Supporting information

Bu₄N⁺ Controlled Addition and Olefination with Ethyl 2-(Trimethylsilyl)acetate via Si activation

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General Experimental.

All of the reactions involving air-sensitive reagents were performed under nitrogen either in oven- or flame-dried glassware using syringe-septum cap technique. All of the solvents were purified and degassed before use. THF was purified under nitrogen over Na/benzophenone ketyl. Pre-weighed amounts of Bu₄NOAc were stored in a desiccator utilizing CaCl₂ as a desiccant. Pre-weighed amounts of Me₃SiOK and Bu₄NCl were stored in a desiccator utilizing P₂O₅ as a desiccant and used immediately upon removal from the desiccator. Potassium acetate was dried in a desiccator utilizing P₂O₅ as a desiccant. Aldehydes were purified by distillation or passed through aluminum oxide column prior to use. Chromatographic separations were carried out on aluminum oxide 60 using flash-column techniques. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm silica gel coated aluminum plates with UV light (254 nm) as the visualizing agent. ¹H and ¹³C NMR spectra were recorded at room-temperature on a 400 MHz spectrometer. The yields are of isolated compounds after purification through column chromatography.
Figure 1. Structure of carbonyl compounds utilized
Experimental procedures for Table 1 (3a and 4a)

**Ethyl 3-hydroxy-3-phenylpropanoate, 3a.**
A solution of ethyl 2-(trimethylsilyl)acetate, 1 (137 µL, 0.75 mmol) and benzaldehyde 2a (51 µL, 0.50 mmol) in anhydrous THF (2.5 mL) was treated with dried Bu₄NOAc (15 mg, 0.05 mmol) under N₂. The resulting solution was stirred at room temperature for 1 h. Aqueous HCl (2 M, 10 mL) was added and stirred for 30 min. The residue was extracted with diethyl ether (15 mL x 3), organic layers combined, washed with brine, dried over sodium sulfate and concentrated under reduced pressure. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (90:10) afforded 3a as a colorless oil (88 mg, 90%).

1H NMR (400 MHz, CDCl₃): δ 7.41 – 7.25 (m, 5H), 5.13 (dd, J = 8.7, 4.1 Hz, 1H), 4.18 (q, J = 7.2 Hz, 2H), 3.32 (bs, 1H), 2.80 – 2.67 (m, 2H), 1.26 (t, J = 7.2 Hz, 3H) ppm. 13C NMR (100 MHz, CDCl₃): δ 172.5, 142.6, 128.7, 127.9, 125.8, 70.4, 61.0, 43.5, 14.3 ppm. MS-ESI [M+H]+: 195.0, C₁₁H₁₅O₃ requires 195.1.

**(E)-Ethyl cinnamate, 4a.**
A solution of benzaldehyde (51 µL, 0.50 mmol) and ethyl 2-(trimethylsilyl)acetate 1 (137 µL, 0.75 mmol) in THF (2.5 mL) was treated with dried Bu₄NCl (42 mg, 0.15 mmol) and Me₃SiOK (19 mg, 0.15 mmol) under N₂. The resulting reaction mixture was stirred at room temperature for 2 h. The reaction mixture was quenched with aqueous HCl (2 M, 10 mL) and stirred for 5 min at rt. The residue was extracted with ethyl acetate (15 mL x 3). Organic layers were combined and washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. Purification by aluminum oxide chromatography eluting with cyclohexane/ethyl acetate (99:1) yielded 4a (77 mg, 87%, E/Z = 99:1) as colorless oil.

1H NMR (CDCl₃, 400 MHz): δ 7.69 (d, J = 16 Hz, 1H), 7.56-7.49 (m, 2H), 7.42-7.35 (m, 3H), 7.45 (d, J = 16 Hz, 1H), 4.27 (q, 2H), 1.31 (t, 3H). 13C NMR (CDCl₃, 100 MHz): δ 166.9, 144.5, 134.5, 130.2, 128.8, 128.0, 118.3, 60.4, 14.2. MS-EI [M]+: 176.1, C₁₁H₁₂O₂ requires 176.1.
Experimental procedures for Table 2 (3b to 3o)

**Ethyl 3-(2-chlorophenyl)-3-hydroxypropanoate, 3b.** A solution of ethyl 2-(trimethylsilyl)acetate, 1 (137 μL, 0.75 mmol) and 2-chlorobenzaldehyde 2b (70 mg, 0.50 mmol) in anhydrous THF (2.5 mL) was treated with dried Bu₄NOAc (15 mg, 0.05 mmol) under N₂. The resulting solution was stirred at room temperature for 1 h. Aqueous HCl (2 M, 10 mL) was added and stirred for 30 min. The residue was extracted with diethyl ether (15 mL x 3), organic layers combined, washed with brine, dried over sodium sulfate and concentrated under reduced pressure. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (90:10) afforded 3b as a colorless oil (91 mg, 80%). ¹H NMR (400 MHz, CDCl₃): δ 7.63 (dd, J = 7.7, 1.6 Hz, 1H), 7.36 – 7.27 (m, 2H), 7.22 (td, J = 7.6, 1.7 Hz, 1H), 5.49 (dd, J = 9.7, 2.5 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.61 (bs, 1H), 2.86 (dd, J = 16.6, 2.7 Hz, 1H), 2.58 (dd, J = 16.6, 9.7 Hz, 1H), 1.28 (t, J = 7.1 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 172.7, 140.0, 131.5, 129.5, 128.9, 127.3, 127.2, 67.2, 61.1, 41.5, 14.3, ppm. MS-ESI [M+H]⁺: 229.0, C₁₁H₁₄O₃Cl requires 229.1.

**Ethyl 3-hydroxy-3-(3-methoxyphenyl)propanoate, 3c.** A solution of ethyl 2-(trimethylsilyl)acetate, 1 (137 μL, 0.75 mmol) and 3-methoxybenzaldehyde 2c (68 mg, 0.50 mmol) in anhydrous THF (2.5 mL) was treated with dried Bu₄NOAc (15 mg, 0.05 mmol) under N₂. The resulting solution was stirred at room temperature for 1 h. Aqueous HCl (2 M, 10 mL) was added and stirred for 30 min. The residue was extracted with diethyl ether (15 mL x 3), organic layers combined, washed with brine, dried over sodium sulfate and concentrated under reduced pressure. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (90:10) afforded 3c as a colorless oil (81 mg, 72%). ¹H NMR (400 MHz, CDCl₃): δ 7.29 – 7.23 (m, 1H), 6.97 – 6.91 (m, 2H), 6.85 – 6.80 (m, 1H), 5.11 (dd, J = 8.6, 4.2 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.81 (s, 3H), 3.35 (bs, 1H), 2.79 – 2.66 (m, 2H), 1.27 (t, J = 7.1 Hz, 3H) ppm.
\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 172.5, 159.9, 144.3, 129.7, 118.0, 113.5, 111.2, 70.3, 61.0, 55.3, 43.5, 14.3, ppm. MS-ESI [M+H]\(^{+}\): 225.0, C\(_{12}\)H\(_{17}\)O\(_4\) requires 225.1.

Ethyl 3-hydroxy-3-(4-methoxyphenyl)propanoate, 3d.\(^1\) A solution of ethyl 2-(trimethylsilyl)acetate, 1 (137 \(\mu\)L, 0.75 mmol) and 4-methoxybenzaldehyde 2d (68 mg, 0.50 mmol) in anhydrous THF (2.5 mL) was treated with dried Bu\(_4\)NOAc (15 mg, 0.05 mmol) under N\(_2\). The resulting solution was stirred at room temperature for 1 h. Aqueous HCl (2 M, 10 mL) was added and stirred for 30 min. The residue was extracted with diethyl ether (15 mL \(\times\) 3), organic layers combined, washed with brine, dried over sodium sulfate and concentrated under reduced pressure. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (90:10) afforded 3d as a colorless oil (89 mg, 79%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.29 (d, \(J = 8.7\) Hz, 2H), 6.88 (d, \(J = 8.7\) Hz, 2H), 5.08 (dd, \(J = 9.2, 3.8\) Hz, 1H), 4.17 (q, \(J = 7.1\) Hz, 1H), 3.80 (s, 3H), 3.24 (bs, 1H), 2.75 (dd, \(J = 16.3, 9.2\) Hz, 1H), 2.66 (dd, \(J = 16.3, 3.8\) Hz, 1H), 1.26 (t, \(J = 7.1\) Hz, 3H), ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 172.6, 159.3, 134.8, 127.1, 114.0, 70.1, 61.0, 55.4, 43.4, 14.3, ppm. MS-ESI [M+H]\(^{+}\): 225.1, C\(_{12}\)H\(_{17}\)O\(_4\) requires 225.1.

Ethyl 3-(4-bromophenyl)-3-hydroxypropanoate, 3e.\(^1\) A solution of ethyl 2-(trimethylsilyl)acetate, 1 (137 \(\mu\)L, 0.75 mmol) and 4-bromobenzaldehyde 2f (93 mg, 0.50 mmol) in anhydrous THF (2.5 mL) was treated with dried Bu\(_4\)NOAc (15 mg, 0.05 mmol) under N\(_2\). The resulting solution was stirred at room temperature for 1 h. Aqueous HCl (2 M, 10 mL) was added and stirred for 30 min. The residue was extracted with diethyl ether (15 mL \(\times\) 3), organic layers combined, washed with brine, dried over sodium sulfate and concentrated under reduced pressure. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (90:10) afforded 3e as a colorless oil (118 mg, 86%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.45 (d, \(J = 8.4\) Hz, 2H), 7.23 (d, \(J = 8.4\) Hz, 2H), 5.06 (dd, \(J = 8.3, 4.6\) Hz, 1H), 4.15 (q, \(J = 7.1\) Hz, 2H),
3.58 (bs, 1H), 2.73 – 2.60 (m, 2H), 1.24 (t, J = 7.1 Hz, 3H), ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 172.3, 141.7, 131.7, 127.5, 121.6, 69.7, 61.1, 43.3, 14.2, ppm. MS-ESI [M+H]$^+$: 273.1, C$_{11}$H$_{14}$O$_3$Br requires 273.0.

![Ethyl 3-hydroxy-3-(3,4,5-trimethoxyphenyl)propanoate](image)

**Ethyl 3-hydroxy-3-(3,4,5-trimethoxyphenyl)propanoate, 3f.** A solution of ethyl 2-(trimethylsilyl)acetate, 1 (137 µL, 0.75 mmol) and 3,4,5-trimethoxybenzaldehyde 2l (98 mg, 0.50 mmol) in anhydrous THF (2.5 mL) was treated with dried Bu$_4$NOAc (15 mg, 0.05 mmol) under N$_2$. The resulting solution was stirred at rt for 1 h. Aqueous HCl (2 M, 10 mL) was added and stirred for 30 min. The residue was extracted with diethyl ether (15 mL x 3), organic layers combined, washed with brine, dried over sodium sulfate and concentrated under reduced pressure. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (75:25) afforded 3f as a colorless oil (119 mg, 84%). $^1$H NMR (400 MHz, CDCl$_3$): δ 6.60 (s, 2H), 5.07 (dd, J = 8.8, 4.0 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.86 (s, 6H), 3.83 (s, 3H), 3.31 (bs, 1H), 2.80 – 2.64 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H), ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 172.6, 153.5, 138.4, 137.5, 102.6, 70.6, 61.1, 61.0, 56.2, 43.6, 14.3, ppm. MS-ESI [M+H]$^+$: 285.2, C$_{14}$H$_{21}$O$_6$ requires 285.1.

![Ethyl 3-hydroxy-3-(naphthalen-2-yl)propanoate](image)

**Ethyl 3-hydroxy-3-(naphthalen-2-yl)propanoate, 3g.** A solution of ethyl 2-(trimethylsilyl)acetate, 1 (137 µL, 0.75 mmol) and 2-napthaldehyde 2m (78 mg, 0.50 mmol) in anhydrous THF (2.5 mL) was treated with dried Bu$_4$NOAc (15 mg, 0.05 mmol) under N$_2$. The resulting solution was stirred at room temperature for 1 h. Aqueous HCl (2 M, 10 mL) was added and stirred for 30 min. The residue was extracted with diethyl ether (15 mL x 3), organic layers combined, washed with brine, dried over sodium sulfate and concentrated under reduced pressure. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate...
(90:10) afforded 3g as a colorless oil (102 mg, 83%). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.89 – 7.79 (m, 4H), 7.53 – 7.43 (m, 3H), 5.31 (dd, $J = 8.2$, 4.4 Hz, 1H), 4.20 (q, $J = 7.1$ Hz, 2H), 3.44 (bs, 1H), 2.89 – 2.75 (m, 2H), 1.27 (t, $J = 7.2$ Hz, 3H), ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 172.6, 140.0, 133.4, 133.1, 128.5, 128.1, 127.8, 126.4, 126.1, 124.6, 123.9, 70.6, 61.1, 43.4, 14.3, ppm. MS-ESI [M+H]$^+$: 245.0, C$_{15}$H$_{17}$O$_3$ requires 245.1.

**Ethyl 3-hydroxy-3-(ferrocenyl)propanoate, 3h.** A solution of ethyl 2-(trimethylsilyl)acetate, 1 (137 µL, 0.75 mmol) and ferrocencarboxaldehyde 2n (107 mg, 0.50 mmol) in anhydrous THF (2.5 mL) was treated with dried Bu$_4$NOAc (150 mg, 0.5 mmol) under N$_2$. The resulting solution was stirred at room temperature for 30 min. Aqueous HCl (2 M, 10 mL) was added and stirred for 30 min. The residue was extracted with diethyl ether (15 mL x 3), organic layers combined, washed with brine, dried over sodium sulfate and concentrated under reduced pressure. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (95:5) afforded 3h as a red oil (85 mg, 56%). $^1$H NMR (400 MHz, CDCl$_3$): δ 4.86 (dd, $J = 7.7$, 5.2 Hz, 1H), 4.28 – 4.14 (m, 11H), 2.82 – 2.65 (m, 3H), 1.28 (t, $J = 7.1$ Hz, 3H), ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 172.2, 91.6, 68.6 (5C), 68.2 (2C), 66.6, 66.5, 66.2, 60.9, 42.9, 14.3, ppm. HRMS-ESI [M+H]$^+$: 303.0690, C$_{15}$H$_{19}$O$_3$Fe requires 303.0684.

**Ethyl 3-(furan-2-yl)-3-hydroxypropanoate, 3i.** A solution of ethyl 2-(trimethylsilyl)acetate, 1 (137 µL, 0.75 mmol) and furan-2-carbaldehyde 2p (48 mg, 0.50 mmol) in anhydrous THF (2.5 mL) was treated with dried Bu$_4$NOAc (15 mg, 0.05 mmol) under N$_2$. The resulting solution was stirred at room temperature for 1 h. Aqueous HCl (0.5 M, 10 mL) was added and stirred for 30 min. The residue was extracted with diethyl ether (15 mL x 3), organic layers combined, washed with brine, dried over sodium sulfate and concentrated under reduced pressure. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (95:5) afforded 3i as a yellow
oil (67 mg, 73%). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.37 (dd, $J = 1.8$, 0.8 Hz, 1H), 6.33 (dd, $J = 3.2$, 1.8 Hz, 1H), 6.29 – 6.25 (m, 1H), 5.13 (dd, $J = 8.5$, 4.1 Hz, 1H), 4.18 (q, $J = 7.1$ Hz, 2H), 3.32 (bs, 1H), 2.90 (dd, $J = 16.5$, 8.5 Hz, 1H), 2.82 (dd, $J = 16.5$, 4.1 Hz, 1H), 1.26 (t, $J = 7.1$ Hz, 3H), ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 172.1, 154.8, 142.4, 110.4, 106.4, 64.3, 61.1, 39.9, 14.2, ppm. MS-ESI [M+H]$^+$: 185.1, C$_9$H$_{13}$O$_4$ requires 185.1.

Ethyl 3-hydroxy-3-(pyridin-4-yl)propanoate, 3j.$^6$ A solution of ethyl 2-(trimethylsilyl)acetate, 1 (137 µL, 0.75 mmol) and 4-pyridinecarbaldehyde 2q (54 mg, 0.50 mmol) in anhydrous THF (2.5 mL) was treated with dried Bu$_4$NOAc (15 mg, 0.05 mmol) under N$_2$. The resulting solution was stirred at room temperature for 1 h. Aqueous HCl (2 M, 10 mL) was added and stirred for 30 min. Reaction mixture was neutralized with saturated aqueous NaHCO$_3$ solution. The residue was extracted with diethyl ether (15 mL x 3), organic layers combined, washed with brine, dried over sodium sulfate and concentrated under reduced pressure. Purification by aluminum oxide chromatography eluting with first cyclohexane/ethyl acetate (80:20) and then dichloromethane/methanol (99:1) afforded 3j as a colorless oil (68 mg, 70%). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.58 – 8.46 (m, 2H), 7.30 (d, $J = 5.6$ Hz, 2H), 5.12 (dd, $J = 7.8$, 4.9 Hz, 1H), 4.16 (q, $J = 7.1$ Hz, 2H), 4.10 (bs, 1H), 2.77 – 2.63 (m, 2H), 1.24 (t, $J = 7.1$ Hz, 3H), ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 172.0, 152.0, 149.9, 120.8, 68.9, 61.2, 42.9, 14.2, ppm. MS-ESI [M+H]$^+$: 196.2, C$_{10}$H$_{14}$NO$_3$ requires 196.1.

Ethyl (E)-3-hydroxyhex-4-enoate, 3k.$^7$ A solution of ethyl 2-(trimethylsilyl)acetate, 1 (4.11 mL, 22.5 mmol) and crotonaldehyde 2s (1.24 mL, 15.0 mmol) in anhydrous THF (75 mL) was treated with dried Bu$_4$NOAc (0.9 g, 3.0 mmol) under N$_2$. The resulting solution was stirred at room temperature for 1 h. Aqueous HCl (2 M, 100 mL) was added and stirred for 30 min. The residue was extracted with diethyl ether (100 mL x 3), organic layers combined, washed with brine, dried over sodium sulfate and concentrated under reduced pressure. Purification by silica
gel chromatography eluting with cyclohexane/ethyl acetate (90:10) afforded 3k as a yellow oil (1.85 g, 78%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 5.74 (dqd, $J = 14.0, 6.5, 1.0$ Hz, 1H), 5.55 – 5.46 (m, 1H), 4.47 (dd, $J = 12.5, 6.4$ Hz, 1H), 4.16 (q, $J = 7.1$ Hz, 2H), 2.89 (bs, 1H), 2.57 – 2.47 (m, 2H), 1.69 (d, $J = 6.5$ Hz, 3H), 1.26 (t, $J = 7.1$ Hz, 3H), ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 172.6, 131.9, 127.7, 69.1, 60.9, 41.6, 17.8, 14.3, ppm. MS-ESI [M+H]$^+$: 159.0, C$_8$H$_{15}$O$_3$ requires 159.1.

Ethyl 3-cyclohexyl-3-hydroxypropanoate, 3l.$^4$ A solution of ethyl 2-(trimethylsilyl)acetate, 1 (137 $\mu$L, 0.75 mmol) and cyclohexanecarbaldehyde 2t (56 mg, 0.50 mmol) in anhydrous THF (2.5 mL) was treated with dried Bu$_4$NOAc (30 mg, 0.1 mmol) under N$_2$. The resulting solution was stirred at room temperature for 1 h. Aqueous HCl (2 M, 10 mL) was added and stirred for 30 min. The residue was extracted with diethyl ether (15 mL x 3), organic layers combined, washed with brine, dried over sodium sulfate and concentrated under reduced pressure. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (90:10) afforded 3l as colorless oil (74 mg, 74%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 4.17 (q, $J = 7.1$ Hz, 2H), 3.81 – 3.72 (m, 1H), 2.89 (bs, 1H), 2.51 (dd, $J = 16.3, 2.9$ Hz, 1H), 2.40 (dd, $J = 16.3, 9.5$ Hz, 1H), 1.90 – 1.61 (m, 5H), 1.43 – 1.31 (m, 1H), 1.27 (t, $J = 7.1$ Hz, 3H), 1.25 – 0.93 (m, 5H), ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 173.7, 72.3, 60.8, 43.2, 38.7, 28.9, 28.4, 26.5, 26.3, 26.2, 14.3, ppm. MS-ESI [M+H]$^+$: 201.2, C$_{11}$H$_{21}$O$_3$ requires 201.1.

Ethyl 3-hydroxy-5-phenylpentanoate, 3m.$^4$ A solution of ethyl 2-(trimethylsilyl)acetate, 1 (137 $\mu$L, 0.75 mmol) and 3-phenylpropanal 2u (67 mg, 0.50 mmol) in anhydrous THF (2.5 mL) was treated with dried Bu$_4$NOAc (30 mg, 0.1 mmol) under N$_2$. The resulting solution was stirred at room temperature for 30 min. Aqueous HCl (2 M, 10 mL) was added and stirred for 1 h. The residue was extracted with diethyl ether (15 mL x 3), organic layers combined, washed with brine, dried over sodium sulfate and concentrated under reduced pressure. Purification by silica
gel chromatography eluting with cyclohexane/ethyl acetate (90:10) afforded 3m as colorless oil (72 mg, 65%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta \) 7.32 – 7.15 (m, 5H), 4.16 (q, \(J = 7.1 \text{ Hz}, 2\)H), 4.07 – 3.96 (m, 1H), 3.11 (bs, 1H), 2.87 – 2.77 (m, 1H), 2.75 – 2.65 (m, 1H), 2.51 (dd, \(J = 16.5, 3.5 \text{ Hz}, 1\)H), 2.44 (dd, \(J = 16.5, 8.6 \text{ Hz}, 1\)H), 1.90 – 1.68 (m, 2H), 1.27 (t, \(J = 7.1 \text{ Hz}, 3\)H), ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta \) 173.2, 141.9, 128.6, 128.5, 126.0, 60.9, 41.4, 38.2, 31.9, 14.3, ppm. MS-ESI [M+H]\(^+\): 223.0, C\(_{13}\)H\(_{19}\)O\(_3\) requires 223.1.

**Ethyl 3-hydroxyheptanoate, 3n.**\(^8\) A solution of ethyl 2-(trimethylsilyl)acetate, 1 (137 \(\mu\)L, 0.75 mmol) and pentanal 2v (43 mg, 0.50 mmol) in anhydrous THF (2.5 mL) was treated with dried Bu\(_4\)NOAc (30 mg, 0.1 mmol) under N\(_2\). The resulting solution was stirred at room temperature for 30 min. Aqueous HCl (2 M, 10 mL) was added and stirred for 1 h. The residue was extracted with diethyl ether (15 mL x 3), organic layers combined, washed with brine, dried over sodium sulfate and concentrated under reduced pressure. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (95:5) afforded 3n as colorless oil (59 mg, 68%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta \) 4.16 (q, \(J = 7.1 \text{ Hz}, 2\)H), 4.03 – 3.92 (m, 1H), 3.15 (bs, 1H), 2.49 (dd, \(J = 16.4, 3.1 \text{ Hz}, 1\)H), 2.38 (dd, \(J = 16.4, 9.0 \text{ Hz}, 1\)H), 1.59 – 1.28 (m, 6H), 1.26 (t, \(J = 7.2 \text{ Hz}, 2\)H), 0.89 (t, \(J = 7.1 \text{ Hz}, 2\)H), ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta \) 173.3, 68.2, 60.8, 41.4, 36.3, 27.8, 22.7, 14.3, 14.1, ppm. MS-ESI [M+H]\(^+\): 175.1, C\(_9\)H\(_{19}\)O\(_3\) requires 175.1.

**Ethyl 3-hydroxy-3-phenylbutanoate, 3o.**\(^9\) A solution of ethyl 2-(trimethylsilyl)acetate, 1 (137 \(\mu\)L, 0.75 mmol) and acetophenone 2w (60 mg, 0.50 mmol) in anhydrous THF (2.5 mL) was treated with dried Bu\(_4\)NOAc (150 mg, 0.5 mmol) under N\(_2\). The resulting solution was stirred at reflux for 4 h. Aqueous HCl (2 M, 10 mL) was added and stirred for 30 min. The residue was extracted with diethyl ether (15 mL x 3), organic layers combined, washed with brine, dried over sodium sulfate and concentrated under reduced pressure. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (90:10) afforded 3o as colorless oil (22 mg, 21%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta \) 7.47 – 7.43 (m, 2H), 7.37 – 7.30 (m, 2H), 7.25 – 7.20
(m, 1H), 4.40 (s, 1H), 4.06 (q, J = 7.1 Hz, 2H), 2.98 (d, J = 15.9 Hz, 1H), 2.79 (d, J = 15.9 Hz, 1H), 1.54 (s, 3H), 1.13 (t, J = 7.1 Hz, 3H), ppm. \[^{13}\text{C}\text{ NMR (100 MHz, CDCl}_3]): \delta 172.9, 147.0, 128.4, 127.0, 124.6, 72.9, 60.9, 46.5, 30.8, 14.1, ppm. \]

**Experimental procedures for Table 2 (4b to 4u)**

**(E)-Ethyl 3-(2-chlorophenyl)acrylate, 4b.**\(^2\) A solution of ethyl trimethylsilylacetae 1 (137 μL, 0.75 mmol) and 2-chlorobenzaldehyde 2b (56 μL, 0.50 mmol) in THF (2.5 mL) was treated with dried Bu₄NCl (42 mg, 0.15 mmol) and Me₃SiOK (19 mg, 0.15 mmol) under N₂, and the resulting reaction mixture was stirred at room temperature for 2 h. The reaction mixture was quenched with aqueous 2 M HCl (10 mL) and stirred for 5 min at rt. The residue was extracted with ethyl acetate (3 × 15 mL). Organic layers were combined and washed with water and brine, dried over Na₂SO₄ and concentrated under reduced pressure. Purification by aluminum oxide chromatography eluting with cyclohexane/ethyl acetate (98:2) yielded 4b (55 mg, 52%) as colorless oil. \[^1\text{H NMR (CDCl}_3, 400 MHz): \delta 8.09 (d, J = 16 Hz, 1H), 7.64-7.59 (m, 1H), 7.44-7.39 (m, 1H), 7.35-7.24 (m, 2H), 6.42 (d, J = 16 Hz, 1H), 4.28 (q, 2H), 1.35 (t, 3H). \]^\[^{13}\text{C}\text{ NMR (CDCl}_3, 100 MHz): \delta 166.5, 140.3, 134.9, 132.8, 130.9, 130.1, 127.6, 127.0, 121.0, 60.7, 14.3. \]**


**(E)-Ethyl-3-(3-methoxyphenyl)acrylate, 4c.**\(^1\) A solution of ethyl trimethylsilylacetae 1 (137 μL, 0.75 mmol) and 3-methoxybenzaldehyde 2c (61 μL, 0.50 mmol) in THF (2.5 mL) was treated with dried Bu₄NCl (42 mg, 0.15 mmol) and Me₃SiOK (19 mg, 0.15 mmol) under N₂, and the resulting reaction mixture was stirred at room temperature for 2 h. The reaction mixture was quenched with 2 M aqueous HCl (10 mL) and stirred for 5 min at rt. The residue was extracted with ethyl acetate (3 × 15 mL). Organic layers were combined and washed with water and brine, dried over Na₂SO₄ and concentrated under reduced pressure. Purification by aluminum oxide chromatography eluting with cyclohexane/ethyl acetate (98:2) yielded 4c (65 mg, 63%) as
colorless oil. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.65 (d, $J = 16$ Hz, 1H), 7.29 (t, $J = 8$ Hz, 1H), 7.15–7.08 (m, 1H), 7.07–7.02 (m, 1H), 6.96–6.90 (m, 1H), 6.42 (d, $J = 16$ Hz, 1H), 4.26 (q, 2H), 3.83 (s, 3H), 1.34 (t, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 166.9, 159.8, 144.5, 135.8, 129.8, 120.7, 118.5, 116.1, 112.8, 60.5, 55.2, 14.3. MS–EI [M]$^+$: 206.0, C$_{12}$H$_{14}$O$_3$ requires 206.1.

(E)-Ethyl-3-(4-methoxyphenyl)acrylate, 4d. $^2$ A solution of ethyl trimethylsilylacetaet 1 (137 µL, 0.75 mmol) and 4-methoxybenzaldehyde 2d (61 µL, 0.50 mmol) in THF (2.0 mL) was treated with dried Bu$_4$NCl (42 mg, 0.15 mmol) and Me$_3$SiOK (19 mg, 0.15 mmol) under N$_2$, and the resulting reaction mixture was stirred at room temperature for 2 h. The reaction mixture was quenched with 2 M aqueous HCl (10 mL) and stirred for 5 min at rt. The residue was extracted with ethyl acetate (3 × 15 mL). Organic layers were combined and washed with water and brine, dried over Na$_2$SO$_4$ and concentrated under reduced pressure. Purification by aluminum oxide chromatography eluting with cyclohexane/ethyl acetate (95:5) yielded 4d (57 mg, 55%, E/Z = 99:1) as colorless oil. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.64 (d, $J = 16$ Hz, 1H), 7.47 (d, $J = 9$ Hz, 2H), 6.90 (d, $J = 9$ Hz, 2H), 6.30 (d, $J = 16$ Hz, 1H), 4.25 (q, 2H), 3.83 (s, 3H), 1.33 (t, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 167.3, 161.2, 144.2, 129.7, 127.2, 115.7, 114.3, 60.3, 55.4, 14.3. HRMS–EI [M]$^+$: 206.0941, C$_{12}$H$_{14}$O$_3$ requires 206.0943.

(E)-Ethyl 3-(4-fluorophenyl)acrylate, 4e. $^2$ A solution of ethyl trimethylsilylacetaet 1 (137 µL, 0.75 mmol) and 4-fluorobenzaldehyde 2e (54 µL, 0.50 mmol) in THF (2.5 mL) was treated with dried Bu$_4$NCl (42 mg, 0.15 mmol) and Me$_3$SiOK (19 mg, 0.15 mmol) under N$_2$, and the resulting reaction mixture was stirred at room temperature for 2 h. The reaction mixture was quenched with 2 M aqueous HCl (10 mL) and stirred for 5 min at rt. The residue was extracted with ethyl acetate (3 × 15 mL). Organic layers were combined and washed with water and brine, dried over Na$_2$SO$_4$ and concentrated under reduced pressure. Purification by aluminum oxide chromatography eluting with cyclohexane/ethyl acetate (99:1) yielded 4e (69 mg, 71%) as a colorless oil. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.64 (d, $J = 16$ Hz, 1H), 7.53–7.48 (m, 2H), 7.12–7.03 (m, 2H), 7.36 (d, $J = 16$ Hz, 1H), 4.26 (q, 2H), 1.34 (t, 3H). $^{13}$C NMR (CDCl$_3$, 400 MHz): $\delta$
166.8, 163.0 (d, $^1J_{C-F} = 250$ Hz), 143.2, 130.7 ($^3J_{C-F} = 3$ Hz), 129.9 ($^3J_{C-F} = 9$ Hz), 118.0 ($^3J_{C-F} = 2$ Hz), 115.9 ($^3J_{C-F} = 22$ Hz), 60.5, 14.3. $^{19}F$ (282 MHz, CDCl$_3$): -(109.7-109.8) (m). HRMS–EI [M$^+$]: 194.0740, C$_{11}$H$_{11}$FO$_2$ requires 194.0743.

(E)-Ethyl 3-(4-bromophenyl)acrylate, 4f. A solution of ethyl trimethylsilylacetate 1 (137 µL, 0.75 mmol) and 4-bromobenzaldehyde 2f (93 mg, 0.50 mmol) in THF (2.5 mL) was treated with dried Bu$_4$NCl (42 mg, 0.15 mmol) and Me$_3$SiOK (19 mg, 0.15 mmol) under N$_2$, and the resulting reaction mixture was stirred at room temperature for 2 h. The reaction mixture was quenched with 2 M aqueous HCl (10 mL) and stirred for 5 min at rt. The residue was extracted with ethyl acetate (3 x 15 mL). Organic layers were combined and washed with water and brine, dried over Na$_2$SO$_4$ and concentrated under reduced pressure. Purification by aluminum oxide chromatography eluting with (cyclohexane/ethyl acetate: 98/2) yielded 4f (87 mg, 70%, E/Z = 99:1) as colorless oil. $^1$H NMR (CDCl$_3$, 400 MHz): δ 7.61 (d, $J = 16$ Hz, 1H), 7.51 (d, $J = 8$ Hz, 2H), 7.38 (d, $J = 8$ Hz, 2H), 6.42 (d, $J = 16$ Hz, 1H), 4.26 (q, 2H), 1.33 (t, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 166.7, 143.2, 133.4, 132.1, 129.4, 124.4, 119.0, 60.6, 14.3. HRMS–EI [M$^+$]: 253.9939 C$_{11}$H$_{11}$O$_2$Br requires 253.9942.

(E)-Ethyl 3-[(4-trifluoromethyl)phenyl]acrylate, 4g. A solution of ethyl trimethylsilylacetate 1 (137 µL, 0.75 mmol) and 4-(trifluoromethyl)benzaldehyde 2g (68 µL, 0.50 mmol) in THF (2.5 mL) was treated with dried Bu$_4$NCl (42 mg, 0.15 mmol) and Me$_3$SiOK (19 mg, 0.15 mmol) under N$_2$, and the resulting reaction mixture was stirred at room temperature for 2 h. The reaction mixture was quenched with 2 M HCl (10 mL) and stirred for 5 min at rt. The residue was extracted with ethyl acetate (3 x 15 mL). Organic layers were combined and washed with water and brine, dried over Na$_2$SO$_4$ and concentrated under reduced pressure. Purification by aluminum oxide chromatography eluting with cyclohexane/ethyl acetate (90:10) yielded 4g (67 mg, 55%) as colorless oil. $^1$H NMR (CDCl$_3$, 400 MHz): δ 7.69 (d, $J = 16$ Hz, 1H), 7.66-7.61 (m,
(E)-Ethyl-3-(4-(dimethylamino)phenyl)acrylate, 4h. A solution of ethyl 2-(trimethylsilyl)acetate 1 (137 µL, 0.75 mmol) and 4-(dimethylamino)benzaldehyde 2h (75 mg, 0.5 mmol) in THF (2.5 mL) was treated with dried Bu₄NCl (42 mg, 0.15 mmol) and Me₃SiOK (19 mg, 0.15 mmol) under N₂ and the resulting solution was stirred at room temperature for 2 h. The reaction mixture was quenched with saturated aqueous NH₄Cl and stirred for 5 min. The residue was extracted with diethyl ether (3 × 15 mL). Organic layers were combined, washed with brine, dried over anhydrous sodium sulfate and concentrated. Purification by aluminum oxide column chromatography eluting with petroleum ether/ethyl acetate (99:1) yielded 4h as yellow solid, mp 58-60 ºC (83 mg, 76 %, E/Z = 97:3). ¹H NMR (400 MHz, CDCl₃): δ 7.62 (d, J = 15.9 Hz, 1H), 7.42 (d, J = 8.9 Hz, 2H), 6.67 (d, J = 8.9 Hz, 2H), 6.22 (d, J = 15.9 Hz, 1H), 4.24 (q, J = 7.1 Hz, 2H), 3.02 (s, 6H), 1.33 (t, J = 7.1 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 168.0, 151.9, 145.2, 129.8, 122.5, 112.8, 112.0, 60.2, 40.3, 14.6. MS-EI [M⁺]:219.2, C₁₃H₁₇NO₂ requires 219.1.

(E)-Ethyl-3-(4-benzyloxyphenyl)acrylate, 4i. A solution of 4-(benzyloxy)benzaldehyde 2i (106 mg, 0.50 mmol) and ethyl trimethylsilylacetate 1 (137 µL, 0.75 mmol) in THF (2.5 mL) was treated with dried Bu₄NCl (42 mg, 0.15 mmol) and Me₃SiOK (19 mg, 0.15 mmol) under N₂, and the resulting reaction mixture was stirred at room temperature for 2 h. The reaction mixture was quenched with 2 M aqueous HCl (10 mL) and stirred for 5 min at rt. The residue was extracted with ethyl acetate (3 × 15 mL). Organic layers were combined and washed with water and brine, dried over Na₂SO₄ and concentrated under reduced pressure. Purification by
aluminum oxide chromatography eluting with cyclohexane/ethyl acetate (95:5) yielded 4i (103 mg, 73%) as a colorless solid, mp 45–47 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.65 (d, $J = 16$ Hz, 1H), 7.47 (d, $J = 9$ Hz, 2H), 7.44–7.32 (m, 5H), 6.98 (d, $J = 9$ Hz, 2H), 6.32 (d, $J = 16$ Hz, 1H), 5.10 (s, 2H), 4.27 (q, 2H), 1.34 (t, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 167.2, 160.4, 144.1, 136.4, 129.6, 128.6, 128.1, 127.4, 115.9, 115.1, 70.0, 60.2, 14.3. HRMS–ESI [M+Na]$^+$: 305.1162, C$_{18}$H$_{18}$O$_3$Na requires 305.1154.

Methyl-(E)-4-(3-ethoxy-3-oxoprop-1-yl)benzoate, 4j. A solution of methyl 4-formylbenzoate 2j (82 mg, 0.5 mmol) and ethyl 2-((trimethylsilyl)acetate 1 (137 µL, 0.75 mmol) in THF (2.5 mL) was treated with dried Bu$_4$NCl (42 mg, 0.15 mmol) and Me$_3$SiOK (19 mg, 0.15 mmol) under N$_2$ and the resulting solution was stirred at room temperature for 2 h. The reaction mixture was quenched with 2M aqueous HCl (10 mL) and stirred for 5 min at rt. The residue was extracted with diethyl ether (3 × 15 mL). Organic layers were combined, washed with brine, dried over anhydrous sodium sulfate and concentrated under reduced pressure. Purification by aluminum oxide chromatography eluting with petroleum ether/ethyl acetate (98:2) yielded 4j as colorless solid, mp 46-47 °C (87 mg, 74 %, E/Z = 99:1). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.04 (d, $J = 8.3$ Hz, 2H), 7.69 (d, $J = 16.1$ Hz, 1H), 7.58 (d, $J = 8.3$ Hz, 2H), 6.51 (d, $J = 16.1$ Hz, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 3.92 (s, 3H), 1.34 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 166.7, 166.6, 143.3, 138.8, 131.5, 130.2, 128.0, 120.8, 60.9, 52.4, 14.4. MS–EI [M$^+$]: 234.3, C$_{13}$H$_{14}$O$_4$ requires 234.1.

(E)-Ethyl-3-(3,4-dimethoxyphenyl)acrylate, 4k. A solution of 3,4-dimethoxybenzaldehyde 2k (83 mg, 0.50 mmol) and ethyl trimethylsilylacetate 1 (137 µL, 0.75 mmol) in THF (2.5 mL) was treated with dried Bu$_4$NCl (42 mg, 0.15 mmol) and Me$_3$SiOK (19 mg, 0.15 mmol) under N$_2$, and the resulting reaction mixture was stirred at room temperature for 2 h. The reaction mixture was quenched with 2M aqueous HCl (10 mL) and stirred for 5 min at rt. The residue was extracted with ethyl acetate (3 × 15 mL). Organic layers were combined and washed with water
and brine, dried over Na$_2$SO$_4$ and concentrated under reduced pressure. Purification by aluminum oxide chromatography eluting with cyclohexane/ethyl acetate (90:10) yielded 4k (67 mg, 57%) as colorless solid, mp: 39–41 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.61 (d, $J = 16$ Hz, 1H), 7.09 (dd, $J = 2$ and 8 Hz, 1H), 7.06–7.02 (m, 1H), 6.85 (d, $J = 8$ Hz, 1H), 6.30 (d, $J = 16$ Hz, 1H), 4.25 (q, 2H), 3.90 (s, 6H), 1.32 (t, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 167.1, 151.0, 149.1, 144.4, 127.4, 122.5, 115.9, 111.0, 109.5, 60.3, 55.9, 55.8, 14.3. HRMS–ESI [M+Na]$^+$: 259.0953, C$_{13}$H$_{16}$O$_4$Na requires 259.0946.

$^{(E)}$-Ethyl-3-(3,4,5-trimethoxyphenyl)acrylate, 4l. A solution of 3,4,5-trimethoxybenzaldehyde 2l (98 mg, 0.50 mmol) and ethyl trimethylsilylacetate 1 (137 µL, 0.75 mmol) in THF (2.5 mL) was treated with dried Bu$_4$NCl (42 mg, 0.15 mmol) and Me$_3$SiOK (19 mg, 0.15 mmol) under N$_2$, and the resulting reaction mixture was stirred at room temperature for 2 h. The reaction mixture was quenched with 2M aqueous HCl (10 mL) and stirred for 5 min at rt. The residue was extracted with ethyl acetate (3 × 15 mL). Organic layers were combined and washed with water and brine, dried over Na$_2$SO$_4$ and concentrated under reduced pressure. Purification by aluminum oxide chromatography eluting with cyclohexane/ethyl acetate (90:10) yielded 4l (95 mg, 71%) as a colorless solid, mp 53-55 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.59 (d, $J = 16$ Hz, 1H), 6.74 (s, 2H), 6.33 (d, $J = 16$ Hz, 1H), 4.25 (q, 2H), 3.87 (s, 9H), 1.33 (t, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 166.9, 153.4, 144.5, 140.1, 129.9, 117.5, 105.2, 60.9, 60.4, 56.1, 26.9, 14.3. MS–EI [M$^+$]: 266.2, C$_{14}$H$_{18}$O$_5$ requires, 266.1.

$^{(E)}$-Ethyl-3-naphthalen-2-yl-acrylate, 4m. A solution of 2-naphthaldehyde 2m (78 mg, 0.50 mmol) and ethyl trimethylsilylacetate 1 (137 µL, 0.75 mmol) in THF (2.5 mL) was treated with dried Bu$_4$NCl (42 mg, 0.15 mmol) and Me$_3$SiOK (19 mg, 0.15 mmol) under N$_2$, and the resulting reaction mixture was stirred at room temperature for 2 h. The reaction mixture was quenched with 2 M HCl (10 mL) and stirred for 5 min at rt. The residue was extracted with ethyl acetate (3
× 15 mL). Organic layers were combined and washed with water and brine, dried over Na₂SO₄ and concentrated under reduced pressure. Purification by aluminum oxide chromatography eluting with cyclohexane/ethyl acetate (99:1) yielded 4m (96 mg, 85%) as yellow solid, mp 52–54 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.93 (s, 1H), 7.89–7.80 (m, 4H), 7.67 (d, J = 9 Hz, 1H), 7.56–7.48 (m, 2H), 6.56 (d, J = 16 Hz, 1H), 4.30 (q, 2H), 1.37 (t, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 167.0, 144.6, 134.2, 133.2, 131.9, 129.8, 128.6, 128.5, 127.7, 127.1, 126.6, 123.5, 118.4, 60.5, 14.3. HRMS-ESI [M+Na]+: 249.0902, C₁₅H₁₄O₂Na requires 249.0891.

(E)-Ethyl-3-(ferrocenyl)acrylate, 4n.¹⁶ A solution of ferrocenecarboxaldehyde 2n (107 mg, 0.50 mmol) ethyl trimethylsilylacetate 1 (137 µL, 0.75 mmol) in THF (2.5 mL) was treated with dried Bu₄NCl (42 mg, 0.15 mmol) and Me₃SiOK (19 mg, 0.15 mmol) under N₂, and the resulting reaction mixture was stirred at room temperature for 2 h. The reaction mixture was quenched with 2 M HCl (10 mL) and stirred for 5 min at rt. The residue was extracted with ethyl acetate (3 × 15 mL). Organic layers were combined and washed with water and brine, dried over Na₂SO₄ and concentrated under reduced pressure. Purification by aluminum oxide chromatography eluting with (cyclohexane/ethyl acetate: 97/3) yielded 4n (95 mg, 67%) as a brown solid, mp 53-55 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.56 (d, J = 16 Hz, 1H), 6.03 (d, J = 16 Hz, 1H), 4.48 (t, 2H), 4.40 (t, 2H), 4.22 (q, 2H), 4.15 (s, 5H), 1.33 (t, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 167.2, 145.6, 114.9, 78.7, 70.8, 69.6, 68.5, 60.1, 14.3. MS-EI [M]+: 284.2, C₁₅H₁₆FeO₂ requires 284.0.

(E,E)-Ethyl-5-phenylpenta-2,4-dienoate, 4o.¹⁷ A solution of (E)-cinnamaldehyde 2o (63 µL, 0.50 mmol) and ethyl trimethylsilylacetate 1 (137 µL, 0.75 mmol) in THF (2.5 mL) was treated with dried Bu₄NCl (42 mg, 0.15 mmol) and Me₃SiOK (19 mg, 0.15 mmol) under N₂, and the resulting reaction mixture was stirred at room temperature for 2 h. The reaction mixture was quenched with 2M aqueous HCl (10 mL) and stirred for 5 min at rt. The residue was extracted
with ethyl acetate (3 × 15 mL). Organic layers were combined and washed with water and brine, dried over Na₂SO₄ and concentrated under reduced pressure. Purification by aluminum oxide chromatography eluting with cyclohexane/ethyl acetate (99:1) yielded 4o (86 mg, 86%) as colorless oil. ¹H NMR (CDCl₃, 400 MHz): δ 7.36-7.27 (m, 3H), 7.26-7.15 (m, 3H), 6.80-6.70 (m, 2H), 5.85 (d, J = 16 Hz, 1H), 4.09 (q, 2H), 1.18 (t, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 167.0, 144.5, 140.3, 129.0, 128.8, 127.1, 126.2, 121.2, 60.3, 14.3. HRMS-EI [M]+: 202.0985, C₁₃H₁₄O₂ requires 202.0994.

(E)-Ethyl 3-(furan-2-yl)acrylate, 4p.¹⁸ A solution of furfural 2p (41 µL, 0.50 mmol) and ethyl trimethylsilylacetate 1 (137 µL, 0.75 mmol) in THF (2.5 mL) was treated with dried Bu₄NCl (42 mg, 0.15 mmol) and Me₃SiOK (19 mg, 0.15 mmol) under N₂, and the resulting reaction mixture was stirred at room temperature for 2 h. The reaction mixture was quenched with phosphate buffer (10 mL) and stirred for 5 min at rt. The residue was extracted with ethyl acetate (3 × 15 mL). Organic layers were combined and washed with water and brine, dried over Na₂SO₄ and concentrated under reduced pressure. Purification by aluminum oxide chromatography eluting with (cyclohexane/ethyl acetate: 99/1) yielded 4p (76 mg, 92%) as yellow oil. ¹H NMR (CDCl₃, 400 MHz): δ 7.48-7.45 (m, 1H), 7.42 (d, J = 16 Hz, 1H), 6.61-6.57 (m, 1H), 6.47-6.43 (m, 1H), 6.30 (d, J = 16 Hz, 1H), 4.24 (q, 2H), 1.31 (t, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 167.0, 150.9, 144.6, 130.9, 115.9, 114.5, 112.2, 60.4, 14.3. HRMS–EI [M]+: 166.0629, C₉H₁₀O₃ requires 166.0630.

Ethyl (E)-3-(pyridin-4-yl)acrylate, 4q.¹⁹ A solution of 4-pyridinecarboxaldehyde 2q (47 µL, 0.50 mmol) and ethyl trimethylsilylacetate 1 (137 µL, 0.75 mmol) in THF (2.5 mL) was treated with dried Bu₄NCl (42 mg, 0.15 mmol) and Me₃SiOK (19 mg, 0.15 mmol) under N₂, and the resulting reaction mixture was stirred at room temperature for 2 h. The reaction mixture was
quenched with phosphate buffer (10 mL) and stirred for 5 min at rt. The residue was extracted with ethyl acetate (3 × 15 mL). Organic layers were combined and washed with water and brine, dried over Na$_2$SO$_4$ and concentrated under reduced pressure. Purification by aluminum oxide chromatography eluting with (cyclohexane/ethyl acetate: 70/30) yielded 4q (55 mg, 58%) as colorless oil. $^1$H NMR (CDCl$_3$, 400 MHz): δ 9.00-8.30 (m, 2H), 7.58 (d, $J = 16$ Hz, 1H), 7.46-7.27 (m, 2H), 6.58 (d, $J = 16$ Hz, 1H), 4.27 (q, 2H), 1.34 (q, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 166.0, 150.5, 141.6, 122.9, 121.9, 60.9, 14.2. MS-ESI [M+H]$^+$: 177.2, C$_{10}$H$_{11}$NO$_2$ requires 117.1.

**tert-Butyl-3-[(E)-2-(ethoxycarbonyl)vinyl]-1H-indole-1-carboxylate, 4r.**$^{18}$ A solution of tert-butyl-3-formyl-1H-indole-1-carboxylate 2r (123 mg, 0.50 mmol) and ethyl trimethylsilylacetate 1 (137 µL, 0.75 mmol) in THF (2.5 mL) was treated with dried Bu$_4$NCl (42 mg, 0.15 mmol) and Me$_3$SiOK (19 mg, 0.15 mmol) under N$_2$, and the resulting reaction mixture was stirred at room temperature for 2 h. The reaction mixture was quenched with phosphate buffer (10 mL) and stirred for 5 min at rt. The residue was extracted with ethyl acetate (3 × 15 mL). Organic layers were combined and washed with water and brine, dried over Na$_2$SO$_4$ and concentrated under reduced pressure. Purification by aluminum oxide chromatography eluting with (cyclohexane/ethyl acetate: 97/3) yielded 4r (50 mg, 32%) as colorless oil. $^1$H NMR (CDCl$_3$, 400 MHz): δ 8.20 (d, $J = 8$ Hz, 1H), 7.89–7.80 (m, 3H), 7.42–7.30 (m, 2H), 6.54 (d, $J = 16$ Hz, 1H), 4.28 (q, 2H), 1.68 (s, 9H), 1.36 (t, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 167.4, 149.1, 136.3, 136.2, 128.5, 127.8, 125.2, 123.5, 120.2, 117.5, 116.8, 115.5, 84.6, 60.4, 28.1, 14.3. HRMS–ESI [M+Na]$^+$: 338.1375, C$_{18}$H$_{21}$NO$_4$Na requires 338.1368.
(E)-Ethyl 3-cyclohexylacrylate, 4s. A solution of cyclohexanecarboxaldehyde 2t (60 mg, 0.50 mmol) and ethyl trimethylsilylacetate 1 (137 µL, 0.75 mmol) in THF (3.0 mL) was treated with dried Bu₄NCl (139 mg, 0.50 mmol) and Me₃SiOK (64 mg, 0.50 mmol) under N₂, and the resulting reaction mixture was heated at 70 °C for 2 h. The reaction mixture cooled to rt and quenched with 2 M HCl (10 mL). The residue was extracted with ethyl acetate (3 × 15 mL). Organic layers were combined and washed with water and brine, dried over Na₂SO₄ and concentrated under reduced pressure. Purification by aluminum oxide chromatography eluting with cyclohexane yielded 4s (19 mg, 21%, E/Z 90:10) as colorless oil. ¹H NMR (CDCl₃, 400 MHz): δ 6.91 (dd, J = 16 Hz, 1H), 5.76 (dd, J = 16 Hz, 1H), 4.18 (q, 2H), 2.18-2.09 (m, 1H), 1.82-1.72 (m, 4H), 1.72-1.65 (m, 1H), 1.29-1.09 (m, 8H). ¹³C NMR (CDCl₃, 100 MHz): δ 154.3, 118.9, 60.1, 40.4, 31.7, 30.3, 25.9, 25.7, 14.3. MS-EI [M⁺]: 182.0, C₁₁H₁₈O₂ requires 182.1.

Ethyl 4,4,4-trifluoro-3-phenylbut-2-enoate, 4t. A solution of 2,2,2-trifluoroacetophenone 2x (70 µL, 0.50 mmol) ethyl trimethylsilylacetate 1 (137 µL, 0.75 mmol) in THF (2.0 mL) was treated with dried Bu₄NCl (42 mg, 0.15 mmol) and Me₃SiOK (19 mg, 0.15 mmol) under N₂, and the resulting reaction mixture was stirred at room temperature for 2 h. The reaction mixture was quenched with 2 M HCl (10 mL) and stirred for 5 min at rt. The residue was extracted with ethyl acetate (3 × 15 mL). Organic layers were combined and washed with water and brine, dried over Na₂SO₄ and concentrated under reduced pressure. Purification by aluminum oxide chromatography eluting with (cyclohexane/ethyl acetate: 99/1) yielded 4t (87 mg, 71%) as a colorless oil. ¹H NMR (CDCl₃, 400 MHz): δ 7.43–7.37 (m, 3H), 7.30–7.27 (m, 2H), 6.63-6.59 (m, 1H), 4.05 (q, 2H), 1.05 (t, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 164.1, 142.2 (²J_C,F = 31 Hz), 131.0, 129.3, 128.6, 128.2, 124.6 (³J_C,F = 6 Hz), 121.1 (⁴J_C,F = 273 Hz), 61.0, 13.7. ¹⁹F (282 MHz, CDCl₃): -68.7 (s). HRMS–EI [M⁺]: 244.0713, C₁₂H₁₄F₂O₂ requires 244.0711.
**Ethyl 3,3-diphenylacrylate, 4u.** A solution of benzophenone 2y (91 mg, 0.50 mmol) and ethyl trimethylsilylacetate 1 (137 µL, 0.75 mmol) in THF (2.0 mL) was treated with dried Bu₄NCl (42 mg, 0.15 mmol) and Me₃SiOK (19 mg, 0.15 mmol) under N₂, and the resulting reaction mixture was stirred at room temperature for 2 h. The reaction mixture was quenched with 2M aqueous HCl (10 mL) and stirred for 5 min at rt. The residue was extracted with ethyl acetate (3 x 15 mL). Organic layers were combined and washed with water and brine, dried over Na₂SO₄ and concentrated under reduced pressure. Purification by aluminum oxide chromatography eluting with (cyclohexane/ethyl acetate: 99/1) yielded 4u (49 mg, 39%) as a colorless oil. 

**1H NMR (CDCl₃, 400 MHz):** δ 7.43-7.27 (m, 8H), 7.24-7.18 (m, 2H), 6.37 (s, 1H), 4.05 (q, 2H), 1.11 (t, 3H). **13C NMR (CDCl₃, 100 MHz):** δ 166.1, 156.4, 140.8, 139.0, 129.3, 129.0, 128.3, 128.2, 128.0, 127.9, 117.5, 60.0, 14.0. HRMS–EI [M]+: 252.1145, C₁₇H₁₆O₂ requires 52.1150.

**Experimental procedures for Scheme 2**

A solution of ethyl 2-(trimethylsilyl)acetate 1 (137 µL, 0.75 mmol) and benzaldehyde 2a (51 µL, 0.50 mmol) in anhydrous THF (2.5 mL) was treated with dried Bu₄NOAc (15 mg, 0.05 mmol) under N₂ and stirred at room temperature for 1 h. The resulted reaction mixture was then treated with dried Bu₄NCl (139 mg, 0.5 mmol) and Me₃SiOK (64 mg, 0.5 mmol) under N₂ and the resulting reaction mixture was stirred at room temperature for 2h. The reaction mixture was quenched with 2M aqueous HCl (10 mL) and stirred for 5 min. The residue was extracted with ethyl acetate (3 x 15 mL). Organic layers were combined and washed with water and brine, dried over Na₂SO₄ and concentrated under reduced pressure. Purification by aluminum oxide chromatography eluting with cyclohexane/ethyl acetate (99:1) yielded 4a (79 mg, 89%) as a colorless oil. 

**1H NMR (CDCl₃, 400 MHz):** δ 7.69 (d, J = 16 Hz, 1H), 7.56-7.49 (m, 2H), 7.42-7.35 (m, 3H), 7.45 (d, J = 16 Hz, 1H), 4.27 (q, 2H), 1.31 (t, 3H). **13C NMR (CDCl₃, 100 MHz):** δ 166.9, 144.5, 134.5, 130.2, 128.8, 128.0, 118.3, 60.4, 14.2.
References:

Ethyl 3-hydroxy-3-phenylpropanoate, 3a.

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
(E)-Ethyl cinnamate, 4a.

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
Ethyl 3-(2-chlorophenyl)-3-hydroxypropanoate, 3b.

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
Ethyl 3-hydroxy-3-(3-methoxyphenyl)propanoate, 3c.

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
Ethyl 3-hydroxy-3-(4-methoxyphenyl)propanoate, 3d.

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
Ethyl 3-(4-bromophenyl)-3-hydroxypropionate, 3e.

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
Ethyl 3-hydroxy-3-(3,4,5-trimethoxyphenyl)propanoate, 3f.

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
Ethyl 3-hydroxy-3-(naphthalen-2-yl)propanoate, 3g.

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
Ethyl 3-hydroxy-3-(ferrocenyl)propanoate, 3h.

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
Ethyl 3-(furan-2-yl)-3-hydroxypropanoate, 3i.

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
Ethyl 3-hydroxy-3-(pyridin-4-yl)propanoate, 3j.

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
Ethyl (E)-3-hydroxyhex-4-enoate, 3k.

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
Ethyl 3-cyclohexyl-3-hydroxypropanoate, 3l.

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
Ethyl 3-hydroxy-5-phenylpentanoate, 3m.

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
Ethyl 3-hydroxyheptanoate, 3n.

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
Ethyl 3-hydroxy-3-phenylbutanoate, 3o.

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
(E)-Ethyl-3-(2-chlorophenyl)acrylate, 4b.

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
(E)-Ethyl-3-(3-methoxyphenyl)acrylate, 4c.

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
(E)-Ethyl-3-(4-methoxyphenyl)acrylate, 4d.

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
(E)-Ethyl-3-(4-fluorophenyl)acrylate, 4e.

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
$^{19}$F NMR (282 MHz, CDCl$_3$)
(E)-Ethyl-3-(4-bromophenyl)acrylate, 4f.

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
(E)-Ethyl-3-[(4-trifluoromethyl)phenyl]acrylate, 4g.

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
$^{19}$F NMR (CDCl$_3$, 282 MHz)
Ethyl (E)-3-(4-(dimethylamino)phenyl)acrylate, 4h.

$^{1}$H NMR (400 MHz, CDCl$_3$)
(E)-Ethyl-3-(4-benzyloxyphenyl)acrylate, 4i.

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
Methyl (E)-4-(3-ethoxy-3-oxoprop-1-en-1-yl)benzoate, 4j.

$^1$H NMR (400 MHz, CDCl$_3$)
(E)-Ethyl-3-(3,4-dimethoxyphenyl)acrylate, 4k.

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
(E)-Ethyl-3-(3,4,5-trimethoxyphenyl)acrylate, 4l.

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
(E)-Ethyl-3-naphthalen-2-yl-acrylate, 4m.

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
(E)-Ethyl-3-(ferrocenyl)acrylate, 4n.

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
(E,E)-Ethyl-5-phenylpenta-2,4-dienoate, 40.

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
(E)-Ethyl-3-(furan-2-yl)acrylate, 4p.

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
(E)-Ethyl-3-(pyridin-4-yl)acrylate, 4q.

\(^1\)H NMR (CDCl\(_3\), 400 MHz)

\(^{13}\)C NMR (CDCl\(_3\), 100 MHz)
tert-Butyl-3-[(E)-2-(ethoxycarbonyl)vinyl]-1H-indole-1-carboxylate, 4r.

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
(E)-ethyl-3-cyclohexylacrylate, 4s.

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
Ethyl-4,4,4-trifluoro-3-phenylbut-2-enoate, 4t.

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
$^{19}\text{F NMR (282 MHz, CDCl}_3\text{)}$
Ethyl-3,3-diphenylacrylate, 4u.

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
Scheme 2

$^1$H NMR (CDCl$_3$, 400 MHz)

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CO$_2$Et + PhCHO $\rightarrow$ Bu$_4$NOAc (10 mol%) THF, rt, 1h

OSiMe$_3$

3a (crude)
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$^1$H NMR (CDCl$_3$, 400 MHz)

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OSiMe$_3$

3a $\rightarrow$ TMSOK/Bu$_4$NCl (1.0 equiv.) rt, 1h

4a
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