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Note

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Carboxylative Cyclization of 2-Butenoates with Carbon Dioxide: Access to Glutaconic Anhydrides

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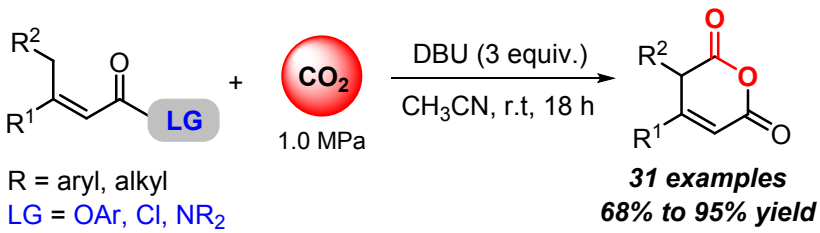
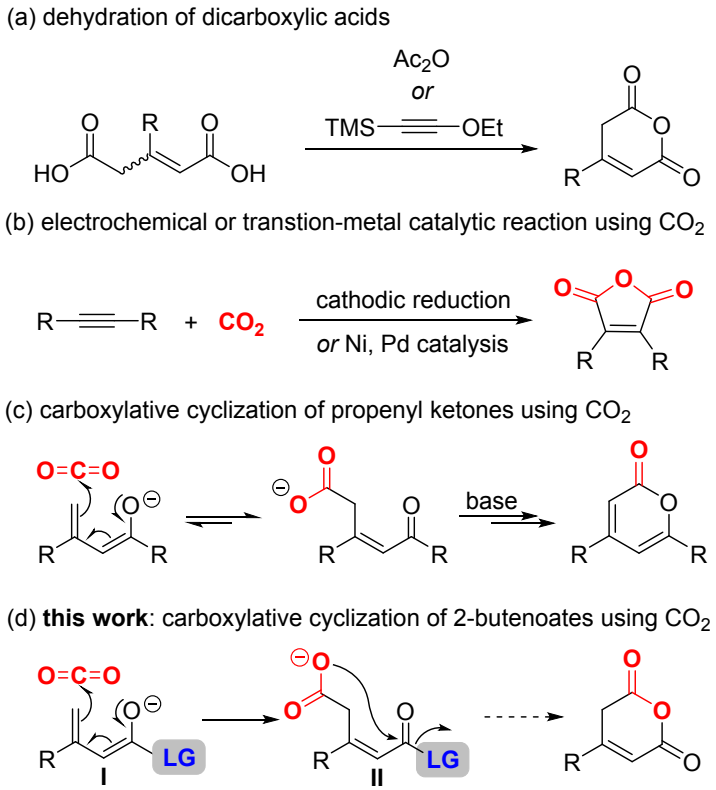


Abstract: Cyclic anhydrides are versatile synthons and functional comonomers. Herein we reported an organic base-promoted carboxylative cyclization of 2-butenoates with carbon dioxide to produce important glutaconic anhydrides in good yields. This metal-free reaction showed broad substrate scopes and proceeded under mild reaction conditions.

Cyclic anhydrides are important acylating agents in organic synthesis[1] and functional monomers for the ring-opening copolymerization with epoxides[2]. Among their diverse derivatives, glutaconic anhydrides are frequently used as formal cycloaddition partners and allenoate precursors to construct various compounds of synthetic and biological interest.[3,4] With regard to the preparation of glutaconic anhydrides, traditional approach heavily relies on the dehydration of dicarboxylic acids[4] (Scheme 1, a). Despite its reliability, this method requires the synthesis of dicarboxylic acid in advance via laborious multistep reactions using stoichiometric oxidants, strong base and other harsh reaction conditions. Therefore, it is highly desirable to develop a more convenient and efficient synthetic route toward glutaconic anhydride in terms of green chemistry.

Scheme 1. Synthesis of Cyclic Anhydrides



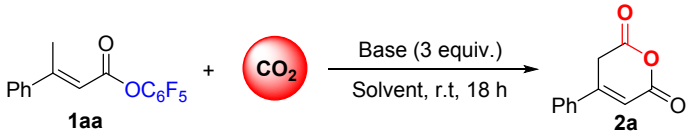
Utilization of carbon dioxide (CO_2) as a renewable C1 building block in organic synthesis has been extensively studied over the past decades.[5] Compared with the previously reported many strategies to convert CO_2 into carboxylic acids, ester, amide and other heterocyclic compounds, direct synthesis of cyclic anhydrides using CO_2 has been less explored. Maleic anhydrides can be accessed by cathodic

dicarboxylation of phenylacetylene with CO_2 using aluminum as the anode[6], or by Ni-catalyzed double carboxylation of alkynes with CO_2 using excess zinc powder as the reductant[7] (Scheme 1, b). Isatoic and other anhydrides can be synthesized by transition-metal catalyzed cyclization reactions with the combined use of CO_2 and CO under redox-neutral conditions[8]. In 2016, we developed a carboxylative cyclization reaction of propenyl ketones with CO_2,[9] in which the cyclization step proceeded via an intramolecular attack of enolate oxygen on the carboxylate group, thus only one oxygen atom of carbon dioxide was incorporated into the α-pyrone product[10] (Scheme 1, c). We envisioned that if 2-butenoates were used as substrates for the base-promoted carboxylative cyclization reaction, the γ-carboxylation of in situ formed enolate **I** with CO_2 and the followed intramolecular cyclization of intermediate **II** via the nucleophilic attack of the carboxylate oxygen would give glutaconic anhydride (Scheme 1, d). Herein, we describe the realization of the above hypothesis via an organic base-promoted metal-free reaction to construct glutaconic anhydride from carbon dioxide in excellent selectivity.

The initial exploration selected the pentafluorophenyl 3-phenyl-2-butenoate (**1aa**) as the model substrates to optimize the reaction conditions due to that pentafluorophenoxide should be a good leaving group (Table 1). When 3.0 equivalent of DBU was used as base and acetonitrile as solvent, the carboxylative cyclization reaction of **1aa** with 1.0 MPa of CO_2 proceeded successfully at the room temperature in the absence of any metal catalyst, affording the desired product 4-phenyl glutaconic anhydride (**2a**) in 90% yield (entry 1). DBN and MTBD were also found to be effective for this reaction despite that the decreased yields of **2a** were obtained (entries 2 and 3). Triethylamine, DMAP, and tested inorganic bases such as cesium carbonate, cesium fluoride or sodium hydride could not promote the reaction and no carboxylated product was observed (entries 4 to 8). THF and DMF were also suitable solvent for this reaction (entries 9 and 10), while the reaction in toluene gave the moderate yields of **2a** (entry 11). The decrease of DBU amount to 1.0 equivalent resulted in the obviously lower yield (32%) (entry 12). The combination use of 1.0 equivalent of DBU and 2.0 equivalent of Cs_2CO_3 gave the same result as the only use of 1.0 equivalent of DBU (entry 13). When DBU amount was slightly increased to 1.5 equivalent, an enhanced yield (64%) of **2a** was obtained (entry 14). This indicated that excess DBU

would be crucial for the formation of anhydride product. It's well-known that CO_2 could be activated by DBU and other strong organic bases by the formation of base–CO_2 adducts.[11] Probably, the excess DBU in this reaction would also capture and activate CO_2, and thus promote the carboxylative cyclization reaction. It is noteworthy that the reaction using CO_2 balloon still underwent efficiently although a slightly decreased yield (84%) of **2a** was obtained (entry 15).

Table 1. Optimization of the reaction conditions [a]



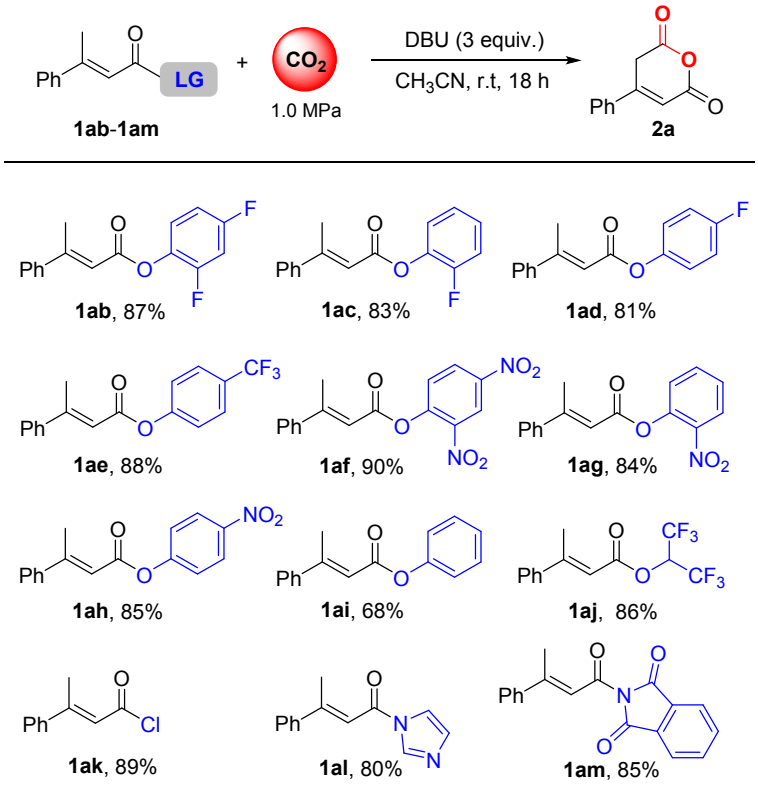
Entry	Base	Solvent	Yield (%)
1	DBU	CH_3CN	90
2	DBN	CH_3CN	77
3	MTBD	CH_3CN	60
4	NEt_3	CH_3CN	<1
5	DMAP	CH_3CN	<1
6	Cs_2CO_3	CH_3CN	<1
7	CsF	CH_3CN	<1
8	NaH	CH_3CN	<1
9	DBU	THF	78
10	DBU	DMF	80
11	DBU	Toluene	55
12[b]	DBU	CH_3CN	32
13[c]	DBU	CH_3CN	32
14[d]	DBU	CH_3CN	64
15[e]	DBU	CH_3CN	84

[a] Reaction conditions: **1aa** (0.1 mmol), CO_2 (1.0 MPa), base (0.3 mmol), solvent (2 mL), r.t, 18 h. [b] 0.1 mmol DBU was used. [c] 0.1 mmol DBU and 0.2 mmol Cs_2CO_3 were used. [d] 0.15 mmol DBU was used. [e] CO_2 balloon was used. DBU: 1,8-diazabicyclo [5.4.0]undec-7-ene. DBN: 1,5-diazabicyclo[4.3.0]non-ene. MTBD: 7-metyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene. DMAP: 4- dimethylaminopyridine.

Since the leaving group played a vital role in the formation of cyclic anhydride products, the carboxylative cyclization of various 2-butenoates bearing different leaving groups were then tested (Scheme 2). 2,4-Difluorophenyl (**1ab**), 4-trifluoromethylphenyl (**1ae**), 2,4-dinitrophenyl (**1af**) and hexafluoroisopropanyl (**1aj**) esters participated in the carboxylative cyclization reaction smoothly and

gave 86-90% yields comparable to pentafluorophenyl ester substrate **1aa**. Mono fluorophenoxide (**1ac**, **1ad**) and mononitrophenyloxide (**1ag** and **1ah**) were found to be good leaving groups, while the unsubstituted phenoxide proved to be less effective and only 68% yield of **2a** was obtained when phenyl 3-phenyl-2-butenoate (**1ai**) was used. Another advantage for the use of those electron-deficient leaving groups is to suppress the alcoholysis of the anhydride product to generate hemiesters by-product. 2-Butenoyl chloride (**1ak**), imidazole (**1al**) and phthalimide (**1am**) were also verified as suitable substrates for this reaction. Considering the easy availability of pentafluorophenyl esters, and facile recovery of pentafluorophenol after the reaction, our explorations still selected pentafluorophenyl 2-butenoate as the substrates.

Scheme 2. Carboxylative Cyclization of Various 2-Butenoates with Carbon Dioxide [a]

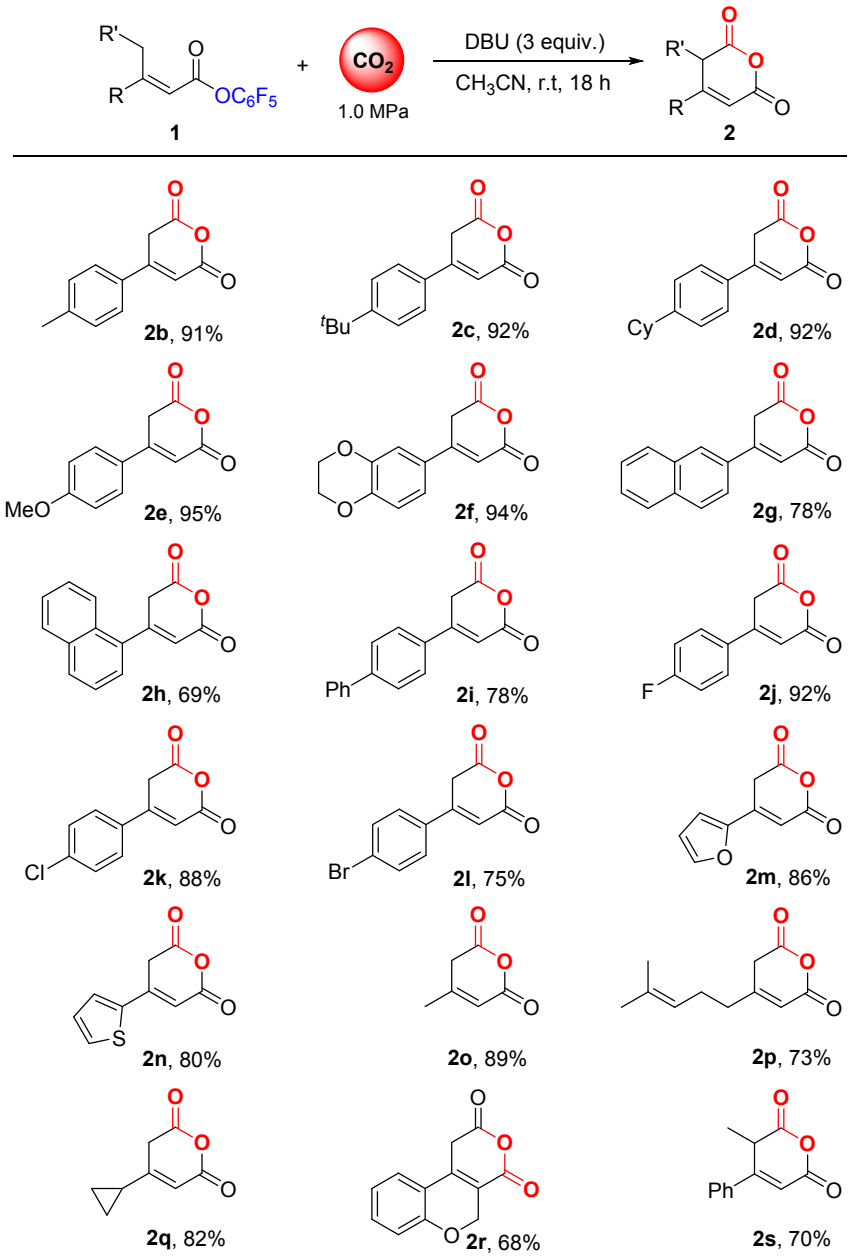


[a] Reaction conditions: **1a** (0.1 mmol), CO_2 (1.0 MPa), DBU (0.3 mmol), CH_3CN (2 mL), r.t, 18 h.

With the optimized reaction conditions in hands, we next investigated the substrate scopes with regard to pentafluorophenyl 2-butenoate using 3.0 equivalent of DBU as base at room temperature in acetonitrile (Scheme 3). 3-Aryl-2-butenoate (**1**) containing various functional groups such as electron-donating alkyl and alkoxy substituents, electron-withdrawing fluoride, chloride, and bromide substituents all conducted

the reaction smoothly to produce the corresponding cyclization products **2b**−**2l** in good yields. The structures of cyclic anhydride products **2b** and **2e** were further confirmed by X-ray crystallography (See SI).[12] 4-Furanyl glutaconic anhydride (**2m**) and 4-thiophenyl glutaconic anhydride (**2n**) could be synthesized by this reaction in 86% and 80% yields respectively. 3-Alkyl-2-butenoate gave the desired products **2o**−**2p** in satisfactory yields and cyclopropanyl group was tolerated (**2q**). Besides the mono-substituted products, 3,4-disubstituted glutaconic anhydrides **2r** and **2s** were obtained in good yields.

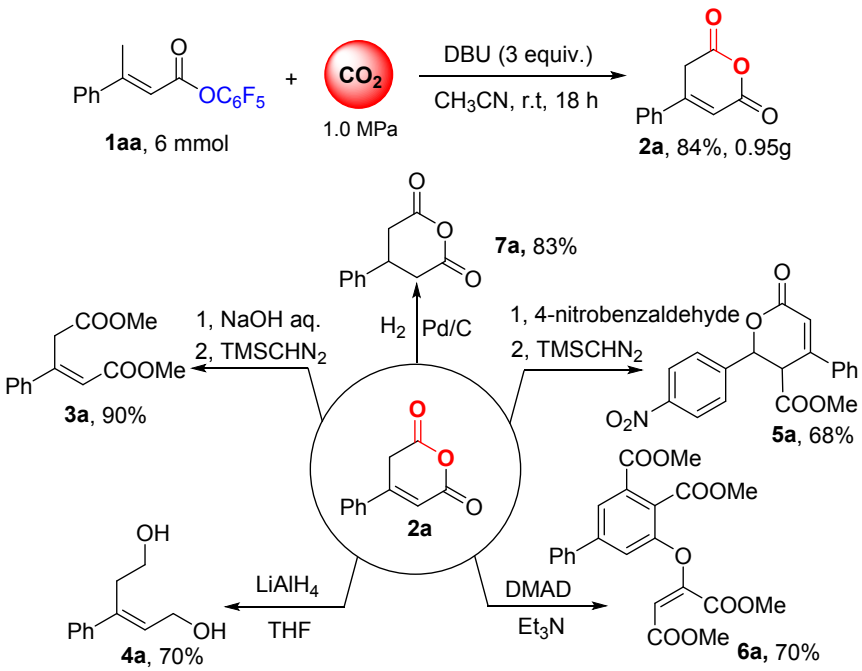
Scheme 3. Carboxylative Cyclization of Various 2-Butenoates with Carbon Dioxide [a]



[a] Reaction conditions: **1** (0.1 mmol), CO_2 (1.0 MPa), DBU (0.3 mmol), CH_3CN (2 mL), r.t, 18 h.

The synthetic utility of this carboxylative cyclization reaction was firstly demonstrated through the gram-scale synthesis of **2a** in 84% yield (Scheme 4, up). Then the obtained cyclic anhydride **2a** was employed as a versatile intermediate to easily transform into other important compounds by simple organic reactions (Scheme 4, down). The hydrolytic reaction of **2a** under basic conditions generated glutaconate **3a** in 90% yield. The reduction of **2a** with lithium aluminum hydride furnished 3-phenyl-2-pentene-1,5-diol **4a** in 70% yield. DMAP promoted cycloaddition of **2a** and 4-nitrobenzaldehyde gave 3, 6-dihydro-6-oxo-2*H*-pyran-3-carboxylate **5a** in moderated yield,[13] while the reaction of **2a** with excess dimethyl acetylenedicarboxylate resulted in an unexpected compound **6a**, which might formed by a cycloaddition-nucleophilic addition reaction sequence. The structure of product **6a** was determined by X-ray crystallography.[12] The hydrogenation of **2a** with H_2 using Pd/C as catalyst readily gave 3-phenylglutaric anhydride **7a** in good yield.

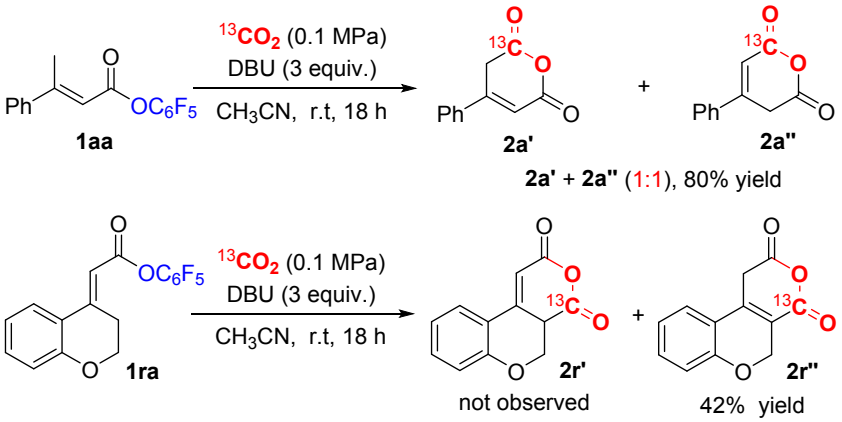
Scheme 4. Gram-Scale Reaction and Synthetic Applications



To illustrate which carbonyl group in the anhydride product come from CO_2, the isotopic labelling reaction was carried out (Scheme 5). According to the $^{13}C\{^1H\}$ NMR spectroscopy (See SI), the reaction of **1aa** with $^{13}CO_2$ gave **2a'** and **2a''** in 1:1 ratio, probably due to the rapid 1,3-hydrogen shift of in the

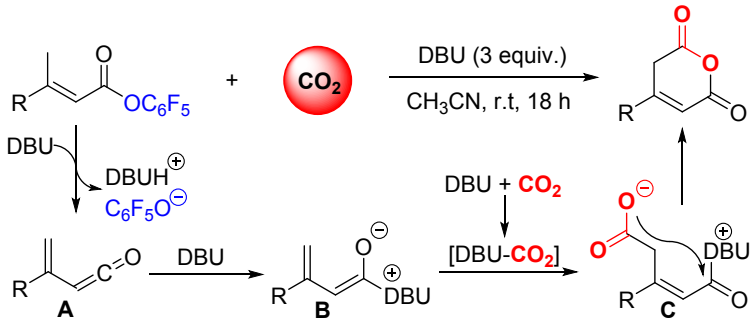
presence of a base. For the reaction of **1ra** with $^{13}CO_2$, the more stable isomer **2r''** was obtained according to the $^{13}C\{^1H\}$ NMR and ^1H-$^{13}C\{^1H\}$ gHMBC spectroscopy (See SI), while **2r'** was not observed.

Scheme 5. Isotopic Labelling Reaction



Based on the control experiments in Table 1, the above labelling experiments and previous reports,[9,10] a possible mechanism for this carboxylative cyclization reaction was proposed (Scheme 6). The reaction of pentafluorophenyl 2-butenoate with DBU would firstly form the substituted vinylketene **A**,[14,15] which continued to react with another DBU to generate zwitterionic dienolate **B**.[14,15] Meanwhile, CO_2 would be activated by the formation of DBU-CO_2 adduct. Then intermediate **B** would conduct γ-carboxylation with DBU-CO_2 to give glutaconate **C**, in which the intramolecular attack of carboxylate group to the carbonyl next to DBU would finally yield the anhydride product.

Scheme 6. Possible Mechanism



In conclusions, we have developed a straightforward access to synthetically important glutaconic anhydrides via an organic base-promoted carboxylative cyclization of 2-butenoate with carbon dioxide. A variety of 2-butenoates bearing electro-deficient leaving groups such as fluorophenoxide, trifluoromethylphenoxide, and nitrophenoxide underwent this reaction smoothly and gave anhydride

products in good yields. This metel-free reaction showed broad substrate scopes and proceeded under very mild reaction conditions.

EXPERIMENTAL SECTION

Unless otherwise stated, all manipulations were performed using standard Schlenk techniques under a dry nitrogen or carbon dioxide atmosphere. CH_3CN was distilled with P_2O_5. THF and toluene were distilled from sodium/benzophenone. All of the solvents were stored over 4A molecular sieves before used. NMR spectra were recorded on 400M or 500M (^{1}H NMR, 400 MHz or 500MHz; ^{13}C NMR, 101 MHz or 126MHz) spectrometer in $CDCl_3$ or DMSO at ambient temperature and chemical shifts are expressed in parts per million (δ, ppm). Proton chemical shifts are referenced to 7.26 ppm ($CHCl_3$) or 2.50 ppm (DMSO) and carbon chemicalshifts are referenced to 77.0 ppm ($CHCl_3$) or 39.5 ppm (DMSO). High resolution mass spectra (HRMS) were recorded on a Q-TOF mass spectrometry equipped with Z-spray ionization source. Infrared spectra (IR) were measured using a Nicolet NEXUS FT-IR spectrophotometer. Carbon dioxide (99.999%), and other commercially available chemicals were used without further purification.

General Procedure for the Preparation of 2-Butenoate Substrate. Except 3-phenyl-2-butenoyl chloride (**1ak**),[14a] 3-phenyl-2-butenoylimidazole (**1al**),[16] 3-phenyl-2-butenoyl phthalimide (**1am**)[17] were prepared according to the literature procedure, Other 2-butenoate substrates were prepared using the following procedure.[18]

A mixture of carboxylic acid (5 mmol), pentafluorophenol or phenol derivatives (6 mmol), DMAP (61.0 mg, 0.5 mmol), and EDCI (1.1 g, 5.5 mmol) in THF (20 mL) was stirred overnight at room temperature. The mixture was diluted cautiously with saturated $NaHCO_3$, and then extracted with EtOAc (3 x 30 mL). The combined organic phase was washed with brine (100 mL). After drying over Na_2SO_4 and filtration, the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (hexanes /ethyl acetate) to afford the desired ester products.

*Perfluorophenyl (E)-3-phenylbut-2-enoate (**1aa**)*. white solid, 1.31 g, 80% yield, R_f = 0.50 (petroleum ether/EtOAc 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.54 (m, 2H), 7.47–7.42 (m, 2H), 6.45–6.42 (m, 1H), 2.68–2.66 (m, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 162.4, 161.9, 141.4 (dm, J = 252.5 Hz), 141.2, 139.3 (dm, J = 252.9 Hz), 137.9 (dm, J = 252.5 Hz), 130.0, 128.7, 126.5, 125.2 (m),113.0, 18.6. ^{19}F NMR (470 MHz, $CDCl_3$) δ -152.53 – -153.60 (m), -158.70 (t, J = 21.7 Hz), -162.73 – -162.84 (m). IR (neat cm^{-1}) ν 2929, 2855, 1759, 1620, 1518, 1005, 896. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{16}H_9F_5O_2$ 328.0523; Found 328.0515.

*2,4-Difluorophenyl (E)-3-phenyl but-2-enoate (**1ab**)*. white solid, 0.86 g, 63% yield, R_f = 0.50 (petroleum ether/EtOAc 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.54 (m, 1H), 7.43–7.41 (m, 4H), 7.19–7.13 (m, 2H), 6.98–6.87 (m, 1H), 6.39 (s, 1H), 2.64 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 163.9, 160.0 (dd, J = 196.9, 10.5 Hz), 159.9, 154.3 (dd, J = 251.8, 12.5 Hz), 141.7, 134.5 (dd, J = 12.9, 4.0 Hz), 129.6, 128.6, 126.4, 124.5 (dd, J = 9.9, 2.0 Hz), 114.7, 111.1 (dd, J = 23.0, 3.8 Hz), 105.0 (dd, J = 26.9, 22.5 Hz), 18.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -113.05 – -113.08 (m), -123.25 – -123.28 (m). IR (neat cm^{-1}) ν 2912, 2852, 1743, 1624, 1119, 850. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{16}H_{12}F_2O_2$ 274.0805; Found 274.0807.

*2-Fluorophenyl (E)-3-phenyl but-2-enoate (**1ac**)*. white solid, 0.67 g, 52% yield, R_f = 0.55 (petroleum ether/EtOAc 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.55 (m, 2H), 7.43–7.41 (m, 3H), 7.23–7.16 (m, 4H), 6.41 (d, J = 1.2 Hz, 1H), 2.64 (d, J = 4.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 163.9, 159.4, 154.3 (d, J = 249.0 Hz), 141.7, 138.1 (d, J = 12.7 Hz), 129.5, 128.6, 126.8 (d, J = 7.2 Hz), 126.4, 124.4 (d, J = 3.8 Hz), 124.0, 116.6 (d, J = 18.4 Hz), 115.0, 18.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -128.20 (dd, J = 14.0, 7.5 Hz). IR (neat cm^{-1}) ν 2954, 2925, 2843, 1744, 1625, 1102, 996, 764. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{16}H_{13}FO_2$ 256.0900; Found 256.0897.

*4-Fluorophenyl (E)-3-phenyl but-2-enoate (**1ad**)*. white solid, 0.77 g, 60% yield, R_f = 0.55 (petroleum ether/EtOAc 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.54 (m, 2H), 7.43–7.41 (m, 3H), 7.14–7.06 (m, 4H), 6.36 (d, J = 1.1 Hz, 1H), 2.65 (d, J = 1.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 165.0, 161.3, 158.9, 146.5 (d, J = 2.8 Hz), 141.8, 129.5, 128.6, 126.4, 123.1 (d, J = 8.4 Hz), 116.1, 115.8 (d, J = 13.9

Hz), 18.2. ^{19}F NMR (470 MHz, $CDCl_3$) δ -117.35 (dd, J = 9.9, 5.6 Hz). IR (neat cm^{-1}) ν 2949, 2925, 1732, 1625, 999, 868. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{16}H_{13}FO_2$ 256.0900; Found 256.0891.

*4-Trifluoromethylphenyl (E)-3-phenylbut-2-enoate (**1ae**)*. white solid, 1.06 g, 69% yield, R_f = 0.50 (petroleum ether/EtOAc 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.5 Hz, 2H), 7.57–7.54 (m, 2H), 7.43–7.42 (m, 3H), 7.29 (d, J = 8.5 Hz, 1H)., 6.38 (d, J = 1.2 Hz, 1H), 2.65 (d, J = 1.2 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.4, 159.8, 153.3, 141.7, 129.6, 128.7, 127.8 (q, J = 32.8 Hz), 126.7 (q, J = 3.7 Hz), 126.4, 124.0 (q, J = 284.0 Hz), 122.3, 115.4, 18.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.18 (s). IR (neat cm^{-1}) ν 2954, 2913, 1737, 1626, 999, 865. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{17}H_{13}F_3O_2$ 306.0868; Found 306.0869.

*2,4-Dinitrophenyl (E)-3-phenylbut-2-enoate (**1af**)*. white solid, 1.23 g, 75% yield, R_f = 0.30 (petroleum ether/EtOAc 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, J = 2.6 Hz, 1H), 8.53 (dd, J = 8.9, 2.7 Hz, 1H), 7.59–7.54 (m, 3H), 7.45-7.43 (m, 3H), 6.42 (d, J = 1.0 Hz, 1H), 2.62 (d, J = 0.9 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.8, 162.6, 148.8, 144.8, 142.1, 141.1, 132.0, 130.1, 128.8, 126.7, 126.5, 121.5, 113.6, 18.6. IR (neat cm^{-1}) ν 1747, 1605, 1537, 1098, 986. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{16}H_{12}N_2O_6$ 328.0695; Found 328.0704.

*2-Nitrophenyl (E)-3-phenylbut-2-enoate (**1ag**)*. white solid, 0.99 g, 70% yield, R_f = 0.35 (petroleum ether/EtOAc 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, J = 8.2, 1.6 Hz, 1H), 7.69–7.65 (m, 1H), 7.58–7.56 (m, 2H), 7.44–7.38 (m, 4H), 7.31 (dd, J = 8.1, 1.2 Hz, 1H), 6.43 (d, J = 1.3 Hz, 1H), 2.64 (d, J = 1.2 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.8, 160.5, 144.1, 142.2, 141.4, 134.5, 129.7, 128.6, 126.4, 126.3, 125.6, 125.3, 114.7, 18.3. IR (neat cm^{-1}) ν 1744, 1625, 1529, 1349, 1113, 993. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{13}NNaO_4$ 306.0742; Found 306.0755.

*4-Nitrophenyl (E)-3-phenylbut-2-enoate (**1ah**)*. white solid, 1.10 g, 78% yield, R_f = 0.40 (petroleum ether/EtOAc 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32–8.28 (m, 2H), 7.57–7.54 (m, 2H), 7.44–7.43 (m, 3H), 7.37–7.33 (m, 2H), 6.37 (d, J = 1.3 Hz, 1H), 2.66 (d, J = 1.2 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.8, 160.6, 155.6, 145.1, 141.5, 129.8, 128.7, 126.4, 125.1, 122.5, 114.9, 18.4. IR (neat cm^{-1})

v 2974, 2913, 2847, 1736, 1614, 1525, 997, 856. HRMS (ESI-TOF) *m*/*z*: $[M+Na]^+$ Calcd for $C_{16}H_{13}NNaO_4$ 306.0742; Found 306.0751.

*Phenyl (E)-3-phenylbut-2-enoate (**1ai**)*. white solid, 0.67 g, 56% yield, R_f = 0.50 (petroleum ether/EtOAc 50:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.62–7.60 (m, 2H), 7.49–7.45 (m, 5H), 7.32–7.29 (m, 1H), 7.25–7.22 (m, 2H), 6.46 (dd, *J* = 2.5, 1.2 Hz, 1H), 2.72 (d, *J* = 1.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 165.0, 158.5, 150.7, 141.9, 129.4, 129.3, 128.6, 126.4, 125.6, 121.7, 116.0, 18.2. IR (neat cm^{-1}) *v* 2933, 1729, 1626, 1592, 994. HRMS (ESI-TOF) *m*/*z*: $[M+Na]^+$ Calcd for $C_{16}H_{14}NaO_2$ 261.0891; Found 261.0899.

*1,1,1,3,3,3-Hexafluoropropan-2-yl (E)-3-phenylbut-2-enoate (**1aj**)*. white solid, 1.30 g, 83% yield, R_f = 0.40 (petroleum ether/EtOAc 50:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.55–7.52 (m, 2H), 7.43–7.40 (m, 3H), 6.26 (d, *J* = 0.9 Hz, 1H), 5.92–5.86 (m, 1H), 2.65 (d, *J* = 0.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.6, 162.3, 141.2, 130.0, 128.7, 126.5, 120.7 (q, *J* = 284.7 Hz), 113.1, 66.0 (dt, *J* = 69.1, 34.5 Hz), 18.6. ^{19}F NMR (470 MHz, $CDCl_3$) δ -73.29 (d, *J* = 6.2 Hz). IR (neat cm^{-1}) *v* 2962, 1743, 1624, 1112, 926, 905, 765. HRMS (EI-TOF) *m*/*z*: $[M]^+$ Calcd for $C_{13}H_{10}F_6O_2$ 312.0585; Found 312.0579.

*(E)-2-(3-phenylbut-2-enoyl)isoindoline-1,3-dione (**1am**)*. white solid, 0.67g, 68% yield, R_f = 0.30 (petroleum ether/EtOAc 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.01–7.99 (m, 2H), 7.80–7.78 (m, 2H), 7.64–7.62 (m, 2H), 7.45–7.43 (m, 3H), 6.96–6.94 (m, 1H), 2.70 (d, *J* = 1.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6) δ 169.6, 165.9, 163.3, 157.4, 141.4, 135.8, 134.6, 132.7, 131.3, 130.2, 129.0, 126.7, 124.2, 123.2, 120.0, 18.4. IR (neat cm^{-1}) *v* 2910, 2860, 1734, 1689, 1281, 1052, 712. HRMS (ESI-TOF) *m*/*z*: $[M+Na]^+$ Calcd for $C_{18}H_{13}NNaO_3$ 314.0793; Found 314.0803.

*Perfluorophenyl (E)-3-(p-tolyl)but-2-enoate (**1ba**)*. white solid, 1.28 g, 75% yield, R_f = 0.50 (petroleum ether/EtOAc 50:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 6.44 (s, 1H), 2.67 (s, 3H), 2.43 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.3, 162.1, 141.5 (dm, *J* = 253.4 Hz), 140.5, 138.2, 139.4, 139.1 (dm, *J* = 252.0 Hz), 137.9 (dm, *J* = 253.4 Hz), 126.4, 125.3 (m), 112.0, 21.2, 18.4. ^{19}F NMR (470 MHz, $CDCl_3$) δ -152.58 – -152.64 (m), -158.88 (t, *J* = 21.6 Hz), -162.84 – -

162.95 (m). IR (neat cm^{-1}) *v* 2962, 2929, 2864, 1756, 1619, 1517, 1098, 896. HRMS (EI-TOF) *m*/*z*: $[M]^+$ Calcd for $C_{17}H_{11}F_5O_2$ 342.0679; Found 342.0675.

*Perfluorophenyl (E)-3-(4-(tert-butyl)phenyl)but-2-enoate (**1ca**)*. white solid, 1.50 g, 78% yield, R_f = 0.50 (petroleum ether/EtOAc 50:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 8.1 Hz, 2H), 6.43 (d, J = 1.1 Hz, 1H), 2.66 (d, J = 1.1 Hz, 3H), 1.36 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 162.2, 162.1, 153.7, 141.5 (dm, J = 252.8 Hz), 139.3 (dm, J = 252.7 Hz), 138.1, 137.9 (dm, J = 252.8 Hz), 126.3, 125.7, 125.3 (m), 112.1, 34.8, 31.2, 18.4. ^{19}F NMR (470 MHz, $CDCl_3$) δ -152.52 – -152.58 (m), -158.82 (t, J = 21.7 Hz), -162.79 – -162.90 (m). IR (neat cm^{-1}) *v* 2966, 2872, 1757, 1619, 1007, 832. HRMS (EI-TOF) *m*/*z*: $[M]^+$ Calcd for $C_{20}H_{17}F_5O_2$ 384.1149; Found 384.1157.

*Perfluorophenyl (E)-3-(4-cyclohexylphenyl)but-2-enoate (**1da**)*. white solid, 1.33 g, 65% yield, R_f = 0.50 (petroleum ether/EtOAc 50:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.3 Hz, 2H), 6.42 (d, J = 1.0 Hz, 1H), 2.65 (d, J = 1.0 Hz, 3H). 2.56 (t, J = 8.1 Hz, 1H), 1.92–1.77 (m, 5H), 1.51–1.27 (m, 5H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 162.4, 162.1, 150.6, 141.4 (dm, J = 251.7 Hz), 139.3 (dm, J = 252.4 Hz), 138.5, 137.9 (dm, J = 251.7 Hz), 127.2, 126.5, 125.3 (m), 112.0, 44.4, 34.3, 26.8, 26.1, 18.4. ^{19}F NMR (470 MHz, $CDCl_3$) δ -152.55 (d, J = 17.8 Hz), -158.83 (t, J = 21.6 Hz), -162.80 – -162.89 (m). IR (neat cm^{-1}) *v* 2928, 2853, 1759, 1618, 1606, 1518, 1100, 896. HRMS (EI-TOF) *m*/*z*: $[M\text{-}C_6F_5O]^+$ Calcd for $C_{16}H_{19}O$ 227.1430; Found 227.1437.

*Perfluorophenyl (E)-3-(4-methoxyphenyl) but-2-enoate (**1ea**)*. white solid, 1.52 g, 85% yield, R_f = 0.40 (petroleum ether/EtOAc 50:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.58–7.54 (m, 2H), 6.97–6.93 (m, 2H), 6.40 (d, J = 1.2 Hz, 1H), 3.87 (s, 3H), 2.65 (d, J = 1.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 162.2, 161.4, 141.5 (dm, J = 252.4 Hz), 139.2 (dm, J = 252.5 Hz), 137.9 (dm, J = 252.4 Hz), 133.2, 128.1, 125.4 (m), 114.1, 110.8, 55.4, 18.2. ^{19}F NMR (470 MHz, $CDCl_3$) δ -152.60 – -152.68 (m), -158.95 (t, J = 21.6 Hz), -162.88 – -162.98 (m). IR (neat cm^{-1}) *v* 2937, 2831, 1754, 1600, 1518, 1098, 896. HRMS (EI-TOF) *m*/*z*: $[M]^+$ Calcd for $C_{17}H_{11}F_5O_3$ 358.0628; Found 358.0648.

*Perfluorophenyl (E)-3-(2,3-dihydrobenzo[b] [1,4] dioxin-6-yl) but-2-enoate (**1fa**)*. white solid, 1.58 g, 82% yield, R_f = 0.35 (petroleum ether/EtOAc 50:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.12–7.10 (m, 2H),

6.91–6.89 (m, 1H), 6.37 (d, J = 1.2 Hz, 1H), 4.32–4.28 (m, 4H), 2.60 (d, J = 1.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.1, 161.5, 145.5, 143.5, 141.4 (dm, J = 253.8 Hz), 139.2 (dm, J = 252.5 Hz), 137.9 (dm, J = 253.9 Hz), 134.2, 125.3 (m), 120.0, 117.4, 115.7, 111.3, 64.6, 64.3, 18.2. ^{19}F NMR (470 MHz, $CDCl_3$) δ -152.56 – -152.62 (m), -158.91 (t, J = 21.7 Hz), -162.85 – -162.96 (m). IR (neat cm^{-1}) v 2978, 2933, 2880, 1751, 1604, 1578, 1007, 891. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{18}H_{11}F_5O_4$ 386.0577; Found 386.0574.

*Perfluorophenyl (E)-3-(naphthalen-2-yl) but-2-enoate (**1ga**)*. white solid, 1.23 g, 65% yield, R_f = 0.45 (petroleum ether/EtOAc 50:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.93–7.86 (m, 3H), 7.68 (d, J = 8.6 Hz, 1H), 7.57–7.54 (m, 2H), 6.58 (s, 1H), 2.77 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 164.4, 161.6, 141.4 (dm, J = 251.1 Hz), 141.1, 139.3 (dm, J = 252.3 Hz), 137.9 (dm, J = 252.8 Hz), 133.8, 129.7, 128.9, 128.6, 126.7, 126.2, 125.3 (m), 125.2, 125.0, 124.3, 116.8, 22.4. ^{19}F NMR (470 MHz, $CDCl_3$) δ -152.50 – -152.56 (m), -158.49 (t, J = 21.7 Hz), -162.60 – -162.69 (m). IR (neat cm^{-1}) v 2966, 2925, 1761, 1630, 1519, 1130, 1003, 899. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{20}H_{11}F_5O_2$ 378.0679; Found 378.0690.

*Perfluorophenyl (E)-3-(naphthalen-1-yl) but-2-enoate (**1ha**)*. white solid, 1.66 g, 88% yield, R_f = 0.40 (petroleum ether/EtOAc 50:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.94–7.89 (m, 2H), 7.87 (s, 1H), 7.59–7.52 (m, 2H), 7.52–7.49 (m, 1H), 7.38 (d, J = 7.0 Hz, 1H), 6.32 (d, J = 1.3 Hz, 1H), 2.74 (d, J = 1.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.1, 162.0, 141.4 (dm, J = 250.9 Hz), 139.3 (dm, J = 252.6 Hz), 138.2, 137.9 (dm, J = 253.7 Hz), 134.0, 133.0, 128.7, 127.6, 127.3, 126.7, 126.6, 125.2 (m), 123.6, 113.2, 18.5. ^{19}F NMR (470 MHz, $CDCl_3$) δ -152.38 – -152.44 (m), -158.68 (t, J = 21.6 Hz), -162.70 – -162.80 (m). IR (neat cm^{-1}) v 2921, 1748, 1613, 1517, 1098, 990, 894. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{20}H_{11}F_5O_2$ 378.0679; Found 378.0669.

*Perfluorophenyl (E)-3-([1,1'-biphenyl]-4-yl) but-2-enoate (**1ia**)*. white solid, 1.66 g, 82% yield, R_f = 0.40 (petroleum ether/EtOAc 50:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.68–7.65 (m, 6H), 7.52–7.48 (m, 2H), 7.44–7.40 (m, 1H), 6.51 (d, J = 1.0 Hz, 1H), 2.71 (d, J = 0.9 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 161.7, 143.0, 141.4 (dm, J = 250.7 Hz), 140.0, 139.8, 139.3 (dm, J = 252.8 Hz), 137.9 (dm, J = 253.5

Hz), 128.9, 127.9, 127.3, 127.1, 127.0, 125.3 (m), 112.7, 18.4. ^{19}F NMR (470 MHz, $CDCl_3$) δ -152.50 – -152.56 (m), -158.68 (t, J = 21.6 Hz), -162.70 – -162.80 (m). IR (neat cm^{-1}) ν 2917, 2880, 1753, 1603, 1518, 1031, 1002, 898. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{22}H_{13}F_5O_2$ 404.0836; Found 404.0844.

*Perfluorophenyl (E)-3-(4-fluorophenyl) but-2-enoate (**1ja**)*. white solid, 1.35 g, 78% yield, R_f = 0.50 (petroleum ether/EtOAc 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.55 (m, 2H), 7.14–7.10 (m, 2H), 6.38 (s, 1H), 2.64 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 163.9 (d, J = 251.0 Hz), 161.8, 161.0, 141.4 (dm, J = 251.1 Hz), 139.3 (dm, J = 252.7 Hz), 137.9 (dm, J = 253.5 Hz), 137.2 (d, J = 3.3 Hz), 128.5 (d, J = 8.5 Hz), 125.2 (m), 115.8 (d, J = 21.7 Hz), 112.9, 18.5. ^{19}F NMR (470 MHz, $CDCl_3$) δ -110.55 (s), -152.60 – -152.67 (m), -158.58 – -158.68 (m), -162.70 – -162.82 (m). IR (neat cm^{-1}) ν 2958, 2929, 2851, 1759, 1624, 1518, 1025, 1009, 834. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{16}H_8F_6O_2$ 346.0428; Found 346.0419.

*Perfluorophenyl (E)-3-(4-chlorophenyl) but-2-enoate (**1ka**)*. white solid, 1.51 g, 83% yield, R_f = 0.45 (petroleum ether/EtOAc 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H), 6.40 (s, 1H), 2.63 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 161.7, 160.8, 141.4 (dm, J = 251.1 Hz), 139.5, 139.3 (dm, J = 252.8 Hz), 137.9 (dm, J = 252.8 Hz), 136.2, 129.0, 127.8, 125.2 (m), 113.4, 18.4. ^{19}F NMR (470 MHz, $CDCl_3$) δ -152.53 – -152.59 (m), -158.50 (t, J = 21.6 Hz), -162.61 – -162.73 (m). IR (neat cm^{-1}) ν 2958, 2913, 2847, 1758, 1622, 1520, 1025, 894. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{16}H_8ClF_5O_2$ 362.0133; Found 362.0128.

*Perfluorophenyl (E)-3-(4-bromophenyl) but-2-enoate (**1la**)*. white solid, 1.42 g, 70% yield, R_f = 0.45 (petroleum ether/EtOAc 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.54 (m, 2H), 7.45–7.41 (m, 2H), 6.41 (d, J = 1.3 Hz, 1H), 2.63 (d, J = 1.3 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 161.7, 160.8, 141.4 (dm, J = 251.6 Hz), 140.0, 139.4 (dm, J = 253.2 Hz), 137.9 (dm, J = 253.5 Hz), 132.0, 128.0, 124.5, 125.1 (m), 113.4, 18.4. ^{19}F NMR (470 MHz, $CDCl_3$) δ -152.52 – -152.57 (m), -158.46 (t, J = 21.6 Hz), -162.59 – -162.68 (m). IR (neat cm^{-1}) ν 2962, 2917, 2843, 1757, 1621, 1518, 1025, 902. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{16}H_8BrF_5O_2$ 405.9628; Found 405.9625.

*Perfluorophenyl (E)-3-(furan-2-yl) but-2-enoate (**1ma**)*. white solid, 1.18 g, 74% yield, R_f = 0.40 (petroleum ether/EtOAc 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 1.5 Hz, 1H), 6.83 (d, J = 3.5 Hz, 1H), 6.63 (d, J = 1.0 Hz, 1H), 6.53 (dd, J = 3.5, 1.8 Hz, 1H), 2.52 (d, J = 1.1 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 162.4, 153.7, 147.7, 145.1, δ 141.5 (dm, J = 251.0 Hz), 139.3 (dm, J = 252.5 Hz), 137.9 (dm, J = 253.2 Hz), 125.3 (m), 113.6, 112.5, 108.1, 15.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -152.59 – -152.64 (m), -158.93 (t, J = 21.6 Hz), -162.89 – -162.99 (m). IR (neat cm^{-1}) v 1752, 1615, 1519, 1022, 1006, 890. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{14}H_7F_5O_3$ 318.0315; Found 318.0322.

*Perfluorophenyl (E)-3-(thiophen-2-yl) but-2-enoate (**1na**)*. white solid, 1.47 g, 88% yield, R_f = 0.40 (petroleum ether/EtOAc 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.45 (m, 2H), 7.13–7.11 (m, 1H), 6.51 (d, J = 0.9 Hz, 1H), 2.68 (d, J = 1.0 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.0, 154.0, 144.5, 141.4 (dm, J = 250.9 Hz), 139.3 (dm, J = 252.8 Hz), 137.9 (dm, J = 253.9 Hz), 128.9, 128.4, 128.31, 125.2 (m), 109.7, 17.9. ^{19}F NMR (470 MHz, $CDCl_3$) δ -152.54 – -152.60 (m), -158.76 (t, J = 21.6 Hz), -162.77 – -162.88 (m). IR (neat cm^{-1}) v 2929, 2847, 1754, 1606, 1518, 1003, 947. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{14}H_7F_5O_2S$ 334.0087; Found 334.0084.

*Perfluorophenyl 3-methyl but-2-enoate (**1oa**)*. colorless oil, 0.89 g, 67% yield, R_f = 0.30 (petroleum ether/EtOAc 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.98 (s, 1H), 2.25 (d, J = 1.1 Hz, 3H), 2.04 (d, J = 1.2 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.3, 161.6, 141.4 (dm, J = 250.8 Hz), 139.2 (dm, J = 252.3 Hz), 137.9 (dm, J = 253.8 Hz), 125.3 (m), 112.7, 27.7, 20.8. ^{19}F NMR (470 MHz, $CDCl_3$) δ -152.86 – -153.90 (m), -159.15 (t, J = 21.6 Hz), -163.07 – -163.18 (m). IR (neat cm^{-1}) v 2986, 2921, 1763, 1644, 1519, 1001, 909. HRMS (EI-TOF) m/z: $[M-C_6F_5O]^+$ Calcd for C_5H_7O 83.0491; Found 83.0491.

*Perfluorophenyl (E)-3,7-dimethylocta-2,6-dienoate (**1pa**)*. colorless oil, 1.39 g, 83% yield, R_f = 0.30 (petroleum ether/EtOAc 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.96 (s, 1H), 5.14–5.09 (m, 1H), 2.31–2.17 (m, 7H), 1.72–1.68 (m, 3H), 1.64–1.61 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.7, 161.8, 141.4 (dm, J = 250.8 Hz), 139.2 (dm, J = 252.6 Hz), 137.9 (dm, J = 253.8 Hz), 133.1, 125.3 (m), 122.4, 112.1, 41.3, 26.0, 19.6, 17.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ -152.74 – -153.80 (m), -159.03 (t, J = 22.3

Hz), -162.96 – -163.07 (m). IR (neat cm^{-1}) *v* 2978, 2917, 2855, 1762, 1634, 1519, 1099, 1003, 902. HRMS (EI-TOF) *m*/*z*: $[M]^+$ Calcd for $C_{16}H_{15}F_5O_2$ 334.0992; Found 334.0981.

*Perfluorophenyl (E)-3-cyclopropyl but-2-enoate (**1qa**)*. colorless oil, 1.17 g, 80% yield, R_f = 0.35 (petroleum ether/EtOAc 100:1). ^1H NMR (400 MHz, $CDCl_3$) δ 5.99 (d, *J* = 3.8 Hz, 1H), 2.02 (d, *J* = 0.9 Hz, 3H), 1.66 (d, *J* = 1.0 Hz, 1H), 0.97–0.91 (m, 2H), 0.89–0.81 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.8, 161.6, 141.5 (dm, *J* = 250.8 Hz), 139.1 (dm, *J* = 252.6 Hz), 137.9 (dm, *J* = 252.7 Hz), 125.4 (m), 109.6, 20.8, 15.4, 7.9. ^{19}F NMR (470 MHz, $CDCl_3$) δ -152.78 – -152.89 (m), -159.28 (td, *J* = 21.6, 7.3 Hz), -163.13 – -163.24 (m). IR (neat cm^{-1}) *v* 2925, 2851, 1758, 1621, 1521, 1025, 1005, 930, 837. HRMS (EI-TOF) *m*/*z*: $[M\text{-}C_6F_5O]^+$ Calcd for C_7H_9O 109.0648; Found 109.0645.

*Perfluorophenyl (E)-2-(chroman-4-ylidene) acetate (**1ra**)*. white solid, 1.30 g, 73% yield, R_f = 0.35 (petroleum ether/EtOAc 50:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.72–7.70 (m, 1H), 7.38–7.34 (m, 1H), 7.00–6.92 (m, 2H), 6.60 (s, 1H), 4.28 (t, *J* = 6.2 Hz, 2H), 3.42–3.39 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.0, 157.4, 154.0, 141.4 (dm, *J* = 250.9 Hz), 139.3 (dm, *J* = 252.8 Hz), 137.9 (dm, *J* = 253.7 Hz), 133.3, 125.2 (m), 124.9, 121.3, 120.0, 118.5, 105.5, 65.3, 27.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -152.57 – -152.63 (m), -158.61 (t, *J* = 21.6 Hz), -162.68 – -162.78 (m). IR (neat cm^{-1}) *v* 2994, 2884, 1753, 1602, 1518, 1002, 874. HRMS (EI-TOF) *m*/*z*: $[M]^+$ Calcd for $C_{17}H_9F_5O_3$ 356.0472; Found 356.0465.

*Perfluorophenyl (E)-3-phenylpent-2-enoate (**1sa**)*. white solid, 1.37 g, 80% yield, R_f = 0.50 (petroleum ether/EtOAc 50:1). ^1H NMR (500 MHz, $CDCl_3$) δ 7.55–7.45 (m, 5H), 6.32 (s, 1H), 3.16 (q, *J* = 7.5 Hz, 2H), 1.14 (t, *J* = 7.5 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 168.9, 161.5, 141.4 (dm, *J* = 251.1 Hz), 140.1, 139.3 (dm, *J* = 252.8 Hz), 137.9 (dm, *J* = 254.0 Hz), 129.9, 128.8, 126.8, 125.3 (m), 112.5, 25.0, 13.4. ^{19}F NMR (470 MHz, $CDCl_3$) δ -152.53 – -152.59 (m), -158.77 (t, *J* = 21.6 Hz), -162.77 – -162.87 (m). IR (neat cm^{-1}) *v* 2937, 2872, 1763, 1615, 1518, 1097, 1026, 955. HRMS (EI-TOF) *m*/*z*: $[M]^+$ Calcd for $C_{17}H_{11}F_5O_2$ 342.0679; Found 342.0689.

General Procedure for Carboxylative Cyclization of 2-Butenoates with CO_2. A 20 mL oven dried autoclave containing a stir bar was charged with 2-butenoate (0.10 mmol), DBU (46 mg, 0.30 mmol) and 2 mL dry CH_3CN in a glove box. After removal from the glove box, the autoclave was purged three times,

and then pressurized to appropriate pressure with carbon dioxide. The reaction mixture was stirred at room temperature for 18 h, and the remaining carbon dioxide was vented slowly. The reaction mixture was then directly loaded into silica gel column, and the products were isolated by flash column chromatography using EtOAc or EtOAc/acetic acid as the eluent.

*4-Phenyl-2H-pyran-2,6(3H)-dione (**2a**).* white solid, 16.9 mg, 90% yield, R_f = 0.35 (EtOAc/acetic acid 30:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.51 (m, 5H), 6.62 (s, 1H), 3.92 (s, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 164.7, 160.2, 152.7, 133.8, 132.1, 129.5, 126.1, 112.1, 33.4. IR (neat cm^{-1}) ν 2956, 2922, 2854, 1794, 1726, 1466, 1122, 974, 767. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ Calcd for $C_{11}H_9O_3$ 189.0552; Found 189.0552..

*4-(p-Tolyl)-2H-pyran-2,6(3H)-dione (**2b**)*. white solid, 18.4 mg, 91% yield, R_f = 0.35 (EtOAc/acetic acid 30:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 6.58 (s, 1H), 3.90 (s, 2H), 2.42 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 164.9, 160.4, 152.6, 142.9, 130.8, 130.1, 126.1, 110.9, 33.3, 21.4. IR (neat cm^{-1}) ν 2923, 2852, 1787, 1728, 1143, 999, 818, 621. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ Calcd for $C_{12}H_{11}O_3$ 203.0708; Found 203.0705.

*4-(4-(tert-Butyl)phenyl)-2H-pyran-2,6(3H)-dione(**2c**)*. white solid, 22.5 mg, 92% yield, R_f = 0.35 (EtOAc/acetic acid 30:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 4H), 6.59 (s, 1H), 3.91 (s, 2H), 1.35 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 164.9, 160.4, 156.0, 152.6, 130.8, 126.4, 126.0, 111.0, 35.0, 33.2, 31.0. IR (neat cm^{-1}) ν 2960, 2924, 1790, 1723, 1629, 1125, 970, 868, 620. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ Calcd for $C_{15}H_{17}O_3$ 245.1178; Found 245.1174.

*4-(4-Cyclohexylphenyl)-2H-pyran-2,6(3H)-dione (**2d**)*. white solid, 24.8 mg, 92% yield, R_f = 0.35 (EtOAc/acetic acid 30:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.3 Hz, 2H), 6.58 (s, 1H), 3.91 (s, 2H), 2.56 (d, J = 2.6 Hz, 1H), 1.88–1.76 (m, 6H), 1.44–1.39 (m, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 165.1, 160.6, 152.9, 152.8, 131.1, 128.0, 126.2, 110.8, 44.5, 34.1, 33.3, 26.7, 26.0. IR (neat cm^{-1}) ν 2925, 2852, 1795, 1737, 1607, 1448, 1122, 1016, 996, 825, 618. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ Calcd for $C_{17}H_{19}O_3$ 271.1334; Found 271.1326.

4-(4-Methoxyphenyl)-2H-pyran-2,6(3H)-dione ***(2e)***. white solid, 20.7 mg, 95% yield, R_f = 0.25 (EtOAc/acetic acid 30:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.9 Hz, 2H), 7.00 (d, J = 8.9 Hz, 2H), 6.53 (s, 1H), 3.89–3.88 (m, 5H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 165.0, 162.8, 160.5, 151.9, 127.9, 125.8, 114.8, 109.4, 55.6, 33.2. IR (neat cm^{-1}) ν 2924, 2852, 1791, 1732, 16256, 1515, 1185, 868, 619. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{11}O_4$ 219.0657; Found 219.0652.

4-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-2H-pyran-2,6(3H)-dione ***(2f)***. white solid, 23.2 mg, 94% yield, R_f = 0.25 (EtOAc/acetic acid 30:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.36–7.32 (m, 2H), 6.95 (d, J = 8.5 Hz, 1H), 6.70 (s, 1H), 4.29 (d, J = 6.1 Hz, 4H), 4.10 (s, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6) δ 166.2, 161.4, 153.5, 146.4, 143.5, 64.4, 63.9, 33.3. IR (neat cm^{-1}) ν 2924, 2853, 1786, 1732, 1626, 1127, 975, 887, 609. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{11}O_5$ 247.0606; Found 247.0604.

4-(Naphthalen-2-yl)-2H-pyran-2,6(3H)-dione ***(2g)***. white solid, 18.6 mg, 78% yield, R_f = 0.35 (EtOAc/acetic acid 30:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.42 (s, 1H), 8.04–7.97 (m, 4H), 7.62 (s, 2H), 6.98 (s, 1H), 4.30 (s, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6) δ 166.2, 161.4, 153.7, 134.0, 132.5, 131.2, 129.0, 128.5, 128.0, 127.7, 127.5, 126.9, 123.2, 111.0, 33.4. IR (neat cm^{-1}) ν 2973, 2929, 1784, 1723, 1622, 1384, 1122, 975, 814, 618. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{11}O_3$ 239.0708; Found 239.0701.

4-(Naphthalen-1-yl)-2H-pyran-2,6(3H)-dione ***(2h)***. white solid, 16.4 mg, 69% yield, R_f = 0.25 (EtOAc/acetic acid 30:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97–793 (m, 2H), 7.88–7.85 (m, 1H), 7.60–7.57 (m, 2H), 7.56–7.52 (m, 1H), 7.39–7.37 (m, 1H), 6.45 (t, J = 1.7 Hz, 1H), 3.94 (d, J = 1.7 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 164.6, 159.8, 155.0, 133.8, 133.6, 130.7, 129.4, 129.0, 127.6, 126.8, 125.1, 124.8, 123.9, 117.8, 36.8. IR (neat cm^{-1}) ν 2964, 2926, 2876, 1794, 1739, 1684, 1519, 1207, 776, 700. HRMS (ESI-TOF) m/z: $[M-H]^-$ Calcd for $C_{15}H_9O_3$ 237.0552; Found 237.0553.

4-([1,1'-Biphenyl]-4-yl)-2H-pyran-2,6(3H)-dione ***(2i)***. white solid, 20.6 mg, 78% yield, R_f = 0.30 (EtOAc/acetic acid 30:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.91 (d, J = 8.1 Hz, 2H), 7.82–7.75 (m, 4H), 7.50 (t, J = 7.5 Hz, 2H), 7.42 (t, J = 7.2 Hz, 1H), 6.87 (s, 1H), 4.21 (s, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6) δ 166.2, 161.4, 153.6, 142.9, 138.8, 132.9, 129.1, 128.2, 127.5, 127.0, 126.8, 110.5, 33.4. IR

(neat cm^{-1}) *v* 2953, 2923, 2851, 1788, 1723, 1630, 1165, 797, 769, 622. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ Calcd for $C_{17}H_{13}O_3$ 265.0865; Found 265.0859.

4-(4-Fluorophenyl)-2H-pyran-2,6(3H)-dione ***(2j)***. white solid, 19.1 mg, 92% yield, R_f = 0.30 (EtOAc/acetic acid 30:1). ^1H NMR (500 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 8.2, 5.2 Hz, 2H), 7.20 (t, *J* = 8.3 Hz, 2H), 6.57 (s, 1H), 3.89 (s, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 164.8 (d, *J* = 255.4 Hz), 164.4, 160.0, 151.4, 129.9, 128.3 (d, *J* = 8.9 Hz), 116.8 (d, *J* = 22.1 Hz), 111.9 (d, *J* = 1.4 Hz), 33.4. IR (neat cm^{-1}) *v* 2952, 2854, 1793, 1738, 1635, 1416, 873, 836, 619. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ Calcd for $C_{11}H_8FO_3$ 207.0457; Found 207.0448.

4-(4-Chlorophenyl)-2H-pyran-2,6(3H)-dione ***(2k)***. white solid, 19.6 mg, 88% yield, R_f = 0.30 (EtOAc/acetic acid 30:1). ^1H NMR (500 MHz, $CDCl_3$) δ 7.49 (s, 4H), 6.60 (s, 1H), 3.88 (s, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 164.3, 159.9, 151.2, 138.5, 132.1, 129.8, 127.4, 33.2. IR (neat cm^{-1}) *v* 2960, 2920, 2850, 1800, 1740, 970, 829. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ Calcd for $C_{11}H_8ClO_3$ 223.0162; Found 223.0156.

4-(4-Bromophenyl)-2H-pyran-2,6(3H)-dione ***(2l)***. yellow solid, 20.0 mg, 75% yield, R_f = 0.35 (EtOAc/acetic acid 30:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 6.61 (s, 1H), 3.89 (s, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 164.2, 159.9, 151.4, 132.8, 132.6, 131.5, 127.5, 126.8, 112.5, 33.2. IR (neat cm^{-1}) *v* 2959, 2917, 2851, 1796, 1741, 1458, 1379, 822, 725. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ Calcd for $C_{11}H_8BrO_3$ 266.9657; Found 266.9654.

4-(Furan-2-yl)-2H-pyran-2,6(3H)-dione ***(2m)***. white solid, 15.3 mg, 86% yield, R_f = 0.35 (EtOAc/acetic acid 30:1). ^1H NMR (400 MHz, DMSO-d_6) δ 8.00 (s, 1H), 7.29 (s, 1H), 6.74 (s, 1H), 6.42 (s, 1H), 4.04 (s, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6) δ 165.6, 161.3, 148.8, 147.4, 142.8, 116.1, 113.2, 105.9, 31.5. IR (neat cm^{-1}) *v* 2925, 2854, 1790, 1733, 1629, 1562, 1004, 971, 841, 617. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ Calcd for $C_9H_7O_4$ 179.0344; Found 179.0339.

4-(Thiophen-2-yl)-2H-pyran-2,6(3H)-dione ***(2n)***. white solid, 15.5 mg, 80% yield, R_f = 0.35 (EtOAc/acetic acid 30:1). ^1H NMR (400 MHz, DMSO-d_6) δ 7.91 (s, 1H), 7.77 (s, 1H), 7.24 (s, 1H), 6.52 (s, 1H), 4.16 (s, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6) δ 165.6, 161.1, 148.0, 138.0, 131.8, 130.7,

128.9, 33.6. IR (neat cm^{-1}) *v* 2954, 2924, 2852, 1684, 1610, 1459, 1377, 855, 703. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ Calcd for $C_9H_7O_3S$ 195.0116; Found 195.0119.

*4-Methyl-2H-pyran-2,6(3H)-dione (**2o**)*. white solid, 11.3 mg, 89% yield, R_f = 0.25 (EtOAc/acetic acid 50:1). ^1H NMR (500 MHz, $CDCl_3$) δ 6.07 (s, 1H), 3.44 (s, 2H), 2.07 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 164.7, 159.7, 155.4, 114.7, 36.3, 22.2. IR (neat cm^{-1}) *v* 2955, 2925, 2854, 1794, 1733, 1659, 1114, 961, 847, 594. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ Calcd for $C_6H_7O_3$ 127.0395; Found 127.0389.

*4-(4-Methylpent-3-en-1-yl)-2H-pyran-2,6(3H)-dione (**2p**)*. white solid, 14.2 mg, 73% yield, R_f = 0.25 (EtOAc/acetic acid 50:1). ^1H NMR (500 MHz, $CDCl_3$) δ 6.06 (s, 1H), 5.03 (t, *J* = 6.4 Hz, 1H), 3.43 (s, 2H), 2.34 (t, *J* = 7.2 Hz, 2H), 2.28–2.24 (m, 2H), 1.70 (s, 3H), 1.62 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 164.9, 159.9, 159.1, 134.4, 121.3, 113.9, 35.7, 35.2, 25.6, 25.0, 17.8. IR (neat cm^{-1}) *v* 2960, 2929, 2855, 1799, 1741, 1653, 1380, 1278, 1118, 966, 598. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ Calcd for $C_{11}H_{15}O_3$ 195.1021; Found 195.1018.

*4-Cyclopropyl-2H-pyran-2,6(3H)-dione (**2q**)*. white solid, 12.5 mg, 82% yield, R_f = 0.25 (EtOAc/acetic acid 30:1). ^1H NMR (400 MHz, $CDCl_3$) δ 5.94 (t, *J* = 1.5 Hz, 1H), 3.34–3.32 (m, 2H), 1.69–1.62 (m, 1H), 1.13–1.08 (m, 2H), 0.88–0.84 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 164.9, 162.0, 159.8, 110.1, 33.2, 16.6, 9.3. IR (neat cm^{-1}) *v* 2954, 2918, 2852, 1792, 1734. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ Calcd for $C_8H_9O_3$ 153.0552; Found 153.0546.

*4a,5-Dihydro-2H,4H-pyrano[3,4-c]chromene-2,4-dione (**2r**)*. white solid, 14.7 mg, 68% yield, R_f = 0.25 (EtOAc/acetic acid 30:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (t, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 5.09 (s, 2H), 3.86 (s, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 163.7, 158.8, 155.8, 141.8, 134.3, 124.8, 122.4, 118.6, 117.4, 113.4, 30.8. IR (neat cm^{-1}) *v* 2929, 2854, 1796, 1723, 1603, 758, 734. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ Calcd for $C_{12}H_9O_4$ 217.0501; Found 217.0495.

*3-Methyl-4-phenyl-2H-pyran-2,6(3H)-dione (**2s**)*. white solid, 14.2 mg, 70% yield, R_f = 0.25 (EtOAc/acetic acid 30:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.46–7.45 (m, 2H), 7.39–7.37 (m, 3H), 6.06 (s, 1H), 3.12 (q, *J* = 7.4 Hz, 1H), 1.08 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.4, 164.7,

140.9, 129.1, 128.6, 127.1, 116.1, 24.5, 13.6. IR (neat cm^{-1}) *v* 2969, 2926, 2871, 1798, 1739, 1684, 1616, 1515, 767, 700. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{11}O_3$ 203.0708; Found 203.0700.

Gram-Scale Synthesis of 2a. A 60 mL oven dried autoclave containing a stir bar was charged with pentafluorophenyl 2-butenoate **1aa** (1.97 g, 6.0 mmol), DBU (2.70 g, 18.0 mmol) and 40 mL dry CH_3CN in a glove box. After removal from the glove box, the autoclave was purged three times, and then pressurized to appropriate pressure with carbon dioxide. The reaction mixture was stirred at room temperature for 18 h, and the remaining carbon dioxide was vented slowly. Then the pH of reaction mixture was adjusted to 3~4 with 0.5 M HCl and extracted with EtOAc (3 × 100 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, concentrated in vacuo and then subjected to column chromatography using EtOAc/acetic acid to afford **2a** as a pale yellow solid. 0.95 g, 84% yield.

Hydrolytic Reaction of 2a. A 25 mL round-bottom flask was charged with **2a** (0.3 mmol, 56 mg) and MeOH (5 mL), then NaOH (2 M, 4 mL) was added with stirring. The reaction mixture was stirred at room temperature until no starting material was detected by TLC. Then the pH of reaction mixture was adjusted to 1.0 with HCl (1 M). The mixture was extracted with diethyl ether (3 × 30 mL). The combined organic layer was washed with brine, dried over Na_2SO_4 and filtration. The solvent was removed under reduced pressure. To the crude product in a mixture solvent (MeOH/DCM=1:1, 6 mL) at room temperature was added $TMSCHN_2$ (1M in hexane, 1 mL) and the reaction mixture was stirred at room temperature for 1 h. The mixture was carefully quenched with HCl (1 M). The organics were extracted EtOAc (5 × 15 mL), dried over Na_2SO_4, filtered, concentrated in vacuo and then subjected to column chromatography using EtOAc-hexane to afford the diester **3a** as a pale yellow oil. 63.2 mg, 90% yield, R_f = 0.25 (petroleum ether/EtOAc 20:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.46–7.42 (m, 2H), 7.39–7.36 (m, 3H), 4.18 (s, 1H), 3.75 (s, 3H), 3.68 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.7, 166.6, 151.2, 140.5, 129.3, 128.7, 126.4, 119.5, 52.1, 51.4, 36.8. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{14}O_4$ 235.0970; Found 235.0957.

Reduction of 2a with Lithium Aluminum Hydride.[19] The **2a** (0.3 mmol, 56 mg) was dissolved in THF (10 mL) under nitrogen and the reaction mixture was cooled to 0 °C. $LiAlH_4$ (1 M in THF, 0.6 mL) was added dropwise with stirring. After the addition was complete, the reaction mixture was heated by oil bath at reflux overnight. The mixture was carefully quenched with EtOAc. Then the pH was adjusted to 4.0 with HCl (1 M). The reaction mixture were extracted with EtOAc (3 × 20 mL), dried over Na_2SO_4, filtered, concentrated in vacuo and then subjected to column chromatography using EtOAc-hexane to afford the diol product **4a** as yellow oil. 37.4 mg, 70% yield, R_f = 0.20 (petroleum ether/EtOAc 1:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.36 (m, 2H), 7.36–7.30 (m, 2H), 7.28–7.25 (m, 1H), 6.13 (t, J = 7.4 Hz, 1H), 4.23 (d, J = 7.4 Hz, 2H), 3.59 (t, J = 5.9 Hz, 2H), 3.33 (bs, 2H), 2.81 (t, J = 5.9 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 141.5, 141.0, 128.9, 128.4, 127.5, 126.5, 59.8, 58.2, 32.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_{15}O_2$ 179.1072; Found 179.1068.

DMAP Promoted Cycloaddition of 2a and 4-Nitrobenzaldehyde.[13] To a mixture of **2a** (0.2 mmol, 37.5 mg) and *p*-nitrobenzaldehyde (0.22 mmol, 33 mg) in dry chloroform (2 ml), DMAP (0.2 mmol, 25 mg) was added. The reaction mixture was stirred at room temperature for 15 h. The mixture was added $TMSCHN_2$ (1M in hexane, 1 mL) and the reaction mixture was stirred at room temperature for 1 h. The mixture was carefully quenched with HCl (1 M) and extracted with EtOAc (3 × 20 mL), dried over Na_2SO_4, filtered, concentrated in vacuo and then subjected to column chromatography using EtOAc-hexane to afford **5a** as a yellow solid. 48.1 mg, 68% yield, R_f = 0.25 (petroleum ether/EtOAc 4:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, J = 16.8 Hz, 1H), 8.18 (d, J = 7.6 Hz, 2H), 7.61 (d, J = 7.6 Hz, 2H), 7.45–7.35 (m, 5H), 6.64 (d, J = 16.8 Hz, 1H), 5.93 (s, 1H), 3.81 (d, J = 5.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.6, 155.0, 147.5, 143.0, 139.1, 136.7, 130.1, 128.9, 128.9, 128.5, 127.9, 123.8, 119.7, 51.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{15}NO_6$ 354.0978; Found 354.0972.

Reaction of 2a with Excess Dimethyl Acetylenedicarboxylate.[20] The **2a** (0.3 mmol, 56 mg) was dissolved in dry DCM (15 mL) under nitrogen atmosphere and then Et_3N (0.06 mmol, 6 mg) was added, and the mixture was stirred for 5 min. DMAD (0.7 mmol, 99 mg) was added dropwise and the mixture was stirred overnight. The mixture was quenched with HCl (1 M) and extracted with ethyl acetate (3 × 20

mL), dried over Na_2SO_4, filtered, concentrated in vacuo and then subjected to column chromatography using EtOAc-hexane to afford **6a** as a white solid. 89.8 mg, 70% yield, R_f = 0.30 (petroleum ether/EtOAc 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 1.6 Hz, 1H), 7.60–7.56 (m, 3H), 7.50–7.43 (m, 3H), 5.25 (s, 1H), 3.96 (s, 3H), 3.93 (s, 3H), 3.93 (s, 3H), 3.68 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 165.7, 165.3, 165.0, 159.6, 150.4, 144.5, 137.8, 130.8, 129.2, 128.9, 127.2, 127.1, 126.5, 100.9, 53.17, 53.0, 52.9, 51.8. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ Calcd for $C_{22}H_{21}O_9$ 429.1186; Found 429.1178.

Hydrogenation of 2a with H_2. A 100 mL oven dried autoclave containing a stir bar was charged with **2a** (0.14 g, 0.76 mmol), Pd/C (5%, 36 mg) and 30 mL dry EtOAc. The autoclave was purged three times with nitrogen, degased at 0 ^{o}C, and then pressurized to 2.0 MPa with H_2. The reaction mixture was stirred at room temperature for 15 h, and the remaining H_2 was vented slowly. After Pd/C was filtered off, the organic solution was concentrated in vacuo and then subjected to column chromatography using EtOAc/hexane to afford **7a** as a white solid. 0.12 g, 83% yield, R_f = 0.25 (petroleum ether/EtOAc 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.36 (m, 2H), 7.36–7.30 (m, 1H), 7.21 (d, J = 7.8 Hz, 2H), 3.47–3.39 (m, 1H), 3.11 (dd, J = 17.3, 4.5 Hz, 2H), 2.87 (dd, J = 17.3, 11.4 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.8, 139.1, 129.36, 128.1, 126.2, 37.1, 34.1. IR (neat cm^{-1}) ν 1800, 1758, 1078, 957, 766, 704. HRMS (ESI-TOF) *m*/*z*: $[M+Na]^+$ Calcd for $C_{11}H_{10}NaO_3$ 213.0528; Found 213.0517.

X-ray Crystallography. Single crystals of **2b** and **2e** were obtained by recrystallization from EtOAc/hexane at room temperature. Recrystallization from EtOAc at 5-10 ^{o}C afforded the single crystal of **6a**. The intensities were collected on a Bruker SMART APEX CCD diffractometer equipped with a graphitemonochromated Mo−Kα (λ = 0.71073 Å) radiation source; the data were acquired using the SMART and SAINT programs. The structures were solved by direct methods and refined on F^2 by fullmatrix least-squares methods using the SHELXTL version 5.1 software.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

X-ray crystallographic data (CIF)

Copies of ^{1}H NMR, $^{13}C\{^{1}H\}$ NMR, ^{19}F NMR spectra for substrates and products

Thermal ellipsoid plots of **2b**, **2e** and **6a**

Spectra of labelled products

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Notes

The authors declare no competing financial interest.

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