Supporting Information
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Intermolecular Addition of Glycosyl Halides to Alkenes Mediated by Visible Light**
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Supporting Information

1. Experimental Section

General. All reagents were reagent grade quality and used as received from Aldrich or Acros unless otherwise indicated. All reactions were conducted under inert conditions (Ar or N\textsubscript{2}) unless otherwise indicated. Anhydrous THF was distilled from sodium/benzophenone prior to use. Anhydrous CH\textsubscript{2}Cl\textsubscript{2} was passed through a column of alumina, sparged with N\textsubscript{2} for 20 minutes, and stored in a sealed Schlenk flask. Anhydrous acetonitrile (MeCN), N,N-diisopropylethylamine (\textit{i}Pr\textsubscript{2}NEt), and diisopropylamine (\textit{i}Pr\textsubscript{2}NH) were distilled from CaH\textsubscript{2} prior to use. Acetobromo-\textalpha-D-glucose (1% CaCO\textsubscript{3}) and acetobromo-\textalpha-D-galactose (1% CaCO\textsubscript{3}) were purified by passing through a silica column prior to use. \textalpha-D-glucopyranosyl bromide tetrabenzoate, \textalpha-D-mannopyranosyl bromide tetrabenzoate were synthesized according to literature procedure.\textsuperscript{i} Ru(bpy)\textsubscript{3}Cl\textsubscript{2} was synthesized by reported procedure,\textsuperscript{ii} and Ru(bpy)\textsubscript{3}(BF\textsubscript{4})\textsubscript{2} was synthesized in an analogous manner to reported anion metathesis.\textsuperscript{iii} Dimethyl 3-vinylcyclopropane-1,1-dicarboxylate was synthesized according to literature procedure.\textsuperscript{iv} Acrylonitrile, acrolein, methyl vinyl ketone, were distilled prior to use. Supercritical fluid chromatography (SFC) was conducted on a Berger Minigram SFC. Column chromatography was performed using Silicycle silica gel 60 as the solid support. All NMR spectra were recorded on Bruker Avance 500 MHz or 400 MHz spectrometer at STP and with CDCl\textsubscript{3} as the NMR solvent unless otherwise indicated. All deuterated solvents were used as received from Cambridge Isotope Laboratories, Inc. \textsuperscript{1}H NMR, \textsuperscript{13}C NMR, and \textsuperscript{31}P NMR chemical shifts are reported in \textdelta units, parts per million (ppm) relative to the chemical shift of residual solvent or an external standard. Reference peaks for chloroform in \textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectra were set at 7.26 ppm and 77.0 ppm, respectively. \textsuperscript{31}P reference peak was set at -18.0 ppm for triphenylphosphite in CDCl\textsubscript{3} as an external standard. High-resolution mass spectra (HRMS) were obtained using a Micromass Q-ToF Ultima or Agilent Accurate LC-TOF Mass Spectrometer (ESI+, 175 eV). Melting point was recorded on Uni-melt (Thomas Hoover) capillary melting point apparatus. Infrared (IR) spectra were obtained using a ASI ReactIR 1000 infrared spectrometer. Specific rotations were obtained using a Jasco DIP-1000 polarimeter with CH\textsubscript{2}Cl\textsubscript{2} as the solvent.
**General Procedures.**

**General Procedure A (liquid alkene):** A flame-dried Schlenk tube equipped with a stir bar under Ar was charged with Ru(bpy)$_3$(BF$_4$)$_2$ (5 mol%), Hantzsch ester 5 (2.2 mol eq) and glycosyl bromide (1 mol eq.). The flask was evacuated and then backfilled with Ar. Solvent (to a sugar concentration of 0.12 mM) was added, forming a bright orange heterogeneous solution, followed by $i$Pr$_2$NEt (3 mol eq.) and alkene (2 mol eq.). The reaction tube was placed 6-10 cm from a 14W fluorescent light bulb and stirred at room temperature until TLC showed consumption of starting material. The reaction was quenched by passing through a plug of silica in Et$_2$O. Flash column chromatography provided the product as a white solid or a colorless oil after removal of solvents.

**General Procedure B (solid alkene):** A flame-dried Schlenk tube equipped with a stir bar under Ar was charged with Ru(bpy)$_3$(BF$_4$)$_2$ (5 mol%), alkene (2 mol eq.), Hantzsch ester 5 (2.2 mol eq) and glycosyl bromide (1 mol eq). The flask was evacuated and then backfilled with Ar. Solvent (to a sugar concentration of 0.12 mM) was added, forming a bright orange heterogeneous solution, followed by $i$Pr$_2$NEt (3 mol eq.). The reaction tube was placed 6-10 cm from a 14W fluorescent light bulb and stirred at room temperature until TLC showed consumption of starting material. The reaction was quenched by passing through a plug of silica in Et$_2$O unless otherwise indicated. Flash column chromatography provided the product as a white solid or a colorless oil after removal of solvents.

**General Procedure for determination of yield by SFC:** The sample for analysis was prepared by adding 100 $\mu$L of 6-t-butyl-2-methyl-phenol (0.588 mmol) to a solution of crude material in 10 mL THF. The sample was injected (5 $\mu$L) onto a silica column (4.6 mm x 250 mm) in 30% THF in CO$_2$ at 100 bar with a 4 mL/min flow rate. Standard retention time = 1.10 min; sample retention time = 2.38 min. The ratio of areas was then compared to a calibration curve to determine yield.
Proton labeling: For the purpose of spectral assignment, the proton labeling outlined in the following box was used throughout the text (including mannosides and galactosides).

Methyl 3-(2,3,4,6-tetra-O-benzoyl-α-D-glucopyranosyl)propanoate (2).
This compound was prepared according to the General Procedure A using α-D-glucopyranosyl bromide tetrabenzoate 1 (80 mg, 0.12 mmol, 2 mol eq.) and methyl acrylate (22 μL, 0.244 mmol, 2 mol eq.). The yield was determined by SFC for reaction optimization. Alternatively, purification of the crude material by flash column chromatography (SiO₂: 20/80 to 30/70 ethyl acetate in hexanes) gave the desired product as a white solid.

Methyl 3-(2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl)propanoate (6).
This compound was prepared according to the General Procedure A using aceto-1-bromo- α-D-glucose (50 mg, 0.12 mmol, 1 mol eq.) and methyl acrylate (22 μL, 0.244 mmol, 2 mol eq.). Flash column chromatography (SiO₂: 40/60 to 50/50 ethyl acetate in hexanes gradient) gave the desired product as a white solid (48 mg, 0.115 mmol, 94% yield).
Methyl 3-(2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl)propyl ketone (7).

This compound was prepared according to the General Procedure A using aceto-1-bromo- α-D-glucose (50 mg, 0.12 mmol, 1 mol eq.) and methyl vinyl ketone (20 µL, 0.244 mmol, 2 mol eq.). Flash column chromatography (SiO₂: 50/50 ethyl acetate in hexanes) gave the desired product as a white solid (42 mg, 0.104 mmol, 86% yield).

3-(2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl)propionaldehyde (8).

This compound was prepared according to the General Procedure A using aceto-1-bromo- α-D-glucose (50 mg, 0.12 mmol, 1 mol eq.) and acrolein (16 µL, 0.244 mmol, 2 mol eq.). Flash column chromatography (SiO₂: 50/50 ethyl acetate in hexanes) gave the desired product as a white solid (40 mg, 0.103 mmol, 85% yield).

3-(2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl)propionitrile (9).

This compound was prepared according to the General Procedure A using aceto-1-bromo- α-D-glucose (50 mg, 0.12 mmol, 1 mol eq.) and acrylonitrile (16 µL, 0.244 mmol, 2 mol eq.). Flash column chromatography (SiO₂ in 50/50 to 60/40 ethyl acetate in hexanes) gave the desired product as a white solid (40 mg, 0.104 mmol, 85% yield).

(2S)-methyl 2-methyl-3-(2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl)propanoate (10).

This compound was prepared according to the General Procedure A using aceto-1-bromo- α-D-glucose (50 mg, 0.12 mmol, 1 mol eq.) and methyl methacrylate (28 µL, 0.244 mmol, 2 mol eq.). Flash column chromatography (SiO₂: 30:70 to 40:60 ethyl acetate in hexanes) gave the desired product as a white solid (52 mg, 0.120 mmol, 98% yield, 1.5:1 dr of isomers).
Diethyl-2-(2,3,4,6-tetra-O-benzoyl-α-D-glucopyranosyl)ethylphosphonate (11).

This compound was prepared according to the General Procedure A using aceto-1-bromo-α-D-glucose (50 mg, 0.12 mmol, 2 mol eq.) and diethyl vinylphosphonate (188 μL, 1.22 mmol, 10 mol eq.). The reaction was placed directly on column for purification. Flash column chromatography (SiO₂: 80/20 ethyl acetate in hexanes) gave the desired product as a white solid (57 mg, 0.077 mmol, 63% yield). [α]D²⁵ = 33.9 (c = 2.45). ¹H NMR (500 MHz, CDCl₃): δ 7.90-8.04 (m, 8H), 7.29-7.53 (m, 12H), 5.96 (t, ³J(H,H) = 9 Hz, 1H, H3), 5.53 (t, ³J(H,H) = 8.5 Hz, 1H, H4), 5.50 (dd, ³J(H,H) = 5.5 and 9 Hz, 1H, H2), 4.60 (dd, ³J(H,H) = 6.5 and 12 Hz, 1H, H6/7), 4.51 (dd, ³J(H,H) = 3 and 12 Hz, 1H, H6/7), 4.44 (m, 1H, H1), 4.28 (ddd, ³J(H,H) = 3, 6.5 and 8.5 Hz, 1H, H5) 2.32 (m, 1H), 1.97 (m, 2H), 1.73 (m, 1H), 1.24 (t, ³J(H,H) = 7.5 Hz, 3H), 1.21 (t, ³J(H,H) = 7 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 166.1, 165.6, 165.4, 165.3, 133.6, 133.5, 133.4, 133.2, 129.91, 129.89, 129.7, 129.6, 128.9, 128.84, 128.78, 128.5, 128.45, 128.43, 72.4, 72.2, 70.9, 70.1, 69.8, 69.3, 63.0, 61.72, 61.66, 21.8, 20.6, 19.67, 19.64, 16.46, 16.43, 16.42, 16.38. ³¹P = δ 30.9. IR (film) ν = 3057, 2988, 2308, 1733, 1652, 1602, 1552, 1420, 1177, 1096, 1069, 1207 cm⁻¹. HRMS (ESI): m/z [M+H]⁺ found 745.2400, calcd 745.2414 for C₄₀H₄₁O₁₂P. m.p. = 123-124°C.

Methyl 4-(2-[2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl]ethyl)benzoate (12).

This compound was prepared according to the General Procedure B using aceto-1-bromo-α-D-glucose (50 mg, 0.122 mmol, 1 mol eq.) and 4-methoxycarbonylstyrene (40 mg, 0.244 mmol, 2 mol eq.). Flash column chromatography (SiO₂: 30/70 to 40/60 ethyl acetate in hexanes) gave the product as a colorless oil (31 mg, 0.063 mmol, 51% yield).
2-((2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl)methylene)dihydrocoumarin (13).

This compound was prepared according to the General Procedure B using aceto-1-bromo-α-D-glucose (492 mg, 1.2 mmol, 1 mol eq.) and 2-methylene-3-hydrocoumarin (16) (384 mg, 2.4 mmol, 2 mol eq.). Flash column chromatography (SiO₂: 30/70 ethyl acetate in hexanes) gave the product as a 1.8:1 mixture of diastereomers as a white solid (525 mg, 1.07 mmol, 89% yield). The material was then recrystallized from benzene/hexanes to give analytically pure product as a 1:1 mixture of diastereomers. [α]D²⁵ = +107.2 (c = 0.60). ¹H NMR (500 MHz, CDCl₃): δ 7.26 (t, 3J(H,H) = 7.7 Hz, 1H + 1H, major + minor) 7.18 (d, 3J(H,H) = 7.1 Hz, 1H + 1H, major + minor), 7.10 (t, 3J(H,H) = 7.5 Hz, 1H + 1H, major + minor), 7.04 (dd, 3J(H,H) = 3.2 and 8 Hz, 1H + 1H, major + minor) 5.36 (t, 3J(H,H) = 9.2 Hz, 1H, H₃, minor), 5.27 (t, 3J(H,H) = 8.5 Hz, 1H, H₃, major), 5.13 (dd, 3J(H,H) = 1.6 and 5.25 Hz, 1H, H₂, major + minor), 5.11 (dd, 3J(H,H) = 3.2 and 5.9 Hz, 1H, H₂, minor), 4.98 (t, 3J(H,H) = 9.1 Hz, 1H, H₄, minor), 4.95 (t, 3J(H,H) = 8.3 Hz, 1H, H₄, major), 4.52 (ddd, 3J(H,H) = 2.8, 5.3 and 11.6 Hz, 1H, H₁, major), 4.39 (ddd, 3J(H,H) = 3.0, 5.8 and 12.5 Hz, 1H, H₁, minor), 4.28-4.17 (m, 1H + 1H, H₆/₇, major + minor), 4.10 (dd, 3J(H,H) = 2.9 and 12.2 Hz, 1H, H₆/₇, major), 3.99 (dd, 3J(H,H) = 2.3 and 12.2 Hz, 1H, H₆/₇, minor), 3.92-3.83 (m, 1H + 1H, H₅, major + minor), 3.10-2.92 (m, 2H + 1H, major + minor), 2.88-2.79 (m, 1H + 2H, major + minor), 2.66 (dt, 3J(H,H) = 2.8 and 13.5 Hz, 1H, minor), 2.20 (ddd, 3J(H,H) = 2.7, 8.3 and 14.8 Hz, 1H, major), 2.09 (s, 3H, OAc), 2.05-1.95 (m, 17H, major + minor), 1.92 (s, 3H, OAc), 1.86 (s, 3H, OAc), 1.71-1.64 (m, 1H, minor). ¹³C NMR (125 MHz, CDCl₃): δ 170.7, 170.6, 170.5, 170.3, 170.0, 169.9, 169.8, 169.6, 169.5, 151.5, 151.4, 128.5, 128.5, 128.1, 127.8, 124.6, 124.4, 122.8, 122.3, 116.7, 116.7, 70.7, 70.1, 70.1, 69.8, 69.7, 69.6, 69.2, 69.1, 68.5, 60.4, 62.2, 62.1, 35.6, 35.1, 31.6, 30.3, 28.2, 26.7, 25.1, 22.7, 20.8, 20.7, 20.7, 20.6, 20.5, 20.4. IR (film) ν = 3057, 2988, 1750, 1617, 1590, 1490, 1459, 1424, 1370, 1227, 1146, 1096, 1038 cm⁻¹. HRMS (ESI): m/z [M+H]⁺ found 493.1698, calcd 493.1710 for C₂₄H₂₈O₁₁.

Methyl 3-(2,3,4,6-tetra-O-benzoyl-α-D-mannopyranosyl)propanoate (14).

This compound was prepared according to a modified General Procedure A using α-D-mannopyranosyl bromide tetrabenzoate (80 mg, 0.12 mmol, 1 mol eq.) and methyl acrylate (22 µL, 0.244 mmol, 2 mol eq.) and Hantzsch ester 4 (34
mg, 0.134 mmol, 1.1 eq). Flash column chromatography (SiO2: 40/60 to 50/50 ethyl acetate in hexanes gradient) gave the desired product as a white solid (66 mg, 0.099 mmol, 81% yield). \([\alpha]_D^{25} = -16.68 \ (c = 1.68)\) 

\(^1\)H NMR (400 MHz, CDCl3): \(\delta 8.09 \ (dd, J_{(H,H)} = 1.6 \text{ and } 6.8 \text{ Hz}, 2H), 8.03 \ (dd, J_{(H,H)} = 1 \text{ and } 8 \text{ Hz}, 2H), 7.98 \ (dd, J_{(H,H)} = 1.2 \text{ and } 6 \text{ Hz}, 2H), 7.3-7.6 \ (m, 12 \text{ H}), 6.02 \ (t, J_{(H,H)} = 9.2 \text{ Hz}, 1 \text{ H}, H4), 5.81 \ (dd, J_{(H,H)} = 3.2 \text{ and } 9.2 \text{ Hz}, 1H, H3), 5.65 \ (t, J_{(H,H)} = 3.2 \text{ Hz}, 1H, H2), 4.60 \ (m, 2H, H6 \text{ and } H7), 4.29 - 4.35 \ (m, 2H, H1 \text{ and } H5), 3.69 \ (s, 3H, -OMe), 2.55 \ (m, 2H), 2.41 \ (m, 1H), 2.10 \ (m, 1H).

\(^13\)C NMR (125 MHz, CDCl3): \(\delta 173.2, 166.2, 165.6, 165.5, 165.4, 133.5, 133.4, 133.3, 129.81, 129.78, 129.73, 129.4, 128.9, 128.5, 128.47, 128.41, 128.40, 74.7, 71.6, 70.6, 69.9, 62.8, 51.8, 30.1, 23.8.\)

IR (film) 3067, 2960, 2929, 2856, 1729, 1605, 1455, 1285, 1250, 1181, 1111, 1073, 1026 cm\(^{-1}\). HRMS (ESI): \(m/z \ [M+H]^+\) found 667.2163, calcd 667.2174 for C\(_{38}\)H\(_{34}\)O\(_{11}\).

\(N,N\)-diisopropylammonium tetrafluoroborate (3·HBF\(_4\)).

To a round bottom flask fitted with a stir bar was added acetone (20 mL) and \(^{1}\)Pr\(_2\)NEt (10 mL, 57 mmol). The solution was cooled to 0\(^{\circ}\) C, and HBF\(_4\)Et\(_2\)O (7.7 mL, 57 mmol) was added dropwise. The solution was allowed to stir for 10 minutes, and a

Methyl 3-(2,3,4,6-tetra-O-acetyl-\(\alpha\)-D-galactopyranosyl)propanoate (15).

This compound was prepared according to the General Procedure A using aceto-1-bromo-\(\alpha\) -D-galactose (50 mg, 0.12 mmol, 1 mol eq.) and methyl acrylate (22 \(\mu\) L, 0.244 mmol, 2 mol eq.). Flash column chromatography (SiO\(_2\): 30/70 to 50/50 ethyl acetate in hexanes gradient) gave the desired product\(^{x}\) as a white solid (41 mg, 0.098 mmol, 80% yield).

(E)-Dimethyl 2-(4-[2,3,4,6-tetra-O-benzoyl-\(\alpha\)-D-glucopyranosyl]but-2-enyl)malonate (16).

This compound was prepared according to the General Procedure A using \(\alpha\) -D-mannopyranosyl bromide tetrabenzoate 1 (80 mg, 0.122 mmol, 1 mol eq.) and dimethyl 3-vinylcyclopropane-1,1-dicarboxylate (450 mg, 2.44 mmol, 20 mol eq.). Flash column chromatography (SiO\(_2\): 25/75 ethyl acetate in hexanes) gave the product as a white powder\(^{y}\) (51 mg, 0.065 mmol, 54% yield).
white precipitate formed. Additional acetone was added to dissolve precipitate. The solution was dried with MgSO$_4$, filtered, and concentrated in vacuo. The resulting solid was redissolved in a minimal amount of acetone, and 200 mL Et$_2$O was added. A white solid formed which was collected via suction filtration and rinsed with Et$_2$O to give the product as a white powder (10.0 g, 81% yield). $^1$H NMR (500 MHz, CDCl$_3$): δ 6.75 (br, 1H, N-H), 3.69 (m, 2H), 3.15 (m, 2H), 1.40 (m, 15H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ 55.3, 43.4, 18.5, 17.1. IR (film) $\tilde{\nu}$ = 3134, 3057, 2991, 2953, 1482, 1424, 1405, 1181, 1131, 1073, 996, 926, 895 cm$^{-1}$.

2-methylene-3-hydrocoumarin (17).

To a flame dry round bottom flask under Ar with a stir bar was added THF (100 mL) and $^3$Pr$_2$NH (6.6 mL, 47 mmol, 3 mol eq.). The flask was cooled to -78° C, and nBuLi (29.3 mL, 1.6 M in hexanes, 47 mmol, 3 mol eq.) was added. The reaction was allowed to stir 10 minutes. Dihydrocoumarin (2 mL, 15.8 mmol, 1 mol eq.) was added as a solution in dry THF (12 mL with an 8 mL rinse). The reaction was allowed to stir 30 minutes at -78° C, and Eschenmoser’s salt (10.2 g, 55.2 mmol, 3.5 mol eq.) was added all at once. A yellow suspension resulted, which was allowed to warm to room temperature and stir for 75 minutes. The reaction was quenched with NH$_4$Cl(aq). The layers were separated, and the aqueous layer was extracted 2 x Et$_2$O. The combined organic layers were rinsed with brine, dried with MgSO$_4$, and filtered. The solvent was evaporated in vacuo to afford the crude product as a yellow oil. The crude mixture was then dissolved in THF (not anhydrous), which resulted in a yellow solution. To this solution was added a stir bar and MeI (5 mL, 80 mmol, 5 mol eq.). The reaction was allowed to stir open to air at room temperature for 18 hours. The resulting suspension was quenched by filtering through a plug of silica and rinsing with Et$_2$O. The solvent was removed in vacuo in order to afford the crude product as a yellow oil. Flash column chromatography (SiO$_2$: 10/90 ethyl acetate in hexanes) afforded the product as a white solid (1.2 g, 7.5 mmol, 47% yield over 2 steps). $^1$H NMR (500 MHz, CDCl$_3$): δ 7.25 (t, $^3$J(H,H) = 8 Hz, 1H), 7.19 (d, $^3$J(H,H) = 7.4 Hz, 1H), 7.12 (t, $^3$J(H,H) = 7.4 Hz, 1H), 7.08 (d, $^3$J(H,H) = 8 Hz, 1H), 6.44 (s, 1H), 5.80 (s, 1H), 3.83 (s, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ 163.3, 150.8, 131.7, 128.6, 128.2, 127.7, 124.5, 121.1, 117.0, 32.0. IR (film) $\tilde{\nu}$ = 3057, 2988, 1749, 1637, 1617, 1557, 1490, 1459, 1424, 1227, 1193, 1170, 1139, 1110. HRMS (ESI): m/z [M+H]$^+$ found 161.0603, calcd 161.0603 for C$_{10}$H$_8$O$_2$. m.p. = 65-67°C.
Time-Resolved EPR Measurements.

Our TREPR apparatus has been described previously in several recent publications. Briefly, a YAG pumped OPO laser system with output at 460 nm (5 mJ) is fired at a repetition rate of 10 Hz, while sampling the direct detection EPR signal from the microwave bridge (CW mode) using a gated boxcar signal averager. The external magnetic field is swept over 2 or 4 minutes with 100 or 300 ns wide gates sampling the EPR signal 5-10 times at each magnetic field point. The flow system was flushed and a solvent blank was run before all experiments. All spectra have center field of 3270 G, sweep width of 200 G, microwave frequency 9.47 GHz, microwave power 10 mW. Samples were flowed through the microwave resonator using a micropump from a reservoir that was constantly purged with nitrogen gas bubbles (for 10 minutes prior to and during TREPR).
2. Spectra

$^{13}$C of 11
$^{31}$P of 11
$^{13}$C of 13
$^{13}\text{C}$ of 14
$^{13}$C of 3-HBF$_4$
$^{13}$C of 17