Supplementary Information

Modular Synthesis of Allyl Vinyl Ethers for the Enantioselective Construction of Functionalized Quaternary Stereocenters

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General procedure for the synthesis of allyl tert-butyl oxalates 7-10:

To a solution of the 3-halo-2-butenol in dichloromethane was added triethyl amine. The mixture was stirred for 5 min at ambient temperature and then cooled to 0 °C. A solution of tert-butyl 2-chloro-2-oxoacetate in dichloromethane was added over 5 min and the mixture was stirred at 0 °C for the specified time. Water was added and the mixture was extracted with dichloromethane. The combined extracts were washed with aqueous HCl (0.1 M), saturated aqueous sodium bicarbonate, brine, dried over Na₂SO₄ and concentrated under reduced pressure to provide the corresponding allyl tert-butyl oxalates. These were used in the next step without purification.

*(E)*-3-Bromobut-2-enyl tert-butyl oxalate (7):

\[
\begin{align*}
\text{Br} & \quad \text{O} \quad \text{CO}_2 \text{Bu} \\
\end{align*}
\]

The reaction of *(E)*-3-bromo-2-butenol (3)\(^1\) (310 mg, 2.06 mmol), triethylamine (0.35 mL, 2.48 mmol) and tert-butyl 2-chloro-2-oxoacetate (405 mg, 2.48 mmol) in dichloromethane (5 mL) for 3 h, according to the general procedure, provided 478 mg (83%) of 7; \(R_f = 0.20\) (hexanes/EtOAc, 96:4).

IR (neat): 2983, 2920, 1760, 1736, 1371, 1327, 1260, 1194, 1138, 943, 841 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl₃): \(\delta 6.09\) (tq, 1H, \(J = 7.8, 1.4, \text{CH}_3\text{C=CH}\)), 4.68 (br d, 2H, \(J = 7.8, \text{OCH}_2\)), 2.36 (m, 3H, \(\text{CH}_3\text{C=CH}\)), 1.56 (s, 9H, \(\text{C(CH}_3)_3\)); \(^{13}\)C NMR (75 MHz, CDCl₃): \(\delta 158.2\) (CO₂(CH₃)₃ or CO₂CH₂), 156.6 (CO₂CH₂ or CO₂(CH₃)₃), 128.5 (BrC=CH), 124.6 (BrC=CH), 85.2 (C(CH₃)₃), 62.5 (OCH₂), 27.7 (C(CH₃)₃), 23.9 (CH₃C=CH); HRMS (ESI, pos.): \(m/z 278.0156\) (278.0154 calc. for C₁₀H₁₅BrO₄ (M⁺)).

*(Z)*-3-Bromobut-2-enyl tert-Butyl oxalate (8):

\[
\begin{align*}
\text{Br} & \quad \text{O} \quad \text{CO}_2 \text{Bu} \\
\end{align*}
\]

The reaction of *(Z)*-3-bromo-2-butenol (4)\(^2\) (2.60 g, 17.33 mmol), triethylamine (2.89 mL, 20.79 mmol) and tert-butyl 2-chloro-2-oxoacetate (3.41 g, 20.8 mmol) in dichloromethane (25 mL) for 2 h, according to the general procedure, provided 4.31 g (89%) of 8; \(R_f = 0.24\) (hexanes/EtOAc, 95:5).

IR (neat): 2982, 1762, 1736, 1371, 1320, 1194, 1135, 950, 843 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl₃): \(\delta 5.92\) (tq, 1H, \(J = 6.3, 1.3, \text{CH}_3\text{C=CH}\)), 4.84 (dq, 2H, \(J = 6.3, 1.3, \text{OCH}_2\)), 2.35 (apparent q, 3H, \(J = 1.3, \text{CH}_3\text{C=CH}\)), 1.56 (s, 9H, \(\text{C(CH}_3)_3\)); \(^{13}\)C NMR (75 MHz, CDCl₃): \(\delta 158.3\) (CO₂(CH₃)₃ or CO₂CH₂), 156.7 (CO₂CH₂ or CO₂(CH₃)₃), 127.8 (BrC=CH), 122.3 (BrC=CH), 85.0 (C(CH₃)₃), 66.0 (OCH₂), 29.0 (CH₃C=CH), 27.7 (C(CH₃)₃); HRMS (APPI, pos.): \(m/z 278.0155\) (278.0154 calc. for C₁₀H₁₅BrO₄ (M⁺)).
(E)-3-Iodobut-2-enyl tert-Butyl oxalate (9):

\[
\begin{array}{c}
\text{I} \\
\text{O} \\
\text{CO}_2\text{Bu}
\end{array}
\]

The reaction of (E)-3-iodo-2-butenol (5)\(^3\) (1.75 g, 8.85 mmol), triethylamine (1.48 mL, 10.6 mmol) and tert-butyl 2-chloro-2-oxoacetate (1.74 g, 10.6 mmol) in dichloromethane (10 mL) for 1 h, according to the general procedure, provided 2.10 g (75%) of 9; \(R_f = 0.21\) (hexanes/EtOAc, 95:5).

IR (neat): 2983, 1761, 1737, 1371, 1310, 1193, 945, 842 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 6.38 (tq, 1H, \(J = 7.4, 1.5\), CH\(_3\)C=CH), 4.64 (br d, \(J = 7.4\), OC\(_2\)H\(_2\)), 2.52 (m, \(J = 3H, CH\(_3\)C=CH), 1.56 (s, 9H, C(C\(_3\)H\(_3\))\(_3\)); \(^13\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 158.1 (CO\(_2\)(CH\(_3\))\(_3\) or CO\(_2\)CH\(_2\)), 156.5 (CO\(_2\)CH\(_2\) or CO\(_2\)(CH\(_3\))\(_3\)), 133.1 (IC=CH), 102.9 (IC=CH), 85.2 (C(CH\(_3\))\(_3\), 62.5 (OCH\(_2\)), 28.3 (CH\(_3\)C=CH), 27.8 (C(CH\(_3\))\(_3\)); HRMS (ESI, pos.): \(m/z\) 326.0015 (326.0015 calc. for C\(_{10}\)H\(_{15}\)IO\(_4\) (M\(^+\))).

(Z)-3-Iodobut-2-enyl tert-Butyl oxalate (10):

\[
\begin{array}{c}
\text{I} \\
\text{O} \\
\text{CO}_2\text{Bu}
\end{array}
\]

The reaction of (Z)-3-iodo-2-butenol (6)\(^4\) (1.58 g, 7.98 mmol), triethylamine (1.34 mL, 9.57 mmol) and tert-butyl 2-chloro-2-oxoacetate (1.57 g, 9.57 mmol) in dichloromethane (10 mL) for 1 h, according to the general procedure, provided 2.01 g (77%) of 10; \(R_f = 0.28\) (hexanes/EtOAc, 95:5).

IR (neat): 2981, 1763, 1735, 1658, 1394, 1370, 1258, 1193, 1139, 1082, 950, 843 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 5.81 (tq, 1H, \(J = 6.1, 1.4\), CH\(_3\)C=CH), 4.77 (dq, \(J = 6.1, 1.4\), OC\(_2\)H\(_2\)), 2.57 (apparent q, \(J = 3H, CH\(_3\)C=CH), 1.56 (s, 9H, C(C\(_3\)H\(_3\))\(_3\)); \(^13\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 158.3 (CO\(_2\)(CH\(_3\))\(_3\) or CO\(_2\)CH\(_2\)), 156.7 (CO\(_2\)CH\(_2\) or CO\(_2\)(CH\(_3\))\(_3\)), 128.5 (C=CH-CH\(_2\)), 105.6 (C=CH-CH\(_2\)), 85.1 (C(CH\(_3\))\(_3\), 70.7 (OCH\(_2\)), 33.9 (CH\(_3\)C=CH), 27.7 (CH\(_3\))\(_3\)); HRMS (ESI, pos.): \(m/z\) 326.0006 (326.0015 calc. for C\(_{10}\)H\(_{15}\)IO\(_4\) (M\(^+\))).

**General procedure for the synthesis of allyl vinyl ethers:**

A CEM Discover\textsuperscript{®} microwave reactor was used for the microwave experiments. All reactions involving microwave heating were conducted in sealed reaction vessels. The temperature of the reaction mixture was monitored with an infrared sensor and the mixture was at the preset temperature (100 °C) in approximately 60s.

To a solution of the allyl tert-butyl oxalate in toluene in a 35 mL microwave vial was added a solution of the Petasis reagent (2.2 equiv.) in toluene.\(^5\) The vial was sealed and the mixture was heated with stirring at 100 °C until completion of the reaction. The mixture was then cooled to ambient temperature, hexane (10 mL) was added, and the mixture was stirred for 5 min. The precipitated solids were removed by filtration through a pad of Celite\textsuperscript{®} and the filtrate was
concentrated under reduced pressure (for the iodo compounds, this residue was briefly treated with aqueous HCl as described). The residue was purified by flash chromatography on silica gel (hexane:EtOAc, 99:1) to provide the allyl vinyl ethers.

**tert-Butyl (E)-2-((3-bromobut-2-enyl)oxy)acrylate (11):**

![Chemical structure](image)

The reaction of 7 (478 mg, 1.71 mmol) and the Petasis reagent (5.60 mL of 0.67 M solution in toluene, 3.76 mmol) for 15 min according to the general procedure, provided after purification by flash column chromatography 190 mg (40%) of 11 as a yellow oil; R_f = 0.26 (hexanes/EtOAc, 96:4).

IR (neat): 2979, 2932, 1729, 1370, 1209, 1153, 1125, 845 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 6.12 (tq, 1H, J = 6.8, 1.3, CH₃C=CH), 5.29 (d, 1H, J = 2.6, C=CHH), 4.53 (d, 1H, J = 2.6, C=CHH), 4.26 (br d, 2H, J = 6.8, OCH₂), 2.32-2.29 (m, 3H, CH₃C=CH), 1.52 (s, 9H, C(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃): δ 162.0 (C=O), 151.7 (C=CH₂), 126.5 (C=CH-CH₂), 125.2 (C=CH-CH₂), 94.0 (C=CH₂), 82.0 (C(CH₃)₃), 65.0 (OCH₂), 28.0 (C(CH₃)₃), 24.0 (CH₃C=C); HRMS (ESI, pos.): m/z 276.0362 (276.0361 calc. for C₁₁H₁₇BrO₃ (M+)).

**tert-Butyl (Z)-2-((3-bromobut-2-enyl)oxy)acrylate (12):**

![Chemical structure](image)

The reaction of 8 (900 mg, 3.22 mmol) and the Petasis reagent (10.6 mL of 0.67 M solution in toluene, 7.08 mmol) for 15 min according to the general procedure, provided after purification by flash column chromatography 540 mg (61%) of 12 as a yellow oil; R_f = 0.27 (hexanes/EtOAc, 95:5).

IR (neat): 2978, 2930, 1727, 1620, 1392, 1368, 1207, 1152, 1036, 849 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 5.97-5.90 (m, 1H, CH₃C=CH), 5.28 (d, 1H, J = 2.6, C=CHH), 4.58 (d, 1H, J = 2.6, C=CHH), 4.45-4.39 (m, 2H, OCH₂), 2.33 (apparent q, 3H, J = 1.3, CH₃C=CH), 1.52 (s, 9H, C(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃): δ 162.1 (C=O), 151.5 (C=CH₂), 124.9 (C=CH-CH₂), 124.5 (C=CH-CH₂), 93.9 (C=CH₂), 82.0 (C(CH₃)₃), 68.2 (OCH₂), 28.8 (CH₃C=C), 28.0 (C(CH₃)₃); HRMS (ESI, pos.): m/z 276.0356 (276.0361 calc. for C₁₁H₁₇BrO₃ (M+)).

**tert-Butyl (E)-2-((3-iodobut-2-en-1-yl)oxy)acrylate (13):**

![Chemical structure](image)

The reaction of 9 (100 mg, 0.30 mmol) and the Petasis reagent (1 mL of 0.67 M solution in toluene, 0.67 mmol) for 5 min according to the general procedure provided the crude product. This was
dissolved in dichloromethane (5 mL), the solution was washed with aqueous HCl (0.2 M, 2 x 3 mL) and the organic phase was concentrated. The residue was purified by flash column chromatography to provide 54 mg (56%) of 13 a yellow oil; $R_f = 0.21$ (hexanes/EtOAc, 96:4).

IR (neat): 2979, 2931, 1727, 1619, 1369, 1328, 1284, 1254, 1149, 1069, 1023, 996, 842 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$): δ 6.41 (tq, 1H, $J = 6.5, 1.5$, CH$_3$C=CH), 5.28 (d, 1H, $J = 2.6$, C=CHH), 4.53 (d, 1H, $J = 2.6$, C=CHH), 4.24 (br d, 2H, $J = 6.5$, OCH$_2$), 2.47 (m, 3H, CH$_3$C=CH), 1.50 (s, 9H, C(CH$_3$)$_3$); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 161.9 (C=O), 151.5 (C=CH$_2$), 135.2 (C=C=CHH), 99.1 (C=C=CHH), 93.8 (C=C=CHH), 82.0 (C(CH$_3$)$_3$), 65.2 (OCH$_2$), 28.3 (CH$_3$C=CH), 28.0 (C(CH$_3$)$_3$); HRMS (APPI, pos.): $m/z$ 324.0236 (324.0222 calc. for C$_{11}$H$_{17}$IO$_3$ (M$^+$)).

**tert-Butyl (Z)-2-((3-iodobut-2-en-1-yl)oxy)acrylate (14):**

The reaction of 10 (270 mg, 0.83 mmol) and the Petasis reagent (2.8 mL of 0.67 M solution in toluene, 1.87 mmol) for 5 min according to the general procedure provided the crude product. This was dissolved in dichloromethane (10 mL) and the solution was washed with aqueous HCl (0.2 M, 2 x 10 mL) and the organic phase was concentrated. The residue was purified by flash column chromatography to provide 153 mg (57%) of 14 a yellow oil; $R_f = 0.24$ (hexanes/EtOAc, 96:4).

IR (neat): 2978, 2934, 1724, 1618, 1392, 1368, 1254, 1206, 1148, 1085, 1031, 847 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$): δ 5.89-5.82 (m, 1H, CH$_3$C=CH), 5.28 (d, 1H, $J = 2.6$, C=CHH), 4.57 (d, 1H, $J = 2.6$, C=CHH), 4.36-4.30 (m, 2H, OCH$_2$), 2.54 (apparent q, 3H, $J = 1.5$, C(CH$_3$)$_3$), 1.52 (s, 9H, C(CH$_3$)$_3$); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 162.0 (C=O), 151.5 (C=C=CH$_2$), 130.7 (C=C=CH$_2$), 102.3 (C=C=CH$_2$), 94.1 (C=C=CH$_2$), 82.0 (C(CH$_3$)$_3$), 73.0 (OCH$_2$), 33.6 (CH$_3$C=CH), 28.0 (C(CH$_3$)$_3$); HRMS (APPI, pos.): $m/z$ 324.0231 (324.0222 calc. for C$_{11}$H$_{17}$IO$_3$ (M$^+$)).

**General Procedure 1 for Suzuki-Miyaura cross-coupling of 13 and 14 with arylboronic acids:**

To the iodoallyl vinyl ether were added the arylboronic acid, KOH, Ag$_2$O and dioxane (purged with N$_2$ for 15 min) at room temperature followed by PdCl$_2$(dpdf)$\cdot$CH$_2$Cl$_2$. The mixture was heated with stirring at 80 °C until consumption of the iodo allyl vinyl ether (TLC). After cooling to ambient temperature, diethyl ether was added and the resulting solution was washed with brine, dried over Na$_2$SO$_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel.

**General Procedure 2 for Suzuki-Miyaura cross-coupling of 13 and 14 with alkylboronic acids:**

To the iodoallyl vinyl ether were added the alkylboronic acid, K$_2$CO$_3$, Ag$_2$O and THF (purged with N$_2$ for 15 min) at room temperature followed by freshly prepared Pd(PPh$_3$)$_4$. The mixture was heated to reflux until consumption of the iodo allyl vinyl ether (TLC). After cooling
to ambient temperature, H₂O (1 mL) was added and the mixture was extracted with diethyl ether (3 x 2 mL) and the combined extracts were washed with saturated NaHCO₃, brine, dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel.

**tert-Butyl (E)-2-(3-methylhept-2-enyloxy)acrylate (15a):**

![Chemical structure](image)

The reaction of 13 (82 mg, 0.25 mmol), butylboronic acid (28 mg, 0.27 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), Ag₂O (145 mg, 0.62 mmol) and K₂CO₃ (103 mg, 0.74 mmol) in THF (1 mL) for 1 h according to General Procedure 2 provided, after purification by flash chromatography on silica gel (hexanes/EtOAc, 95:5), 39 mg (63%) of 15a as a clear oil; Rₜ = 0.23 (hexanes/EtOAc, 97:3).

IR (neat): 2932, 1726, 1617, 1263, 1153, 909 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 5.42 (tq, 1H, J = 6.4, 1.3, CH₃C=C), 5.23 (d, 1H, J = 2.3, C=CH₂), 4.53 (d, 1H, J = 2.3, C=C), 4.31 (br d, 2H, J = 6.6, OCH₂), 2.06-1.98 (m, 2H, C=CH₂), 1.67 (s, 3H, CH₃C=C), 1.51 (s, 9H, C(CH₃)₃), 1.46-1.24 (m, 4H, C₂H₂), 0.90 (t, 3H, J = 7.2, CH₂CH₂); ¹³C NMR (75 MHz, CDCl₃): δ 162.3 (C=O), 152.1 (C=CH₂), 141.0 (C≡CH₂), 118.8 (CH₃C=CH), 93.1 (C=CH₂), 81.6 (C(CH₃)₂), 65.5 (OCH₂), 39.2 (C(C(CH₃)₃), 29.8 (CH₂CH₂ or CH₃CH₂CH₂), 28.0 (C(CH₃)₃), 22.4 (CH₃CH₂CH₂ or CH₃CH₂CH₂), 16.6 (CH₃C=CH or CH₃CH₂CH₂), 14.0 (CH₃CH₂CH₂ or CH₃C=CH); HRMS (APPI, neg.): m/z 254.1875 (254.1882 calc. for C₁₅H₂₆O₃ (M⁻)).

**tert-Butyl (E)-2-(3,5-dimethylhex-2-enyloxy)acrylate (15b):**

The reaction of 13 (80 mg, 0.25 mmol), (2-methylpropyl)boronic acid (28 mg, 0.27 mmol), Pd(PPh₃)₄ (28 mg, 0.025 mmol), Ag₂O (142 mg, 0.61 mmol) and K₂CO₃ (102 mg, 0.74 mmol) in THF (1 mL) for 2h according to General Procedure 2 provided, after purification by flash chromatography on silica gel (hexanes/EtOAc, 95:5), 37 mg (61%) of 15b as a clear oil; Rₜ = 0.24 (hexanes/EtOAc, 97:3).

IR (neat): 2932, 2928, 2871, 1726, 1617, 1369, 1316, 1206, 1150, 1026, 847 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 5.40 (br t, 1H, J = 6.4, CH₃C=C), 5.23 (d, 1H, J = 2.3, C=CH₂), 4.53 (d, 1H, J = 2.3, C=C), 4.33 (br d, 2H, J = 6.4, OCH₂), 1.89 (br d, 2H, J = 7.4, CH₂CH(CH₃)₂), 1.81-1.71 (m, 1H, CH(CH₃)₂), 1.66-1.62 (br s, 3H, CH₃C=CH), 1.51 (s, 9H, C(CH₃)₃), 0.85 (d, 6H, J = 6.5, CH(CH₃)₂); ¹³C NMR (75 MHz, CDCl₃): δ 162.3 (C=O), 152.1 (C=CH₂), 139.8 (i-BuC=CH), 120.3 (CH₃C=CH), 93.1 (C=CH₂), 81.6 (C(CH₃)₃), 65.5 (OCH₂), 49.2 (CH₂CH(CH₃)₂), 28.0 (C(CH₃)₃), 26.0 (CH(CH₃)₂), 22.4 (CH(CH₃)₂), 16.5 (CH₃C=CH); HRMS (APPI, pos.): m/z 254.1875 (254.1882 calc. for C₁₅H₂₆O₃ (M⁺)).
**tert-Butyl (E)-2-(3-cyclopropylbut-2-enyloxy)acrylate (15c):**

The reaction of **13** (80 mg, 0.25 mmol), cyclopropyl boronic acid (23 mg, 0.27 mmol), Pd(PPh₃)₄ (28 mg, 0.024 mmol), Ag₂O (142 mg, 0.61 mmol) and K₂CO₃ (102 mg, 0.74 mmol) in THF (1 mL) for 1 h according to General Procedure 2 provided, after purification by flash chromatography on silica gel (hexanes/EtOAc, 95:5), 37 mg (65%) of **15c** as a clear oil; Rᵢ = 0.23 (hexanes/EtOAc, 97:3).

IR (neat): 2978, 2932, 1725, 1616, 1368, 1319, 1206, 1148, 1019 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 5.51-5.43 (br t, 1H, J = 6.8, CH₃C=CH₂), 5.23 (d, 1H, J = 2.3, C=CH₂), 4.53 (d, 1H, J = 2.3, C=CH₂), 4.31 (d, 2H, J = 6.5, OC₂H₂), 1.57 (s, 3H, C(CH₃)₃), 1.51 (s, 9H, C(C(CH₃)₃)), 1.45-1.36 (m, 1H, CH₃CH₂CH₂), 0.64-0.54 (m, 2H, CH₂CH₂), 0.53-0.44 (m, 2H, C(CH₂)₂); ¹³C NMR (75 MHz, CDCl₃): δ 162.3 (C=O), 152.0 (C=CH₂), 141.5 (CH₃C=CH), 117.3 (CH₃C=CH), 93.1 (C=CH₂), 81.7 (C(CH₃)₃), 65.4 (OC₂H₂), 28.0 (C(CH₃)₃), 15.7 (CH₃CH₂CH₂ or CH₃), 14.4 (CH₃ or CHCH₂CH₂), 4.74 (CH₂CH₂); HRMS (APPI, neg.): m/z 238.1569 (238.1569 calc. for C₁₄H₂₂O₃ (M⁻)).

**tert-Butyl (E)-2-(3-(naphthalen-2-yl)but-2-enyloxy)acrylate (15d):**

The reaction of **13** (110 mg, 0.34 mmol), 2-naphthylboronic acid (58 mg, 0.34 mmol), PdCl₂(dppf)-CH₂Cl₂ (4.10 mg, 0.005 mmol), Ag₂O (79 mg, 0.34 mmol) and KOH (19 mg, 0.34 mmol) in dioxane (1.2 mL) for 40 min according to General Procedure 1 provided, after purification by flash chromatography on silica gel (hexanes/EtOAc, 95:5), 75 mg (68%) of **15d** as a clear oil; Rᵢ = 0.22 (hexanes/EtOAc, 95:5).

IR (neat): 2978, 2932, 1724, 1616, 1368, 1349, 1327, 1206, 1148, 1022, 850, 812 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.86-7.77 (m, 4H, ArH), 7.6 (dd, 1H, J = 8.6, 1.9, ArH), 7.50-7.40 (m, 2H, ArH), 6.17 (tq, 1H, J = 6.1, 1.3, CC=CH₂), 5.31 (d, 1H, J = 2.4, C=CH₂), 4.64 (d, 1H, J = 2.4, C=CH₂), 4.59 (d, 2H, J = 6.1, OCH₂), 2.20 (m, 3H, CH₃C=CH), 1.54 (s, 9H, C(CH₃)₃), 13C NMR (75 MHz, CDCl₃): δ 162.3 (C=O), 152.0 (C=CH₂), 139.7 (ArCᵢₚs₀), 138.4 (ArC=C), 133.4 (ArCᵢₚs₀), 132.8 (ArCᵢₚs₀), 128.2 (ArC), 127.8 (ArC), 127.5 (ArC), 126.2 (ArC), 125.9 (ArC), 124.5 (ArC), 124.2 (ArC), 122.9 (ArC=CH₂), 93.6 (C=CH₂), 81.9 (C(CH₃)₃), 66.1 (OCH₂), 28.0 (CH₃)₃, 16.3 (CH₃); HRMS (APPI, pos.): m/z 324.1722 (324.1725 calc. for C₂₁H₂₄O₃ (M⁺)).
**tert-Butyl (E)-2-(3-phenylbut-2-enyloxy)acrylate (15e):**

![Chemical structure of 15e]

The reaction of 13 (100 mg, 0.31 mmol), phenylboronic acid (38 mg, 0.31 mmol), PdCl2(dppf)·CH2Cl2 (3.70 mg, 0.004 mmol), Ag2O (72 mg, 0.31 mmol) and KOH (56 mg, 0.31 mmol) in dioxane (1.1 mL) for 20 min according to General Procedure 1 provided, after purification by flash chromatography on silica gel (hexanes/EtOAc, 95:5), 73 mg (87%) of 15e as a clear oil; Rf = 0.21 (hexanes/EtOAc, 97:3).

IR (neat): 2979, 2931, 1726, 1618, 1369, 1337, 1317, 1207, 1150, 1032, 848 cm⁻¹; ¹H NMR (300 MHz, CDCl3): δ 7.44-7.38 (m, 2H, ArH), 7.36-7.26 (m, 3H, ArH), 6.00 (tq, 1H, J = 6.2, 1.3, CC=C=H), 5.29 (d, 1H, J = 2.4, C=CH), 4.60 (d, 1H, J = 2.4, C=CH), 4.53 (d, 2H, J = 6.2, OCH₂), 2.11-2.07 (m, 3H, C₃H₇C=C), 1.52 (s, 9H, C(C₃H₃)₃); ¹³C NMR (75 MHz, CDCl₃): δ 162.3 (C=O), 159.1 (ArCipso), 152.0 (C=CH₂), 142.5 (ArCipso), 138.6 (PhC=CH), 128.3 (2 × ArC), 127.4 (ArC), 125.8 (2 × ArC), 122.3 (PhC=CH), 93.5 (C=CH₂), 81.8 (C(CH₃)₃), 66.0 (OCH₂), 28.0 (C(CH₃)₃), 16.4 (CH₃C=CH); HRMS (APPI, pos.): m/z 274.1581 (274.1569 calc. for C₁₇H₂₂O₃ (M⁺)).

**tert-Butyl (E)-2-((3-(4-methoxyphenyl)but-2-en-1-yl)oxy)acrylate (15f):**

The reaction of 13 (85 mg, 0.26 mmol), 4-methoxyphenylboronic acid (39 mg, 0.26 mmol), PdCl2(dppf)·CH₂Cl₂ (3.30 mg, 0.004 mmol), Ag₂O (60 mg, 0.26 mmol) and KOH (14 mg, 0.26 mmol) in dioxane (1 mL) for 35 min according to General Procedure 1 provided, after purification by flash chromatography on silica gel (hexanes/EtOAc, 9:1), 60 mg (77%) of 15f as a clear oil; Rf = 0.21 (hexanes/EtOAc, 97:3).

IR (neat): 2978, 2932, 1726, 1618, 1512, 1370, 1248, 1207, 1152, 1032 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.36 (d, 2H, J = 8.8, ArH), 6.85 (d, 2H, J = 8.8, ArH), 5.93 (tq, 1H, J = 6.3, 1.3, CC=CH), 5.28 (d, 1H, J = 2.4, C=CH₂), 4.60 (d, 1H, J = 2.4, C=CH₂), 4.51 (d, 2H, J = 6.3, OCH₂), 3.81 (s, 3H, OCH₃), 2.07 (m, 3H, CH₃C=C), 1.52 (s, 9H, C(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃): δ 162.2 (C=O), 159.1 (ArCipso), 152.0 (C=CH₂), 138.1 (ArCipso), 135.0 (ArC=CH), 126.9 (2 × ArC), 120.6 (ArC=CH), 113.6 (2 × ArC), 93.4 (C=CH₂), 81.8 (C(CH₃)₃), 66.0 (OCH₂), 55.3 (OCH₃), 28.0 (CH₃), 16.3 (CH₃); HRMS (APPI, neg.): m/z 304.1669 (304.1675 calc. for C₁₈H₂₂O₄ (M⁺)).
**tert-Butyl (E)-2-(3-(3-methoxyphenyl)but-2-enyloxy)acrylate (15g):**

\[
\text{MeO}\quad \begin{array}{c}
\text{O} \\
\text{COO'}\text{Bu}
\end{array}
\]

The reaction of 13 (114 mg, 0.35 mmol), 3-methoxyphenylboronic acid (53 mg, 0.35 mmol), PdCl\(_2\)(dpff)·CH\(_2\)Cl\(_2\) (4.10 mg, 0.005 mmol), Ag\(_2\)O (81 mg, 0.35 mmol) and KOH (20 mg, 0.35 mmol) in dioxane (1.2 mL) for 20 min according to General Procedure 1 provided, after purification by flash chromatography on silica gel (hexanes/EtOAc, 93:7), 87 mg (82%) of 15g as a clear oil; \(R_f = 0.22\) (hexanes/EtOAc, 93:7).

IR (neat): 2979, 2936, 1725, 1614, 1580, 1370, 1319, 1288, 1207, 1149, 1038 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)): δ 7.23 (t, 1H, \(J = 8.0\), Ar\(H\)), 7.03-6.99 (m, 1H, Ar\(H\)), 6.96-6.94 (m, 1H, Ar\(H\)), 6.81 (br dd, 1H, \(J = 8.2, 2.5\), Ar\(H\)), 6.01 (tq, 1H, \(J = 6.1, 1.3\), CH\(_3\)C=CH\(H\)), 5.29 (d, 1H, \(J = 2.4\), C=CH\(H\)), 4.60 (d, 1H, \(J = 2.4\), C=CH\(H\)), 4.52 (br dd, 2H, \(J = 6.1, 1.3\), OCH\(_2\)), 3.82 (s, 3H, OCH\(_3\)); \(^13\)C NMR (75 MHz, CDCl\(_3\)): δ 162.2 (C=O), 159.5 (ArC ipso), 152.0 (C=CH\(_2\)), 144.1 (ArC ipso), 138.4 (CH\(_3\)C=CH), 129.2 (ArC), 122.5 (CH\(_3\)C=CH), 118.3 (ArC), 112.8 (ArC), 111.6 (ArC), 93.5 (C=CH\(_2\)), 81.8 (C(CH\(_3\))\(_3\)), 65.9 (OCH\(_2\)), 55.3 (OCH\(_3\)), 28.0 (CH\(_3\))\(_3\), 16.4 (CH\(_3\)); HRMS (APPI, neg.): m/z 304.1668 (304.1675 calc. for C\(_{18}\)H\(_{24}\)O\(_4\) (M\(^+\))).

**tert-Butyl (E)-2-((3-(thiophen-2-yl)but-2-en-1-yl)oxy)acrylate (15h):**

\[
\text{S} \\
\text{O} \\
\text{COO'}\text{Bu}
\]

The reaction of 13 (101 mg, 0.31 mmol), 2-thienylboronic acid (0.31 mmol), PdCl\(_2\)(dpff)·CH\(_2\)Cl\(_2\) (0.004 mmol), Ag\(_2\)O (0.31 mmol) and KOH (0.31 mmol) in dioxane (1.1 mL) for 4h according to General Procedure 1 provided, after purification by flash chromatography on silica gel (hexanes/EtOAc, 95:5), 37 mg (43%) of 15h as clear oil; \(R_f = 0.20\) (hexanes/EtOAc, 97:3).

IR (neat): 2979, 1723, 1617, 1369, 1315, 1206, 1148, 849 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)): δ 7.16 (dd, 1H, \(J = 5.1, 1.2\), Ar\(H\)), 7.05 (dd, 1H, \(J = 3.6, 1.2\), Ar\(H\)), 6.97 (dd, 1H, \(J = 5.1, 3.6\), Ar\(H\)), 6.13 (tq, 1H, \(J = 6.4, 1.3\), CH\(_3\)C=CH\(H\)), 5.29 (d, 1H, \(J = 2.5\), C=CH\(H\)), 4.59 (d, 1H, \(J = 2.5\), C=CH\(H\)), 4.50 (br d, 2H, \(J = 6.4\), OCH\(_2\)), 2.12-2.09 (m, 3H, CH\(_3\)C=CH\(H\)), 1.52 (s, 9H, C(CH\(_3\))\(_3\)); \(^13\)C NMR (75 MHz, CDCl\(_3\)): δ 162.2 (C=O), 152.0 (C=CH\(_2\)), 146.4 (ArC ipso), 132.7 (CH\(_3\)C=CH), 127.3 (CH\(_3\)C=CH), 124.3 (ArC), 123.4 (ArC), 120.5 (ArC), 93.6 (C=CH\(_2\)), 81.9 (C(CH\(_3\))\(_3\)), 65.5 (OCH\(_2\)), 28.0 (CH\(_3\))\(_3\), 16.3 (CH\(_3\)); HRMS (APPI, neg.): m/z 280.1120 (280.1133 calc. for C\(_{18}\)H\(_{20}\)O\(_3\)S (M\(^+\))).
**tert-Butyl (E)-2-((3-2-cyanophenyl)but-2-en-1-yl)oxy)acrylate (15i):**

The reaction of 13 (90 mg, 0.27 mmol), 2-cyanophenylboronic acid (0.27 mmol), PdCl₂(dppf)·CH₂Cl₂ (0.004 mmol), Ag₂O (0.27 mmol) and KOH (0.27 mmol) in dioxane (1 mL) for 4h according to General Procedure 1 provided, after purification by flash chromatography on silica gel (hexanes/EtOAc, 9:1), 38 mg (47%) of 15i as clear oil; Rᶠ = 0.20 (hexanes/EtOAc, 93: 7).

IR (neat): 2979, 2933, 2225, 1724, 1619, 1370, 1336, 1317, 1288, 1206, 1148, 1030 cm⁻¹;¹H NMR (300 MHz, CDCl₃): δ 7.66 (dd, 1H, J = 8.0, 1.4, ArH), 7.54 (dt, 1H, J = 7.7, 1.4, ArH), 7.38-7.32 (m, 1H, ArH), 5.87 (tq, 1H, J = 6.0, 1.4, CC=C), 5.32 (d, 1H, J = 2.6, C=CH), 4.64 (d, 1H, J = 2.6, C=CH₂), 4.55 (d, 2H, J = 6.0, OCH₂), 3.81 (s, 3H, OCH₃), 2.15 (m, 3H, CH₃C=C), 1.52 (s, 9H, C(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃): δ 162.1 (C=O), 151.8 (C=CH₂), 148.2 (ArCₐρso), 136.9 (ArC=CH), 133.3 (ArC), 132.6 (ArC), 128.5 (ArC), 127.6 (ArC=CH or ArC), 127.5 (ArC or ArC=CH), 118.4 (CN), 110.6 (ArCₐρso (C-CN)), 93.8 (C=CH₂), 81.9 (C(CH₃)₃), 65.4 (OCH₂), 28.0 (CH₃), 18.0 (CH₃); HRMS (APPI, neg.): m/z 299.1520 (299.1521 calc. for C₁₈H₂₁NO₃ (M⁺)).

**tert-Butyl (E)-2-((3-(4-bromophenyl)but-2-en-1-yl)oxy)acrylate (15j):**

The reaction of 13 (97 mg, 0.30 mmol), 4-bromophenylboronic acid (60 mg, 0.30 mmol), PdCl₂(dppf)·CH₂Cl₂ (3.30 mg, 0.004 mmol), Ag₂O (69 mg, 0.30 mmol) and KOH (17 mg, 0.30 mmol) in dioxane (1.1 mL) for 40 min according to General Procedure 1 provided, after purification by flash chromatography on silica gel (hexanes/EtOAc, 9:1), 63 mg (60%) of 15j as a clear oil; Rᶠ = 0.26 (hexanes/EtOAc, 92:8).

IR (neat): 2979, 2932, 1724, 1617, 1484, 1368, 1335, 1316, 1206, 1148, 1007, 848, 812 cm⁻¹;¹H NMR (300 MHz, CDCl₃): δ 7.43 (d, 2H, J = 8.5, ArH), 7.27 (d, 2H, J = 8.5, ArH), 6.00 (tq, 1H, J = 6.1, 1.3, CC=CH), 5.29 (d, 1H, J = 2.5, C=CHH), 4.59 (d, 1H, J = 2.5, C=CHH), 4.50 (d, 2H, J = 6.1, OCH₂), 2.06 (m, 3H, CH₃C=C), 1.52 (s, 9H, C(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃): δ 162.1 (C=O), 151.9 (C=CH₂), 141.4 (ArCₐρso), 137.6 (ArC=CH), 131.4 (2 x ArC), 127.4 (2 x ArC), 122.9 (ArCₐρso (C-Br) or ArC=CH), 121.3 (ArC=CH or ArCₐρso (C-Br)), 93.5 (C=CH₂), 81.9 (C(CH₃)₃), 65.8 (OCH₂), 28.0 (CH₃), 16.3 (CH₃); HRMS (APPI, neg.): m/z 352.0684 (352.0674 calc. for C₁₇H₂₁BrO₃ (M⁺)).
**tert-Butyl (Z)-2-(3-methylhept-2-enyloxy)acrylate (16a):**

\[
\begin{align*}
&\text{The reaction of 14 (75 mg, 0.23 mmol), butylboronic acid (26 mg, 0.25 mmol), Pd(PPh_3)_4 (26 mg, 0.023 mmol), Ag}_2\text{O (133 mg, 0.57 mmol) and K}_2\text{CO}_3 (95 mg, 0.69 mmol) in THF (1 mL) for 1 h according to General Procedure 2 provided, after purification by flash chromatography on silica gel (hexanes/EtOAc, 95:5), 38 mg (67%) of 16a as a clear oil; } R_f = 0.24 \text{ (hexanes/EtOAc, 97:3).}
\end{align*}
\]

IR (neat): 2961, 2931, 2867, 1729, 1617, 1370, 1207, 1154, 848 cm\(^{-1}\); 1H NMR (300 MHz, CDCl\(_3\)): δ 5.46-5.41 (br t, 1H, \(J = 6.3\), CH\(_3\)C=CH\(_2\)), 5.23 (d, 1H, \(J = 2.3\), C=CH\(_2\)), 4.53 (d, 1H, \(J = 2.3\), C=CH\(_2\)), 4.28 (br d, 2H, \(J = 6.6\), OCH\(_2\)), 2.06 (t, 2H, \(J = 7.3\), CH\(_2\)CH(CH\(_3\))\(_2\)), 1.74 (m, 3H, C=CH\(_2\)H), 1.51 (s, 9H, C(CH\(_3\))\(_3\)), 1.44-1.26 (m, 4H, CH\(_2\)CH(CH\(_3\))\(_2\)); 13C NMR (75 MHz, CDCl\(_3\)): δ 162.2 (C=O), 152.1 (CH\(_3\)C=CH\(_2\)), 141.7 (BuC=C), 119.4 (C=CH), 92.9 (C=CH\(_2\)), 81.6 (C(CH\(_3\))\(_3\)), 65.0 (OCH\(_2\)), 32.0, 30.2, 27.9, 23.4, 22.6, 13.9; HRMS (APPI, neg.): m/z 254.1879 (254.1882 calc. for C\(_{15}\)H\(_{26}\)O\(_3\) (M\(^+\))).

**tert-Butyl (Z)-2-(3,5-dimethylhex-2-enyloxy)acrylate (16b):**

\[
\begin{align*}
&\text{The reaction of 14 (50 mg, 0.15 mmol), (2-methylpropyl)boronic acid (17 mg, 0.014 mmol), Pd(PPh_3)_4 (17 mg, 0.014 mmol), Ag}_2\text{O (87 mg, 0.37 mmol) and K}_2\text{CO}_3 (62 mg, 0.45 mmol) in THF (1 mL) for 3 h according to General Procedure 2 provided, after purification by flash chromatography on silica gel (hexanes/EtOAc, 95:5), 24 mg (63%) of 16b as a clear oil; } R_f = 0.24 \text{ (hexanes/EtOAc, 97:3).}
\end{align*}
\]

IR (neat): 2957, 2930, 2871, 1729, 1617, 1369, 1317, 1254, 1206, 1150, 1019 cm\(^{-1}\); 1H NMR (300 MHz, CDCl\(_3\)): δ 5.54-5.46 (br t, 1H, \(J = 6.5\), CH\(_3\)C=CH\(_2\)), 5.23 (d, 1H, \(J = 2.3\), C=CH\(_2\)), 4.28 (br d, 2H, \(J = 7.3\), OCH\(_2\)), 2.06 (t, 2H, \(J = 7.3\), CH\(_2\)CH(CH\(_3\))\(_2\)), 1.85-1.75 (m, 1H, CH(CH\(_3\))\(_2\)), 1.75-1.70 (m, 3H, CH\(_3\)C=C), 1.51 (s, 9H, C(CH\(_3\))\(_3\)), 0.86 (d, 6H, \(J = 6.5\), CH(CH\(_3\))\(_2\)); 13C NMR (75 MHz, CDCl\(_3\)): δ 162.3 (C=O), 152.1 (CH\(_3\)C=CH\(_2\)), 140.4 (iBuC=C), 120.7 (C=CH), 93.0 (C=CH\(_2\)), 81.7 (C(CH\(_3\))\(_3\)), 65.1 (OCH\(_2\)), 41.6 (CH\(_2\)CH(CH\(_3\))\(_2\)), 28.0 (C(CH\(_3\))\(_3\)), 26.7 (CH(CH\(_3\))\(_2\) or CH(CH\(_3\))\(_3\)), 23.7 (CH\(_3\)C=C or CH(CH\(_3\))\(_2\)), 22.5 (CH(CH\(_3\))\(_2\)); HRMS (APPI, pos.): m/z 254.1882 (254.1882 calc. for C\(_{15}\)H\(_{26}\)O\(_3\) (M\(^+\))).
**tert-Butyl (Z)-2-(3-(3,4-dimethoxyphenyl)but-2-enyloxy)acrylate (16c):**

The reaction of 14 (88 mg, 0.27 mmol), 3,4-dimethoxyphenylboronic acid (49 mg, 0.27 mmol), PdCl₂(dppf)·CH₂Cl₂ (3.30 mg, 0.004 mmol), Ag₂O (62 mg, 0.27 mmol) and KOH (15 mg, 0.27 mmol) in dioxane (1 mL) for 30 min according to General Procedure 1 provided, after purification by flash chromatography on silica gel (hexanes/EtOAc, 93:7), 60 mg (67%) of 16c as a clear oil; R_f = 0.21 (hexanes/EtOAc, 95:5).

IR (neat): 2976, 2937, 1724, 1616, 1513, 1460, 1370, 1318, 1255, 1205, 1146, 1025, 911, 849 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 6.88-6.81 (d, 1H, J = 8.0, ArH), 6.79-6.72 (m, 2H, ArH), 5.78-5.72 (tq, 1H, J = 7.0, 1.4, CC=CH₂), 5.16 (d, 1H, J = 2.3, CC=CH₂), 4.37 (d, 1H, J = 2.3, CC=CH₂), 4.20 (br dd, 2H, J = 7.0, 1.1, CH₂), 3.89 (s, 3H, ArOC₃), 3.85 (s, 3H, ArOC₃), 2.10 (m, 3H, C=CC₃), 1.51 (s, 9H, C(C₃)₃); ¹³C NMR (75 MHz, CDCl₃): δ 162.2 (C=O), 151.7 (ArCipso), 148.5 (ArCipso), 148.3 (C=CH₂), 142.4 (PhC=CH), 133.2 (ArCipso), 121.0 (ArC=CH), 120.0 (ArC), 111.2 (ArC), 110.9 (ArC), 93.2 (C=CH₂), 81.7 (C(CH₃)₃), 66.1 (CH₂-O), 55.87 (OCH₃), 55.80 (OCH₃), 28.0 (CH₃), 25.3 (CH₃); HRMS (APPI, pos.): m/z 334.1778 (334.1780 calc. for C₁₉H₂₆O₅ (M⁺)).

**tert-Butyl (Z)-2-(3-(4-(benzyloxycarbonylamino)phenyl)but-2-enyloxy)acrylate (16d):**

The reaction of 14 (95 mg, 0.29 mmol), 4-Cbz-aminophenylboronic acid boronic acid (79 mg, 0.29 mmol), PdCl₂(dppf)·CH₂Cl₂ (3.60 mg, 0.004 mmol), Ag₂O (67 mg, 0.29 mmol) and KOH (16 mg, 0.29 mmol) in dioxane (1.1 mL) for 30 min according to General Procedure 1 provided, after purification by flash chromatography on silica gel (hexanes/EtOAc, 85:15), 102 mg (84%) of 16d as a clear oil; R_f = 0.25 (hexanes/EtOAc, 85:15); IR (neat): 3350, 2977, 1710, 1614, 1593, 1525, 1316, 1208, 1149, 1050 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.45-7.27 (br m, 7H, ArH), 7.12 (br d, 2H, ArH, J = 6.8), 6.95-6.65 (br, 1H, NH) 5.73 (br t, 1H, J = 6.8, C=CH₂), 5.20 (br s, 2H, ArCH₂O), 5.15 (d, 1H, 2.3, C=CH₂H), 4.33 (d, 1H, 2.3, CC=CH₂H), 4.20 (br d, 2H, J = 6.8, OCH₂), 2.07 (br s, 3H, C=CC₃H₃), 1.50 (s, 9H, C(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃): δ 162.3 (C=O), 153.4 (C(O)NH₂), 151.6 (C=CH₂), 141.2 (ArCipso), 137.1 (ArCipso), 136.0 (ArCipso), 135.6 (PhC=CH), 128.6 (2 x ArC) 128.5 (2 x ArC), 128.38 (2 x ArC), 128.33 (2 x ArC), 121.6 (ArC=CH), 118.4
tert-Butyl (Z)-2-(3-phenylbut-2-enyloxy)acrylate (16e):

The reaction of 14 (100 mg, 0.30 mmol), phenylboronic acid (36 mg, 0.30 mmol), PdCl2(dppe)-CH2Cl2 (3.30 mg, 0.004 mmol), Ag2O (69 mg, 0.30 mmol) and KOH (17 mg, 0.30 mmol) in dioxane (1.1 mL) for 20 min according to General Procedure 1 provided, after purification by flash chromatography on silica gel (hexanes/Et2O, 9:1), 59 mg (72%) of 16e as a clear oil; Rf = 0.22 (hexanes/Et2O, 96:4); IR (neat): 2978, 2935, 1723, 1617, 1368, 1319, 1205, 1148, 912 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.38-7.23 (m, 3H, ArH), 7.21-7.14 (m, 2H, ArH), 5.77 (t, J = 6.7, 1.4, C=CCH2), 5.14 (d, J = 2.3, C=CHH), 4.33 (d, J = 2.3, C=CCHH), 4.21 (br dq, J = 6.7, 1.4 OC₂H), 2.10 (m, 3H, C₃H₃C=CH), 1.51 (s, 9H, COC(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃): δ 162.2 (C=O), 151.7 (C=CH₂), 141.8 (PhC=CH), 140.5 (ArCipso), 128.2 (2 x ArC), 127.7 (2 x ArC), 127.4 (ArC), 121.7 (PhC=CH), 93.2 (C=CH₂), 81.7 (C(CH₃)₃), 66.1 (CH₂O), 28.0 (CH₃)₃, 25.3 (C=CCH₃); HRMS (APPI, neg.): m/z 274.1556 (274.1569 calc. for C₁₇H₂₂O₃ (M⁻)).

tert-Butyl (Z)-2-((3-(furan-3-yl)but-2-en-1-yl)oxy)acrylate (16f):

The reaction of 14 (99 mg, 0.30 mmol), 3-furanylboronic acid (34 mg, 0.30 mmol), PdCl2(dppe)-CH2Cl2 (3.67 mg, 0.004 mmol), Ag2O (69 mg, 0.30 mmol) and KOH (17 mg, 0.30 mmol) in dioxane (1.2 mL) for 3h according to General Procedure 1 provided, after purification by flash chromatography on silica gel (hexanes/EtOAc, 97:3), 51 mg (65%) of 16f as a clear oil; Rf = 0.24 (hexanes/EtOAc, 97:3); IR (neat): 2923, 2853, 1727, 1619, 1456, 1368, 1320, 1256, 1206, 1152, 1023, 956, 873 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.41 (d, J = 1.4, ArH), 6.41 (t, J = 1.4, ArH), 5.71 (tq, J = 6.6, 1.3, CH₃C=CH), 5.23 (d, J = 2.4, C=CHH), 4.48 (d, J = 2.4, C=CHH), 4.37 (br m, 2H, J = 6.6, OCH₂), 2.04 (br q, 3H, J = 1.3, CH₃C=CH), 1.52 (s, 9H, C(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃): δ 162.2 (C=O), 151.7 (C=CH₂), 140.5 (ArC), 140.4 (ArC), 132.2 (CH₃C=CH or ArCipso), 124.3 (ArCipso or CH₃C=CH), 121.7 (CH₃C=CH), 110.1 (ArC), 93.4 (C=CH₂), 81.8 (C(CH₃)₃), 65.8 (OCH₂), 28.0 (C(CH₃)₃), 24.1 (CH₃C=CH); HRMS (APPI, pos.): m/z 264.1345 (264.1362 calc. for C₁₅H₂₆O₄ (M⁺)).
**tert-Butyl (Z)-2-(3-(biphenyl-4-yl)but-2-enyloxy)acrylate (16g):**

![Chemical Structure](image)

The reaction of 14 (98 mg, 0.30 mmol), 4-biphenylboronic acid (59 mg, 0.30 mmol), PdCl$_2$(dpff)·CH$_2$Cl$_2$ (3.70 mg, 0.004 mmol), Ag$_2$O (69 mg, 0.30 mmol) and KOH (17 mg, 0.30 mmol) in dioxane (1.1 mL) for 30 min according to General Procedure 1 provided, after purification by flash chromatography on silica gel (hexanes/EtOAc, 93:7), 70 mg (67%) of 16g as a clear oil; R$_f$ = 0.25 (hexanes/EtOAc, 93:7).

IR (neat): 2976, 2935, 1724, 1616, 1368, 1318, 1205, 1147, 1012 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$): δ 7.63-7.53 (m, 4H, ArH), 7.47-7.40 (m, 2H, ArH), 7.37-7.25 (m, 3H, ArH), 5.81 (tq, 1H, $J$ = 6.7, 1.4, C=CH), 5.17 (d, 1H, $J$ = 2.3, C=CH), 4.37 (d, 1H, $J$ = 2.3, C=CH), 4.27 (br dd, 2H, $J$ = 6.7, 1.2, OC$_2$H), 2.14 (m, 3H, C=CC$_3$), 1.51 (s, 9H, C(C$_3$H$_3$)$_3$); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 162.3 (C=O), 151.7 (C=CH$_2$), 141.4 (ArC$_{ipso}$), 140.7 (ArC$_{ipso}$), 140.2 (ArC$_{ipso}$), 139.5 (PhC=CH), 128.8 (2 x ArC), 128.2 (2 x ArC), 127.4 (ArC), 127.0 (2 x ArC), 126.9 (2 x ArC), 122.0 (ArC=CH), 93.3 (C=CH$_2$), 81.7 (C(CH$_3$)$_3$), 66.1 (OCH$_2$), 28.0 (CH$_3$)$_3$, 25.2 (CH$_3$); HRMS (APPI, neg.): m/z 423.2047 (423.2046 calc. for C$_{25}$H$_{29}$NO$_5$ (M$^+$)).

**tert-Butyl (Z)-2-(3-(naphthalen-1-yl)but-2-enyloxy)acrylate (16h):**

The reaction of 14 (101 mg, 0.31 mmol), 1-naphthylboronic acid (53 mg, 0.31 mmol), PdCl$_2$(dpff)·CH$_2$Cl$_2$ (3.80 mg, 0.004 mmol), Ag$_2$O (72 mg, 0.31 mmol) and KOH (17 mg, 0.31 mmol) in dioxane (1.1 mL) for 1 h according to General Procedure 1 provided, after purification by flash chromatography on silica gel (hexanes/EtOAc, 93:7), 80 mg (80%) of 16h as clear oil; R$_f$ = 0.22 (hexanes/EtOAc, 93:7).

IR (neat): 2975, 2934, 1724, 1617, 1368, 1316, 1205, 1147, 1020 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$): δ 7.90-7.74 (m, 3H, ArH), 7.51-7.40 (m, 3H, ArH), 7.27-7.22 (m, 1H, ArH), 6.02 (tq, 1H, $J$ = 6.4, 1.5, CH$_3$C=CH), 5.04 (d, 1H, $J$ = 2.4, C=CHH), 4.19 (d, 1H, $J$ = 2.4, C=CHH), 3.99-3.91 (br m, 2H, OC$_2$H), 2.16 (br q, 3H, $J$ = 1.4, CH$_3$C=CH), 1.48 (s, 9H, C(CH$_3$)$_3$); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 162.2 (C=O), 151.7 (C=CH$_2$), 140.0 (ArC$_{ipso}$), 138.8 (ArC=CH), 133.7 (ArC$_{ipso}$), 130.6 (ArC$_{ipso}$), 128.4 (ArC), 127.5 (ArC), 126.2 (ArC), 125.9 (ArC), 125.5 (ArC), 125.2 (ArC), 124.9 (ArC), 123.9 (ArC=CH), 93.2 (C=CH$_2$), 81.6 (C(CH$_3$)$_3$), 66.4 (OCH$_2$), 28.0 (C(CH$_3$)$_3$), 26.1 (CH$_3$C=CH); HRMS (APPI, neg.): m/z 324.1721 (324.1725 calc. for C$_{21}$H$_{26}$NO$_5$ (M$^+$)).
General procedure for the rearrangement of 15 to 17:

To a suspension of Cu(OTf)₂ in ether was added 15 and the mixture was stirred at ambient temperature for 1 h. To the resulting solution was added a solution of the allyl vinyl ether in ether. The resulting solution was stirred at ambient temperature for the specified time. The solution was concentrated and the residue was purified by flash chromatography on silica gel to provide 17.

**tert-Butyl (S)-4-methyl-2-oxo-4-vinloctanoate (17a):**

![Chemical Structure](image)

Treatment of 15a (60 mg, 0.24 mmol) with the complex derived from Cu(OTf)₂ (8.7 mg, 0.024 mmol) and (R,R)-2,2'-isopropylidene-bis(4-phenyl-2-oxazoline) (8 mg, 0.024 mmol) in ether (1 mL) for 92 h according to the general procedure provided, after purification by flash chromatography on silica gel (hexanes/EtOAc, 97:3), 35 mg (58%) of 17a as a clear oil; R_f = 0.27 (hexanes/EtOAc, 97:3).

IR (neat): 3084, 2958, 2930, 1720, 1460, 1370, 1283, 1257, 1155, 1056, 914, 866 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 5.81 (dd, 1H, J = 17.5, 10.8, CH=CH₂), 5.00 (dd, 1H, J = 10.8, 1.0, CH=CH₂), 4.93 (dd, 1H, J = 17.5, 1.0, CH=CH₂), 2.90 (d, 1H, J = 14.2, CH₂C(O)), 2.68 (d, 1H, J = 14.2, CH₂C(O)), 1.54 (s, 9H, C(CH₃)₃), 1.45-1.35 (m, 2H, CH₂CH₂), 1.30-1.15 (m, 4H, CH₂CH₂), 1.09 (s, 3H, CH₃), 0.88 (t, 3H, J = 7.0, CH₂CH₃); ¹³C NMR (75 MHz, CDCl₃): δ 195.2 (C(O)CO₂tBu), 161.3 (CO₂tBu), 145.1 (CH=CH₂), 112.6 (CH=CH₂), 83.7 (C(CH₃)₃), 47.9 (CH₂C(O)), 40.7 (CH₂), 39.8 (Cquat.), 27.8 (C(CH₃)₃), 26.2 (CH₂), 23.2 (CH₂), 22.7 (CH₃), 14.0 (CH₃); HRMS (APPI, pos.): m/z 254.1875 (254.1882 calc. for C₁₅H₂₆O₃ (M⁺)); HPLC: Chiralpak AS-H (hexane/i-PrOH, 99.5:0.5, flow rate 1 mL min⁻¹, λ= 254 nm): t_major = 3.70; t_minor 3.25 min; 98% ee.

**tert-Butyl (S)-4-methyl-2-oxo-4-phenylhex-5-enoate (17e):**

![Chemical Structure](image)

Treatment of 15e (30 mg, 0.11 mmol) with the complex derived from Cu(OTf)₂ (4 mg, 0.011 mmol) and (R,R)-2,2'-isopropylidenebis(4-phenyl-2-oxazoline) (3.70 mg, 0.011 mmol) in ether (0.5 mL) for 67 h according to the general procedure provided, after purification by flash chromatography on silica gel (hexanes/EtOAc, 98:2), 16 mg (53%) of 17e as a clear oil; R_f = 0.21 (hexanes/EtOAc, 98:2).

IR (neat): 3084, 2958, 2930, 1720, 1460, 1370, 1283, 1257, 1155, 1056, 914, 866 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.32-7.28 (m, 4H, ArH), 7.23-7.15 (m, 1H, ArH), 6.15 (dd, 1H, J = 17.4, 10.7, CH=CH₂), 5.14 (dd, 1H, J = 10.7, 0.8, CH=CHH), 5.09 (dd, 1H, J = 17.4, 0.8, CH=CHH), 3.29 (s,
2H, CH₂C(O)), 1.52 (s, 3H, CH₃), 1.45 (s, 9H, C(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃): δ 194.3 (C(O)CO₂tBu), 160.8 (CO₂tBu), 145.6 (ArCipso), 128.4 (2 x ArC), 126.5 (ArC), 126.3 (2 x ArC), 112.8 (CH=CH₂), 83.7 (C(CH₃)₃), 48.0 (CH₂C(O)), 43.6 (Ar-C-CH₃), 27.7 (C(CH₃)₃), 25.2 (Ar-C-CH₃); HRMS (APPI, pos.): m/z 274.1575 (274.1569 calc. for C₁₇H₂₂O₃ (M⁺)); HPLC: Chiralpak AD-H (hexane/i-PrOH, 99.6/0.4, flow rate 1 mL min⁻¹, λ= 254 nm): t_major = 6.77; t_minor 7.50 min; 45% ee.

tert-Butyl (S)-4-(4-bromophenyl)-4-methyl-2-oxohex-5-enoate (17j):

Treatment of 15j (50 mg, 0.14 mmol) with the complex derived from Cu(OTf)₂ (5.2 mg, 0.014 mmol) and (R,R)-2,2'-isopropylidenebis(4-phenyl-2-oxazoline) (4.8 mg, 0.014 mmol) in ether (0.5 mL) for 120 h according to the general procedure provided, after purification by flash chromatography on silica gel (hexanes/EtOAc, 98:2), 49 mg (48%) of 17j as a clear oil; R_f = 0.22 (hexanes/EtOAc, 98:2).

IR (neat): 2979, 2935, 1720, 1490, 1396, 1370, 1290, 1256, 1155, 1054, 1008, 921, 824 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.41 (d, 2H, J = 8.7, ArH), 7.18 (d, 2H, J = 8.7, ArH), 6.08 (dd, 1H, J = 17.4, 10.7, CH=CH₂), 5.15 (dd, 1H, J = 10.7, 0.7, CH=CHH), 5.08 (dd, 1H, J = 17.4, 0.7, CH=CHH), 3.26 (AB system, 2H, J = 15.3, C(CH₂)₃), 1.49 (s, 3H, CH₃), 1.46 (s, 9H, C(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃): δ 193.8 (C(O)CO₂tBu), 160.7 (CO₂tBu), 144.57 (ArCipso), 131.4 (2 x ArC), 128.3 (2 x ArC), 120.5 (ArC-Br), 113.2 (CH=CH₂), 84.0 (C(CH₃)₃), 47.8 (CH₂C(O)), 43.3 (Ar-C-CH₃), 27.7 (C(CH₃)₃), 25.2 (Ar-C-CH₃); HRMS (APPI, pos.): m/z 352.0667 (352.0674 calc. for C₁₇H₂₁BrO₃ (M⁺)); HPLC: Chiralpak AD-H (hexane/i-PrOH, 99.6/0.4, flow rate 1 mL min⁻¹, λ= 254 nm): t_major = 8.06; t_minor 9.04 min; 56% ee.

References

5. J. F. Payack, D. L. Hughes, D. Cai, I. F. Cottrell and T. R. Verhoeven Org. Prep. Proc. Int., 1995, 27, 707. In our studies, the purity of titanocene dichloride used to prepare the Petasis reagent was found to be critical for the successful methylenation of 9 and 10. The reported yields of 13 and 14 were obtained when 99+% pure, commercial titanocene dichloride was used. The use of titanocene dichloride with lower purity (97%, commercial) significantly reduced the yield of the methylenation reaction.
$\text{Br}^{\text{7}}\text{CO}_2\text{Bu}$

$^1\text{H NMR (300 MHz, CDCl}_3)$

$\text{Br}^{\text{7}}\text{CO}_2\text{Bu}$

$^{13}\text{C NMR (75 MHz, CDCl}_3)$
$^1$H NMR (300 MHz, CDCl$_3$)

$^1$C NMR (75 MHz, CDCl$_3$)
\[ \text{\(}^{1}H\text{ NMR (300 MHz, CDCl}\text{)} \text{)} \]

\[ \text{\(}^{13}C\text{ NMR (75 MHz, CDCl}\text{)} \text{)} \]
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$^{13}C$ NMR (75 MHz, CDCl$_3$)
1H NMR (300 MHz, CDCl₃)

13C NMR (75 MHz, CDCl₃)

GM-05-81 purified
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$^{13}$C NMR (75 MHz, CDCl$_3$)
$^{1}H$ NMR (300 MHz, CDCl$_3$)

$^{13}C$ NMR (75 MHz, CDCl$_3$)
$^{13}$C NMR (75 MHz, CDCl$_3$)

$^{1}$H NMR (300 MHz, CDCl$_3$)
15d

$^1$H NMR (300 MHz, CDCl$_3$)

15d

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^{1}$$H$ NMR (300 MHz, CDCl$_3$)

$^{13}$$C$ NMR (75 MHz, CDCl$_3$)
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$^{13}$C NMR (75 MHz, CDCl$_3$)

$^{1}$H NMR (300 MHz, CDCl$_3$)
**1H NMR (300 MHz, CDCl₃)**

![1H NMR Spectrum](image1)

**13C NMR (75 MHz, CDCl₃)**

![13C NMR Spectrum](image2)
16a

$^1$H NMR (300 MHz, CDCl$_3$)

16a

$^{13}$C NMR (75 MHz, CDCl$_3$)
**1H NMR (300 MHz, CDCl₃)**

**13C NMR (75 MHz, CDCl₃)**
1H NMR (300 MHz, CDCl₃)

13C NMR (75 MHz, CDCl₃)
$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
16e

$^{1}H$ NMR (300 MHz, CDCl$_3$)

16e

$^{13}C$ NMR (75 MHz, CDCl$_3$)
$^{1}H$ NMR (300 MHz, CDCl$_3$)

$^{13}C$ NMR (75 MHz, CDCl$_3$)
$\text{H NMR (300 MHz, CDCl}_3\text{)}$

$16h$

$\text{H NMR (300 MHz, CDCl}_3\text{)}$

$16h$

$\text{H NMR (300 MHz, CDCl}_3\text{)}$

$16h$
17a

$^1$H NMR (300 MHz, CDCl$_3$)

17a

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^{1}H$ NMR (300 MHz, CDCl$_3$)

$^{13}C$ NMR (75 MHz, CDCl$_3$)
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- **17a (racemic)**

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Page: 1 of 1
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![Chromatogram Image]

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49
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![Graph](image_url)

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