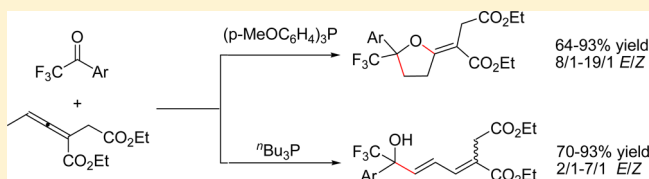


# Phosphine Catalyst-Controlled Cycloaddition or Dienylation Reactions of Trifluoromethyl Aryl Ketones with Bis-Substituted Allenates

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## S Supporting Information

**ABSTRACT:** A chemoselective phosphine-catalyzed cycloaddition or dienylation reaction between trifluoromethyl-substituted ketones and bis-substituted allenates 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<sub>3</sub>-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 allenates and carbonyl compounds.



## INTRODUCTION

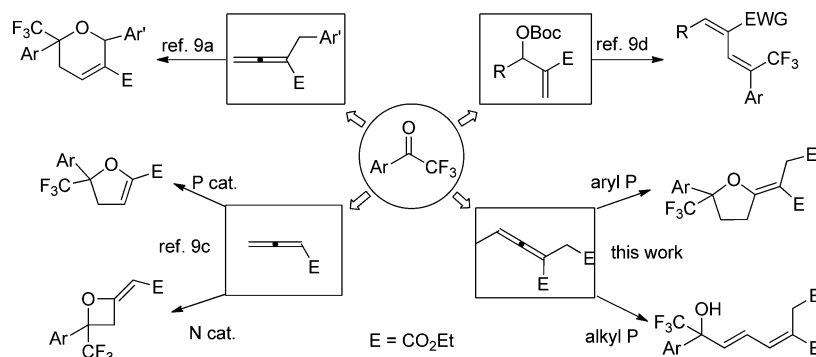
The trifluoromethyl-substituted quaternary carbon center is an important structural motif occurring in a range of pharmaceuticals and drug candidate molecules such as anti-HIV agent efavirenz,<sup>1a</sup> antimalarial agent dihydroartemisinin (DHA),<sup>1b</sup> and nonsteroidal selective glucocorticoid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

In 2009, He and co-workers<sup>10</sup> reported the [3 + 2] annulation between  $\gamma$ -substituted allenates and aromatic aldehyde,<sup>11,12</sup> 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<sup>13</sup> chemoselective cycloaddition or dienylation reaction between bis-substituted allenates and trifluoromethyl ketones. In this system, two skeletally different products, CF<sub>3</sub>-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  $\alpha$ -trifluoromethyl ketones also enables satisfying improvement in substrate generality and chemo- and stereoselectivity as compared with analogous examples.<sup>10a,c</sup>

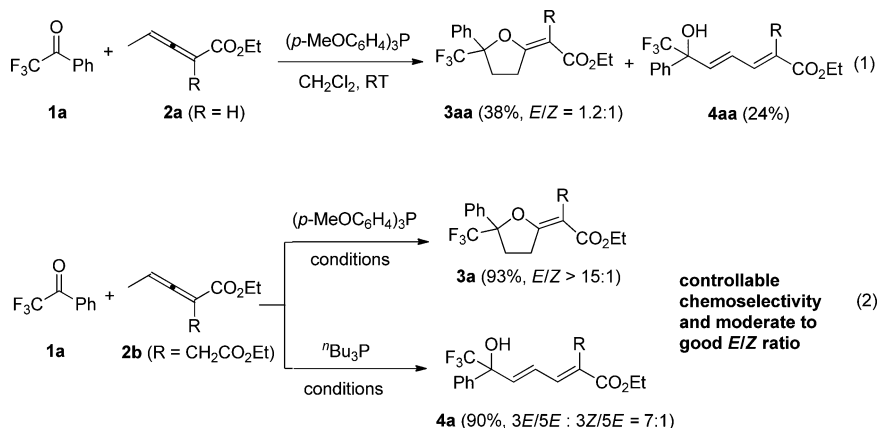
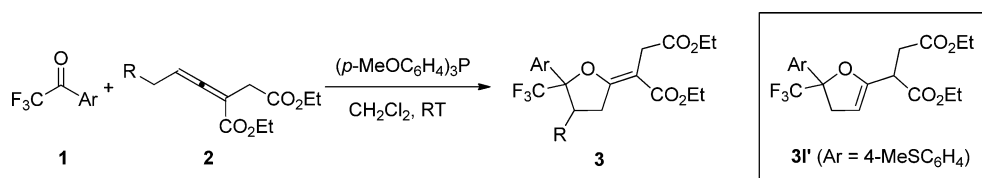
## RESULTS AND DISCUSSION

Initially,  $\gamma$ -methyl allenoate **2a** was reacted with CF<sub>3</sub>-substituted acetophenone **1a** in the presence of (*p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P, 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  $\alpha,\gamma$ -bis-substituted allenoate **2b** led to excellent chemo- and stereoselectivity: the use of (*p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P 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<sub>3</sub>-substituted dienyl tertiary alcohol **4a** with excellent chemo-

Received: July 12, 2013

Scheme 1. Nucleophilic Phosphine-Catalyzed Reactions of  $\alpha$ -Trifluoromethyl Ketones and Allenates or Their Surrogates

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

Table 1. Catalytic [3 + 2] Cycloadditions of Trifluoromethyl Aryl Ketones **1** with Allenates **2** Catalyzed by Tris(4-methoxyphenyl)phosphine<sup>a</sup>

entry	1, Ar	2, R	product	yield <sup>b</sup> (%)	E/Z <sup>c</sup>
1	1a, Ph	2b, H	3a	93	15/1
2	1b, 4-BrC <sub>6</sub> H <sub>4</sub>	2b, H	3b	83	12/1
3	1c, 4-FC <sub>6</sub> H <sub>4</sub>	2b, H	3c	90	11/1
4	1d, 4-ClC <sub>6</sub> H <sub>4</sub>	2b, H	3d	85	19/1
5	1e, 4-MeOC <sub>6</sub> H <sub>4</sub>	2b, H	3e	69	9/1
6	1f, 3-MeOC <sub>6</sub> H <sub>4</sub>	2b, H	3f	71	8/1
7	1g, 4-EtOC <sub>6</sub> H <sub>4</sub>	2b, H	3g	70	15/1
8	1h, 4-EtC <sub>6</sub> H <sub>4</sub>	2b, H	3h	64	9/1
9	1i, 4-MeC <sub>6</sub> H <sub>4</sub>	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 <sup>d</sup>	1a, Ph	2c, Me	3ac, 3ac'	69	19/1
13 <sup>e</sup>	1l, 4-MeSC <sub>6</sub> H <sub>4</sub>	2b, H	3l	64	8/1

<sup>a</sup>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<sub>2</sub>Cl<sub>2</sub> (1.0 mL) for 3 h at rt. <sup>b</sup>Yields of isolated *E* isomer. <sup>c</sup>Determined by <sup>1</sup>H NMR analysis of crude products. <sup>d</sup>The diastereoselectivity ratio of **3ac** and **3ac'** was determined as 56/44 by isolated yield. <sup>e</sup>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<sub>3</sub>P 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

reactions; see Kwon and He's reports<sup>7d,10a</sup>) was not detected, which may be ascribed to the steric hindrance of the CF<sub>3</sub> 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 allenolate **2b** and various aryl trifluoromethyl ketones proceeded smoothly to provide a range of synthetically valuable tetrahydrofurans containing a CF<sub>3</sub>-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  $\gamma$ -ethyl allenolate **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. Meanwhile, 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.

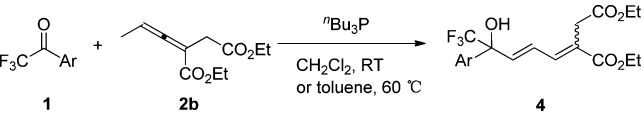
Subsequently, the scope of Bu<sub>3</sub>P-catalyzed dienylation reaction of trifluoromethyl ketone was tested, and the results are summarized in Table 2. The reaction provided facile access to CF<sub>3</sub>-substituted dienyl tertiary alcohols with generally high yields, which could also be a unique complement to the current strategies for accessing the diene motif of high synthetic

interest.<sup>14</sup> Different from the observation in the (*p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P catalysis, the Bu<sub>3</sub>P-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 substituents 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<sup>15</sup> via <sup>1</sup>H 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.

Recently, significant advances have been made in the applications of chiral phosphines for asymmetric allenolate reaction. However, the development of P-catalyzed enantioselective reactions involving carbonyl electrophiles or  $\gamma$ -substituted allenolate (in the case in which the  $\gamma$ -substituents participate in the reaction) has not been reported.<sup>16</sup> The stereocontrolled  $\delta$  addition of a phosphine–allenolate intermediate was still a challenging goal due to the remote distance between the chiral center of the catalyst and the  $\delta$  carbon of the allenolate. Herein we also performed some preliminary research on the enantioselective cycloaddition with activated ketones catalyzed by our previously developed chiral bifunctional phosphines (Scheme 3).<sup>17</sup> With the trifluoromethyl ketone **1a** in the presence of catalyst **5a**, the reaction with allenolates **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,  $\alpha$ -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 allenolate or its surrogate and carbonyl compounds. Moreover, the investigation of asymmetric catalysis revealed that the reaction pathway was also tunable by changing the  $\alpha$ -substituent patterns of  $\gamma$ -methyl allenolates (Scheme 3, eq 1). Notably, chemoselectivities in these asymmetric reactions were generally excellent with no byproducts detected.

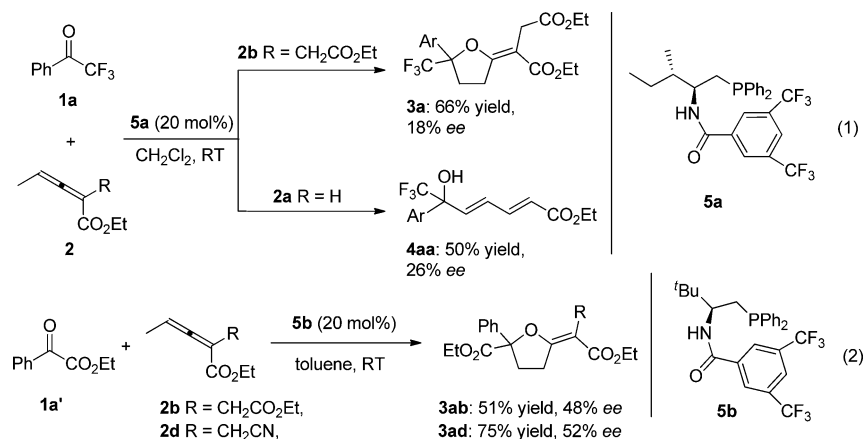
On the basis of previous reports<sup>18,10a</sup> and our own observation, a tentative mechanistic rationale for the chemoselective reaction is illustrated in Scheme 4. Upon the nucleophilic addition of phosphine, the allenolate is first converted to zwitterionic intermediate **A**, which undergoes 1,4-H 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,<sup>18d</sup> 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.<sup>18a</sup> Thus, in this case, together with steric factors, the open-chained

**Table 2. Catalytic Additions of Trifluoromethyl Aryl Ketones **1** with Allenolate **2b** Catalyzed by Tributylphosphine<sup>a</sup>**

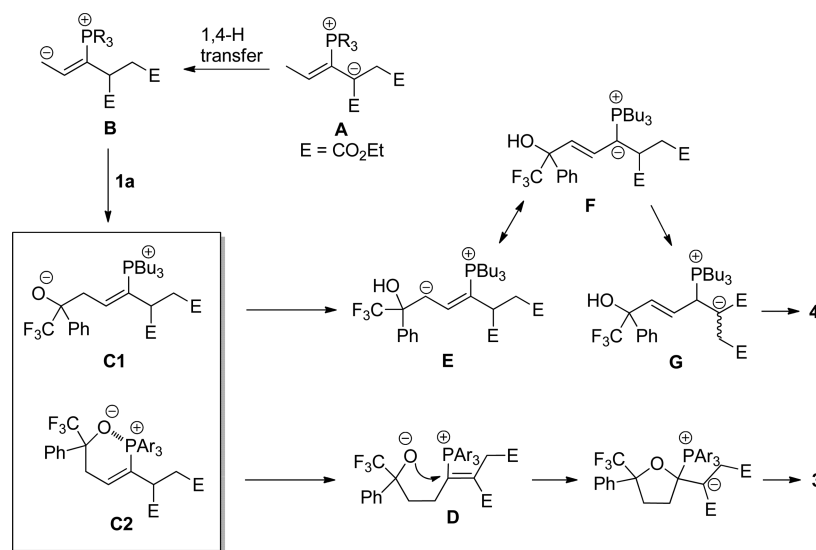


entry	<b>1</b> , Ar	<b>4</b>	yield of <b>4</b> <sup>b</sup> (%)	<i>E,E/Z,E</i> <sup>c</sup>	yield of <b>3</b> <sup>d</sup> (%)
1	<b>1a</b> , Ph	<b>4a</b>	90	7/1	5
2 <sup>e</sup>	<b>1b</b> , 4-BrC <sub>6</sub> H <sub>4</sub>	<b>4b</b>	86	2/1	10
3 <sup>e</sup>	<b>1c</b> , 4-FC <sub>6</sub> H <sub>4</sub>	<b>4c</b>	88	2.3/1	8
4 <sup>e</sup>	<b>1d</b> , 4-ClC <sub>6</sub> H <sub>4</sub>	<b>4d</b>	80	2/1	12
5	<b>1e</b> , 4-MeOC <sub>6</sub> H <sub>4</sub>	<b>4e</b>	88	6/1	5
6	<b>1f</b> , 3-MeOC <sub>6</sub> H <sub>4</sub>	<b>4f</b>	93	6/1	5
7	<b>1g</b> , 4-EtOC <sub>6</sub> H <sub>4</sub>	<b>4g</b>	83	6.5/1	4
8	<b>1h</b> , 4-EtC <sub>6</sub> H <sub>4</sub>	<b>4h</b>	88	6.5/1	5
9	<b>1i</b> , 4-MeC <sub>6</sub> H <sub>4</sub>	<b>4i</b>	84	7/1	4
10 <sup>e</sup>	<b>1j</b> , 2-thienyl	<b>4j</b>	80	3/1	12
11 <sup>e</sup>	<b>1k</b> , 1-naphthyl	<b>4k</b>	70	3/1	12
12	<b>1l</b> , 4-MeSC <sub>6</sub> H <sub>4</sub>	<b>4l</b>	82	6/1	4

<sup>a</sup>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<sub>2</sub>Cl<sub>2</sub> (2.0 mL) for 3 h at rt. <sup>b</sup>Isolated yields of *E,E* and *Z,E* isomers. <sup>c</sup>Determined by <sup>1</sup>H NMR analysis of crude products. <sup>d</sup>Isolated yields of *E* isomers. <sup>e</sup>The reaction was run at 60 °C for 2 h.

Scheme 3. Exploration of the Asymmetric Annulation of Activated Ketone and  $\gamma$ -Substituted Allenolate

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 allenolate with commercially available simple phosphine catalysts. These findings not only enrich the chemistry of reactions of allenolates under nucleophilic catalysis, but also enable easy access to two sets of skeletally diverse products bearing  $\text{CF}_3$  quaternary 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 allenolate 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  $\gamma$ -substituted allenolates were prepared according to a modified version of the literature procedure<sup>8e,19a</sup> and stored at 4 °C prior to use. All trifluoromethyl aryl ketones were prepared following reported procedures<sup>19b,c</sup> or purchased from commercial suppliers. All acyl-protected aminophosphines were synthesized according to procedures reported previously.<sup>17a</sup>

**Representative Procedure for the Triarylphosphine-Catalyzed Cycloadditions.** To a stirred solution of trifluoromethyl ketone **1** (0.1 mmol) and phosphine (0.02 mmol) in  $\text{CH}_2\text{Cl}_2$  (1 mL) was added  $\gamma$ -substituted allenolate (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  $^1\text{H}$  NMR data with those of cycloadduct **3aa**, which were compared with those of known analogues.<sup>10a</sup>

**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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 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,



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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta = 171.6$ , 169.8, 167.4, 135.4, 129.3, 128.5, 126.3, 124.4 (q,  $J_{\text{C-F}} = 248$  Hz), 99.1, 88.8 (q,  $J_{\text{C-F}} = 30.1$  Hz), 60.6, 60.2, 32.1, 32.0, 30.1, 14.3, 14.2;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz)  $\delta = -79.6$ ; IR (film,  $\text{cm}^{-1}$ ) 2983, 1738, 1656, 1454, 1370, 1309, 1186, 1101, 1042, 891, 768, 723; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{21}\text{F}_3\text{O}_5\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  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)  $t_{\text{major}} = 14.6$  min,  $t_{\text{minor}} = 10.6$  min,  $\lambda = 254$  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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.54$  (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,  $J_{\text{AB}} = 16.8$  Hz, 1H), 3.47 (d,  $J_{\text{AB}} = 16.8$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta = 171.5$ , 169.4, 167.3, 134.5, 131.8, 128.1, 124.1 (q,  $J_{\text{C-F}} = 285$  Hz), 99.5, 88.5 (q,  $J_{\text{C-F}} = 30.1$  Hz), 60.7, 60.3, 32.1, 32.0, 30.0, 14.3, 14.2;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz)  $\delta = -79.6$ ; IR (film,  $\text{cm}^{-1}$ ) 2982, 2935, 1739, 1713, 1658, 1490, 1369, 1312, 1173, 1113, 1048, 1009, 898, 821, 781, 736; HRMS (MALDI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{20}\text{BrF}_3\text{O}_5\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.48$  (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,  $J_{\text{AB}} = 16.8$  Hz, 1H), 3.50 (d,  $J_{\text{AB}} = 16.8$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta = 171.5$ , 169.5, 167.3, 163.23 (d,  $J_{\text{C-F}} = 249$  Hz), 131.3 (d,  $J_{\text{C-F}} = 3.6$  Hz), 128.3 (d,  $J_{\text{C-F}} = 8.1$  Hz), 124.3 (q,  $J_{\text{C-F}} = 284$  Hz), 115.5 (d,  $J_{\text{C-F}} = 22$  Hz), 99.3, 88.4 (q,  $J_{\text{C-F}} = 30$  Hz), 60.6, 60.3, 32.2, 32.0, 30.1, 14.3, 14.2;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz)  $\delta = -76.5$ ,  $-109.3$ ; IR (film,  $\text{cm}^{-1}$ ) 2983, 2937, 1738, 1702, 1657, 1513, 1370, 1312, 1238, 1176, 1128, 1048, 837, 781; HRMS (MALDI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{20}\text{F}_4\text{O}_5\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.43$ –7.37 (m, 4H), 4.17 (q,  $J = 7.0$  Hz, 4H), 3.53 (d,  $J_{\text{AB}} = 16.8$  Hz, 1H), 3.48 (d,  $J_{\text{AB}} = 16.8$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta = 171.5$ , 169.4, 167.3, 135.6, 134.0, 128.8, 127.8, 124.2 (q,  $J_{\text{C-F}} = 285$  Hz), 99.4, 88.3 (q,  $J_{\text{C-F}} = 30.1$  Hz), 60.7, 60.3, 32.1, 32.0, 30.0, 14.3, 14.2;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz)  $\delta = -79.6$ ; IR (film,  $\text{cm}^{-1}$ ) 2982, 2936, 1720, 1660, 1494, 1463, 1369, 1311, 1255, 1175, 1086, 1048, 1012, 826, 738; HRMS (MALDI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{20}\text{ClF}_3\text{O}_5\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  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;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta = 7.42$  (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,  $J_{\text{AB}} = 16.8$  Hz, 1H), 3.47 (d,  $J_{\text{AB}} = 16.8$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta = 171.6$ , 169.9, 167.5, 160.3, 127.7, 127.3, 124.4 (q,  $J_{\text{C-F}} = 284$  Hz), 113.9, 99.0, 88.7 (q,  $J_{\text{C-F}} = 30.1$  Hz), 60.6, 60.2, 55.3, 32.0, 30.2, 29.7, 14.3, 14.2;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz)  $\delta = -79.8$ ; IR (film,  $\text{cm}^{-1}$ ) 2981, 2937, 2843, 1736, 1655, 1612, 1516, 1463, 1369, 1302, 1254, 1172, 1087, 1047, 897, 832; HRMS (MALDI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{23}\text{F}_3\text{O}_6\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.34$  (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,  $J_{\text{AB}} = 16.8$  Hz, 1H), 3.52 (d,  $J_{\text{AB}} = 16.8$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta = 171.6$ , 169.8, 167.4, 159.7, 136.9, 127.3, 124.4 (q,  $J_{\text{C-F}} = 284$  Hz), 118.5, 114.4, 112.6, 99.1, 88.7 (q,  $J_{\text{C-F}} = 30.1$  Hz), 60.6, 60.2, 55.3, 32.2, 32.0, 30.1, 14.3, 14.2;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz)  $\delta = -79.4$ ; IR (film,  $\text{cm}^{-1}$ ) 2981, 2936, 2851, 1738, 1712, 1657, 1604, 1586, 1493, 1465, 1369, 1295, 1178, 1101, 1047, 883, 784, 728; HRMS (MALDI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{23}\text{F}_3\text{O}_6\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.39$  (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,  $J_{\text{AB}} = 16.8$  Hz, 1H), 3.51 (d,  $J_{\text{AB}} = 16.8$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta = 171.6$ , 169.9, 167.5, 127.6, 127.1, 124.5 (q,  $J_{\text{C-F}} = 285$  Hz), 114.4, 99.0, 88.7 (q,  $J_{\text{C-F}} = 30.1$  Hz), 63.6, 60.6, 60.2, 32.0, 30.2, 29.7, 14.7, 14.3, 14.2;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz)  $\delta = -76.6$ ; IR (film,  $\text{cm}^{-1}$ ) 2982, 2935, 1740, 1713, 1653, 1514, 1300, 1252, 1172, 1118, 1047, 898, 834, 808; HRMS (MALDI)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{25}\text{F}_3\text{O}_6\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  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;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta = 7.37$  (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,  $J_{\text{AB}} = 16.7$  Hz, 1H), 3.47 (d,  $J_{\text{AB}} = 17.0$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta = 171.6$ , 169.9, 167.5, 145.5, 132.6, 128.0, 126.3, 124.5 (q,  $J_{\text{C-F}} = 284$  Hz), 99.0, 88.8 (q,  $J_{\text{C-F}} = 30.1$  Hz), 60.6, 60.2, 32.1, 30.1, 29.7, 28.5, 15.3, 14.3, 14.2;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz)  $\delta = -79.6$ ; IR (film,  $\text{cm}^{-1}$ ) 2969, 2930, 2855, 1741, 1713, 1656, 1515, 1462, 1415, 1369, 1316, 1175, 1090, 1047, 830, 785; HRMS (MALDI)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{25}\text{F}_3\text{O}_5\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.38$  (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,  $J_{\text{AB}} = 16.8$  Hz, 1H), 3.52 (d,  $J_{\text{AB}} = 16.8$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta = 171.6$ , 169.9, 167.5, 139.3, 132.4, 129.2, 126.2, 124.4 (q,  $J_{\text{C-F}} = 285$  Hz), 99.0, 88.8 (q,  $J_{\text{C-F}} = 30.1$  Hz), 60.6, 60.2, 32.0, 30.1, 29.7, 21.1, 14.3, 14.2;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz)  $\delta = -79.7$ ; IR (film,  $\text{cm}^{-1}$ ) 2982, 2933, 1740, 1713, 1658, 1515, 1461, 1369, 1315, 1174, 1121, 1088, 1048, 899, 815; HRMS (MALDI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{23}\text{F}_3\text{O}_5\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.39$  (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,  $J_{\text{AB}} = 17.1$  Hz, 1H), 3.48 (d,  $J_{\text{AB}} = 16.8$  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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta = 171.4$ , 169.3, 167.3, 137.9, 127.2, 127.0, 126.8, 123.8 (q,  $J_{\text{C-F}} = 284$  Hz), 99.7, 87.5 (q,  $J_{\text{C-F}} = 30.4$  Hz), 60.6, 60.3, 33.2, 31.9, 30.1, 14.3, 14.2;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz)  $\delta = -76.8$ ; IR (film,  $\text{cm}^{-1}$ ) 3107, 2982, 2936, 2358, 1740, 1713, 1462, 1369, 1299, 1175, 1089, 1046, 883, 843, 781, 710; HRMS (MALDI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{19}\text{F}_3\text{O}_5\text{SNa}$  [ $\text{M} + \text{Na}$ ] $^+$  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;  $R_f =$

0.33 (petroleum ether/ethyl acetate, 80/20); viscous, colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 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,  $J_{\text{AB}}$  = 16.9 Hz, 1H), 3.59 (d,  $J_{\text{AB}}$  = 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  = 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;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz)  $\delta$  = –75.1; IR (film,  $\text{cm}^{-1}$ ) 2982, 2934, 1738, 1712, 1653, 1463, 1361, 1311, 1178, 1129, 1098, 1078, 1049, 962, 803, 777; HRMS (MALDI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{23}\text{F}_3\text{O}_5\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  = 173.7, 135.5, 129.3, 128.5, 126.3, 92.4, 59.6, 31.7, 29.4, 14.2;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz)  $\delta$  = –72.7; IR (film,  $\text{cm}^{-1}$ ) 3027, 2939, 1718, 1653, 1621, 1481, 1387, 1345, 1261, 1129, 1035, 1001, 956, 821; HRMS (MALDI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{15}\text{F}_3\text{O}_3\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  = 165.2, 135.6, 129.3, 128.5, 126.5, 91.2, 59.6, 30.7, 29.7, 14.4;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz)  $\delta$  = –73.1; IR (film,  $\text{cm}^{-1}$ ) 3031, 2899, 1724, 1619, 1601, 1487, 1347, 1325, 1274, 1131, 1045, 1015, 959, 764; HRMS (MALDI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{15}\text{F}_3\text{O}_3\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  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;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  = 166.5, 142.3, 137.5, 136.7, 130.8, 129.1, 128.6, 126.6, 126.1, 124.3, 60.6, 14.2;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz)  $\delta$  = –76.3; IR (film,  $\text{cm}^{-1}$ ) 3427, 2984, 1698, 1645, 1619, 1451, 1370, 1305, 1241, 1166, 1077, 1001, 941, 706; HRMS (MALDI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{15}\text{F}_3\text{O}_3\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  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)  $t_{\text{major}}$  = 19.7 min,  $t_{\text{minor}}$  = 12.3 min,  $\lambda$  = 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  $^1\text{H}$  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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  = 171.6, 169.2, 167.6, 132.4, 129.0, 128.4, 126.4, 126.3, 123.6, 99.2, 91.1 (q,  $J_{\text{C-F}}$  = 30.1 Hz), 60.6, 60.2, 38.6, 36.7, 31.9, 17.3, 14.3, 14.2;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz)  $\delta$  = –76.6; IR (film,  $\text{cm}^{-1}$ ) 2982, 2936, 1739, 1712, 1657, 1450, 1369, 1314, 1298, 1178, 1101, 1071, 1051, 934, 729; HRMS (MALDI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{23}\text{F}_3\text{O}_5\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 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);  $^{13}\text{C}$  NMR

( $\text{CDCl}_3$ , 100 MHz)  $\delta$  = 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;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz)  $\delta$  = –73.4; IR (film,  $\text{cm}^{-1}$ ) 2983, 2937, 1739, 1712, 1657, 1369, 1312, 1168, 1111, 1052, 1029, 724, 699; HRMS (MALDI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{23}\text{F}_3\text{O}_5\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 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,  $J_{\text{AB}}$  = 16.8 Hz, 1H), 3.48 (d,  $J_{\text{AB}}$  = 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  = 171.6, 169.7, 167.4, 140.5, 131.9, 126.7, 126.1, 124.3 (q,  $J_{\text{C-F}}$  = 28.5 Hz), 99.2, 88.6 (q,  $J_{\text{C-F}}$  = 30.1 Hz), 60.6, 60.2, 32.0, 30.1, 29.7, 15.4, 14.3, 14.2;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz)  $\delta$  = –79.6; IR (film,  $\text{cm}^{-1}$ ) 2982, 2935, 1740, 1713, 1653, 1514, 1300, 1252, 1172, 1118, 1047, 898, 834, 808; HRMS (MALDI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{23}\text{F}_3\text{O}_5\text{SNa}$  [ $\text{M} + \text{Na}$ ] $^+$  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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  = 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;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz)  $\delta$  = –81.9, –82.0; IR (film,  $\text{cm}^{-1}$ ) 2983, 2928, 1740, 1599, 1495, 1446, 1373, 1306, 1253, 1165, 1069, 1030, 863, 818, 736, 688; HRMS (MALDI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{23}\text{F}_3\text{O}_5\text{SNa}$  [ $\text{M} + \text{Na}$ ] $^+$  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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.48 (m, 2H), 7.35 (m, 3H), 4.17 (q,  $J$  = 7.1 Hz, 6H), 3.58 (d,  $J_{\text{AB}}$  = 16.8 Hz, 1H), 3.51 (d,  $J_{\text{AB}}$  = 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  = 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,  $\text{cm}^{-1}$ ) 2981, 2932, 2854, 1736, 1650, 1449, 1368, 1304, 1259, 1176, 1094, 1058, 887, 860, 781; HRMS (MALDI)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{26}\text{O}_7\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  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)  $t_{\text{major}}$  = 15.5 min,  $t_{\text{minor}}$  = 14.4 min,  $\lambda$  = 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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.55 (m, 2H), 7.42 (m, 3H), 4.25 (m, 4H), 3.61 (d,  $J_{\text{AB}}$  = 16.8 Hz, 1H), 3.58 (d,  $J_{\text{AB}}$  = 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  = 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,  $\text{cm}^{-1}$ ) 2998, 2936, 2812, 2230, 1741, 1622, 1519, 1327, 1291, 1252, 1186, 1095, 1027, 897, 856, 763; HRMS (MALDI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{21}\text{O}_5\text{NNa}$  [ $\text{M} + \text{Na}$ ] $^+$  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)  $t_{\text{major}}$  = 41.4 min,  $t_{\text{minor}}$  = 39.7 min,  $\lambda$  = 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 allenolate **2b** (0.12 mmol) in  $\text{CH}_2\text{Cl}_2$  (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



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 allenolate **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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.66 (dd,  $J$  = 15.6, 11.3 Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 7.60 (m, 2H; both isomers, *ArH*), 7.45–7.44 (m, 1H; major,  $\text{CH}=\text{CHCH}$ ), 7.43–7.40 (m, 3H; both isomers, *ArH*), 6.84 (dd,  $J$  = 15.1, 11.3 Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 6.66 (d,  $J$  = 15.0 Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 6.57 (d,  $J$  = 11.0 Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 6.46 (d,  $J$  = 15.6 Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 4.28–4.22 (m, 2H; both isomers,  $\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ ), 4.17–4.11 (m, 2H; both isomers,  $\text{OCH}_2\text{CH}_3$ ), 3.46 (s, 2H; major,  $\text{CH}_2\text{CO}$ ), 3.36 (s, 2H; minor,  $\text{CH}_2\text{CO}$ ), 3.33 (s, 1H; major, *OH*), 3.23 (s, 1H; minor, *OH*), 1.34–1.30 (t,  $J$  = 7.0 Hz, 3H; both isomers,  $\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ ), 1.26–1.23 (t,  $J$  = 7.3 Hz, 3H; both isomers,  $\text{OCH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  = 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);  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz)  $\delta$  = –78.8 (minor), –78.9 (major); IR (film,  $\text{cm}^{-1}$ ) 3441, 2985, 2940, 1714, 1644, 1614, 1450, 1371, 1162, 1028, 1004, 979, 769, 710; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{21}\text{F}_3\text{O}_5\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.63 (dd,  $J$  = 15.6, 11.3 Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 7.54 (d,  $J$  = 8.7 Hz, 2H; both isomers, *ArH*), 7.47 (d,  $J$  = 8.6 Hz, 2H; both isomers, *ArH*), 7.42 (d,  $J$  = 11.3 Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 6.82 (dd,  $J$  = 15.1, 11.3 Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 6.61 (d,  $J$  = 15.2 Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 6.56 (d,  $J$  = 11.0 Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 6.41 (d,  $J$  = 15.6 Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 4.28–4.22 (m, 2H; both isomers,  $\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ ), 4.17–4.11 (m, 2H; both isomers,  $\text{OCH}_2\text{CH}_3$ ), 3.46 (s, 2H; major,  $\text{CH}_2\text{CO}$ ), 3.35 (s, 2H; minor,  $\text{CH}_2\text{CO}$ ), 1.34–1.30 (t,  $J$  = 7.0 Hz, 3H; both isomers,  $\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ ), 1.26–1.22 (t,  $J$  = 7.3 Hz, 3H; both isomers,  $\text{OCH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  = 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;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz)  $\delta$  = –79.6 (major), –79.7 (minor); IR (film,  $\text{cm}^{-1}$ ) 3425 (br), 2985, 2936, 1713, 1645, 1466, 1371, 1095, 1029, 978, 901, 853, 714; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{20}\text{BrF}_3\text{O}_5\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.63 (dd,  $J$  = 15.5, 11.0 Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 7.58 (m, 2H; both isomers, *ArH*), 7.43 (d,  $J$  = 11.6 Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 7.09 (m, 2H; both isomers, *ArH*), 6.82 (dd,  $J$  = 15.1, 11.3 Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 6.63 (d,  $J$  = 15.1 Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 6.57 (d,  $J$  = 11.1 Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 6.43 (d,  $J$  = 15.5 Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 4.28–4.23 (m, 2H; both isomers,  $\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ ), 4.16–4.11 (m, 2H; both isomers,  $\text{OCH}_2\text{CH}_3$ ), 3.69 (br, 1H; major, *OH*), 3.53 (br, 1H; minor, *OH*), 3.46 (s, 2H; major,  $\text{CH}_2\text{CO}$ ), 3.36 (s, 2H; minor,  $\text{CH}_2\text{CO}$ ), 1.34–1.30 (t,  $J$  = 7.0 Hz, 3H; both isomers,  $\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ ), 1.26–1.22 (t,  $J$  = 7.3 Hz, 3H; both isomers,  $\text{OCH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  = 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;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz)  $\delta$  = –79.0 ( $\text{CF}_3$ , minor), –79.1 ( $\text{CF}_3$ , major), –113.2 (*ArF*, major), –113.6 (*ArF*, minor); IR (film,  $\text{cm}^{-1}$ ) 3440 (br), 2985, 2936, 1714, 1645, 1604, 1466, 1447, 1371, 1240, 1179, 1096, 1029, 839, 731; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{20}\text{F}_4\text{O}_5\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.63 (dd,  $J$  = 15.6, 11.3 Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 7.54 (m, 2H; both isomers, *ArH*), 7.42 (d,  $J$  = 11.5 Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 7.38 (m, 2H; both isomers, *ArH*), 6.82 (dd,  $J$  = 15.1, 11.3 Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 6.62 (d,  $J$  = 15.3 Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 6.56 (d,  $J$  = 11.1 Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 6.42 (d,  $J$  = 15.6 Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 4.28–4.23 (m, 2H; both isomers,  $\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ ), 4.16–4.11 (m, 2H; both isomers,  $\text{OCH}_2\text{CH}_3$ ), 3.46 (s, 2H; major,  $\text{CH}_2\text{CO}$ ), 3.35 (s, 2H; minor,  $\text{CH}_2\text{CO}$ ), 1.34–1.30 (t,  $J$  = 7.2 Hz, 3H; both isomers,  $\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ ), 1.26–1.22 (t,  $J$  = 7.0 Hz, 3H; both isomers,  $\text{OCH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  = 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;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz)  $\delta$  = –79.0 (minor), –79.1 (major); IR (film,  $\text{cm}^{-1}$ ) 3437 (br), 2984, 2937, 1713, 1645, 1498, 1371, 1241, 1162, 1097, 1029, 979, 932, 830, 732; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{20}\text{ClF}_3\text{O}_5\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  443.0849, found 443.0843.

**Data for (E)-diethyl 2-((E)-5,5,5-trifluoro-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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.64 (dd,  $J$  = 15.6, 11.3 Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 7.51 (d,  $J$  = 8.8 Hz, 2H; both isomers, *ArH*), 7.44 (d,  $J$  = 11.3 Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 6.94 (d,  $J$  = 9.0 Hz, 2H; both isomers, *ArH*), 6.84 (dd,  $J$  = 15.1, 11.3 Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 6.64 (d,  $J$  = 15.1 Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 6.57 (d,  $J$  = 11.0 Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 6.44 (d,  $J$  = 15.5 Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 4.26 (q,  $J$  = 7.0 Hz, 2H; both isomers,  $\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ ), 4.14 (q,  $J$  = 7.1 Hz, 2H; both isomers,  $\text{OCH}_2\text{CH}_3$ ), 3.84 (s, 3H; major,  $\text{OCH}_3$ ), 3.47 (s, 2H; major,  $\text{CH}_2\text{CO}$ ), 3.36 (s, 2H; minor,  $\text{CH}_2\text{CO}$ ), 3.33 (br, 1H; major, *OH*), 1.33 (t,  $J$  = 7.0 Hz, 3H; both isomers,  $\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ ), 1.25 (t,  $J$  = 7.0 Hz, 3H; both isomers,  $\text{OCH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  = 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);  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz)  $\delta$  = –78.9 (minor), –79.0 (major); IR (film,  $\text{cm}^{-1}$ ) 3443 (br), 2983, 2937, 2842, 1714, 1644, 1611, 1514, 1465, 1371, 1254, 1160, 1031, 1000, 979, 834, 736; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{23}\text{F}_3\text{O}_6\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  439.1344, found 439.1341.

**Data for (E)-diethyl 2-((E)-5,5,5-trifluoro-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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.64 (dd,  $J$  = 15.5, 11.0 Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 7.42 (d,  $J$  = 11.5 Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 7.33 (m, 1H; both isomers, *ArH*), 7.17 (m, 2H; both isomers, *ArH*), 6.93 (dd,  $J$  = 8.0, 2.3 Hz, 1H; both isomers, *ArH*), 6.84 (dd,  $J$  = 15.3, 11.6 Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 6.63 (d,  $J$  = 15.3 Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 6.56 (d,  $J$  = 11.0 Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 6.43 (d,  $J$  = 15.6 Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 4.25 (q,  $J$  = 7.0 Hz, 2H; both isomers,  $\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ ), 4.13 (q,  $J$  = 7.1 Hz, 2H; both isomers,  $\text{OCH}_2\text{CH}_3$ ), 3.84 (s, 3H; major,  $\text{OCH}_3$ ), 3.59 (br, 1H; major, *OH*), 3.46 (s, 2H; major,  $\text{CH}_2\text{CO}$ ), 3.35 (s, 2H; minor,  $\text{CH}_2\text{CO}$ ), 1.32 (t,  $J$  = 7.0 Hz, 3H; both isomers,  $\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ ), 1.24 (t,  $J$  = 7.0 Hz, 3H; both isomers,  $\text{OCH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  = 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

broadenings are observed due to diastereoisomers);  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz)  $\delta = -78.6$  (minor),  $-78.7$  (major); IR (film,  $\text{cm}^{-1}$ ) 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  $\text{C}_{20}\text{H}_{23}\text{F}_3\text{O}_6\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.64$  (dd,  $J = 15.6, 11.1$  Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 7.33 (d,  $J = 8.8$  Hz, 2H; both isomers,  $\text{ArH}$ ), 7.43 (d,  $J = 11.3$  Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 6.91 (d,  $J = 8.8$  Hz, 2H; both isomers,  $\text{ArH}$ ), 6.84 (dd,  $J = 15.3, 11.6$  Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 6.63 (d,  $J = 15.0$  Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 6.58 (d,  $J = 11.3$  Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 6.43 (d,  $J = 15.5$  Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 4.25 (q,  $J = 7.0$  Hz, 2H; both isomers,  $\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ ), 4.15 (q,  $J = 7.3$  Hz, 2H; both isomers,  $\text{OCH}_2\text{CH}_3$ ), 4.06 (q,  $J = 7.1$  Hz, 2H; both isomers,  $\text{ArOCH}_2\text{CH}_3$ ), 3.46 (s, 2H; major,  $\text{CH}_2\text{CO}$ ), 3.35 (s, 2H; minor,  $\text{CH}_2\text{CO}$ ), 1.44 (t,  $J = 7.0$  Hz, 3H; both isomers,  $\text{ArOCH}_2\text{CH}_3$ ), 1.32 (t,  $J = 7.0$  Hz, 3H; both isomers,  $\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ ), 1.24 (t,  $J = 7.3$  Hz, 3H; both isomers,  $\text{OCH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta = 170.6, 166.9, 159.4, 138.8, 138.6, 137.6, 128.7, 128.0, 127.2, 127.1, 126.2, 123.4, 114.4, 63.5, 61.2, 61.1, 32.7, 29.7, 14.7, 14.2, 14.0$  (additional peaks and line broadenings are observed due to diastereoisomers);  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz)  $\delta = -78.9$  (minor),  $-79.0$  (major); IR (film,  $\text{cm}^{-1}$ ) 3449, 2983, 2936, 1731, 1716, 1643, 1611, 1512, 1393, 1297, 1242, 1154, 1117, 1031, 1000, 924, 837; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{25}\text{F}_3\text{O}_6\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.64$  (dd,  $J = 15.5, 11.3$  Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 7.50 (d,  $J = 8.0$  Hz, 2H; both isomers,  $\text{ArH}$ ), 7.44 (d,  $J = 11.3$  Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 7.25 (d,  $J = 8.2$  Hz, 2H; both isomers,  $\text{ArH}$ ), 6.85 (dd,  $J = 15.1, 11.5$  Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 6.65 (d,  $J = 15.1$  Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 6.57 (d,  $J = 11.0$  Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 6.45 (d,  $J = 15.3$  Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 4.25 (q,  $J = 7.3$  Hz, 2H; both isomers,  $\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ ), 4.14 (q,  $J = 7.1$  Hz, 2H; both isomers,  $\text{OCH}_2\text{CH}_3$ ), 3.47 (s, 2H; major,  $\text{CH}_2\text{CO}$ ), 3.44 (br, 1H; major,  $\text{OH}$ ), 3.35 (s, 2H; minor,  $\text{CH}_2\text{CO}$ ), 3.31 (br, 1H; minor,  $\text{OH}$ ), 2.68 (q,  $J = 7.5$  Hz, 2H; both isomers,  $\text{ArCH}_2\text{CH}_3$ ), 1.32 (t,  $J = 7.0$  Hz, 3H; both isomers,  $\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ ), 1.28–1.23 (m, 6H; both isomers, and  $\text{OCH}_2\text{CH}_3$  and  $\text{ArCH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta = 170.5, 166.9, 145.2, 138.8, 138.6, 134.2, 128.0, 127.9, 127.1, 126.6, 124.8$  (q,  $J_{\text{C-F}} = 286$  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);  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz)  $\delta = -78.7$  (minor),  $-78.8$  (major); IR (film,  $\text{cm}^{-1}$ ) 3451, 2970, 2953, 2875, 1730, 1713, 1643, 1514, 1464, 1371, 1163, 1030, 1001, 933, 834, 777; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{25}\text{F}_3\text{O}_5\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.64$  (dd,  $J = 15.6, 11.3$  Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 7.47 (d,  $J = 8.0$  Hz, 2H; both isomers,  $\text{ArH}$ ), 7.43 (d,  $J = 11.3$  Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 7.23 (d,  $J = 8.3$  Hz, 2H; both isomers,  $\text{ArH}$ ), 6.84 (dd,  $J = 15.1, 11.6$  Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 6.64 (d,  $J = 15.1$  Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 6.57 (d,  $J = 11.3$  Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 6.44 (d,  $J = 15.5$  Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 4.25 (q,  $J = 7.0$  Hz, 2H; both isomers,  $\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ ), 4.15 (q,  $J = 7.3$  Hz, 2H; both isomers,  $\text{OCH}_2\text{CH}_3$ ), 3.46 (s, 2H; major,  $\text{CH}_2\text{CO}$ ), 3.35 (s, 2H; minor,  $\text{CH}_2\text{CO}$ ), 3.27 (s, 1H; major,  $\text{OH}$ ), 3.17 (s, 1H; minor,  $\text{OH}$ ), 2.39 (s, 3H; both isomers,  $\text{ArCH}_3$ ), 1.33 (t,  $J = 7.0$  Hz, 3H; both isomers,  $\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ ), 1.25 (t,  $J = 7.0$  Hz, 3H; both isomers,  $\text{OCH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta = 170.5,$

166.9, 139.0, 138.7, 138.5, 133.9, 129.2, 129.1, 127.2, 126.5, 124.7 (q,  $J_{\text{C-F}} = 286$  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);  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz)  $\delta = -78.8$  (minor),  $-78.9$  (major); IR (film,  $\text{cm}^{-1}$ ) 3444 (br), 2984, 2930, 1730, 1644, 1613, 1514, 1447, 1371, 1158, 1029, 978, 932, 818; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{23}\text{F}_3\text{O}_5\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.70$  (dd,  $J = 15.5, 11.3$  Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 7.44 (d,  $J = 11.5$  Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 7.38 (m, 1H; both isomers,  $\text{ArH}$ ), 7.21 (m, 1H; both isomers,  $\text{ArH}$ ), 7.06 (m, 1H; both isomers,  $\text{ArH}$ ), 6.92 (dd,  $J = 14.8, 11.6$  Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 6.58 (d,  $J = 11.3$  Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 6.55 (d,  $J = 14.8$  Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 6.37 (d,  $J = 15.3$  Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 4.25 (q,  $J = 7.0$  Hz, 2H; both isomers,  $\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ ), 4.15 (q,  $J = 7.3$  Hz, 2H; both isomers,  $\text{OCH}_2\text{CH}_3$ ), 3.49 (s, 2H; major,  $\text{CH}_2\text{CO}$ ), 3.36 (s, 2H; minor,  $\text{CH}_2\text{CO}$ ), 1.33 (t,  $J = 7.0$  Hz, 3H; both isomers,  $\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ ), 1.25 (t,  $J = 7.3$  Hz, 3H; both isomers,  $\text{OCH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta = 171.0, 170.6, 166.9, 165.9, 140.5, 140.3, 140.1, 138.4, 136.9, 136.0, 129.6, 127.6, 127.2, 127.1, 126.9, 126.7, 126.6, 126.5, 126.6, 61.2, 61.1, 61.0, 40.3, 32.8, 29.7, 14.2, 14.1, 14.0$  (additional peaks and line broadenings are observed due to diastereoisomers);  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz)  $\delta = -78.9$  (minor),  $-79.0$  (major); IR (film,  $\text{cm}^{-1}$ ) 3434, 2983, 2935, 1714, 1645, 1489, 1371, 1240, 1162, 1077, 1028, 1010, 932, 823; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{19}\text{F}_3\text{O}_5\text{NaS}$  [ $\text{M} + \text{Na}$ ] $^+$  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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.49$ –8.47 (m, 1H; both isomers,  $\text{ArH}$ ), 7.92–7.87 (m, 2H; both isomers,  $\text{ArH}$ ), 7.82–7.80 (m, 1H; both isomers,  $\text{ArH}$ ), 7.51–7.47 (m, 3H; both isomers,  $\text{ArH}$ ), 7.40 (d,  $J = 10.5$  Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 6.73 (dd,  $J = 15.6, 10.8$  Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 6.68 (d,  $J = 15.3$  Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 6.55 (d,  $J = 11.3$  Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 6.50 (d,  $J = 15.8$  Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 4.22 (q,  $J = 7.0$  Hz, 2H; major,  $\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ ), 4.14 (q,  $J = 7.0$  Hz, 2H; minor,  $\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$  and  $\text{OCH}_2\text{CH}_3$ ), 4.05 (q,  $J = 7.0$  Hz, 2H; major,  $\text{OCH}_2\text{CH}_3$ ), 3.35 (s, 2H; major,  $\text{CH}_2\text{CO}$ ), 3.31 (s, 2H; minor,  $\text{CH}_2\text{CO}$ ), 1.30 (t,  $J = 7.3$  Hz, 3H; both isomers,  $\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ ), 1.19 (t,  $J = 7.1$  Hz, 3H; major,  $\text{OCH}_2\text{CH}_3$ ), 1.10 (t,  $J = 7.0$  Hz, 3H; minor,  $\text{OCH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta = 170.9, 170.3, 166.9, 166.0, 140.1, 139.2, 138.7, 137.9, 134.9, 132.4, 132.1, 131.1, 130.8, 130.6, 129.1, 129.0, 128.9, 127.3, 127.1, 126.1, 126.0, 125.8, 125.7, 124.5, 61.2, 61.0, 60.9, 40.2, 32.7, 29.7, 14.2, 14.0, 13.8$  (additional peaks and line broadenings are observed due to diastereoisomers);  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz)  $\delta = -75.6$  (minor),  $-75.8$  (major); IR (film,  $\text{cm}^{-1}$ ) 3431 (br), 2983, 2934, 1716, 1643, 1465, 1370, 1266, 1088, 1055, 1029, 978, 802; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{23}\text{F}_3\text{O}_5\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  459.1395, found 459.1395.

**Data for (E)-diethyl 2-((E)-5,5,5-trifluoro-4-hydroxy-4-(4-methylthiophenyl)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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.63$  (dd,  $J = 15.5, 11.1$  Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 7.50 (d,  $J = 8.3$  Hz, 2H; both isomers,  $\text{ArH}$ ), 7.43 (d,  $J = 11.3$  Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 7.27 (d,  $J = 8.5$  Hz, 2H; both isomers,  $\text{ArH}$ ), 6.83 (dd,  $J = 15.0, 11.3$  Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 6.62 (d,  $J = 15.1$  Hz, 1H; major,  $\text{CH}=\text{CHCH}$ ), 6.56 (d,  $J = 11.1$  Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 6.42 (d,  $J = 15.5$  Hz, 1H; minor,  $\text{CH}=\text{CHCH}$ ), 4.25 (q,  $J = 7.0$  Hz, 2H; both isomers,  $\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ ), 4.13 (q,  $J = 7.3$  Hz, 2H; both isomers,  $\text{OCH}_2\text{CH}_3$ ), 3.57 (br, 1H; major,  $\text{OH}$ ), 3.46 (s, 2H; major,  $\text{CH}_2\text{CO}$ ), 3.35 (s, 2H; minor,  $\text{CH}_2\text{CO}$ ), 2.51 (s, 3H; major,



ArSCH<sub>3</sub>), 1.32 (t, *J* = 7.0 Hz, 3H; both isomers, CH<sub>2</sub>CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.24 (t, *J* = 7.3 Hz, 3H; both isomers, OCH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  = 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); <sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz)  $\delta$  = -78.8 (minor), -78.9 (major); IR (film, cm<sup>-1</sup>) 3438, 2983, 2927, 1739, 1713, 1644, 1598, 1495, 1466, 1370, 1240, 1095, 979, 931, 819; HRMS (ESI) *m/z* calcd for C<sub>20</sub>H<sub>23</sub>F<sub>3</sub>O<sub>5</sub>NaS [M + Na]<sup>+</sup> 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, <sup>1</sup>H NMR and <sup>13</sup>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.

## ■ ACKNOWLEDGMENTS

We gratefully acknowledge financial support from the National Basic Research Program of China (973 Program, Grant 2010CB833200), the National Natural Science Foundation of China (Grants 21032006 and 21272247), the Science and Technology Commission of Shanghai Municipality (Grant 11XD1406400), the Excellent Young Scholars Foundation of the National Natural Science Foundation of China (Grant 20525208), and the supporting fund for young researchers of the Hefei University of Technology (to H.X.).

## ■ REFERENCES

- (1) (a) Corbett, J. W.; Ko, S.; Rodgers, S. J. M.; Gearhart, L. A.; Magnus, N. A.; Bacheler, L. T.; Diamond, S.; Jeffrey, S.; Klabe, R. M.; Cordova, B. C.; Garber, S.; Logue, K.; Trainor, G. L.; Anderson, P. S.; Erickson-Viitanen, S. K. *J. Med. Chem.* **2000**, *43*, 2019. (b) Magueur, G.; Crousse, B.; Charneau, S.; Grellier, P.; Bégué, J.-P.; Bonnet-Delpon, D. *J. Med. Chem.* **2004**, *47*, 2694. (c) Schäcke, H.; Schottelius, A.; Döcke, W.-D.; Strehlke, P.; Jaroch, S.; Schmees, N.; Rehwinkel, H.; Hennekes, H.; Asadullah, K. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 227.
- (2) (a) Shen, X.; Zhang, W.; Ni, C.; Gu, Y.; Hu, J. *J. Am. Chem. Soc.* **2012**, *134*, 16999. (b) Sun, J.; Shi, D.; Ma, M.; Li, S.; Wang, S.; Han, L.; Yang, Y.; Fan, X.; Shi, J.; He, L. *J. Nat. Prod.* **2005**, *68*, 915.
- (3) (a) Nie, J.; Guo, H.-C.; Cahard, D.; Ma, J.-A. *Chem. Rev.* **2011**, *111*, 455. (b) Yearick, K.; Wolf, C. *Org. Lett.* **2008**, *10*, 3915. (c) Motoki, R.; Kanai, M.; Shibasaki, M. *Org. Lett.* **2007**, *9*, 2997. (d) Blay, G.; Fernández, I.; Monleón, A.; Pedro, J. R.; Vila, C. *Org. Lett.* **2007**, *9*, 2997. (e) Martina, S. L. X.; Jagt, R. B. C.; de Vries, J. G.; Feringa, B. L.; Minnaard, A. J. *Chem. Commun.* **2006**, 4093.
- (4) For reviews on phosphine-catalyzed reactions, see: (a) Lu, X.; Zhang, C.; Xu, Z. *Acc. Chem. Res.* **2001**, *34*, 535. (b) Methot, J. L.; Roush, W. R. *Adv. Synth. Catal.* **2004**, *346*, 1035. (c) Ye, L.-W.; Zhou, J.; Tang, Y. *Chem. Soc. Rev.* **2008**, *37*, 1140. (d) Cowen, B. J.; Miller, S. J. *Chem. Soc. Rev.* **2009**, *38*, 3102. (e) Marinetti, A.; Voituriez, A. *Synlett* **2010**, 174. (f) Zhao, Q.-Y.; Lian, Z.; Wei, Y.; Shi, M. *Chem. Commun.* **2012**, *48*, 1724.
- (5) For the latest examples, see: (a) Meng, W.; Zhao, H.-T.; Nie, J.; Zheng, Y.; Fu, A.; Ma, J.-A. *Chem. Sci.* **2012**, *3*, 3053. (b) Zhao, L.; Wen, M.; Wang, Z.-X. *Eur. J. Org. Chem.* **2012**, 3587. (c) Zhang, X.-N.; Shi, M. *ACS Catal.* **2013**, *3*, 507. (d) Deng, J.-C.; Chan, F.-W.; Kuo, C.-W.; Cheng, C.-A.; Huang, C.-Y.; Chuang, S.-C. *Eur. J. Org. Chem.* **2012**, 5738. (e) Tian, J.; He, Z. *Chem. Commun.* **2013**, *49*, 2058. (f) Duvvuru, D.; Retailleau, P.; Betzer, J.-F.; Marinetti, A. *Eur. J. Org. Chem.* **2012**, 897. (g) Gomez, C.; Gicquel, M.; Carry, J.-C.; Schio, L.; Retailleau, P.; Voituriez, A.; Marinetti, A. *J. Org. Chem.* **2013**, *78*, 1488. (6) (a) Zhang, C.; Lu, X. *J. Org. Chem.* **1995**, *60*, 2906. (b) Xu, Z.; Lu, X. *Tetrahedron Lett.* **1997**, *38*, 3461.
- (7) For catalytic reaction of aldehyde with allenic esters, see: (a) Zhu, X.-F.; Schaffner, A.-P.; Li, R. C.; Kwon, O. *Org. Lett.* **2005**, *7*, 2977. (b) Creech, G. S.; Kwon, O. *Org. Lett.* **2008**, *10*, 429. (c) Selig, P.; Turočkin, A.; Raven, W. *Adv. Synth. Catal.* **2013**, *351*, 1685. (d) Zhu, X.-F.; Henry, C. E.; Wang, J.; Dudding, T.; Kwon, O. *Org. Lett.* **2005**, *7*, 1387.
- (8) For phosphine-mediated reaction of aldehyde with allenic esters, see: (a) Xu, S.; Chen, R.; He, Z. *J. Org. Chem.* **2011**, *76*, 7528. (b) Xu, S.; Zou, W.; Wu, G.; Song, H.; He, Z. *Org. Lett.* **2010**, *12*, 3556. (c) Ma, R.; Xu, S.; Tang, X.; Wu, G.; He, Z. *Tetrahedron* **2011**, *67*, 1053. (d) Xu, S.; Zhou, L.; Zeng, S.; Ma, R.; Wang, Z.; He, Z. *Org. Lett.* **2009**, *11*, 3498. (e) Xu, S.; Zhou, L.; Ma, R.; Song, H.; He, Z. *Org. Lett.* **2010**, *12*, 544. (f) Zhou, R.; Wang, C.; Song, H.; He, Z. *Org. Lett.* **2010**, *12*, 976. (g) Jacobsen, M. J.; Funder, E. D.; Cramer, J. R.; Gothelf, K. V. *Org. Lett.* **2011**, *13*, 3418. (h) Deng, J.-C.; Chuang, S.-C. *Org. Lett.* **2011**, *13*, 2248.
- (9) (a) Wang, T.; Ye, S. *Org. Lett.* **2010**, *12*, 4168. (b) Wang, T.; Ye, S. *Org. Biomol. Chem.* **2011**, *9*, 5260. (c) Saunders, L. B.; Miller, S. J. *ACS Catal.* **2011**, *1*, 1347. (d) Wang, T.; Shen, L.-T.; Ye, S. *Synthesis* **2011**, 3359.
- (10) (a) Xu, S.; Zhou, L.; Ma, R.; Song, H.; He, Z. *Chem.—Eur. J.* **2009**, *15*, 8698. (b) Meng, X.; Huang, Y.; Zhao, H.; Xie, P.; Ma, J.; Chen, R. *Org. Lett.* **2009**, *11*, 991. (c) Jose, A.; Lakshmi, K. C. S.; Suresh, E.; Nair, V. *Org. Lett.* **2013**, *15*, 1858. (d) Li, E.; Huang, Y.; Liang, L.; Xie, P. *Org. Lett.* **2013**, *15*, 3138.
- (11) For related reactions of activated ketone, see: (a) Li, J.; Liu, Y.; Li, C.; Jia, X. *Chem.—Eur. J.* **2011**, *17*, 7409. (b) Basavaiah, D.; Badsara, S. S.; Sahu, B. C. *Chem.—Eur. J.* **2013**, *19*, 2961. (c) Lian, Z.; Shi, M. *Org. Biomol. Chem.* **2012**, *10*, 8048. (d) Yang, L.; Xie, P.; Li, E.; Li, X.; Huang, Y.; Chen, R. *Org. Biomol. Chem.* **2012**, *10*, 7628. (e) Liu, X.-G.; Wei, Y.; Shi, M. *Eur. J. Org. Chem.* **2010**, 1977. (f) Wei, Y.; Liu, X.-G.; Shi, M. *Eur. J. Org. Chem.* **2012**, 2386.
- (12) For annulation of allenolates and ketimines, see: (a) Chen, X.-Y.; Lin, R.-C.; Ye, S. *Chem. Commun.* **2012**, *48*, 1317. (b) Chen, X.-Y.; Ye, S. *Eur. J. Org. Chem.* **2012**, 5723.
- (13) For related studies, see: (a) Tran, Y. S.; Kwon, O. *J. Am. Chem. Soc.* **2007**, *129*, 12632. (b) Li, E.; Xie, P.; Yang, L.; Liang, L.; Huang, Y. *Chem.—Asian J.* **2013**, *8*, 603. (c) Evans, C. A.; Miller, S. J. *J. Am. Chem. Soc.* **2003**, *125*, 12394. (d) Xie, P.; Li, E.; Zheng, J.; Li, X.; Huang, Y.; Chen, R. *Adv. Synth. Catal.* **2013**, *355*, 161.
- (14) Delcamp, J. H.; Gormisky, P. A.; White, M. C. *J. Am. Chem. Soc.* **2013**, *135*, 8460.
- (15) Wang, S. R.; Zhu, C.-Y.; Sun, X.-L.; Tang, Y. *J. Am. Chem. Soc.* **2009**, *131*, 4192.
- (16) For N-containing chiral catalysts for reactions of allenes with carbonyl compounds, see: (a) Pei, C.-K.; Shi, M. *Chem.—Eur. J.* **2012**, *18*, 6712. (b) Pei, C.-K.; Jiang, Y.; Wei, Y.; Shi, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 11328. For recent examples of asymmetric phosphine-catalyzed reaction, see: (c) Chen, S.; Salo, E. C.; Wheeler, K. A.; Kerrigan, N. J. *Org. Lett.* **2012**, *14*, 1784. (d) Lundgren, R. J.; Wilsily, A.; Marion, N.; Ma, C.; Chung, Y. K.; Fu, G. C. *Angew. Chem., Int. Ed.* **2013**, *52*, 2525. (e) Takizawa, S.; Nguyen, T. M.-N.; Grossmann, A.; Enders, D.; Sasai, H. *Angew. Chem., Int. Ed.* **2012**, *51*, 5423. (f) Zhang, X.; Deng, H.-P.; Huang, L.; Wei, Y.; Shi, M. *Chem. Commun.* **2012**, *48*, 8664. (g) Shi, Z.; Yu, P.; Loh, T.-P.; Zhong, G. *Angew. Chem., Int. Ed.* **2012**, *51*, 7825.

(17) (a) Xiao, H.; Chai, Z.; Zheng, C.-W.; Yang, Y.-Q.; Liu, W.; Zhang, J.-K.; Zhao, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 4467. (b) Xiao, H.; Chai, Z.; Wang, H.-F.; Wang, X.-W.; Cao, D.-D.; Liu, W.; Lu, Y.-P.; Yang, Y.-Q.; Zhao, G. *Chem.—Eur. J.* **2011**, *17*, 10562. (c) Xiao, H.; Chai, Z.; Cao, D.; Wang, H.; Chen, J.; Zhao, G. *Org. Biomol. Chem.* **2012**, *10*, 3195.

(18) (a) Zhu, X.-F.; Henry, C. E.; Kwon, O. *J. Am. Chem. Soc.* **2007**, *129*, 6722. (b) Khong, S. N.; Tran, Y. S.; Kwon, O. *Tetrahedron* **2010**, *66*, 4760. (c) Liang, Y.; Liu, S.; Xia, Y.; Li, Y.; Yu, Z.-X. *Chem.—Eur. J.* **2008**, *14*, 4361. (d) Vedejs, E.; Steck, P. L. *Angew. Chem., Int. Ed.* **1999**, *38*, 2788. We thank one of our reviewers for proposing this rationale.

(19) (a) Zhu, X.-F.; Lan, J.; Kwon, O. *J. Am. Chem. Soc.* **2003**, *125*, 4716. (b) Dishart, K. T.; Levine, R. *J. Am. Chem. Soc.* **1956**, *78*, 2268. (c) Simons, J. H.; Black, W. T.; Clark, R. F. *J. Am. Chem. Soc.* **1953**, *75*, 5621.