

Supporting Information

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SI Text

Materials and Methods. Unless noted, all reactions were performed in flame-dried glassware and carried out under an atmosphere of argon with magnetic stirring. HPLC grade chloroform preserved with pentane was purchased from Fisher Scientific. Tetrahydrofuran, diethylether, and dichloromethane were degassed with argon and passed through two columns of neutral alumina. Toluene was degassed with argon and passed through one column of neutral alumina and one column of Q5 reagent. Column chromatography was performed on SiliCycle® SilicaFlash® P60, 40–63 μm 60 Å and in general were performed according to the guidelines reported by Still et al. (1). Thin-layer chromatography was performed on SiliCycle® 250 μm 60 Å plates. Visualization was accomplished with UV light or KMnO_4 stain followed by heating.

^1H NMR spectra were recorded on Varian 300 or 400 MHz spectrometers at ambient temperature unless otherwise stated. Data are reported as follows: chemical shift in parts per million (δ , ppm) from CDCl_3 (7.26 ppm), toluene- d_8 (7.09, 7.0, 6.98, 2.09 ppm), or benzene- d_6 (7.16 ppm) multiplicity (s, singlet; bs, broad singlet; d, doublet; t, triplet; q, quartet; and m, multiplet), coupling constants (hertz). ^{13}C NMR was recorded on Varian 300 or 400 MHz spectrometers (at 75 or 100 MHz) at ambient temperature. Chemical shifts are reported in ppm from CDCl_3 (77.2 ppm) or toluene- d_8 (137.86 (1), 129.4 (3), 128.33 (3), 125.49 (3), 20.4 (5) ppm). High-resolution mass spectra [electrospray ionization (ESI)] were obtained by Donald Dick of Colorado State University.

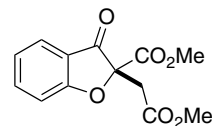
Salicylaldehydes **7a–c**, **7e**, and **7g–j**, dimethyl acetylenedicarboxylate (DMAD) (**8a**), and catechol **14a** were purchased from Aldrich or Acros and used without subsequent purification. Salicylaldehydes **7d** (2) and **7f** (3), phosphonate ester **8e** (4, 5), allenes **19a** (6), and **19b** (7), and triazolium precatalysts **4b** and **ent-4b** (8) were prepared according to literature procedures.

General Procedure for the One-Pot, One-Step Multicatalytic Michael/Stetter Reaction. A 1-dram vial was equipped with a magnetic stir bar under argon and charged sequentially with DMAD (**8a**) or activated alkyne **8b–d** (0.15 mmol), salicylaldehyde **7** (0.16 mmol), and triazolium salt **4b** (14 mg, 0.030 mmol). Toluene (1.5 mL) was added, and the mixture was cooled to 0 °C. Quinuclidine (**11**) (3.0 mg, 0.030 mmol) or 1,4-diazabicyclo[2.2.2]octane (DABCO) (**10**) (3.0 mg, 0.030 mmol) was added in one portion, and the reaction was monitored by TLC (acetone/hexanes). When the reaction was observed to be complete, the mixture was quenched with glacial acetic acid (1–2 drops), filtered through a plug of silica with Et_2O (~40 mL), and concentrated in vacuo. The resulting crude product **9** was purified via flash chromatography.

General Procedure for the One-Pot, Two-Step Michael/Stetter Reaction of Salicylaldehydes **7 and DMAD (**8a**) in the Presence or Absence of Catechol.** A 1-dram vial was equipped with a magnetic stir bar under argon and charged with DMAD (**8a**) (21 mg, 0.15 mmol) and salicylaldehyde **7** (0.16 mmol). Toluene (1.5 mL) was added, and the mixture was cooled to 0 °C. Quinuclidine (**11**) (3.0 mg, 0.030 mmol) or DABCO (**10**) (3.0 mg, 0.030 mmol) was added in one portion, and the reaction was monitored by TLC (EtOAc/hexanes) until consumption of **8a** was observed to be complete. Triazolium salt precatalyst **4b** (14 mg, 0.030 mmol) was added at this time, and the reaction was again monitored by TLC (acetone/hexanes). If catechol (0.015 mmol) was added to the reaction, it was added at this time

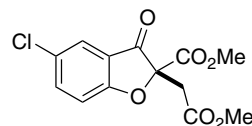
followed by triazolium salt precatalyst **4b** (14 mg, 0.030 mmol). When the reaction was observed to be complete by TLC, the mixture was quenched with glacial acetic acid (1–2 drops), filtered through a plug of silica with Et_2O (~40 mL), and concentrated in vacuo. The resulting crude product **9** was purified via flash chromatography.

Procedure for the Preparation of **9aa on 7.0 mmol Scale.** A 250-mL, flame-dried, round-bottom flask was charged with triazolium salt **4b** (164 mg, 0.350 mmol) and evacuated for 3 min, then filled with argon. After the evacuation procedure was repeated an additional two times, DMAD (**8a**) (1.01 g, 7.12 mmol), salicylaldehyde (**7a**) (933 mg, 7.64 mg), and toluene (72 mL) were added sequentially, and the reaction mixture was cooled to 0 °C. Quinuclidine (**11**) (156 mg, 1.40 mmol) was added portionwise to the reaction mixture. After stirring at 0 °C for 9 h, the reaction was quenched with glacial acetic acid (150 μL) and poured directly onto a silica gel column (5:1-1:1 hexanes/EtOAc) to give 1.48 g (79% yield) **9aa** as a clear, amorphous solid.



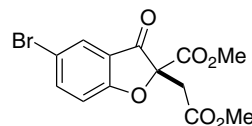
[**9aa**]

($c = 0.0156$ g/mL, CHCl_3); HPLC analysis—Chiracel IC column, 60:40 hexanes:iPrOH, 0.7 mL/min, major enantiomer: 14.9 min, minor enantiomer: 27.0 min, 89% enantiomeric excess (ee); ^1H NMR (400 MHz, CDCl_3) δ 7.66 (m, 2H), 7.22 (d, 1H, $J = 8.4$ Hz), 7.14 (t, 1H, $J = 7.5$ Hz), 3.76 (s, 3H), 3.64 (s, 3H), 3.47 (d, 1H, $J = 17.5$ Hz), 3.10 (d, 1H, $J = 17.5$); ^{13}C NMR (100 MHz, CDCl_3) δ 194.6, 172.3, 169.0, 165.6, 138.7, 125.1, 123.1, 119.5, 113.7, 88.0, 53.8, 52.4, 38.5; IR (thin film/NaCl) 2950, 1747, 1727, 1614, 1465, 1214 cm^{-1} ; high-resolution mass spectrometry (HRMS) (ESI) m/z [$\text{C}_{13}\text{H}_{13}\text{O}_6$] $^+$ calculated 265.0707, found 265.0710.



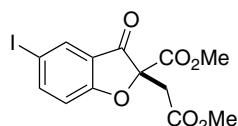
[**9ba**]

($c = 0.0146$ g/mL, CHCl_3); HPLC analysis—Chiracel IC column, 50:50 hexanes:iPrOH, 0.7 mL/min, major enantiomer: 13.7 min, minor enantiomer: 20.7 min, 89% ee; ^1H NMR (400 MHz, CDCl_3) δ 7.65 (d, 1H, $J = 2.3$ Hz), 7.60 (dd, 1H, $J = 8.8, 2.3$ Hz), 7.17 (d, 1H, $J = 8.8$ Hz), 3.77 (s, 3H), 3.65 (s, 3H), 3.45 (d, 1H, $J = 17.6$ Hz), 3.21 (d, 1H, $J = 17.6$); ^{13}C NMR (100 MHz, CDCl_3) δ 193.6, 170.7, 168.8, 165.2, 138.4, 128.7, 124.4, 121.0, 115.0, 88.9, 53.9, 52.5, 38.4; IR (thin film/NaCl) 2956, 1756, 1735, 1606, 1463, 1212 cm^{-1} ; HRMS (ESI) m/z [$\text{C}_{13}\text{H}_{11}\text{ClNaO}_6$] $^+$ calculated 321.0136, found 321.0137.



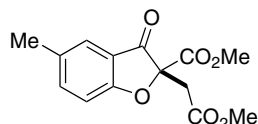
[**9ca**]

(*c* = 0.0160 g/mL, CHCl₃); HPLC analysis—Chiracel IC column, 50:50 hexanes:iPrOH, 0.7 mL/min, major enantiomer, 94% ee; 14.2 min, minor enantiomer: 20.5 min; ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, 1H, *J* = 1.6 Hz), 7.72 (dd, 1H, *J* = 8.8, 1.6 Hz), 7.12 (d, 1H, *J* = 8.8 Hz), 3.75 (s, 3H), 3.63 (s, 3H), 3.43 (d, 1H, *J* = 17.6 Hz), 3.20 (d, 1H, *J* = 17.6); ¹³C NMR (100 MHz, CDCl₃) δ 193.4, 171.0, 168.8, 165.2, 141.1, 127.5, 121.5, 115.6, 115.3, 88.7, 53.9, 52.5, 38.4; IR (thin film/NaCl) 2950, 1757, 1737, 1609, 1460, 1440, 1214 cm⁻¹; HRMS (ESI) *m/z* [C₁₃H₁₁BrNaO₆]⁺ calculated 364.9631, found 364.9637.



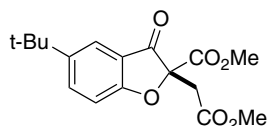
[9da]

(*c* = 0.0219 g/mL, CHCl₃); HPLC analysis—Chiracel IC column, 60:40 hexanes:iPrOH, 0.7 mL/min, major enantiomer: 16.5 min, minor enantiomer: 22.4 min, 94% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.98 (s, 1H), 7.88 (d, 1H, *J* = 8.7 Hz), 7.02 (d, 1H, *J* = 8.7 Hz), 3.75 (s, 3H), 3.64 (s, 3H), 3.43 (d, 1H, *J* = 17.6), 3.20 (d, 1H, *J* = 17.6 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 193.1, 171.7, 168.8, 165.1, 146.6, 133.6, 122.1, 115.8, 88.3, 85.3, 53.9, 52.4, 38.4; IR (thin film/NaCl) 2955, 1756, 1737, 1603, 1455, 1434, 1209 cm⁻¹; HRMS (ESI) *m/z* [C₁₃H₁₁INaO₆]⁺ calculated 412.9493, found 412.9497.



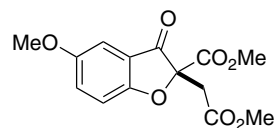
[9ea]

(*c* = 0.0160 g/mL, CHCl₃); HPLC analysis—Chiracel IC column, 60:40 hexanes:iPrOH, 0.7 mL/min, major enantiomer: 15.6 min, minor enantiomer: 19.7 min, 86% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.47 (m, 2H), 7.12 (m, 1H), 3.76 (s, 3H), 3.65 (s, 3H), 3.46 (d, 1H, *J* = 17.4 Hz), 3.09 (d, 1H, *J* = 17.4 Hz), 2.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 194.7, 170.9, 169.0, 165.8, 140.0, 132.8, 124.5, 119.4, 113.3, 88.3, 53.7, 52.4, 38.6, 20.7; IR (thin film/NaCl) 2953, 1747, 1721, 1619, 1490, 1440, 1209 cm⁻¹; HRMS (ESI) *m/z* [C₁₃H₁₅O₆]⁺ calculated 279.0863, found 279.0865.



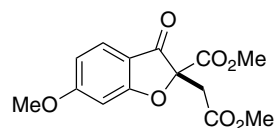
[9fa]

(*c* = 0.0195 g/mL, CHCl₃); HPLC analysis—Chiracel IC column, 90:10 hexanes:iPrOH, 0.7 mL/min, major enantiomer: 20.8 min, minor enantiomer: 16.4 min, 85% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.73 (dd, 1H, *J* = 8.8, 2.0 Hz), 7.65 (d, 1H, *J* = 1.7 Hz), 7.16 (d, 1H, *J* = 8.8 Hz), 3.76 (s, 3H), 3.66 (s, 3H), 3.48 (d, 1H, *J* = 17.4 Hz), 3.04 (d, 1H, *J* = 17.4 Hz), 1.31 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 194.8, 170.8, 169.1, 165.8, 146.4, 137.0, 121.0, 118.8, 113.1, 88.5, 53.7, 52.4, 38.6, 34.7, 31.4; IR (thin film/NaCl) 2960, 2905, 1747, 1726, 1619, 1491, 1210 cm⁻¹; HRMS (ESI) *m/z* [C₁₇H₂₁O₆]⁺ calculated 321.1333, found 321.1337.



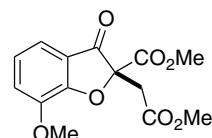
[9ga]

(*c* = 0.0148 g/mL, CHCl₃); HPLC analysis—Chiracel IC column, 50:50 hexanes:iPrOH, 0.7 mL/min, major enantiomer: 19.9 min, minor enantiomer: 14.5 min, 86% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.29 (dd, 1H, *J* = 9.0, 2.8 Hz), 7.16 (d, 1H, *J* = 9.0 Hz), 7.07 (d, 1H, *J* = 2.8 Hz), 3.81 (s, 3H), 3.78 (s, 3H), 3.67 (s, 3H), 3.47 (d, 1H, *J* = 17.4 Hz), 3.11 (d, 1H, *J* = 17.4); ¹³C NMR (100 MHz, CDCl₃) δ 194.8, 169.0, 167.8, 165.8, 155.8, 128.7, 119.5, 114.6, 104.8, 88.8, 56.0, 53.8, 52.4, 38.6; IR (thin film/NaCl) 2955, 1747, 1716, 1491, 1440, 1209 cm⁻¹; HRMS (ESI) *m/z* [C₁₄H₁₅O₇]⁺ calculated 295.0812, found 295.0809.



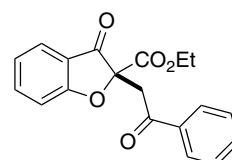
[9ha]

(*c* = 0.0171 g/mL, CHCl₃); HPLC analysis—Chiracel IC column, 50:50 hexanes:iPrOH, 1.0 mL/min, major enantiomer: 40.7 min, minor enantiomer: 24.5 min, 85% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, 1H, *J* = 8.6 Hz), 6.68 (m, 2H), 3.88 (s, 3H), 3.77 (s, 3H), 3.67 (s, 3H), 3.48 (d, 1H, *J* = 17.4 Hz), 3.00 (d, 1H, *J* = 17.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 192.0, 175.0, 169.2, 169.0, 165.9, 126.2, 112.9, 112.2, 96.6, 88.9, 56.1, 53.7, 52.4, 38.5; IR (thin film/NaCl) 2950, 1747, 1711, 1614, 1440, 1286 cm⁻¹; HRMS (ESI) *m/z* [C₁₄H₁₅O₇]⁺ calculated 295.0812, found 295.0812.



[9ia]

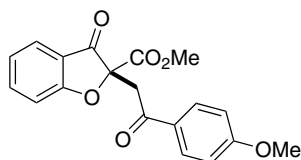
(*c* = 0.0085 g/mL, CHCl₃); HPLC analysis—Chiracel IC column, 60:40 hexanes:iPrOH, 0.7 mL/min, major enantiomer: 19.9 min, minor enantiomer: 33.5 min, 92% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.28 (dd, 1H, *J* = 7.7, 1.2 Hz), 7.16 (dd, 1H, *J* = 7.9, 1.1 Hz), 7.09 (t, 1H, *J* = 7.8 Hz), 3.96 (s, 3H), 3.75 (s, 3H), 3.63 (s, 3H), 3.46 (d, 1H, *J* = 17.6 Hz), 3.30 (d, 1H, *J* = 17.6 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 195.0, 168.8, 165.6, 162.4, 146.5, 123.6, 121.1, 119.3, 116.0, 88.3, 56.4, 53.9, 52.4, 38.4; IR [attenuated total reflectance (ATR)] 2956, 1723, 1617, 1504, 1438, 1206 cm⁻¹; HRMS (ESI) *m/z* [C₁₄H₁₄NaO₇]⁺ calculated 317.0632, found 317.0637.



[9ab]

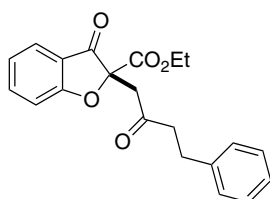
(*c* = 0.0105 g/mL, CHCl₃); HPLC analysis—Chiracel IC column, 90:10 hexanes:iPrOH, 0.7 mL/min, major enantiomer: 21.8 min, minor enantiomer: 18.6 min, 12% ee; ¹H NMR

(400 MHz, CDCl₃) δ 7.93 (m, 2H), 7.65 (m, 3H), 7.46 (m, 2H), 7.19 (m, 2H), 4.24 (m, 3H), 3.69 (d, 1H, *J* = 18.2 Hz), 1.24 (t, 3H, *J* = 7.1 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 195.7, 194.2, 172.5, 165.6, 138.6, 135.9, 133.9, 128.9, 128.3, 125.0, 122.9, 119.7, 113.8, 88.4, 63.0, 43.4, 14.1; IR (thin film/NaCl) 2978, 1747, 1726, 1690, 1614, 1460, 1224 cm⁻¹; HRMS (ESI) *m/z* [C₁₉H₁₇O₅]⁺ calculated 325.1071, found 325.1078.



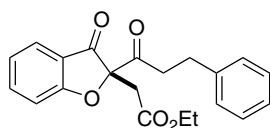
[9ac]

(*c* = 0.0136 g/mL, CHCl₃); HPLC analysis—Chiracel IC column, 85:15 hexanes:iPrOH, 0.7 mL/min, major enantiomer: 38.3 min, minor enantiomer: 42.5 min, 18% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, 2H, *J* = 8.9 Hz), 7.73 (d, 1H, *J* = 7.7 Hz), 7.66 (m, 1H), 7.23 (d, 1H, *J* = 8.4 Hz), 7.16 (t, 1H, *J* = 7.5 Hz), 6.92 (d, 2H, *J* = 8.9 Hz), 4.19 (d, 1H, *J* = 18.1 Hz), 3.86 (s, 3H), 3.79 (s, 3H), 3.67 (d, 1H, *J* = 18.1 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 195.6, 192.6, 172.3, 166.3, 164.1, 138.6, 130.7, 128.9, 125.0, 122.9, 119.7, 114.0, 113.8, 88.5, 55.6, 53.7, 43.2; IR (thin film/NaCl) 2955, 1753, 1722, 1679, 1600, 1462, 1264, 1233 cm⁻¹; HRMS (ESI) *m/z* [C₁₉H₁₆NaO₆]⁺ calculated 363.0839, found 363.0845.



[9ad]

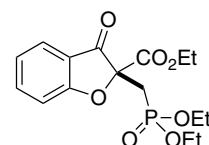
(*c* = 0.0037 g/mL, CHCl₃); HPLC analysis—Chiracel IC column, 90:10 hexanes:iPrOH, 0.7 mL/min, major enantiomer: 47.0 min, minor enantiomer: 39.6 min, 51% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.66 (m, 2H), 7.20 (m, 7H), 4.22 (dq, 1H, *J* = 10.8, 7.1 Hz), 4.19 (dq, 1H, *J* = 10.8, 7.1 Hz), 3.61 (d, 1H, *J* = 18.2 Hz), 3.13 (d, 1H, *J* = 18.2 Hz), 2.78 (m, 2H), 2.75 (m, 2H), 1.22 (t, 3H, *J* = 7.1 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 204.0, 195.3, 172.4, 165.4, 140.6, 138.6, 128.7, 128.4, 126.4, 125.0, 122.9, 119.6, 113.7, 88.2, 63.0, 46.7, 44.3, 29.5, 14.0; IR (thin film/NaCl) 2981, 1751, 1722, 1612, 1462, 1247 cm⁻¹; HRMS (ESI) *m/z* [C₂₁H₂₀NaO₅]⁺ calculated 375.1203, found 375.1199.



[15ad]

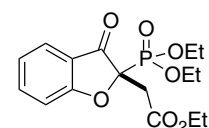
*R*_f = 0.29 (2:1 pentane/Et₂O); HPLC analysis—Chiracel IC column, 90:10 hexanes:iPrOH, 0.7 mL/min, major enantiomer: 19.2 min, minor enantiomer: 60.5 min, 89% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.68 (m, 2H), 7.08–7.26 (m, 7H), 4.09 (q, 2H, *J* = 7.2 Hz), 3.52 (d, 1H, *J* = 17.2 Hz), 3.21 (ddd, 1H, *J* = 18.5, 9.9, 5.6 Hz), 2.96 (d, 1H, *J* = 17.2 Hz), 2.89 (ddd, 1H, *J* = 14.6, 9.6, 5.4 Hz), 2.80 (ddd, 1H, *J* = 14.6, 10.0, 5.3 Hz), 2.52 (ddd, 1H, *J* = 18.5, 9.8, 5.6 Hz), 1.16 (t, 3H, *J* = 7.2 Hz); IR (thin film/NaCl) 2981, 1739, 1711, 1611, 1462,

1205 cm⁻¹; HRMS (ESI) *m/z* [C₂₁H₂₀NaO₅]⁺ calculated 375.1203, found 375.1211.



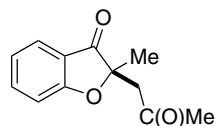
[9ae]

A 1-dram vial was equipped with a magnetic stir bar under argon and charged with phosphonate **8e** (51 mg, 0.22 mmol), salicylaldehyde (**7a**) (28 mg, 0.23 mmol), and toluene (2.2 mL). Quinuclidine (**11**) (5.0 mg, 0.040 mmol) was added in one portion, and the reaction mixture was stirred for 25 h at 23 °C. At this point, the reaction mixture was cooled to 0 °C, and triazolium salt **4b** (20 mg, 0.040 mmol) was added. After an additional 75 min of stirring, the mixture was quenched with glacial acetic acid (2 drops), filtered through a plug of silica with Et₂O (~40 mL), and concentrated in vacuo. Flash chromatography yielded 28 mg (36% yield) of partially purified **9ae**, which was contaminated with about 20% chromene impurity which coeluted in a variety of solvent systems. *R*_f = 0.35 (95:5 CH₂Cl₂/MeOH); [α]_D²⁵ = +32.4° (*c* = 0.0023 g/mL, CHCl₃); HPLC analysis—Chiracel ASH column, 85:15 hexanes:iPrOH, 1.0 mL/min, major enantiomer: 10.0 min, minor enantiomer: 8.2 min, 86% ee; ¹H NMR (400 MHz, CDCl₃) δ 7.67 (m, 2H), 7.26 (m, 1H), 7.15 (m, 1H), 4.23 (q, 2H, *J* = 7.1 Hz), 4.00–4.07 (m, 4H), 2.98 (dd, 1H, *J* = 16.9, 15.9 Hz), 2.62 (dd, 1H, *J* = 18.1, 15.8 Hz), 1.23 (m, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 195.1 (d, *J* = 7.3 Hz), 172.3, 165.4 (d, *J* = 12.8 Hz), 138.7, 125.2, 123.0, 119.4, 113.7, 87.4 (d, *J* = 7.4 Hz), 63.2, 62.3 (d, *J* = 5.6 Hz), 62.1 (d, *J* = 6.8 Hz), 30.7 (d, *J* = 145.0 Hz), 16.4 (d, *J* = 6.9 Hz), 14.1; IR (thin film/NaCl) 2984, 2930, 1753, 1729, 1613, 1463, 1247, 1026 cm⁻¹; HRMS (ESI) *m/z* [C₁₆H₂₂O₇P]⁺ calculated 357.1098, found 357.1099.



[15ae]

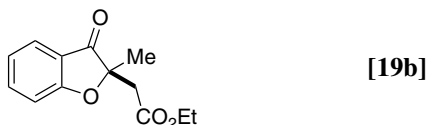
¹H NMR (400 MHz, CDCl₃) δ 7.73 (m, 1H), 7.61 (m, 1H), 7.16 (m, 2H), 4.21 (m, 4H), 3.94 (m, 2H), 3.51 (dd, 1H, *J* = 17.1, 3.1 Hz), 3.34 (dd, 1H, *J* = 17.1, 9.2 Hz), 1.32 (t, 3H, *J* = 7.1 Hz), 1.22 (t, 3H, *J* = 7.1 Hz), 0.96 (t, 3H, *J* = 7.2 Hz).



[19a]

A 1-dram vial was equipped with a magnetic stir bar under argon and charged with allenone **18a** (27 mg, 0.33 mmol), salicylaldehyde (**7a**) (37 mg, 0.30 mmol), and THF (1.5 mL). Quinuclidine (**11**) (6.7 mg, 0.060 mmol) was added in one portion, and the reaction mixture was stirred at 23 °C until consumption of **7a** was observed to be complete by TLC (hexanes/EtOAc). At this point, the reaction mixture was cooled to 0 °C, triazolium salt **4b** (28 mg, 0.060 mmol) was added, and the reaction was again monitored by TLC (hexanes/acetone). When the reaction was observed to be complete, the mixture was quenched with glacial acetic acid (2 drops), filtered through a plug of silica with Et₂O (~40 mL), and concentrated in vacuo. Flash chromatography yielded 37 mg (60% yield) of **19a**. *R*_f = 0.22 (3:1 hexanes/EtOAc); [α]_D²⁵ = -5.6° (*c* = 0.0184 g/mL, CHCl₃); HPLC analysis—Chiracel ADH column, 97:3 hexanes:iPrOH, 1.0 mL/min,

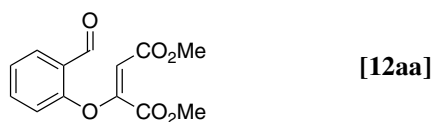
major enantiomer: 14.4 min, minor enantiomer: 16.5 min, 78% ee; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.70 (ddd, 1H, $J = 7.7, 1.4, 0.6$ Hz), 7.59 (ddd, 1H, $J = 8.5, 7.3, 1.5$ Hz), 7.071 (m, 2H), 3.15 (d, 1H, $J = 17.3$ Hz), 3.09 (d, 1H, $J = 17.2$ Hz), 2.11 (s, 3H), 1.42 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 203.4, 203.1, 170.8, 137.7, 124.7, 122.0, 120.8, 113.3, 86.4, 50.1, 30.4, 22.5; IR (thin film/NaCl) 2359, 1712, 1610, 1462, 1367 cm^{-1} ; HRMS (ESI) m/z $[\text{C}_{12}\text{H}_{13}\text{O}_3]^+$ calculated 205.0859, found 205.0863.



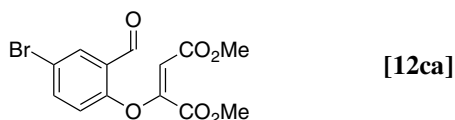
A 1-dram vial was equipped with a magnetic stir bar under argon and charged with allenolate **18b** (47 mg, 0.42 mmol), salicylaldehyde (**7a**) (46 mg, 0.38 mmol), and solvent (1.5 mL). Quinuclidine (**11**) (8.4 mg, 0.076 mmol) was added in one portion, and the reaction mixture was stirred at 23 °C until consumption of **7a** was observed to be complete by TLC ($\text{CH}_2\text{Cl}_2/\text{EtOAc}$). At this point, triazolium salt **4b** (35 mg, 0.076 mmol) was added, and the reaction was again monitored by TLC (hexanes/acetone). When the reaction was observed to be complete, the mixture was quenched with glacial acetic acid (2 drops), filtered through a plug of silica with Et_2O (~40 mL), and concentrated in vacuo. Flash chromatography yielded 52 mg (59% yield) of **19b**. $R_f = 0.27$ (4:1 hexanes/ EtOAc); $[\alpha]_D^{25} = -11.3^\circ$ ($c = 0.0092$ g/mL, CHCl_3); HPLC analysis—Chiracel IC column, 50:50 hexanes:*i*PrOH, 0.7 mL/min, major enantiomer: 44.0 min, minor enantiomer: 25.9 min, 96% ee; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.70 (m, 1H), 7.60 (m, 1H), 7.09 (m, 2H), 3.99 (dq, 1H, $J = 10.8, 7.1$ Hz), 3.93 (dq, 1H, $J = 10.8, 7.1$ Hz), 3.05 (d, 1H, $J = 16.3$ Hz), 2.92 (d, 1H, $J = 16.3$ Hz), 1.46 (s, 3H), 0.98 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 202.8, 171.1, 168.6, 137.9, 124.7, 122.0, 120.7, 113.4, 86.5, 61.0, 41.8, 22.7, 13.8; IR (thin film/NaCl) 2980, 1721, 1612, 1464, 1213 cm^{-1} ; HRMS (ESI) m/z $[\text{C}_{13}\text{H}_{15}\text{O}_4]^+$ calculated 235.0965, found 235.0967.

General Procedure for the Preparation of Intermediate Aldehydes 12.

A 50-mL, flame-dried, round-bottom flask was charged with DMAD (**8a**) (2.0 mmol), salicylaldehyde (**7a**) (2.1 mmol), and toluene (20 mL) under argon. The mixture was cooled to 0 °C, and quinuclidine (**11**) or DABCO (**10**) (0.40 mmol) was added in one portion. After stirring for 30–60 min, the reaction mixture was concentrated in vacuo, and the resulting crude product **12** was purified via flash chromatography.

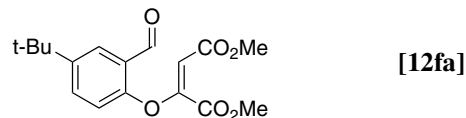


Characterization data for **12aa** agreed with that reported in the literature (9).



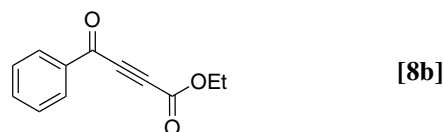
$R_f = 0.24$ (3:1 hexanes/ EtOAc); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 10.21 (s, 1H), 8.06 (d, 1H, $J = 2.5$ Hz), 7.75 (dd, 1H, $J = 8.7, 2.5$ Hz), 7.10 (d, 1H, $J = 8.7$ Hz), 5.32 (s, 1H), 3.91 (s, 3H), 3.71 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 186.4, 165.0,

162.3, 158.8, 154.3, 138.8, 132.1, 129.1, 123.3, 120.3, 103.4, 53.5, 52.2; IR (ATR) 2953, 1747, 1712, 1687, 1645, 1627, 1360, 1126 cm^{-1} ; HRMS (ESI) m/z $[\text{C}_{13}\text{H}_{11}\text{BrNaO}_6]^+$ calculated 364.9631, found 364.9631.

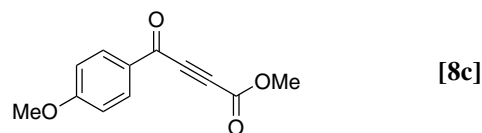


$R_f = 0.24$ (4:1 hexanes/ EtOAc); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 10.25 (s, 1H), 7.96 (d, 1H, $J = 2.6$ Hz), 7.68 (dd, 1H, $J = 8.6, 2.6$ Hz), 7.12 (d, 1H, $J = 8.6$ Hz), 5.18 (s, 1H), 3.93 (s, 3H), 3.68 (s, 3H), 1.34 (s, 9H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 188.1, 165.4, 162.8, 160.7, 153.0, 150.5, 133.4, 127.2, 125.9, 121.5, 100.9, 53.4, 52.1, 35.0, 31.3; IR (thin film/NaCl) 2958, 2870, 1754, 1726, 1695, 1639, 1365, 1133 cm^{-1} ; HRMS (ESI) m/z $[\text{C}_{17}\text{H}_{21}\text{NaO}_6]^+$ calculated 343.1152, found 343.1153.

General Procedure for the Preparation of Ketoalkynoates 8b–d. Ketoalkynoates were oxidized from the corresponding propargylic alcohols, which were prepared according to a modified literature procedure (10):

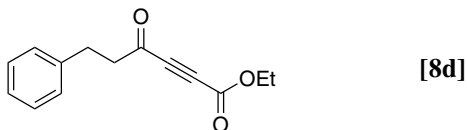


To a solution of LiHMDS (2.53 g, 15.1 mmol) in THF (30 mL) at -78°C was added ethyl propiolate (1.36 g, 13.9 mmol) in THF (13 mL) over 30 min via syringe pump. The resultant mixture was stirred for 30 min, at which point a solution of benzaldehyde (1.34 g, 12.6 mmol) in THF (6.0 mL) was added via syringe pump over 30 min. After an additional 45 min of stirring, the reaction mixture was quenched with saturated NH_4Cl and allowed to warm to room temperature. The organic layer was diluted with Et_2O , washed with NH_4Cl , H_2O and brine, and dried over MgSO_4 . Concentration and flash chromatography gave 1.77 g (69% yield) of the partially purified propargylic alcohol. To a solution of the crude alcohol (494 mg, 2.42 mmol) in CH_2Cl_2 (2.4 mL) at 0 °C was added dropwise a solution of MnO_2 (1.48 g, 17.0 mmol) in CH_2Cl_2 (1.2 mL). The ice bath was removed, and the reaction mixture was allowed to stir at 23 °C for 4 h. Filtration through celite and purification via flash chromatography gave 260 mg of **8b** (36% yield over two steps) as a light yellow oil. $R_f = 0.35$ (5:1 hexanes/ EtOAc); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.12 (dd, 2H, $J = 8.0, 0.4$ Hz), 7.67 (t, 1H, $J = 7.2$ Hz), 7.52 (t, 2H, $J = 8.0$ Hz), 4.35 (q, 2H, $J = 7.2$ Hz), 1.37 (t, 3H, $J = 7.2$ Hz); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 176.3, 152.4, 135.7, 135.3, 129.9, 129.0, 80.6, 79.9, 63.2, 14.1; IR (thin film/NaCl) 2986, 1719, 1653, 1450, 1262 cm^{-1} ; low-resolution mass spectrometry (LRMS) (GC) m/z $[\text{C}_{12}\text{H}_{10}\text{O}_3]$ calculated 202, found 202. HRMS (ESI) resulted in excessive substrate decomposition: m/z $[\text{C}_{10}\text{H}_9\text{O}_2]^+$ calculated 161.0597, found 161.0592, m/z $[\text{C}_{11}\text{H}_9\text{O}_3]^+$ calculated 189.0546, found 189.0541, m/z $[\text{C}_{12}\text{H}_{13}\text{O}_4]^+$ calculated 221.0808, found 221.0805, m/z $[\text{C}_{13}\text{H}_{15}\text{O}_4]^+$ calculated 235.0965, found 235.0962.



To a solution of LiHMDS (836 mg, 5.00 mmol) in THF (10 mL) at -78°C was added methyl propiolate (386 mg, 4.59 mmol) in

THF (4.2 mL) over 30 min via syringe pump. The resultant mixture was stirred for 30 min, at which point a solution of *p*-anisaldehyde (566 mg, 4.16 mmol) in THF (2.0 mL) was added via syringe pump over 20 min. After an additional 45 min of stirring, the reaction mixture was quenched with saturated NH_4Cl and allowed to warm to room temperature. The organic layer was diluted with Et_2O , washed with NH_4Cl , H_2O and brine, and dried over MgSO_4 . Concentration and flash chromatography gave 744 mg (81% yield) of the partially purified propargylic alcohol. To a solution of the crude alcohol (473 mg, 2.15 mmol) in CH_2Cl_2 (11 mL) at 0°C was added Dess-Martin Periodinane (DMP) (1.01 g, 2.38 mmol) portionwise. After stirring for 90 min at 0°C and another 2 h at 23°C , the reaction mixture was again cooled to 0°C and another portion of DMP (275 mg, 0.650 mmol) was added. The reaction was placed in the fridge (-5°C) overnight and quenched 12 h later with a 1:1 mixture of $\text{Na}_2\text{S}_2\text{O}_3/\text{NaHCO}_3$ (12 mL). The biphasic mixture was stirred until both layers cleared, at which point the organic layer was diluted with Et_2O , washed with H_2O and brine, and dried over MgSO_4 . Concentration and purification via flash chromatography gave 154 mg of **8c** (26% yield over two steps) as a white powder. $R_f = 0.26$ (7:2 hexanes/ EtOAc); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.08 (d, 2H, $J = 9.0$ Hz), 6.97 (d, 2H, $J = 9.0$ Hz), 3.90 (s, 3H), 3.88 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 174.6, 165.5, 153.0, 132.4, 129.2, 114.4, 80.5, 79.7, 55.9, 53.5; IR (thin film/ NaCl) 2959, 1712, 1638, 1596, 1254 cm^{-1} ; HRMS (ESI) m/z [$\text{C}_{12}\text{H}_{11}\text{O}_4$] $^+$ calculated 219.0652, found 219.0653.



To a solution of LiHMDS (2.55 g, 15.2 mmol) in THF (30 mL) at -78°C was added ethyl propiolate (1.37 g, 13.9 mmol) in THF

(13 mL) over 30 min via syringe pump. The resultant mixture was stirred for 30 min, at which point a solution of hydrocinnamaldehyde (1.70 g, 12.7 mmol) in THF (6.0 mL) was added via syringe pump over 20 min. After an additional 45 min of stirring, the reaction mixture was quenched with saturated NH_4Cl and allowed to warm to room temperature. The organic layer was diluted with Et_2O , washed with NH_4Cl , H_2O and brine, and dried over MgSO_4 . Concentration and flash chromatography gave 1.81 g (62% yield) of the partially purified propargylic alcohol. To a solution of the crude alcohol (465 mg, 2.00 mmol) in CH_2Cl_2 (10 mL) at 0°C was added DMP (938 mg, 2.21 mmol) portionwise. The reaction was stirred for 3 h at 23°C and then placed in the fridge (-5°C) overnight. Another portion of DMP (155 mg, 0.365 mmol) was added at this point, and the reaction was allowed to stir for an additional 4 h at 23°C before it was quenched with a 1:1 mixture of $\text{Na}_2\text{S}_2\text{O}_3/\text{NaHCO}_3$ (13 mL). The biphasic mixture was stirred until both layers cleared, at which point the organic layer was diluted with Et_2O , washed with H_2O and brine and dried over MgSO_4 . Concentration and purification via flash chromatography gave 373 mg of **8d** (50% yield over two steps) as a clear oil. $R_f = 0.48$ (4:1 hexanes/ EtOAc); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.30 (m, 2H), 7.21 (m, 3H), 4.31 (q, 2H, $J = 7.2$ Hz), 2.99 (m, 4H), 1.34 (t, 3H, $J = 7.2$ Hz); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 184.9, 152.2, 139.6, 128.7, 128.4, 126.6, 80.5, 78.6, 63.1, 46.8, 29.3, 14.0; IR (thin film/ NaCl) 3029, 2985, 1721, 1689, 1496, 1244 cm^{-1} ; LRMS (GC) m/z [$\text{C}_{14}\text{H}_{14}\text{O}_3$] calculated 230, found 230. HRMS (ESI) resulted in excessive substrate decomposition: m/z [$\text{C}_{42}\text{H}_{43}\text{O}_9$] $^+$ calculated 691.2902, found 691.2902, m/z [$\text{C}_{42}\text{H}_{42}\text{NaO}_9$] $^+$ calculated 713.2721, found 713.2726, m/z [$\text{C}_{43}\text{H}_{46}\text{NaO}_{10}$] $^+$ calculated 745.2983, found 745.2986, m/z [$\text{C}_{56}\text{H}_{56}\text{NaO}_{12}$] $^+$ calculated 943.3664, found 943.3671, m/z [$\text{C}_{84}\text{H}_{84}\text{NaO}_{18}$] $^+$ calculated 1403.5550, found 1403.5551, m/z [$\text{C}_{85}\text{H}_{88}\text{NaO}_{19}$] $^+$ calculated 1435.5812, found 1435.5808.

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Table S1. Crystal data and structure refinement for 9da

Identification code	rovis93_0m	
Empirical formula	C ₁₃ H ₁₁ O ₆	
Formula weight	390.12	
Temperature	120 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	a = 7.5599(2) Å b = 7.9027(2) Å c = 23.7479(6) Å	a = 90° b = 90° g = 90°
Volume	1418.79(6) Å ³	
Z	4	
Density (calculated)	1.826 Mg/m ³	
Absorption coefficient	2.278 mm ⁻¹	
F(000)	760	
Crystal size	0.32 × 0.27 × 0.10 mm ³	
Theta range for data collection	2.72–36.65°	
Index ranges	–12 & lt; i>h & lt; i>h & lt; i>h = 12, –13 & lt; i>k & lt; i>k & lt; i>k = 13, –39 & lt; i>l & lt; i>l & lt; i>l = 39	
Reflections collected	52,652	
Independent reflections	7,026 [R _{int} = 0.0303]	
Completeness to theta = 36.65°	99.7%	
Absorption correction	Semiempirical from equivalents	
Max and min transmission	0.8042 and 0.5292	
Refinement method	Full-matrix least-squares on F ²	
Data/restraints/parameters	7,026/0/184	
Goodness-of-fit on F ²	1.095	
Final R indices [I > 2sigma(I)]	R1 = 0.0216, wR2 = 0.0487	
R indices (all data)	R1 = 0.0238, wR2 = 0.0496	
Absolute structure parameter	–0.001(9)	
Largest diff. peak and hole	1.224 and –1.370 e.Å ⁻³	

Table S2. Atomic coordinates (×10⁴) and equivalent isotropic displacement parameters (Å² × 10³) for 9da; U(eq) is defined as one-third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
C(1)	6686(1)	7236(2)	8020(1)	12(1)
C(2)	5610(2)	6323(2)	8915(1)	14(1)
C(3)	4290(2)	7079(2)	8597(1)	13(1)
C(4)	2559(2)	7219(2)	8790(1)	16(1)
C(5)	2217(2)	6575(2)	9323(1)	19(1)
C(6)	3555(2)	5814(2)	9648(1)	18(1)
C(7)	5274(2)	5665(2)	9450(1)	17(1)
C(8)	7217(2)	6317(2)	8576(1)	14(1)
C(9)	7003(2)	6082(1)	7519(1)	14(1)
C(10)	6738(2)	6994(2)	6968(1)	14(1)
C(11)	7790(2)	8854(1)	7968(1)	14(1)
C(12)	7097(3)	6798(2)	5987(1)	28(1)
C(13)	7997(2)	11778(2)	8100(1)	21(1)
I(1)	2902(1)	4789(1)	10435(1)	28(1)
O(1)	4830(1)	7618(1)	8079(1)	14(1)
O(2)	8663(1)	5719(1)	8671(1)	20(1)
O(3)	6094(2)	8386(1)	6917(1)	22(1)
O(4)	6969(1)	10230(1)	8152(1)	16(1)
O(5)	9296(1)	8800(1)	7796(1)	22(1)
O(7)	7312(1)	6054(1)	6537(1)	19(1)

Table S4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 9da

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
C(1)	10(1)	11(1)	16(1)	1(1)	0(1)	0(1)
C(2)	14(1)	14(1)	14(1)	0(1)	0(1)	-1(1)
C(3)	13(1)	12(1)	14(1)	1(1)	0(1)	-1(1)
C(4)	13(1)	18(1)	19(1)	2(1)	2(1)	0(1)
C(5)	17(1)	20(1)	19(1)	1(1)	5(1)	-1(1)
C(6)	22(1)	20(1)	13(1)	1(1)	3(1)	-3(1)
C(7)	18(1)	19(1)	14(1)	1(1)	-1(1)	0(1)
C(8)	13(1)	14(1)	16(1)	0(1)	0(1)	-1(1)
C(9)	15(1)	11(1)	16(1)	0(1)	0(1)	0(1)
C(10)	14(1)	13(1)	16(1)	0(1)	0(1)	-1(1)
C(11)	14(1)	12(1)	16(1)	-1(1)	0(1)	0(1)
C(12)	37(1)	32(1)	16(1)	3(1)	1(1)	9(1)
C(13)	20(1)	12(1)	31(1)	1(1)	-1(1)	-3(1)
I(1)	34(1)	34(1)	17(1)	6(1)	7(1)	-1(1)
O(1)	11(1)	14(1)	16(1)	3(1)	1(1)	0(1)
O(2)	14(1)	24(1)	23(1)	3(1)	-2(1)	3(1)
O(3)	29(1)	16(1)	20(1)	3(1)	2(1)	6(1)
O(4)	15(1)	11(1)	21(1)	-1(1)	1(1)	-2(1)
O(5)	14(1)	18(1)	34(1)	-4(1)	7(1)	-4(1)
O(7)	25(1)	18(1)	15(1)	0(1)	2(1)	4(1)

The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^2U^{11} + \dots + 2hka^*b^*U^{12}]$.