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Reaction of Baylis–Hillman Adducts with Fluorinated Silanes

Artem A. Zemtsov,[a] Vitalij V. Levin,[a] Alexander D. Dilman,*[a] Marina I. Struchkova,[a] Pavel A. Belyakov,[a] Vladimir A. Tartakovsky,[a] and Jinbo Hu[b]

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Reactions of acylated Baylis–Hillman adducts bearing nitrile, ester, or ketone groups with C_6F_5-substituted silicon reagents $Me_nSi(C_6F_5)_{4-n}$ (n = 1–3) have been studied. The reactions are initiated by Bu_4NOAc (5 mol-%) in MeCN or DMF under mild conditions and afford products of allylic substitution of the acetoxy group by the C_6F_5 carbanion in good yields. Predominant or exclusive formation of one geometrical isomer was observed in all cases (*Z* for nitriles, *E* for esters and ketones). For substrates containing carbonyl groups, nucleophilic attack of the C_6F_5 carbanion chemoselectively occurred at the C=C bond. Reactions of acylated Baylis–Hillman adducts with Me_3SiCF_3 were found to be inefficient, as the CF_3 carbanion had the propensity to attack the C=O bond of substrates with ester or ketone substituents.

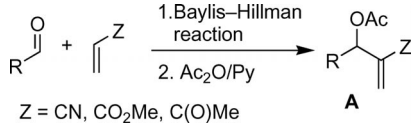
Introduction

Organosilanes bearing a perfluorinated group have become valuable reagents for the introduction of fluorinated substituents into organic molecules.[1,2] Thus, in the presence of basic activators (e.g., fluoride or acetate ions) the silicon reagents are activated to generate pentacoordinate species, which serve as a source of fluorinated carbanion in reactions with electrophiles [Equation (1)].

R_F = CF_3, C_6F_5; X = F, OAc Y = O, NR, CR_2 (1)

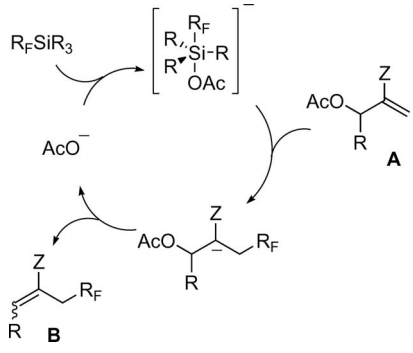
Although the use of silanes for the nucleophilic addition of fluorinated groups to C=O and C=N bonds has been extensively investigated,[1,3,4] the addition to electron-deficient alkenes is still considered a challenging problem. The difficulties in performing such transformations are associated with low reactivity of typical Michael acceptors bearing nitrile or ester substituents, whereas α,β-unsaturated aldehydes and ketones undergo preferential attack at the carbonyl carbon atom.[5]

Recently, we reported an approach for the nucleophilic trifluoromethylation of alkenes bearing either two geminal nitrile groups[6] or Meldrum's acid,[7] which renders such substrates highly electrophilic.[8] Here we report the results of studies to extend the scope of the Michael reaction by using fluorinated silanes. We employed compounds of type **A** as Michael acceptors, which can be obtained from aldehydes and simple electron-deficient alkenes by Baylis–Hillman reactions followed by acylation [Equation (2)].



Z = CN, CO_2Me, C(O)Me (2)

The presence of the acetoxy group in substrates **A** serves two purposes. Firstly, due to its electron-withdrawing effect, it enhances the electrophilicity of the alkene double bond.[9] Secondly, after the nucleophilic addition at the C=C bond, the acetoxy group is eliminated, and if acetate anion serves as a Lewis base,[3b] the process can become catalytic in acetate.[10] (Scheme 1).



Scheme 1. Proposed reaction mechanism.

The overall transformation may be viewed as an allylic S_N2' substitution leading to products **B**. The trisubstituted

[a] N. D. Zelinsky Institute of Organic Chemistry,
119991 Moscow, Leninsky Prospect 47, Russian Federation
Fax: +7-499-135-53-28
E-mail: adil25@mail.ru
[b] Key Laboratory of Organofluorine Chemistry,
Shanghai Institute of Organic Chemistry,
Chinese Academy of Sciences,
345 Ling-Ling Road, Shanghai 200032, P. R. China
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double bond of products **B** is anticipated to be less reactive than the terminal double bond of **A**. Another important variable is the nature of the silicon reagent. Indeed, we have previously shown that the efficiency of reactions involving silanes is strongly influenced by the number of perfluorinated and heteroatom groups borne by the silicon.[11] In the case of the trifluoromethyl group, the only available silane is Me_3SiCF_3 (Ruppert–Prakash reagent). Synthesis of other CF_3-containing silanes is complicated.[12] At the same time, various C_6F_5-substituted silanes can be readily synthesized by using pentafluorophenylmagnesium bromide and chlorosilanes.[13] Inspired by this realization, we first studied reactions of substrates **A** with C_6F_5-substituted silanes and then with the Ruppert–Prakash reagent.

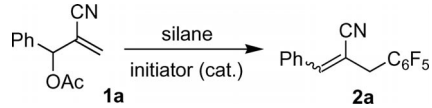
Results and Discussion

Nitrile **1a** was selected as a model substrate and its pentafluorophenylation was carried out. Silanes were employed in ratios leading to 1.5 equivalents of C_6F_5 per equivalent of substrate (Table 1). The addition of sodium acetate (10 mol-%) to a solution of **1a** and $MeSi(C_6F_5)_3$ in DMF at room temperature was exothermic, leading to complete consumption of starting **1a**. Disappointingly, product **2a** was obtained in only 36% yield under these conditions. The reaction led predominantly to a complex mixture (Table 1, Entry 1). Lowering the reaction temperature to –20 °C led to a doubling of the yield of **2a** although longer reaction times were necessary (Table 1, Entry 3). To screen the effectiveness of different solvents, we resorted to the exclusive use of tetrabutylammonium acetate as the acetate source given its high solubility in a variety of media.[3b] It was ultimately determined that the cleanest reaction occurred in MeCN using 0.05 equivalents of acetate and furnishing **2a** in 82% isolated yield as a 94:6 mixture of *Z*/*E* isomers (Table 1, Entry 9).

Attempts to vary the silicon reagent did not lead to further yield improvement (Table 1, Entries 10–14). For example, silanes $Me_2Si(C_6F_5)_2$ and $Me_3SiC_6F_5$ reacted readily but provided complex mixtures, whereas the use of $(EtO)_3SiC_6F_5$ afforded lower yields. Notably, the use of fluorosilane $FSi(C_6F_5)_3$, which has been shown to be the most effective silane in reactions mediated by weak Lewis acids,[11] was completely unproductive.

Under the optimized conditions, a series of nitriles **1** was subjected to pentafluorophenylation using $MeSi(C_6F_5)_3$[14] (Table 2). The rate of the reaction was found to be sensitive to the nature of the substituent R of substrates **1**. Electron-rich systems or, most notably, substrates with aliphatic groups were found to react slowly (e.g., Table 2, Entries 6 and 7). Nevertheless, good yields of products could be achieved for all substrates. The *Z* isomers of **2** were formed predominantly in all cases. The preference for *Z* isomer formation can be rationalized by the greater thermodynamic stability of these isomers relative to the corresponding *E* isomers, which suffer from strong 1,3-allylic interactions between the R and CH_2 groups during the course of the reaction. The assignment of configuration was made on the basis of 2D NOESY data for **2a**,**b**,**d**–**f**; the configurations of **2c** and **2g** were assigned by analogy to the former products.

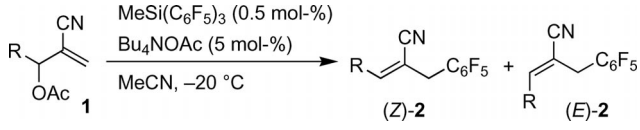
Table 1. Pentafluorophenylation of nitrile **1a**.



Entry	Silane[a]	Initiator (equiv.)	Solvent	*T* [°C]	Time [h]	Yield [%][b]
1	$MeSi(R_F)_3$	NaOAc (0.1)	DMF	20	2	36
2	$MeSi(R_F)_3$	NaOAc (0.1)	DMF	0	3	52
3	$MeSi(R_F)_3$	NaOAc (0.1)	DMF	–20	18	72
4	$MeSi(R_F)_3$	DABCO (0.05)	DMF	–20	18	57
5	$MeSi(R_F)_3$	$Et_3N{\cdot}HF$ (0.05)	DMF	0	18	47
6	$MeSi(R_F)_3$	Bu_4NOAc (0.02)	DMF	0	18	56
7	$MeSi(R_F)_3$	Bu_4NOAc (0.02)	THF	0	18	46
8	$MeSi(R_F)_3$	Bu_4NOAc (0.05)	MeCN	0	18	63
9	$MeSi(R_F)_3$	Bu_4NOAc (0.05)	MeCN	–20	18	82[c]
10	$Me_2Si(R_F)_2$	Bu_4NOAc (0.05)	DMF	0	18	24
11	$Me_2Si(R_F)_2$	Bu_4NOAc (0.05)	MeCN	0	18	40
12	Me_3SiR_F	Bu_4NOAc (0.05)	MeCN	0	18	14
13	$FSi(R_F)_3$	Bu_4NOAc (0.05)	MeCN	20	18	–[d]
14	$(EtO)_3SiR_F$	Bu_4NOAc (0.05)	MeCN	0	18	73

[a] R_F = C_6F_5, $MeSi(R_F)_3$ (0.5 equiv.); $Me_2Si(R_F)_2$ (0.75 equiv.); Me_3SiR_F (1.5 equiv.); $FSi(R_F)_3$ (0.5 equiv.); $(EtO)_3SiR_F$ (1.5 equiv). [b] Determined by NMR spectroscopy with internal standard, unless otherwise noted. [c] Isolated yield. [d] No reaction.

Table 2. Pentafluorophenylation of nitriles **1**.

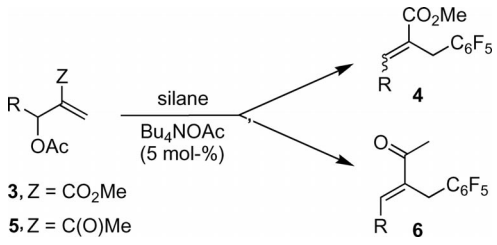


Entry	R	Time [h]	**2**	Yield of **2** [%][a]	*Z*/*E*
1	Ph	18	**2a**	82	94:6
2[b]	4-$MeOC_6H_4$	6	**2b**	80	93:7
3	4-$NO_2C_6H_4$	3	**2c**	93	>99:1
4	1-naphthyl	72	**2d**	85	>99:1
5	2-furyl	72	**2e**	81	91:9
6[b]	Et	18	**2f**	71	96:4
7[b]	cyclohexyl	20	**2g**	77	86:14

[a] Isolated yield of *Z* and *E* isomeric mixture. [b] Reaction performed at 0 °C.

We next evaluated the reactivity of substrates in which the double bond was activated by ester or keto groups (Table 3). The reaction of methyl ester **3a** (R = Ph) with $MeSi(C_6F_5)_3$ afforded only 50% yield of desired product **4a** regardless of temperature, solvent, and amount of activator (Table 3, Entries 1–4). The use of other silanes in DMF led to increased yields with the optimum case being with $Me_3SiC_6F_5$ (Table 3, Entry 9). Ester substrates **3b**–**f** were also subjected to the optimized pentafluorophenylation conditions and products **4b**–**f** were furnished in high yield

Table 3. Pentafluorophenylation of substrates **3** and **5**.



Entry	*Z*	R	Substrate	Silane (equiv.)	Solvent	*T* [°C]	Time [h]	Conv. [%]	Product	Yield[a] [%]	*E*/*Z*
1	CO_2Me	Ph	**3a**	$MeSi(C_6F_5)_3$ (0.5)	MeCN	–20	18	54	**4a**	[b]	
2			**3a**	$MeSi(C_6F_5)_3$ (0.5)	MeCN	20	24	41	**4a**	(27)	85:15
3[c]			**3a**	$MeSi(C_6F_5)_3$ (0.5)	THF	–20→20	18	25	**4a**	[b]	
4			**3a**	$MeSi(C_6F_5)_3$ (0.5)	DMF	20	18	52	**4a**	(25)	89:11
5			**3a**	$Me_2Si(C_6F_5)_2$ (0.75)	MeCN	–20	18	91	**4a**	(23)	92:8
6			**3a**	$Me_2Si(C_6F_5)_2$ (0.75)	DMF	–20	18	76	**4a**	(58)	89:11
7			**3a**	$Me_2Si(C_6F_5)_2$ (0.75)	DMF	–20→0	18	100	**4a**	(55)	88:12
8			**3a**	$Me_3SiC_6F_5$ (1.5)	DMF	–20→0	18	100	**4a**	(73)	89:11
9			**3a**	$Me_3SiC_6F_5$ (1.5)	DMF	–20	18	100	**4a**	83	87:13
10		4-$NO_2C_6H_4$	**3b**	$Me_3SiC_6F_5$ (1.5)	DMF	–20	4	100	**4b**	85	94:6
11		4-$MeOC_6H_4$	**3c**	$Me_3SiC_6F_5$ (1.5)	DMF	–20	18	100	**4c**	91	88:12
12		2-pyridyl	**3d**	$Me_3SiC_6F_5$ (1.5)	DMF	–20	3	100	**4d**	70	>99:1
13		2-thienyl	**3e**	$Me_3SiC_6F_5$ (1.5)	DMF	–20	18	100	**4e**	80	82:18
14		Et	**3f**	$Me_3SiC_6F_5$ (1.5)	DMF	–20	20	100	**4f**	86	81:19
15	C(O)Me	Ph	**5a**	$MeSi(C_6F_5)_3$ (0.5)	MeCN	–20→0	18	100	**6a**	61	>99:1
16			**5a**	$MeSi(C_6F_5)_3$ (0.5)	DMF	–20	72	87	**6a**	62	>99:1
17			**5a**	$Me_3SiC_6F_5$ (1.5)	DMF	–20	8	100	**6a**	(80)[d]	>99:1
18			**5a**	$Me_2Si(C_6F_5)_2$ (0.75)	DMF	–20	18	100	**6a**	88	>99:1
19		4-$NO_2C_6H_4$	**5b**	$Me_2Si(C_6F_5)_2$ (0.75)	DMF	–20	3	100	**6b**	80	>99:1
20		$PhCH_2CH_2$	**5c**	$Me_2Si(C_6F_5)_2$ (0.75)	DMF	–20	21	100	**6c**	88	>99:1

[a] Isolated yield. The yields in parenthesis were determined by NMR spectroscopy with internal standard. [b] Complex mixture was formed with yield of desired product <20%. [c] 0.2 equiv. Bu_4NOAc was used. [d] Small amounts of unidentified byproducts were observed.

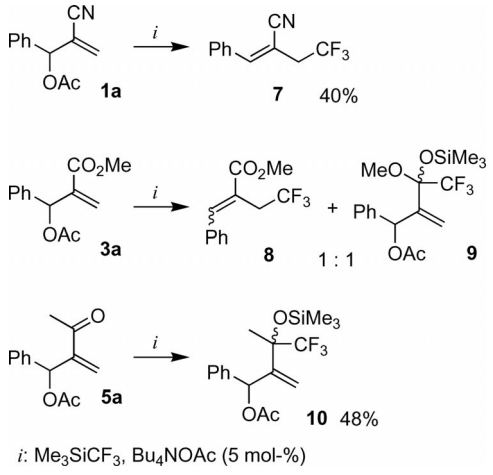
(Table 3, Entries 10–14). In contrast to nitrile products **2**, which bore predominantly the *Z* configuration, esters **4** were produced primarily as *E* isomers with a *trans* arrangement of the R substituent and the bulkier ester group. The assignment of configuration of **4a**,**f** was made on the basis of 2D NOESY; configuration of **4b**–**e** was established by analogy according to systematic chemical shift differences.[15]

Reactions of ketones **5** proceed to completion even at low temperature, reflecting the enhanced reactivity of these Michael acceptors compared to esters **3**. Brief variation of the silane performed with substrate **5a** (R = Ph) demonstrated that $Me_2Si(C_6F_5)_2$ is the ideal C_6F_5 source. The substrates with aromatic and aliphatic groups reacted cleanly to afford desired products **6a**–**c** in excellent yields exclusively as the *E* isomers (Table 3, Entries 18–20) The *E* configuration of **6a**–**c** was established by 2D NOESY spectra. Products arising from nucleophilic addition at the C=O bond were not detected in crude material.

It is clear that for pentafluorophenylation reactions all substrates (nitriles, esters, and ketones) can be effectively converted in good yields although different silicon reagents $Me_nSi(C_6F_5)_{4-n}$ (n = 1–3) have to be employed for each type of substrate. Although the underlying reason for this phenomenon is not clear at present, we propose that the efficiency of particular silane/substrate combinations depends on the reactivity of the corresponding five-coordinate siliconate species, which serves as the nucleophile.

We next studied reactions of Baylis–Hillman adducts with the Ruppert–Prakash reagent, which would lead to CF_3-containing products. Trifluoromethylation of substrates **1a**, **3a**, and **5a** was performed in the presence of Bu_4NOAc (5 mol-%), and the results are summarized in Scheme 2.

Trifluoromethylation of nitrile **1a** gave desired product **7** in moderate yield, and all attempts to improve the efficiency of this process were unsuccessful. Ester substrate **3a** gave an inseparable mixture containing compounds **8** and **9** (both existing as isomeric mixtures) in a combined yield of 30%. Reaction of ketone **5a** with the Ruppert–Prakash reagent furnished **10** as a mixture of two diastereoisomers (1.5:1 *dr*); Michael addition products were not observed. The results obtained using **3a** and **5a** suggest that, for reactions with Me_3SiCF_3, the increase in C=C bond electrophilicity in changing from an ester to a ketone substituent is overwhelmed by the increased reactivity of the ketone carbonyl group. This observation contrasts the results obtained with reactions of **3a** and **5a** with C_6F_5-substituted silanes in which the only products observed result from nucleophilic attack at the C=C bond.



Scheme 2. Trifluoromethylation reactions.

Conclusions

The reactions of acylated Baylis–Hillman adducts with C_6F_5-substituted silicon reagents proceed under mild conditions by using catalytic amounts of tetrabutylammonium acetate and furnish the corresponding products in good yields. However, the optimized conditions require different silicon reagents $Me_nSi(C_6F_5)_{4-n}$ (n = 1–3) for different substrate types. The products are formed either as predominantly *Z* isomers in the case of nitrile substrates, or as predominantly *E* isomers in case of ester or ketone substrates. Of special note is that ketone substrates underwent exclusive nucleophilic attack by the C_6F_5 carbanion at the C=C bond in preference to the carbonyl group. The reactions of Baylis–Hillman adducts with Me_3SiCF_3 are inefficient with nucleophilic attack at the carbonyl group being a serious undesirable pathway.

Experimental Section

General Remarks: All reactions were performed under an argon atmosphere. DMF was distilled under vacuum from P_2O_5 and stored over 4 Å MS. MeCN was successively distilled from P_2O_5 and CaH_2 and stored over 4 Å MS. Column chromatography was carried out on Merck silica gel (Kieselgel 60, 230–400 mesh). Silica gel plates coated with F-254 indicator were used for thin-layer analytical chromatography and compounds were visualized with UV and/or acidic aq. $KMnO_4$ solution. NMR spectra were recorded with a Bruker AM-300 instrument. For minor isomers characteristic signals are given. Microanalyses were performed with a Karlo Erba 1106 instrument. For the synthesis of Baylis–Hillman acetates, see the Supporting Information.

General Procedure for Pentafluorophenylation of Nitriles 1 (Procedure A): Tetrabutylammonium acetate (15 mg, 0.05 mmol) was added to a mixture of **1** (1.0 mmol) and $(C_6F_5)_3SiMe$ (272 mg, 0.5 mmol) in MeCN (2 mL) at –20 °C, and the resulting suspension was stirred under conditions described in Table 2. For workup, the mixture was quenched with 0.5 M HCl (12 mL), and the aqueous phase was extracted with Et_2O (3 × 5 mL). The combined organic layer was filtered through Na_2SO_4 and concentrated, and the residue was purified by column chromatography.

General Procedure for Pentafluorophenylation of Esters 3: Tetrabutylammonium acetate (15 mg, 0.05 mmol) was added to a mixture of **3** (1.0 mmol) and $C_6F_5SiMe_3$ (360 mg, 1.5 mmol) in DMF (2 mL) at –20 °C. The reaction mixture was kept at this temperature for the time given in Table 3 and worked up as described in procedure A.

General Procedure for Pentafluorophenylation of Enones 5: Tetrabutylammonium acetate (15 mg, 0.05 mmol) was added to a mixture of **5** (1.0 mmol) and $(C_6F_5)_2SiMe_2$ (294 mg, 0.75 mmol) in DMF (2 mL) at –20 °C. The reaction mixture was kept at this temperature for the time given in Table 3 and worked up as described in procedure A.

2-[(Pentafluorophenyl)methyl]-3-phenylacrylonitrile (2a): Yield: 254 mg (82%), *E*/*Z* = 6:94. M.p. 68–70 °C. R_f = 0.21 (hexane/EtOAc, 8:1). ^{1}H NMR (300 MHz, $CDCl_3$, *Z* isomer): δ = 3.82 (s, 2 H, CH_2), 7.11 (s, 1 H, CH), 7.38–7.51 (m, 3 H, CH_{Ar}), 7.69–7.81 (m, 2 H, CH_{Ar}) ppm. ^{1}H NMR (300 MHz, $CDCl_3$, *E* isomer): δ = 3.91 (s, 2 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, *Z* isomer): δ = 28.6 (m), 106.3, 110.1 (tm, J = 17.9 Hz), 117.5, 128.8, 128.9, 130.7, 132.6, 137.7 (dm, J = 247.6 Hz), 140.9 (dm, J = 247.6 Hz), 145.4 (dm, J = 248.8 Hz), 145.5 ppm. ^{13}C NMR (75 MHz, $CDCl_3$, *E* isomer): δ = 22.7, 129.8, 133.2, 146.2 ppm. ^{19}F (282 MHz, $CDCl_3$, *Z* isomer): δ = –164.6 (ddd, J = 21.2, 21.2, 8.5 Hz, 2 F, *meta*), –157.6 (t, J = 21.2 Hz, F, *para*), –145.5 (dd, J = 21.2, 8.5 Hz, *ortho*) ppm. ^{19}F (282 MHz, $CDCl_3$, *E* isomer): δ = –164.8 (m, 2F, *meta*), –145.1 (dd, J = 21.2, 8.5 Hz, 1 F, *ortho*) ppm. $C_{16}H_8F_5N$ (309.23): calcd. C 62.14, H 2.61, N 4.53; found C 62.07, H 2.65, N 4.35.

3-(4-Methoxyphenyl)-2-[(pentafluorophenyl)methyl]acrylonitrile (2b): Yield: 271 mg (80%), *E*/*Z* = 7:93. M.p. 50–52 °C. R_f = 0.21 (hexane/EtOAc, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$, *Z* isomer): δ = 3.78 (s, 2 H, CH_2), 3.85 (s, 3 H, OMe), 6.93 (d, J = 8.8 Hz, 2 H, CH_{Ar}), 7.02 (s, 1 H, =CH), 7.72 (d, J = 8.8 Hz, 2 H, CH_{Ar}) ppm. ^{1}H NMR (300 MHz, $CDCl_3$, *E* isomer): δ = 3.87 (s, 3 H, OMe), 3.91 (s, 2 H, =CH), 7.31 (s, 1 H, =CH), 7.36 (d, J = 8.8 Hz, 2 H, CH_{Ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, *Z* isomer): δ = 28.5, 55.4, 103.1, 110.5 (tm, J = 18.1 Hz), 114.3, 118.1, 125.6, 138.7, 137.7 (dm, J = 247.6 Hz), 140.8 (dm, J = 248.2 Hz), 145.1, 145.4 (dm, J = 248.2 Hz), 161.5 ppm. ^{13}C NMR (75 MHz, $CDCl_3$, *E* isomer): δ = 114.4, 131.2, 145.7 ppm. ^{19}F (282 MHz, $CDCl_3$, *Z* isomer): δ = –164.7 (ddd, J = 21.2, 21.2, 6.4 Hz, 2 F, *meta*), –157.9 (t, J = 21.2 Hz, 1 F, *para*), –145.6 (dd, J = 21.2, 6.4 Hz, 2 F, *ortho*) ppm. ^{19}F (282 MHz, $CDCl_3$, *E* isomer): –164.8 (m, 2 F, *meta*), –157.7 (t, J = 21.2 Hz, 1 F, *para*), –145.2 (dd, J = 21.2, 6.4 Hz, 2 F, *ortho*) ppm. $C_{17}H_{10}F_5NO$ (339.26): calcd. C 60.18, H 2.97, N 4.13; found C 60.11, H 3.03, N 4.07.

(2*Z*)-3-(4-Nitrophenyl)-2-[(pentafluorophenyl)methyl]acrylonitrile (2c): Yield: 329 mg (93%), *E*/*Z* = <1:99. M.p. 80–82 °C. R_f = 0.22 (hexane/EtOAc, 4:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.88 (s, 2 H, CH_2), 7.18 (s, 1 H, =CH), 7.89 (d, J = 8.8 Hz, 2 H, CH_{Ar}), 8.28 (d, J = 8.8 Hz, 2 H, CH_{Ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.7, 109.3 (tm, J = 18.1 Hz), 111.2, 116.6, 124.1, 129.6, 137.7 (dm, J = 247.6 Hz), 138.7, 141.0 (dm, J = 247.1 Hz), 142.6, 145.4 (dm, J = 248.0 Hz), 148.5 ppm. ^{19}F (282 MHz, $CDCl_3$): δ = –164.0 (ddd, J = 21.2, 21.2, 8.5 Hz, 2 F, *meta*),–156.7 (t, J = 21.2 Hz, 1 F, *para*), –145.3 (dd, J = 21.2, 8.5 Hz, 2 F, *ortho*) ppm. $C_{16}H_7F_5N_2O_2$ (354.23): calcd. C 54.25, H 1.99, N 7.91; found C 54.27, H 1.98, N 7.74.

(2*Z*)-3-(Naphthalen-1-yl)-2-[(pentafluorophenyl)methyl]acrylonitrile (2d): Yield: 305 mg (85%). M.p. 126–128 °C. R_f = 0.30 (hexane/EtOAc, 6:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.93 (s, 2 H, CH_2), 7.48–7.65 (m, 3 H, CH_{Ar}), 7.80–7.98 (m, 5 H, 4 CH_{Ar}, =CH), 7.90

(s, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.3 (m), 110.1 (tm, J = 18.1 Hz), 110.2, 117.1, 122.9, 125.3, 126.4, 126.7, 127.0, 128.8, 130.1, 130.7, 131.0, 133.3, 137.7 (dm, J = 247.6 Hz), 140.9 (dm, J = 247.8 Hz), 144.0, 145.3 (dm, J = 248.2 Hz) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –161.9 (ddd, J = 21.2, 21.2, 8.5 Hz, 2 F, *meta*), –154.9 (t, J = 21.2 Hz, 1 F, *para*), –143.1 (dd, J = 21.2, 8.5 Hz, 2 F, *ortho*) ppm. $C_{20}H_{10}F_5NO$ (359.29): calcd. C 66.86, H 2.81, N 3.90; found C 66.75, H 2.84, N 3.75.

3-(2-Furyl)-2-[(pentafluorophenyl)methyl]acrylonitrile (2e): Yield: 242 mg (81%), *E*/*Z* = 9:91. M.p. 74–75 °C. R_f = 0.31 (hexane/EtOAc, 6:1). ^{1}H NMR (300 MHz, $CDCl_3$, *Z* isomer): δ = 3.75 (s, 2 H, CH_2), 6.52 (dd, J = 3.7, 1.8 Hz, 1 H, OCH=C*H*), 6.88 (s, 1 H, NC–C=CH), 7.00 (d, J = 3.7 Hz, 1 H, C=CH), 7.55 (d, J = 1.8 Hz, 1 H, OCH) ppm. ^{1}H NMR (300 MHz, $CDCl_3$, *E* isomer): 4.16 (s, 2 H, CH_2), 6.58 (dd, J = 3.7, 1.8 Hz, 1 H, OCH=C*H*), 6.72 (d, J = 3.7 Hz, 1 H, C=CH), 6.96 (s, 1 H, NC-C=CH), 7.63 (d, J = 1.8 Hz, 1 H, OCH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, *Z* isomer): δ = 27.6, 102.5, 110.1 (tm, J = 18.1 Hz), 112.5, 115.1, 117.5, 132.1, 137.6 (dm, J = 247.6 Hz), 140.9 (dm, J = 247.6 Hz), 145.0, 145.4 (dm, J = 247.6 Hz), 149.0 ppm. ^{19}F (282 MHz, $CDCl_3$, *Z* isomer): δ = –161.8 (ddd, J = 21.2, 21.2, 8.5 Hz, 2 F, *meta*), –155.1 (t, J = 21.2 Hz, 1 F, *para*), –143.1 (dd, J = 21.2, 8.5 Hz, 2 F, *ortho*) ppm. ^{19}F (282 MHz, $CDCl_3$, *E* isomer): –162.5 (m, 2 F, *meta*), –155.6 (t, J = 21.2 Hz, *para*), –142.5 (dd, J = 21.2, 8.5 Hz, *ortho*) ppm. $C_{14}H_6F_5NO$ (299.20): calcd. C 56.20, H 2.02, N 4.68; found C 56.25, H 2.02, N 4.68.

2-[(Pentafluorophenyl)methyl]pent-2-enenitrile (2f): Yield: 185 mg (71%), *E*/*Z* = 4:96. Oil. R_f = 0.26 (hexane/EtOAc, 10:1). ^{1}H NMR (300 MHz, $CDCl_3$, *Z* isomer): δ = 1.08 (t, J = 7.5 Hz, 3 H, CH_3), 2.39 (qd, J = 7.5, 7.4 Hz, 2 H, CH_2CH), 3.61 (s, 2 H, CH_2), 6.32 (t, J = 7.4, = Hz, 1 HCH) ppm. ^{1}H NMR (300 MHz, $CDCl_3$, *E* isomer): δ = 1.11 (t, J = 7.2 Hz, 3 H, CH_3), 6.47 (t, J = 7.7 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, *Z* isomer): δ = 12.7, 25.0, 26.8 (m), 109.6, 110.2 (tm, J = 18.0 Hz), 116.2, 137.7 (dm, J = 247.6 Hz), 140.9 (dm, J = 247.2 Hz), 145.3 (dm, J = 248.2 Hz), 151.7 ppm. ^{19}F (282 MHz, $CDCl_3$, *Z* isomer): δ = –165.0 (ddd, J = 21.2, 21.2, 8.5 Hz, 2 F, *meta*), –158.2 (t, J = 21.2 Hz, F, *para*), –146.0 (dd, J = 21.2, 8.5 Hz, 2 F, *ortho*) ppm. ^{19}F (282 MHz, $CDCl_3$, *E* isomer: –145.6 (dd, J = 21.2, 8.5 Hz, 2 F, *ortho*) ppm. $C_{12}H_8F_5N$ (261.19): calcd. C 55.18, H 3.09, N 5.36; found C 55.07, H 3.17, N 5.37.

3-Cyclohexyl-2-[(pentafluorophenyl)methyl]acrylonitrile (2g): Yield: 243 mg (77%), *E*/*Z* = 14:86. Oil. R_f = 0.28 (hexane/EtOAc, 12:1). ^{1}H NMR (300 MHz, $CDCl_3$, *Z* isomer): δ = 1.06–1.43 (m, 5 H, 5CH_{Cy}), 1.63–1.81 (m, 5 H, 5 CH_{Cy}), 2.53 (dtt, J = 10.5, 10.5, 3.3 Hz, 1 H, CH_{Cy}), 3.59 (s, 2 H, C_6F_5-CH_2), 6.16 (d, J = 9.9 Hz, 1 H, C=CH) ppm. ^{1}H NMR (300 MHz, $CDCl_3$, *E* isomer): 3.65 (s, 2 H, CH_2), 6.31 (dt, J = 10.3, 1.5 Hz, 1 H, C=CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, *Z* isomer): δ = 25.1, 25.5, 27.0 (m), 31.5, 31.8, 40.8, 109.9–110.7 (m), 137.4 (dm, J = 247.5 Hz), 140.9 (dm, J = 247.5 Hz), 145.2, (dm, J = 247.5 Hz), 155.4 ppm. ^{13}C NMR (75 MHz, $CDCl_3$, *E* isomer): δ = 25.2, 26.2, 31.5, 38.2, 155.2 ppm. ^{19}F (282 MHz, $CDCl_3$, *Z* isomer): δ = –162.3 (ddd, J = 21.2, 21.2, 8.5 Hz, 2 F, *meta*),–155.5 (t, J = 21.2 Hz, 1 F, *para*), –143.4 (dd, J = 21.2, 8.5 Hz, 2 F, *ortho*) ppm. ^{19}F (282 MHz, $CDCl_3$, *E* isomer): δ = –155.4 (m, 1 F, *para*), –143.0 (dd, J = 21.2, 8.5 Hz, 2 F, *ortho*) ppm. $C_{16}H_{14}F_5N$ (315.28): calcd. C 60.95, H 4.48, N 4.44; found C 61.04, H 4.54, N 4.45.

Methyl 2-[(Pentafluorophenyl)methyl]-3-phenylacrylate (4a): Yield: 284 mg (83%), *E*/*Z* = 87:13. Oil. R_f = 0.24 (hexane/EtOAc, 10:1). ^{1}H NMR (300 MHz, $CDCl_3$, *E* isomer): δ = 3.78 (s, 3 H, OMe), 3.95 (s, 2 H, CH_2), 7.31–7.47 (m, 5 H, CH_{Ar}), 7.92 (s, 1 H, =CH) ppm. ^{1}H NMR (300 MHz, $CDCl_3$, *Z* isomer): δ = 3.63 (s, 3 H, OMe), 3.82 (s, 2 H, CH_2), 6.72 (s, 1 H, =CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, *E* isomer): δ = 21.5 (m), 52.1, 112.4 (tm, J = 16.5 Hz), 128.2, 128.5, 128.7, 135.1, 137.3 (dm, J = 251.4 Hz), 139.6 (dm, J = 250.8 Hz), 141.9, 145.4 (dm, J = 250.8 Hz), 167.3 ppm. ^{19}F (282 MHz, $CDCl_3$, *E* isomer): δ =–164.1 (ddd, J = 21.2, 21.2, 8.5 Hz, 2 F, *meta*), –158.3 (t, J = 21.2 Hz, 1 F, *para*), –142.7 (dd, J = 21.2, 8.5 Hz, *ortho*) ppm. $C_{17}H_{11}F_5O_2$ (342.26): calcd. C 59.66, H 3.24; found C 59.71, H 3.31.

Methyl 3-(4-Nitrophenyl)-2-[(pentafluorophenyl)methyl]acrylate (4b): Yield: 329 mg (85%), *E*/*Z* = 94:6. M.p. 104–106 °C. R_f = 0.23 (hexane/EtOAc, 6:1). ^{1}H NMR (300 MHz, $CDCl_3$, *E* isomer): δ = 3.79 (s, 3 H, OMe), 3.88 (s, 2 H, CH_2), 7.52 (d, J = 8.8 Hz, 2 H, CH_{Ar}), 7.91 (s, 1 H, =CH), 8.28 (d, J = 8.8 Hz, 2 H, CH_{Ar}) ppm. ^{1}H NMR (300 MHz, $CDCl_3$, *Z* isomer): δ = 3.65 (s, 3 H, OMe), 6.78 (s, 1 H, =CH), 7.39 (d, J = 8.8 Hz, 2 H, CH_{Ar}), 8.17 (d, J = 8.8 Hz, 2 H, CH_{Ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, *E* isomer): δ = 21.4, 52.4, 111.9–112.1 (m), 123.4, 123.8, 129.0, 129.5, 131.1, 137.3 (dm, J = 252.0 Hz), 139.7 (dm, J = 250.1 Hz), 145.2 (m, J = 250.1 Hz), 147.6, 166.5 ppm. ^{19}F (282 MHz, $CDCl_3$, *E* isomer): δ = –163.4 (ddd, J = 21.2, 21.2, 8.5 Hz, 2 F, *meta*),–157.2 (t, J = 21.2 Hz, 1 F, *para*), –142.7 (dd, J = 21.2, 8.5 Hz, 2 F, *ortho*) ppm. *Z* isomer: δ = –162.6 (ddd, J = 21.2, 21.2, 8.5 Hz, 2 F, *meta*), –156.0 (t, J = 21.2 Hz, 1 F, *para*), –143.2 (dd, J = 21.2, 8.5 Hz, 2 F, *ortho*) ppm. $C_{17}H_{10}F_5NO_4$ (387.26): calcd. C 52.73, H 2.60, N 3.62; found C 52.69, H 2.54, N 3.61.

Methyl 3-(4-Methoxyphenyl)-2-[(pentafluorophenyl)methyl]acrylate (4c): Yield: 339 mg (91%), *E*/*Z* = 88:12. Oil. R_f = 0.26 (hexane/EtOAc, 8:1). ^{1}H NMR (300 MHz, $CDCl_3$, *E* isomer): δ = 3.76 (s, 3 H, OMe), 3.83 (s, 3 H, CO_2Me), 3.97 (s, 2 H, CH_2), 6.93 (d, J = 8.8 Hz, 2 H, CH_{Ar}), 7.33 (d, J = 8.8 Hz, 2 H, CH_{Ar}), 7.84 (s, 1 H, =CH) ppm. ^{1}H NMR (300 MHz, $CDCl_3$, *Z* isomer): δ = 3.67 (s, 3 H, OCH_3), 3.78 (s, 2 H, CH_2), 3.79 (s, 3 H, CO_2Me), 6.67 (s, 1 H, =CH), 6.82 (d, J = 8.8 Hz, 2 H, CH_{Ar}), 7.21 (d, J = 8.8 Hz, 2 H, CH_{Ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, *E* isomer): δ = 21.5 (m), 51.9, 55.2, 113.1 (tm, J = 18.2 Hz), 114.0, 126.0, 127.3, 130.7, 137.3 (dm, J = 250.5 Hz), 139.7 (dm, J = 250.9 Hz), 141.5, 145.4 (dm, J = 250.9 Hz), 160.1, 167.6 ppm. ^{19}F (282 MHz, $CDCl_3$, *E* isomer): δ = –164.2 (ddd, J = 21.2, 21.2, 8.5 Hz, 2 F, *meta*), –158.6 (t, J = 21.2 Hz, 1 F, *para*), –142.9 (dd, J = 21.2, 8.5 Hz, 2 F, *ortho*) ppm. $C_{18}H_{13}F_5O_3$ (372.29): calcd. C 58.07, H 3.52; found C 58.20, H 3.53.

Methyl (2*E*)-2-[(Pentafluorophenyl)methyl]-3-(pyridin-2-yl)acrylate (4d): Yield: 240 mg (70%). M.p. 61–63 °C. R_f = 0.24 (hexane/EtOAc, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.80 (s, 3 H, OMe), 4.66 (s, 2 H, CH_2), 7.23 (ddd, J = 7.7, 4.7, 1.2 Hz, 1 H, N–CH=CH), 7.37 (ddd, J = 7.7, 1.2, 1.0 Hz, 1 H, N–C=C*H*), 7.68–7.76 (m, 2 H, =CH, N–C=CH–C*H*), 8.65 (ddd, J = 4.7, 1.8, 1.0 Hz, 1 H, N–CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.1 (m), 52.3, 113.9 (tm, J = 16.5 Hz), 123.2, 126.9, 131.2, 136.5, 137.3 (dm, J = 250.6 Hz), 138.2, 139.5 (dm, J = 250.6 Hz), 145.6 (dm, J = 248.5 Hz), 149.3, 154.0, 167.8 ppm. ^{19}F (282 MHz, $CDCl_3$), δ = –164.8 (ddd, J = 21.2, 21.2, 8.5 Hz, 2 F, *meta*), –159.4 (t, J = 21.2 Hz, 1 F, *para*), –142.7 (dd, J = 21.2, 8.5 Hz, 2 F, *ortho*) ppm. $C_{16}H_{10}F_5NO_2$ (343.25): calcd. C 55.99, H 2.94, N 4.08; found C 55.94, H 2.91, N 4.05.

Methyl 2-[(Pentafluorophenyl)methyl]-3-(2-thienyl)acrylate (4e): Yield: 279 mg (80%), *E*/*Z* = 82:18. M.p. 46–48 °C. R_f = 0.37 (hexane/EtOAc, 8:1). ^{1}H NMR (300 MHz, $CDCl_3$, *E* isomer): δ = 3.77 (s, 3 H, OMe), 4.12 (s, 2 H, CH_2), 7.13 (dd, J = 5.1, 3.7 Hz, 1 H, S–CH=C*H*), 7.34 (d, J = 4.7 Hz, 1 H, S–C=CH), 7.52 (d, J = 5.1 Hz, 1 H, S–CH), 8.00 (s, 1 H, =CH) ppm. ^{1}H NMR (300 MHz,

$CDCl_3$, *Z* isomer): δ = 3.82 (s, 3 H, OMe), 7.00 (s, 1 H, =CH), 7.03 (dd, *J* = 5.1, 3.7 Hz, 1 H, S–CH=C*H*), 7.26 (d, *J* = 3.7 Hz, 1 H, C=CH), 7.44 (d, *J* = 5.1 Hz, 1 H, S–CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, *E* isomer): δ = 22.3 (m), 52.1, 112.5 (tm, *J* = 16.2 Hz), 123.6, 127.4, 129.7, 133.3, 133.9, 137.4 (dm, *J* = 250.3 Hz), 137.5, 139.8 (dm, *J* = 250.3 Hz), 145.6 (dm, *J* = 250.3 Hz), 175.2 ppm. ^{19}F (282 MHz, $CDCl_3$, *E* isomer): δ =–164.0 (ddd, *J* = 21.2, 21.2, 8.5 Hz, 2 F, *meta*), –158.2 (t, *J* = 21.2 Hz, 1 F, *para*), –142.5 (dd, *J* = 21.2, 8.5 Hz, 2 F, *ortho*) ppm. ^{19}F (282 MHz, $CDCl_3$, *Z* isomer): δ = –163.3 (ddd, *J* = 21.2, 21.2, 8.5 Hz, 2 F, *meta*), –157.2 (t, *J* = 21.2 Hz, 1 F, *para*), –143.2 (dd, *J* = 21.2, 8.5 Hz, 2 F, *ortho*) ppm. $C_{15}H_9F_5O_2S$ (348.29): calcd. C 51.73, H 2.60; found C 51.67, H 2.61.

Methyl 2-[(Pentafluorophenyl)methyl]pent-2-enoate (4f): Yield: 253 mg (86%), *E*/*Z* = 81:19. Oil. R_f = 0.27 (hexane/EtOAc, 25:1). ^{1}H NMR (300 MHz, $CDCl_3$, *E* isomer): δ = 1.10 (t, *J* = 7.5 Hz, 3 H, CH_2CH$_3$), 2.34 (qd, *J* = 7.5, 7.4 Hz, 2 H, CH_2CH$_3$), 3.70 (s, 3 H, OMe), 6.92 (t, *J* = 7.4, 1 HCH) ppm. ^{1}H NMR (300 MHz, $CDCl_3$, *Z* isomer): δ = 1.01 (t, *J* = 7.5, 3 H, CH_2CH$_3$), 2.48 (qd, *J* = 7.5, 7.4 Hz, 2 H, CH_2CH$_3$), 3.72 (s, 3 H, OMe), 5.93 (t, *J* = 7.5 Hz, 1 H, =CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, *E* isomer): δ = 12.9, 20.3 (m), 22.2 (t, *J* = 1.4 Hz), 51.8, 113.2 (tm, *J* = 18.5 Hz), 126.7, 137.4 (dm, *J* = 251.4 Hz), 139.8 (dm, *J* = 251.4 Hz), 145.5 (dm, *J* = 251.4 Hz), 147.4, 167.2 ppm. ^{19}F (282 MHz, $CDCl_3$, *E* isomer): δ =–164.1 (ddd, *J* = 21.2, 21.2, 8.5 Hz, 2 F, *meta*),–158.4 (t, *J* = 21.2 Hz, 1 F, *para*), –143.1 (dd, *J* = 21.2, 8.5 Hz, *ortho*) ppm. $C_{13}H_{11}F_5O_2$ (294.22): calcd. C 53.07, H 3.77; found C 52.89, H 3.65.

(3*E*)-3-[(Pentafluorophenyl)methyl]-4-phenylbut-3-en-2-one (6a): Yield: 287 mg (88%). Oil. R_f = 0.22 (hexane/EtOAc, 10:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.46 (s, 3 H, CH_3), 3.89 (s, 2 H, CH_2), 7.29–7.46 (m, 5 H, CH_{Ar}), 7.74 (s, 1 H, =CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.6 (m), 25.7, 113.3 (tm, *J* = 16.5 Hz), 128.61, 128.63, 128.9, 135.0, 137.2 (dm, *J* = 250.8 Hz), 137.9, 139.4 (dm, *J* = 250.8 Hz), 142.1 (dm, *J* = 250.8 Hz), 142.2, 198.7 ppm. ^{19}F (282 MHz, $CDCl_3$): δ = –164.3 (ddd, *J* = 21.2, 21.2, 8.5 Hz, 2 F, *meta*), –158.9 (t, *J* = 21.2 Hz, 1 F, *para*), –143.0 (dd, *J* = 21.2, 8.5 Hz, 2 F, *ortho*) ppm. $C_{17}H_{11}F_5O$ (326.26): calcd. C 62.58, H 3.40; found C 62.62, H 3.48.

(3*E*)-4-(4-Nitrophenyl)-3-[(pentafluorophenyl)methyl]but-3-en-2-one (6b): Yield: 297 mg (80%). M.p. 108–109 °C. R_f = 0.21 (hexane/EtOAc, 4:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.47 (s, 3 H, CH_3), 3.82 (s, 2 H, CH_2), 7.52 (d, *J* = 8.6 Hz, 2 H, CH_{Ar}), 7.73 (s, 1 H, =CH), 8.28 (d, *J* = 8.6 Hz, 2 H, CH_{Ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.6, 25.7, 112.4 (tm, *J* = 17.3 Hz), 123.9, 129.5, 137.2 (dm, *J* = 250.2 Hz), 139.2, 139.7 (dm, *J* = 251.4 Hz), 140.3, 141.6, 145.0 (dm, *J* = 250.2 Hz), 147.7, 198.0 ppm. ^{19}F (282 MHz, $CDCl_3$): δ = –163.6 (ddd, *J* = 21.2, 21.2, 8.5 Hz, 2 F, *meta*), –157.8 (t, *J* = 21.2 Hz, 1 F, *para*), –142.9 (dd, *J* = 21.2, 8.5 Hz, 2 F, *ortho*) ppm. $C_{17}H_{10}F_5NO_3$ (371.26): calcd. C 55.00, H 2.71, N 3.77; found C 55.14, H 2.71, N 3.64.

(3*E*)-3-[(Pentafluorophenyl)methyl]-6-phenylhex-3-en-2-one (6c): Yield: 312 mg (88%). Oil. R_f = 0.24 (hexane/EtOAc, 6:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.29 (t, *J* = 7.5 Hz, 3 H, CH_3), 2.68 (dt, *J* = 7.2, 7.2 Hz, 2 H, PhCH$_2$CH_2), 2.82 (t, 2 H, PhCH_2), 3.62 (s, 2 H, $C_6F_5CH_2$), 6.79 (t, *J* = 7.2 Hz, 1 H, CH), 7.15–7.35 (m, 5 H, CH_{Ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.1, 25.4, 31.0, 34.6, 113.3 (tm, *J* = 17.8 Hz), 126.4, 128.3, 128.6, 137.2 (dm, *J* = 251.0 Hz), 138.0, 139.6 (dm, *J* = 251.1 Hz), 145.0, 145.2 (dm, *J* = 251.1 Hz), 198.0 ppm. ^{19}F (282 MHz, $CDCl_3$): δ = –164.0 (ddd, *J* = 21.2, 21.2, 8.5 Hz, 2 F, *meta*), –158.7 (t, *J* = 21.2 Hz, 1 F, *para*), –142.9 (dd, *J* = 21.2, 8.5 Hz, 2 F, *ortho*) ppm. $C_{19}H_{15}F_5O$ (354.31): calcd. C 64.41, H 4.27; found C 64.46, H 4.28.

(2*Z*)-3-Phenyl-2-(2,2,2-trifluoroethyl)acrylonitrile (7) (Procedure B): Tetrabutylammonium acetate (15 mg, 0.05 mmol) was added to a mixture of nitrile **1a** (201 mg, 1.0 mmol) and CF_3SiMe_3 (221 μL, 1.5 mmol) in MeCN (2 mL) at –20 °C, and the resulting suspension was stirred at 0 °C for 18 h. For workup, the mixture was quenched by the addition of 0.5 M HCl (4 mL) and water (8 mL). The aqueous phase was extracted with Et_2O (3 × 5 mL), and the combined organic layer was filtered through Na_2SO_4 and concentrated. The residue was purified by column chromatography (hexane/EtOAc, 5:1) to give the product (187 mg) containing ca. 7% of an unidentified impurity (based on ^{19}F NMR), thereby corresponding to ca. 40% yield of compound **7**. Subsequent recrystallization from a large amount of hexane/EtOAc (6:1) afforded analytically pure material. M.p. 62–66 °C R_f = 0.27 (hexane/EtOAc, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.18 (q, *J* = 9.6 Hz, 2 H, CH_2), 7.17 (s, 1 H, =CH), 7.44–7.52 (m, 3 H, CH_{Ar}), 7.76–7.85 (m, 2 H, CH_{Ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.1 (q, *J* = 31.3 Hz), 99.4, 117.5, 124.6 (q, *J* = 277.8 Hz), 129.0, 129.1, 131.3, 132.5, 150.2 ppm. ^{19}F (282 MHz, $CDCl_3$): δ = –66.7 (t, *J* = 9.6 Hz, 3 F, CF_3) ppm. $C_{11}H_8F_3N$ (211.18): calcd. C 62.56, H 3.82, N 6.63; found C 62.61, H 3.72, N 6.54. The *Z* configuration was established by 2D NOESY experiments.

Trifluoromethylation of Ester 3a: Production of **3a** was performed in a fashion similar to procedure B, but using DMF as solvent and stirring at –20 °C for 18 h. The crude material contained equimolar amounts of compounds **8** and **9** as well as unidentified impurities. Column chromatography (hexane/EtOAc, 20:1) afforded an inseparable mixture of compounds **8** and **9**, which was analyzed by ^{19}F NMR spectroscopy with $PhCF_3$ as an internal standard.

Methyl 3-Phenyl-2-(2,2,2-trifluoroethyl)acrylate (8): Mixture of isomers, 4:1. Oil. R_f = 0.24 (hexane/EtOAc, 20:1). ^{1}H NMR (300 MHz, $CDCl_3$, major isomer): δ = 3.46 (q, *J* = 10.2 Hz, 2 H, CH_2CF_3), 3.88 (s, 3 H, OMe), 8.01 (s, 1 H, =CH), 7.23–7.50 (m, 5 H, Ph) ppm. ^{1}H NMR (300 MHz, $CDCl_3$, minor isomer): δ = 3.68 (s, 3 H, OMe), 7.00 (s, 1 H, =CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, major isomer): δ = 32.2 (q, *J* = 30.7 Hz), 52.5, 125.6 (q, *J* = 278.1 Hz), 167.6 ppm. ^{13}C NMR (75 MHz, $CDCl_3$, minor isomer): δ = 39.3 (q, *J* = 30.4 Hz), 52.0, 168.0 ppm. ^{19}F (282 MHz, $CDCl_3$, major isomer): δ = –64.1 (t, *J* = 9.5 Hz, 3 F, CF_3) ppm. ^{19}F (282 MHz, $CDCl_3$, minor isomer): δ = –66.7 (t, *J* = 10.6 Hz, 3 F, CF_3) ppm.

1-Phenyl-2-{2,2,2-trifluoro-1-methoxy-1-[(trimethylsilyl)oxy]-ethyl}prop-2-en-1-yl Acetate (9): Mixture of isomers, 1:1; characteristic signals are given. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.09 and 0.22 (s, 9 H, 2SiMe_3), 2.07 and 2.12 (s, 3 H, 2 CH_3COO), 3.14 and 3.29 (s, 3 H, 2OMe), 5.54–5.80 (m, 2 H, 2H_2C=), 6.50 and 6.51 (s, 1 H, 2 C*H*-OAc) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.9 (m) and 1.0 (m), 50.0 and 50.2, 122.2 (q, *J* = 289.3 Hz) ppm. ^{19}F (282 MHz, $CDCl_3$): δ = –82.6 and –82.0 (s, 3 F, CF_3) ppm.

1-Phenyl-2-{2,2,2-trifluoro-1-methyl-1-[(trimethylsilyl)oxy]-ethyl}prop-2-en-1-yl Acetate (10): Trifluoromethylation of ketone **5a** was performed according to procedure B, but with stirring at –20 °C for 18 h. The residue was purified by column chromatography (hexane/EtOAc, 20:1). Yield: 173 mg (48%). Mixture of isomers, 1.5:1. Oil. R_f = 0.28 (hexane/EtOAc, 20:1). ^{1}H NMR (300 MHz, $CDCl_3$, major isomer): δ = –0.02 (s, 9 H, $SiMe_3$), 1.62 (s, 3 H, C-CH_3), 2.07 (s, 3 H, CH_3CO_2), 5.58 (s, 1 H, =CH_AH$_B$), 5.63 (s, 1 H, =CH$_A$$H_B$), 6.65 (C*H*-OAc), 7.27–7.41 (m, 5 H, CH_{Ar}) ppm. ^{1}H NMR (300 MHz, $CDCl_3$, minor isomer): δ = 0.17 (s, 9 H, $SiMe_3$), 1.60 (s, 3 H, C-CH_3), 2.10 (s, 3 H, CH_3CO_2), 5.48

(s, 1 H, =CH_AH$_B$), 5.64 (s, 1 H, =CH$_A$$H_B$), 6.59 (C*H*-OAc), 7.27–7.41 (m, 5 H, CH$_{Ar}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, major isomer): δ = 1.8, 21.2, 22.6 (q, J = 1.4 Hz), 73.5 (q, J = 1.4 Hz), 77.6 (q, J = 29.2 Hz), 118.8 (q, J = 1.4 Hz), 125.20 (q, J = 287.6 Hz), 127.9, 128.1, 128.4, 139.4, 147.0, 169.4 ppm. ^{13}C NMR (75 MHz, $CDCl_3$, minor isomer): δ = 2.0, 21.3, 23.1 (q, J = 1.4 Hz), 73.2 (q, J = 1.4 Hz), 77.4 (q, J = 29.0 Hz), 119.0 (q, J = 1.6 Hz), 125.22 (q, J = 287.6 Hz), 127.5, 128.0, 128.3, 139.1, 147.4, 169.5 ppm. ^{19}F (282 MHz, $CDCl_3$, major isomer): δ = –81.6 (s, 3 F, CF_3) ppm. ^{19}F (282 MHz, $CDCl_3$, minor isomer): δ = –80.9 (s, 3 F, CF_3). $C_{17}H_{23}F_3O_3Si$ (360.44): calcd. C 56.65, H 6.43; found C 56.45, H 6.27.

Supporting Information (see footnote on the first page of this article): Synthesis and characterization of starting compounds.

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[14] The use of MeSi(C_6F_5)$_3$ is quite convenient, as this compound is tolerant of air and moisture and can be readily prepared from the cheap reagents C_6F_5Br and $MeSiCl_3$; see ref.[13]

[15] In the ^{1}H NMR spectra of compounds **4a**–**f**, the chemical shift of CH= of the *E* isomer appears ca. 1 ppm downfield relative to that of the *Z* isomer.

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