

Supplementary Information

Divergent Synthesis of δ -Valerolactones and Furanones via Palladium or Copper-Catalyzed α -Hydroxycyclopropanol Ring Opening Cyclizations

Pedro de Andrade Horn,^{a,d} Michael J. E. Collins,^{b,d} Cyrus C. Gudeman,^b Alexandra A. Fresh,^a
and Mingji Dai^{*b,c}

^aDepartment of Chemistry, Purdue University, West Lafayette, IN 47907, USA

^bDepartment of Chemistry, Emory University, Atlanta, GA 30022, USA

Email: mingji.dai@emory.edu. Tel: 001-404-727-4299

^cDepartment of Pharmacology and Chemical Biology, Emory University, Atlanta, GA 30022, USA

^dContributed Equally

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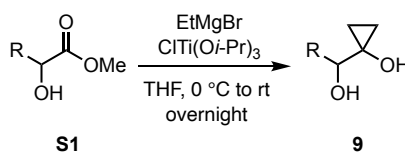
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Part 1. Experimental procedures and spectral data.

General Methods

NMR spectra were recorded on Bruker spectrometers (^1H at 400 MHz, 500 MHz, ^{13}C at 100 MHz, 125 MHz, and ^{19}F at 376 MHz, 470 MHz). Chemical shifts (δ) were given in ppm with reference to solvent signals [^1H NMR: CHCl_3 (7.26), CD_3OD (3.30); ^{13}C NMR: CDCl_3 (77.2), CD_3OD (49.0)]. ^1H NMR data are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (Hz), and integration. High-resolution mass measurements for compound characterization were carried out using a Thermo Exact Plus spectrometer using APCI. IR spectra were collected either on a Nicolet iS10 FT-IR or Nicolet iS50 ATR-IR from Thermo Scientific. Column chromatography was performed on silica gel. All reactions requiring heating were heated in an oil bath. All reactions sensitive to air or moisture were conducted under argon atmosphere in dry solvents under anhydrous conditions, unless otherwise noted. Carbon monoxide balloon was used to introduce carbon monoxide to the reactions (Note: Carbon monoxide is toxic and needs to be handled with caution; the carbon monoxide tank is kept in a fume hood with excellent ventilation). Anhydrous THF, CH_2Cl_2 , DMF, MeCN, and toluene were obtained from a Solvent Purification System (Cabinet Mount SPS from Pure Process Technology). All other solvents and reagents were used as obtained from commercial sources without further purification. Room temperature (rt) is around 23 °C.

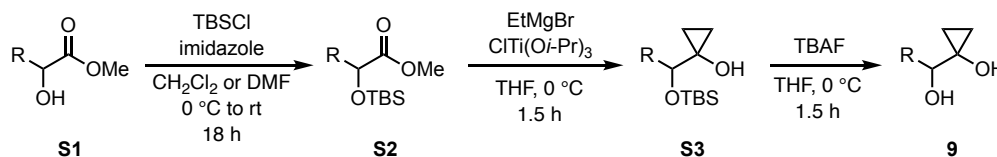
Representative procedure I for the synthesis of α -hydroxycyclopropanols:^{1,2}



To a solution of α -hydroxy methyl esters **S1** (1.0 equiv) in THF (0.2 M), $\text{ClTi}(\text{O}i\text{-Pr})_3$ (2.0 equiv) was added in a single portion. The reaction was then cooled to 0 °C. Next, EtMgBr (3.0 M in Et_2O , 4.0 equiv) was added dropwise over a 10-minute period. The reaction was warmed to room temperature overnight. EtOAc was then added at 0 °C to quench the excess EtMgBr, followed by NH_4Cl . The aqueous phase was extracted another three times with EtOAc, and the combined

organic layers were dried over MgSO₄, filtered through a short celite pad, and concentrated under reduced pressure. The crude residue was purified using column chromatography to afford α -hydroxycyclopropanol **15**.

Representative procedure II for the synthesis of α -hydroxycyclopropanols:¹⁻⁴

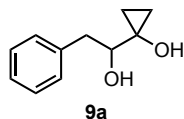


To a solution of the α -hydroxy methyl ester **S1** (1.0 equiv) and imidazole (2.4 equiv) in CH₂Cl₂ or DMF (0.15 M), TBSCl (1.2 equiv) was added in one portion at 0 °C. The reaction mixture was stirred for 18 h at room temperature before it was quenched with a saturated NaHCO₃ solution. Layers were separated and the aqueous layer was extracted three more times with CH₂Cl₂. The organic layers were combined and dried over MgSO₄, filtered through a short celite pad, and concentrated under reduced pressure to give the crude product which was purified using column chromatography to afford α -siloxy methyl ester **S2**.

To a solution of the above α -siloxy methyl ester **S2** (1.0 equiv) in THF (0.1 M), ClTi(Oi-Pr)₃ (2.0 equiv) was added in a single portion. The reaction was then cooled to 0 °C. Next, EtMgBr (3.0 M in Et₂O, 4.0 equiv) was added dropwise over a 10-minute period. The reaction was stirred at 0 °C for 1.5 h. EtOAc was then added at 0 °C to quench the excess EtMgBr, followed by NH₄Cl. The aqueous phase was extracted another three times with EtOAc, and the combined organic layers were dried over MgSO₄, filtered through a short celite pad, and concentrated under reduced pressure. The crude residue was purified using column chromatography to afford α -siloxycyclopropanol **S3**.

To a solution of the above α -siloxycyclopropanol **S3** in THF (0.06 M) at 0 °C, TBAF (1 M in THF, 1.2 equiv) was added dropwise over 5 min. The reaction mixture was stirred at 0 °C for another 1.5 h. After the starting material was consumed, the volatiles were removed under reduced pressure and the crude was dissolved in EtOAc and transferred to a separatory funnel. A saturated NH₄Cl

solution was added, and the aqueous layer was extracted two more times with EtOAc. The combined organic layers were washed with brine, dried over MgSO₄, filtered through a short celite pad. The solvents were removed under reduced pressure to give the crude product which was purified using column chromatography to give the desired α -hydroxycyclopropanol **9**.



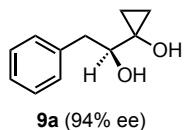
Synthesized following general procedure II; 39% yield over 3 steps.

¹H NMR (500 MHz, CDCl₃) δ 7.37-7.29 (m, 2H), 7.28-7.22 (m, 3H), 3.37 (dd, J = 9.1, 4.3 Hz, 1H), 3.04 (dd, J = 13.7, 4.3 Hz, 1H), 2.95 (dd, J = 13.8, 9.2, 1H), 2.60 (bs, 1H), 1.96 (bs, 1H), 0.93-0.74 (m, 2H), 0.63-0.56 (m, 1H), 0.52-0.45 (m, 1H).

¹³C NMR (125 MHz, CDCl₃) δ 138.3, 129.4, 128.7, 126.6, 77.8, 58.1, 39.8, 13.0, 11.1.

IR (ATR, cm⁻¹) 3349, 3277, 2948, 2925, 2904, 1603, 1496, 1453, 1420, 1217, 1067.

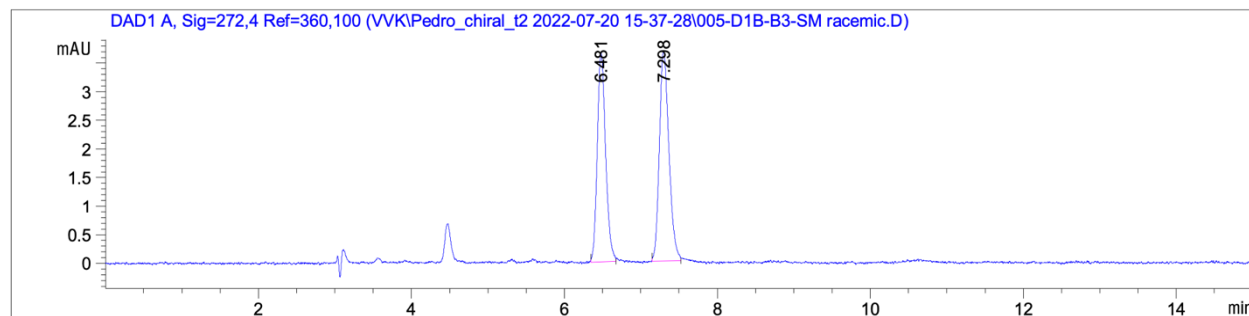
HRMS (APCI+) m/z calcd for C₁₁H₁₅O₂ [M+H]⁺: 179.1066; found: 179.1068.



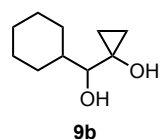
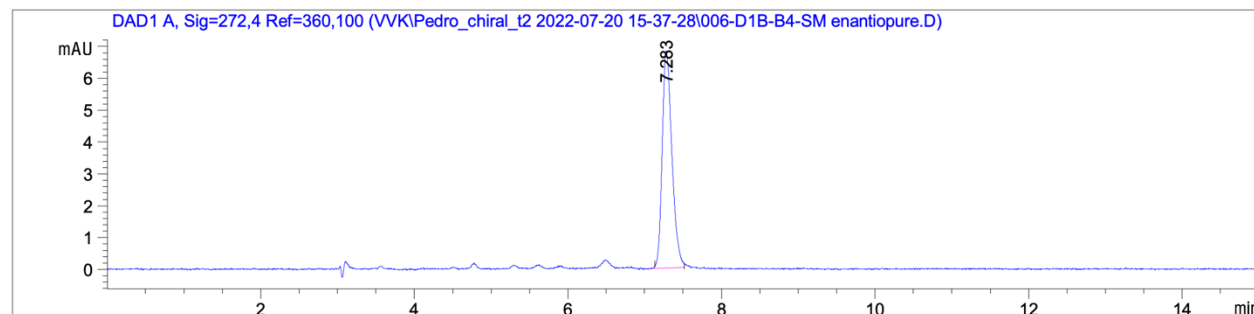
Synthesized following general procedure I; 41% yield; 94% *ee*.

SFC (Chiralpak IA column) 3% MeOH/CO₂ (2.0 mL/min, λ = 210 nm)

Racemic 9a			
	RT (min)	Area (mAU*s)	% Area
1	6.481	573.93634	46.2609
2	7.298	575.50488	53.7391



Enantio-enriched 9a			
	RT (min)	Area (mAU*s)	% Area
1	15.495	37.39734	3.0239
2	16.766	1056.44800	96.9761



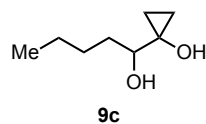
Synthesized following general procedure II; 37% yield over 3 steps.

¹H NMR (500 MHz, CDCl₃) δ 2.68 (d, *J* = 8.7 Hz, 1H), 2.14-1.91 (m, 4H), 1.81-1.71 (m, 3H), 1.70-1.63 (m, 1H), 1.35-1.21 (m, 2H), 1.19-1.14 (m, 1H), 1.05-0.93 (m, 3H), 0.73-0.62 (m, 2H), 0.51-0.44 (m, 1H).

¹³C NMR (125 MHz, CDCl₃) δ 81.8, 57.5, 41.0, 29.9, 29.4, 26.5, 26.1, 26.0, 13.1, 11.3.

IR (ATR, cm⁻¹) 3343, 2918, 2846, 2360, 1738, 1448, 1420, 1285, 1228, 1023, 1012.

HRMS (APCI+) *m/z* calcd for C₁₀H₁₉O₂ [M+H]⁺: 171.1379; found: 171.1381.



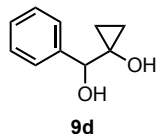
Synthesized following general procedure II; 83% yield over 3 steps.

¹H NMR (500 MHz, CDCl₃) δ 3.14 (dd, *J* = 8.2, 5.3 Hz, 1H), 2.06 (bs, 2H), 1.72-1.57 (m, 2H), 1.51-1.42 (m, 1H), 1.42-1.29 (m, 3H), 0.92 (t, *J* = 7.1 Hz, 3H), 0.88-0.84 (m, 1H), 0.81-0.76 (m, 1H), 0.59-0.51 (m, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 77.0 (hidden behind solvent peak), 58.7, 32.9, 28.2, 22.8, 14.0, 12.6, 11.3.

IR (ATR, cm^{-1}) 3236, 2953, 2933, 2871, 2856, 1736, 1464, 1454, 1429, 1284, 1220, 1066, 1006.

HRMS (APCI+) m/z calcd for $\text{C}_8\text{H}_{17}\text{O}_2$ $[\text{M}+\text{H}]^+$: 145.1223; found: 145.1225.



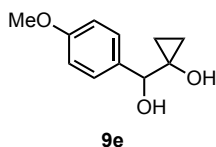
Synthesized following general procedure I; 23% yield.

^1H NMR (500 MHz, CDCl_3) δ 7.46-7.42 (m, 2H), 7.40-7.35 (m, 2H), 7.34-7.29 (m, 1H), 4.49 (s, 1H), 0.93-0.87 (m, 1H), 0.86-0.80 (m, 1H), 0.79-0.68 (m, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 140.8, 128.4, 128.0, 126.6, 78.0, 59.4, 12.1, 11.4.

IR (ATR, cm^{-1}) 3174, 2882, 2360, 1450, 1418, 1280, 1198, 1039, 1024.

HRMS (APCI+) m/z calcd for $\text{C}_{10}\text{H}_{13}\text{O}_2$ $[\text{M}+\text{H}]^+$: 165.0910; found: 165.0913.



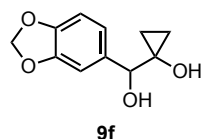
Synthesized following general procedure I; 20% yield.

^1H NMR (500 MHz, CDCl_3) δ 7.39-7.34 (m, 2H), 6.95-6.87 (m, 2H), 4.46 (d, $J = 3.8$ Hz, 1H), 3.81 (s, 3H), 2.30-2.24 (m, 2H), 0.89 (ddd, $J = 10.1, 5.4, 3.6$ Hz, 1H), 0.81 (ddd, $J = 9.3, 5.6, 4.2$ Hz, 1H), 0.75-0.66 (m, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 159.4, 132.9, 127.8, 113.8, 77.5, 59.4, 55.3, 12.0, 11.2.

IR (ATR, cm^{-1}) 3426, 2963, 2935, 2839, 2586, 1778, 1696, 1674, 1600, 1574, 1512, 1246, 1172, 1027.

HRMS (APCI+) m/z calcd for $\text{C}_{11}\text{H}_{11}\text{O}_3$ $[\text{M}+\text{H}]^+$: 191.0702; found: 191.0703.



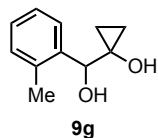
Synthesized following general procedure II; 38% yield over 3 steps.

^1H NMR (500 MHz, CD_3OD) δ 6.98 (d, $J = 1.7$ Hz, 1H), 6.87 (dd, $J = 8.0, 1.7$ Hz, 1H), 6.75 (d, $J = 8.0$ Hz, 1H), 5.90 (s, 2H), 4.36 (s, 1H), 0.75-0.66 (m, 3H), 0.65-0.60 (m, 1H).

^{13}C NMR (125 MHz, CD_3OD) δ 147.4, 146.8, 136.2, 120.2, 107.3, 107.1, 100.7, 76.8, 57.9, 11.0, 9.8.

IR (ATR, cm^{-1}) 3310, 2891, 2359, 1737, 1500, 1485, 1434, 1285, 1238, 1216, 1182, 1054, 1037.

HRMS (APCI+) m/z calcd for $\text{C}_{11}\text{H}_{13}\text{O}_4$ $[\text{M}+\text{H}]^+$: 209.0808; found: 209.0810.



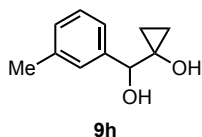
Synthesized following general procedure II; 60% yield over 3 steps.

^1H NMR (500 MHz, CDCl_3) δ 7.55 (dd, $J = 7.2, 2.0$ Hz, 1H), 7.23-7.15 (m, 2H), 7.13 (dd, $J = 7.1, 1.9$ Hz, 1H), 5.09 (s, 1H), 3.07 (bs, 1H), 2.76 (bs, 1H), 2.34 (s, 3H), 0.83 (ddd, $J = 10.7, 6.8, 5.1$ Hz, 1H), 0.73 (ddd, $J = 10.6, 6.7, 5.5$ Hz, 1H), 0.64 (ddd, $J = 10.7, 6.8, 5.3$ Hz, 1H), 0.38 (ddd, $J = 10.6, 6.7, 5.1$ Hz, 1H).

^{13}C NMR (125 MHz, CDCl_3) δ 138.5, 135.7, 130.3, 127.7, 126.4, 126.0, 73.9, 58.6, 19.7, 11.9, 9.9.

IR (ATR, cm^{-1}) 3372, 2248, 1778, 1202, 1025, 905.

HRMS (APCI+) m/z calcd for $\text{C}_{11}\text{H}_{13}\text{O}_2$ $[\text{M}+\text{H}]^+$: 117.0910; found: 117.0912.



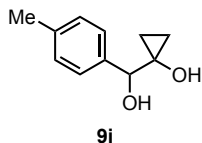
Synthesized following general procedure II; 49% yield over 3 steps.

^1H NMR (500 MHz, CDCl_3) δ 7.29-7.19 (m, 3H), 7.14-7.10 (m, 1H), 4.43 (s, 1H), 2.41 (bs, 2H), 2.87 (s, 3H), 0.88 (ddd, $J = 10.6, 6.2, 4.3$ Hz, 1H), 0.81 (ddd, $J = 10.2, 6.3, 4.9$ Hz, 1H), 0.78-0.65 (m, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 140.8, 138.1, 128.7, 128.3, 127.3, 123.7, 78.0, 59.3, 21.5, 12.1, 11.4.

IR (ATR, cm^{-1}) 3239, 3034, 3008, 2917, 1607, 1466, 1424, 1412, 1375, 1291, 1235, 1209, 1149, 1029, 1021.

HRMS (APCI+) m/z calcd for $\text{C}_{11}\text{H}_{13}\text{O}_2$ $[\text{M}+\text{H}]^+$: 177.0910; found: 177.0911.



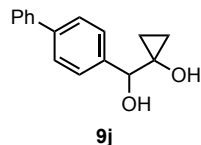
Synthesized following general procedure I; 20% yield.

¹H NMR (500 MHz, CDCl₃) δ 7.36-7.33 (m, 2H), 7.23-7.18 (m, 2H), 4.48 (s, 1H), 2.40-2.36 (m, 4H), 2.34 (bs, 1H), 0.93-0.88 (m, 1H), 0.86-0.81 (m, 1H), 0.79-0.68 (m, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 137.8, 137.7, 129.1, 126.5, 77.8, 59.4, 21.1, 12.0, 11.3.

IR (ATR, cm⁻¹) 3370, 2921, 2648, 1701, 1683, 1605, 1413, 1207, 1177, 1034, 1019.

HRMS (APCI+) *m/z* calcd for C₁₁H₁₅O₂ [M+H]⁺: 179.1066; found: 179.1066.



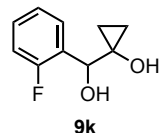
Synthesized following general procedure I; 21% yield.

¹H NMR (500 MHz, CDCl₃) δ 7.63-7.57 (m, 4H), 7.54-7.50 (m, 2H), 7.47-7.42 (m, 2H), 7.38-7.33 (m, 1H), 4.53 (s, 1H), 2.46-2.31 (m, 2H), 0.96-0.90 (m, 1H), 0.90-0.84 (m, 1H), 0.83-0.72 (m, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 140.9, 140.8, 139.8, 128.8, 127.4, 127.2, 127.1, 127.1, 77.8, 59.4, 12.2, 11.5.

IR (ATR, cm⁻¹) 3272, 3032, 2901, 2359, 1737, 1486, 1409, 1203, 1191, 1037, 1018, 1003.

HRMS (APCI+) *m/z* calcd for C₁₆H₁₇O₂ [M+H]⁺: 241.1223; found: 241.1225.



Synthesized following general procedure I; 22% yield.

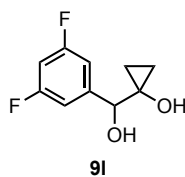
¹H NMR (500 MHz, CDCl₃) δ 7.64-7.61 (m, 1H), 7.32-7.26 (m, 1H), 7.20-7.17 (m, 1H), 7.07-7.03 (m, 1H), 4.84 (s, 1H), 2.45 (bs, 1H), 2.36 (bs, 1H), 0.93 (ddd, *J* = 10.5, 7.2, 4.9 Hz, 1H), 0.84-0.74 (m, 2H), 0.70 (ddd, *J* = 10.0, 7.0, 4.9 Hz, 1H).

¹³C NMR (125 MHz, CDCl₃) δ 159.8 (d, *J* = 245.7 Hz), 129.3 (d, *J* = 8.4 Hz), 128.4 (d, *J* = 4.2 Hz), 127.8 (d, *J* = 13.1 Hz), 124.2 (d, *J* = 3.5 Hz), 115.3 (d, *J* = 22.3 Hz), 72.0, 59.0, 12.8, 11.0.

¹⁹F NMR (470 MHz, CDCl₃) δ -118.9.

IR (ATR, cm⁻¹) 3347, 2919, 1616, 1587, 1488, 1454, 1274, 1225, 1030.

HRMS (APCI+) *m/z* calcd for C₁₀H₁₂O₂F [M+H]⁺: 183.0815; found: 183.0819.



Synthesized following general procedure II; 45% yield over 3 steps.

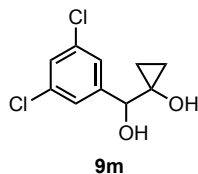
¹H NMR (500 MHz, CDCl₃) δ 7.04-6.95 (m, 2H), 6.77-6.73 (m, 1H), 4.38 (s, 1H), 2.49 (bs, 1H), 2.27 (bs, 1H), 0.99-0.86 (m, 2H), 0.80-0.76 (m, 1H), 0.75-0.70 (m, 1H).

¹³C NMR (125 MHz, CDCl₃) δ 163.0 (dd, *J* = 248.6, 12.5 Hz), 144.9 (t, *J* = 8.7 Hz), 109.6 (dd, *J* = 19.9, 6.2 Hz), 103.2 (t, *J* = 25.3 Hz), 77.3 (under CHCl₃ residual peak), 59.2, 12.4, 11.8

¹⁹F NMR (470 MHz, CDCl₃) δ -110.6.

IR (ATR, cm⁻¹) 3340, 1625, 1595, 1453, 1315, 1278, 1222, 1200, 1115, 1059, 1019.

HRMS (APCI+) *m/z* calcd for C₁₀H₁₁O₂F₂ [M+H]⁺: 201.0721; found: 201.0723.



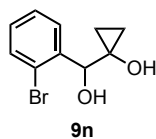
Synthesized following general procedure II; 31% yield over 3 steps.

¹H NMR (500 MHz, CDCl₃) δ = 7.35 (dd, *J* = 1.88, 0.65 Hz, 2H), 7.31 (t, *J* = 1.99 Hz, 1H), 4.35 (s, 1H), 0.96-0.89 (m, 2H), 0.80-0.71 (m, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 144.3, 135.0, 128.0, 125.2, 77.1, 59.2, 12.4, 11.8.

IR (ATR, cm⁻¹) 3342, 3280, 1593, 1572, 1422, 1382, 1215, 1195, 1100, 1046, 1013.

HRMS (APCI-) *m/z* calcd for C₁₀H₉O₂³⁵Cl₂ [M-H]⁻: 230.9985; found: 230.9984.



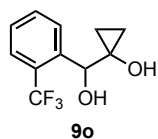
Synthesized following general procedure I; 20% yield.

¹H NMR (500 MHz, CDCl₃) δ 7.69 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.53 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.36-7.32 (m, 1H), 7.16 (ddd, *J* = 8.0, 7.3, 1.8 Hz, 1H), 5.10 (s, 1H), 2.71 (bs, 2H), 0.90 (ddd, *J* = 10.6, 6.7, 5.1 Hz, 1H), 0.82 (ddd, *J* = 10.5, 6.8, 5.5 Hz, 1H), 0.76 (ddd, *J* = 10.6, 6.8, 5.4 Hz, 1H), 0.58 (ddd, *J* = 10.3, 6.8, 5.1 Hz, 1H).

¹³C NMR (125 MHz, CDCl₃) δ 139.7, 132.7, 129.4, 129.0, 127.5, 123.2, 76.1, 58.6, 12.8, 10.4.

IR (ATR, cm⁻¹) 3351, 2958, 2922, 2852, 1716, 1467, 1435, 1275, 1196, 1038, 1017.

HRMS (APCI+) m/z calcd for $C_{10}H_{12}O_2^{79}Br$ $[M+H]^+$: 243.0015; found: 243.0015.



Synthesized following general procedure II; 37% yield over 3 steps.

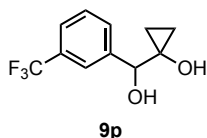
1H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, $J = 7.9$ Hz, 1H), 7.64 (d, $J = 7.9$ Hz, 1H), 7.57-7.53 (m, 1H), 7.41-7.26 (m, 1H), 5.06 (s, 1H), 3.14 (bs, 2H), 0.90-0.80 (m, 1H), 0.77-0.64 (m, 2H), 0.54-0.46 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 139.4, 132.0, 129.1, 128.0, 127.9 (q, $J = 30.3$ Hz), 125.6 (q, $J = 6.3$ Hz), 124.2 (q, $J = 274.0$ Hz), 72.6, 58.8, 13.3, 10.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.2.

IR (ATR, cm^{-1}) 3358, 1455, 1309, 1202, 1158, 1114, 1063, 1041, 1027.

HRMS (ESI-) m/z calcd for $C_{11}H_{10}O_2F_3$ $[M-H]^-$: 231.0627; found: 231.0630.



Synthesized following general procedure II; 60% yield over 3 steps.

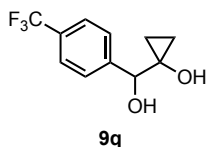
1H NMR (500 MHz, $CDCl_3$) δ 7.74-7.70 (m, 1H), 7.64 (d, $J = 7.9$ Hz, 1H), 7.58 (dd, $J = 8.2, 1.5$ Hz, 1H), 7.49 (t, $J = 7.7$ Hz, 1H), 4.50 (s, 1H), 2.62-2.19 (m, 2H), 0.99-0.84 (m, 2H), 0.81-0.68 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 141.8, 130.8 (q, $J = 33.0$ Hz), 130.0, 128.8, 124.7 (q, $J = 3.8$ Hz), 124.1 (q, $J = 272.6$ Hz), 123.5 (q, $J = 3.6$ Hz), 77.6, 59.3, 12.4, 11.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6.

IR (ATR, cm^{-1}) 3353, 2886, 1707, 1452, 1327, 1216, 1159, 1111, 1099, 1071, 1042, 1016.

HRMS (APCI+) m/z calcd for $C_{11}H_{12}O_2F_3$ $[M+H]^+$: 233.0783; found: 233.0786.



Synthesized following general procedure II; 63% yield over 3 steps.

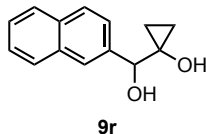
1H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, $J = 8.1$ Hz, 2H), 7.57 (d, $J = 8.1$ Hz, 2H), 4.49 (s, 1H), 2.58-2.15 (m, 2H), 0.97-0.84 (m, 2H), 0.82-0.67 (m, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 144.7, 130.1 (q, $J = 32.2$ Hz), 127.0, 125.3 (q, $J = 3.9$ Hz), 124.1 (q, $J = 272.0$ Hz), 77.6, 59.4, 12.4, 11.6.

^{19}F NMR (470 MHz, CDCl_3) δ -63.7.

IR (ATR, cm^{-1}) 3274, 2359, 1618, 1413, 1375, 1257, 1163, 1108, 1064, 1054, 1014.

HRMS (APCI+) m/z calcd for $\text{C}_{11}\text{H}_{12}\text{O}_2\text{F}_3$ $[\text{M}+\text{H}]^+$: 233.0783; found: 233.0786.



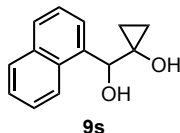
Synthesized following general procedure II; 33% yield over 3 steps.

^1H NMR (500 MHz, CDCl_3) δ 7.93-7.89 (m, 1H), 7.87-7.79 (m, 3H), 7.55 (dd, $J = 8.5, 1.8$ Hz, 1H), 7.52-7.46 (m, 2H), 4.65 (s, 1H), 2.36 (bs, 2H), 0.93 (ddd, $J = 9.7, 6.8, 4.6$ Hz, 1H), 0.84 (dddd, $J = 16.5, 9.9, 6.5, 5.1$ Hz, 2H), 0.75 (ddd, $J = 10.0, 6.9, 4.6$ Hz, 1H).

^{13}C NMR (125 MHz, CDCl_3) δ 138.2, 133.2, 133.1, 128.14, 128.08, 127.7, 126.3, 126.1, 125.5, 124.7, 78.1, 59.5, 12.1, 11.5.

IR (ATR, cm^{-1}) 3264, 3177, 2359, 1601, 1414, 1281, 1193, 1037.

HRMS (APCI+) m/z calcd for $\text{C}_{14}\text{H}_{15}\text{O}_2$ $[\text{M}+\text{H}]^+$: 215.1066; found: 215.1068.



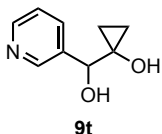
Synthesized following general procedure I; 16% yield.

^1H NMR (500 MHz, CDCl_3) δ 8.08-8.01 (m, 1H), 7.88-7.81 (m, 1H), 7.79-7.73 (m, 2H), 7.53-7.39 (m, 3H), 5.60 (s, 1H), 3.49 (bs, 2H), 0.83 (dt, $J = 11.7, 6.1$ Hz, 1H), 0.73 (dt, $J = 11.1, 6.1$ Hz, 1H), 0.63 (dt, $J = 11.8, 6.2$ Hz, 1H), 0.35 (dt, $J = 11.1, 6.0$ Hz, 1H).

^{13}C NMR (125 MHz, CDCl_3) δ 136.1, 133.6, 131.2, 128.8, 128.4, 126.2, 125.6, 125.3, 124.5, 123.5, 74.0, 59.0, 13.0, 10.5.

IR (ATR, cm^{-1}) 3343, 3050, 3009, 2923, 1711, 1597, 1414, 1395, 1270, 1199, 1062, 1018, 994, 783.

HRMS (APCI+) m/z calcd for $\text{C}_{14}\text{H}_{15}\text{O}_2$ $[\text{M}+\text{H}]^+$: 215.1066; found: 215.1068.



Synthesized following general procedure II; 22% yield over 3 steps.

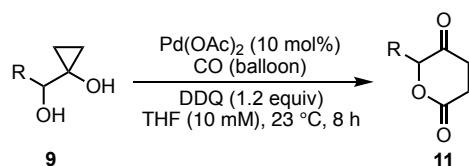
¹H NMR (400 MHz, CD₃OD) δ 8.61 (d, *J* = 1.72 Hz, 1H), 8.42 (dd, *J* = 6.75, 1.72 Hz, 1H), 7.94 (dt, *J* = 8.0, 1.76 Hz, 1H), 7.41 (ddd, *J* = 7.9, 4.9, 0.9 Hz), 4.42 (s, 1H), 3.31-3.28 (m, 1H), 0.86-0.76 (m, 2H), 0.77-0.73 (m, 1H), 0.70-0.65 (m, 1H).

¹³C NMR (100 MHz, CD₃OD) δ 147.6, 147.2, 139.1, 135.8, 123.4, 74.7, 57.7, 10.8, 10.2.

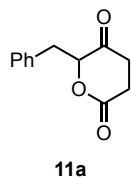
IR (ATR, cm⁻¹) 3340, 3073, 2697, 1596, 1580, 1481, 1284, 1059, 1042.

HRMS (APCI-) *m/z* calcd for C₉H₁₂O₂N [M+H]⁺: 166.0968; found: 166.0852.

Representative procedure for the palladium-catalyzed carbonylative lactonization:



To a stirred solution of α-hydroxycyclopropanol **9** (1.0 equiv, 0.1 mmol) and DDQ (1.2 equiv, 0.12 mmol, 27.2 mg) in THF (0.01 M, 10 mL) under carbon monoxide atmosphere (the reactor was evacuated and backfilled three times using a carbon monoxide balloon) was added Pd(OAc)₂ (0.1 equiv, 0.01 mmol, 2.24 mg) in one portion. The resulting solution was stirred at room temperature for 8 h. The volatiles were then removed. The residue was dissolved in EtOAc (30 mL) and transferred into a separatory funnel. Next, the organic layer was washed two times with a saturated Na₂S₂O₃ solution (10 mL), two times with a saturated NaHCO₃ solution (10 mL), and two times with brine (10 mL). The organic layer was then dried over MgSO₄, filtered through a short celite plug, and concentrated under reduced pressure. The crude residue was purified using column chromatography to afford 4-keto-δ-valerolactone **11**.



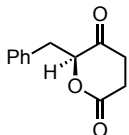
12.1 mg, 59%; 581 mg, 51% (1.0 gram scale)

¹H NMR (500 MHz, CDCl₃) δ 7.35-7.18 (m, 5H), 4.93-4.87 (m, 1H), 3.27 (dd, *J* = 14.5, 4.3 Hz, 1H), 3.19 (ddt, *J* = 14.5, 6.1, 1.5 Hz, 1H), 2.74-2.59 (m, 2H), 2.50-2.36 (m, 1H), 2.34-2.23 (m, 1H).

^{13}C NMR (125 MHz, CDCl_3) δ 204.8, 169.4, 135.1, 130.0, 128.8, 127.4, 83.9, 37.3, 34.0, 27.5.

IR (ATR, cm^{-1}) 2924, 1752, 1727, 1497, 1454, 1304, 1257, 1159, 1136, 1071, 1030, 1018.

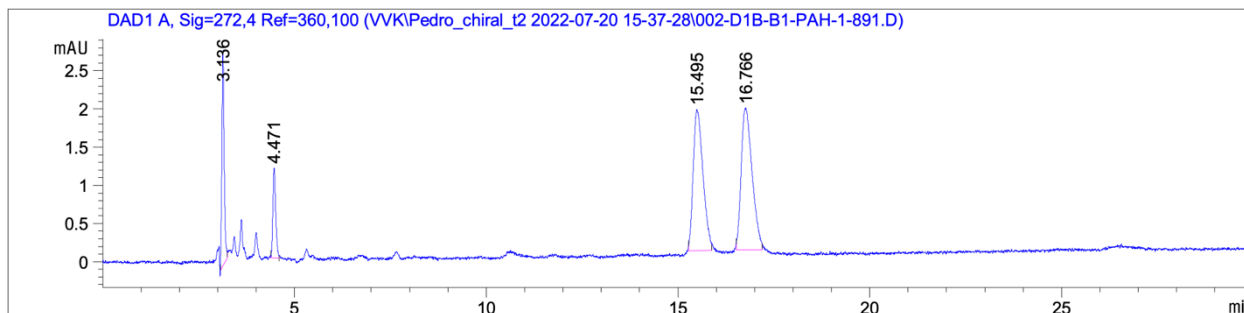
HRMS (APCI+) m/z calcd for $\text{C}_{12}\text{H}_{13}\text{O}_3$ $[\text{M}+\text{H}]^+$: 205.0859; found: 205.0861.



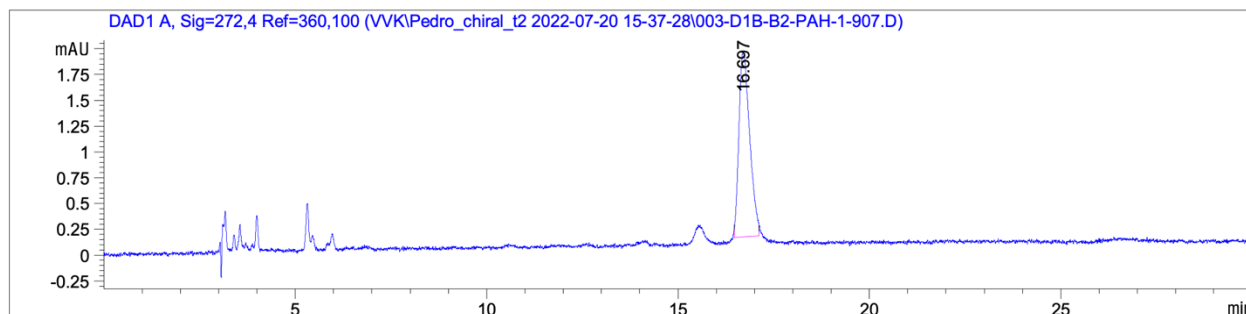
11a (55%, 85% ee)

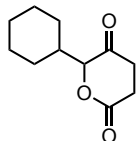
SFC (Chiralpak IA column) 3% MeOH/ CO_2 (2.0 mL/min, $\lambda = 210$ nm)

Racemic 11a			
	RT (min)	Area (mAU*s)	% Area
1	15.495	6816.87354	47.1827
2	16.766	7630.96143	52.8173



Enantio-enriched 11a			
	RT (min)	Area (mAU*s)	% Area
1	15.553	582.559	7.3821
2	16.702	7308.97	92.6179





11b

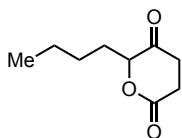
7.0 mg, 36%.

¹H NMR (500 MHz, CDCl₃) δ 4.47 (d, *J* = 3.4 Hz, 1H), 2.94-2.88 (m, 1H), 2.87-2.79 (m, 1H), 2.77-2.69 (m, 1H), 2.66-2.57 (m, 1H), 2.14-2.04 (m, 1H), 1.83-1.71 (m, 2H), 1.69-1.61 (m, 2H), 1.54-1.40 (m, 2H), 1.34-1.10 (m, 4H).

¹³C NMR (125 MHz, CDCl₃) δ 205.5, 170.1, 87.5, 39.9, 34.7, 29.0, 28.1, 26.3, 26.2, 25.9, 25.7.

IR (ATR, cm⁻¹) 2927, 2854, 1752, 1729, 1450, 1263, 1176, 1162, 1101.

HRMS (APCI+) *m/z* calcd for C₁₁H₁₇O₃ [M+H]⁺: 197.1172; found: 197.1175.



11c

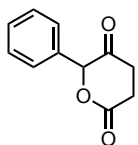
6.5 mg, 38%.

¹H NMR (500 MHz, CDCl₃) δ 4.64 (dd, *J* = 8.0, 4.1 Hz, 1H), 2.97-2.83 (m, 2H), 2.79-2.60 (m, 2H), 2.01-1.91 (m, 1H), 1.86-1.75 (m, 1H), 1.52-1.26 (m, 4H), 0.91 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 205.5, 170.1, 83.3, 33.8, 30.5, 28.2, 26.8, 22.3, 13.8.

IR (ATR, cm⁻¹) 2957, 2928, 2872, 2861, 1731, 1466, 1410, 1266, 1170, 1078.

HRMS (APCI+) *m/z* calcd for C₉H₁₅O₃ [M+H]⁺: 171.1015; found: 171.1017.



11d

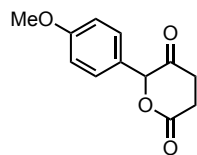
10.0 mg, 52%.

¹H NMR (500 MHz, CDCl₃) δ 7.46-7.33 (m, 5H), 5.71 (s, 1H), 2.97-2.87 (m, 1H), 2.87-2.75 (m, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 202.8, 169.6, 133.0, 129.1, 129.1, 125.9, 84.4, 33.4, 27.9.

IR (ATR, cm⁻¹) 1732, 1271, 1176, 1043.

HRMS (APCI+) *m/z* calcd for C₁₁H₁₁O₃ [M+H]⁺: 191.0702; found: 191.0705.



11e

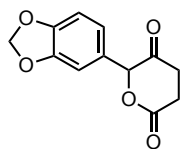
9.7 mg, 44%.

¹H NMR (500 MHz, CDCl₃) δ 7.30-7.22 (m, 2H), 6.97-6.89 (m, 2H), 5.65 (s, 1H), 3.81 (s, 3H), 2.95-2.88 (m, 1H), 2.88-2.76 (m, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 203.2, 169.8, 160.2, 127.5, 125.0, 114.5, 84.3, 55.4, 33.4, 28.0.

IR (ATR, cm⁻¹) 2961, 2922, 2852, 1733, 1614, 1520, 1461, 1270, 1257, 1175, 1027.

HRMS (APCI+) *m/z* calcd for C₁₂H₁₃O₄ [M+H]⁺: 221.0808; found: 221.0810.



11f

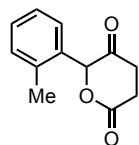
10.3 mg, 44%.

¹H NMR (500 MHz, CDCl₃) δ 6.86-6.76 (m, 3H), 5.99 (s, 2H), 5.59 (s, 1H), 2.96-2.84 (m, 2H), 2.84-2.76 (m, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 202.9, 169.6, 148.4 (2C), 126.6, 120.0, 108.6, 106.7, 101.6, 84.2, 33.4, 28.0.

IR (ATR, cm⁻¹) 2923, 1755, 1734, 1503, 1490, 1445, 1248, 1171, 1135, 1102, 1035.

HRMS (APCI+) *m/z* calcd for C₁₂H₁₁O₅ [M+H]⁺: 235.0601; found: 235.0605.



11g

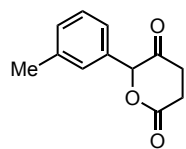
13.2 mg, 64%.

¹H NMR (500 MHz, CDCl₃) δ 7.36-7.15 (m, 4H), 5.83 (s, 1H), 3.07-3.01 (m, 2H), 2.92-2.83 (m, 2H), 2.34 (s, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 203.8, 169.7, 137.1, 131.9, 131.2, 129.6, 127.8, 126.3, 83.3, 33.9, 28.4, 19.7.

IR (ATR, cm⁻¹) 3023, 2923, 1733, 1331, 1259, 1172, 1136, 1037, 1016.

HRMS (APCI+) m/z calcd for $C_{12}H_{13}O_3$ $[M+H]^+$: 205.0859; found: 205.0862.



11h

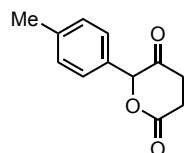
11.4 mg, 56%.

1H NMR (500 MHz, $CDCl_3$) δ 7.33-7.26 (m, 1H), 7.21-7.12 (m 3H), 5.66 (s, 1H), 2.95-2.87 (m, 1H), 2.86-2.77 (m, 3H), 2.36 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 202.9, 169.8, 139.0, 132.9, 129.9, 129.0, 126.4, 122.9, 84.5, 33.4, 27.9, 21.5.

IR (ATR, cm^{-1}) 2952, 2923, 2854, 1758, 1737, 1261, 1164, 1153, 1136, 1047.

HRMS (APCI+) m/z calcd for $C_{12}H_{13}O_3$ $[M+H]^+$: 205.0859; found: 205.0862.



11i

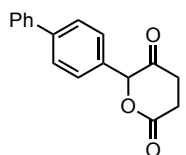
10.6 mg, 52%.

1H NMR (500 MHz, $CDCl_3$) δ 7.29-7.14 (m, 4H), 5.67 (s, 1H), 2.95-2.86 (m, 1H), 2.86-2.73 (m, 3H), 2.36 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 203.0, 169.8, 139.1, 130.1, 129.8, 125.9, 84.5, 33.4, 27.9, 21.2.

IR (ATR, cm^{-1}) 2955, 2921, 2853, 1732, 1266, 1177, 1131, 1039, 1020.

HRMS (APCI+) m/z calcd for $C_{12}H_{13}O_3$ $[M+H]^+$: 205.0859; found: 205.0862.



11j

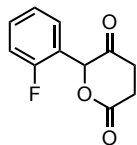
14.0 mg, 53%.

1H NMR (500 MHz, $CDCl_3$) δ 7.67-7.61 (m, 2H), 7.60-7.56 (m, 2H), 7.48-7.42 (m, 4H), 7.41-7.33 (m, 1H), 5.75 (s, 1H), 2.99-2.90 (m, 1H), 2.90-2.79 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 202.8, 169.6, 142.1, 140.1, 131.9, 128.9, 127.80, 127.77, 127.2, 126.4, 84.3, 33.5, 27.9.

IR (ATR, cm^{-1}) 2922, 1733, 1489, 1410, 1334, 1269, 1162, 1140, 1036, 1021.

HRMS (APCI+) m/z calcd for $\text{C}_{17}\text{H}_{15}\text{O}_3$ $[\text{M}+\text{H}]^+$: 267.1015; found: 267.1020.



11k

10.0 mg, 48%.

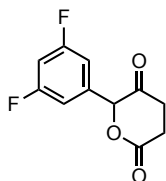
^1H NMR (500 MHz, CDCl_3) δ 7.45-7.36 (m, 1H), 7.32 (td, $J = 7.4, 1.8$ Hz, 1H), 7.19 (tdd, $J = 7.6, 3.4, 1.2$ Hz, 1H), 7.16-7.08 (m, 1H), 5.83 (s, 1H), 3.09-3.02 (m, 2H), 2.94-2.85 (m, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 202.4, 169.2, 160.5 (d, $J = 248.9$ Hz), 131.6 (d, $J = 9.5$ Hz), 130.1 (d, $J = 3.4$ Hz), 124.5 (d, $J = 3.6$ Hz), 121.2 (d, $J = 13.6$ Hz), 115.9 (d, $J = 21.0$ Hz), 80.5, 33.5, 28.3.

^{19}F NMR (470 MHz, CDCl_3) δ -116.6.

IR (ATR, cm^{-1}) 2922, 1759, 1738, 1494, 1458, 1263, 1235, 1171, 1136, 1041, 1030.

HRMS (APCI+) m/z calcd for $\text{C}_{11}\text{H}_{10}\text{O}_3\text{F}$ $[\text{M}+\text{H}]^+$: 209.0608; found: 209.0611.



11l

14.2 mg, 63%.

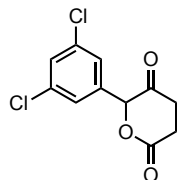
^1H NMR (500 MHz, CDCl_3) δ 7.00-6.91 (m, 2H), 6.84 (tt, $J = 8.8, 2.3$ Hz, 1H), 5.66 (s, 1H), 3.03-2.91 (m, 1H), 2.90-2.76 (m, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 201.5, 168.6, 163.3 (dd, $J = 250.5, 12.5$ Hz), 136.4 (t, $J = 9.4$ Hz), 109.3 (dd, $J = 20.7, 7.2$ Hz), 104.6 (t, $J = 25.1$ Hz), 82.9, 33.4, 27.8.

^{19}F NMR (470 MHz, CDCl_3) δ -108.6.

IR (ATR, cm^{-1}) 2956, 2922, 2851, 1744, 1731, 1601, 1456, 1306, 1121.

HRMS (APCI+) m/z calcd for $\text{C}_{11}\text{H}_9\text{O}_3\text{F}_2$ $[\text{M}+\text{H}]^+$: 227.0514; found: 227.0519.



11m

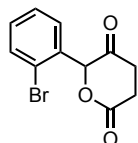
12.9 mg, 48%.

¹H NMR (500 MHz, CDCl₃) δ 7.39-7.37 (m, 1H), 7.30-7.27 (m, 2H), 5.63 (s, 1H), 2.98 (ddd, *J* = 17.4, 9.4, 6.4 Hz, 1H), 2.93-2.88 (m, 1H), 2.87-2.77 (m, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 201.6, 168.7, 135.9, 135.7, 129.4, 124.7, 82.7, 33.4, 27.8.

IR (ATR, cm⁻¹) 2922, 2852, 1741, 1731, 1572, 1434, 1269, 1180, 1158, 1050.

HRMS (APCI+) *m/z* calcd for C₁₁H₉O₃³⁵Cl₂ [M+H]⁺: 258.9923; found: 258.9927.



11n

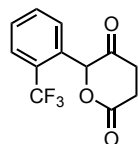
16.0 mg, 60%.

¹H NMR (500 MHz, CDCl₃) δ 7.64-7.59 (m, 1H), 7.39-7.32 (m, 2H), 7.30-7.26 (m, 1H), 6.02 (s, 1H), 3.18-3.02 (m, 2H), 2.97-2.83 (m, 2H).

¹³C{¹H} NMR (125 MHz, CDCl₃) δ 201.9, 169.4, 133.2, 132.9, 131.0, 130.0, 127.8, 123.8, 84.1, 33.5, 28.5.

IR (ATR, cm⁻¹) 2923, 1759, 1738, 1262, 1172, 1137, 1056, 1039, 1028.

HRMS (APCI+) *m/z* calcd for C₁₁H₁₀O₃⁷⁹Br [M+H]⁺: 268.9807; found: 268.9812.



11o

16.5 mg, 64%.

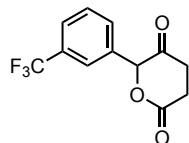
¹H NMR (500 MHz, CDCl₃) δ 7.74-7.71 (m, 1H), 7.64-7.59 (m, 1H), 7.55-7.50 (m, 1H), 7.47-7.43 (m, 1H), 6.03 (s, 1H), 3.17 (ddd, *J* = 16.5, 13.8, 6.4 Hz, 1H), 3.06 (ddd, *J* = 16.5, 5.7, 2.4 Hz, 1H), 2.92 (ddd, *J* = 18.9, 6.5, 2.4 Hz, 1H), 2.81 (ddd, *J* = 19.1, 13.9, 5.7 Hz, 1H).

¹³C NMR (125 MHz, CDCl₃) δ 201.9, 169.3, 132.4, 131.2, 129.9, 129.6, 128.8 (q, *J* = 30.7 Hz), 126.3 (q, *J* = 5.7 Hz), 123.9 (q, *J* = 273.9 Hz), 120.6, 80.9, 33.1, 28.5.

¹⁹F NMR (470 MHz, CDCl₃) δ -59.1.

IR (ATR, cm⁻¹) 2959, 2923, 2853, 1764, 1741, 1313, 1261, 1158, 1118, 1048, 1033.

HRMS (APCI+) *m/z* calcd for C₁₂H₁₀O₃F₃ [M+H]⁺: 259.0576; found: 259.0578.



11p

10.9 mg, 42%.

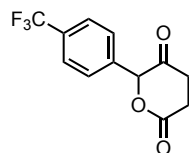
¹H NMR (500 MHz, CDCl₃) δ 7.69-7.62 (m, 2H), 7.61-7.53 (m, 2H), 5.75 (s, 1H), 3.04-2.95 (m, 1H), 2.95-2.79 (m, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 202.1, 168.9, 133.8, 131.5 (q, *J* = 33.3 Hz), 129.7, 129.5, 126.0 (q, *J* = 5.4 Hz), 123.7 (q, *J* = 271.5 Hz), 123.2 (q, *J* = 3.7 Hz), 83.5, 33.4, 27.9.

¹⁹F NMR (470 MHz, CDCl₃) δ -63.9.

IR (ATR, cm⁻¹) 2924, 1761, 1738, 1328, 1259, 1163, 1121, 1074.

HRMS (APCI+) *m/z* calcd for C₁₂H₁₀O₃F₃ [M+H]⁺: 259.0576; found: 259.0579.



11q

18.0 mg, 70%.

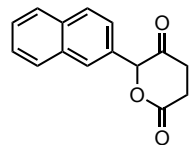
¹H NMR (500 MHz, CDCl₃) δ 7.68 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 5.76 (s, 1H), 3.03-2.94 (m, 1H), 2.92-2.76 (m, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 202.0, 169.0, 136.6, 131.4 (q, *J* = 32.7 Hz), 126.5, 125.9 (q, *J* = 3.6 Hz), 123.7 (q, *J* = 272.5 Hz), 83.6, 33.4, 27.9

¹⁹F NMR (470 MHz, CDCl₃) δ -64.0.

IR (ATR, cm⁻¹) 2920, 1736, 1330, 1272, 1180, 1159, 1110, 1068, 1047.

HRMS (APCI+) *m/z* calcd for C₁₂H₁₀O₃F₃ [M+H]⁺: 259.0576; found: 259.0580.



11r

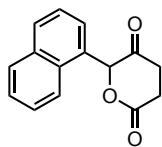
15.3 mg, 64%.

¹H NMR (500 MHz, CDCl₃) δ 7.93-7.78 (m, 4H), 7.56-7.43 (m, 3H), 5.87 (s, 1H), 3.00-2.79 (m, 4H).

^{13}C NMR (125 MHz, CDCl_3) δ 202.8, 169.7, 133.3, 133.0, 130.3, 129.2, 128.2, 127.8, 127.0, 126.9, 125.2, 123.1, 84.6, 33.5, 27.9.

IR (ATR, cm^{-1}) 2922, 1756, 1735, 1261, 1170, 1156, 1123, 1039.

HRMS (APCI+) m/z calcd for $\text{C}_{15}\text{H}_{13}\text{O}_3$ $[\text{M}+\text{H}]^+$: 241.0859; found: 241.0864.



11s

9.2 mg, 38%.

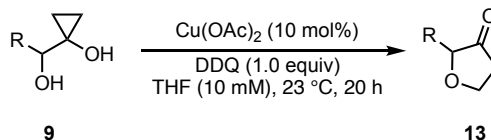
^1H NMR (500 MHz, CDCl_3) δ 7.94-7.84 (m, 3H), 7.59-7.51 (m, 2H), 7.47 (t, $J = 7.7$ Hz, 1H), 7.42 (t, $J = 7.1$ Hz, 1H), 6.31 (s, 1H), 3.12-3.06 (m, 2H), 3.06-2.90 (m, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 203.5, 169.6, 134.1, 130.9, 130.6, 129.4, 129.0, 127.1, 126.3 (2C), 124.9, 123.8, 83.4, 33.9, 28.4.

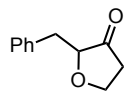
IR (ATR, cm^{-1}) 3052, 2923, 1735, 1260, 1164, 1137, 1030.

HRMS (APCI+) m/z calcd for $\text{C}_{15}\text{H}_{13}\text{O}_3$ $[\text{M}+\text{H}]^+$: 241.0859; found: 241.0860.

Representative procedure for the copper-catalyzed ring opening cyclizations:



To a flame dried vial under argon was added α -hydroxycyclopropanol **9** (1.0 equiv, 0.1 mmol), followed by $\text{Cu}(\text{OAc})_2$ (0.1 equiv, 0.01 mmol, 1.83 mg) and DDQ (1.0 equiv, 0.1 mmol, 22.7 mg). The mixture was then dissolved in THF (0.01 M, 10 mL). The reaction was then stirred for 20 h at room temperature. After completion the mixture was filtered through a short pad of celite, then quenched with DI water (50 mL), and diluted with EtOAc (50 mL). The aqueous phase was washed three times with EtOAc (20 mL). The organic phases were combined and washed with brine (50 mL). The organic phase was then dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The resulting crude residue was then dissolved in CHCl_3 and filtered, once again, through a pad of celite to give the crude product, which was purified by column chromatography to afford 3-furanone **13**.



13a

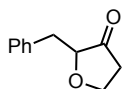
16.4 mg, 93%; 788 mg, 80% (1.0 gram scale).

¹H NMR (500 MHz, CDCl₃) δ 7.32-7.27 (m, 2H), 7.26-7.21 (m, 3H), 4.18-4.23 (m, 1H), 4.05-3.97 (m, 1H), 3.98 (dd, *J* = 7.8, 3.7 Hz, 1H), 3.08 (dd, *J* = 14.5, 3.8 Hz, 1H), 2.86 (dd, *J* = 14.5, 7.7 Hz, 1H), 2.46 (ddd, *J* = 18.1, 7.1, 4.0 Hz, 1H), 2.36-2.29 (m, 1H).

¹³C NMR (125 MHz, CDCl₃) δ 215.5, 137.1, 129.4, 128.4, 126.7, 80.6, 64.5, 37.0, 36.9.

IR (ATR, cm⁻¹) 3029, 2920, 2874, 1753, 1496, 1454, 1403, 1146, 1075, 994.

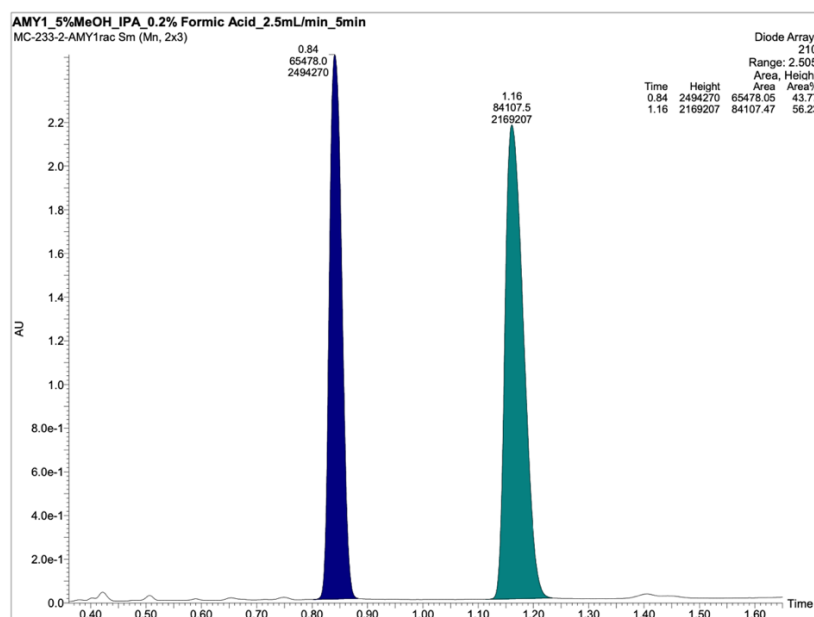
HRMS (APCI+) *m/z* calcd for C₁₁H₁₃O₂ [M+H]⁺: 177.0910; found: 177.0909.



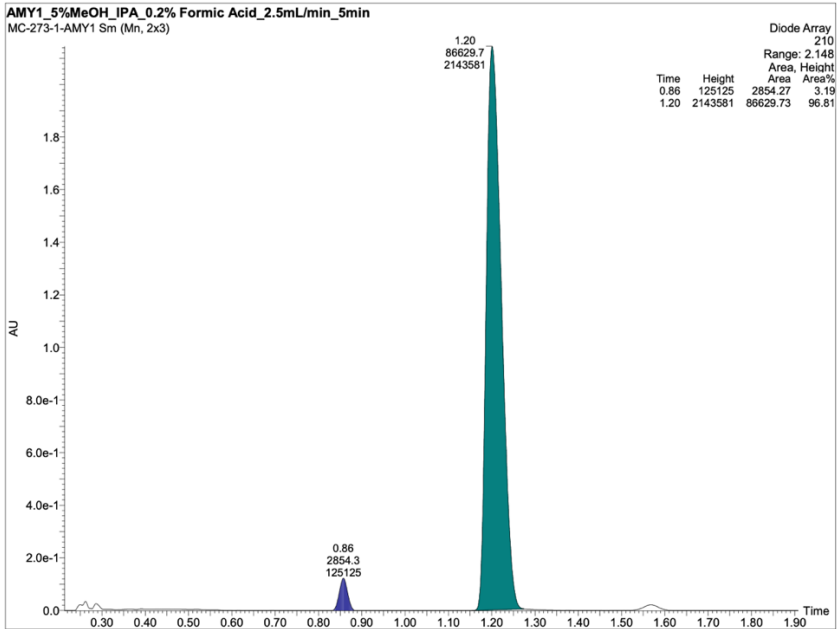
13a (80%, 94% ee)

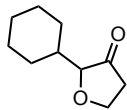
AMY1_5%MeOH_IPA_0.2% Formic Acid_2.5mL/min_5min

Racemic 13a			
	RT (min)	Area (mAU*s)	% Area
1	0.84	65478.05	43.7700
2	16.766	84107.47	56.2300



Enantio-enriched 13a			
	RT (min)	Area (mAU*s)	% Area
1	0.86	2854.27	3.1900
2	1.20	86629.73	96.8100





13b

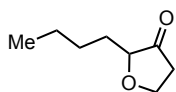
13.5 mg, 80%.

¹H NMR (400 MHz, CDCl₃) δ 4.29 (m, 1H), 4.08-4.00 (m, 1H), 3.53 (d, *J* = 3.9 Hz, 1H), 2.52-2.37 (m, 2H), 1.80-1.70 (m, 4H), 1.67-1.61 (m, 1H), 1.52-1.46 (m, 1H), 1.32-1.11 (m, 5H).

¹³C NMR (125 MHz, CDCl₃) δ 216.5, 83.7, 64.5, 39.8, 38.0, 29.3, 27.1, 26.3, 26.1, 26.0.

IR (ATR, cm⁻¹) 2925, 2853, 1753, 1450, 1404, 1158, 1139, 1028.

HRMS (APCI+) *m/z* calcd for C₁₀H₁₇O₂ [M+H]⁺: 169.1223; found: 169.1223.



13c

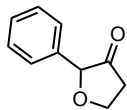
5.0 mg, 35%.

¹H NMR (500 MHz, CDCl₃) δ 4.32-4.28 (m, 1H), 4.08-4.02 (m, 1H), 3.69 (dd, *J* = 7.9, 4.2 Hz, 1H), 2.52-2.43 (m, 2H), 1.77-1.67 (m, 1H), 1.61-1.50 (m, 2H), 1.50-1.27 (m, 3H), 0.90 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 216.4, 80.0, 64.3, 37.1, 30.3, 27.5, 22.5, 13.9.

IR (ATR, cm⁻¹) 2957, 2930, 2861, 2360, 2341, 1756, 1728, 1466, 1286, 1159, 1128, 1088, 1037.

HRMS (APCI+) *m/z* calcd for C₈H₁₅O₂ [M+H]⁺: 143.1066; found: 143.1067.



13d

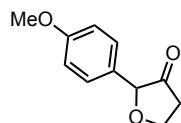
13.0 mg, 80%.

¹H NMR (400 MHz, CDCl₃) δ 7.43-7.30 (m, 5H), 4.75 (s, 1H), 4.50 (ddd, *J* = 9.4, 7.2, 6.3 Hz, 1H), 4.30 (m, 1H), 2.65-2.61 (m, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 213.0, 135.6, 128.6, 128.2, 126.0, 80.9, 64.8, 36.6.

IR (ATR, cm⁻¹) 3062, 3032, 2917, 2876, 1755, 1719, 1494, 1452, 1403, 1142, 1055, 987.

HRMS (APCI+) *m/z* calcd for C₁₀H₁₁O₂ [M+H]⁺: 163.0753; found: 163.0756.



13e

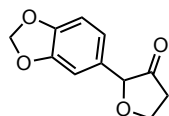
11.3 mg, 59%.

¹H NMR (500 MHz, CDCl₃) δ 7.33-7.29 (m, 2H), 6.93-6.88 (m, 2H), 4.69 (s, 1H), 4.51-4.43 (m, 1H), 4.25 (ddd, *J* = 9.4, 8.4, 7.5 Hz, 1H), 3.80 (s, 3H), 2.71-2.55 (m, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 213.5, 159.6, 127.8, 127.5, 114.1, 80.8, 64.6, 55.3, 36.7.

IR (ATR, cm⁻¹) 3001, 2958, 2926, 2838, 1779, 1677, 1600, 1577, 1512, 1463, 1247, 1177, 1071, 1031.

HRMS (APCI+) *m/z* calcd for C₁₁H₁₃O₃ [M+H]⁺: 193.0859; found: 193.0859.



13f

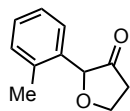
19.2 mg, 93%.

¹H NMR (400 MHz, CDCl₃) δ 6.87-6.85 (m, 2H), 6.81-6.79 (m, 1H), 5.95 (d, *J* = 0.7 Hz, 2H), 4.64 (s, 1H), 4.50-4.41 (m, 1H), 4.27-4.21 (m, 1H), 2.64-2.60 (m, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 213.1, 148.0, 147.6, 129.4, 119.8, 108.4, 106.7, 101.2, 80.9, 64.7, 36.5.

IR (ATR, cm⁻¹) 2916, 2850, 1753, 1503, 1487, 1442, 1402, 1239, 1144, 1099, 1034, 926.

HRMS (APCI+) *m/z* calcd for C₁₁H₁₁O₄ [M+H]⁺: 207.0651; found: 207.0651.



13g

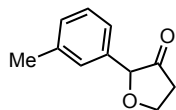
13.2 mg, 75%.

¹H NMR (500 MHz, CDCl₃) δ 7.32-7.27 (m, 1H), 7.24-7.16 (m, 3H), 4.96 (s, 1H), 4.55 (m, 1H), 4.25 (m, 1H), 2.73 (m, 1H), 2.62 (m, 1H), 2.42 (s, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 213.5, 136.6, 134.4, 130.8, 128.3, 126.5, 126.0, 79.9, 64.7, 37.0, 19.6.

IR (ATR, cm⁻¹) 3023, 2955, 2921, 2871, 1753, 1490, 1462, 1403, 1216, 1140, 1050, 1037, 986.

HRMS (APCI+) *m/z* calcd for C₁₁H₁₃O₂ [M+H]⁺: 177.0910; found: 177.0909.



13h

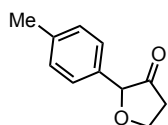
14.6 mg, 83%.

¹H NMR (400 MHz, CDCl₃) δ 7.29-7.19 (m, 3H), 7.14-7.12 (m, 1H), 4.71 (s, 1H), 4.52-4.47 (m, 1H), 4.30-4.24 (m, 1H), 2.65-2.61 (m, 2H), 2.36 (s, 3H).

¹³C{¹H} NMR (100 MHz, CDCl₃) δ 213.2, 138.3, 135.6, 129.0, 128.5, 126.7, 123.2, 81.0, 64.8, 36.6, 21.5.

IR (ATR, cm⁻¹) 2956, 2923, 2870, 1756, 1720, 1607, 1489, 1461, 1403, 1278, 1140, 1054, 985.

HRMS (APCI+) *m/z* calcd for C₁₁H₁₃O₂ [M+H]⁺: 177.0910; found: 177.0909.



13i

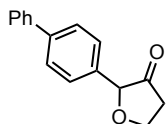
12.4 mg, 70%.

¹H NMR (500 MHz, CDCl₃) δ 7.30-7.26 (m, 2H), 7.20-7.16 (m, 2H), 4.71 (s, 1H), 4.52-4.44 (m, 1H), 4.27 (m, 1H), 2.65-2.58 (m, 2H), 2.34 (s, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 213.3, 138.0, 132.7, 129.3, 126.0, 81.0, 64.7, 36.6, 21.2.

IR (ATR, cm⁻¹) 2922, 2879, 2360, 1759, 1449, 1328, 1163, 1121, 1073.

HRMS (APCI+) *m/z* calcd for C₁₁H₁₃O₂ [M+H]⁺: 177.0910; found: 177.0910.



13j

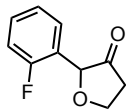
19.3 mg, 81%.

¹H NMR (400 MHz, CDCl₃) δ 7.62-7.56 (m, 4H), 7.50-7.42 (m, 4H), 7.37-7.33 (m, 1H), 4.80 (s, 1H), 4.56-4.50 (m, 1H), 4.34 (m, 1H), 2.68-2.64 (m, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 213.1, 141.2, 140.7, 134.6, 128.8, 127.4, 127.4, 127.2, 126.4, 80.8, 64.9, 36.6.

IR (ATR, cm⁻¹) 3055, 3030, 2918, 2870, 1755, 1487, 1402, 1141, 1050, 1007.

HRMS (APCI+) *m/z* calcd for C₁₆H₁₅O₂ [M+H]⁺: 239.1066; found: 239.1063.



13k

12.1 mg, 67%.

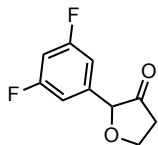
¹H NMR (400 MHz, CDCl₃) δ 7.35-7.30 (m, 2H), 7.17-7.06 (m, 2H), 4.90 (s, 1H), 4.87 (m, 1H), 4.57-4.51 (m, 1H), 4.29-4.22 (m, 1H), 2.83-2.74 (m, 1H), 2.68-2.61 (m, 1H).

¹³C NMR (125 MHz, CDCl₃) δ 212.8, 160.8 (d, *J* = 248.2 Hz), 130.6 (d, *J* = 8.6 Hz), 129.8 (d, *J* = 4.7 Hz), 124.3 (d, *J* = 3.0 Hz), 123.8 (d, *J* = 13.8 Hz), 115.9 (d, *J* = 21.4 Hz), 77.7, 65.2, 36.7.

¹⁹F NMR (470 MHz, CDCl₃) δ -117.3.

IR (ATR, cm⁻¹) 2922, 2876, 1758, 1617, 1587, 1492, 1457, 1403, 1233, 1143, 1052, 1030, 986.

HRMS (APCI+) *m/z* calcd for C₁₀H₁₀O₂F [M+H]⁺ = 181.0659; found 181.0660.



13l

14.5 mg, 73%, 36 h.

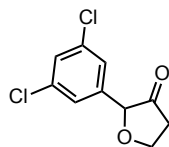
¹H NMR (400 MHz, CDCl₃) δ 7.04-7.00 (m, 2H), 6.79-6.74 (m, 1H), 4.72 (s, 1H), 4.53-4.47 (m, 1H), 4.35-4.26 (m, 1H), 2.69-2.62 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 211.3, 163.1 (dd, *J* = 249.0, 12.6 Hz), 139.3 (t, *J* = 9.2 Hz), 108.7 (dd, *J* = 20.5, 6.4 Hz), 103.5 (t, *J* = 25.6 Hz), 79.5 (t, *J* = 2.4 Hz), 64.9, 36.2.

¹⁹F NMR (376 MHz, CDCl₃) δ -109.1.

IR (ATR, cm⁻¹) 3092, 2887, 1759, 1728, 1624, 1596, 1443, 1326, 1228, 1137, 1118, 986.

HRMS (APCI+) *m/z* calcd for C₁₀H₉O₂F₂ [M+H]⁺: 199.0565; found: 199.0565.



13m

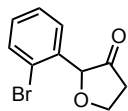
13.4 mg, 58%, 36 h.

¹H NMR (400 MHz, CDCl₃) δ 7.34-7.22 (m, 3H), 4.67 (s, 1H), 4.52-4.46 (m, 1H), 4.33-4.26 (m, 1H), 2.65-2.61 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 211.4, 138.7, 135.2, 128.3, 124.2, 79.4, 65.0, 36.3.

IR (ATR, cm^{-1}) 3080, 2992, 2919, 2879, 1759, 1587 1569, 1427, 1402, 1204, 1139, 1102, 1070, 989.

HRMS (APCI+) m/z calcd for $\text{C}_{10}\text{H}_9\text{O}_2^{35}\text{Cl}_2$ $[\text{M}+\text{H}]^+$: 230.9974; found: 230.9978.



13n

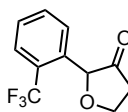
18.8 mg, 78%.

^1H NMR (500 MHz, CDCl_3) δ 7.62-7.57 (m, 1H), 7.35-7.27 (m, 2H), 7.21-7.17 (m, 1H), 5.13 (s, 1H), 4.59-4.54 (m, 1H), 4.30-4.24 (m, 1H), 2.80-2.73 (m, 1H), 2.68-2.62 (m, 1H).

^{13}C NMR (125 MHz, CDCl_3) δ 211.8, 135.5, 133.3, 130.0, 128.9, 127.6, 123.5, 81.5, 64.9, 36.9.

IR (ATR, cm^{-1}) 3064, 2920, 2874, 2359, 2337, 1757, 1472, 1439, 1402, 1137, 1063, 1023, 988.

HRMS (APCI+) m/z calcd for $\text{C}_{10}\text{H}_{10}\text{O}_2^{79}\text{Br}$ $[\text{M}+\text{H}]^+$: 240.9858; found: 240.9856.



13o

16.6 mg, 72%.

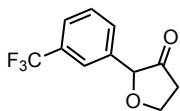
^1H NMR (400 MHz, CDCl_3) δ 7.72-7.69 (m, 1H), 7.57-7.54 (m, 1H), 7.46-7.42 (m, 2H), 5.03 (s, 1H), 4.60-4.54 (m, 1H), 4.28-4.22 (m, 1H), 2.80-2.63 (m, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 211.7, 134.7, 132.1, 129.3 (q, $J = 31.3$ Hz), 129.0, 128.6, 126.3 (q, $J = 6.3$ Hz), 124.0 (q, $J = 272.5$ Hz), 78.6, 64.8, 36.8.

^{19}F NMR (470 MHz, CDCl_3) δ -58.8.

IR (ATR, cm^{-1}) 2920, 2850, 1759, 1587, 1455, 1405, 1310, 1275, 1203, 1159, 1109, 1048, 1033.

HRMS (APCI+) m/z calcd for $\text{C}_{11}\text{H}_{10}\text{O}_2\text{F}_3$ $[\text{M}+\text{H}]^+$: 231.0627; found: 231.0625.



13p

17.0 mg, 74%.

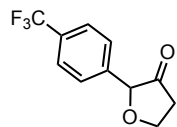
^1H NMR (400 MHz, CDCl_3) δ 7.72-7.72 (m, 1H), 7.64-7.56 (m, 2H), 7.52-7.48 (m, 1H), 4.78 (s, 1H), 4.55-4.50 (m, 1H), 4.35-4.28 (m, 1H), 2.67-2.63 (m, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 212.0, 136.5, 131.0 (q, $J = 32.5$ Hz), 129.3, 129.0, 124.9 (q, $J = 3.7$ Hz), 124.0 (q, $J = 271.3$ Hz), 122.5 (q, $J = 3.61$ Hz), 80.1, 64.9, 36.4.

¹⁹F NMR (470 MHz, CDCl₃) δ -63.8.

IR (ATR, cm⁻¹) 2951, 2920, 2872, 2360, 1757, 1514, 1404, 1143, 1057, 1020, 985.

HRMS (APCI+) *m/z* calcd for C₁₁H₁₀O₂F₃ [M+H]⁺: 231.0627; found: 231.0626.



13q

13.1 mg, 57%.

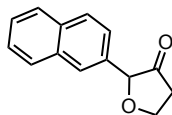
¹H NMR (400 MHz, CDCl₃) δ 7.65-7.62 (m, 2H), 7.58-7.56 (m, 2H), 4.80 (s, 1H), 4.55-4.49 (m, 1H), 4.35-4.29 (m, 1H), 2.66-2.62 (m, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 211.9, 139.4, 130.3 (q, *J* = 32.5 Hz), 126.0, 125.4 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 271.3 Hz), 80.2, 64.9, 36.4.

¹⁹F NMR (470 MHz, CDCl₃) δ -63.8.

IR (ATR, cm⁻¹) 2917, 2882, 1760, 1619, 1415, 1323, 1162, 1120, 1110, 1066, 1017.

HRMS (APCI+) *m/z* calcd for C₁₁H₁₀O₂F₃ [M+H]⁺: 231.0627; found: 231.0629.



13r

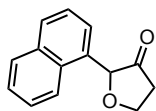
17.2 mg, 81%.

¹H NMR (400 MHz, CDCl₃) δ 7.89-7.82 (m, 4H), 7.54-7.46 (m, 3H), 4.92 (s, 1H), 4.60-4.54 (m, 1H), 4.38-4.32 (m, 1H), 2.70-2.66 (m, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 213.0, 133.2, 133.0, 128.5, 128.1, 127.8 (2C), 126.3, 126.2, 125.1, 123.7, 81.0, 64.9, 36.6.

IR (ATR, cm⁻¹) 3056, 2919, 2973, 1756, 1507, 1402, 1142, 1123, 1057.

HRMS (APCI+) *m/z* calcd for C₁₄H₁₃O₂ [M+H]⁺: 213.0910; found: 213.0905



13s

13.4 mg, 63%.

¹H NMR (400 MHz, CDCl₃) δ 8.12-8.09 (m, 1H), 7.89-7.82 (m, 2H), 7.58-7.44 (m, 4H), 5.51 (s, 1H), 4.64-4.59 (m, 1H), 4.41-4.34 (m, 1H), 2.88-4.29 (m, 1H), 2.75-2.68 (m, 1H).

¹³C NMR (125 MHz, CDCl₃) δ 212.9, 134.0, 131.7, 131.2, 129.1, 128.7, 126.4, 125.9, 125.1, 124.3, 124.2, 79.4, 64.9, 37.0.

IR (ATR, cm⁻¹) 3050, 2921, 1752, 1714, 1595, 1510, 1398, 1243, 1138, 1087.

HRMS (APCI+) *m/z* calcd for C₁₄H₁₃O₂ [M+H]⁺: 213.0910; found: 213.0909.

Part 2: References

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- 3) J. A. Malone, K. Cariou, A. J. Frontier, *J. Am. Chem. Soc.*, 2009, **131**, 7560-7561.
- 4) M. Podunavac, J. J. Lacharity, K. E. Jones, A. Zakarian, *Org. Lett.*, 2018, **20**, 4867-4870.

Part 3: ^1H , ^{13}C , and ^{19}F NMR spectra

