Supporting Information

Vinylalumination for the Synthesis of Functionalized Allyl Alcohols, Vinylepoxides, and α -Alkylidene- β -hydroxy- γ -lactones.

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Materials: All reactions were carried out under nitrogen atmosphere. Tetrahydrofuran was distilled from sodium benzophenone ketyl prior to use. The NMR chemical shifts () are reported in ppm.

Experimental procedure for vinylalumination using β -unsubstituted reagent (1):

Preparation of ethyl 2-(hydroxyphenylmethyl)acrylate (5a): To a stirred suspension of NMO (2.3 g, 20 mmol) in anhydrous THF (50 mL) was added DIBAL-H (2.7 mL, 15 mmol) at 0 °C and stirred for 0.5 h wherein the NMO went into solution. Ethyl propiolate (1.0 mL, 10 mmol) was added and the mixture was stirred at 0 °C for 1 h, followed by the addition of benzaldehyde (**4a**) (1.2 mL, 12 mmol). The mixture was warmed to rt, and stirred for 4 h, quenched with 10 mL of 1.0 M HCl, and the product extracted with ether (3×50 mL). The combined ether layers were washed with brine and dried over MgSO₄. Removal of the solvents and purification by column chromatography over silica gel (95:5, hexanes:ethyl acetate) provided 2.5 g (9.5 mmol, 95%) of **5a**.

Experimental procedure for vinylalumination using β -substituted reagents (2, 3, 11):

Preparation of ethyl (2Z)-2-(hydroxyphenylmethyl)-3-phenylacrylate (7a): To a stirred suspension of NMO (2.3 g, 20 mmol) in anhydrous THF (50 mL) was added DIBAL-H (2.7 mL, 15 mmol) at 0 °C and stirred for 0.5 h wherein the NMO went into solution. Ethyl phenylpropiolate (1.4 mL, 8.5 mmol) was added, the mixture was warmed to rt and stirred for 4 h, followed by the addition of benzaldehyde (**4a**) (1.0 mL, 10 mmol) and overnight stirring. The reaction was quenched with 10 mL of 1.0 M HCl, and the product was extracted with ether (3×50 mL). The combined ether layers were washed with brine and dried over MgSO₄. Removal of the solvents and purification by column chromatography over silica gel (95:5, hexanes:ethyl acetate) provided 1.8 g (6.8 mmol, 80%) of **7a**.

Experimental procedure for vinylalumination of unactivated ketones: Preparation of ethyl 2-(1-hydroxy-1-phenylethyl)acrylate (5e): To a stirred suspension of NMO (4.17 g, 35.6 mmol) in anhydrous THF (30 mL) was added DIBAL-H (1 M in hexanes; 32 mL, 32 mmol) at 0 °C and stirred for 0.5 h wherein the NMO went into solution. Ethyl propiolate (2.8 mL, 27.5 mmol) was added and the mixture was stirred at 0 °C for 1 h, followed by the addition of acetophenone (**4e**) (1.8 mL, 15.3 mmol) and BF₃.OEt₂ (1.9 mL, 15.3 mmol). The mixture was warmed to rt and stirred for 4 h, quenched with 10 mL of 1.0 M HCl, and the product was extracted with ether (3×50 mL). The combined ether layers were washed with brine and dried over MgSO₄. Removal of the solvents and purification by column chromatography over silica gel (95:5, hexanes:ethyl acetate) provided 2.5 g (11.3 mmol, 74%) of **5e**.

Note: For the α -substituted vinylaluminium reagents (**2**, **3**), the solution has to be stirred for 4 h at rt prior to addition of the ketones.

Experimental procedure for vinylalumination of acyl cyanides using β -unsubstituted reagent (1): Preparation of ethyl 2-(1-cyano-1-hydroxyethyl)acrylate (5p): To a solution of HMPA (3.5 mL, 20 mmol) in anhydrous THF (50 mL) was added DIBAL-H (2.7 mL, 15 mmol) at 0 °C. Ethyl propiolate (1.0 mL, 10 mmol) was added and the mixture was stirred at 0 °C for 1 h, followed by the addition of pyruvonnitrile (**4p**) (0.85 mL, 12 mmol). The mixture was warmed to rt and stirred for 4 h, quenched with 10 mL of 1.0 M HCl, and the product was extracted with ether (3×50 mL). The combined ether layers were washed with brine and dried over MgSO₄. Removal of the solvents and purification by column chromatography over silica gel (95:5, hexanes:ethyl acetate) provided 1.4 g (8.6 mmol, 72%) of **5p**.

Note: For the α -substituted vinylaluminium reagents (**2**, **3**), the solution has to be stirred for 4 h at rt prior to addition of the ketones.

Preparation of 2-methyl-1,3-dithiane-2-carbaldehyde (4z): To 2-methyl-1,3-dithiane (10.7 g, 80 mmol) diluted with THF (50 mL) and cooled to -18 °C was added *n*BuLi (2.5 M in hexanes; 32 mL, 80 mmol) and the mixture was stirred for 0.5 h, then DMF (24 mL, 390 mmol) was added and after stirring for 3 h at -18 °C the reaction was quenched with aqueous 10% HCl (20 mL). The product was extracted with pentane (3×100 mL), washed with water (3×100 mL) and with brine and evaporated under reduced pressure to afford **4z** in 63% yield (8.2 g, 58 mmol). ¹H NMR (300 MHz, CDCl₃): 9.04 (s, 1H), 2.82-3.39 (m, 2H), 2.52-2.61 (m, 2H), .02-2.12 (m, 1H), 1.66-1.82 (m, 1H), 1.46 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): 189.3, 52.4, 27.0, 23.8, 22.0. MS: EI/CI: M⁺ = 162.

Ethyl 2-(1-hydroxy-2-methylpropyl)acrylate (5c): ¹H NMR (300 MHz, CDCl₃): δ•0.82 (d, *J* = 6.87 Hz), 0.89 (d, *J* = 6.78 Hz, 3H), 1.25 (t, *J* = 7.14 Hz, 3H), 1.86 (m, 1H), 2.79 (d, *J* = 7.44, 1H), 4.05 (t, *J* = 6.87 Hz, 1H), 4.17 (q, *J* = 7.14 Hz, 2H), 5.70 (s, 1H), 6.19 (s, 1H); ¹³C NMR (75 MHz, CDCl₃): •δ14.0, 17.4, 19.5, 32.7, 60.7, 77.3, 125.6, 141.8, 166.7; IR (CDCl₃) 3486, 1701, 1625 cm⁻¹; MS (EI) *m/z* (relative intensity): 154 (M-H₂O, 0.7), 83 (100); (CI) *m/z* 173 (m+H, 75).

Ethyl 2-(1-hydroxy-2,2-dimethylpropyl)acrylate (5d): ¹H NMR (300 MHz, CDCl₃) δ•0.84 (s, 9H), 1.25 (t, *J* = 7.14 Hz, 3H), 3.0 (br s, 1H), 4.16 (q, *J* = 7.14 Hz, 2H), 4.25 (s, 1H), 5.70 (s, 1H), 6.22 (s, 1H); ¹³C NMR (75 MHz, CDCl₃)•: δ14.0, 25.7, 35.8, 60.8, 78.5, 126.5, 141.1, 167.7. MS (EI) *m/z* (relative intensity): 171 (M-CH₃, 0.3), 57 (100) (CI) *m/z* 187 (m+H, 25), 169 (M+H-H₂O, 100).

Ethyl 2-(1-hydroxy-1-phenylethyl)acrylate (5e): ^1H NMR (300 MHz, CDCl_3)

δ 1.18 (t, $J=7.14$ Hz, 3H), 1.67 (s, 3H), 4.10 (m, 2H), 4.62 (s, 1H), 5.95 (s, 1H), 6.40 (s, 1H), 7.35 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3): δ 13.9, 29.2, 61.1, 75.4, 124.6, 124.7, 126.9, 128.2, 144.6, 146.9, 167.4. IR (CDCl_3): 3492, 1695, 1621 cm^{-1} . MS (EI) m/z (relative intensity): 220 (M^+ , 0.5), 43 (100); (CI) m/z 203 ($\text{M}+\text{H}-\text{H}_2\text{O}$).

Ethyl 2-(1-hydroxy-1-methylpropyl)acrylate (5f): ^1H NMR (300 MHz, CDCl_3):

δ 0.77 (t, $J=7.44$ Hz, 3H), 1.25 (t, $J=7.14$ Hz, 3H), 1.31 (s, 3H), 1.70 (m, 2H), 3.50 (br s, 1H), 4.15 (q, $J=7.14$ Hz, 2H), 5.69 (s, 1H), 6.13 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 8.4, 14.02, 25.9, 33.8, 60.8, 74.1, 124.0, 145.0, 167.4. IR (CDCl_3): 3499, 1698, 1618 cm^{-1} . MS (EI) m/z (relative intensity): 157 ($\text{M}-\text{CH}_3$, 8), 97 (100); (CI) m/z 173 ($\text{M}+\text{H}$, 3.5), 155 (100).

Ethyl 2-(2,2,2-trifluoro-1-hydroxyethyl)acrylate (5g): ^1H NMR (300 MHz, CDCl_3):

δ 1.27 (t, $J=7.14$ Hz, 3H), 4.22 (q, $J=7.14$ Hz, 2H), 4.62 (br s, 1H), 4.91 (quint, $J=6.57$ Hz, 1H), 6.12 (s, 1H), 6.52 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 13.7, 61.6, 69.1 (q, $J=32.5$ Hz), 123.9 (q, $J=282.8$ Hz), 131.0, 134.1, 165.7; ^{19}F NMR (282 MHz, CDCl_3): δ -79.7 (d, $J=6.8$ Hz). IR (CDCl_3): 3466, 1705, 1628 cm^{-1} . MS (EI) m/z (relative intensity): 153 ($\text{m}-\text{OEt}$, 90), 83 (100); (CI) m/z 199 ($\text{m}+\text{H}$).

Ethyl 2-[hydroxy(pentafluorophenyl)methyl]acrylate (5i): ^1H NMR (300 MHz, CDCl_3):

δ 1.25 (t, $J=7.14$ Hz, 3H), 4.15 (m, 2H), 4.76 (br s, 1H), 5.87 (s, 1H), 6.09 (s, 1H)

6.47 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 13.7, 61.3, 64.0, 126.5, 136-148 (m), 165.5; ^{19}F NMR (282 MHz, CDCl_3): δ -143.7 (m, 2F), -156.2 (m, 1F), -163.8 (m, 2F). IR (CDCl_3): 3453, 1705, 1651 cm^{-1} . MS (EI) m/z (relative intensity): 296 (M^+ , 37), 279 (M-OH, 50); (CI) m/z 297 (m+H).

Ethyl 2-(2,2,2-trifluoro-1-hydroxy-1-methylethyl)acrylate (5j): ^1H NMR (300

MHz, CDCl_3): δ 1.27 (t, $J=7.14$ Hz, 3H), 1.52 (s, 1H), 4.22 (q, $J=7.14$ Hz, 2H), 5.99 (s, 1H), 6.19 (s, 1H), 6.50 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 13.6, 21.2, 61.8, 74.8 (q, $J=29.29$ Hz), 125.3 (q, $J=286.6$ Hz), 130.6, 136.4, 167.4; ^{19}F NMR (282 MHz, CDCl_3): δ -82.7 (s). IR (CDCl_3): 3431, 1675, 1621 cm^{-1} . MS (EI) m/z (relative intensity): 197 (m- CH_3), 5), 97 (100); (CI) m/z 213 (m+H).

Ethyl 2-(2,2,2-trifluoro-1-hydroxy-1-phenylethyl)acrylate (5k): ^1H NMR (300

MHz, CDCl_3): δ 1.24 (t, $J=7.11$ Hz, 3H), 4.17 (m, 2H), 5.74 (s, 1H), 6.14 (s, 1H), 6.65 (s, 1H), 7.40 (m, 3H), 7.60 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 13.8, 61.9, 79.1 (q, $J=28.95$), 124.2 (q, $J=285.3$ Hz), 126.9, 128.3, 128.7, 128.9, 136.4, 137.2, 167.1; ^{19}F NMR (282 MHz, CDCl_3): δ -76.7 (s). IR (CDCl_3): 3439, 1698, 1621 cm^{-1} . MS (EI) m/z (relative intensity): 257 (m-OH, 8.5), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100); (CI) m/z 275 (m+H, 100), 257 (m- H_2O , 51); HRMS: 274.0817 (calc.), 274.0826 (actual).

Ethyl 2-[2,2,2-trifluoro-1-hydroxy-1-(thien-2-yl)ethyl]acrylate (5l): ^1H

NMR (300 MHz, CDCl_3): δ 1.31 (t, $J=7.14$ Hz, 3H), 4.27 (m, 2H), 6.06 (s, 1H), 6.60 (s, 1H), 6.73 (s, 1H), 7.01 (m, 1H), 7.13 (m, 1H), 7.36 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 14.0, 62.2, 77.7

(q, $J=30.33$ Hz), 124.0 (q, $J=286.1$ Hz), 126.7, 126.9, 130.6, 135.5, 141.4, 167.4; ^{19}F NMR (282 MHz, CDCl_3) δ -78.2 (s). IR (CDCl_3): 3346, 1692, 1618 cm^{-1} . MS (EI) m/z (relative intensity): 280 (M^+ , 20), 263 (m-OH, 15.5), 111 (100); (CI) m/z 281 (m+H, 2), 263 (m+H- H_2O , 100); HRMS: 280.0381 (calc.), 280.0391 (actual).

Ethyl 2-(2,2,2-trichloro-1-hydroxyethyl)acrylate (5m): ^1H NMR (300 MHz,

CDCl_3): δ 1.29 (t, $J=7.14$ Hz, 3H), 4.25 (q, $J=7.14$ Hz, 2H), 4.97 (br s, 1 H), 5.14 (s, 1H), 6.19 (s, 1H), 6.57 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 14.0, 61.7, 81.1, 102.2, 132.5, 134.9, 166.7; IR (CDCl_3) 3446, 1715, 1625 cm^{-1} ; MS (EI) m/z (relative intensity) 201/203/205 (m-OEt, 4.4/4.0/1.5), 83 (100); (CI) m/z 247/249/251 (m+H).

Diethyl 2-hydroxy-2-methyl-3-methylenesuccinate (5n): ^1H NMR (300

MHz, CDCl_3): δ 1.11 (t, $J=7.14$ Hz, 3H), 1.15 (t, $J=7.14$ Hz, 3H), 1.57 (s, 3H), 3.81 (br s, 1H), 4.09 (q, 4H), 5.81 (s, 1H), 6.22 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 13.8, 13.9, 23.7, 61.0, 61.7, 125.1, 142.1, 165.9, 174.6. IR (neat): 3450, 1730, 1715, 1650 cm^{-1} .

4-Ethyl 1-methyl 2-hydroxy-3-methylene-2-phenylsuccinate (5o): ^1H NMR

(300 MHz, CDCl_3): δ 1.25 (t, $J=7.14$ Hz, 3H), 3.73 (s, 3H), 4.20 (m, 2H), 4.38 (s, 1H), 5.29 (s, 1H), 6.30 (s, 1H), 7.30 (m, 3H), 7.58 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 14.0, 53.2, 61.3, 78.4, 126.7, 128.6, 128.2, 128.3, 137.2, 143.0, 166.5, 173.4. MS (EI) m/z (relative intensity): 247 (M-OH, 0.7), 105 (100); (CI) 265 (m+H, 60), 201 (100).

Ethyl 2-(1-cyano-1-hydroxyethyl)acrylate (5p): ^1H NMR (300 MHz, CDCl_3):

δ 1.30 (t, J = 7.17 Hz, 3H), 1.78 (s, 3H), 4.27 (q, J = 7.17 Hz, 2H), 4.82 (br s, 1H), 6.09 (s, 1H), 6.42 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3): 13.9, 26.6, 62.0, 67.4, 120.4, 127.4, 139.0, 165.2.

Ethyl 3-hydroxy-3-methyl-2-methylene-pent-4-ynoate (5q): ^1H NMR (300

MHz, CDCl_3): 1.33 (t, J =7.14 Hz, 3H), 1.73 (s, 3H), 2.53 (s, 1H), 4.28 (q, J =7.14 Hz, 2H), 4.42 (br s, 1H), 6.06 (s, 1H), 6.26 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3): 14.1, 28.6, 61.4, 67.5, 72.3, 85.7, 124.9, 142.12, 166.6.

Ethyl 2-(1-hydroxy-2-methyl-3-oxopropyl)acrylate (5r): ^1H NMR (300 MHz,

CDCl_3): 1.28 (t, J = 7.14 Hz, 3H), 1.48 (s, 3H), 2.22 (s, 3H), 4.20 (q, J = 7.14 Hz, 2H), 4.38 (br s, 1H), 5.98 (s, 1H), 6.37 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3): 14.0, 22.8, 235, 61.3, 78.5, 125.8, 142.6, 166.4, 209.7. IR: 3459, 1715, 1628 cm^{-1} .

Ethyl 2-(1-ethyl-1-hydroxy-2-oxobutyl)acrylate (5s): ^1H NMR (300 MHz,

CDCl_3): δ 0.81 (t, J =7.38 Hz, 3H), 1.09 (t, J =7.26 Hz, 3H), 1.26 (t, J =7.14 Hz, 3H), 1.91 (m, 2H), 2.47 (m, 2H), 4.17 (q, J =7.14 Hz, 2H), 4.41 (s, 1H), 5.92 (s, 1H), 6.32 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 7.1, 7.7, 14.0, 28.4, 29.3, 61.2, 80.6, 125.4, 142.7, 166.6, 211.1; IR (CDCl_3) 3459, 1715, 1625 cm^{-1} ; MS (EI) m/z (relative intensity) 197 (M-OH, 4), 57 (100) (CI) m/z 215 ($m+H$); HRMS: 215.1283 (calc.), 215.1287 (actual).

Ethyl 2-(1-hydroxy-2-oxo-1,2-diphenylethyl)acrylate (5t): ^1H NMR (300

MHz, CDCl_3): δ 1.30 (t, $J=7.14$ Hz, 3H), 4.26 (q, $J=7.14$ Hz, 2H), 5.16 (s, 1H), 5.40 (s, 1H), 6.33 (s, 1H), 7.35 (m, 6H), 7.60 (m, 2H), 7.95 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 14.0, 61.6, 84.7, 126.5, 127.8, 128.2, 128.5, 130.6, 132.5, 134.6, 137.1, 144.4, 168.4, 200.39; IR (CDCl_3) 3486, 1682, 1628, 1595 cm^{-1} ; MS (EI) m/z (relative intensity) 205 ($\text{M}-\text{C}_6\text{H}_5\text{CO}$, 30), 105 (100) (CI) m/z 311 ($\text{M}+\text{H}$, 7), 293 (100); HRMS: 310.1205 (calc.), 310.1198 (actual).

Ethyl 3-hydroxy-3-methyl-2-methylene-4-oxo-hexanoate (5u): ^1H NMR

(300 MHz, CDCl_3): δ 0.97 (t, $J=7.26$ Hz, 3H), 1.16 (t, $J=7.14$ Hz, 3H), 1.35 (s, 3H), 2.45 (q, $J=7.26$ Hz, 2H), 4.08 (q, $J=7.14$ Hz, 2H), 4.28 (s, 1H), 5.85 (s, 1H), 6.24 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 7.7, 13.8, 23.1, 27.9, 61.1, 78.3, 125.6, 142.5, 166.4, 211.9; IR (CDCl_3) 3452, 1718, 1628 cm^{-1} ; MS (EI) m/z (relative intensity) 171 ($\text{M}-\text{Et}$, 8), 111 (100) (CI) m/z 201 ($\text{M}+\text{H}$); HRMS: 201.1127 (calc.), 201.1132 (actual).

Ethyl 3-ethyl-3-hydroxy-2-methylene-4-oxo-pentanoate (5'u): ^1H NMR (300

MHz, CDCl_3): δ 0.72 (t, $J=7.44$ Hz, 3H), 1.16 (t, $J=7.14$ Hz, 3H), 1.81 (m, 2H), 2.05 (s, 3H), 4.08 (q, $J=7.14$ Hz), 4.25 (s, 1H), 5.85 (s, 1H), 6.23 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 6.9, 13.8, 23.7, 28.7, 61.1, 80.6, 125.6, 142.5, 166.4, 208.2; IR (CDCl_3) 3452, 1718, 1628 cm^{-1} ; MS (EI) m/z (relative intensity): 171 ($\text{M}-\text{Et}$, 8), 111 (100) (CI) m/z 201 ($\text{M}+\text{H}$); HRMS: 201.1127 (calc.), 201.1132 (actual).

Ethyl 2-(1-hydroxy-2-oxo-1-phenylpropyl)acrylate (5v): ^1H NMR (300 MHz,

CDCl_3): δ 1.31 (t, $J=7.14$ Hz, 3H), 2.22 (s, 3H), 4.25 (q, $J=7.14$ Hz, 2H), 5.00 (s, 1H), 5.33 (s, 1H), 6.35 (s, 1H), 7.35 (m, 3H), 7.47 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 14.0, 24.9, 61.7, 84.4, 126.7, 128.3, 128.4, 129.1, 136.1, 143.2, 168.1, 209.2. IR (CDCl_3): 3492, 1711, 1688, 1625 cm^{-1} . MS (EI) m/z (relative intensity): 231 (M-OH, 1), 105 (100); (CI) m/z 249 (M+H, 60), 231 (100); HRMS: 249.1127 (calc.), 249.1135 (actual)

Ethyl 2-(1-hydroxy-1-methyl-2-oxo-2-phenylethyl) (5'v): ^1H NMR (300

MHz, CDCl_3): δ 1.15 (t, $J=7.14$ Hz, 3H), 1.65 (s, 3H), 4.05 (m, 2H), 4.84 (s, 1H), 6.18 (s, 1H), 6.42 (s, 1H), 7.35 (m, 3H), 7.47 (m, 2H), 8.05 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 13.8, 25.0, 61.2, 80.7, 125.4, 127.3, 128.3, 129.5, 133.1, 143.9, 166.0, 200.3. IR (CDCl_3): 3439, 1711, 1675, 1595 cm^{-1} . MS (EI) m/z (relative intensity): 231 (M-OH, 1), 105 (100); (CI) m/z 249 (M+H, 60), 231 (100); HRMS: 249.1127 (calc.), 249.1135 (actual).

Ethyl 2-(2-bromo-1-hydroxyethyl)acrylate (5w): ^1H NMR (300 MHz,

CDCl_3): δ 1.33 (t, $J=7.1$ Hz, 3H), 2.97 (d, $J=6.8$ Hz, 1H), 3.53 (dd, $J=10.3$ and 6.7 Hz, 1H), 3.71 (dd, $J=10.3$ and 4.5 Hz, 1H), 4.25 (q, $J=7.1$ Hz, 2H), 4.67 (q, $J=6.8$ Hz, 1H), 6.00 (s, 1H), 6.41 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 14.1, 37.8, 61.2, 70.8, 127.6, 138.9, 165.7.

Ethyl 2-(2-bromo-1-hydroxy-1-phenylethyl)acrylate (5x): ^1H NMR (300

MHz, CDCl_3): δ 1.23 (t, $J=7.14$ Hz, 3H), 2.88 (d, $J=10.9$ Hz, 1H), 4.04 (d, 10.9 Hz, 1H), 4.15

(m, 2H), 4.47 (s, 1 H), 6.09 (s, 1H), 6.53 (s, 1H), 7.32 (m, 3H), 7.48 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 13.9, 40.7, 61.4, 76.5, 125.8, 127.2, 128.0, 128.4, 128.7, 133.4, 141.1, 142.0, 166.6.

Ethyl 2-[1-(bromomethyl)-2,2,2-trifluoro-1-hydroxyethyl]acrylate (5y): ^1H

NMR (300 MHz, CDCl_3): δ 1.35 (t, $J=7.1$ Hz, 3H), 3.78 (d, $J=11.2$ Hz, 1H), 3.94 (d, $J=11.2$, 1H), 4.29 (q, $J=7.1$ Hz, 2H), 5.95 (s, 1H), 6.15 (s, 1H), 6.75 (s, 1H); ^{19}F NMR (282 MHz, CDCl_3): δ -80.1; ^{13}C NMR (75 MHz, CDCl_3): δ 13.9, 34.2, 62.2, 76.7, 123.5 (q, $J=288$ Hz), 132.6, 133.1, 166.6.

Ethyl (2Z)-2-(1-hydroxybutyl)but-2-enoate (6b): ^1H NMR (300 MHz,

CDCl_3): δ 0.85 (t, $J=7.35$ Hz, 3H), 1.26 (t, $J=7.14$ Hz, 3H), 1.35 (m, 2H), 1.50 (m, 2H), 1.91 (d, $J=7.29$ Hz, 3H), 2.79 (br s, 1H), 4.18 (t, $J=5.8$ Hz, 1H), 4.18 (q, $J=7.11$ Hz, 2H), 6.16 (q, $J=7.14$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 13.8, 14.2, 15.3, 19.1, 38.7, 60.3, 73.7, 135.4, 136.3, 167.7. IR (CDCl_3): 3446, 1698, 1651 cm^{-1} . MS (EI) m/z (relative intensity): 186 (M^+ , 2), 97 (100); (CI) m/z 187 ($\text{M}+\text{H}$, 4), 169 (100).

Ethyl (2Z)-2-(1-hydroxy-1-phenylethyl)but-2-enoate (6e): ^1H NMR (300 MHz,

CDCl_3): δ 1.08 (t, $J=7.14$ Hz, 3H), 1.62 (s, 3H), 1.99 (d, $J=7.17$ Hz, 3H), 4.07 (m, 2H), 4.36 (s, 1H), 6.35 (q, $J=7.17$ Hz, 1H), 7.35 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3): δ 13.9, 15.7, 29.2, 60.6, 76.1, 124.9, 126.8, 128.0, 133.7, 138.2, 147.3, 168.8. IR (CDCl_3): 3466, 1681, 1598 cm^{-1} . MS (EI) m/z (relative intensity): 234 (M^+ , 0.1), 43 (100); (CI) m/z 217 ($\text{M}+\text{H}-\text{H}_2\text{O}$).

Ethyl (2Z)-2-(1-hydroxy-1-methylpropyl)but-2-enoate (6f): ^1H NMR (300

MHz, CDCl_3): δ 0.79 (t, $J=7.50$ Hz, 3H), 1.27 (t, $J=7.14$ Hz, 3H), 1.29 (s, 3H), 1.62 (m, 2H), 1.77 (d, $J=7.17$ Hz, 3H), 2.85 (br s, 1H), 4.20 (q, $J=7.11$ Hz, 2H), 5.96 (q, $J=7.08$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 8.4, 14.1, 15.2, 26.4, 34.1, 60.4, 74.3, 129.3, 139.8, 169.2. IR (CDCl_3): 3486, 1701, 1651 cm^{-1} . MS (EI) m/z (relative intensity): 171 ($\text{M}-\text{CH}_3$, 1.5), 111 (100); (CI) m/z 187 ($\text{M}+\text{H}$, 1), 169 (100).

Ethyl (2Z)-2-(2,2,2-trifluoro-1-hydroxyethyl)but-2-enoate (6g): ^1H NMR (300

MHz, CDCl_3): δ 1.32 (t, $J=7.14$ Hz, 3H), 2.08 (d, $J=7.2$ Hz, 3H), 4.28 (q, $J=7.14$ Hz, 2H), 4.33 (d, $J=8.52$ Hz, 1H), 4.69 (quint, $J=7.47$ Hz, 1H), 6.54 (q, $J=7.14$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 14.0, 15.9, 61.3, 72.5 (q, $J=32.2$ Hz), 124.2 (q, $J=283.3$ Hz), 126.1, 144.8, 167.0; ^{19}F NMR (282 MHz, CDCl_3): δ -79.62 (d, $J=6.8$ Hz). IR (CDCl_3): 3453, 1698, 1651 cm^{-1} . MS (EI) m/z (relative intensity): 212 (M^+ , 1), 97 (100); (CI) m/z 213 ($\text{m}+\text{H}$).

Diethyl (3Z)-3-ethylidene-2-hydroxy-2-methylsuccinate (6n): ^1H NMR

(300 MHz, CDCl_3): 1.18 (m, 6H), 1.47 (s, 3H), 1.93 (d, $J=7.17$ Hz, 3H), 3.79 (br s, 1H), 4.18 (m, 4H), 6.29 (q, $J=7.20$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): 13.9, 14.0, 15.5, 24.4, 60.6, 61.9, 74.7, 135.2, 135.3, 167.0, 175.3; IR (CDCl_3): 3506, 1728, 1711 cm^{-1} . MS (EI) m/z (relative intensity): 213 (M^+ , 1), 111 (100); (CI) m/z 231 ($\text{m}+\text{H}$).

4-Ethyl 1-methyl (3Z)-3-ethylidene-2-hydroxy-2-phenylsuccinate (6o): ^1H

NMR (300 MHz, CDCl_3): δ 1.32 (t, $J=7.14$ Hz, 3H), 1.95 (d, $J=7.26$ Hz), 3.81 (s, 3H), 4.28 (q, $J=7.14$ Hz, 2H), 4.32 (s, 1H), 5.83 (q, $J=7.26$ Hz, 1H), 7.34 (m, 3H), 7.61 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 14.1, 15.8, 53.2, 60.9, 80.5, 127.0, 128.2, 128.2, 136.1, 138.4, 141.4, 167.5, 174.4. IR (CDCl_3): 3506, 1731, 1715, 1651 cm^{-1} . MS (EI) m/z (relative intensity): 219 (M-COOMe, 18), 105 (100); (CI) m/z 279 (m+H, 8), 261 (100).

Ethyl (2Z)-2-ethylidene-3-hydroxy-3-methylpent-4-ynoate (6q): ^1H NMR

(300 MHz, CDCl_3): δ 1.35 (t, $J=7.11$ Hz, 3H), 1.69 (s, 3H), 1.94 (d, $J=7.2$ Hz, 3H), 2.54 (s, 1H), 4.05 (s, 1H), 4.32 (q, $J=7.14$ Hz, 2H), 6.53 (q, $J=7.29$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 14.2, 15.5, 28.9, 61.0, 69.8, 72.5, 86.0, 133.9, 135.9, 168.1. IR (CDCl_3): 3466, 2110, 1708, 1654 cm^{-1} . MS (EI) m/z (relative intensity): 182 (M^+ , 0.2), 121 (100); (CI) m/z 183 (m+H, 1.5), 165 (M+H- H_2O , 100).

Ethyl (2Z)-2-(1-hydroxy-1-methyl-2-oxopropyl)but-2-enoate (6r): ^1H

NMR (300 MHz, CDCl_3): δ 1.23 (t, $J=7.14$ Hz, 3H), 1.39 (s, 3H), 1.96 (d, $J=7.11$ Hz, 3H), 2.18 (s, 3H), 4.17 (m, 2H), 4.31 (s, 1H), 6.28 (q, $J=7.29$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 14.0, 15.5, 23.1, 23.2, 60.8, 79.4, 134.8, 136.0, 167.2, 209.6. IR: 3446, 1715, 1682 cm^{-1} . MS (EI/CI) 201 (m+H); HRMS: 201.1127 (calc.), 201.1120 (actual).

Ethyl 3-hydroxy-3-methyl-2-(2-methyl-methylene)-4-oxo-hexanoate (6u):

^1H NMR (300 MHz, CDCl_3): δ •1.08 (t, J =7.29 Hz, 3H), 1.23 (t, J =7.14 Hz, 3H), 1.39 (s, 3H), 1.93 (d, J =7.3 Hz, 3H), 2.50 (m, 2H), 4.15 (q, J =7.14 Hz, 2H), 4.37 (s, 1H), 6.27 (q, J =7.14 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3)•: δ 8.0, 14.0, 15.6, 23.6, 28.0, 60.8, 79.3, 134.6, 136.4, 167.3, 212.4; IR (CDCl_3) 3445, 1715 cm^{-1} ; MS (EI) m/z (relative intensity) 171 (M-COMe, 8), 69 (100); (CI) m/z 215 (m+H, 17), 197 (100).

Ethyl 3-ethyl-3-hydroxy-2-(2-methyl-methylene)-4-oxo-pentanoate (6'u): ^1H

NMR (300 MHz, CDCl_3): δ •0.78 (t, J =7.44 Hz, 3H), 1.23 (t, J =7.14 Hz, 3H), 1.82 (m, 2H), 1.93 (d, J =7.3 Hz, 3H), 2.15 (s, 3H), 4.15 (q, J =7.14 Hz, 2H), 4.28 (s, 1H), 6.01 (q, J =7.14 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3)•: δ 6.9, 14.0, 15.5, 23.3, 28.4, 60.8, 81.6, 133.0, 136.4, 167.4, 208.7; IR (CDCl_3) 3445, 1715 cm^{-1} ; MS (EI) m/z (relative intensity) 197 (M-OH, 0.5), 69 (100); (CI) m/z 215 (m+H, 3), 197 (100).

Ethyl (2Z)-2-(1-hydroxy-2-oxo-1-phenylpropyl)but-2-enoate (6v): ^1H NMR

(300 MHz, CDCl_3): δ •1.33 (t, J =7.11 Hz, 3H), 1.92 (d, J =7.26 Hz, 3H), 2.19 (s, 3H), 4.29 (m, 2H), 5.03 (s, 1H), 5.79 (q, J =7.23 Hz, 1H), 7.35 (m, 3H), 7.49 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3)•: δ 14.1, 15.7, 25.0, 61.2, 85.9, 127.0, 128.1, 128.3, 136.5, 136.9, 141.2, 169.2, 209.8. IR (CDCl_3): 3473, 1711, 1681, 1625 cm^{-1} . MS (EI) m/z (relative intensity): 245 (M-OH, 2), 105 (100); (CI) m/z 363 (M+H, 9), 245 (100); HRMS: 263.1283 (calc.), 263.1280 (actual).

Ethyl (2Z)-2-(1-hydroxy-1-methyl-2-oxo-2-phenylethyl)but-2-enoate (6'v):

^1H NMR (300 MHz, CDCl_3): δ 1.16 (t, $J=7.14$ Hz, 3H), 1.65 (s, 3H), 2.10 (d, $J=7.32$ Hz, 3H), 4.11 (m, 2H), 4.87 (s, 1H), 6.56 (q, $J=7.14$ Hz, 1H), 7.38 (m, 3H), 8.03 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 13.8, 15.8, 25.3, 60.8, 78.6, 127.3, 128.3, 129.5, 132.9, 135.9, 136.7, 166.9, 201.1. IR (CDCl_3): 3432, 1711, 1675, cm^{-1} . MS (EI) m/z (relative intensity): 245 (M-OH, 2), 105 (100); (CI) m/z 363 (M+H, 9), 245 (100); HRMS: 263.1283 (calc.), 263.1280 (actual).

Ethyl (2Z)-2-(1-hydroxy-1-phenylmethyl)-3-phenylacrylate (7a):

^1H NMR (300 MHz, CDCl_3): δ 0.97 (t, $J=7.14$ Hz, 3H), 3.40 (d, $J=6.75$ Hz, 1H), 4.03 (q, $J=7.14$ Hz, 2H), 5.61 (d, $J=5.50$ Hz, 1H), 6.96 (s, 1H), 7.35 (m, 10H); ^{13}C NMR (75 MHz, CDCl_3): δ 13.6, 60.9, 75.6, 126.7, 127.9, 128.1, 128.2, 128.5, 128.5, 134.7, 135.5, 136.0, 141.1, 168.7. IR (CDCl_3): 3465, 1701 cm^{-1} . MS (EI) m/z (relative intensity): 282 (M^+ , 5), 105 (100); (CI) m/z 265 (m+H- H_2O , 100).

Ethyl (2Z)-2-(1-hydroxybutyl)-3-phenylacrylate (7b):

^1H NMR (300 MHz, CDCl_3): δ 0.95 (t, $J=7.38$ Hz, 3H), 1.09 (t, $J=7.17$ Hz, 3H), 1.45 (m, 2H), 1.68 (q, $J=7.5$ Hz, 2H), 2.87 (br s, 1H), 4.13 (q, $J=7.14$ Hz, 2H), 4.41 (t, $J=6.0$ Hz, 1H), 6.83 (s, 1H), 7.26 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3): δ 13.7, 13.9, 19.0, 38.4, 60.9, 74.0, 128.0, 128.1, 128.3, 132.8, 135.6, 137.1, 168.9. IR (CDCl_3): 3432, 1701, 1638 cm^{-1} . MS (EI) m/z (relative intensity): 248 (M^+ , 0.6), 159 (100); (CI) m/z 231 (M+H- H_2O).

Ethyl (2Z)-2-(1-hydroxy-1-phenylethyl)-3-phenylacrylate (7e): ^1H NMR (300 MHz, CDCl_3): δ 0.85 (t, $J=7.14$ Hz, 3H), 1.81 (s, 3H), 3.92 (m, 2H), 4.13 (s, 1H), 7.04 (s, 1H), 7.31 (m, 3H), 7.53 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 13.3, 28.9, 60.9, 76.3, 124.5, 125.5, 127.2, 128.2, 128.3, 132.3, 133.7, 135.9, 139.3, 145.8, 170.0. IR (CDCl_3): 3472, 1684 cm^{-1} . MS (EI) m/z (relative intensity): 296 (M^+ , 0.1), 77 (100); (CI) m/z 279 ($\text{M}+\text{H}-\text{H}_2\text{O}$).

Ethyl (2Z)-2-(1-hydroxy-1-methylpropyl)-3-phenylacrylate (7f): ^1H NMR (300 MHz, CDCl_3): δ 0.95 (t, $J=7.44$ Hz, 3H), 1.06 (t, $J=7.17$ Hz, 3H), 1.47 (s, 3H), 1.79 (m, 2H), 2.55 (br s, 1H), 4.15 (q, $J=7.17$ Hz, 2H), 6.82 (s, 1H), 7.25 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3): δ 8.3, 13.6, 26.9, 34.2, 60.9, 74.6, 127.8, 128.0, 128.2, 129.5, 135.9, 141.0, 170.0. IR (CDCl_3): 3479, 1708 cm^{-1} . MS (EI): 248 (M^+); (CI) m/z 231 ($\text{M}+\text{H}-\text{H}_2\text{O}$).

Ethyl (2Z)-2(2,2,2-trifluoro-1-hydroxyethyl)-3-phenylacrylate (7g): ^1H NMR (300 MHz, CDCl_3): δ 1.08 (t, $J=7.14$ Hz, 3H), 4.15 (q, $J=7.14$ Hz, 2H), 4.54 (br s, 1H), 4.90 (quint, $J=6.57$ Hz, 1H), 7.23 (s, 1H), 7.33 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3): δ 13.4, 61.7, 72.4 (q, $J=32.4$ Hz), 124.1 (q, $J=283.4$ Hz), 126.4, 128.2, 128.51, 129.0, 134.5, 140.7, 168.0; ^{19}F NMR (282 MHz, CDCl_3): δ -79.20 (d, $J=6.8$ Hz). IR (CDCl_3): 344, 1698, 1638 cm^{-1} . MS (EI) m/z (relative intensity): 274 (M^+ , 17), 205 ($\text{M}-\text{CF}_3$, 27), 159 (100); (CI) m/z 275 ($\text{m}+\text{H}$).

Ethyl (2Z)-2-[hydroxy(pentafluorophenyl)methyl]-3-phenylacrylate (7i):

^1H NMR (300 MHz, CDCl_3): δ 1.06 (t, $J=7.14$ Hz, 3H), 3.48 (d, $J=7.14$ Hz, 1H), 4.09 (q, $J=7.14$ Hz, 2H), 5.99 (d, $J=6.30$ Hz, 1H), 7.15 (s, 1H), 7.30 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3): δ 13.4, 61.3, 66.5, 114.9, 128.1, 128.4, 128.5, 132.1, 134.9, 135.6, 135.0, 146.8, 167.54; ^{19}F NMR (282 MHz, CDCl_3): δ -143.60 (m, 2F), -155.6 (t, $J=21.2$ Hz, 1F), -163.2 (m, 2F). IR (CDCl_3): 3426, 1695, 1651 cm^{-1} . MS (EI) m/z (relative intensity): 372 (M^+ , 23), 355 (M-OH, 31), 131 (100); (CI) m/z 373 (M+H, 1), 355 (100).

Ethyl (2Z)-2-(2,2,2-trifluoro-1-hydroxy-1-methylethyl)-3-phenylacrylate (7j):

^1H NMR (300 MHz, CDCl_3): δ 1.02 (t, $J=7.14$ Hz, 3H), 1.71 (s, 1H), 4.10 (m, 2H), 4.75 (s, 1H), 7.17 (s, 1H), 7.3 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3): δ 13.3, 21.3, 61.8, 75.0 (q, $J=29.41$ Hz), 125.5 (q, $J=286.8$ Hz), 128.1, 128.3, 128.7, 131.2, 135.0, 136.6, 169.3; ^{19}F NMR (282 MHz, CDCl_3): δ -81.8 (s). IR (CDCl_3): 3431, 1675, 1621 cm^{-1} . MS (EI) m/z (relative intensity): 288 (M^+ , 24) 173 (100); (CI) m/z 289 (M+H, 100), 271 (80).

Ethyl (2Z)-2-(2,2,2-trifluoro-1-hydroxy-1-phenylethyl)-3-phenylacrylate (7k):

^1H NMR (300 MHz, CDCl_3): δ 0.92 (t, $J=7.14$ Hz, 3H), 4.02 (q, $J=7.14$ Hz, 2H), 5.34 (s, 1H), 7.06 (s, 1H), 7.39 (m, 8H), 7.75 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 13.2, 61.9, 79.6 (q, $J=28.83$ Hz), 124.7 (q, $J=286.7$ Hz), 127.5, 128.2, 128.3, 128.9, 129.1, 131.1, 134.9, 136.0, 137.8, 169.6; ^{19}F NMR (282 MHz, CDCl_3): δ -75.5 (s). IR (CDCl_3): 3446, 1685, 1655 cm^{-1} . MS

(EI) m/z (relative intensity): 350 (M^+ , 12), 105 ($C_6H_5CO^+$, 100); (CI) m/z 351 ($M+H$, 8) 333 ($M+H-H_2O$, 100).

Ethyl (2Z)-2-(2,2,2-trichloro-1-hydroxyethyl)-3-phenylacrylate (7m): 1H NMR (300 MHz, $CDCl_3$): δ 1.05 (t, $J=7.17$ Hz, 3H), 4.12 (q, $J=7.14$ Hz, 2H), 5.11 (s, 2 H), 7.30 (s, 1H), 7.33 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.4, 61.7, 84.4 (q, $J=32.5$ Hz), 102.3, 127.5, 128.2, 128.4, 128.9, 134.7, 142.7, 168.8. IR ($CDCl_3$): 3446, 1715, 1625 cm^{-1} . MS (EI) m/z (relative intensity): 277/279/281 (m-OEt, 1.3/1.1/0.4); (CI) m/z 323/325/327 (m+H).

Diethyl (3Z)-3-benzylidene-2-hydroxy-2-methylsuccinate (7n): 1H NMR (300 MHz, $CDCl_3$): δ 1.06 (t, $J=7.14$ Hz, 3H), 1.30 (t, $J=7.14$ Hz, 3H), 1.71 (s, 3H), 3.91 (s, 3H), 4.10 (q, $J=7.14$ Hz, 2H), 4.28 (m, 2H), 7.02 (s, 1H), 7.31 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.6, 14.0, 24.7, 61.0, 62.6, 75.2, 128.2, 128.3, 132.9, 135.4, 136.5, 168.2, 174.8. IR ($CDCl_3$): 3492, 1721, 1634 cm^{-1} . MS (EI) m/z (relative intensity): 275, 219 (m-COOEt), 173 (100); (CI) m/z 293 (m+H).

4-Ethyl 1-methyl (3Z)-3-benzylidene-2-hydroxy-2-phenylsuccinate (7o): 1H NMR (300 MHz, $CDCl_3$): δ 1.05 (t, $J=7.14$ Hz, 3H), 3.90 (s, 3H), 4.13 (m, 2H), 4.45 (s, 1H), 6.57 (s, 1H), 7.30 (m, 8H), 7.72 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.5, 53.5, 61.2, 72.1, 80.8, 126.6, 127.1, 128.0, 128.2, 128.3, 128.4, 128.6, 135.3, 136.6, 138.3, 168.6, 173.9. MS (EI)

m/z (relative intensity): 323 (M-OH, 1), 105 (100); (CI) m/z 341 (m+H, 0.6), 323 (m+H-H₂O, 100).

Ethyl (2Z)-2-(1-cyano-1-hydroxyethyl)-3-phenylacrylate 3 (7p): ¹H NMR (300

MHz, CDCl₃): δ 1.23 (t, *J*=7.14 Hz, 3H), 2.38 (s, 3H), 4.30 (q, *J*=7.14 Hz), 4.8 (br s, 1 H), 7.40 (m, 5H), 7.54 (s, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 13.9, 14.0, 22.7, 26.5, 31.6, 61.7, 128.8, 129.5, 130.7, 132.9, 134.7, 141.3, 167.7, 194.7. MS (EI) m/z (relative intensity): 245 (M⁺, 1), 218 (100); (CI) m/z 246 (M+H, 48), 219 (M+H-HCN, 100).

Ethyl (2Z)-2-benzylidene-3-hydroxy-3-methyl-pent-4-ynoate (7q): ¹H NMR

(300 MHz, CDCl₃) δ 1.09 (t, *J*=7.14 Hz, 3H), 1.82 (s, 3H), 2.65 (s, 1H), 3.57 (s, 1H), 4.17 (q, *J*=7.14 Hz, 2H), 7.22 (s, 1H), 7.30 (m, 5H); ¹³C NMR (75 MHz, CDCl₃): δ 13.7, 29.6, 61.4, 69.1, 73.7, 85.3, 128.3, 128.4, 128.6, 131.6, 135.1, 137.3, 169.0; IR (CDCl₃): 3466, 3305, 2250, 1715, 1635 cm⁻¹. MS (EI) m/z (relative intensity): 244 (M⁺, 1), 183 (100); (CI) m/z 245 (M+H, 0.36).

Ethyl (2Z)-2-(1-hydroxy-1-methyl-2-oxopropyl)-3-phenylacrylate (7r): ¹H

NMR (300 MHz, CDCl₃): δ 1.04 (t, *J*=7.14 Hz, 3H), 1.60 (s, 3H), 2.35 (s, 3H), 4.09 (q, *J*=7.14 Hz, 2H), 4.46 (s, 1H), 6.99 (s, 1H), 7.31 (m, 5H); ¹³C NMR (75 MHz, CDCl₃): δ 13.5, 23.1, 23.2, 61.2, 79.8, 128.2, 128.3, 128.5, 133.3, 135.0, 136.7, 168.4, 208.4. IR (CDCl₃): 3439, 1715, 1635 cm⁻¹. MS (EI) m/z (relative intensity): 219 (M-COCH₃, 37), 173 (100); (CI) m/z 263 (m+H, 27), 245 (100); HRMS: 263.1283 (calc.), 263.1285 (actual).

Ethyl (2Z)-2-(1-hydroxy-1-methyl-2-oxobutyl)-3-phenylacrylate (7u): ^1H NMR (300 MHz, CDCl_3) δ •1.03 (t, J =7.14 Hz, 3H), 1.17 (t, J =7.20 Hz, 3H), 1.59 (s, 3H), 1.93 (d, J =7.30 Hz, 3H), 2.70 (m, 2H), 4.08 (m, 2H), 4.52 (s, 1H), 6.97 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 8.1, 13.5, 23.5, 28.6, 61.1, 79.6, 128.2, 128.3, 125.5, 133.1, 135.1, 137.0, 168.4, 211.4; IR (CDCl_3): 3449, 1715 cm^{-1} ; MS (EI) m/z (relative intensity) 259 (M-OH, 3), 131 (100); (CI) m/z 277 (m+H, 17), 259 (100).

Ethyl (2Z)-2-(1-ethyl-1-hydroxy-2-oxopropyl)-3-phenylacrylate (7'u): ^1H NMR (300 MHz, CDCl_3): δ •0.90 (t, J =7.38 Hz, 3H), 1.05 (t, J =7.14 Hz, 3H), 2.03 (m, 2H), 2.31 (s, 3H), 4.08 (m, 2H), 4.41 (s, 1H), 6.96 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 7.0, 13.5, 23.3, 28.0, 61.1, 82.2, 128.1, 128.2, 128.5, 132.6, 135.1, 136.7, 168.4, 207.9; IR (CDCl_3): 3439, 1715 cm^{-1} . MS (EI) m/z (relative intensity) 259 (M-OH, 3), 131 (100); (CI) m/z 277 (m+H, 17), 259 (100).

Ethyl (2Z)-1-(1-hydroxy-2-oxo-1-phenylpropyl)-3-phenylacrylate (7v): ^1H NMR (300 MHz, CDCl_3): δ •1.01 (t, J =7.14 Hz, 3H), 2.31 (s, 3H), 4.10 (m, 2H), 5.20 (s, 1H), 6.59 (s, 1H), 7.14 (m, 2H), 7.21 (m, 3H), 7.38 (m, 3H), 7.59 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 13.4, 25.5, 61.3, 86.1, 127.2, 128.0, 128.4, 128.5, 128.5, 135.4, 136.7, 137.1, 139.3, 170.4, 209.0. IR (CDCl_3): 3452, 1711, 1682, 1608 cm^{-1} . MS (EI) m/z (relative intensity): 281

(M-COCH₃, 9), 105 (100); (CI) m/z 325 (M+H, 1), 307 (100); HRMS: 325.1440 (calc.), 325.1450 (actual).

Ethyl 2-oxiran-2-ylacrylate (8w): ¹H NMR (300 MHz, CDCl₃): δ1.33 (t, *J*=7.1 Hz, 3H), 2.54 (dd, *J*=6.0 and 2.5 Hz, 1H), 2.99 (dd, *J*=6.0 and 4.1 Hz, 1H), 3.75 (m, 1H), 4.27 (q, *J*=7.10 Hz, 2H), 5.79 (s, 1 H), 6.24 (s, 1H); ¹³C NMR (75 MHz, CDCl₃): δ14.2, 49.3, 50.5, 60.9, 124.3, 138.8, 165.4. IR (neat): 2978, 1712, 1631 cm⁻¹. MS (EI) m/z (relative intensity): 114 (20), 59 (100); (CI) m/z 143 (M+H, 53), 97 (100).

Preparation of ethyl 2-(2-phenyloxiran-2-yl)acrylate (8x): 13.8 g (100 mmol) of K₂CO₃ was added to 3.0 g (10 mmol) of **5x** dissolved in acetone (40 mL) and the mixture was stirred vigorously for 6 h. After filtration, concentration under reduced pressure, and purification by column chromatography over silica gel, 1.92 g (88% yield) of **8x** was obtained. ¹H NMR (300 MHz, CDCl₃): δ1.18 (t, *J*=7.10 Hz, 3H), 3.14 (d, *J*=5.40 Hz, 1H), 3.18 (d, *J*=5.50 Hz, 1H), 4.15 (q, *J*=7.10 Hz, 2H), 6.07 (s, 1 H), 6.48 (s, 1H), 7.2-7.38 (m, 5H); ¹³C NMR (75 MHz, CDCl₃): δ14.0, 55.8, 59.9, 60.9, 126.4, 128.1, 128.2, 128.7, 138.4, 140.0, 165.2.

Ethyl 2-[2-(trifluoromethyl)oxiran-2-yl]acrylate (8w): ¹H NMR (300 MHz, CDCl₃): δ1.32 (t, *J*=7.1 Hz, 3H), 2.91 (m, 1H), 3.36 (d, *J*=5.0, 1H), 4.28 (m, 2H), 6.21 (s, 1 H), 6.64 (s, 1H); ¹⁹F NMR (282 MHz, CDCl₃): δ-76.7; ¹³C NMR (75 MHz, CDCl₃): δ14.0, 50.7, 58.7, 61.4, 122.6 (q, *J*=279 Hz), 133.0, 133.1, 163.9. IR (neat): 2985, 1725, 1634 cm⁻¹. MS (EI) m/z (relative intensity): 182 (12), 59 (100); (CI) m/z 211 (M+H, 100).

Preparation of (3Z)-3-dodec-11-enylidene-4-hydroxy-5-methyl-

dihydro-furan-2-one (Listenolide A₁) (10): To hydroxyester **16** (0.093 g, 0.33 mmol) in CH₂Cl₂ (5 mL) were added a few drops of CF₃COOH and the mixture was refluxed for 3 h. Excess trifluoroacetic acid was quenched with saturated aq. NaHCO₃ (5 mL), the product was extracted with Et₂O (3×10 mL) and dried with MgSO₄. The volatiles were evaporated and the residue was purified on silica gel (hexanes:ethyl acetate 4:1) to give **10** in 99% yield as a thick oil (0.093 g, 0.32 mmol). ¹H NMR (300 MHz, CDCl₃): 6.54 (t, *J*=7.56 Hz, 1H), 5.74-5.87 (m, 1H), 4.90-5.01 (m, 3H), 4.33-4.37 (m, 2H), 2.67-2.79 (m, 2H), 2.00-2.05 (m, 2H), 1.26-1.48 (m, 17H); ¹³C NMR (75 MHz, CDCl₃): 149.8, 149.4, 139.3, 128.8, 114.1, 81.4, 75.6, 33.8, 29.7, 29.5, 29.4, 29.2, 29.1, 29.0, 28.9, 27.8, 19.2, 14.1. MS: (EI/CI) *M*⁺ = 281; HRMS: 280.2042 (actual), 280.2038 (calc.).

4-Hydroxy-5-methyl-3-methylenedihydrofuran-2(3*H*)-one (9): ¹H NMR (300 MHz, CDCl₃): δ6.43 (s, 1H), 5.97 (s, 1H), 4.34-4.49 (m, 2H), 2.27 (br s, 1H), 1.45 (d, *J*=7.41 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ168.3, 138.8, 125.9, 81.6, 74.4, 19.1. EI/CI: *M*⁺ = 129; HRMS: 129.0556 (actual), 129.0552 (calc.).

Preparation of ethyl (2Z)-2-(1-hydroxy-2-oxopropyl)-tetradeca-2,13-

dienoate (14): To NMO (5.24 g, 44 mmol) slurred in THF (30 mL) and cooled to 0 °C was added DIBAL-H (6.7 mL, 37 mmol) in THF (23 mL) and the reaction was stirred for 0.5 h at 0 °C,

followed by addition of ethyl tetradec-13-en-2-ynoate (5.57 g, 22 mmol). The mixture was warmed to rt, stirred for 4 h, and **4z** (3.08 g, 19 mmol) was added. After overnight stirring at rt, the reaction was quenched with saturated aq. NH_4Cl , product was extracted with Et_2O (3×50 mL) and washed with brine. After removal of the volatiles, the product was filtered through silica gel (hexanes:ethyl acetate 98:2) to give the desired dithiane **12** in 46% yield (2.83 g, 8.74 mmol). The dithiane **12** (0.07 g, 0.17 mmol) in CH_3CN (1 mL) was rapidly added to a vigorously stirring solution of NCS (0.10 g, 0.8 mmol) and AgNO_3 (0.14 g, 0.85 mmol) in CH_3CN (10 mL) and H_2O (3 mL). White precipitate immediately formed and the mixture was stirred for 5 min., and then were added saturated aqueous (1 mL each): Na_2SO_3 , NaHCO_3 , and NaCl . After addition of hexanes (5 mL) and CH_2Cl_2 (5 mL), the mixture was filtered, organic layer was separated and purified on silica gel (flash; hexanes:ethyl acetate 98:2) to afford **15** as a thick oil in 82% yield (0.05 g, 0.14 mmol). ^1H NMR (300 MHz, CDCl_3): 6.32 (t, $J=7.42$ Hz, 1H), 5.74-5.88 (m, 1H), 4.91-5.02 (m, 2H), 4.52 (s, 1H), 4.18-4.22 (m, 2H), 4.07 (d, $J=1.17$ Hz, 1H), 2.48-2.59 (m, 2H), 2.19 (s, 3H), 2.00-2.07 (m, 2H), 1.24-1.48 (m, 17H); ^{13}C NMR (75 MHz, CDCl_3): 206.4, 165.7, 149.0, 130.3, 114.1, 80.6, 76.6, 60.8, 33.8, 30.3, 29.6, 29.4, 29.3, 29.1, 29.0, 28.9, 24.7, 14.0. EI/CI: $\text{M}^+ = 325$; HRMS: 325.2376 (actual), 325.2379 (calc.).

Ethyl 2-(1-hydroxy-2-oxopropyl)acrylate (14): ^1H NMR (300 MHz, CDCl_3): 6.44 (s, 1H), 5.97 (s, 1H), 4.79 (d, $J=4.68$ Hz, 1H), 4.24 (q, $J=7.14$ Hz, 2H), 4.08 (d, $J=4.74$ Hz, 1H), 2.19 (s, 3H), 1.27 (t, $J=7.14$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): 205.7, 165.3, 138.5, 129.9, 76.6, 61.4, 25.0, 14.1. EI/CI: $\text{M}^+ = 173$; HRMS: 173.0806 (actual), 173.0814 (calc.).

Preparation of ethyl (2Z)-2-(1,2-dihydroxypropyl)tetradeca-2,13-

dienoate (17): Ketone **15** (0.132 g, 0.40 mmol) was diluted with Et₂O (0.7 mL) and cooled to 0 °C. To that mixture was added Zn(BH₄)₂ (6.8 M in H⁻ in THF; 0.12 mL, 0.20 mmol) and it was stirred at 0 °C for 2 h. The excess of Zn(BH₄)₂ was quenched with aq. 10% HCl, the product was extracted with ether (3×20 mL), washed with brine, and dried with MgSO₄. The solvent was removed under aspirator vacuum and the residue was purified on silica gel (hexanes:ethyl acetate 3:1) to give **17** in 93% yield (0.122 g, 0.37 mmol) in 5:95 *syn:anti* ratio (determined by ¹H NMR as the ratio of multiplets at 3.93 and 3.82). ¹H NMR (300 MHz, CDCl₃): 6.15 (t, *J*=7.47 Hz, 1H), 5.74-5.87 (m, 1H), 4.91-5.01 (m, 2H), 4.13-4.29 (m, 3H), 3.90-3.94 (m, 1H), 3.18 (d, *J*=7.8 Hz) and 3.11 (d, *J*=5.76 Hz, 1H), 2.38-2.45 (m, 3H), 2.01-2.08 (m, 2H), 1.20-1.41 (m, 20H); ¹³C NMR (75 MHz, CDCl₃): 168.3, 145.3, 144.3, 139.3, 130.6, 114.2, 78.1, 69.8, 60.9, 33.8, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 28.9, 18.4, 14.2. MS: (EI/CI) M⁺ = 327; HRMS: 327.2533 (actual), 327.2535 (calc.).

Ethyl 2-(1,2-dihydroxypropyl)acrylate (16): ¹H NMR (300 MHz, CDCl₃):

δ1.26 (d, *J*=6.12 Hz) and 1.13 (d, *J*=6.57 Hz, 3H), 1.32 (t, *J*=7.44 Hz, 3H), 2.27 (br s, 1H), 3.04 (br s, 1H), 4.00-4.08 (m, 1H), 4.24 (q, *J*=7.07 Hz, 2H), 4.44 (d, *J*=3.18 Hz, 1H), 5.91 (s, 1H), 6.35 (s, 1H); ¹³C NMR (300 MHz, CDCl₃): δ14.1, 17.6, 69.1, 61.3, 75.2, 127.4, 139.1, 168.8. MS: EI/CI: M⁺ = 175; HRMS: 175.0969 (actual), 175.0970 (calc.).

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