JOC Article

Efficient and Stereoselective Synthesis of β-Trifluoromethyl α,β-Unsaturated Esters via Iron(III) Porphyrin-Catalyzed Olefination of Ketones

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β-Trifluoromethyl α,β-unsaturated esters were efficiently prepared by reactions of fluorine-containing ketones with diazo compounds via metalloporphyrin-catalyzed olefination in the presence of triphenylphosphine. The commercially available Fe(III)(TPP)Cl (TPP: tetraphenylporphyrin) is effective for catalyzing the olefination of a variety of trifluoromethyl ketones with different diazoacetate esters under mild conditions. The reactions proceeded with high yields (up to 95% isolated yield) and high stereoselectivity (up to 99% (*E*)-selectivity).

Introduction

Trifluoromethylated compounds have found numerous important applications in organic, materials, medicinal, and agricultural chemistry due to their unique physical, chemical, and biological properties.[1] As a result, methods for the synthesis of trifluoromethylated compounds have attracted growing interest in recent years.[1,2] Among trifluoromethylated compounds, β-trifluoromethyl α,β-unsaturated esters are a class of important compounds.[1,3] In addition to methods based on trifluoromethylacetylenic esters,[4] β-trifluoromethyl α,β-unsaturated esters are generally synthesized through intramolecular[5] or intermolecular[6] Wittig-type reactions. To avoid the basic conditions required for the generation of phosphorane precursors and to improve the yields and stereoselectivity of these Wittig-type reactions,[5,6] it is desirable to develop alternative protocols for the synthesis of β-trifluoromethyl α,β-unsaturated esters under neutral conditions.

Recently, we have developed general and efficient catalytic systems, based on commercially available Fe(TPP)Cl and Ru(TPP)(CO) (Figure 1), for highly selective olefination of a wide variety of aldehydes with ethyl diazoacetate (EDA) in the presence of triphenylphosphine under mild conditions.[7] Herein, we extend our methodology to trifluoromethyl ketones, leading to efficient and stereoselective synthesis of β-trifluoromethyl α,β-unsaturated esters. Although several metal complex-based catalytic systems have been disclosed for olefination of aldehydes with diazo compounds,[7,8] this report, to the best of our knowledge, represents the first application of metal complex-based olefinations for fluorine-containing ketone substrates that lead to the synthesis of fluorinated α,β-unsaturated esters.[9] The Fe(TPP)Cl-catalyzed reactions can be effectively carried out in a one-pot protocol under mild conditions and are suitable for a variety of trifluoromethyl ketones and different diazoacetate esters,

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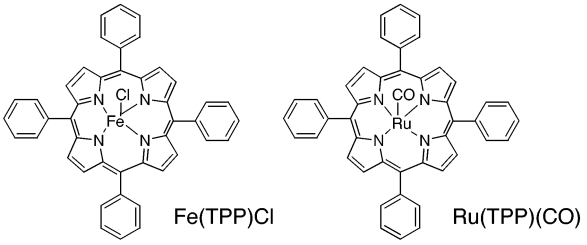
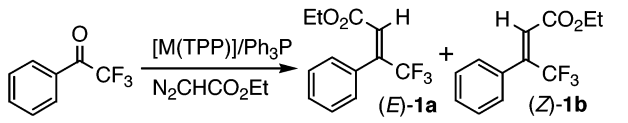


FIGURE 1. Structures of Fe(TPP)Cl and Ru(TPP)(CO).

TABLE 1. Olefination of Trifluoroacetophenone with EDA Catalyzed by Metal Tetraphenylporphyrin (TPP)[a]



entry	[M(TPP)] (mol %)	temp (°C)	time (h)[b]	yield (%)[c]	*E*/*Z*[d]
1	Fe(TPP)Cl (1.5)	80	17	93	89/11
2	Fe(TPP)Cl (1.5)	80	2.0	95[g]	93/7
3	Fe(TPP)Cl (1.5)	80	1.0	90	89/11
4[e]	Fe(TPP)Cl (1.5)	68	1.0	92	89/11
5	Fe(TPP)Cl (1.5)	50	1.0	77	91/9
6[f]	Fe(TPP)Cl (1.5)	50	1.0	51[g]	93/7
7	Fe(TPP)Cl (1.5)	23	1.0	31[g]	
8	Fe(TPP)Cl (1.5)	23	4.0	68[g]	94/6
9	Fe(TPP)Cl (1.5)	23	7.0	90	93/7
10[e]	Fe(TPP)Cl (1.5)	23	7.0	92	92/8
11[f]	Fe(TPP)Cl (1.5)	23	7.0	21[g]	
12	Fe(TPP)Cl (0.1)	80	1.0	86	90/10
13	Ru(TPP)CO (1.5)	80	1.0	93	90/10
14	Co(TPP) (1.5)	80	1.0	66[g]	88/12

[a] Reactions were carried out in toluene under N_2 with 1.0 equiv of trifluoroacetophenone, 1.2 equiv of EDA, 1.2 equiv of Ph_3P, and catalytic [M(TPP)]. Concentration: 0.5 mmol of ketone/2 mL of toluene. [b] Reaction times have not been fully optimized. [c] Yields represent isolated yields of >95% purity as determined by GC and ^{1}H NMR. [d] Ratio of *E*:*Z* isomers was determined by GC or ^{1}H NMR. [e] Reaction was carried out in THF. [f] Reaction was carried out in the air. [g] Yields were determined by GC.

affording the desired *β*-trifluoromethyl α,*β*-unsaturated esters in high yields and high (*E*)-selectivity.

Results and Discussion

We first evaluated the catalytic activity of Fe(TPP)Cl for olefination of trifluoroacetophenone under various conditions for the synthesis of the *β*-trifluoromethyl α,*β*-unsaturated ester **1** (Table 1). The reactions were typically carried out in toluene or THF under a nitrogen atmosphere at different temperatures for various times with 1.2 equiv of EDA using 1.5 mol % Fe(TPP)Cl in the presence of 1.2 equiv of Ph_3P per trifluoroacetophenone at a trifluoroacetophenone concentration of 0.25 M (0.50 mmol of ketone/2 mL of solvent). The reaction can be performed in a one-pot fashion without the need for slow addition of the EDA. The initial overnight reaction at 80 °C gave the desired olefin in high yield and good (*E*)-selectivity (Table 1, entry 1). It was found later that the reaction time, at the same temperature, could be shortened to 1−2 h without significantly affecting the yields and stereoselectivity (Table 1, entries 2 and 3). Although the reaction was also effective at 68 °C (Table 1, entry 4), further decreases in the reaction temperature resulted in low yields of the desired product in 1 h (Table 1, entries 5 and 7) due to incomplete conversion of the starting material. With longer reaction times (4 h), however, the yield at room temperature was considerably improved (Table 1, entry 8). Within 7 h, the reaction could be carried out efficiently and stereoselectively at room temperature in toluene (Table 1, entry 9) or in THF (Table 1, entry 10). When the same reaction was performed in the air (Table 1, entries 6 and 11), a dramatic decrease of the yield was observed, indicating the necessity of an inert reaction atmosphere. With a slight decrease of yield, the reaction could also be carried out with low catalyst loading of 0.1 mol % Fe(TPP)Cl (Table 1, entry 12). In addition to Fe(TPP)Cl, we found that Co(TPP) and Ru(TPP)(CO) can also catalyze the olefination reaction of trifluoroacetophenone to give the *β*-trifluoromethyl α,*β*-unsaturated ester **1**. While Co(TPP) showed a modest catalytic activity (Table 1, entry 14) due to competitive formation of an azine product ($PhC(CF_3)$═N−N═$CHCO_2Et$), the catalytic efficiency of the relatively more expensive Ru(TPP)(CO) was found to equal that of Fe(TPP)Cl (Table 1, entry 13). This similar catalytic activity pattern among the three metalloporphyrins was also observed in the olefination reaction of aldehydes.[7]

The catalytic procedure can be applied to a variety of trifluoromethyl ketones, affording a series of *β*-trifluoromethyl α,*β*-unsaturated esters, as shown in Table 2. Although the reactions can be carried out at room temperature, an elevated temperature condition such as 80 °C was preferred due to the fast reaction rate. Complete conversions of starting materials can be therefore reached in shorter reaction times. For example, a variety of 4-substituted trifluoroacetophenone derivatives can be catalytically converted to the corresponding *β*-trifluoromethyl α,*β*-unsaturated ethyl esters in 1 h at 80 °C by reaction with EDA. The yield ranged from 80% for an electron-withdrawing substituent (Table 2, entry 4) to 92% for an electron-neutral substituent (Table 2, entry 2) but decreased to 64% for an electron-donating substituent (Table 2, entry 6). The (*E*)-selectivity of these reactions remained high in the range of 90−93%. With a longer reaction time, the yield of the *β*-trifluoromethyl α,*β*-unsaturated ester from trifluoroacetophenone with an electron-donating substituent increased to 93% (Table 2, entry 5), although no obvious changes were observed in the cases with electron-withdrawing and electron-neutral substituents (Table 2, entries 1 and 3). When sterically hindered 2,2,2-trifluoro-2′,4′,6′-trimethylacetophenone was used, however, no formation of the desired product **5** was observed (Table 2, entry 7). Good yield and excellent (*E*)-selectivity were also obtained for the olefination of α,*β*-unsaturated trifluoromethyl ketone, leading

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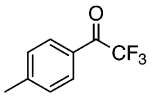
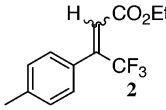
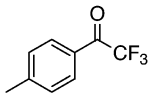
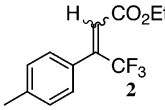
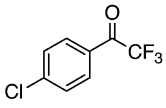
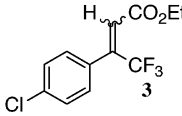
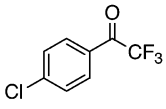
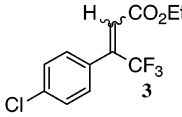
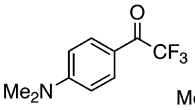
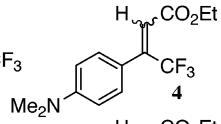
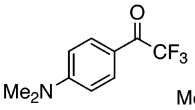
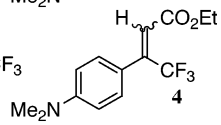
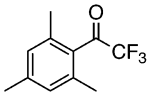
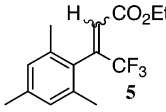
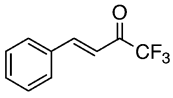
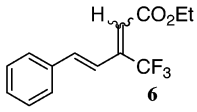
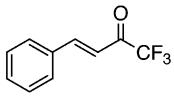
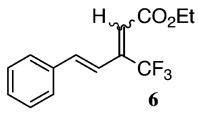
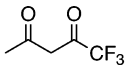
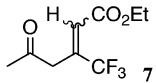
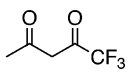
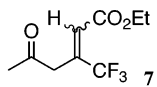
(9) For a recent report on rhodium(I)-catalyzed methylenenation of fluorinated ketones using trimethylsilyldiazomethane, see: Lebel, H.; Paquet, V. *Org. Lett.* **2002**, *4*, 1671.

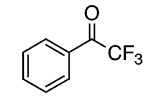
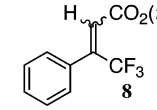
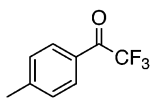
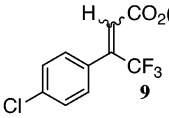
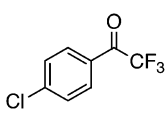
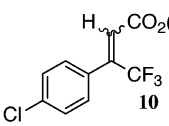
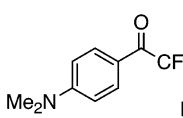
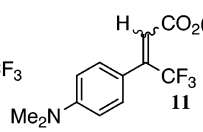
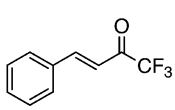
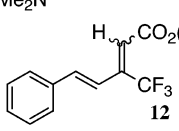
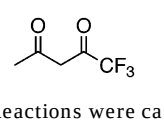
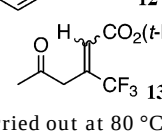
TABLE 2. Olefination of Trifluoromethyl Ketones with Ethyl Diazoacetate (EDA) Catalyzed by Fe(TPP)Cl[a]

entry	substrate	product	time (h)[b]	yield (%)[c]	*E*/*Z*[d]
1		 **2**	15	88	88/12
2		 **2**	1.0	92	90/10
3		 **3**	7.0	85	91/9
4		 **3**	1.0	80	92/8
5		 **4**	24	93	87/13
6		 **4**	1.0	64[e]	93/7
7		 **5**	21	0	– –
8		 **6**	16	77	>99/1
9		 **6**	1.0	73	>99/1
10		 **7**	2.0	84	69/31
11		 **7**	1.0	73	61/39

[a] Reactions were carried out at 80 °C in toluene under N_2 with 1.0 equiv of ketone, 1.2 equiv of EDA, 1.2 equiv of Ph_3P, and 1.5 mol % Fe(TPP)Cl. Concentration: 0.5 mmol of ketone/2 mL of toluene. [b] Reaction times have not been fully optimized. [c] Yields represent isolated yields of >95% purity as determined by GC and ^{1}H NMR. [d] Ratio of *E*:*Z* isomers was determined by GC or ^{1}H NMR. [e] Yields were determined by GC.

to the synthesis of β-trifluoromethylated conjugated diene ester **6** (Table 2, entries 8 and 9). High regioselectivity was achieved when trifluoro-2,4-pentanedione was used as a substrate, affording the β-trifluoromethyl α,β-unsaturated ester **7** from the reaction of the activated ketone (Table 2, entries 10 and 11). No product was observed from the reaction of the nonactivated ketone of the dione. This is consistent with our results that the Fe(TPP)Cl catalytic system is inactive toward normal ketone substrates such as acetophenone or 2-hexanone.

TABLE 3. Olefination of Trifluoromethyl Ketones with *tert*-Butyl Diazoacetate (*t*-BDA) Catalyzed by Fe(TPP)Cl[a]

entry	substrate	product	time (h)[b]	yield (%)[c]	*E*/*Z*[d]
1		 **8**	4.0	90	85/15
2		 **9**	4.0	94	83/17
3		 **10**	4.0	80	91/9
4		 **11**	24	95	81/19
5		 **12**	4.0	80	>99/1
6		 **13**	4.0	73	62/38

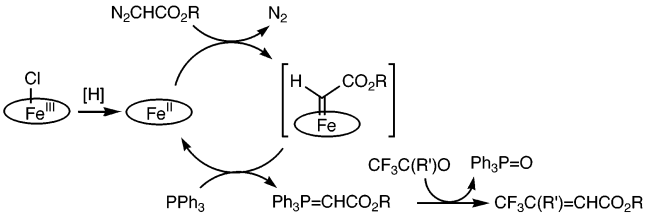
[a] Reactions were carried out at 80 °C in toluene under N_2 with 1.0 equiv of ketone, 1.4 equiv of *t*-BDA, 1.2 equiv of Ph_3P, and 1.5 mol % Fe(TPP)Cl. Concentration: 0.5 mmol of ketone/2 mL of toluene. [b] Reaction times have not been fully optimized. [c] Yields represent isolated yields of >95% purity as determined by GC and ^{1}H NMR. [d] Ratio of *E*:*Z* isomers was determined by GC or ^{1}H NMR.

The stereoselectivity of the formation of **7** was, however, only in the range of 60−70%.

In addition to ethyl diazoacetate, the catalytic system can also be applied to the sterically hindered *tert*-butyl diazoacetate (*t*-BDA), as shown in Table 3. Within 4 h, trifluoroacetophenone was converted to the desired β-trifluoromethyl α,β-unsaturated *tert*-butyl ester **8** in 90% yield and 85% (*E*)-selectivity at 80 °C using 1.5 mol % Fe(TPP)Cl (Table 3, entry 1). The same catalytic conditions were also effective for trifluoroacetophenone derivatives with para substituents such as methyl (Table 3, entry 2) and chloro (Table 3, entry 3) groups. A longer reaction time was required for the electron-rich dimethylamino derivate (Table 3, entry 4). Similar to the case of the diene ethyl ester **6** (Table 2, entries 8 and 9), the same excellent (*E*)-selectivity was also obtained for the synthesis of β-trifluoromethylated conjugated diene *tert*-butyl ester **12** (Table 3, entry 5). Although the (*E*)-selectivity was only 62%, complete regioselectivity toward the activated ketone was observed when the trifluoro-2,4-pentanedione was used, affording the corresponding β-trifluoromethyl α,β-unsaturated *tert*-butyl ester **13** in 73% yield.

At least three possible mechanisms have been proposed in the literature for transition metal complex-catalyzed olefination of aldehydes with diazo reagents. While two of them are associated with a metal-carbene intermediate,[8a−d,f−j] the third mechanism requires no formation of metal-carbene species.[8e] The noncarbene mechanism

SCHEME 1. Proposed Olefination Mechanism by Fe(TPP)Cl



involves the activation of diazo reagent through nitrogen coordination to the metal center, followed by nucleophilic attack of Ph_3P to generate a phosphorane that reacts with aldehydes as in the Wittig reaction.[8e] The two carbene mechanisms differ from each other with the role of the metal-carbene intermediate in the catalytic cycle. The first carbene mechanism requires direct reaction of the metal-carbene with aldehdyde to form an oxo-metallacyclobutane species that produces the olefin product.[8a,g–j] The second carbene mechanism necessitates the carbene transfer from the metal center to Ph_3P for the formation of a phosphorane.[8b–d,f] We presume that the current olefination of trifluoromethyl ketones operates by the second carbene mechanism, which is similar to the one proposed for olefination of aldehydes by metalloporphyrins, as outlined in Scheme 1.[7,8c,d] The Fe(III) center of Fe(TPP)Cl is assumed to be reduced in situ to Fe(II) by EDA,[10] and it then reacts with diazo reagent to afford a neutral iron-carbene intermediate. Carbene transfer from the neutral iron-carbene intermediate to Ph_3P generates a phosphorane that reacts with trifluoromethyl ketones to afford β-trifluoromethyl α,β-unsaturated esters. Alternatively, the Fe(III) center of Fe(TPP)Cl could directly interact with diazo compound to give a cation iron-carbene intermediate, as demonstrated for the Rh(III) center of Rh(TTP)I in catalytic cyclopropanation reaction.[11] The cation iron-carbene intermediate should be capable of functioning as the neutral iron-carbene intermediate in Scheme 1 for turning over the catalytic cycle.

Conclusion

In summary, we have developed an efficient catalytic system, based on commercially available Fe(TPP)Cl, for highly stereoselective olefination of a variety of trifluoromethyl ketones under mild conditions, leading to the synthesis of a series of β-trifluoromethyl α,β-unsaturated esters. This new one-pot catalytic system should find practical applications in organic synthesis for the construction of trifluoromethylated unsaturated esters.

Experimental Section

General Considerations. All reactions were carried out in oven-dried glassware using standard Schlenk techniques. Toluene and tetrahydrofuran were distilled under nitrogen from sodium benzophenone ketyl. Proton, carbon, and fluorine nuclear magnetic resonance spectra (^{1}H NMR, ^{13}C NMR, and ^{19}F NMR) were recorded on a 300 MHz spectrometer and referenced with respect to internal TMS standard, residual solvent, or internal $CFCl_3$. Infrared spectra were obtained using a FT-IR spectrometer. Samples were prepared as films on a NaCl plate by evaporating $CHCl_3$ solutions. Thin-layer chromatography was carried out on Silica Gel 60 F-254 TLC plates.

General Procedures for Olefination Reaction. A certain mol % Fe(TPP)Cl and 1.2 equiv of triphenylphosphine were placed in an oven-dried, resealable Schlenk tube. The tube was capped with a Teflon screwcap, evacuated, and backfilled with nitrogen. The screwcap was replaced with a rubber septum, and 1.0 equiv of ketone (0.5 mmol) was added via syringe, followed by solvent (2 mL) and 1.2 equiv of EDA or 1.4 equiv of *t*-BDA. The tube was purged with nitrogen for 2 min, and its contents were stirred at a constant temperature in an oil bath. After the reaction was finished, the resulting mixture was cooled to room temperature and concentrated. The residue was purified by flash silica gel chromatography to give the product.

Ethyl (*E*)-4,4,4-Trifluoro-3-phenylbut-2-enoate (1)[12] was synthesized from α,α,α-trifluoroacetophenone. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40(m, 3H), 7.31(m, 2H), 6.61(q, 1H, J = 1.5 Hz), 4.03(q, 2H, J = 7.2 Hz), 1.04(t, 3H, J = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.0, 142.2, 129.5, 129.3, 128.6, 128.1, 124.5, 120.7, 61.0, 13.6. ^{19}F NMR (282 MHz, $CDCl_3$): δ −68.06. IR: 1736, 1656, 1497 cm^{-1}. HRMS-EI ([M$^+$]): calcd for $C_{12}H_{11}F_3O_2$, 244.0711; found, 244.0713 with an isotope distribution pattern that is the same as the calculated one.

Ethyl (*E*)-4,4,4-Trifluoro-3-(4-methylphenyl)but-2-enoate (2)[13] was synthesized from 4-(trifluoroacetyl)toluene. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.19(s, 4H), 6.58(q, 1H, J = 1.5 Hz), 4.06(q, 2H, J = 7.2 Hz), 2.37(s, 3H), 1.09(t, 3H, J = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.2, 142.5, 139.3, 128.9, 128.4, 124.1, 120.7, 61.0, 21.2, 13.7. ^{19}F NMR (282 MHz, $CDCl_3$): δ −68.01. IR: 1737, 1654, 1614, 1515 cm^{-1}. HRMS-EI ([M$^+$]): calcd for $C_{13}H_{13}F_3O_2$, 258.0868; found, 258.0874 with an isotope distribution pattern that is the same as the calculated one.

Ethyl (*E*)-4,4,4-Trifluoro-3-(4-chlorophenyl)but-2-enoate (3)[14] was synthesized from 4′-chloro-2,2,2-trifluoroacetophenone. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38(d, 2H. J = 8.7 Hz), 7.23(d, 2H, J = 8.7 Hz), 6.62(q, 1H, J = 1.5 Hz), 4.07(q, 2H, J = 7.2 Hz), 1.11(t, 3H, J = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.7, 141.5, 135.6, 130.0, 128.5, 125.0, 120.4, 61.2, 13.7. ^{19}F NMR (282 MHz, $CDCl_3$): δ −68.09. IR: 1735, 1655, 1595, 1493 cm^{-1}. HRMS-EI ([M$^+$]): calcd for $C_{12}H_{10}ClF_3O_2$, 278.0321; found, 278.0328 with an isotope distribution pattern that is the same as the calculated one.

Ethyl (*E*)-4,4,4-Trifluoro-3-(4-dimethylaminophenyl)-but-2-enoate (4)[15] was synthesized from 4′-(dimethylamino)-2,2,2-trifluoroacetophenone. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20(d, 2H, J = 8.7 Hz), 6.67(d, 2H, J = 8.7 Hz), 6.47(q, 1H, J = 1.5 Hz), 4.10(q, 2H, J = 7.2 Hz), 2.97(s, 6H), 1.14(t, 3H, J = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.8, 150.9, 142.4, 129.8, 122.0, 117.6, 111.2, 60.8, 40.0, 13.8. ^{19}F NMR (282 MHz, $CDCl_3$): δ −67.17. IR: 1733, 1611, 1527 cm^{-1}. HRMS-EI ([M$^+$]): calcd for $C_{14}H_{16}F_3NO_2$, 287.1133; found, 287.1122 with an isotope distribution pattern that is the same as the calculated one.

Ethyl 5-Phenyl-3-trifluoromethyl-penta-2*E*,4*E*-dienoate (6)[16] was synthesized from *trans*-1,1,1-trifluoro-4-phenyl-3-buten-2-one. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14(d, 1H, J = 17.1 Hz), 7.56−7.34(m, 5H), 7.12(dd, 1H, J = 17.1, 2.4 Hz), 6.29(s, 1H), 4.27(q, 2H, J = 7.2 Hz), 1.33(t, 3H, J = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.9, 140.5, 138.3, 136.0, 129.5, 128.8, 127.6, 124.4, 120.7, 119.5, 118.0, 61.0, 14.1. ^{19}F NMR

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(11) (a) Bartley, D. W.; Kodadek, T. *J. Am. Chem. Soc.* **1993**, *115*, 1656. (b) Maxwell, J. L.; Brown, K. C.; Bartley, D. W.; Kodadek, T. *Science* **1992**, *256*, 1544.
(12) Shen, Y.; Gao, S. *J. Org. Chem.* **1993**, *58*, 4564.
(13) Pan, R.-Q.; Wang, P.-A.; Deng, M.-Z. *Heteroat. Chem.* **2002**, *13*, 287.
(14) Gong, Y.; Kato, K.; Kimoto, H. *J. Fluorine Chem.* **2000**, *105*, 169.
(15) Il'chenko, A. Y.; Koval'chuk, R. E.; Yagupol'skii, L. M. *Zhumal Organicheskoi Khimii* **1977**, *13*, 1992.
(16) Shen, Y.; Zhang Z.; Sun J. *J. Fluorine Chem.* **2001**, *111*, 189.

(282 MHz, $CDCl_3$): δ −64.07. IR: 1719, 1629, 1558, 1541 cm^{-1}. HRMS-EI ([M^+]): calcd for $C_{14}H_{13}F_3O_2$, 270.0868; found, 270.0871 with an isotope distribution pattern that is the same as the calculated one.

Ethyl 3-Trifluoromethyl-5-one-2-hexenote (7) was synthesized from trifluoro-2,4-pentanedione. **(*E*)-Isomer**. ^1H NMR (300 MHz, $CDCl_3$): δ 6.49(q, 1H, J = 1.5 Hz), 4.15(q, 2H, J = 7.2 Hz), 3.79(s, 2H), 2.21(s, 3H), 1.24(t, 3H, J = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.7, 164.4, 138.4, 124.7, 120.8, 61.1, 41.0, 29.6, 13.9. ^{19}F NMR (282 MHz, $CDCl_3$): δ −71.04. **(*Z*)-Isomer**. ^1H NMR (300 MHz, $CDCl_3$): δ 6.78(s, 1H), 4.12-(q, 2H, J = 7.2 Hz), 3.58(s, 2H), 2.29(s, 3H),1.22(t, 3H, J = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.6, 168.0, 135.0, 129.6, 121.0, 61.3, 31.8, 29.6, 14.0. ^{19}F NMR (282 MHz, $CDCl_3$): δ −70.81. IR: 1730, 1651, 1541 cm^{-1}. HRMS-EI ([$M^+ - OC_2H_5$]): calcd for $C_9H_{10}F_3O_2$, 179.0320; found, 179.0312 with an isotope distribution pattern that is the same as the calculated one.

***tert*-Butyl (*E*)-4,4,4-Trifluoro-3-phenylbut-2-enoate (8)**[12] was synthesized from α,α,α-trifluoroacetophenone. ^1H NMR (300 MHz, $CDCl_3$): δ 7.40(m, 3H), 7.29(m, 2H), 6.54(q, 1H, J = 1.5 Hz), 1.22(s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.5, 140.3, 129.1, 128.8, 128.1, 126.4, 124.5, 120.8, 82.2, 27.5. ^{19}F NMR (282 MHz, $CDCl_3$): δ −67.98. IR: 1730, 1672, 1621 cm^{-1}. HRMS-EI ([M^+]): calcd for $C_{14}H_{15}F_3O_2$, 272.1024, found, 272.1012 with an isotope distribution pattern that is the same as the calculated one.

***tert*-Butyl (*E*)-4,4,4-Trifluoro-3-(4-methylphenyl)but-2-enoate (9)** was synthesized from 4-(trifluoroacetyl)toluene. ^1H NMR (300 MHz, $CDCl_3$): δ 7.18(s, 4H), 6.51(q, 1H, J = 0.9 Hz), 2.36(s, 3H), 1.25(s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.6, 140.6, 139.1, 128.8, 128.6, 126.1, 124.5, 120.9, 82.0, 27.5, 21.2. ^{19}F NMR (282 MHz, $CDCl_3$): δ −67.94. IR 1730. 1652, 1614, 1515 cm^{-1}; HRMS-EI ([M^+]): calcd for $C_{15}H_{17}F_3O_2$, 286.1181; found, 286.1170 with an isotope distribution pattern that is the same as the calculated one.

***tert*-Butyl (*E*)-4,4,4-Trifluoro-3-(4-chlorophenyl)but-2-enoate (10)** was synthesized from 4′-chloro-2,2,2-trifluoroacetophenone. ^1H NMR (300 MHz, $CDCl_3$): δ 7.38(d, 2H. J = 8.7 Hz), 7.22(d, 2H, J = 8.7 Hz), 6.55(q, 1H, J = 1.5 Hz), 1.27-(s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.1, 139.4, 135.4, 130.2, 128.5, 126.9, 124.2, 120.6, 82.5, 27.6. ^{19}F NMR (282 MHz, $CDCl_3$): δ −68.01. IR: 1729, 1654, 1596, 1494 cm^{-1}. HRMS-EI ([M^+]): calcd for $C_{14}H_{14}ClF_3O_2$, 306.0634; found, 306.0651 with an isotope distribution pattern that is the same as the calculated one.

***tert*-Butyl (*E*)-4,4,4-Trifluoro-3-(4-dimethylaminophenyl)but-2-enoate (11)** was synthesized from 4′-(dimethylamino)-2,2,2-trifluoroacetophenone. ^1H NMR (300 MHz, $CDCl_3$): δ 7.17(d, 2H, J = 8.7 Hz), 6.67(d, 2H, J = 8.7 Hz), 6.42(q, 1H, J = 0.9 Hz), 2.96(s, 6H), 1.32(s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.4, 150.8, 140.7, 129.8, 128.5, 124.2, 118.2, 111.3, 81.7, 40.1, 27.7. ^{19}F NMR (282 MHz, $CDCl_3$): δ −67.25. IR: 1727, 1611, 1526 cm^{-1}. HRMS-EI ([M^+]): calcd for $C_{16}H_{20}F_3NO_2$, 315.1446; found, 315.1447 with an isotope distribution pattern that is the same as the calculated one.

***tert*-Butyl 5-Phenyl-3-trifluoromethyl-penta-2*E*,4*E*-dienoate (12)** was synthesized from *trans*-1,1,1-trifluoro-4-phenyl-3-buten-2-one. ^1H NMR (300 MHz, $CDCl_3$): δ 8.09(dd, 1H, J = 17.1, 0.9 Hz), 7.53(d, 2H, J = 7.5 Hz), 7.34(m, 3H), 7.09(d, 1H, J = 17.1 Hz), 6.23(s, 1H), 1.53(s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.2, 139.6, 137.8, 136.1, 129.3, 128.8, 127.5, 124.6, 121.6, 118.0, 81.8, 28.0. ^{19}F NMR (282 MHz, $CDCl_3$): δ −64.05. IR 1714, 1628 cm^{-1}. HRMS-EI ([M^+]): calcd for $C_{16}H_{17}F_3O_2$, 298.1181; found, 298.1177 with an isotope distribution pattern that is the same as the calculated one.

***tert*-Butyl 3-Trifluoromethyl-5-one-2-hexenote (13)** was synthesized from trifluoro-2,4-pentanedione. **(*E*)-Isomer**.:^1H NMR (300 MHz, $CDCl_3$): δ 6.47(q, 1H, J = 0.9 Hz), 3.81(s, 2H), 2.26(s, 3H), 1.47(s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): 200.9, 163.6, 136.9, 129.3, 121.0, 82.1, 40.8, 29.6, 27.8.^{19}F NMR: (282 MHz, $CDCl_3$) −70.86. **(*Z*)-Isomer**. ^1H NMR (300 MHz, $CDCl_3$): δ 6.79(s, 1H), 3.56(s, 2H), 2.34(s, 3H), 1.45(s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.5, 167.1, 135.2, 126.5, 124.6, 81.7, 32.9, 31.8, 27.8. ^{19}F NMR (282 MHz, $CDCl_3$): δ −70.71. IR: 1723, 1611, 1526 cm^{-1}. HRMS-EI ([M^+]): calcd for $C_{11}H_{15}F_3O_3$, 252.0973; found, 252.0192 with an isotope distribution pattern that is the same as the calculated one.

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