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Phosphine Catalyst-Controlled Cycloaddition or Dienylation Reactions of Trifluoromethyl Aryl Ketones with Bis-Substituted Allenoates

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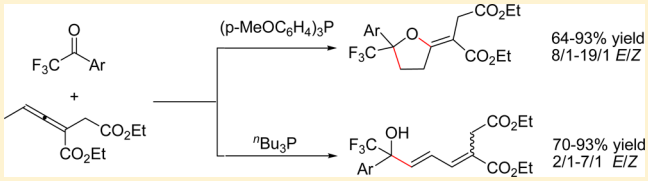
Supporting Information

ABSTRACT: A chemoselective phosphine-catalyzed cycloaddition or dienylation reaction between trifluoromethyl-substituted ketones and bis-substituted allenoates was described. Under the catalysis of triarylphosphine, the reaction gave a range of trifluoromethylated tetrahydrofurans with broad substrate tolerance and good to excellent stereoselectivity, while the use of trialkylphosphine switched the reaction pathway to furnish CF_3-substituted dienyl tertiary alcohols chemoselectively. Moreover, a preliminary study on the asymmetric version of the reaction was also performed, which represents the first example of a phosphine-catalyzed asymmetric reaction between allenoates and carbonyl compounds.



INTRODUCTION

The trifluoromethyl-substituted quaternary carbon center is an important structural motif occurring in a range of pharmaceuticals and drug candidate molecules such as anti-HIV agent efavirenz,[1a] antimalarial agent dihydroartemisinin (DHA),[1b] and nonsteroidal selective glucocorticoid receptor (GR) agonist ZK216348.[1c] Particularly, the CF_3-substituted tetrahydrofuran and tertiary alcohol are substructures present in some bioactive molecules with great potential value in medicinal chemistry.[2] Owing to the higher electrophilicity of α-trifluoromethyl ketones as compared with their nonfluorinated counterparts, they are more prone to attack by carbon nucleophiles, which constitutes a simple and direct way to the CF_3-substituted tertiary alcohols and their analogues.[3] On the other hand, the phosphine-catalyzed cycloaddition reactions of allenoates or their surrogates with various electrophiles have emerged as a versatile platform for the synthesis of valuable five- and six-membered cyclic structures.[4,5] Unlike the widely studied electron-deficient olefins,[6a] imines,[6b] and aldehydes,[7,8] the use of CF_3-activated ketones as electrophiles in the allenoate reaction was not disclosed until recently by Ye et al.[9] The products of the reaction with α-trifluoromethyl ketones are highly dependent on the structures of the allenoates: the use of simple allenoates gave CF_3-substituted 1,2-dihydrofurans (under phosphine catalysis) or oxetanes (under tertiary amine catalysis), while the use of α-branched allenoates provided CF_3-substituted dihydropyrans and the use of Morita–Baylis–Hillman adducts furnished dienes (Scheme 1). Up to now, the nucleophile-catalyzed γ- or bis-substituted allenoate reaction with trifluoromethyl ketone had remained unexplored.

In 2009, He and co-workers[10] reported the [3 + 2] annulation between γ-substituted allenoates and aromatic aldehyde,[11,12] which served as a facile entry to tetrahydrofurans with modest stereoselectivities. The chemoselective formation of tetrahydrofurans was achieved in refluxing xylene. Herein we disclosed a novel catalyst-dependent[13] chemoselective cycloaddition or dienylation reaction between bis-substituted allenoates and trifluoromethyl ketones. In this system, two skeletally different products, CF_3-substituted tetrahydrofurans and dienyl tertiary alcohols, could be obtained chemoselectively by judicious choice of the phosphine catalyst (Scheme 1). Moreover, the presented cycloaddition reaction using α-trifluoromethyl ketones also enables satisfying improvement in substrate generality and chemo- and stereoselectivity as compared with analogous examples.[10a,c]

RESULTS AND DISCUSSION

Initially, γ-methyl allenoate **2a** was reacted with CF_3-substituted acetophenone **1a** in the presence of $(p\text{-}CH_3OC_6H_4)_3P$, giving a mixture of [3 + 2] cycloadduct **3aa** and tertiary alcohol **4aa** in poor product ratio and *E*,*E*/*Z*,*E* ratio (Scheme 2, eq 1). To our surprise, the use of α,γ-bis-substituted allenoate **2b** led to excellent chemo- and stereoselectivity: the use of $(p\text{-}CH_3OC_6H_4)_3P$ gave [3 + 2] cycloadduct **3a** as the sole product with 93% yield (*E*/*Z* > 15/1) under the optimized reaction conditions (for details, see the Supporting Information), and the use of tributylphosphine provided CF_3-substituted dienyl tertiary alcohol **4a** with excellent chemo-

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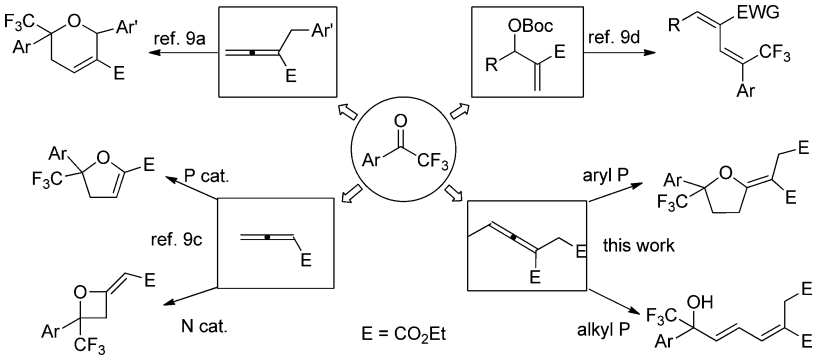
Scheme 1. Nucleophilic Phosphine-Catalyzed Reactions of α-Trifluoromethyl Ketones and Allenoates or Their Surrogates



Scheme 2. Chemoselective Reaction between Bis-Substituted Allenoate and Trifluoromethyl Ketone

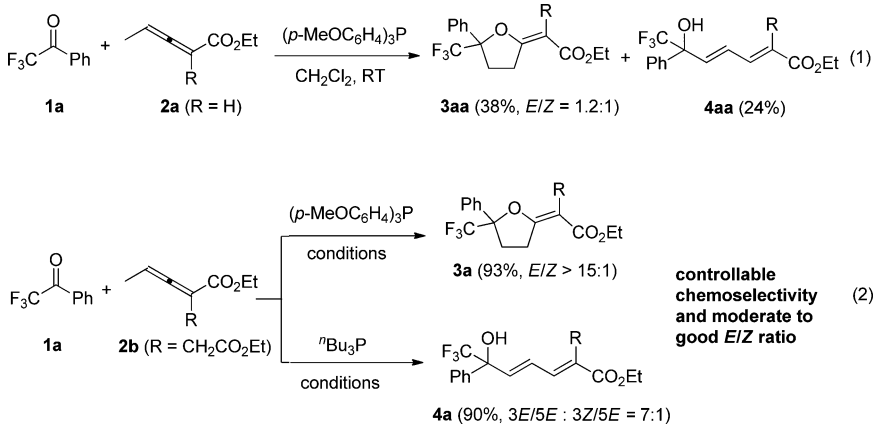
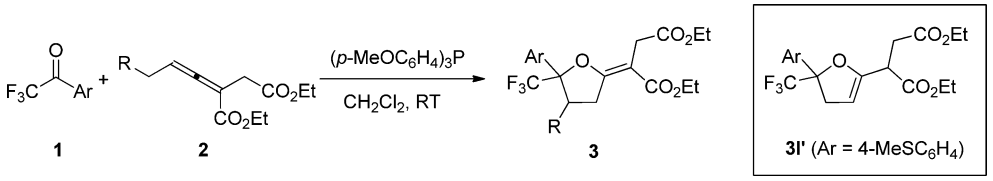


Table 1. Catalytic [3 + 2] Cycloadditions of Trifluoromethyl Aryl Ketones 1 with Allenoates 2 Catalyzed by Tris(4-methoxyphenyl)phosphine[a]



entry	1, Ar	2, R	product	yield[b] (%)	E/Z[c]
1	**1a**, Ph	**2b**, H	**3a**	93	15/1
2	**1b**, 4-BrC_6H_4	**2b**, H	**3b**	83	12/1
3	**1c**, 4-FC_6H_4	**2b**, H	**3c**	90	11/1
4	**1d**, 4-ClC_6H_4	**2b**, H	**3d**	85	19/1
5	**1e**, 4-MeOC_6H_4	**2b**, H	**3e**	69	9/1
6	**1f**, 3-MeOC_6H_4	**2b**, H	**3f**	71	8/1
7	**1g**, 4-EtOC_6H_4	**2b**, H	**3g**	70	15/1
8	**1h**, 4-EtC_6H_4	**2b**, H	**3h**	64	9/1
9	**1i**, 4-MeC_6H_4	**2b**, H	**3i**	70	8/1
10	**1j**, 2-thienyl	**2b**, H	**3j**	89	12/1
11	**1k**, 1-naphthyl	**2b**, H	**3k**	77	11/1
12[d]	**1a**, Ph	**2c**, Me	**3ac**, **3ac′**	69	19/1
13[e]	**1l**, 4-MeSC_6H_4	**2b**, H	**3l**	64	8/1

[a]Unless otherwise noted, all reactions were carried out with **1** (0.1 mmol) and **2** (0.15 mmol) in the presence of phosphine (0.02 mmol) in CH_2Cl_2 (1.0 mL) for 3 h at rt. [b]Yields of isolated *E* isomer. [c]Determined by ^{1}H NMR analysis of crude products. [d]The diastereoselectivity ratio of **3ac** and **3ac′** was determined as 56/44 by isolated yield. [e]The double bond migration product **3l′** was obtained in 28% yield and with 1.2/1 diastereoselectivity concurrently.

selectivity and moderate *E*,*E* selectivity, which may be viewed as a double vinylic analogue of Mosher's ester (Scheme 2, eq 2). The presence of Bu_3P also gave the isomerization product of allenoate **2b** itself concomitantly (for details, see the Supporting Information). Notably, in all cases examined above, 1,3-dioxane derivatives (common byproduct in aldehyde

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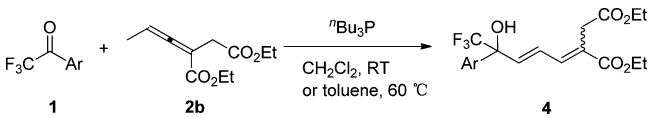
reactions; see Kwon and He's reports[7d,10a]) was not detected, which may be ascribed to the steric hindrance of the CF_3 group.

The reaction scope under the catalysis of tris(4-methoxyphenyl)phosphine was first examined (Table 1). The [3 + 2] cycloaddition reaction between bis-substituted allenoate **2b** and various aryl trifluoromethyl ketones proceeded smoothly to provide a range of synthetically valuable tetrahydrofurans containing a CF_3-substituted quaternary stereogenic center in 64−93% yields and with good to excellent *E* selectivities as the only products. An obvious electronic effect on the reactivity was observed: aromatic ketones containing electron-withdrawing substituents in general gave higher yields and stereoselectivities than those with electron-donating substituents. The heteroaryl ketone **1j** and the sterically demanding substrate **1k** were also well-tolerated in the cycloaddition (entries 10 and 11). However, aliphatic substrates were totally unsuitable (the aliphatic ketones generally remained unreacted under the typical reaction conditions). The reaction proceeded uneventfully when γ-ethyl allenoate **2c** was employed as the substrate, albeit with a poor diastereoselectivity (entry 12). To our surprise, the relatively electron-rich ketone **1l** was reactive enough to achieve full conversion, furnishing the normal cycloadduct in 72% yield with a moderate *E*/*Z* ratio. Meanwile, an unprecedented double bond migration product, **3l′**, was also isolated in 28% yield with statistically random diastereoselectivity (entry 13). Further study revealed such migration of an exocyclic double bond is thermodynamically favored: when the reaction time was prolonged, all tested aryl ketones yielded a trace amount of migrated products.

Subsequently, the scope of Bu_3P-catalyzed dienylation reaction of trifluoromethyl ketone was tested, and the results are summarized in Table 2. The reaction provided facile access to CF_3-substituted dienyl tertiary alcohols with generally high yields, which could also be a unique complement to the current strategies for accessing the diene motif of high synthetic interest.[14] Different from the observation in the $(p\text{-}CH_3OC_6H_4)_3P$ catalysis, the Bu_3P-catalyzed reaction of substrates **1b**, **1c**, and **1d** bearing electron-withdrawing substituents required a higher reaction temperature in toluene to give high yields of the diene products, albeit with low *E*,*E*/*Z*,*E* selectivities (entries 2−4). Similar results were also observed with heteroaryl ketone **1j** and 1-naphthyl ketone **1k** (entries 10 and 11). In comparison, the reaction of substrates with electron-neutral or electron-donating substitutents could be run at rt to provide higher yields and *E*,*E*/*Z*,*E* selectivities. The configuration of diene **4a** was assigned by comparison with literature analogues[15] via ^1H NMR analysis, and the configurations of the others were assigned accordingly. Notably, in the cases examined, small amounts of tetrahydrofuran products **3** were also formed concomitantly.

Table 2. Catalytic Additions of Trifluoromethyl Aryl Ketones 1 with Allenoate 2b Catalyzed by Tributylphosphine[a]



1 2b 4

entry	1, Ar	4	yield of 4[b] (%)	*E*,*E*/*Z*,*E*[c]	yield of 3[d] (%)
1	**1a**, Ph	**4a**	90	7/1	5
2[e]	**1b**, 4-BrC_6H_4	**4b**	86	2/1	10
3[e]	**1c**, 4-FC_6H_4	**4c**	88	2.3/1	8
4[e]	**1d**, 4-ClC_6H_4	**4d**	80	2/1	12
5	**1e**, 4-$MeOC_6H_4$	**4e**	88	6/1	5
6	**1f**, 3-$MeOC_6H_4$	**4f**	93	6/1	5
7	**1g**, 4-$EtOC_6H_4$	**4g**	83	6.5/1	4
8	**1h**, 4-EtC_6H_4	**4h**	88	6.5/1	5
9	**1i**, 4-MeC_6H_4	**4i**	84	7/1	4
10[e]	**1j**, 2-thienyl	**4j**	80	3/1	12
11[e]	**1k**, 1-naphthyl	**4k**	70	3/1	12
12	**1l**, 4-$MeSC_6H_4$	**4l**	82	6/1	4

[a]Unless otherwise noted, all reactions were carried out with **1** (0.1 mmol) and **2** (0.12 mmol) in the presence of phosphine (0.015 mmol) in CH_2Cl_2 (2.0 mL) for 3 h at rt. [b]Isolated yields of *E*,*E* and *Z*,*E* isomers. [c]Determined by ^1H NMR analysis of crude products. [d]Isolated yields of *E* isomers. [e]The reaction was run at 60 °C for 2 h.

Recently, significant advances have been made in the applications of chiral phosphines for asymmetric allenoate reaction. However, the development of P-catalyzed enantioselective reactions involving carbonyl electrophiles or γ-substituted allenoate (in the case in which the γ-substitutents participate in the reaction) has not been reported.[16] The stereocontrolled δ addition of a phosphine−allenoate intermediate was still a challenging goal due to the remote distance between the chiral center of the catalyst and the δ carbon of the allenoate. Herein we also performed some preliminary research on the enantioselective cycloaddition with activated ketones catalyzed by our previously developed chiral bifunctional phosphines (Scheme 3).[17] With the trifluoromethyl ketone **1a** in the presence of catalyst **5a**, the reaction with allenoates **2a** and **2b** proceeded uneventfully to provide the diene and tetrahydrofuran products in moderate yields (for details on chiral catalyst screening, see the Supporting Information), albeit with poor enantioselectivities (Scheme 3, eq 1). To our delight, the reaction with another type of activated carbonyl, α-keto ester **1a′**, worked well to give the corresponding tetrahydrofuran **3ad** with superior ee with catalyst **5b**. To our knowledge, this is the first example of enantioselective P-catalyzed reaction between allenoate or its surrogate and carbonyl compounds. Moreover, the investigation of asymmetric catalysis revealed that the reaction pathway was also tunable by changing the α-substituent patterns of γ-methyl allenoates (Scheme 3, eq 1). Notably, chemoselectivities in these asymmetric reactions were generally excellent with no byproducts detected.

On the basis of previous reports[18,10a] and our own observation, a tentative mechanistic rationale for the chemoselective reaction is illustrated in Scheme 4. Upon the nucleophilic addition of phosphine, the allenoate is first converted to zwitterionic intermediate **A**, which undergoes 1,4-H migration immediately to give intermediate **B**. The vinylic phosphonium **B**, stabilized by its phosphorus ylide resonance form, attacks the carbonyl group of the trifluoromethyl ketone to furnish intermediate **C1** or **C2**. Depending on the phosphine catalysts used, two pathways are possible: (1) due to the P−O interaction,[18d] triarylphosphine-derived zwitterions might form a six-membered ring, **C2**, which is suitable for ring closure after a double bond migration to give intermediate **D**, and the latter would undergo a *5-exo-trig* process to produce the tetrahydrofuran product **3** with release of the phosphine; (2) for trialkylphosphine-derived zwitterions, the more electron-rich substituent (*n*-butyl group) on the phosphorus center could stabilize its positive charge more efficiently, and less P−O interaction might be expected.[18a] Thus, in this case, together with steric factors, the open-chained

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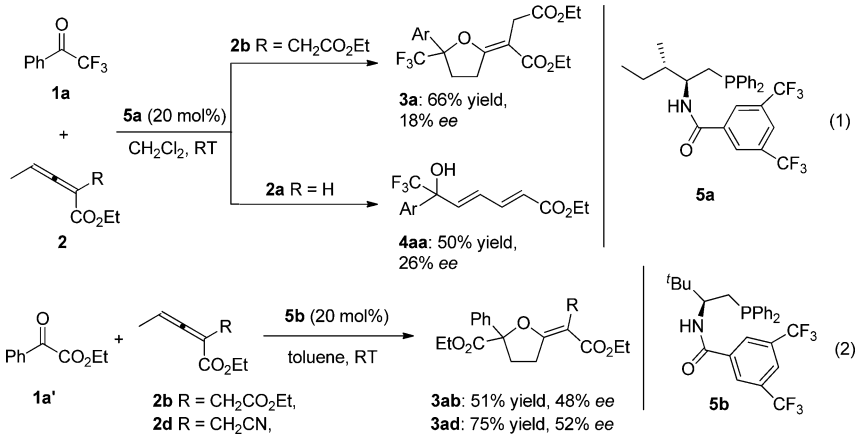
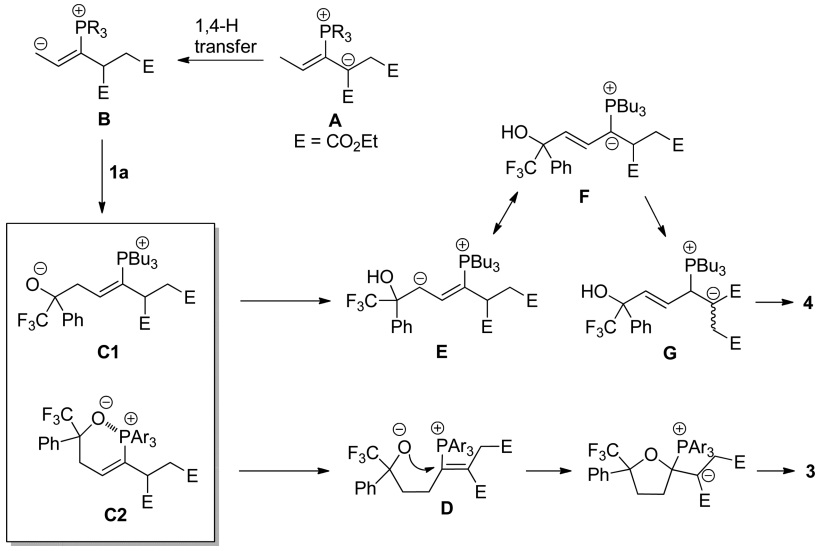
Scheme 3. Exploration of the Asymmetric Annulation of Activated Ketone and γ-Substituted Allenoate



Scheme 4. Plausible Reaction Mechanism



C1 would be favored, which was transformed to intermediate **G** through some internal proton transfer processes (via **E** and **F**) to provide the diene compound. A full understanding of the intrinsic factors determining such chemoselectivity of this reaction still requires further study.

CONCLUSION

In conclusion, we have demonstrated a catalyst-controlled chemoselective cycloaddition or dienylation reaction between trifluoromethyl ketone and bis-substituted allenoate with commercially available simple phosphine catalysts. These findings not only enrich the chemistry of reactions of allenoates under nucleophilic catalysis, but also enable easy access to two sets of skeletally diverse products bearing CF_3 quarternary stereogenic centers, namely, trifluoromethylated tetrahydrofurans and dienyl tertiary alcohols, in good yields and *E* selectivity. Furthermore, a preliminary study on the first asymmetric P-catalyzed annulation reaction of allenoate with carbonyls was also performed with promising results for further research. Efforts toward a highly enantioselective version of the reaction are currently under way in our laboratories.

EXPERIMENTAL SECTION

General Methods. Unless otherwise indicated, chemicals and solvents were purchased from commercial suppliers or purified by standard techniques. All reactions were carried out employing oven-dried glassware. Various γ-substituted allenoates were prepared according to a modificated version of the literature procedure[8e,19a] and stored at 4 °C prior to use. All trifluoromethyl aryl ketones were prepared following reported procedures[19b,c] or purchased from commercial suppliers. All acyl-protected aminophosphines were synthesized according to procedures reported previously.[17a]

Representative Procedure for the Triarylphosphine-Catalyzed Cycloadditions. To a stirred solution of trifluoromethyl ketone **1** (0.1 mmol) and phosphine (0.02 mmol) in CH_2Cl_2 (1 mL) was added γ-substituted allenoate (0.15 mmol) via a microsyringe in one portion. Then the resulting mixture was vigorously stirred at rt and monitored by TLC. After the reaction was complete, the mixture was directly purified by column chromatography on silica gel (petroleum ether/ethyl acetate (10/1) as the eluent) to furnish the corresponding product. The *E*/*Z* geometries of the main products were determined by comparison of ^{1}H NMR data with those of cycloadduct **3aa**, which were compared with those of known analogues.[10a]

*Data for (E)-diethyl 2-(5-phenyl-5-(trifluoromethyl)dihydrofuran-2(3H)-ylidene)succinate (**3a**):* 36 mg, 93% yield; R_f = 0.4 (petroleum ether/ethyl acetate, 80/20); viscous, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47−7.46 (m, 2H), 7.41−7.39 (m, 3H), 4.17 (q, *J* = 7.0 Hz, 4H), 3.55 (d, J_{AB} = 16.8 Hz, 1H), 3.49 (d, J_{AB} = 16.8 Hz,

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1H), 3.42−3.33 (m, 1H), 3.21−3.13 (m, 1H), 2.90−2.83 (m, 1H), 2.55−2.47 (m, 1H), 1.27 (t, J = 7.0 Hz, 3H), 1.26 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 171.6, 169.8, 167.4, 135.4, 129.3, 128.5, 126.3, 124.4 (q, J_{C-F} = 248 Hz), 99.1, 88.8 (q, J_{C-F} = 30.1 Hz), 60.6, 60.2, 32.1, 32.0, 30.1, 14.3, 14.2; ^{19}F NMR ($CDCl_3$, 282 MHz) δ = −79.6; IR (film, cm^{-1}) 2983, 1738, 1656, 1454, 1370, 1309, 1186, 1101, 1042, 891, 768, 723; HRMS (ESI) m/z calcd for $C_{19}H_{21}F_3O_5Na$ [M + Na]$^+$ 409.1239, found 409.1238. Data for the chiral product (best ee obtained with a trifluoromethyl ketone, catalyzed by phenylalanine-derived phosphine **5i**; for details, see Table 4S in the Supporting Information): enantiometric excess 33%; HPLC analysis (Chiralpak AD-H column, hexane/*i*-PrOH, 90/10, flow rate 0.60 mL/min) t_{major} = 14.6 min, t_{minor} = 10.6 min, λ = 254 nm.

*Data for (E)-diethyl 2-(5-(4-bromophenyl)-5-(trifluoromethyl)-dihydrofuran-2(3H)-ylidene)succinate (**3b**):* 38 mg, 83% yield; R_f = 0.38 (petroleum ether/ethyl acetate, 80/20); viscous, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.54 (d, J = 8.5 Hz, 2H), 7.35 (d, J = 8.5 Hz, 2H), 4.17 (q, J = 7.0 Hz, 4H), 3.53 (d, J_{AB} = 16.8 Hz, 1H), 3.47 (d, J_{AB} = 16.8 Hz, 1H), 3.42−3.33 (m, 1H), 3.21−3.13 (m, 1H), 2.89−2.82 (m, 1H), 2.50−2.42 (m, 1H), 1.27 (t, J = 7.0 Hz, 3H), 1.26 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 171.5, 169.4, 167.3, 134.5, 131.8, 128.1, 124.1 (q, J_{C-F} = 285 Hz), 99.5, 88.5 (q, J_{C-F} = 30.1 Hz), 60.7, 60.3, 32.1, 32.0, 30.0, 14.3, 14.2; ^{19}F NMR ($CDCl_3$, 282 MHz) δ = −79.6; IR (film, cm^{-1}) 2982, 2935, 1739, 1713, 1658, 1490, 1369, 1312, 1173, 1113, 1048, 1009, 898, 821, 781, 736; HRMS (MALDI) m/z calcd for $C_{19}H_{20}BrF_3O_5Na$ [M + Na]$^+$ 487.0338, found 487.0344.

*Data for (E)-diethyl 2-(5-(4-fluorophenyl)-5-(trifluoromethyl)-dihydrofuran-2(3H)-ylidene)succinate (**3c**):* 36 mg, 90% yield; R_f = 0.4 (petroleum ether/ethyl acetate, 80/20); viscous, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.48 (dd, J = 8.5, 6.0 Hz, 2H), 7.12 (dd, J = 8.8, 8.5 Hz, 2H), 4.20 (q, J = 7.0 Hz, 2H), 4.19 (q, J = 7.0 Hz, 2H), 3.55 (d, J_{AB} = 16.8 Hz, 1H), 3.50 (d, J_{AB} = 16.8 Hz, 1H), 3.45−3.36 (m, 1H), 3.25−3.16 (m, 1H), 2.92−2.85 (m, 1H), 2.54−2.47 (m, 1H), 1.29 (t, J = 7.0 Hz, 3H), 1.28 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 171.5, 169.5, 167.3, 163.23 (d, J_{C-F} = 249 Hz), 131.3 (d, J_{C-F} = 3.6 Hz), 128.3 (d, J_{C-F} = 8.1 Hz), 124.3 (q, J_{C-F} = 284 Hz), 115.5 (d, J_{C-F} = 22 Hz), 99.3, 88.4 (q, J_{C-F} = 30 Hz), 60.6, 60.3, 32.2, 32.0, 30.1, 14.3, 14.2; ^{19}F NMR ($CDCl_3$, 282 MHz) δ = −76.5, −109.3; IR (film, cm^{-1}) 2983, 2937, 1738, 1702, 1657, 1513, 1370, 1312, 1238, 1176, 1128, 1048, 837, 781; HRMS (MALDI) m/z calcd for $C_{19}H_{20}F_4O_5Na$ [M + Na]$^+$ 427.1145, found 427.1139.

*Data for (E)-diethyl 2-(5-(4-chlorophenyl)-5-(trifluoromethyl)-dihydrofuran-2(3H)-ylidene)succinate (**3d**):* 36 mg, 85% yield; R_f = 0.38 (petroleum ether/ethyl acetate, 80/20); viscous, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43−7.37 (m, 4H), 4.17 (q, J = 7.0 Hz, 4H), 3.53 (d, J_{AB} = 16.8 Hz, 1H), 3.48 (d, J_{AB} = 16.8 Hz, 1H), 3.42−3.34 (m, 1H), 3.22−3.13 (m, 1H), 2.89−2.82 (m, 1H), 2.50−2.43 (m, 1H), 1.27 (t, J = 7.0 Hz, 3H), 1.26 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 171.5, 169.4, 167.3, 135.6, 134.0, 128.8, 127.8, 124.2 (q, J_{C-F} = 285 Hz), 99.4, 88.3 (q, J_{C-F} = 30.1 Hz), 60.7, 60.3, 32.1, 32.0, 30.0, 14.3, 14.2; ^{19}F NMR ($CDCl_3$, 282 MHz) δ = −79.6; IR (film, cm^{-1}) 2982, 2936, 1720, 1660, 1494, 1463, 1369, 1311, 1255, 1175, 1086, 1048, 1012, 826, 738; HRMS (MALDI) m/z calcd for $C_{19}H_{20}ClF_3O_5Na$ [M + Na]$^+$ 443.0849, found 443.0844.

*Data for (E)-diethyl 2-(5-(4-methoxyphenyl)-5-(trifluoromethyl)-dihydrofuran-2(3H)-ylidene)succinate (**3e**):* 28 mg, 69% yield; R_f = 0.35 (petroleum ether/ethyl acetate, 80/20); viscous, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.42 (d, J = 8.5 Hz, 2H), 6.91 (d, J = 8.5 Hz, 2H), 4.16 (q, J = 7.0 Hz, 4H), 3.81 (s, 3H), 3.54 (d, J_{AB} = 16.8 Hz, 1H), 3.47 (d, J_{AB} = 16.8 Hz, 1H), 3.39−3.30 (m, 1H), 3.20−3.09 (m, 1H), 2.86−2.76 (m, 1H), 2.53−2.43 (m, 1H), 1.27 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 171.6, 169.9, 167.5, 160.3, 127.7, 127.3, 124.4 (q, J_{C-F} = 284 Hz), 113.9, 99.0, 88.7 (q, J_{C-F} = 30.1 Hz), 60.6, 60.2, 55.3, 32.0, 30.2, 29.7, 14.3, 14.2; ^{19}F NMR ($CDCl_3$, 282 MHz) δ = −79.8; IR (film, cm^{-1}) 2981, 2937, 2843, 1736, 1655, 1612, 1516, 1463, 1369, 1302, 1254, 1172, 1087, 1047, 897, 832; HRMS (MALDI) m/z calcd for $C_{20}H_{23}F_3O_6Na$ [M + Na]$^+$ 439.1344, found 439.1339.

*Data for (E)-diethyl 2-(5-(3-methoxyphenyl)-5-(trifluoromethyl)-dihydrofuran-2(3H)-ylidene)succinate (**3f**):* 29 mg, 71% yield; R_f = 0.35 (petroleum ether/ethyl acetate, 80/20); viscous, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34 (dd, J = 8.2, 8.1 Hz, 1H), 7.01 (d, J = 8.2 Hz, 2H), 6.95 (m, 1H), 4.20 (q, J = 7.0 Hz, 4H), 3.85 (s, 3H), 3.57 (d, J_{AB} = 16.8 Hz, 1H), 3.52 (d, J_{AB} = 16.8 Hz, 1H), 3.45−3.36 (m, 1H), 3.22−3.14 (m, 1H), 2.90−2.83 (m, 1H), 2.57−2.50 (m, 1H), 1.29 (t, J = 7.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 171.6, 169.8, 167.4, 159.7, 136.9, 127.3, 124.4 (q, J_{C-F} = 284 Hz), 118.5, 114.4, 112.6, 99.1, 88.7 (q, J_{C-F} = 30.1 Hz), 60.6, 60.2, 55.3, 32.2, 32.0, 30.1, 14.3, 14.2; ^{19}F NMR ($CDCl_3$, 282 MHz) δ = −79.4; IR (film, cm^{-1}) 2981, 2936, 2851, 1738, 1712, 1657, 1604, 1586, 1493, 1465, 1369, 1295, 1178, 1101, 1047, 883, 784, 728; HRMS (MALDI) m/z calcd for $C_{20}H_{23}F_3O_6Na$ [M + Na]$^+$ 439.1344, found 439.1339.

*Data for (E)-diethyl 2-(5-(4-ethoxyphenyl)-5-(trifluoromethyl)-dihydrofuran-2(3H)-ylidene)succinate (**3g**):* 30 mg, 70% yield; R_f = 0.36 (petroleum ether/ethyl acetate, 80/20); viscous, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39 (d, J = 8.7 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 4.20 (q, J = 7.3 Hz, 4H), 4.07 (q, J = 7.0 Hz, 2H), 3.56 (d, J_{AB} = 16.8 Hz, 1H), 3.51 (d, J_{AB} = 16.8 Hz, 1H), 3.44−3.35 (m, 1H), 3.23−3.14 (m, 1H), 2.89−2.81 (m, 1H), 2.55−2.48 (m, 1H), 1.44 (t, J = 7.0 Hz, 3H), 1.29 (t, J = 7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 171.6, 169.9, 167.5, 127.6, 127.1, 124.5 (q, J_{C-F} = 285 Hz), 114.4, 99.0, 88.7 (q, J_{C-F} = 30.1 Hz), 63.6, 60.6, 60.2, 32.0, 30.2, 29.7, 14.7, 14.3, 14.2; ^{19}F NMR ($CDCl_3$, 282 MHz) δ = −76.6; IR (film, cm^{-1}) 2982, 2935, 1740, 1713, 1653, 1514, 1300, 1252, 1172, 1118, 1047, 898, 834, 808; HRMS (MALDI) m/z calcd for $C_{21}H_{25}F_3O_6Na$ [M + Na]$^+$ 453.1501, found 453.1496.

*Data for (E)-diethyl 2-(5-(4-ethylphenyl)-5-(trifluoromethyl)-dihydrofuran-2(3H)-ylidene)succinate (**3h**):* 26 mg, 69% yield; R_f = 0.38 (petroleum ether/ethyl acetate, 80/20); viscous, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.37 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 8.2 Hz, 2H), 4.16 (q, J = 7.0 Hz, 2H), 4.15 (q, J = 7.1 Hz, 2H), 3.53 (d, J_{AB} = 16.7 Hz, 1H), 3.47 (d, J_{AB} = 17.0 Hz, 1H), 3.39−3.31 (m, 1H), 3.23−3.09 (m, 1H), 2.88−2.78 (m, 1H), 2.65 (q, J = 7.6 Hz, 2H), 2.54−2.45 (m, 1H), 1.26−1.24 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 171.6, 169.9, 167.5, 145.5, 132.6, 128.0, 126.3, 124.5 (q, J_{C-F} = 284 Hz), 99.0, 88.8 (q, J_{C-F} = 30.1 Hz), 60.6, 60.2, 32.1, 30.1, 29.7, 28.5, 15.3, 14.3, 14.2; ^{19}F NMR ($CDCl_3$, 282 MHz) δ = −79.6; IR (film, cm^{-1}) 2969, 2930, 2855, 1741, 1713, 1656, 1515, 1462, 1415, 1369, 1316, 1175, 1090, 1047, 830, 785; HRMS (MALDI) m/z calcd for $C_{21}H_{25}F_3O_5Na$ [M + Na]$^+$ 437.1552, found 437.1546.

*Data for (E)-diethyl 2-(5-(p-tolyl)-5-(trifluoromethyl)-dihydrofuran-2(3H)-ylidene)succinate (**3i**):* 28 mg, 70% yield; R_f = 0.36 (petroleum ether/ethyl acetate, 80/20); viscous, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.1 Hz, 2H), 4.20 (q, J = 7.0 Hz, 4H), 3.57 (d, J_{AB} = 16.8 Hz, 1H), 3.52 (d, J_{AB} = 16.8 Hz, 1H), 3.44−3.36 (m, 1H), 3.23−3.14 (m, 1H), 2.90−2.83 (m, 1H), 2.56−2.49 (m, 1H), 2.39 (s, 3H), 1.30 (t, J = 7.0 Hz, 3H), 1.29 (t, J = 7.0 Hz, 3H); ^{13}C NMR (CDCl3, 100 MHz) δ = 171.6, 169.9, 167.5, 139.3, 132.4, 129.2, 126.2, 124.4 (q, J_{C-F} = 285 Hz), 99.0, 88.8 (q, J_{C-F} = 30.1 Hz), 60.6, 60.2, 32.0, 30.1, 29.7, 21.1, 14.3, 14.2; ^{19}F NMR ($CDCl_3$, 282 MHz) δ = −79.7; IR (film, cm^{-1}) 2982, 2933, 1740, 1713, 1658, 1515, 1461, 1369, 1315, 1174, 1121, 1088, 1048, 899, 815; HRMS (MALDI) m/z calcd for $C_{20}H_{23}F_3O_5Na$ [M + Na]$^+$ 423.1395, found 423.1390.

*Data for (E)-diethyl 2-(5-(thiophene-2-yl)-5-(trifluoromethyl)-dihydrofuran-2(3H)-ylidene)succinate (**3j**):* 35 mg, 89% yield; R_f = 0.33 (petroleum ether/ethyl acetate, 80/20); viscous, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39 (dd, J = 5.0, 1.0 Hz, 1H), 7.18 (d, J = 3.5 Hz, 1H), 7.06 (dd, J = 5.0, 3.7 Hz, 1H), 4.19 (q, J = 7.0 Hz, 4H), 3.51 (d, J_{AB} = 17.1 Hz, 1H), 3.48 (d, J_{AB} = 16.8 Hz, 1H), 3.46−3.42 (m, 1H), 3.25−3.17 (m, 1H), 2.86−2.79 (m, 1H), 2.63−2.56 (m, 1H), 1.29 (t, J = 7.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 171.4, 169.3, 167.3, 137.9, 127.2, 127.0, 126.8, 123.8 (q, J_{C-F} = 284 Hz), 99.7, 87.5 (q, J_{C-F} = 30.4 Hz), 60.6, 60.3, 33.2, 31.9, 30.1, 14.3, 14.2; ^{19}F NMR ($CDCl_3$, 282 MHz) δ = −76.8; IR (film, cm^{-1}) 3107, 2982, 2936, 2358, 1740, 1713, 1462, 1369, 1299, 1175, 1089, 1046, 883, 843, 781, 710; HRMS (MALDI) m/z calcd for $C_{17}H_{19}F_3O_5SNa$ [M + Na]$^+$ 415.0803, found 415.0798.

*Data for (E)-diethyl 2-(5-(naphthalen-1-yl)-5-(trifluoromethyl)-dihydrofuran-2(3H)-ylidene)succinate (**3k**):* 33 mg, 77% yield; R_f =

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0.33 (petroleum ether/ethyl acetate, 80/20); viscous, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.31 (br, 1H), 7.93 (dd, J = 8.1, 7.5 Hz, 2H), 7.82 (br, 1H), 7.59 (m, 1H), 7.53 (m, 2H), 4.25−4.17 (m, 4H), 3.64 (d, J_{AB} = 16.9 Hz, 1H), 3.59 (d, J_{AB} = 16.8 Hz, 1H), 3.44−3.40 (m, 2H), 3.34−3.29 (m, 1H), 2.94−2.86 (m, 1H), 1.30 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 171.5, 167.5, 134.5, 131.5, 130.9, 129.3, 127.1, 126.5, 125.7, 124.7, 123.7, 98.9, 60.7, 60.2, 32.3, 29.7, 14.3, 14.2; ^{19}F NMR ($CDCl_3$, 282 MHz) δ = −75.1; IR (film, cm^{-1}) 2982, 2934, 1738, 1712, 1653, 1463, 1369, 1311, 1178, 1129, 1098, 1078, 1049, 962, 803, 777; HRMS (MALDI) m/z calcd for $C_{23}H_{23}F_3O_5Na$ [M + Na]$^+$ 459.1390, found 459.1395.

*Data for (E)-ethyl 2-(5-phenyl-5-(trifluoromethyl)dihydrofuran-2(3H)-ylidene)acetate (**3aa**):* 6 mg, 21% yield; R_f = 0.4 (petroleum ether/ethyl acetate, 80/20); viscous, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.53 (m, 2H), 7.44 (m, 3H), 5.63 (m, 1H), 4.18 (q, J = 7.0 Hz, 2H), 3.37 (m, 1H), 3.15 (m, 1H), 2.88 (m, 1H), 2.53 (m, 1H), 1.30 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 173.7, 135.5, 129.3, 128.5, 126.3, 92.4, 59.6, 31.7, 29.4, 14.2; ^{19}F NMR ($CDCl_3$, 282 MHz) δ = −72.7; IR (film, cm^{-1}) 3027, 2939, 1718, 1653, 1621, 1481, 1387, 1345, 1261, 1129, 1035, 1001, 956, 821; HRMS (MALDI) m/z calcd for $C_{15}H_{15}F_3O_3Na$ [M + Na]$^+$ 323.0871, found 323.0873.

*Data for (Z)-ethyl 2-(5-phenyl-5-(trifluoromethyl)dihydrofuran-2(3H)-ylidene)acetate (**3aa′**):* 5 mg, 17% yield; R_f = 0.25 (petroleum ether/ethyl acetate, 80/20); viscous, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.60 (m, 2H), 7.41 (m, 3H), 4.98 (m, 1H), 4.21 (q, J = 7.0 Hz, 2H), 2.99 (m, 1H), 2.83 (m, 1H), 2.73 (m, 1H), 2.43 (m, 1H), 1.32 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 165.2, 135.6, 129.3, 128.5, 126.5, 91.2, 59.6, 30.7, 29.7, 14.4; ^{19}F NMR ($CDCl_3$, 282 MHz) δ = −73.1; IR (film, cm^{-1}) 3031, 2899, 1724, 1619, 1601, 1487, 1347, 1325, 1274, 1131, 1045, 1015, 959, 764; HRMS (MALDI) m/z calcd for $C_{15}H_{15}F_3O_3Na$ [M + Na]$^+$ 323.0871, found 323.0875.

*Data for (2E,4E)-ethyl 7,7,7-trifluoro-6-hydroxy-6-phenylhepta-2,4-dienoate (**4aa**):* 7 mg, 24% yield; R_f = 0.3 (petroleum ether/ethyl acetate, 80/20); viscous, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.58−7.56 (m, 2H), 7.41−7.37 (m, 3H), 7.30 (dd, J = 15.6, 5.0 Hz, 1H), 6.64 (dd, J = 15.2, 10.3 Hz, 1H), 6.56 (d, J = 15.5 Hz, 1H), 5.96 (d, J = 15.3 Hz, 1H), 4.20 (q, J = 7.0 Hz, 2H), 3.04 (br, 1H), 1.29 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 166.5, 142.3, 137.5, 136.7, 130.8, 129.1, 128.6, 126.6, 126.1, 124.3, 60.6, 14.2; ^{19}F NMR ($CDCl_3$, 282 MHz) δ = −76.3; IR (film, cm^{-1}) 3427, 2984, 1698, 1645, 1619, 1451, 1370, 1305, 1241, 1166, 1077, 1001, 941, 706; HRMS (MALDI) m/z calcd for $C_{15}H_{15}F_3O_3Na$ [M + Na]$^+$ 323.0871, found 323.0875. Data for the chiral product from the catalysis of phosphine **5i**: yield 50%; enantiometric excess 26%; HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 90/10, flow rate 0.70 mL/min) t_{major} = 19.7 min, t_{minor} = 12.3 min, λ = 254 nm.

*trans-(E)-Diethyl 2-(4-Methyl-5-phenyl-5-(trifluoromethyl)-dihydrofuran-2(3H)-ylidene)succinate (**3ac**).* The diastereoisomers were separable by silica gel chromatography, which could be discriminated by ^{1}H NMR data. The diagnostic feature is the chemical shift differences of the methyl group caused by the shielding effect of the adjacent phenyl group. Data for **3ac**: 15 mg, 38% yield; R_f = 0.35 (petroleum ether/ethyl acetate, 80/20); viscous, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45−7.43 (m, 5H), 4.22 (q, J = 7.3 Hz, 2H), 4.20 (q, J = 7.0 Hz, 2H), 3.65−3.49 (m, 3H), 3.13−3.04 (m, 1H), 2.86 (dd, J = 18.1, 6.3 Hz, 1H), 1.30 (m, 6H), 0.86 (d, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 171.6, 169.2, 167.6, 132.4, 129.0, 128.4, 126.4, 126.3, 123.6, 99.2, 91.1 (q, J_{C-F} = 30.1 Hz), 60.6, 60.2, 38.6, 36.7, 31.9, 17.3, 14.3, 14.2; ^{19}F NMR ($CDCl_3$, 282 MHz) δ = −76.6; IR (film, cm^{-1}) 2982, 2936, 1739, 1712, 1657, 1450, 1369, 1314, 1298, 1178, 1101, 1071, 1051, 934, 729; HRMS (MALDI) m/z calcd for $C_{20}H_{23}F_3O_5Na$ [M + Na]$^+$ 423.1395, found 423.1390.

*Data for cis-(E)-diethyl 2-(4-methyl-5-phenyl-5-(trifluoromethyl)-dihydrofuran-2(3H)-ylidene)succinate (**3ac′**):* 12 mg, 31% yield; R_f = 0.33 (petroleum ether/ethyl acetate, 80/20); viscous, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58−7.56 (m, 2H), 7.44−7.42 (m, 3H), 4.20 (m, 4H), 3.60−3.46 (m, 3H), 3.07−2.98 (m, 1H), 2.93−2.85 (m, 1H), 1.53 (dd, J = 7.1, 1.8 Hz, 3H), 1.30 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 171.6, 168.8, 167.5, 136.5, 129.1, 128.5, 125.7, 99.0, 60.6, 60.2, 42.0, 39.2, 31.9, 15.4, 14.3, 14.2; ^{19}F NMR ($CDCl_3$, 282 MHz) δ = −73.4; IR (film, cm^{-1}) 2983, 2937, 1739, 1712, 1657, 1369, 1312, 1168, 1111, 1052, 1029, 724, 699; HRMS (MALDI) m/z calcd for $C_{20}H_{23}F_3O_5Na$ [M + Na]$^+$ 423.1395, found 423.1390.

*Data for (E)-diethyl 2-(5-(4-(methylthio)phenyl)-5-(trifluoromethyl)dihydrofuran-2(3H)-ylidene)succinate (**3l**):* 28 mg, 64% yield; R_f = 0.35 (petroleum ether/ethyl acetate, 80/20); viscous, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 8.5 Hz, 2H), 4.17 (q, J = 7.0 Hz, 4H), 3.53 (d, J_{AB} = 16.8 Hz, 1H), 3.48 (d, J_{AB} = 16.9 Hz, 1H), 3.42−3.33 (m, 1H), 3.20−3.11 (m, 1H), 2.87−2.80 (m, 1H), 2.49 (m, 4H), 1.27 (t, J = 7.3 Hz, 3H), 1.26 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 171.6, 169.7, 167.4, 140.5, 131.9, 126.7, 126.1, 124.3 (q, J_{C-F} = 285 Hz), 99.2, 88.6 (q, J_{C-F} = 30.1 Hz), 60.6, 60.2, 32.0, 30.1, 29.7, 15.4, 14.3, 14.2; ^{19}F NMR ($CDCl_3$, 282 MHz) δ = −79.6; IR (film, cm^{-1}) 2982, 2935, 1740, 1713, 1653, 1514, 1300, 1252, 1172, 1118, 1047, 898, 834, 808; HRMS (MALDI) m/z calcd for $C_{20}H_{23}F_3O_5SNa$ [M + Na]$^+$ 455.1116, found 455.1111.

*Data for diethyl 2-(5-(4-(methylthio)phenyl)-5-(trifluoromethyl)-4,5-dihydrofuran-2-yl)succinate (**3l′**):* 12 mg, 28% yield; R_f = 0.38 (petroleum ether/ethyl acetate, 80/20); dr = 1.18/1, the mixture of diastereoisomers was unseparable by column chromatography; viscous, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41−7.38 (m, 2H), 7.27−7.24 (m, 2H), 4.85 (m, 1H), 4.21−4.13 (m, 4H), 3.84−3.81 (m, 1H), 3.38 (dd, J = 16.8, 7.0 Hz, 1H), 3.09−2.98 (m, 2H), 2.71 (ddd, J = 16.8, 9.3, 5.5 Hz, 1H), 2.49 (s, 3H), 1.27−1.24 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 171.1, 170.2, 139.8, 134.4, 126.8, 126.7, 126.1, 96.7, 96.5, 61.6, 61.5, 60.9, 41.0, 40.9, 39.5, 34.3, 34.1, 29.7, 15.5, 14.1, 14.0; ^{19}F NMR ($CDCl_3$, 282 MHz) δ = −81.9, −82.0; IR (film, cm^{-1}) 2983, 2928, 1740, 1599, 1495, 1446, 1373, 1306, 1253, 1165, 1069, 1030, 863, 818, 736, 688; HRMS (MALDI) m/z calcd for $C_{20}H_{23}F_3O_5SNa$ [M + Na]$^+$ 455.1116, found 455.1111.

*Data for (E)-diethyl 2-(5-(ethoxycarbonyl)-5-phenyldihydrofuran-2(3H)-ylidene)succinate (**3ab**):* 20 mg, 51% yield; R_f = 0.34 (petroleum ether/ethyl acetate, 80/20); viscous, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.48 (m, 2H), 7.35 (m, 3H), 4.17 (q, J = 7.1 Hz, 6H), 3.58 (d, J_{AB} = 16.8 Hz, 1H), 3.51 (d, J_{AB} = 16.8 Hz, 1H), 3.22 (m, 1H), 3.16 (m, 1H), 2.97 (m, 1H), 2.38 (dt, J = 12.6, 8.5 Hz, 1H), 1.26 (m, 6H), 1.21 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 171.9, 170.7, 170.2, 167.8, 138.6, 128.5, 128.4, 125.1, 98.3, 90.6, 62.1, 60.5, 60.0, 35.4, 32.0, 30.3, 14.4, 14.3, 13.9; IR (film, cm^{-1}) 2981, 2932, 2854, 1736, 1650, 1449, 1368, 1304, 1259, 1176, 1094, 1058, 887, 860, 781; HRMS (MALDI) m/z calcd for $C_{21}H_{26}O_7Na$ [M + Na]$^+$ 413.1576, found 413.1558. Data for the chiral product: enantiometric excess 48%; HPLC analysis (Chiralpak AD-H column, hexane/*i*-PrOH, 90/10, flow rate 0.60 mL/min) t_{major} = 15.5 min, t_{minor} = 14.4 min, λ = 254 nm.

*Data for (E)-ethyl 5-(3-cyano-1-ethoxy-1-oxopropan-2-ylidene)-2-phenyltetrahydrofuran-2-carboxylate (**3ad**):* 26 mg, 75% yield; R_f = 0.34 (petroleum ether/ethyl acetate, 80/20); viscous, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55 (m, 2H), 7.42 (m, 3H), 4.25 (m, 4H), 3.61 (d, J_{AB} = 16.8 Hz, 1H), 3.58 (d, J_{AB} = 16.8 Hz, 1H), 3.29 (m, 1H), 3.16 (m, 1H), 3.03 (m, 1H), 2.47 (dt, J = 12.5, 9.1 Hz, 1H), 1.35 (t, J = 7.0 Hz, 3H), 1.21 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 171.9, 170.3, 166.3, 137.8, 128.8, 128.7, 125.1, 118.3, 94.6, 91.6, 62.4, 60.7, 35.1, 30.8, 29.7, 15.0, 14.4, 13.9; IR (film, cm^{-1}) 2998, 2936, 2812, 2230, 1741, 1622, 1519, 1327, 1291, 1252, 1186, 1095, 1027, 897, 856, 763; HRMS (MALDI) m/z calcd for $C_{19}H_{21}O_5NNa$ [M + Na]$^+$ 366.1317, found 366.1313. Data for the chiral product: enantiometric excess 52%; HPLC analysis (Chiralpak OD column and AD-H column in series, hexane/*i*-PrOH, 90/10, flow rate 0.50 mL/min) t_{major} = 41.4 min, t_{minor} = 39.7 min, λ = 254 nm.

General Procedure for the Tributylphosphine-Catalyzed Alkenylations. *Conditions at rt.* To a stirred solution of trifluoromethyl ketone **1** (0.1 mmol) and bis-substituted allenoate **2b** (0.12 mmol) in CH_2Cl_2 (2 mL) was added tributylphosphine (0.015 mmol) via a microsyringe in one portion. Then the resulting mixture was vigorously stirred at rt and monitored by TLC. After the reaction was complete, the mixture was directly purified by column

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chromatography on silica gel (petroleum ether/ethyl acetate (10/1) as the eluent) to furnish the corresponding product.

Conditions at 60 °C. The solution of trifluoromethyl ketone **1** (0.1 mmol) in toluene (2 mL) was warmed to 60 °C before the bis-substituted allenoate **2b** (0.12 mmol) and tributylphosphine (0.015 mmol) were added sequentially via a microsyringe in one portion. Then the resulting mixture was vigorously stirred at 60 °C and monitored by TLC. After the reaction was complete, the mixture was allowed to cool to rt and directly purified by column chromatography on silica gel (petroleum ether/ethyl acetate (10/1) as the eluent) to furnish the corresponding product.

*Data for (E)-diethyl 2-((E)-5,5,5-trifluoro-4-hydroxy-4-phenylpent-2-en-1-ylidene)succinate (**4a**):* mixture of *E,E/Z,E* isomers (major and minor), *E,E/Z,E* = 7/1; 35 mg, 90% yield; R_f = 0.3 (petroleum ether/ethyl acetate, 80/20); viscous, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.66 (dd, *J* = 15.6, 11.3 Hz, 1H; minor, CH═C*H*CH), 7.60 (m, 2H; both isomers, Ar*H*), 7.45−7.44 (m, 1H; major, CH═CHC*H*), 7.43−7.40 (m, 3H; both isomers, Ar*H*), 6.84 (dd, *J* = 15.1, 11.3 Hz, 1H; major, CH═C*H*CH), 6.66 (d, *J* = 15.0 Hz, 1H; major, C*H*═CHCH), 6.57 (d, *J* = 11.0 Hz, 1H; minor, CH═CHC*H*), 6.46 (d, *J* = 15.6 Hz, 1H; minor, C*H*═CHCH), 4.28−4.22 (m, 2H; both isomers, $CH_2CO_2CH_2CH_3$), 4.17−4.11 (m, 2H; both isomers, OCH_2CH_3), 3.46 (s, 2H; major, CH_2CO), 3.36 (s, 2H; minor, CH_2CO), 3.33 (s, 1H; major, O*H*), 3.23 (s, 1H; minor, O*H*), 1.34−1.30 (t, *J* = 7.0 Hz, 3H; both isomers, $CH_2CO_2CH_2CH_3$), 1.26−1.23 (t, *J* = 7.3 Hz, 3H; both isomers, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 170.5, 166.9, 138.6, 138.4, 138.3, 136.9, 136.8, 129.0, 128.8, 128.5, 128.4, 127.4, 126.6, 61.2, 61.1, 32.7, 14.2, 14.1 (additional peaks and line broadenings are observed due to diastereoisomers); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = −78.8 (minor), −78.9 (major); IR (film, cm^{-1}) 3441, 2985, 2940, 1714, 1644, 1614, 1450, 1371, 1162, 1028, 1004, 979, 769, 710; HRMS (ESI) *m/z* calcd for $C_{19}H_{21}F_3O_5Na$ [M + Na]$^+$ 409.1239, found 409.1231.

*Data for (E)-diethyl 2-((E)-4-(4-bromophenyl)-5,5,5-trifluoro-4-hydroxypent-2-en-1-ylidene)succinate (**4b**):* mixture of *E,E/Z,E* isomers (major and minor), *E,E/Z,E* = 2/1; 40 mg, 86% yield; R_f = 0.3 (petroleum ether/ethyl acetate, 80/20); viscous, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.63 (dd, *J* = 15.6, 11.3 Hz, 1H; minor, CH═C**H**CH), 7.54 (d, *J* = 8.7 Hz, 2H; both isomers, Ar*H*), 7.47 (d, *J* = 8.6 Hz, 2H; both isomers, Ar*H*), 7.42 (d, *J* = 11.3 Hz, 1H; major, CH═CHC*H*), 6.82 (dd, *J* = 15.1, 11.3 Hz, 1H; major, CH═C*H*CH), 6.61 (d, *J* = 15.2 Hz, 1H; major, C*H*═CHCH), 6.56 (d, *J* = 11.0 Hz, 1H; minor, CH═CHC*H*), 6.41 (d, *J* = 15.6 Hz, 1H; minor, C*H*═CHCH), 4.28−4.22 (m, 2H; both isomers, $CH_2CO_2CH_2CH_3$), 4.17−4.11 (m, 2H; both isomers, OCH_2CH_3), 3.46 (s, 2H; major, CH_2CO), 3.35 (s, 2H; minor, CH_2CO), 1.34−1.30 (t, *J* = 7.0 Hz, 3H; both isomers, $CH_2CO_2CH_2CH_3$), 1.26−1.22 (t, *J* = 7.3 Hz, 3H; both isomers, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 170.9, 170.5, 166.8, 165.9, 140.2, 138.5, 137.8, 136.7, 135.9, 131.6, 131.5, 129.8, 128.6, 128.5, 127.8, 127.6, 127.1, 125.9, 123.4, 123.2, 61.3, 61.2, 61.1, 40.2, 32.7, 29.7, 14.2, 14.1, 14.0; ^{19}F NMR ($CDCl_3$, 282 MHz) δ = −79.6 (major), −79.7 (minor); IR (film, cm^{-1}) 3425 (br), 2985, 2936, 1713, 1645, 1466, 1371, 1095, 1029, 978, 901, 853, 714; HRMS (ESI) *m/z* calcd for $C_{19}H_{20}BrF_3O_5Na$ [M + Na]$^+$ 487.0344, found 487.0339.

*Data for (E)-diethyl 2-((E)-5,5,5-trifluoro-4-(4-fluorophenyl)-4-hydroxypent-2-en-1-ylidene)succinate (**4c**):* mixture of *E,E/Z,E* isomers (major and minor), *E,E/Z,E* = 2.3/1; 36 mg, 88% yield; R_f = 0.3 (petroleum ether/ethyl acetate, 80/20); viscous, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.63 (dd, *J* = 15.5, 11.0 Hz, 1H; minor, CH═C*H*CH), 7.58 (m, 2H; both isomers, Ar*H*), 7.43 (d, *J* = 11.6 Hz, 1H; major, CH═CHC*H*), 7.09 (m, 2H; both isomers, Ar*H*), 6.82 (dd, *J* = 15.1, 11.3 Hz, 1H; major, CH═C*H*CH), 6.63 (d, *J* = 15.1 Hz, 1H; major, C*H*═CHCH), 6.57 (d, *J* = 11.1 Hz, 1H; minor, CH═CHC*H*), 6.43 (d, *J* = 15.5 Hz, 1H; minor, C*H*═CHCH), 4.28−4.23 (m, 2H; both isomers, $CH_2CO_2CH_2CH_3$), 4.16−4.11 (m, 2H; both isomers, OCH_2CH_3), 3.69 (br, 1H; major, O*H*), 3.53 (br, 1H; minor, O*H*), 3.46 (s, 2H; major, CH_2CO), 3.36 (s, 2H; minor, CH_2CO), 1.34−1.30 (t, *J* = 7.0 Hz, 3H; both isomers, $CH_2CO_2CH_2CH_3$), 1.26−1.22 (t, *J* = 7.3 Hz, 3H; both isomers, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 170.9, 170.6, 166.8, 165.9, 164.2, 161.8, 140.4, 138.5, 138.1, 137.1, 132.7, 129.6, 128.8, 128.7, 127.6, 127.4, 126.9, 115.5, 115.4, 115.3, 115.2, 61.3, 61.2, 61.1, 60.0, 40.2, 32.7, 29.7, 14.2, 14.1, 14.0; ^{19}F NMR ($CDCl_3$, 282 MHz) δ = −79.0 (CF_3, minor), −79.1 (CF_3, major), −113.2 (ArF, major), −113.6 (ArF, minor); IR (film, cm^{-1}) 3440 (br), 2985, 2936, 1714, 1645, 1604, 1466, 1447, 1371, 1240, 1179, 1096, 1029, 839, 731; HRMS (ESI) *m/z* calcd for $C_{19}H_{20}F_4O_5Na$ [M + Na]$^+$ 427.1145, found 427.1141.

*Data for (E)-diethyl 2-((E)-4-(4-chlorophenyl)-5,5,5-trifluoro-4-hydroxypent-2-en-1-ylidene)succinate (**4d**):* mixture of *E,E/Z,E* isomers (major and minor), *E,E/Z,E* = 2.2/1; 33 mg, 80% yield; R_f = 0.3 (petroleum ether/ethyl acetate, 80/20); viscous, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.63 (dd, *J* = 15.6, 11.3 Hz, 1H; minor, CH═C*H*CH), 7.54 (m, 2H; both isomers, Ar*H*), 7.42 (d, *J* = 11.5 Hz, 1H; major, CH═CHC*H*), 7.38 (m, 2H; both isomers, Ar*H*), 6.82 (dd, *J* = 15.1, 11.3 Hz, 1H; major, CH═C*H*CH), 6.62 (d, *J* = 15.3 Hz, 1H; major, C*H*═CHCH), 6.56 (d, *J* = 11.1 Hz, 1H; minor, CH═CHC*H*), 6.42 (d, *J* = 15.6 Hz, 1H; minor, C*H*═CHCH), 4.28−4.23 (m, 2H; both isomers, $CH_2CO_2CH_2CH_3$), 4.16−4.11 (m, 2H; both isomers, OCH_2CH_3), 3.46 (s, 2H; major, CH_2CO), 3.35 (s, 2H; minor, CH_2CO), 1.34−1.30 (t, *J* = 7.2 Hz, 3H; both isomers, $CH_2CO_2CH_2CH_3$), 1.26−1.22 (t, *J* = 7.0 Hz, 3H; both isomers, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 170.9, 170.6, 166.8, 165.9, 140.3, 138.5, 137.8, 136.8, 135.5, 135.4, 135.2, 135.0, 129.7, 128.8, 128.6, 128.5, 128.2, 127.8, 127.6, 127.0, 126.0, 123.1, 61.3, 61.2, 61.1, 40.2, 32.7, 29.7, 14.2, 14.1, 14.0, 13.9; ^{19}F NMR ($CDCl_3$, 282 MHz) δ = −79.0 (minor), −79.1 (major); IR (film, cm^{-1}) 3437 (br), 2984, 2937, 1713, 1645, 1498, 1371, 1241, 1162, 1097, 1029, 979, 932, 830, 732; HRMS (ESI) *m/z* calcd for $C_{19}H_{20}ClF_3O_5Na$ [M + Na]$^+$ 443.0849, found 443.0843.

*Data for (E)-diethyl 2-((E)-5,5,5-trifluoro-4-hydroxy-4-(4-methoxyphenyl)pent-2-en-1-ylidene)succinate (**4e**):* mixture of *E,E/Z,E* isomers (major and minor), *E,E/Z,E* = 6/1; 37 mg, 88% yield; R_f = 0.28 (petroleum ether/ethyl acetate, 80/20); viscous, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 (dd, *J* = 15.6, 11.3 Hz, 1H; minor, CH═C*H*CH), 7.51 (d, *J* = 8.8 Hz, 2H; both isomers, Ar*H*), 7.44 (d, *J* = 11.3 Hz, 1H; major, CH═CHC*H*), 6.94 (d, *J* = 9.0 Hz, 2H; both isomers, Ar*H*), 6.84 (dd, *J* = 15.1, 11.3 Hz, 1H; major, CH═C*H*CH), 6.64 (d, *J* = 15.1 Hz, 1H; major, C*H*═CHCH), 6.57 (d, *J* = 11.0 Hz, 1H; minor, CH═CHC*H*), 6.44 (d, *J* = 15.5 Hz, 1H; minor, C*H*═CHCH), 4.26 (q, *J* = 7.0 Hz, 2H; both isomers, $CH_2CO_2CH_2CH_3$), 4.14 (q, *J* = 7.1 Hz, 2H; both isomers, OCH_2CH_3), 3.84 (s, 3H; major, OCH_3), 3.47 (s, 2H; major, CH_2CO), 3.36 (s, 2H; minor, CH_2CO), 3.33 (br, 1H; major, O*H*), 1.33 (t, *J* = 7.0 Hz, 3H; both isomers, $CH_2CO_2CH_2CH_3$), 1.25 (t, *J* = 7.0 Hz, 3H; both isomers, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 170.5, 166.9, 160.0, 138.7, 138.5, 128.9, 128.0, 127.2, 127.1, 113.9, 113.8, 61.2, 61.1, 55.3, 32.7, 29.7, 14.2, 14.1 (additional peaks and line broadenings are observed due to diastereoisomers); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = −78.9 (minor), −79.0 (major); IR (film, cm^{-1}) 3443 (br), 2983, 2937, 2842, 1714, 1644, 1611, 1514, 1465, 1371, 1254, 1160, 1031, 1000, 979, 834, 736; HRMS (ESI) *m/z* calcd for $C_{20}H_{23}F_3O_6Na$ [M + Na]$^+$ 439.1344, found 439.1341.

*Data for (E)-diethyl 2-((E)-5,5,5-trifluoro-4-hydroxy-4-(3-methoxyphenyl)pent-2-en-1-ylidene)succinate (**4f**):* mixture of *E,E/Z,E* isomers (major and minor), *E,E/Z,E* = 6/1; 39 mg, 93% yield; R_f = 0.28 (petroleum ether/ethyl acetate, 80/20); viscous, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 (dd, *J* = 15.5, 11.0 Hz, 1H; minor, CH═C*H*CH), 7.42 (d, *J* = 11.5 Hz, 1H; major, CH═CHC*H*), 7.33 (m, 1H; both isomers, Ar*H*), 7.17 (m, 2H; both isomers, Ar*H*), 6.93 (dd, *J* = 8.0, 2.3 Hz, 1H; both isomers, Ar*H*), 6.84 (dd, *J* = 15.3, 11.6 Hz, 1H; major, CH═C*H*CH), 6.63 (d, *J* = 15.3 Hz, 1H; major, C*H*═CHCH), 6.56 (d, *J* = 11.0 Hz, 1H; minor, CH═CHC*H*), 6.43 (d, *J* = 15.6 Hz, 1H; minor, C*H*═CHCH), 4.25 (q, *J* = 7.0 Hz, 2H; both isomers, $CH_2CO_2CH_2CH_3$), 4.13 (q, *J* = 7.1 Hz, 2H; both isomers, OCH_2CH_3), 3.84 (s, 3H; major, OCH_3), 3.59 (br, 1H; major, O*H*), 3.46 (s, 2H; major, CH_2CO), 3.35 (s, 2H; minor, CH_2CO), 1.32 (t, *J* = 7.0 Hz, 3H; both isomers, $CH_2CO_2CH_2CH_3$), 1.24 (t, *J* = 7.0 Hz, 3H; both isomers, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 170.6, 166.9, 159.7, 138.7, 138.4, 138.3, 129.5, 127.3, 127.2, 118.9, 114.2, 112.7, 61.2, 61.1, 55.3, 32.7, 29.7, 14.2, 14.0 (additional peaks and line

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broadenings are observed due to diastereoisomers); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = −78.6 (minor), −78.7 (major); IR (film, cm^{-1}) 3444 (br), 2984, 2939, 2839, 1730, 1713, 1644, 1604, 1491, 1466, 1370, 1241, 1085, 1031, 979, 853, 785, 721; HRMS (ESI) m/z calcd for $C_{20}H_{23}F_3O_6Na$ [M + Na]$^+$ 439.1344, found 439.1339.

*Data for (E)-diethyl 2-((E)-4-(4-ethoxyphenyl)-5,5,5-trifluoro-4-hydroxypent-2-en-1-ylidene)succinate (**4g**):* mixture of *E,E/Z,E* isomers (major and minor), *E,E/Z,E* = 6.5/1; 35 mg, 83% yield; R_f = 0.3 (petroleum ether/ethyl acetate, 80/20); viscous, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 (dd, *J* = 15.6, 11.1 Hz, 1H; minor, CH=C*H*CH), 7.33 (d, *J* = 8.8 Hz, 2H; both isomers, Ar*H*), 7.43 (d, *J* = 11.3 Hz, 1H; major, CH=CHC*H*), 6.91 (d, *J* = 8.8 Hz, 2H; both isomers, Ar*H*), 6.84 (dd, *J* = 15.3, 11.6 Hz, 1H; major, CH=C*H*CH), 6.63 (d, *J* = 15.0 Hz, 1H; major, C*H*=CHCH), 6.58 (d, *J* = 11.3 Hz, 1H; minor, CH=CHC*H*), 6.43 (d, *J* = 15.5 Hz, 1H; minor, C*H*=CHCH), 4.25 (q, *J* = 7.0 Hz, 2H; both isomers, $CH_2CO_2CH_2CH_3$), 4.15 (q, *J* = 7.3 Hz, 2H; both isomers, OCH_2CH_3), 4.06 (q, *J* = 7.1 Hz, 2H; both isomers, $ArOCH_2CH_3$), 3.46 (s, 2H; major, CH_2CO), 3.35 (s, 2H; minor, CH_2CO), 1.44 (t, *J* = 7.0 Hz, 3H; both isomers, $ArOCH_2CH_3$), 1.32 (t, *J* = 7.0 Hz, 3H; both isomers, $CH_2CO_2CH_2CH_3$), 1.24 (t, *J* = 7.3 Hz, 3H; both isomers, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 170.6, 166.9, 159.4, 138.8, 138.6, 137.6, 128.7, 128.0, 127.2, 127.1, 126.2, 123.4, 114.4, 63.5, 61.2, 61.1, 32.7, 29.7, 14.7, 14.2, 14.0 (additional peaks and line broadenings are observed due to diastereoisomers); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = −78.9 (minor), −79.0 (major); IR (film, cm^{-1}) 3449, 2983, 2936, 1731, 1716, 1643, 1611, 1512, 1393, 1297, 1242, 1154, 1117, 1031, 1000, 924, 837; HRMS (ESI) m/z calcd for $C_{21}H_{25}F_3O_6Na$ [M + Na]$^+$ 453.1501, found 453.1496.

*Data for (E)-diethyl 2-((E)-4-(4-ethylphenyl)-5,5,5-trifluoro-4-hydroxypent-2-en-1-ylidene)succinate (**4h**):* mixture of *E,E/Z,E* isomers (major and minor), *E,E/Z,E* = 6.5/1; 36 mg, 88% yield; R_f = 0.3 (petroleum ether/ethyl acetate, 80/20); viscous, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 (dd, *J* = 15.5, 11.3 Hz, 1H; minor, CH=C*H*CH), 7.50 (d, *J* = 8.0 Hz, 2H; both isomers, Ar*H*), 7.44 (d, *J* = 11.3 Hz, 1H; major, CH=CHC*H*), 7.25 (d, *J* = 8.2 Hz, 2H; both isomers, Ar*H*), 6.85 (dd, *J* = 15.1, 11.5 Hz, 1H; major, CH=C*H*CH), 6.65 (d, *J* = 15.1 Hz, 1H; major, C*H*=CHCH), 6.57 (d, *J* = 11.0 Hz, 1H; minor, CH=CHC*H*), 6.45 (d, *J* = 15.3 Hz, 1H; minor, C*H*=CHCH), 4.25 (q, *J* = 7.3 Hz, 2H; both isomers, $CH_2CO_2CH_2CH_3$), 4.14 (q, *J* = 7.1 Hz, 2H; both isomers, OCH_2CH_3), 3.47 (s, 2H; major, CH_2CO), 3.44 (br, 1H; major, O*H*), 3.35 (s, 2H; minor, CH_2CO), 3.31 (br, 1H; minor, O*H*), 2.68 (q, *J* = 7.5 Hz, 2H; both isomers, $ArCH_2CH_3$), 1.32 (t, *J* = 7.0 Hz, 3H; both isomers, $CH_2CO_2CH_2CH_3$), 1.28−1.23 (m, 6H; both isomers, and OCH_2CH_3 and $ArCH_2CH_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 170.5, 166.9, 145.2, 138.8, 138.6, 134.2, 128.0, 127.9, 127.1, 126.6, 124.8 (q, J_{C-F} = 286 Hz), 61.2, 61.1, 61.0, 60.9, 40.3, 32.7, 29.7, 28.4, 15.3, 14.2, 14.1, 14.0 (additional peaks and line broadenings are observed due to diastereoisomers); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = −78.7 (minor), −78.8 (major); IR (film, cm^{-1}) 3451, 2970, 2953, 2875, 1730, 1713, 1643, 1514, 1464, 1371, 1163, 1030, 1001, 933, 834, 777; HRMS (ESI) m/z calcd for $C_{21}H_{25}F_3O_5Na$ [M + Na]$^+$ 437.1552, found 437.1548.

*Data for (E)-diethyl 2-((E)-5,5,5-trifluoro-4-hydroxy-4-(p-tolyl)-pent-2-en-1-ylidene)succinate (**4i**):* mixture of *E,E/Z,E* isomers (major and minor), *E,E/Z,E* = 7/1; 34 mg, 84% yield; R_f = 0.3 (petroleum ether/ethyl acetate, 80/20); viscous, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 (dd, *J* = 15.6, 11.3 Hz, 1H; minor, CH=C*H*CH), 7.47 (d, *J* = 8.0 Hz, 2H; both isomers, Ar*H*), 7.43 (d, *J* = 11.3 Hz, 1H; major, CH=CHC*H*), 7.23 (d, *J* = 8.3 Hz, 2H; both isomers, Ar*H*), 6.84 (dd, *J* = 15.1, 11.6 Hz, 1H; major, CH=C*H*CH), 6.64 (d, *J* = 15.1 Hz, 1H; major, C*H*=CHCH), 6.57 (d, *J* = 11.3 Hz, 1H; minor, CH=CHC*H*), 6.44 (d, *J* = 15.5 Hz, 1H; minor, C*H*=CHCH), 4.25 (q, *J* = 7.0 Hz, 2H; both isomers, $CH_2CO_2CH_2CH_3$), 4.15 (q, *J* = 7.3 Hz, 2H; both isomers, OCH_2CH_3), 3.46 (s, 2H; major, CH_2CO), 3.35 (s, 2H; minor, CH_2CO), 3.27 (s, 1H; major, O*H*), 3.17 (s, 1H; minor, O*H*), 2.39 (s, 3H; both isomers, $ArCH_3$), 1.33 (t, *J* = 7.0 Hz, 3H; both isomers, $CH_2CO_2CH_2CH_3$), 1.25 (t, *J* = 7.0 Hz, 3H; both isomers, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 170.5, 166.9, 139.0, 138.7, 138.5, 133.9, 129.2, 129.1, 127.2, 126.5, 124.7 (q, J_{C-F} = 286 Hz), 61.2, 61.1, 40.3, 32.7, 29.7, 21.1, 14.2, 14.1, 14.0 (additional peaks and line broadenings are observed due to diastereoisomers); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = −78.8 (minor), −78.9 (major); IR (film, cm^{-1}) 3444 (br), 2984, 2930, 1730, 1644, 1613, 1514, 1447, 1371, 1158, 1029, 978, 932, 818; HRMS (ESI) m/z calcd for $C_{20}H_{23}F_3O_5Na$ [M + Na]$^+$ 423.1395, found 423.1392.

*Data for (E)-diethyl 2-((E)-5,5,5-trifluoro-4-hydroxy-4-(thiophene-2-yl)pent-2-en-1-ylidene)succinate (**4j**):* mixture of *E,E/Z,E* isomers (major and minor), *E,E/Z,E* = 3/1; 31 mg, 80% yield; R_f = 0.28 (petroleum ether/ethyl acetate, 80/20); viscous, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (dd, *J* = 15.5, 11.3 Hz, 1H; minor, CH=C*H*CH), 7.44 (d, *J* = 11.5 Hz, 1H; major, CH=CHC*H*), 7.38 (m, 1H; both isomers, Ar*H*), 7.21 (m, 1H; both isomers, Ar*H*), 7.06 (m, 1H; both isomers, Ar*H*), 6.92 (dd, *J* = 14.8, 11.6 Hz, 1H; major, CH=C*H*CH), 6.58 (d, *J* = 11.3 Hz, 1H; minor, CH=CHC*H*), 6.55 (d, *J* = 14.8 Hz, 1H; major, C*H*=CHCH), 6.37 (d, *J* = 15.3 Hz, 1H; minor, C*H*=CHCH), 4.25 (q, *J* = 7.0 Hz, 2H; both isomers, $CH_2CO_2CH_2CH_3$), 4.15 (q, *J* = 7.3 Hz, 2H; both isomers, OCH_2CH_3), 3.49 (s, 2H; major, CH_2CO), 3.36 (s, 2H; minor, CH_2CO), 1.33 (t, *J* = 7.0 Hz, 3H; both isomers, $CH_2CO_2CH_2CH_3$), 1.25 (t, *J* = 7.3 Hz, 3H; both isomers, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 171.0, 170.6, 166.9, 165.9, 140.5, 140.3, 140.1, 138.4, 136.9, 136.0, 129.6, 127.6, 127.2, 127.1, 126.9, 126.7, 126.6, 126.5, 126.6, 61.2, 61.1, 61.0, 40.3, 32.8, 29.7, 14.2, 14.1, 14.0 (additional peaks and line broadenings are observed due to diastereoisomers); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = −78.9 (minor), −79.0 (major); IR (film, cm^{-1}) 3434, 2983, 2935, 1714, 1645, 1489, 1371, 1240, 1162, 1077, 1028, 1010, 932, 823; HRMS (ESI) m/z calcd for $C_{17}H_{19}F_3O_5NaS$ [M + Na]$^+$ 415.0803, found 415.0803.

*Data for (E)-diethyl 2-((E)-5,5,5-trifluoro-4-hydroxy-4-(naphthalen-1-yl)pent-2-en-1-ylidene)succinate (**4k**):* mixture of *E,E/Z,E* isomers (major and minor), *E,E/Z,E* = 3/1; 31 mg, 70% yield; R_f = 0.28 (petroleum ether/ethyl acetate, 80/20); viscous, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.49−8.47 (m, 1H; both isomers, Ar*H*), 7.92−7.87 (m, 2H; both isomers, Ar*H*), 7.82−7.80 (m, 1H; both isomers, Ar*H*), 7.51−7.47 (m, 3H; both isomers, Ar*H*), 7.40 (d, *J* = 10.5 Hz, 1H; major, CH=CHC*H*), 6.73 (dd, *J* = 15.6, 10.8 Hz, 1H; major, CH=C*H*CH), 6.68 (d, *J* = 15.3 Hz, 1H; major, C*H*=CHCH), 6.55 (d, *J* = 11.3 Hz, 1H; minor, CH=CHC*H*), 6.50 (d, *J* = 15.8 Hz, 1H; minor, C*H*=CHCH), 4.22 (q, *J* = 7.0 Hz, 2H; major, $CH_2CO_2CH_2CH_3$), 4.14 (q, *J* = 7.0 Hz, 2H; minor, $CH_2CO_2CH_2CH_3$ and OCH_2CH_3), 4.05 (q, *J* = 7.0 Hz, 2H; major, OCH_2CH_3), 3.35 (s, 2H; major, CH_2CO), 3.31 (s, 2H; minor, CH_2CO), 1.30 (t, *J* = 7.3 Hz, 3H; both isomers, $CH_2CO_2CH_2CH_3$), 1.19 (t, *J* = 7.1 Hz, 3H; major, OCH_2CH_3), 1.10 (t, *J* = 7.0 Hz, 3H; minor, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 170.9, 170.3, 166.9, 166.0, 140.1, 139.2, 138.7, 137.9, 134.9, 132.4, 132.1, 131.1, 130.8, 130.6, 129.1, 129.0, 128.9, 127.3, 127.1, 126.1, 126.0, 125.8, 125.7, 124.5, 61.2, 61.0, 60.9, 40.2, 32.7, 29.7, 14.2, 14.0, 13.8 (additional peaks and line broadenings are observed due to diastereoisomers); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = −75.6 (minor), −75.8 (major); IR (film, cm^{-1}) 3431 (br), 2983, 2934, 1716, 1643, 1465, 1370, 1266, 1088, 1055, 1029, 978, 802; HRMS (ESI) m/z calcd for $C_{23}H_{23}F_3O_5Na$ [M + Na]$^+$ 459.1395, found 459.1395.

*Data for (E)-diethyl 2-((E)-5,5,5-trifluoro-4-hydroxy-4-(4-(methylthio)phenyl)pent-2-en-1-ylidene)succinate (**4l**):* mixture of *E,E/Z,E* isomers (major and minor), *E,E/Z,E* = 6/1; 34 mg, 82% yield; R_f = 0.3 (petroleum ether/ethyl acetate, 80/20); viscous, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.63 (dd, *J* = 15.5, 11.1 Hz, 1H; minor, CH=C*H*CH), 7.50 (d, J = 8.3 Hz, 2H; both isomers, Ar*H*), 7.43 (d, *J* = 11.3 Hz, 1H; major, CH=CHC*H*), 7.27 (d, *J* = 8.5 Hz, 2H; both isomers, Ar*H*), 6.83 (dd, *J* = 15.0, 11.3 Hz, 1H; major, CH=C*H*CH), 6.62 (d, *J* = 15.1 Hz, 1H; major, C*H*=CHCH), 6.56 (d, *J* = 11.1 Hz, 1H; minor, CH=CHC*H*), 6.42 (d, *J* = 15.5 Hz, 1H; minor, C*H*=CHCH), 4.25 (q, *J* = 7.0 Hz, 2H; both isomers, $CH_2CO_2CH_2CH_3$), 4.13 (q, *J* = 7.3 Hz, 2H; both isomers, OCH_2CH_3), 3.57 (br, 1H; major, O*H*), 3.46 (s, 2H; major, CH_2CO), 3.35 (s, 2H; minor, CH_2CO), 2.51 (s, 3H; major,

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ArSCH_3), 1.32 (t, J = 7.0 Hz, 3H; both isomers, $CH_2CO_2CH_2CH_3$), 1.24 (t, J = 7.3 Hz, 3H; both isomers, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 171.0, 170.6, 166.9, 166.0, 140.5, 140.1, 139.7, 138.7, 137.2, 133.4, 129.4, 127.4, 127.3, 127.1, 127.0, 126.1, 123.3, 61.2, 61.1, 61.0, 32.7, 29.7, 15.4, 14.7, 14.2, 14.0 (additional peaks and line broadenings are observed due to diastereoisomers); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = −78.8 (minor), −78.9 (major); IR (film, cm^{-1}) 3438, 2983, 2927, 1739, 1713, 1644, 1598, 1495, 1466, 1370, 1240, 1095, 979, 931, 819; HRMS (ESI) m/z calcd for $C_{20}H_{23}F_3O_5NaS$ $[M + Na]^+$ 455.1116, found 455.1111.

■ ASSOCIATED CONTENT

Supporting Information

Tables giving information on the screening of phosphine catalysts for the reaction of trifluoromethyl ketone and catalyst screening for asymmetric cycloaddition reaction and condition surveys for cycloaddition and dienylation reactions, ^{1}H NMR and ^{13}C NMR spectra for **3a**−**3l**, **3aa**, **3aa′**, **3ac**, **3ac′**, **3l′**, **3ab**, **3ad**, **4aa**, and **4a**−**4l**, and chiral HPLC spectra of **3a**, **3ab**, **3ad**, and **4aa**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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