0 equiv.), and DMSO (20.0 mL). After 8 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by flash column chromatography (pentane) provided the title compound (76 mg, 0.39 mmol, 78%) as a colorless oil. IR (film) ν_max 2956, 2921, 2852, 1448, 966 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.89 (3H, t, J = 6.8, (CH₂)₅C₆H₃), 1.04–1.16 (3H, m, C₆H₂), 1.21–1.36 (11H, m, C₆H₂), 1.59–1.75 (4H, m, CH₂), 1.84–1.93 (1H, m, CHCH=CH), 1.94–2.00 (2H, m, CH=CHC₆H₃), 5.31–5.40 (2H, m, CHC=CH + CHCH=C₆H₃); ¹³C NMR (126 MHz, CDCl₃) δ 14.1, 22.6, 26.1, 26.2, 26.9, 28.8, 29.7, 30.2, 31.8, 32.7, 33.3, 40.7, 127.7, 136.4; HRMS (ESI-TOF) m/z calcd. for C₁₄H₂₇ ([M+H]⁺) 195.2107, found 195.2108.

trans-rose oxide

Prepared following the general procedure outlined above using 1-bromo-2-methylprop-1-ene (52 µL, 0.50 mmol, 1.0 equiv.), 4-methyltetrahydro-2H-pyran-2-carboxylic acid (144 mg, 1.0 mmol, 2.0 equiv.), Ir[dF(Me)ppy]₂(dtbbpy)PF₆ (5.1 mg, 5.0 µmol, 0.010 equiv.), NiCl₂-glyme (5.5 mg, 25 µmol, 0.05 equiv.), dtbbpy (6.7 mg, 25 µmol, 0.05 equiv.), Cs₂CO₃ (326 mg, 1.0 mmol, 2.0 equiv.), and DMSO (20.0 mL). After 18 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by flash column chromatography (5% Et₂O/pentane) provided the title compound (61 mg, 0.40 mmol, 79%, 5:1 d.r.). The inseparable diastereomers were characterized as a mixture. IR (film) ν_max 2954, 2919, 2849, 1669, 1453, 1377, 1184, 1078, 1053, 881, 833, 733 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.83–0.99 (0.8H, m), 1.07 (3H, d, J = 7.0), 1.19–1.30 (1.2 H, m), 1.34–1.41 (1H, m), 1.50–1.64 (2.4H, m), 1.68–1.81 (7.2H, m), 1.97–2.07 (1H, m), 3.39–3.51 (0.4H, m), 3.67–3.79 (2H, m), 3.95–4.07 (0.4H, m), 4.37 (1H, td, J = 8.2, 3.3), 5.17 (0.2 H, dt, J = 8.3, 1.6), 5.29 (1H, dt, J = 7.9, 1.5); ¹³C NMR (126 MHz, CDCl₃) δ 18.3, 19.1, 22.3, 24.9, 25.7, 25.8, 30.3, 32.4, 34.4, 38.2, 40.8, 62.2, 67.9, 68.4,
69.1, 74.6, 80.1, 125.4, 126.3, 135.6; HRMS (ESI-TOF) m/z calcd. for C₁₀H₁₉O ([M+H]⁺) 155.1430, found 155.1432.

7) Experimental Data for Additional Examples

\((E)-\text{dodec-5-en-1-yl}\)benzene (S1)

Prepared following the general procedure outlined above using \((E)-1\)-iodooct-1-ene (87 µL, 0.50 mmol, 1.0 equiv.), 5-phenylvaleric acid (267 mg, 1.5 mmol, 3.0 equiv.), \(\text{Ir}[\text{dF(CF}_3\text{ppy)}]{_2}(\text{dtbbpy})\text{PF}_6\) (5.6 mg, 5.0 µmol, 0.010 equiv.), \(\text{NiCl}_2\cdot\text{glyme}\) (5.5 mg, 25 µmol, 0.05 equiv.), dtbbpy (6.7 mg, 25 µmol, 0.05 equiv.), \(\text{Cs}_2\text{CO}_3\) (489 mg, 1.5 mmol, 3.0 equiv.), and DMSO (20.0 mL). After 24 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by flash column chromatography (pentane) provided the title compound (14 mg, 0.06 mmol, 11%) as a colorless oil. IR (film) \(\nu_{\text{max}}\) 2926, 2854, 1454 cm⁻¹; \(^1H\) NMR (500 MHz, CDCl₃) \(\delta\) 0.89 (3H, t, \(J = 6.7\), \(\text{CH}_2\)₅C₃H₃), 1.22–1.37 (8H, m, \(\text{CH}_2\)), 1.36–1.45 (2H, m, \(\text{CH}_2\)), 1.59–1.67 (2H, m, \(\text{CH}_2\)), 1.93–2.05 (4H, m, \(\text{CH}_2\text{CH}=\text{CHCH}_2\)), 2.61 (2H, t, \(J = 7.8\), \(\text{CH}_2\text{Ph}\)), 5.39 (2H, m, \(J = 4.7\), \(\text{CH}=\text{CH}\)), 7.17–7.30 (5H, m, ArH); \(^{13}C\) NMR (126 MHz, CDCl₃) \(\delta\) 14.1, 22.7, 28.9, 29.3, 29.6, 31.0, 31.8, 32.5, 32.6, 35.9, 125.6, 128.2, 128.4, 130.0, 130.7, 142.9; HRMS (ESI-TOF) m/z calcd. for C₁₆H₂₉ ([M+H]⁺) 245.2264, found 245.2256.

\((E)-1\)-methoxy-4-(non-2-en-1-yl)benzene (S2)

Prepared following the general procedure outlined above using \((E)-1\)-iodooct-1-ene (87 µL, 0.50 mmol, 1.0 equiv.), 2-(4-methoxyphenyl)acetic acid (125 mg, 0.75 mmol, 1.50 equiv.), \(\text{Ir}[\text{dF(CF}_3\text{ppy)}]{_2}(\text{dtbbpy})\text{PF}_6\) (5.6 mg, 5.0 µmol, 0.010 equiv.), \(\text{NiCl}_2\cdot\text{glyme}\) (11 mg, 50 µmol, 0.10 equiv.), dtbbpy (20 mg, 75 µmol, 0.15 equiv.), \(\text{Cs}_2\text{CO}_3\) (277 mg, 0.85 mmol, 1.70 equiv.), and DMF (25.0 mL). After 72 h, the reaction mixture was subjected to the workup protocol
outlined in the general procedure. Purification by flash column chromatography (0–5% Et2O/pentane) provided the title compound (112 mg, 0.482 mmol, 96%) as a colorless oil. IR (film) νmax 2955, 2924, 2854, 1510, 1038, 966, 818 cm⁻¹; 1H NMR (500 MHz, CDCl₃) δ 0.89 (3H, t, J = 6.7, CH₃), 1.21–1.43 (8H, m, (CH₂)₄CH₃), 2.02 (2H, q, J = 6.8, CH=CHCH₂), 2.80 (2H, d, J = 6.0, CH₂Ph), 3.80 (3H, s, OCH₃), 5.43–5.60 (2H, m, CH=CH), 6.82–6.86 (2H, m, ArH), 7.07–7.15 (2H, m, ArH); 13C NMR (126 MHz, CDCl₃) δ 14.1, 22.6, 28.9, 29.5, 31.7, 32.5, 38.1, 55.3, 113.7, 129.1, 129.3, 131.8, 133.2, 157.8; HRMS (ESI-TOF) m/z calcd. for C₁₅H₂₁ ([M+H]⁺) 233.1900, found 233.1896.

(E)-1-chloro-3-(non-2-en-1-yl)benzene (S3)
Prepared following the general procedure outlined above using (E)-1-iodooct-1-ene (87 µL, 0.50 mmol, 1.0 equiv.), 2-(3-chlorophenyl)acetic acid (128 mg, 0.75 mmol, 1.50 equiv.), Ir[dF(CF₃ppy)]₂(dtbbpy)PF₆ (5.6 mg, 0.010 equiv.), NiCl₂·glyme (11 mg, 50 µmol, 0.10 equiv.), dtbbpy (20 mg, 75 µmol, 0.15 equiv.), Cs₂CO₃ (277 mg, 0.85 mmol, 1.70 equiv.), and DMF (25.0 mL). After 72 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by flash column chromatography (0–5% Et₂O/pentane) provided the title compound (80 mg, 0.338 mmol, 68%) as a clear oil. IR (film) νmax 2956, 2924, 2854, 1597, 1431, 1078, 966, 776, 682 cm⁻¹; 1H NMR (500 MHz, CDCl₃) δ 0.89 (3H, t, J = 6.6, CH₃), 1.21–1.45 (8H, m, (CH₂)₄CH₃), 2.01–2.05 (2H, m, CH=CHCH₂), 3.31 (2H, d, J = 4.1, CH₂Ar), 5.47–5.60 (2H, m, CH=CH), 7.05–7.24 (4H, m, ArH); 13C NMR (126 MHz, CDCl₃) δ 14.1, 22.6, 28.9, 29.3, 31.7, 32.5, 38.7, 126.0, 126.6, 127.7, 128.6, 129.5, 132.9, 134.1, 143.2; HRMS (ESI-TOF) m/z calcd. for C₁₅H₂₁ ([M+H]⁺) 237.1405, found 237.1409.

8) Spectral Data
16

16
9) References Cited