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Synthesis of Penta-2,4-dienenitriles by the Horner–Wadsworth–Emmons Olefination of Enones

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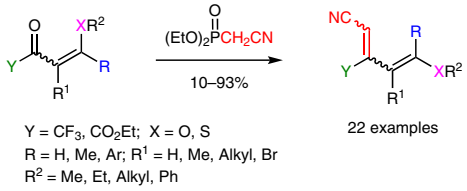

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Abstract Three new series of compounds, 5-alkoxy-3-(trifluoromethyl)penta-2,4-dienenitriles, 5-(phenylthio)-3-(trifluoromethyl)penta-2,4-dienenitriles, and ethyl 4-alkoxy-2-(cyanomethylene)but-3-enoates, obtained from the olefination reaction of the respective enones with diethyl cyanomethylphosphonate via the Horner–Wadsworth–Emmons olefination are reported. All products were obtained as single regioisomers; however, the composition of the stereoisomers changed according to the enone substituents. A study based on ^{1}H and ^{13}C NMR chemical shifts, ^{1}H–^{19}F and ^{13}C–^{19}F NMR coupling constants, ^{1}H NMR signal integrals, and HSQC, HMBC, and NOESY experiments was performed in order to assign the structure and percentage of each stereoisomer obtained.

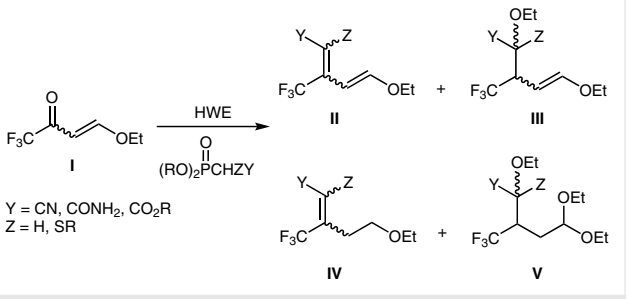
Key words pentadienenitriles, olefination, enones, diethyl cyanomethylphosphonate, Horner–Wadsworth–Emmons reaction

The Horner–Wadsworth–Emmons (HWE) reaction is one of the most reliable and widespread synthetic tools for the olefination of aldehydes and ketones. It has proven a valuable synthetic tool for preparing simple as well as highly functionalized and complex molecular scaffolds. For example, the HWE reaction has been used in the synthesis of α,β-unsaturated esters and ketones,[1] which have been used as building blocks for the synthesis of fluorinated retinoids,[2] insect sex pheromones,[3] and pyrethoids,[4] and of α,β-unsaturated nitriles,[5] which have been used to synthesize carbocycles[6] and heterocycles.[7] The HWE reaction has also been used for the synthesis of natural products[8] and vinylic sulfoximines,[9] the olefination of epimerizable aldehyde groups adjacent to stereocenters,[10] and inter- and intramolecular reactions for preparing *trans*-bicyclic enones,[11] among other things.[12]

Penta-2,4-dienenitriles are useful building blocks that have been used as precursors in organic synthesis, in order to obtain various heterocyclic compounds such as Diels–Alder adducts,[13] piperidazines,[14] pyridines,[15] indoles,[16] aromatic polycycles,[17] flavonoid pigments,[18] dyes,[19] and organic light-emitting diodes.[20]

Currently, the main methods for obtaining penta-2,4-dienenitriles are: (a) the pyrolysis reaction of esters,[21] (b) Peterson's reaction between aldehydes and α-silyl carbanions,[22] (c) oxidative reactions catalyzed by metals,[23] (d) the Knoevenagel condensation reaction,[24] and (e) the HWE reaction via double olefination of diethyl (1-cyanoethyl)phosphonate.[25]

Although the HWE reaction has been applied to a variety of aldehydes and ketones, the use of such a reaction for the olefination of trifluoromethylated enones has been explored very little. In fact, a literature search revealed only one use of this reaction, involving 4-ethoxy-1,1,1-trifluorobut-3-en-2-one (**I**), in a patent reported by Gebhardt and co-workers (Scheme 1).[26] This reaction provided a mixture of four different products, which are represented by structures **II**–**V**.



Scheme 1 Mixture of products from the HWE reaction of 4-ethoxy-1,1,1-trifluorobut-3-en-2-one

As outlined in Scheme 1, this reaction gave a complex mixture of products when enone **I** was reacted with HWE reagents. Since only enone **I** was used in the study,[26] we decided to perform the HWE olefination reaction on a range of substituted enones. Thus, the aim of our study was to perform the HWE olefination reaction on a series of enones with the general structures **VI**, **VII**, and **VIII** (Figure 1) using diethyl cyanomethylphosphonate, in order to generate new and valuable building blocks for organic synthesis.

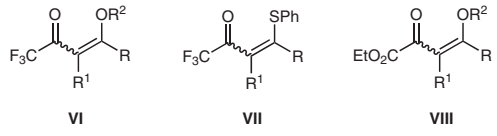
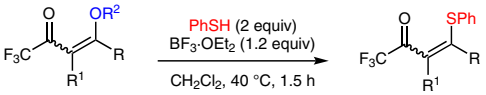


Figure 1 General structures of the enones used in this study

This study began with the preparation of the enones with the general structure **VI**, which were obtained in accordance with our previously developed method,[27] and enones **VIII**, which were also obtained in accordance with our previously reported methods.[28] The enones of general structure **VII** were prepared by the reaction of alkoxy-substituted enones **VI** with benzenethiol in dichloromethane and in the presence of boron trifluoride–diethyl ether complex, following similar procedures reported by Martins and co-workers[29] for the synthesis of 1,1,1-trihalo-4-(phenylseleno)alk-3-en-2-ones. For the compounds of structure **VII**, only compounds **2a** and **2h** were known; however, compound **2a** was synthesized previously by the acylation of a vinyl sulfide,[30] whereas compound **2h** was obtained by the reaction of enone **1h** with benzenethiol catalyzed by hydrated indium trichloride.[31] This reaction furnished product **2h** in low yield (27%), together with a mixture of side products including diphenyl disulfide (18%) and 1,1,1-trifluoro-3,4-bis(phenylthio)but-3-en-2-one (39%); whereas, using our method, compound **2h** was obtained in 71% yield, and no side products were observed (Table 1).

The best conditions for the HWE reaction of the enones with diethyl cyanomethylphosphonate were established using enone **1a**, following the method developed by Thomas and Boutagy.[32] The reaction was performed in a one-pot, two-step procedure. In the first step, the phosphonate anion **4′** was generated by the reaction of diethyl cyanomethylphosphonate (**4**) with a base and a solvent, as indicated in Table 2. For this step, the temperature was maintained at 0 °C for 30 minutes. In the second step, enone **1a** was added to the reaction flask, and various parameters, such as temperature, reaction time, and stoichiometric amounts of the reagents, were investigated (Table 2).

Table 1 Optimized Reaction Conditions for Obtaining Compounds **2**



1 **2**

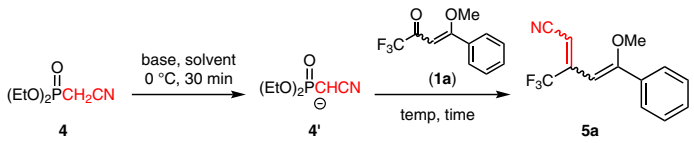
Enone	R	R^1	R^2	Product	Yield (%)[a]
1a	C_6H_5	H	Me	**2a**	85[b]
1c	4-BrC_6H_4	H	Me	**2c**	60
1d	4-MeC_6H_4	H	Me	**2d**	60
1e	4-$MeOC_6H_4$	H	Me	**2e**	78
1h	H	Br	Et	**2h**	71[c]

[a] Yield of product after purification by crystallization or column chromatography.
[b] Known compound.[30]
[c] Known compound.[31]

The amounts of enone **1a** and diethyl cyanomethylphosphonate (**4**) were always kept constant, namely 1.0:1.2 equivalents, respectively. The type and amount of the base and the reaction conditions were systematically changed. Sodium hydride in tetrahydrofuran were the first conditions studied, in accordance with reported HWE olefination reactions.[32] A very low yield was obtained when the reaction was performed at 30 °C for 2 hours (Table 2, entry 1); however, the yield was improved by refluxing the reaction, again for 2 hours (Table 2, entries 2–4). When 1.0 or 2.0 equivalents of base was used, the reaction yield was basically the same (Table 2, entries 4 and 2, respectively); however, when 1.5 equivalents of base was used, a slightly better yield was obtained (Table 2, entry 3). For shorter reaction times, such as 0.5 and 1.0 hour, the reaction furnished lower yields (Table 2, entries 5 and 6), and the reaction for 4 hours under reflux also gave a very low yield, probably due to decomposition of product **5a** (Table 2, entry 7). Other bases, such as triethylamine, pyridine, 1,8-diazabicyclo[5.4.0]undec-7-ene, 1,4-diazabicyclo[2.2.2]octane, *N*,*N*-diisopropylethylamine, sodium hydroxide, and sodium carbonate, were tested, but all resulted in low yields (Table 2, entries 8–15). Other solvents, such as water, diethyl ether, and dioxane, were tested; however, they either did not improve the yield or no reaction was observed (Table 2, entries 14–17).

The optimized conditions for obtaining compound **5a** (Table 2, entry 3) were applied to the synthesis of all other products **5** of this series. Enones **1a–k** with different substituents at the α- and the β-position were submitted to the reaction with diethyl cyanomethylphosphonate (**4**) in order to test the regioselectivity and stereoselectivity of the reaction (Table 3).

Table 2 Optimization of the Reaction Conditions for Obtaining Compound **5a**



4 4' 5a

Entry	Base	Molar ratio[a]	Solvent	Temp (°C)	Time (h)	Yield (%)[b]
1	NaH	1:1.2:2	THF	30	2	10
2	NaH	1:1.2:2	THF	reflux	2	53
3	NaH	1:1.2:1.5	THF	reflux	2	60
4	NaH	1:1.2:1	THF	reflux	2	54
5	NaH	1:1.2:1.5	THF	reflux	0.5	5
6	NaH	1:1.2:1.5	THF	reflux	1	41
7	NaH	1:1.2:1.5	THF	reflux	4	5
8	Et_3N	1:1.2:1.5	THF	reflux	2	[c]
9	Py	1:1.2:1.5	THF	reflux	2	[c]
10	DBU	1:1.2:1.5	THF	reflux	2	30
11	DABCO	1:1.2:1.5	THF	reflux	2	17
12	DIPEA	1:1.2:1.5	THF	reflux	2	[c]
13	NaOH	1:1.2:1.5	THF	reflux	2	[c]
14	NaOH	1:1.2:1.5	H_2O	reflux	2	18
15	Na_2CO_3	1:1.2:1.5	H_2O	reflux	2	35
16	NaH	1:1.2:1.5	Et_2O	reflux	2	36
17	NaH	1:1.2:1.5	dioxane	reflux	2	46

[a] Molar ratio of **1a**/**4**/base.
[b] Yield of product after purification by column chromatography.
[c] Enone **1a** was recovered.

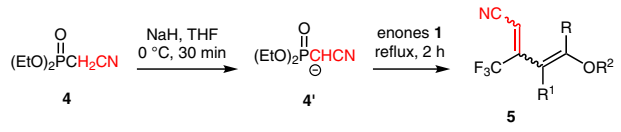
The same conditions were also applied to the reaction of enones **2** with diethyl cyanomethylphosphonate (**4**), which furnished the expected 5-(phenylthio)-3-(trifluoromethyl)penta-2,4-dienenitriles **6** in moderate yields (Table 4).

The reaction of diethyl cyanomethylphosphonate (**4**) was also tested with a series of ethyl 4-alkoxy-2-oxobut-3-enoates **3** as the enone component (Table 5). The reaction conditions used were the same as those used for the series of enones **1** and **2**. The products obtained from this reaction were the ethyl 4-alkoxy-2-(cyanomethylene)but-3-enoates **7**, which had the corresponding structure and similar yields as the previous series of compounds **5** and **6**.

Only a single compound, similar to structure **II** in Scheme 1, was formed in all of the reactions studied (Tables 3–5); compounds corresponding to structures **III**, **IV**, and **V** were not observed. As a general rule, β-substituted enones, such as **1a–f**, **2a**,**c–e**, and **3a–d**, furnished products **5a–f** or the corresponding compounds **6a**,**c–e** and **7a–d** in moderate to very good yields, except for enone **1f**, which gave compound **5f** in low yield. However, α-substituted enones, such as **1g–k**, **2h**, and **3j**,**k**, furnished the corresponding products **5g–k**, **6h**, and **7j**,**k**, respectively, in poor yields, except for enones **1j**,**k**, **2h**, and **3j**, which gave products **5j**,**k**, **6h**, and **7j** in yields of 70%, 55%, 67%, and 60%, respectively (Tables 3–5). The low yields obtained with α-substituted enones are likely due to a steric effect between the α-substituent and the trifluoromethyl or the ethyl carboxylate group, which leads to the carbonyl being removed from the double-bond plane, thus decreasing the reactivity of the carbonyl group.[33] In comparison with the five-membered ring of the dihydrofuran **1i**, the more flexible six-membered ring of the dihydropyrans **1j**,**k** probably accounts for the better yields of products **5j**,**k**.

As mentioned previously, the products obtained from the reaction of enones **1**, **2**, or **3** with diethyl cyanomethylphosphonate (**4**) were exclusively formed as a single regioisomer and, in all cases, the major stereoisomer obtained was (2*E*,4*E*) configured (see Table 6), thus indicating a greater stability of this isomer compared to the other possible stereoisomers.

Table 3 Optimized Reaction Conditions for Obtaining Compounds **5a–k**

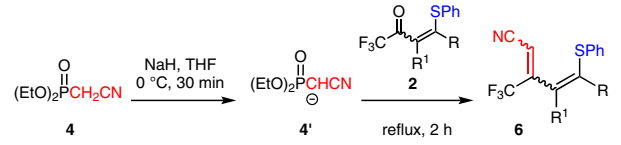


4 **4'** **5**

Enone	R	R^1	R^2	Product	Yield (%)[a]
1a	C_6H_5	H	Me	**5a**	60
1b	4-FC_6H_4	H	Me	**5b**	64
1c	4-BrC_6H_4	H	Me	**5c**	84
1d	4-MeC_6H_4	H	Me	**5d**	93
1e	4-$MeOC_6H_4$	H	Me	**5e**	75
1f	Me	H	Me	**5f**	28
1g	H	Me	Et	**5g**	10
1h	H	Br	Et	**5h**	36
1i	H	$-(CH_2)_2-$		**5i**	20
1j	H	$-(CH_2)_3-$		**5j**	70
1k	H	$-(CH_2)_2CH(OEt)-$		**5k**	55

[a] Yield of product after purification by column chromatography.

Table 4 Optimized Reaction Conditions for Obtaining Compounds **6**



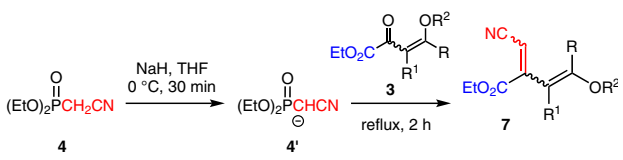
4 **4'** **6**

Enone	R	R^1	Product	Yield (%)[a]
2a	C_6H_5	H	**6a**	67
2c	4-BrC_6H_4	H	**6c**	50
2d	4-MeC_6H_4	H	**6d**	58
2e	4-$MeOC_6H_4$	H	**6e**	44
2h	H	Br	**6h**	67

[a] Yield of product after purification by column chromatography.

Compounds **5a–e**, which are derived from β-substituted trifluoromethylated enones, were obtained as a mixture of four stereoisomers, in which the stereoisomer with the (2*E*,4*E*) configuration represents 45–61% of the product, whereas the stereoisomers with the (2*Z*,4*E*), (2*E*,4*Z*), and (2*Z*,4*Z*) configurations represent 10–38%, 8–23%, and 4–19% of the product, respectively (see Table 6). Surprisingly, product **5f** was composed of only two stereoisomers: (2*E*,4*E*) and (2*Z*,4*E*), in 70% and 30%, respectively. Compounds **6a**,**c–e** had a stereoisomeric composition comparable to compounds **5a**,**c–e** (Table 6). In this series, the stereoisomer with the (2*E*,4*E*) configuration contributed 43–60%,

Table 5 Optimized Reaction Conditions for Obtaining Compounds **7**



4 **4'** **7**

Enone	R	R^1	R^2	Product	Yield (%)[a]
3a	C_6H_5	H	Me	**7a**	57
3b	4-FC_6H_4	H	Me	**7b**	66
3c	4-BrC_6H_4	H	Me	**7c**	79
3d	4-MeC_6H_4	H	Me	**7d**	62
3j	H	$-(CH_2)_3-$		**7j**	60
3k	H	$-(CH_2)_2CH(OEt)-$		**7k**	33

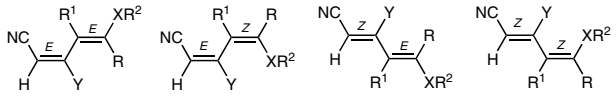
[a] Yield of product after purification by column chromatography.

whereas the stereoisomers with the (2*Z*,4*E*), (2*E*,4*Z*), and (2*Z*,4*Z*) configurations contributed 12–22%, 10–28%, and 8–17%, respectively.

Compounds **7a–d**, which are derived from β-substituted ethyl carboxylate enones, also had a stereoisomeric composition comparable to that of compounds **5a–e**. Compounds **7a** and **7d** were obtained as a mixture of four stereoisomers, in which the stereoisomer with the (2*E*,4*E*) configuration represented 64% and 37% of the product, respectively; the stereoisomer with the (2*Z*,4*E*) configuration represented 28% and 13%, respectively; the stereoisomer with the (2*E*,4*Z*) configuration represented 4% and 48%, respectively, while the (2*Z*,4*Z*) configuration represented less than 5% of the product (Table 6). On the other hand, compounds **7b** and **7c** were obtained as a mixture of two stereoisomers, in which the stereoisomer with the (2*E*,4*E*) configuration represented at least 81% of the product, whereas the stereoisomer with the (2*Z*,4*E*) configuration contributed 14–19%. Products **5g–k** and **7j**,**k**, which were derived from the α-substituted enones **1g–k** and **3j**,**k**, furnished only two stereoisomers: usually the stereoisomer with the (2*E*,4*E*) configuration was predominant over the (2*Z*,4*E*) configuration (see Table 6). An exception was product **5k**, which was composed of one stereoisomer only, the (2*E*,4*E*) isomer.

The characterization of products **5**, **6**, and **7** was unambiguously elucidated by GC-MS, and ^1H and ^{13}C NMR spectroscopy, as well as by two-dimensional NMR experiments such as heteronuclear single quantum coherence (HSQC), heteronuclear multiple bond correlation (HMBC), and nuclear Overhauser effect spectroscopy (NOESY). The structure and percentage of each stereoisomer obtained was determined via a study based on ^1H and ^{13}C NMR chemical shifts, $^1H–^{19}F$ and $^{13}C–^{19}F$ NMR coupling constants, ^1H NMR signal integrals, and NOESY experiments on the representative compounds **5a**, **6a**, and **7a**. Figure 2 shows some of the

Table 6 Proportion of the Stereoisomers Obtained for Compounds **5**, **6**, and **7**[a]



(2*E*,4*E*) (2*E*,4*Z*) (2*Z*,4*E*) (2*Z*,4*Z*)

Compd **5**, X = O; Y = CF_3; R, R^1, and R^2 are defined in Table 3
Compd **6**, X = S; Y = CF_3; R, R^1, and R^2 are defined in Table 4
Compd **7**, X = O; Y = CO_2Et; R, R^1, and R^2 are defined in Table 5

Nitrile	(2*E*,4*E*)	(2*Z*,4*E*)	(2*E*,4*Z*)	(2*Z*,4*Z*)
5a	48	38	8	6
5b	57	18	21	4
5c	61	10	10	19
5d	46	22	15	17
5e	45	25	23	7
5f	70	30	–	–
5g	87	13	–	–
5h	50	50	–	–
5i	65	35	–	–
5j	75	25	–	–
5k	100	–	–	–
6a	50	12	28	10
6c	60	22	10	8
6d	47	16	23	14
6e	43	16	24	17
6h	69	31	–	–
7a	64	28	4	4
7b	86	14	–	–
7c	81	19	–	–
7d	37	13	48	2
7j	84	16	–	–
7k	85	15	–	–

[a] Percentage of the stereoisomers, as determined from ^{1}H NMR signal integrals. A dash indicates <1% of that stereoisomer.

important data that enables the elucidation of the four stereoisomers of compound **5a**, referred to as **5a**, **5a′**, **5a″**, and **5a‴**. H2 and H4 are strategic nuclei for the entire assignment of the structure of each stereoisomer. The ^{1}H NMR signal integrals enable the assignment of every H2 and H4 that belongs to the same stereoisomer. After each stereoisomer was recognized by its respective signal intensities, a sequence of HSQC and HMBC experiments enabled the absolute assignment of all carbon atoms of each stereoisomer. For example, the HSQC spectrum allows the assignment of H2/C2 and H4/C4, based on the respective cross-peaks between them ($^1J_{C-H}$). In the HMBC spectrum, H2 shows cross-peaks with C1, C3, and C4, while H4 has cross-peaks with C2, C3, C5, and the *ipso*-carbon of the phenyl ring. The configuration of each stereoisomer was subsequently identified through a combination of the NOESY data and interpretation of the ^{1}H–^{19}F and ^{13}C–^{19}F NMR coupling constants. For example, the NOESY spectrum of the two major stereoisomers of compound **5a** (**5a** and **5a′**) showed cross-peaks between the methyl of the methoxy group and H4, which allows assignment of the (4*E*) configuration for the double bond at the 4-position for these two stereoisomers (Figure 2). However, the same NOESY spectrum did not indicate any cross-peak between the hydrogens of the phenyl group and H2; this lack of cross-peaks does not allow assignment of the stereochemistry of the double bond at the 2-position from this spectrum. Thus, the configuration of the double bond at the 2-position was provided by an interpretation of the ^{1}H–^{19}F and ^{13}C–^{19}F NMR coupling constants, as shown in Figure 2. It was observed that the 'through-space' coupling constant between H2 and the fluorine atoms of the CF_3 group is a little larger than the 'through-bond' coupling constant. Additionally, the coupling constant between C2 and the fluorine atoms of the CF_3 group is much larger for the (2*E*) configuration (6.1 and 7.2 Hz for **5a** and **5a″**, respectively) than for the (2*Z*) configuration (3.3 and 3.5 Hz for **5a′** and **5a‴**, respectively), while the coupling constant between C4 and the fluorine atoms of the CF_3 group is smaller for the (2*E*) configuration (1.4 and 0.0 Hz for **5a** and **5a″**, respectively) than the (2*Z*) configuration (3.0 Hz for both **5a′** and **5a‴**). Furthermore, it was observed that the chemical shift of H2 is more shielded on the (2*Z*) configuration than it is on the (2*E*) configuration. Thus, the major stereoisomer of compound **5a** was assigned the (2*E*,4*E*) configuration, while the second (**5a′**), third (**5a″**), and minor stereoisomer (**5a‴**) were assigned the (2*Z*,4*E*), (2*E*,4*Z*), and (2*Z*,4*Z*) configuration, respectively (Figure 2).

A very reliable trend with respect to the NMR assignments of the four stereoisomers of compound **5a** was also observed for all other compounds **5** of this series. A similar study was also done for compounds **6a** and **7a**, in order to provide the correct assignment of all other compounds **6** and **7** of these two series. The regions of the ^{1}H NMR spectra in which H2 and H4 appear were expanded for a better observation of the discussed trends (see the Supporting Information). The ^{1}H and ^{13}C NMR chemical shifts of only the two major stereoisomers of each compound are reported in the experimental section. The GC-MS spectra are the same for both stereoisomers reported in the experimental section; the data are given for only one of the stereoisomers.

Compounds **5**, **6**, and **7** can be considered to be attractive intermediates for organic synthesis due to the various electrophilic and nucleophilic centers, as shown in Figure 3. The carbon atoms shown in red (i.e., A, B, and C) are electrophilic centers. Carbon A can undergo Michael-type reactions by either nucleophilic addition, or nucleophilic addition followed by elimination of an alcohol or a benzenethiol molecule. Carbon atoms B and C are electrophilic centers

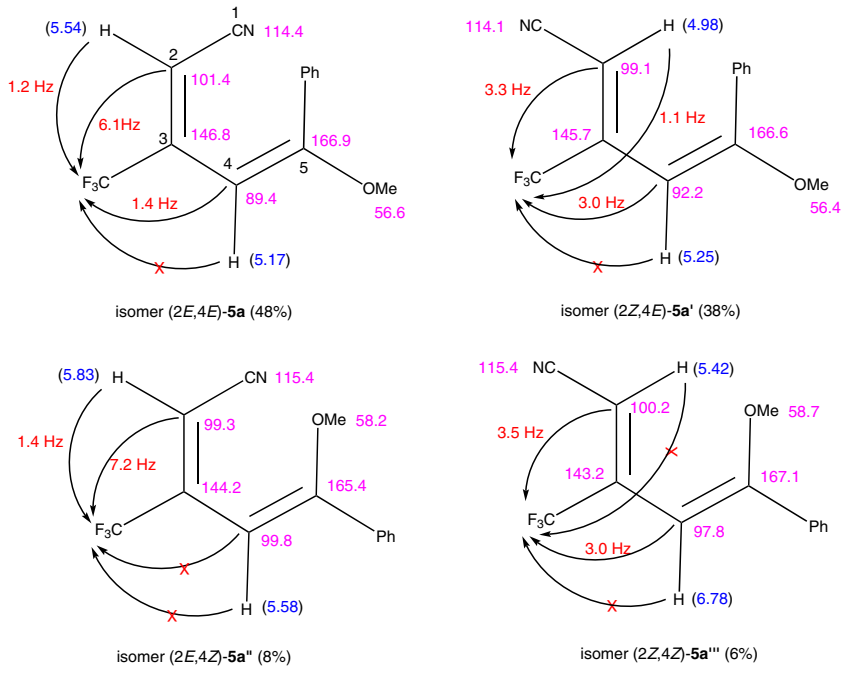


Figure 2 ^{1}H and ^{13}C NMR chemical shifts (blue and pink, respectively), and ^{1}H–^{19}F and ^{13}C–^{19}F NMR coupling constants (red) of H2/C2 and H4/C4 with the fluorine atoms of the CF_3 group

and are suitable for nucleophilic addition, while carbons D and E, and the nitrogen F of the nitrile group are nucleophilic centers. Additionally, products **7** have an ethoxycarbonyl group, which is an electrophilic center suitable for nucleophilic addition/elimination reactions.

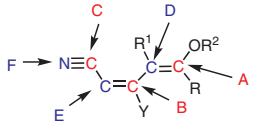


Figure 3 Reaction sites of the penta-2,4-dienenitriles

Despite the products being obtained as a mixture of stereoisomers, which could impose difficulties in controlling the stereochemistry for some types of reactions, the penta-2,4-dienenitriles **5**, **6**, and **7** obtained in this study could be efficiently used for preparing important heterocyclic compounds, such as pyran-2-ones, pyridin-2-imines, and pyridin-2-ones.

In summary, an efficient synthesis of three new series of compounds, 5-alkoxy-3-(trifluoromethyl)penta-2,4-dienenitriles, 5-(phenylthio)-3-(trifluoromethyl)penta-2,4-dienenitriles, and ethyl 4-alkoxy-2-(cyanomethylene)but-3-enoates, obtained from the olefination reaction of the respective enones via the Horner–Wadsworth–Emmons reaction has been outlined. All products were obtained as single regioisomers; however, the composition of the stereoisomers changed according to the enone substituents. A study based on ^{1}H and ^{13}C NMR chemical shifts, ^{1}H–^{19}F and ^{13}C–^{19}F NMR coupling constants, ^{1}H NMR signal integrals, and HSQC, HMBC, and NOESY experiments enabled the determination of the structure and percentage of each stereoisomer obtained. We believe that the penta-2,4-dienenitriles obtained in this study may be suitable as starting materials for the synthesis of important heterocyclic compounds, such as pyran-2-ones, pyridin-2-imines, and pyridin-2-ones; studies in this direction are under development in our laboratory, and the results will be disclosed in the near future.

Low-resolution mass spectra were recorded in EI mode on an Agilent 5975B GC/MSD spectrometer. The GC was equipped with a split/splitless injector, autosampler, and cross-linked HP-5 capillary column (30 m, 0.32 mm internal diameter), and helium was used as the carrier gas. High-resolution mass spectra were recorded on a Bruker LC/MS-QTOF spectrometer in ESI mode. CHN microanalyses were performed on an elemental analyzer. ^{1}H and ^{13}C NMR spectra were acquired on a Bruker DPX 200 spectrometer operating at 200 MHz for ^{1}H NMR and at 50 MHz for ^{13}C NMR, or on a Bruker Avance III spectrometer operating at 400 MHz for ^{1}H NMR and at 100 MHz for ^{13}C NMR, on solutions in $CDCl_3$ and using TMS as the internal reference. All two-dimensional NMR experiments (HSQC, HMBC, and NOESY) were registered at 400 MHz. ^{19}F NMR spectra of selected compounds were acquired on a Bruker Avance III 600 spectrometer (operating at 565 MHz), on solutions in $CDCl_3$ and using fluorobenzene as the external reference with the chemical shifts reported relative to the $CFCl_3$ standard.

1,1,1-Trifluoro-4-(phenylthio)alk-3-en-2-ones 2; General Procedure

To a solution of benzenethiol (1.03 mL, 10.0 mmol) and an enone **1** (5.0 mmol) in anhydrous dichloromethane (5.0 mL), under stirring and argon atmosphere, was added dropwise a solution of $BF_3{\cdot}OEt_2$ (0.74 mL, 6.0 mmol) in anhydrous dichloromethane (5.0 mL). After the addition, the reaction mixture was gradually warmed to 40 °C and stirred at this temperature for 1.5 h. For the workup, the mixture was washed with a 5% solution of sodium carbonate (2 × 50 mL) and distilled water (2 × 50 mL). The organic layer was dried over anhydrous sodium sulfate and filtered, and the solvent was evaporated. (Phenylthio)alkenones **2a** and **2h** were purified by crystallization from hexane, whereas **2c–e** were purified by column chromatography using silica gel (230–400 mesh) and hexane as the eluent.

1,1,1-Trifluoro-4-phenyl-4-(phenylthio)but-3-en-2-one (2a)

Yellow solid; yield: 131 mg (85%); mp 71–74 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.20–7.08 (m, 10 H, Ar), 6.69 (d, *J* = 0.7 Hz, 1 H, H3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 177.4 (q, $^2J_{C-F}$ = 35.2 Hz, C2), 172.5 (C4), 137.5–127.9 (Ar), 116.3 (q, $^1J_{C-F}$ = 290.8 Hz, C1), 113.7 (C3).

GC-MS (EI, 70 eV): *m*/*z* (%) = 308 (49) [M$^+$], 239 (100), 211 (44), 178 (24), 149 (47), 121 (21), 109 (34).

Anal. Calcd for $C_{16}H_{11}F_3OS$ (308.32): C, 62.33; H, 3.60. Found: C, 62.44; H, 3.61.

4-(4-Bromophenyl)-1,1,1-trifluoro-4-(phenylthio)but-3-en-2-one (2c)

Brown oil; yield: 116 mg (60%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.56–6.96 (m, 9 H, Ar), 6.66 (d, *J* = 0.6 Hz, 1 H, H3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 177.8 (q, $^2J_{C-F}$ = 35.2 Hz, C2), 171.3 (C4), 136.8–112.6 (Ar), 116.7 (q, $^1J_{C-F}$ = 290.8 Hz, C1), 108.1 (q, $^3J_{C-F}$ = 11.5 Hz, C3).

GC-MS (EI, 70 eV): *m*/*z* (%) = 388 (9) [M + 2], 386 (9) [M$^+$], 319 (100), 317 (100), 291 (12), 289 (12), 229 (32), 227 (32), 210 (40), 109 (48).

HRMS (ESI): *m*/*z* [M + Na] calcd for $C_{16}H_{10}BrF_3OSNa$: 408.9486; found: 408.9482.

1,1,1-Trifluoro-4-(phenylthio)-4-*p*-tolylbut-3-en-2-one (2d)

Brown oil; yield: 104 mg (60%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.59–6.92 (m, 9 H, Ar), 6.69 (s, 1 H, H3), 2.23 (s, 3 H, Me).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 177.7 (q, $^2J_{C-F}$ = 35.2 Hz, C2), 173.0 (C4), 141.2–128.6 (Ar), 116.8 (q, $^1J_{C-F}$ = 296.8 Hz, C1), 114.0 (C3), 21.6 (Me).

GC-MS (EI, 70 eV): *m*/*z* (%) = 322 (9) [M$^+$], 253 (100), 225 (17), 163 (57), 135 (24), 109 (25).

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{17}H_{14}F_3OS$: 323.0712; found: 323.0715.

1,1,1-Trifluoro-4-(4-methoxyphenyl)-4-(phenylthio)but-3-en-2-one (2e)

Brown oil; yield: 132 mg (78%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.58–6.67 (m, 9 H, Ar), 6.63 (s, 1 H, H3), 3.71 (s, 3 H, OMe).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 177.2 (q, $^2J_{C-F}$ = 34.7 Hz, C2), 171.8 (C4), 160.6 (Ar), 134.9–113.3 (Ar), 116.8 (q, $^1J_{C-F}$ = 285.3 Hz, C1), 108.4 (C3), 55.2 (OMe).

GC-MS (EI, 70 eV): *m*/*z* (%) = 338 (10) [M$^+$], 269 (83), 229 (64), 179 (100), 151 (46), 132 (52), 109 (30).

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{17}H_{14}F_3O_2S$: 339.0661; found: 339.0666.

3-Bromo-1,1,1-trifluoro-4-(phenylthio)but-3-en-2-one (2h)

Yellow solid; yield: 110 mg (71%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.54 (d, *J* = 0.7 Hz, 1 H, H4), 7.56–7.44 (m, 5 H, Ar).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.2 (q, $^2J_{C-F}$ = 35.2 Hz, C2), 157.5 (q, $^3J_{C-F}$ = 4.0 Hz, C3), 131.9–129.8 (Ar), 115.7 (q, $^1J_{C-F}$ = 290.8 Hz, C1), 112.4 (C4).

GC-MS (EI, 70 eV): *m*/*z* (%) = 312 (100) [M + 2], 310 (100) [M$^+$], 243 (83), 241 (81), 134 (67.5), 109 (38).

Anal. Calcd for $C_{10}H_6BrF_3OS$ (311.12): C, 38.60; H, 1.94. Found: C, 38.62; H, 1.96.

Penta-2,4-dienenitriles 5, 6, and 7; General Procedure

To a solution of diethyl cyanomethylphosphonate (**4**; 0.19 mL, 1.2 mmol) in THF (10 mL), under stirring at 0 °C, sodium hydride (0.36 g, 1.5 mmol) was added and the reaction mixture was stirred at 0 °C for 0.5 h. Then, the enone **1**, **2**, or **3** (1.0 mmol) was added to the reaction mixture, which was gradually warmed to reflux and stirred at this temperature for 2.0 h. For the workup, the mixture was washed with ammonium chloride solution (4 × 50 mL). The organic layer was dried over anhydrous sodium sulfate and filtered, and the solvent was evaporated. All penta-2,4-dienenitriles **5**, **6**, and **7** were purified by column chromatography using silica gel (230–400 mesh) and chloroform as the eluent.

5-Methoxy-5-phenyl-3-(trifluoromethyl)penta-2,4-dienenitrile (5a)

Brown oil; yield: 152 mg (60%).

For the (2*E*,4*E*) isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.24 (m, 5 H, Ar), 5.54 (q, *J* = 1.2 Hz, 1 H, H2), 5.17 (s, 1 H, H4), 3.86 (s, 3 H, OMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9 (C5), 146.8 (q, $^2J_{C-F}$ = 31.2 Hz, C3), 134.3–127.8 (Ar), 122.2 (q, $^1J_{C-F}$ = 275.7 Hz, CF_3), 114.4 (C1), 101.4 (q, $^3J_{C-F}$ = 6.1 Hz, C2), 89.4 (q, $^3J_{C-F}$ = 1.4 Hz, C4), 56.6 (OMe).

^{19}F NMR (565 MHz, $CDCl_3$): δ = –68.8 (CF_3).

For the (2*Z*,4*E*) isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.24 (m, 5 H, Ar), 5.25 (s, 1 H, H4), 4.98 (q, *J* = 1.1 Hz, 1 H, H2), 3.82 (s, 3 H, OMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6 (C5), 145.7 (q, $^2J_{C-F}$ = 31 Hz, C3), 133.7–127.8 (Ar), 121.8 (q, $^1J_{C-F}$ = 276 Hz, CF_3), 114.1 (C1), 99.1 (q, $^3J_{C-F}$ = 3.3 Hz, C2), 92.2 (q, $^3J_{C-F}$ = 3.0 Hz, C4), 56.4 (OMe).

^{19}F NMR (565 MHz, $CDCl_3$): δ = –65.7 (CF_3).

GC-MS (EI, 70 eV): *m*/*z* (%) = 253 (98) [M$^+$], 202 (33), 184 (100), 169 (45), 140 (24), 77 (34).

HRMS (ESI): *m*/*z* [M + Na] calcd for $C_{13}H_{10}F_3NONa$: 276.0612; found: 276.0605.

5-(4-Fluorophenyl)-5-methoxy-3-(trifluoromethyl)penta-2,4-dienenitrile (5b)

Red oil; yield: 153 mg (64%).

For the (2*E*,4*E*) isomer:

^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.02–7.02 (m, 4 H, Ar), 5.57 (q, *J* = 1.2 Hz, 1 H, H2), 5.17 (s, 1 H, H4), 3.87 (s, 3 H, OMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.8 (C5), 160.0 (d, $^1J_{C-F}$ = 266.9 Hz, Ar), 146.8 (q, $^2J_{C-F}$ = 31.5 Hz, C3), 130.8 (d, $^3J_{C-F}$ = 8.7 Hz, 2 C, Ar), 122.1 (q, $^1J_{C-F}$ = 275.6 Hz, CF_3), 115.3 (d, $^2J_{C-F}$ = 21.9 Hz, 2 C, Ar), 114.1 (C1), 101.6 (q, $^3J_{C-F}$ = 5.9 Hz, C2), 89.5 (q, $^3J_{C-F}$ = 1.2 Hz, C4), 56.6 (OMe).

^{19}F NMR (565 MHz, $CDCl_3$): δ = –68.8 (CF_3), –109.7 (ArF).

For the (2*E*,4*Z*) isomer:

^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.02–7.02 (m, 4 H, Ar), 5.85 (q, *J* = 1.4 Hz, 1 H, H2), 5.56 (s, 1 H, H4), 3.66 (s, 3 H, OMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.2 (C5), 163.7 (d, $^1J_{C-F}$ = 250.8 Hz, Ar), 144.1 (q, $^2J_{C-F}$ = 32.1 Hz, C3), 130.7 (d, $^3J_{C-F}$ = 8.5 Hz, 2 C, Ar), 121.6 (q, $^1J_{C-F}$ = 277.2 Hz, CF_3), 116.3 (d, $^2J_{C-F}$ = 21.9 Hz, 2 C, Ar), 113.9 (C1), 99.6 (q, $^3J_{C-F}$ = 1.7 Hz, C4), 99.6 (q, $^3J_{C-F}$ = 7.7 Hz, C2), 56.4 (OMe).

^{19}F NMR (565 MHz, $CDCl_3$): δ = –67.2 (CF_3), –109.4 (ArF).

GC-MS (EI, 70 eV): *m*/*z* (%) = 271 (95) [M$^+$], 220 (33), 202 (100), 187 (36), 158 (28), 123 (30), 95 (31).

HRMS (ESI): *m*/*z* [M + Na] calcd for $C_{13}H_9F_4NONa$: 294.0518; found: 294.0523.

5-(4-Bromophenyl)-5-methoxy-3-(trifluoromethyl)penta-2,4-dienenitrile (5c)

Brown oil; yield: 278 mg (84%).

For the (2*E*,4*E*) isomer:

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.61–7.26 (m, 4 H, Ar), 5.58 (s, 1 H, H2), 5.18 (s, 1 H, H4), 3.86 (s, 3 H, OMe).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 165.7 (C5), 146.7 (q, $^2J_{C-F}$ = 31.7 Hz, C3), 133.2–129.4 (Ar), 122.0 (q, $^1J_{C-F}$ = 275.4 Hz, CF_3), 114.5 (C1), 101.9 (q, $^3J_{C-F}$ = 5.7 Hz, C2), 89.7 (q, $^3J_{C-F}$ = 1.5 Hz, C4), 56.8 (OMe).

For the (2*Z*,4*Z*) isomer:

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.61–7.26 (m, 4 H, Ar), 6.79 (s, 1 H, H4), 5.44 (s, 1 H, H2), 3.68 (s, 3 H, OMe).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 165.6 (C5), 142.8 (q, $^2J_{C-F}$ = 30.0 Hz, C3), 132.5–129.4 (Ar), 121.6 (q, $^1J_{C-F}$ = 277.2 Hz, CF_3), 115.2 (C1), 100.0 (q, $^3J_{C-F}$ = 1.4 Hz, C4), 99.8 (q, $^3J_{C-F}$ = 7.0 Hz, C2), 58.8 (OMe).

GC-MS (EI, 70 eV): *m*/*z* (%) = 333 (25) [M + 2], 331 (26) [M$^+$], 252 (100), 232 (58), 183 (74), 140 (44).

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{13}H_{10}BrF_3NO$: 331.9892; found: 331.9891.

5-Methoxy-5-*p*-tolyl-3-(trifluoromethyl)penta-2,4-dienenitrile (5d)

Brown oil; yield: 248 mg (93%).

For the (2*E*,4*E*) isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.16 (m, 4 H, Ar), 5.52 (s, 1 H, H2), 5.14 (s, 1 H, H4), 3.85 (s, 3 H, OMe), 2.35 (s, 3 H, Me).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1 (C5), 147.0 (q, $^2J_{C-F}$ = 31.5 Hz, C3), 140.3–127.6 (Ar), 122.2 (q, $^1J_{C-F}$ = 275.5 Hz, CF_3), 114.6 (C1), 101.1 (q, $^3J_{C-F}$ = 5.9 Hz, C2), 89.1 (q, $^3J_{C-F}$ = 1.6 Hz, C4), 56.5 (OMe), 21.3 (Me).

For the (2*Z*,4*E*) isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.16 (m, 4 H, Ar), 5.22 (s, 1 H, H4), 5.01 (s, 1 H, H2), 3.68 (s, 3 H, OMe), 2.40 (s, 3 H, Me).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.2 (C5), 143.1 (q, $^2J_{C-F}$ = 29.1 Hz, C3), 140.8–127.9 (Ar), 121.7 (q, $^1J_{C-F}$ = 276.9 Hz, CF_3), 115.4 (C1), 98.6 (q, $^3J_{C-F}$ = 3.2 Hz, C2), 92.0 (q, $^3J_{C-F}$ = 3.0 Hz, C4), 58.5 (OMe), 21.3 (Me).

GC-MS (EI, 70 eV): *m*/*z* (%) = 267 (49) [M$^+$], 252 (100), 237 (25), 232 (37), 198 (31), 183 (37), 140 (14), 91 (18).

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{14}H_{13}F_3NO$: 268.0944; found: 268.0940.

5-Methoxy-5-(4-methoxyphenyl)-3-(trifluoromethyl)penta-2,4-dienenitrile (5e)

Brown oil; yield: 212 mg (75%).

For the (2*E*,4*E*) isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94–6.86 (m, 4 H, Ar), 5.53 (s, 1 H, H2), 5.11 (s, 1 H, H4), 3.84 (s, 3 H, OMe), 3.80 (s, 3 H, OMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8 (C5), 161.0 (Ar), 147.0 (q, $^2J_{C-F}$ = 30.1 Hz, C3), 130.2–126.3 (Ar), 122.2 (q, $^1J_{C-F}$ = 274.9 Hz, CF_3), 114.5 (2 C, Ar), 114.0 (C1), 100.6 (q, $^3J_{C-F}$ = 6.6 Hz, C2), 88.7 (q, $^3J_{C-F}$ = 1.5 Hz, C4), 56.2 (OMe), 55.1 (OMe).

For the (2*Z*,4*E*) isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94–6.86 (m, 4 H, Ar), 5.19 (q, *J* = 1.4 Hz, 1 H, H2), 5.06 (s, 1 H, H4), 3.83 (s, 3 H, OMe), 3.80 (s, 3 H, OMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.3 (C5), 161.2 (Ar), 144.4 (q, $^2J_{C-F}$ = 32.0 Hz, C3), 130.0–126.2 (Ar), 122.0 (q, $^1J_{C-F}$ = 275.0 Hz, CF_3), 114.4 (C1), 113.9 (Ar), 98.2 (q, $^3J_{C-F}$ = 3.0 Hz, C2), 91.6 (q, $^3J_{C-F}$ = 3.0 Hz, C4), 56.4 (OMe), 55.2 (OMe).

GC-MS (EI, 70 eV): *m*/*z* (%) = 283 (100) [M$^+$], 257 (35), 252 (72), 232 (39), 214 (98), 199 (34), 183 (24), 135 (31).

HRMS (ESI): *m*/*z* [M + Na] calcd for $C_{14}H_{12}F_3NO_2Na$: 306.0718; found: 306.0727.

5-Methoxy-3-(trifluoromethyl)hexa-2,4-dienenitrile (5f)

Brown oil; yield: 54 mg (28%).

For the (2*E*,4*E*) isomer:

^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.43 (s, 1 H, H2), 5.10 (s, 1 H, H4), 3.68 (s, 3 H, OMe), 2.07 (s, 3 H, Me).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.8 (C5), 147.7 (q, $^2J_{C-F}$ = 31.6 Hz, C3), 121.9 (q, $^1J_{C-F}$ = 275.6 Hz, CF_3), 112.4 (C1), 99.8 (q, $^3J_{C-F}$ = 5.9 Hz, C2), 89.4 (q, $^3J_{C-F}$ = 1.7 Hz, C4), 55.4 (OMe), 19.0 (Me).

For the (2*Z*,4*E*) isomer:

^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.84 (s, 1 H, H4), 5.08 (s, 1 H, H2), 3.69 (s, 3 H, OMe), 2.00 (s, 3 H, Me).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.9 (C5), 146.6 (q, $^2J_{C-F}$ = 30.7 Hz, C3), 121.6 (q, $^1J_{C-F}$ = 276.8 Hz, CF_3), 112.3 (C1), 96.9 (q, $^3J_{C-F}$ = 3.0 Hz, C2), 91.8 (q, $^3J_{C-F}$ = 3.0 Hz, C4), 55.4 (OMe), 19.0 (Me).

GC-MS (EI, 70 eV): *m*/*z* (%) = 191 (100) [M$^+$], 164 (71), 149 (16), 121 (18), 95 (33), 65 (21).

HRMS (ESI): *m*/*z* [M + H] calcd for $C_8H_9F_3NO$: 192.0631; found: compound did not ionize.

5-Ethoxy-4-methyl-3-(trifluoromethyl)penta-2,4-dienenitrile (5g)

Brown oil; yield: 21 mg (10%).

For the (2*E*,4*E*) isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.83 (s, 1 H, H5), 5.40 (s, 1 H, H2), 4.05 (q, *J* = 7.1 Hz, 2 H, H6), 1.78 (s, 3 H, Me), 1.33 (t, *J* = 7.1 Hz, 3 H, H7).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.2 (C5), 147.6 (q, $^2J_{C-F}$ = 30.1 Hz, C3), 121.7 (q, $^1J_{C-F}$ = 278.0 Hz, CF_3), 114.9 (C1), 108.1 (C2), 93.5 (q, $^3J_{C-F}$ = 3.6 Hz, C4), 70.1 (C6), 15.2 (Me), 10.9 (C7).

For the (2*Z*,4*E*) isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.77 (s, 1 H, H5), 5.67 (s, 1 H, H2), 4.05 (q, *J* = 7.1 Hz, 2 H, H6), 1.90 (s, 3 H, Me), 1.33 (t, *J* = 7.1 Hz, 3 H, H7).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.3 (C5), 146.6 (q, $^2J_{C-F}$ = 29.9 Hz, C3), 122.0 (q, $^1J_{C-F}$ = 276.8 Hz, CF_3), 115.8 (C1), 106.2 (C2), 96.6 (q, $^3J_{C-F}$ = 7.1 Hz, C4), 69.6 (C6), 15.3 (Me), 11.3 (C7).

GC-MS (EI, 70 eV): *m*/*z* (%) = 205 (32) [M$^+$], 150 (100), 149 (22), 122 (12), 101 (7), 69 (7).

HRMS (ESI): *m*/*z* [M + H] calcd for $C_9H_{11}F_3NO$: 206.0787; found: compound did not ionize.

4-Bromo-5-ethoxy-3-(trifluoromethyl)penta-2,4-dienenitrile (5h)

Brown oil; yield: 97 mg (36%).

For the (2*E*,4*E*) isomer:

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.24 (s, 1 H, H5), 5.94 (q, *J* = 1.3 Hz, 1 H, H2), 4.23 (q, *J* = 7.1 Hz, 2 H, H6), 1.40 (t, *J* = 7.1 Hz, 3 H, H7).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 154.0 (C5), 143.0 (q, $^2J_{C-F}$ = 31.2 Hz, C3), 120.4 (q, $^1J_{C-F}$ = 278.6 Hz, CF_3), 114.2 (C1), 103.6 (q, $^3J_{C-F}$ = 6.1 Hz, C2), 86.2 (q, $^3J_{C-F}$ = 1.0 Hz, C4), 71.6 (C6), 15.2 (C7).

For the (2*Z*,4*E*) isomer:

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.08 (s, 1 H, H5), 6.16 (s, 1 H, H2), 4.19 (q, *J* = 7.1 Hz, 2 H, H6), 1.40 (t, *J* = 7.1 Hz, 3 H, H7).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 152.7 (C5), 145.4 (q, $^2J_{C-F}$ = 32.4 Hz, C3), 121.1 (q, $^1J_{C-F}$ = 276.8 Hz, CF_3), 114.2 (C1), 100.5 (q, $^3J_{C-F}$ = 3.0 Hz, C2), 95.2 (q, $^3J_{C-F}$ = 0.8 Hz, C4), 70.9 (C6), 15.3 (C7).

GC-MS (EI, 70 eV): *m*/*z* (%) = 271 (37) [M + 2], 269 (38) [M$^+$], 243 (18), 241 (20), 216 (95), 214 (100), 196 (10), 194 (10), 142 (11), 107 (12), 69 (13).

HRMS (ESI): *m*/*z* [M + Na] calcd for $C_8H_7BrF_3NONa$: 291.9561; found: 291.9570.

3-(4,5-Dihydrofuran-3-yl)-4,4,4-trifluorobut-2-enenitrile (5i)

Brown oil; yield: 38 mg (20%).

For the (2*E*,4*E*) isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.12 (q, *J* = 1.76 Hz, 1 H, H5), 5.52 (q, *J* = 0.48 Hz, 1 H, H2), 4.64–4.56 (m, 2 H, H6), 3.32 (tq, J_t = 9.44 Hz, J_q = 0.68 Hz, 2 H, H7).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.1 (q, $^4J_{C-F}$ = 3.0 Hz, C5), 141.8 (q, $^2J_{C-F}$ = 31.0 Hz, C3), 122.0 (q, J_{C-F} = 276.0 Hz, CF_3), 116.1 (C1), 109.5 (C4), 91.6 (q, $^3J_{C-F}$ = 7.0 Hz, C2), 72.6 (C6), 29.5 (C7).

For the (2*Z*,4*E*) isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.08 (q, *J* = 1.48 Hz, 1 H, H5), 5.10 (d, *J* = 0.72 Hz, 1 H, H2), 4.64–4.56 (m, 2 H, H6), 2.81 (tq, J_t = 9.56 Hz, J_q = 0.68 Hz, 2 H, H7).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.5 (q, $^4J_{C-F}$ = 4.0 Hz, C5), 142.2 (q, $^2J_{C-F}$ = 32.0 Hz, C3), 121.5 (q, J_{C-F} = 276.0 Hz, CF_3), 114.9 (C1), 110.3 (C4), 92.4 (q, $^3J_{C-F}$ = 3.0 Hz, C2), 71.6 (C6), 29.6 (C7).

GC-MS (EI, 70 eV): *m*/*z* (%) = 189 (100) [M$^+$], 188 (39), 162 (29), 134 (45), 114 (33), 92 (15), 69 (11).

HRMS (ESI): *m*/*z* [M + H] calcd for $C_8H_7F_3NO$: 190.0474; found: compound did not ionize.

3-(3,4-Dihydro-2*H*-pyran-5-yl)-4,4,4-trifluorobut-2-enenitrile (5j)

Brown oil; yield: 142 mg (70%).

For the (2*E*,4*E*) isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.06 (s, 1 H, H5), 5.67 (q, J_{H-F} = 1.32 Hz, 1 H, H2), 4.11–4.06 (m, 2 H, H6), 2.14 (t, *J* = 6.28 Hz, 2 H, H8), 2.03–1.96 (m, 2 H, H7).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.9 (q, $^4J_{C-F}$ = 1.0 Hz, C5), 148.3 (q, $^2J_{C-F}$ = 30.0 Hz, C3), 122.0 (q, J_{C-F} = 276.0 Hz, CF_3), 115.8 (C1), 105.9 (C4), 96.2 (q, $^3J_{C-F}$ = 7.0 Hz, C2), 66.3 (C6), 21.8 (8), 21.2 (C7).

^{19}F NMR (565 MHz, $CDCl_3$): δ = –64.3 (CF_3).

For the (2*Z*,4*E*) isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.14 (s, 1 H, H5), 5.35 (s, 1 H, H2), 4.11–4.06 (m, 2 H, H6), 2.42 (t, *J* = 6.32 Hz, 2 H, H8), 2.03–1.96 (m, 2 H, H7).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.7 (q, $^4J_{C-F}$ = 4.0 Hz, C5), 146.7 (q, $^2J_{C-F}$ = 30.0 Hz, C3), 121.6 (q, J_{C-F} = 276.0 Hz, CF_3), 114.9 (C1), 107.0 (C4), 92.6 (q, $^3J_{C-F}$ = 3.0 Hz, C2), 66.2 (C6), 21.1 (C8), 21.0 (C7).

^{19}F NMR (565 MHz, $CDCl_3$): δ = –58.8 (CF_3).

GC-MS (EI, 70 eV): *m*/*z* (%) = 203 (100) [M$^+$], 202 (11), 188 (19), 174 (55), 147 (25), 127 (47), 106 (34), 79 (26).

HRMS (ESI): *m*/*z* [M + H] calcd for $C_9H_9F_3NO$: 204.0631; found: 204.0641.

3-(2-Ethoxy-3,4-dihydro-2*H*-pyran-5-yl)-4,4,4-trifluorobut-2-enenitrile (5k)

Brown oil; yield: 140 mg (55%).

Only the (2*E*,4*E*) isomer:

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.02 (s 1 H, H5), 5.39 (s, 1 H, H2), 5.13 (t, *J* = 8.6 Hz, 1 H, H6), 3.92–3.53 (m, 2 H, H9), 2.35–1.84 (m, 4 H, H7, H8), 1.21 (t, *J* = 7.1 Hz, 3 H, H10).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.1 (q, *J* = 4.0 Hz, C5), 146.5 (q, $^2J_{C-F}$ = 30.7 Hz, C3), 121.4 (q, $^1J_{C-F}$ = 278.3 Hz, CF_3), 114.6 (C1), 107.8 (C6), 96.9 (C4), 93.4 (q, $^3J_{C-F}$ = 3.5 Hz, C2), 64.4 (C9), 25.6 (C8), 17.5 (C7), 14.9 (C10).

^{19}F NMR (565 MHz, $CDCl_3$): δ = –58.9 (CF_3).

GC-MS (EI, 70 eV): *m*/*z* (%) = 247 (50) [M$^+$], 202 (31), 192 (18), 163 (18), 148 (8), 127 (15), 104 (9), 72 (100).

HRMS (ESI): *m*/*z* [M + Na] calcd for $C_{11}H_{12}F_3NO_2Na$: 270.0718; found: 270.0714.

5-Phenyl-5-(phenylthio)-3-(trifluoromethyl)penta-2,4-dienenitrile (6a)

Brown oil; yield: 220 mg (67%).

For the (2*E*,4*E*) isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.12 (m, 10 H, Ar), 6.42 (s, 1 H, H4), 6.11 (q, *J* = 1.1 Hz, 1 H, H2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.5 (C5), 145.9 (q, $^2J_{C-F}$ = 32.2 Hz, C3), 134.8–127.5 (Ar), 121.5 (q, $^1J_{C-F}$ = 275.6 Hz, CF_3), 118.3 (q, $^3J_{C-F}$ = 1.5 Hz, C4), 114.4 (C1), 104.4 (q, $^3J_{C-F}$ = 6.1 Hz, C2).

^{19}F NMR (565 MHz, $CDCl_3$): δ = –67.9 (CF_3).

For the (2*E*,4*Z*) isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.12 (m, 10 H, Ar), 6.48 (s, 1 H, H4), 6.44 (q, *J* = 0.9 Hz, 1 H, H2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.1 (C5), 143.1 (q, $^2J_{C–F}$ = 30.4 Hz, C3), 135.0–128.1 (Ar), 121.4 (q, $^1J_{C–F}$ = 277.4 Hz, CF_3), 119.3 (q, $^3J_{C–F}$ = 3.0 Hz, C4), 113.8 (C1), 102.3 (q, $^3J_{C–F}$ = 3.4 Hz, C2).

^{19}F NMR (565 MHz, $CDCl_3$): δ = –64.6 (CF_3).

GC-MS (EI, 70 eV): *m*/*z* (%) = 331 (46) [M$^+$], 304 (100), 253 (22), 222 (32), 202 (68), 152 (17), 121 (27), 110 (26), 77 (16).

HRMS (ESI): *m*/*z* [M + Na] calcd for $C_{18}H_{12}F_3NSNa$: 354.0540; found: 354.0523.

5-(4-Bromophenyl)-5-(phenylthio)-3-(trifluoromethyl)penta-2,4-dienenitrile (6c)

Yellow oil; yield: 210 mg (50%).

For the (2*E*,4*E*) isomer:

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.56–7.11 (m, 9 H, Ar), 6.41 (s, 1 H, H4), 6.11 (q, *J* = 1.0 Hz, 1 H, H2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.1 (C5), 150.3, 146.9 (Ar), 145.6 (q, $^2J_{C–F}$ = 32.4 Hz, C3), 137.2–127.8 (Ar), 121.5 (q, $^1J_{C–F}$ = 275.8 Hz, CF_3), 118.8 (q, $^3J_{C–F}$ = 1.5 Hz, C4), 114.2 (C1), 104.9 (q, $^3J_{C–F}$ = 6.1 Hz, C2).

For the (2*Z*,4*E*) isomer:

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.56–7.11 (m, 9 H, Ar), 5.67 (s, 1 H, H4), 5.55 (q, *J* = 1.0 Hz, 1 H, H2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.8 (C5), 149.5 (Ar), 146.4 (q, $^2J_{C–F}$ = 32.1 Hz, C3), 137.3–123.8 (Ar), 121.5 (q, $^1J_{C–F}$ = 275.7 Hz, CF_3), 111.7 (q, $^3J_{C–F}$ = 1.1 Hz, C4), 111.7 (C1), 103.0 (q, $^3J_{C–F}$ = 6.2 Hz, C2).

GC-MS (EI, 70 eV): *m*/*z* (%) = 411 (20) [M + 2], 409 (20) [M$^+$], 384 (12), 382 (11), 342 (7), 340 (7), 302 (1), 300 (12), 252 (13), 221 (100), 201 (21), 171 (15), 152 (14), 110 (23), 109 (35).

HRMS (ESI): *m*/*z* [M + Na] calcd for $C_{18}H_{11}BrF_3NSNa$: 431.9645; found: 431.9639.

5-(Phenylthio)-5-*p*-tolyl-3-(trifluoromethyl)penta-2,4-dienenitrile (6d)

Brown oil; yield: 200 mg (58%).

For the (2*E*,4*E*) isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.06 (m, 9 H, Ar), 6.42 (s, 1 H, H4), 6.08 (q, *J* = 1.2 Hz, 1 H, H2), 2.30 (s, 3 H, Me).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.2 (C5), 145.9 (q, $^2J_{C–F}$ = 32.1 Hz, C3), 139.7–127.3 (Ar), 121.6 (q, $^1J_{C–F}$ = 275.7 Hz, CF_3), 117.9 (q, $^3J_{C–F}$ = 0.9 Hz, C4), 114.5 (C1), 104.2 (q, $^3J_{C–F}$ = 5.9 Hz, C2), 21.1 (Me).

^{19}F NMR (565 MHz, $CDCl_3$): δ = –67.9 (CF_3).

For the (2*E*,4*Z*) isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.06 (m, 9 H, Ar), 6.50 (s, 1 H, H4), 6.44 (q, *J* = 0.7 Hz, 1 H, H2), 2.40 (s, 3 H, Me).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.8 (C5), 143.2 (q, $^2J_{C–F}$ = 30.1 Hz, C3), 139.9–127.9 (Ar), 121.3 (q, $^1J_{C–F}$ = 277.4 Hz, CF_3), 119.3 (q, $^3J_{C–F}$ = 3.0 Hz, C4), 114.4 (C1), 102.1 (q, $^3J_{C–F}$ = 3.3 Hz, C2), 21.3 (Me).

^{19}F NMR (565 MHz, $CDCl_3$): δ = –64.6 (CF_3).

GC-MS (EI, 70 eV): *m*/*z* (%) = 345 (33) [M$^+$], 318 (100), 267 (13), 236 (61), 216 (52), 167 (22), 135 (22), 110 (14), 91 (5).

HRMS (ESI): *m*/*z* [M + Na] calcd for $C_{19}H_{14}F_3NSNa$: 368.0697; found: 368.0694.

5-(4-Methoxyphenyl)-5-(phenylthio)-3-(trifluoromethyl)penta-2,4-dienenitrile (6e)

Brown oil; yield: 160 mg (44%).

For the (2*E*,4*E*) isomer:

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.53–6.74 (m, 9 H, Ar), 6.37 (s, 1 H, H4), 6.06 (q, *J* = 1.0 Hz, 1 H, H2), 3.75 (s, 3 H, OMe).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 160.7 (Ar), 150.7 (C5), 145.9 (q, $^2J_{C–F}$ = 32.0 Hz, C3), 134.8–127.3 (Ar), 121.6 (q, $^1J_{C–F}$ = 275.7 Hz, CF_3), 117.1 (q, $^3J_{C–F}$ = 0.9 Hz, C4), 114.9 (C1), 103.9 (q, $^3J_{C–F}$ = 6.1 Hz, C2), 55.2 (OMe).

For the (2*E*,4*Z*) isomer:

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.53–6.74 (m, 9 H, Ar), 6.44 (s, 1 H, H4), 6.41 (q, *J* = 1.2 Hz, 1 H, H2), 3.83 (s, 3 H, OMe).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 160.8 (Ar), 150.4 (C5), 143.1 (q, $^2J_{C–F}$ = 30.3 Hz, C3), 134.6–129.2 (Ar), 121.5 (q, $^1J_{C–F}$ = 277.4 Hz, CF_3), 118.6 (q, $^3J_{C–F}$ = 2.9 Hz, C4), 114.6 (C1), 101.6 (q, $^3J_{C–F}$ = 3.2 Hz, C2), 55.3 (OMe).

GC-MS (EI, 70 eV): *m*/*z* (%) = 361 (33) [M$^+$], 334 (21), 284 (5), 252 (100), 232 (31), 209 (9), 189 (9), 151 (12).

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{19}H_{15}F_3NOS$: 362.0821; found: 362.0817.

4-Bromo-5-(phenylthio)-3-(trifluoromethyl)penta-2,4-dienenitrile (6h)

Brown oil; yield: 220 mg (67%).

For the (2*E*,4*E*) isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55–7.37 (m, 5 H, Ar), 7.51 (s, 1 H, H5), 6.00 (q, *J* = 1.2 Hz, 1 H, H2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.6 (q, $^2J_{C–F}$ = 32.6 Hz, C3), 143.9 (C4), 143.4 (C5), 138.2–128.9 (Ar), 120.7 (q, $^1J_{C–F}$ = 279.3 Hz, CF_3), 113.8 (C1), 104.3 (q, $^3J_{C–F}$ = 6.0 Hz, C2).

For the (2*Z*,4*E*) isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55–7.37 (m, 5 H, Ar), 7.51 (s, 1 H, H5), 6.22 (s, 1 H, H2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.1 (q, $^2J_{C–F}$ = 30.2 Hz, C3), 145.6 (C5), 144.7 (C4), 137.2–129.2 (Ar), 120.3 (q, $^1J_{C–F}$ = 278.8 Hz, CF_3), 113.7 (C1), 102.9 (q, $^3J_{C–F}$ = 2.3 Hz, C2).

GC-MS (EI, 70 eV): *m*/*z* (%) = 335 (100) [M + 2], 333 (100), 254 (60), 221 (25), 190 (18), 109 (75), 65 (23).

HRMS (ESI): *m*/*z* [M + Na$^+$] calcd for $C_{12}H_8BrF_3NS$: 355.9332; found: 355.9313.

Ethyl 2-(Cyanomethylene)-4-methoxy-4-phenylbut-3-enoate (7a)

Yellow oil; yield: 150 mg (57%).

For the (2*E*,4*E*) isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.32 (m, 5 H, Ar), 5.81 (s, 1 H, H2), 5.70 (d, *J* = 1.2 Hz, 1 H, H4), 3.90 (s, 3 H, OMe), 3.61 (q, *J* = 7.1 Hz, 2 H, H7), 0.96 (t, *J* = 7.2 Hz, 3 H, H8).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.4 (C6), 150.6 (C5), 135.5 (C3), 130.0–128.2 (Ar), 116.3 (C4), 100.4 (C1), 94.8 (C2), 61.7 (C7), 56.4 (OMe), 13.4 (C8).

For the (2*Z*,4*E*) isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.32 (m, 5 H, Ar), 5.58 (s, 1 H, H4), 5.30 (d, *J* = 0.9 Hz, 1 H, H2), 3.84 (q, *J* = 7.1 Hz, 2 H, H7), 3.82 (s, 3 H, OMe), 1.16 (t, *J* = 7.2 Hz, 3 H, H8).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.8 (C6), 149.8 (C5), 134.6 (C3), 130.1 (Ar), 128.8–128.4 (Ar), 116.2 (C4), 98.4 (C1), 96.7 (C2), 61.9 (C7), 56.2 (OMe), 13.5 (C8).

GC-MS (EI, 70 eV): *m*/*z* (%) = 257 (30) [M$^+$], 228 (26), 210 (21), 184 (100), 169 (44), 140 (25), 115 (18), 77 (24).

HRMS (ESI): *m*/*z* [M + Na] calcd for $C_{15}H_{15}NO_3Na$: 280.0950; found: 280.0951.

Ethyl 2-(Cyanomethylene)-4-(4-fluorophenyl)-4-methoxybut-3-enoate (7b)

Red oil; yield: 182 mg (66%).

For the (2*E*,4*E*) isomer:

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.38–7.31 (m, 2 H, Ar), 7.09–7.00 (m, 2 H, Ar), 5.79 (s, 1 H, H2), 5.74 (d, *J* = 1.2 Hz, 1 H, H4), 3.91 (s, 3 H, OMe), 3.71 (q, *J* = 7.2 Hz, 2 H, H7), 1.02 (t, *J* = 7.1 Hz, 3 H, H8).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.4 (C6), 164.7 (C5), 163.3 (d, $^1J_{C-F}$ = 250.7 Hz, Ar), 150.3 (Ar), 131.8 (C3), 130.7 (d, $^3J_{C-F}$ = 8.6 Hz, 2 C, Ar), 116.4 (C4), 115.3 (d, $^2J_{C-F}$ = 21.8 Hz, 2 C, Ar), 100.9 (C1), 94.8 (C2), 62.0 (C7), 56.5 (OMe), 13.6 (C8).

For the (2*Z*,4*E*) isomer:

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.38–7.31 (m, 2 H, Ar), 7.09–7.00 (m, 2 H, Ar), 5.57 (s, 1 H, H2), 5.35 (d, *J* = 1.0 Hz, 1 H, H4), 3.84 (s, 3 H, OMe), 3.71 (q, *J* = 7.2 Hz, 2 H, H7), 1.19 (t, *J* = 7.2 Hz, 3 H, H8).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.4 (C6), 164.1 (C5), 163.3 (d, $^1J_{C-F}$ = 250.7 Hz, Ar), 149.8 (Ar), 131.7 (C3), 131.0 (d, $^3J_{C-F}$ = 8.6 Hz, 2 C, Ar), 116.2 (C4), 115.5 (d, $^2J_{C-F}$ = 21.8 Hz, 2 C, Ar), 98.7 (C1), 96.9 (C2), 62.1 (C7), 56.4 (OMe), 13.6 (C8).

GC-MS (EI, 70 eV): *m*/*z* (%) = 275 (40) [M^{2+}], 202 (100), 158 (26), 123 (26), 95 (22).

HRMS (ESI): *m*/*z* [M + Na] calcd for $C_{15}H_{14}FNO_3Na$: 298.0855; found: 298.0862.

Ethyl 4-(4-Bromophenyl)-2-(cyanomethylene)-4-methoxybut-3-enoate (7c)

Yellow oil; yield: 270 mg (79%).

For the (2*E*,4*E*) isomer:

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 8.6 Hz, 2 H, Ar), 7.22 (d, *J* = 8.6 Hz, 2 H, Ar), 5.79 (s, 1 H, H2), 5.76 (d, *J* = 1.2 Hz, 1 H, H4), 3.90 (s, 3 H, OMe), 3.72 (q, *J* = 7.1 Hz, 2 H, H7), 1.00 (t, *J* = 7.2 Hz, 3 H, H8).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.4 (C6), 164.0 (C5), 149.5 (Ar), 133.5 (C3), 131.7–124.6 (Ar), 116.1 (C4), 99.2 (C1), 97.0 (C2), 62.2 (C7), 56.4 (OMe), 13.6 (C8).

For the (2*Z*,4*E*) isomer:

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 8.5 Hz, 2 H, Ar), 7.25 (d, *J* = 8.0 Hz, 2 H, Ar), 5.57 (s, 1 H, H2), 5.36 (d, *J* = 1.0 Hz, 1 H, H4), 3.83 (s, 3 H, OMe), 3.72 (q, *J* = 7.1 Hz, 2 H, H7), 1.19 (t, *J* = 7.2 Hz, 3 H, H8).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.4 (C6), 164.0 (C5), 149.5 (Ar), 133.5 (C3), 132.1–124.6 (Ar), 116.1 (C4), 99.1 (C1), 96.7 (C2), 62.2 (C7), 56.4 (OMe), 13.6 (C8).

GC-MS (EI, 70 eV): *m*/*z* (%) = 337 (16) [M + 2], 335 (16) [M$^+$], 264 (20), 262 (21), 210 (23), 184 (65), 183 (100), 169 (18), 153 (18), 140 (35).

HRMS (ESI): *m*/*z* [M + Na] calcd for $C_{15}H_{14}BrNO_3Na$: 358.0055; found: 358.0070.

Ethyl 2-(Cyanomethylene)-4-methoxy-4-*p*-tolylbut-3-enoate (7d)

Brown oil; yield: 170 mg (62%).

For the (2*E*,4*E*) isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.14 (m, 4 H, Ar), 5.80 (s, 1 H, H2), 5.68 (d, *J* = 0.9 Hz, 1 H, H4), 3.90 (s, 3 H, OMe), 3.63 (q, *J* = 7.1 Hz, 2 H, H7), 2.35 (s, 3 H, Me), 0.98 (t, *J* = 7.2 Hz, 3 H, H8).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.2 (C6), 165.6 (C5), 151.0 (Ar), 140.3 (C3), 128.9–125.4 (Ar), 116.5 (C4), 99.9 (C1), 94.6 (C2), 61.8 (C7), 56.4 (OMe), 21.3 (Me), 13.5 (C8).

For the (2*E*,4*Z*) isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.14 (m, 4 H, Ar), 6.01 (s, 1 H, H2), 5.52 (s, 1 H, H4), 4.33 (q, *J* = 7.0 Hz, 2 H, H7), 3.53 (s, 3 H, OMe), 2.40 (s, 3 H, Me), 1.37 (t, *J* = 7.2 Hz, 3 H, H8).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.7 (C6), 163.9 (C5), 149.1 (Ar), 140.6 (C3), 129.4–124.0 (Ar), 116.1 (C4), 104.7 (C1), 97.8 (C2), 61.9 (C7), 58.4 (OMe), 21.3 (Me), 14.1 (C8).

GC-MS (EI, 70 eV): *m*/*z* (%) = 271 (39) [M$^+$], 256 (14), 228 (20), 210 (36), 198 (95), 184 (100), 183 (55), 169 (17), 154 (21), 140 (28), 119 (24), 91 (29).

HRMS (ESI): *m*/*z* [M + Na] calcd for $C_{16}H_{17}NO_3Na$: 294.1106; found: 294.1103.

Ethyl 3-Cyano-2-(3,4-dihydro-2*H*-pyran-5-yl)acrylate (7j)

Yellow oil; yield: 120 mg (60%).

For the (2*E*,4*E*) isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.98 (s, 1 H, H5), 5.09 (s, 1 H, H2), 4.36 (q, *J* = 7.2 Hz, 2 H, H10), 4.05 (t, *J* = 5.4 Hz, 2 H, H6), 2.10 (t, *J* = 6.4 Hz, 2 H, H8), 1.96 (q, *J* = 6.0 Hz, 2 H, H7), 1.36 (t, *J* = 7.1 Hz, 3 H, H11).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.3 (C9), 152.4 (C5), 150.7 (C3), 116.8 (C4), 109.3 (C1), 89.3 (C2), 66.5 (C6), 62.4 (C10), 21.0 (C8), 19.7 (C7), 13.9 (C11).

For the (2*Z*,4*E*) isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.99 (s, 1 H, H5), 5.73 (s, 1 H, H2), 4.24 (q, *J* = 7.1 Hz, 2 H, H10), 4.07 (t, *J* = 5.3 Hz, 2 H, H6), 2.45 (t, *J* = 6.3 Hz, 2 H, H8), 1.96 (q, *J* = 6.0 Hz, 2 H, H7), 1.30 (t, *J* = 7.1 Hz, 3 H, H11).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.4 (C9), 153.1 (C5), 151.1 (C3), 117.0 (C4), 108.9 (C1), 97.8 (C2), 66.3 (C6), 62.2 (C10), 22.1 (C7), 21.4 (C8), 14.0 (C11).

GC-MS (EI, 70 eV): *m*/*z* (%) = 207 (1) [M$^+$], 170 (24), 141 (100), 125 (8), 113 (12), 95 (32), 69 (12).

HRMS (ESI): *m*/*z* [M – H] calcd for $C_{11}H_{14}NO_3$: 206.0817; found: 206.0831.

Ethyl 3-Cyano-2-(2-ethoxy-3,4-dihydro-2*H*-pyran-5-yl)acrylate (7k)

Brown oil; yield: 83 mg (33%).

For the (2*E*,4*E*) isomer:

^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.80 (s, 1 H, H5), 5.10 (s, 1 H, H2), 5.04 (t, *J* = 3.0 Hz, 1 H, H6), 4.31 (q, *J* = 7.1 Hz, 2 H, C(O)OCH_2), 3.82–3.46 (m, 2 H, OCH_2), 1.98–1.91 (m, 4 H, H7, H8), 1.31 (t, *J* = 7.1 Hz, 3 H, O–C–CH_3), 1.11 (t, *J* = 7.1 Hz, 3 H, C(O)O–C–CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 165.6 (C=O), 153.1 (C5), 149.5 (C3), 117.1 (C4), 110.4 (C1), 97.8 (C2), 90.6 (C6), 64.8 (OCH_2), 62.9 (C(O)OCH_2), 25.9–16.7 (C7, C8), 15.4–14.3 (O–C–CH_3, C(O)O–C–CH_3).

For the (2*Z*,4*E*) isomer:

^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.80 (s, 1 H, H5), 5.75 (s, 1 H, H2), 5.04 (t, *J* = 3.0 Hz, 1 H, H6), 4.19 (q, *J* = 7.2 Hz, 2 H, C(O)OCH_2), 3.82–3.46 (m, 2 H, OCH_2), 2.26–2.03 (m, 4 H, H7, H8), 1.31 (t, *J* = 7.1 Hz, 3 H, O–C–CH_3), 1.11 (t, *J* = 7.1 Hz, 3 H, C(O)O–C–CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 165.6 (C=O), 151.1 (C5), 147.8 (C3), 117.2 (C4), 110.1 (C1), 99.3 (C6), 97.6 (C2), 64.6 (OCH_2), 62.6 (C(O)OCH_2), 26.3–19.1 (C7, C8), 15.5–14.4 (O–C–CH_3, C(O)O–C–CH_3).

GC-MS (EI, 70 eV): *m*/*z* (%) = 251 (9) [M^+], 205 (12), 178 (14), 159 (16), 134 (21), 93 (8), 72 (100), 65 (17).

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{13}H_{18}NO_4$: 252.1230; found: 252.1234.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1590871. Included are copies of ^{1}H, ^{13}C, and ^{19}F NMR spectra, HSQC, HMBC, and NOESY data for selected compounds, and mass spectra.

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