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Nucleophilic trifluoromethylation of arylidenemalononitriles

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ABSTRACT

A method for the nucleophilic trifluoromethylation of arylidenemalononitriles using Me_3SiCF_3 is described. The reaction is carried out in dimethylformamide in the presence of AcONa as a Lewis base, and affords products of Michael addition in high yield.

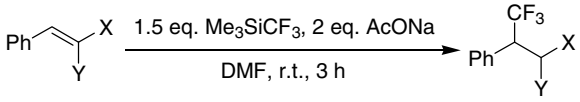
Nucleophilic trifluoromethylation reactions using the Ruppert–Prakash reagent (Me_3SiCF_3) have attracted significant attention in recent years.[1] In particular, procedures for the addition of a trifluoromethyl carbanion to C=O and C=N bonds have been the subject of a number of papers.[1–3]

At the same time, examples of the employment of Me_3SiCF_3 in Michael addition reactions have remained virtually unexplored. There are several reports on the successful Michael addition of Me_3SiCF_3 to unconventional Michael acceptors—2-perfluoroalkylchromones and 2-perfluoroalkyl-4-quinolones.[4] In another publication, the trifluoromethylation of cyclohex-2-enone in combination with sterically bulky aluminum reagents was studied, but the yields of the products of conjugate addition were moderate.[5] It should be noted that in these reports strongly basic activators such as Me_4NF and *t*-BuOK were employed for the activation of Me_3SiCF_3.

Within the framework of our research devoted to the applications of fluorinated silanes,[6,7] we decided to study the behavior of different electron deficient alkenes toward Me_3SiCF_3. As a basic activator we used sodium acetate in DMF, since this system had been efficient for many other processes.[2b,6a,b]

As model substrates we employed benzylidene derivatives, bearing a methoxycarbonyl or a cyano group (Table 1). The trifluoromethylation reactions were performed at room temperature for 3 h, and then quenched with aqueous hydrochloric acid. Methyl cinnamate was completely unreactive (entry 1), whereas dimethyl benzylidenemalonate gave a complex mixture containing mostly starting substrate (ca. 60%) (entry 2). The cyanoacetic ester derivative provided the corresponding product in 66% yield, with the remainder of the material balance being unreacted starting alkene (entry 3). Rewardingly, benzylidenemalononitrile afforded the desired product in an excellent 94% yield (entry 4).

Table 1
Variation of the alkene in trifluoromethylation reactions



Entry	X	Y	Product	Yield[a] (%)
1	CO_2Me	H		0
2	CO_2Me	CO_2Me		[b]
3	CO_2Me	CN	**1**	66[c]
4	CN	CN	**2a**	94

[a] Isolated yield.
[b] In the ^1H NMR spectrum of the crude mixture, the signals attributed to the product did not exceed 15%.
[c] The product was formed as a mixture of diastereomers in a 2.2:1 ratio.

Given the greater stability of the malononitrile anion compared to the dialkylmalonate anion,[8] these data suggest that the efficiency of trifluoromethylation depends on the electrophilicity of the alkene substrate.[9]

Various arylidenemalononitriles were examined in the reaction with Me_3SiCF_3 (Table 2). The aromatic ring of the substrate may contain electron-withdrawing or -donating substituents with both leading to products in high yields. Interestingly, in the case of a substrate possessing two sites for possible nucleophilic attack, only one product, corresponding to attack at the position adjacent to the malononitrile moiety, was obtained (entry 7).

Besides the trifluoromethyl group, pentafluoroethyl-, pentafluorophenyl-, and dichlorofluoromethyl groups can be transferred to

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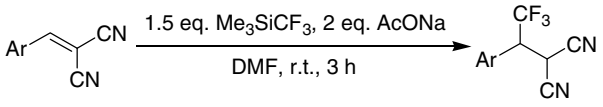
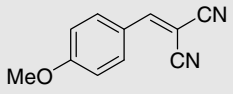
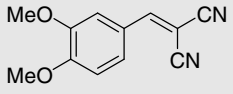
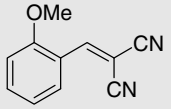
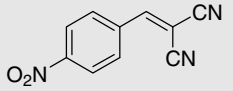
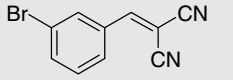
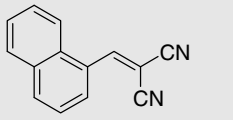
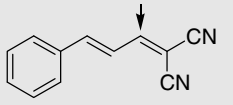
Table 2
Trifluoromethylation of arylidenemalononitriles



Entry	Substrate	Product	Yield[a] (%)
1		**2b**	95
2		**2c**	98
3		**2d**	96
4		**2e**	75
5		**2f**	83
6		**2g**	84
7		**2h**	87[b]

[a] Isolated yield.
[b] 2-[3-Phenyl-1-(trifluoromethyl)prop-2-enyl]malononitrile was obtained as the sole product.

benzylidenemalononitrile from the corresponding silanes[10] under the reported conditions (Scheme 1).

In summary, a convenient method for the Michael addition of a trifluoromethyl group, as well as other fluorinated fragments, to arylidenemalononitriles has been elaborated. The reaction proceeds under mildly basic conditions and leads to the products in high yields.[11] Importantly, this method provides ready access to functionalized compounds bearing a fluorinated group at the β-position, which are difficult to synthesize by other means. Our current research is focused on further development of the methodology of conjugate addition reactions using fluorinated silanes.

Acknowledgments

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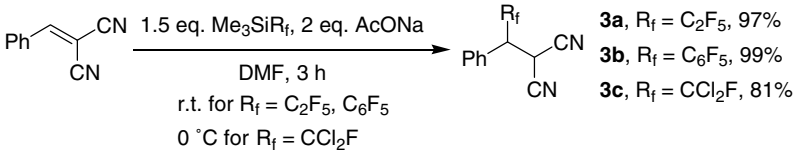
References and notes

1. For reviews on the chemistry of Me_3SiCF_3, see: (a) Prakash, G. K. S.; Yudin, A. K. *Chem. Rev.* **1997**, *97*, 757; (b) Prakash, G. K. S.; Mandal, M. *J. Fluorine Chem.* **2001**, *112*, 123; (c) Singh, R. P.; Shreeve, J. M. *Tetrahedron* **2000**, *56*, 7613; (d) Ma, J.-A.; Cahard, D. *J. Fluorine Chem.* **2007**, *128*, 975.
2. For addition to C=O bonds, see: (a) Prakash, G. K. S.; Panja, C.; Vaghoo, H.; Surampudi, V.; Kultyshev, R.; Mandal, M.; Rasul, G.; Mathew, T.; Olah, G. A. *J. Org. Chem.* **2006**, *71*, 6806; (b) Kawano, Y.; Kaneko, N.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1133; (c) Mizuta, S.; Shibata, N.; Akiti, S.; Fujimoto, H.; Nakamura, S.; Toru, T. *Org. Lett.* **2007**, *9*, 3707; (d) Fustero, S.; Albert, L.; Acena, J. L.; Sanz-Cervera, J. F.; Asensio, A. *Org. Lett.* **2008**, *10*, 605.
3. For addition to C=N bonds, see: (a) Prakash, G. K. S.; Mandal, M.; Olah, G. A. *Synlett* **2001**, 77; (b) Prakash, G. K. S.; Mogi, R.; Olah, G. A. *Org. Lett.* **2006**, *8*, 3589; (c) Kirij, N. V.; Babadzhanova, L. A.; Movchun, V. N.; Yagupolskii, Y. L.; Tyrra, W.; Naumann, D.; Fischer, H. T. M.; Scherer, H. *J. Fluorine Chem.* **2008**, *129*, 14; (d) Nelson, D. W.; Owens, J.; Hiraldo, D. *J. Org. Chem.* **2001**, *66*, 2572.
4. (a) Sosnovskikh, V. Ya.; Sevenard, D. V.; Usachev, B. I.; Röschenthaler, G.-V. *Tetrahedron Lett.* **2003**, *44*, 2097; (b) Sosnovskikh, V. Ya. V. Ya.; Usachev, B. I.; Sevenard, D. V.; Röschenthaler, G.-V. *J. Org. Chem.* **2003**, *68*, 7747; (c) Sosnovskikh, V. Ya. V. Ya.; Usachev, B. I.; Sevenard, D. V.; Röschenthaler, G.-V. *J. Fluorine Chem.* **2005**, *126*, 779; (d) Sosnovskikh, V. Ya. V. Ya.; Usachev, B. I.; Permyakov, M. N.; Sevenard, D. V.; Röeschenthaler, G.-V. *Russ. Chem. Bull.* **2006**, *55*, 1687.
5. Sevenard, D. V.; Sosnovskikh, V. Ya.; Kolomeitsev, A. A.; Königsmann, M. H.; Röschenthaler, G.-V. *Tetrahedron Lett.* **2003**, *44*, 7623.
6. For reactions using Me_3SiCF_3, see: (a) Dilman, A. D.; Arkhipov, D. E.; Levin, V. V.; Belyakov, P. A.; Korlyukov, A. A.; Struchkova, M. I.; Tartakovsky, V. A. *J. Org. Chem.* **2007**, *72*, 8604; (b) Levin, V. V.; Kozlov, M. A.; Song, Y.-H.; Dilman, A. D.; Belyakov, P. A.; Struchkova, M. I.; Tartakovsky, V. A. *Tetrahedron Lett.* **2008**, *49*, 3108; (c) Dilman, A. D.; Gorokhov, V. V.; Belyakov, P. A.; Struchkova, M. I.; Tartakovsky, V. A. *Russ. Chem. Bull.* **2007**, *56*, 1522.
7. For reactions of C_6F_5-substituted silanes, see: (a) Dilman, A. D.; Belyakov, P. A.; Korlyukov, A. A.; Struchkova, M. I.; Tartakovsky, V. A. *Org. Lett.* **2005**, *7*, 2913; (b) Dilman, A. D.; Levin, V. V.; Karni, M.; Apeloig, Y. *J. Org. Chem.* **2006**, *71*, 7214; (c) Dilman, A. D.; Levin, V. V.; Belyakov, P. A.; Struchkova, M. I.; Tartakovsky, V. A. *Synthesis* **2006**, 447; (d) Levin, V. V.; Dilman, A. D.; Belyakov, P. A.; Korlyukov, A. A.; Struchkova, M. I.; Antipin, M. Y.; Tartakovsky, V. A. *Synthesis* **2006**, 489; (e) Levin, V. V.; Dilman, A. D.; Belyakov, P. A.; Korlyukov, A. A.; Struchkova, M. I.; Tartakovsky, V. A. *Mendeleev Commun.* **2007**, 105; (f) Dilman, A. D.; Gorokhov, V. V.; Belyakov, P. A.; Struchkova, M. I.; Tartakovsky, V. A. *Tetrahedron Lett.* **2006**, *47*, 6217; (g) Levin, V. V.; Dilman, A. D.; Belyakov, P. A.; Struchkova, M. I.; Tartakovsky, V. A. *Tetrahedron Lett.* **2006**, *47*, 8959.
8. Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456.
9. For the electrophilicity parameters of arylidenemalononitriles, see: Lemek, T.; Mayr, H. *J. Org. Chem.* **2003**, *68*, 6880.
10. For the synthesis of silanes, see: (a) $Me_3SiC_2F_5$: Bardin, V. V.; Pressman, L. S.; Cherstkov, V. F. *Synth. Commun.* **1995**, *25*, 2425; $Me_3SiC_6F_5$: (b) Eaborn, C.; Treverton, J. A.; Walton, D. R. M. . D. R. M. . *J. Organomet. Chem.* **1967**, *9*, 259; Me_3SiCCl_2F: (c) Joste, R.; Ruppert, I. *J. Organomet. Chem.* **1987**, *329*, 313.
11. *General procedure:* Sodium acetate (164 mg, 2 mmol) was added to a solution of arylidenemalononitrile (1 mmol) and Me_3SiR_f (1.5 mmol) in DMF (2 mL) and the mixture was stirred for 3 h at room temperature [in the case of Me_3SiCCl_2F, the temperature was 0 °C]. For the work-up, the reaction flask was cooled to 0 °C, aq HCl (1.07 mL of 1.4 M) was added, the mixture was stirred for an additional 2 min, then diluted with water (10 mL), and extracted with ether (3 × 5 mL). The combined organic phase was filtered through Na_2SO_4, concentrated under vacuum, and the crude product was chromatographed on silica gel eluting with hexanes/ethyl acetate.
Methyl 2-cyano-4,4,4-trifluoro-3-phenylbutanoate (**1**): Oil, R_f = 0.27 (hexanes/EtOAc, 5:1). Mixture of isomers, ratio 2.2:1. ^{1}H NMR (300 MHz, $CDCl_3$): 3.69 (s, 3H, Me, minor), 3.75 (s, 3H, Me, major), 4.03 (d, 1H, *J* = 7.3, CHCN, minor), 4.12–4.23 (m, 1H, $CHCF_3$, both isomers), 4.25 (d, 1H, *J* = 5.5, CHCN, major), 7.39–7.52 (m, 5H, Ph, both isomers). ^{13}C NMR (75 MHz, $CDCl_3$). Major isomer: 38.5, 49.0 (q, *J* = 29.3), 54.0, 113.5, 125.0 (q, *J* = 280.9), 129.1, 129.3, 129.7, 130.4, 163.8. Minor isomer: 38.5, 49.6 (q, *J* = 28.8), 53.9, 113.6, 124.8 (q, *J* = 280.9), 128.8, 129.1, 129.6, 130.5, 163.7. ^{19}F NMR (282 MHz, $CDCl_3$): −68.6 (d, *J* = 8.5, major), −67.2 (d, *J* = 8.5, minor). Calcd for $C_{12}H_{10}F_3NO_2$ (257.21): C, 56.04; H, 3.92; N, 5.45. Found: C, 56.28; H, 3.72; N, 5.33.



Scheme 1.

2-(2,2,2-Trifluoro-1-phenylethyl)malononitrile (**2a**): Oil, R_f = 0.20 (hexanes/EtOAc, 6:1). ^{1}H NMR (300 MHz, $CDCl_3$): 3.96 (qd, 1H, J = 6.5, 8.2, $CHCF_3$), 4.40 (d, 1H, J = 6.5, $CH(CN)_2$), 7.40–7.68 (m, 5H, Ph). ^{13}C NMR (50 MHz, $CDCl_3$): 24.8 (q, J = 2.5), 50.2 (q, 29.0), 109.8, 110.1, 124.0 (q, J = 282.1), 128.0 (q, J = 1.5), 128.9, 129.7, 130.7. ^{19}F NMR (282 MHz, $CDCl_3$): −67.6 (d, J = 8.2). Anal. Calcd for $C_{11}H_7F_3N_2$ (224.18): C, 58.93; H, 3.15; N, 12.50. Found: C, 59.02; H, 3.11; N, 12.44.

2-[2,2,2-Trifluoro-1-(4-methoxyphenyl)ethyl]malononitrile (**2b**): Mp 40–41 °C, R_f = 0.26 (hexanes/EtOAc, 4:1). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 3.83 (s, 3H, OMe), 3.91 (dq, 1H, J = 8.4, 6.4, $CHCF_3$), 4.37 (d, 1H, J = 6.4, $CH(CN)_2$), 6.99 (d,2H, J = 8.8, $2H_{Ar}$), 7.38 (d, 2H, J = 8.8, $2H_{Ar}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 24.9 (q, J = 2.6), 49.4 (q, J = 29.3), 55.2, 110.0, 110.3, 115.0, 119.7 (q, J = 1.4), 124.1 (q, J = 281.4), 130.2, 161.2. ^{19}F NMR (282 MHz, $CDCl_3$) δ: −68.0 (d, 3F, J = 8.4). Anal. Calcd for $C_{12}H_9F_3N_2O$ (254.21): C, 56.70; H, 3.57; N, 11.02. Found: C, 56.71; H, 3.52; N, 10.92.

2-[1-(3,4-Dimethoxyphenyl)-2,2,2-trifluoroethyl]malononitrile (**2c**): Mp 110–111 °C, R_f = 0.3 (hexanes/EtOAc, 2:1). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 3.79–3.98 (m, 7H, 2OMe + $CHCF_3$), 4.40 (d, 1H, J = 6.1, $CH(CN)_2$), 6.92 (d, 1H, J = 8.3, $1H_{Ar}$), 6.95 (s, 1H, $1H_{Ar}$), 7.00 (d, 1H, J = 8.3, $1H_{Ar}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 25.0 (q, J = 2.6), 49.9 (q, J = 29.3), 55.9, 56.0, 110.0, 110.2, 111.5 (q, J = 1.1), 111.7, 120.0 (q, J = 1.7), 122.0, 124.0 (q, J = 281.4), 149.6, 150.8. ^{19}F NMR (282 MHz, $CDCl_3$) δ: −67.9 (d, 3F, J = 8.5). Anal. Calcd for $C_{13}H_{11}F_3N_2O_2$ (284.23): C, 54.93; H, 3.90; N, 9.86. Found: C, 54.91; H, 3.91; N, 9.84.

2-[2,2,2-Trifluoro-1-(2-methoxyphenyl)ethyl]malononitrile (**2d**): Oil, R_f = 0.26 (hexanes/EtOAc, 4:1). ^{1}H NMR (200 MHz, $CDCl_3$): 3.91 (s, 3H, OMe), 4.50 (d, 1H, J = 7.1, $CH(CN)_2$), 4.63–4.80 (m, 1H, $CHCF_3$), 7.00–7.14 (m, 2H, CH_{Ar}), 7.43–7.54 (m, 2H, CH_{Ar}). ^{13}C NMR (50 MHz, $CDCl_3$): 23.6 (q, J = 2.2), 42.6 (q, J = 29.8), 55.7, 110.3, 110.4, 111.4, 116.5 (q, J = 1.5), 121.3, 124.3 (q, J = 281.4), 128.8 (q, J = 1.5), 131.7, 157.1. ^{19}F NMR (282 MHz, $CDCl_3$): −66.8 (d, J = 8.5). Anal. Calcd for $C_{12}H_9F_3N_2O$ (254.21): C, 56.70; H, 3.57; N, 11.02. Found: C, 56.77; H, 3.58; N, 10.88.

2-[2,2,2-Trifluoro-1-(4-nitrophenyl)ethyl]malononitrile (**2e**): Oil, R_f = 0.24 (hexanes/EtOAc, 4:1). Mp 97–98 °C. ^{1}H NMR (200 MHz, $CDCl_3$): 4.05–4.22 (m, 1H, $CHCF_3$), 4.53 (d, 1H, J = 5.9, $CH(CN)_2$), 7.74 (d, 2H, J = 8.9, CH_{Ar}), 8.39 (d, 2H, J = 8.9, CH_{Ar}). ^{13}C NMR (50 MHz, $CDCl_3$): 24.4 (q, J = 2.5), 49.6 (q, J = 29.8), 109.4, 109.6, 123.5 (q, J = 281.8), 124.7, 130.4, 134.5, 149.3. ^{19}F NMR (282 MHz, $CDCl_3$): −67.3 (d, J = 6.8). Anal. Calcd for $C_{11}H_6F_3N_3O_2$ (269.18): C, 49.08; H, 2.25; N, 15.61. Found: C, 49.18; H, 2.19; N, 15.56.

2-[1-(3-Bromophenyl)-2,2,2-trifluoroethyl]malononitrile (**2f**): Oil, R_f = 0.29 (hexanes/EtOAc, 5:1). ^{1}H NMR (200 MHz, $CDCl_3$): 3.85–4.02 (m, 1H, $CHCF_3$), 4.40 (d, 1H, J = 6.4, $CH(CN)_2$), 7.34–7.50 (m, 2H, CH_{Ar}), 7.48–7.74 (m, 2H, CH_{Ar}). ^{13}C NMR (50 MHz, $CDCl_3$): 24.6 (q, J = 2.8), 49.6 (q, J = 29.1), 109.6, 109.8, 123.5, 123.6 (q, J = 281.3), 127.5, 129.9 (q, J = 1.4), 131.1, 132.0 (q, J = 1.4), 134.0. ^{19}F NMR (282 MHz, $CDCl_3$): −67.5 (d, J = 8.5). Anal. Calcd for $C_{11}H_6BrF_3N_2$ (303.08): C, 43.59; H, 2.00; N, 9.24. Found: C, 43.54; H, 1.98; N, 9.28.

2-[2,2,2-Trifluoro-1-(1-naphthyl)ethyl]malononitrile (**2g**): Oil, R_f = 0.21 (hexanes/EtOAc, 6:1). ^{1}H NMR (200 MHz, $CDCl_3$): 4.56 (d, 1H, J = 7.3, $CH(CN)_2$), 5.00–5.19 (m, 1H, $CHCF_3$), 7.55–7.73 (m, 3H, CH_{Ar}), 7.84 (d, 1H, J = 7.3, CH_{Ar}), 7.95–8.06 (m, 3H, CH_{Ar}). ^{13}C NMR (50 MHz, $CDCl_3$): 24.6 (q, J = 2.5), 43.4 (q, J = 29.0), 110.1, 110.3, 121.2, 124.3 (q, J = 281.9), 124.3, 125.1, 126.0 (br s, $\Delta\nu_{1/2}$ = 5.9 Hz), 126.6, 127.8, 129.5, 131.2, 131.4, 134.0. ^{19}F NMR (282 MHz, $CDCl_3$): −66.8 (d, J = 8.5). Anal. Calcd for $C_{15}H_9F_3N_2$ (274.24): C, 65.69; H, 3.31; N, 10.21. Found: C, 65.51; H, 3.35; N, 10.02.

2-[(2E)-3-Phenyl-1-(trifluoromethyl)prop-2-enyl]malononitrile (**2h**): Oil, R_f = 0.22 (hexanes/EtOAc, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 3.47–3.60 (m, 1H, $CHCF_3$), 4.23 (d, 1H, J = 4.2, $CH(CN)_2$), 6.16 (dd, 1H, J = 15.8, 9.7, =*CH*CHCF$_3$), 6.94 (d, 1H, J = 15.8, PhC*H*=), 7.33–7.54 (m, 5H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 24.2 (q, J = 2.8), 48.6 (q, J = 29.7), 109.4, 110.1, 113.4 (q, J = 2.0), 123.8 (q, J = 281.4), 127.2, 128.9, 129.6, 134.2, 142.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ: −69.9 (d, 3F, J = 8.5). Anal. Calcd for $C_{13}H_9F_3N_2$ (250.22): C, 62.40; H, 3.63; N, 11.20. Found: C, 62.45; H, 3.69; N, 10.97.

2-(2,2,3,3,3-Pentafluoro-1-phenylpropyl)malononitrile (**3a**): Oil, R_f = 0.26 (hexanes/EtOAc, 6:1). ^{1}H NMR (300 MHz, $CDCl_3$): 3.96 (dt, 1H, J = 23.6, 5.6, CHC_2F_5), 4.53 (d, 1H, J = 5.6, $CH(CN)_2$), 7.46–7.56 (m, 5H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): 24.3 (m), 47.7 (t, J = 19.6), 110.2, 110.4, 114.0 (ddq, J = 264.3, 259.3, 37.6), 118.1 (qt, J = 287.5, 35.4), 127.6 (d, J = 5.5), 129.3 (d, J = 2.2), 129.6, 130.8. ^{19}F NMR (282 MHz, $CDCl_3$): −122.5 (dd, 1F, J = 23.6, 270.0, CF_AF_B), −111.3 (dd, 1F, J = 270.0, 5.6, CF_AF_B), −82.3 (s, 3F, CF_3). Anal. Calcd for $C_{12}H_7F_5N_2$ (274.19): C, 52.57; H, 2.57; N, 10.22. Found: C, 52.64; H, 2.59; N, 10.14.

2-[(Pentafluorophenyl)(phenyl)methyl]malononitrile (**3b**): Mp 89–90 °C, R_f = 0.30 (hexanes/EtOAc, 6:1). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 4.79 (d, 1H, J = 12.1, $CH(CN)_2$), 5.00 (d, 1H, J = 12.1, CHC_6F_5), 7.30–7.55 (m, 5H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 26.8 (t, J = 5.3), 43.2, 111.0, 111.1, 111.3 (tm, J = 14.6), 127.4 (t, J = 1.4), 129.7, 129.8, 134.0, 138.0 (dm, J = 251.0), 141.4 (dm, J = 257.6), 144.9 (dm, J = 247.7). ^{19}F NMR (282 MHz, $CDCl_3$) δ: −159.8 (m, 2F), −152.0 (t, 1F, J = 21.1), −141.8 (d, 2F, J = 17.8). Anal. Calcd for $C_{16}H_7F_5N_2$ (322.23): C, 59.64; H, 2.19; N, 8.69. Found: C, 59.54; H, 2.02; N, 8.57.

2-(2,2-Dichloro-2-fluoro-1-phenylethyl)malononitrile (**3c**): Mp 77–78 °C, R_f = 0.25 (hexanes/EtOAc, 6:1). ^{1}H NMR (200 MHz, $CDCl_3$): 4.16 (dd, 1H, J = 5.6, 16.2, $CHCCl_2F$), 4.77 (d, 1H, J = 5.6, $CH(CN)_2$), 7.45–7.63 (m, 5H, Ph). ^{13}C NMR (50 MHz, $CDCl_3$): 26.1, 60.5 (d, J = 20.8), 110.2, 110.6, 119.7 (d, J = 302.9), 129.4, 129.5 (d, J = 2.2), 130.1, 130.6. ^{19}F NMR (282 MHz, $CDCl_3$): −55.7 (d, J = 16.2). Anal. Calcd for $C_{11}H_7Cl_2FN_2$ (257.09): C, 51.39; H, 2.74; N, 10.90. Found: C, 51.27; H, 2.63; N, 10.79.