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# Synthesis of pyrazoles with fluorinated side-chain by cyclization of fluoroalkylated triketides

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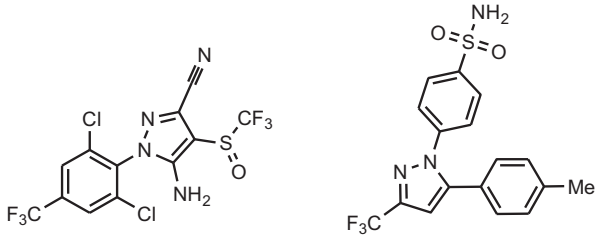
ABSTRACT

The cyclization of fluoroalkylated 3,5-dioxoesters with hydrazines, carried out in glacial acetic acid, afforded pyrazines with fluoroalkylated side-chain. The cyclization of 3,5-dioxoesters with hydroxylamine afforded hydroxylated fluoroalkylated dihydroisoxazoles. All reactions proceeded with good to very good regioselectivity.



## 1. Introduction

Fluoroalkylated heterocycles are of considerable relevance in medicinal and agricultural chemistry, due to their solubility, bioavailability and metabolic stability.[1–4] Perfluoroalkylated molecules are also of importance as liquid crystals[5] and as ligands[6] in catalytic reactions in fluorous solvent systems and as organocatalysts.[7] Perfluoroalkylated 1,3,5-tricarbonyl compounds represent versatile building blocks for the synthesis of hetero- and carbocycles. Fluorinated 1,3,5-triketones were studied by Röschenthaler and coworkers.[8] In 2011, we reported a convenient synthesis of fluoroalkylated 3,5-dioxoalkanoates based on the condensation of the dianion of ethyl acetoacetate with perfluoroalkanoates.[9] The tautomeric equilibria of the products in solution were also analyzed in detail. The chemistry of these new and potentially useful building blocks has, to the best of our knowledge, not been studied so far.[10] Herein, we report the synthesis of pyrazoles containing perfluoroalkyl side chains by cyclization reactions of fluoroalkylated 3,5-dioxoalkanoates with hydrazines. Trifluoromethylated pyrazoles are of considerable relevance in medicinal chemistry. For example, the clinically used drug celecoxib represents a non-steroidal antirheumatic agent,[11] while fipronil® is highly active against parasites[12] (Scheme 1).




Fipronil®  Celecoxib

**Scheme 1.** Structures of fipronil® and celecoxib.

## 2. Results and discussion

It is known for more than one century that pyrazoles can be prepared by cyclization of hydrazine with 1,3-diketones.[13] The cyclization of perfluoroalkylated 3,5-dioxoalkanoates **1b** and **1c**, available by condensation of the dianion of ethyl acetoacetate with

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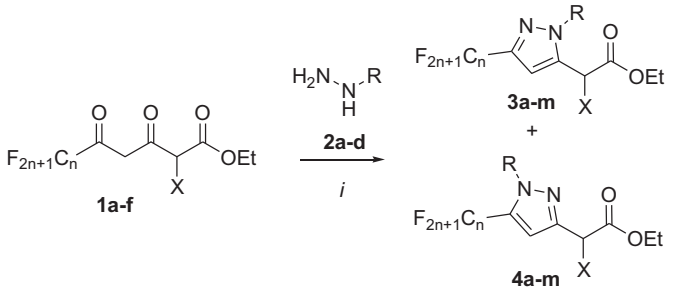
the corresponding perfluoroalkylated esters,[9] with hydrazine hydrate (**2a**) afforded pyrazoles **3a** and **3b**, respectively (Scheme 2, Table 1). The reactions were carried out in glacial acetic acid (25 °C, 2 h). The cyclization of **1b** and **1c** with methyl hydrazine gave



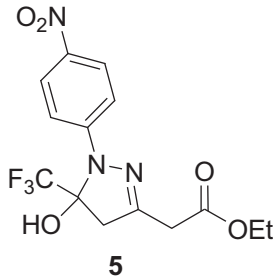

**Scheme 2.** Synthesis of **3a**–**m**; *conditions*: *i*, HOAc, 25 °C, 2 h.

**Table 1**
Synthesis of **3a**–**m**

| 1 | 2 | 3,4 | $C_nF_{2n+1}$ | X | R | 3[a] | 4[a] |
|---|---|---|---|---|---|---|---|
| **b** | **a** | **a** | $C_2F_5$ | H | H | 59 | 0 |
| **c** | **a** | **b** | $C_3F_7$ | H | H | 55 | 0 |
| **b** | **b** | **c** | $C_2F_5$ | H | Me | 66 | 16 |
| **c** | **b** | **d** | $C_3F_7$ | H | Me | 67 | 17 |
| **a** | **c** | **e** | $CF_3$ | H | 4-$(NO_2)C_6H_4$ | 37[b] | 0 |
| **b** | **c** | **f** | $C_2F_5$ | H | 4-$(NO_2)C_6H_4$ | 35 | 0 |
| **c** | **c** | **g** | $C_3F_7$ | H | 4-$(NO_2)C_6H_4$ | 31 | 0 |
| **a** | **d** | **h** | $CF_3$ | H | 4-$MeC_6H_4$ | 67 | 0 |
| **b** | **d** | **i** | $C_2F_5$ | H | 4-$MeC_6H_4$ | 25 | 4 |
| **c** | **d** | **j** | $C_3F_7$ | H | 4-$MeC_6H_4$ | 20[c] | |
| **d** | **d** | **k** | $CF_3$ | Cl | 4-$MeC_6H_4$ | 75 | 0 |
| **e** | **d** | **l** | $C_2F_5$ | Cl | 4-$MeC_6H_4$ | 70[d] | 15 |
| **f** | **d** | **m** | $C_3F_7$ | Cl | 4-$MeC_6H_4$ | 20[c] | |

[a] Yields of isolated products.
[b] Product **5** was isolated as a by-product in 31% yield (structure see Scheme 3).
[c] Unseparable mixture of regioisomers.
[d] The reaction was carried out at 50 °C, 6 h (for 25 °C, 2 h: 42% yield).

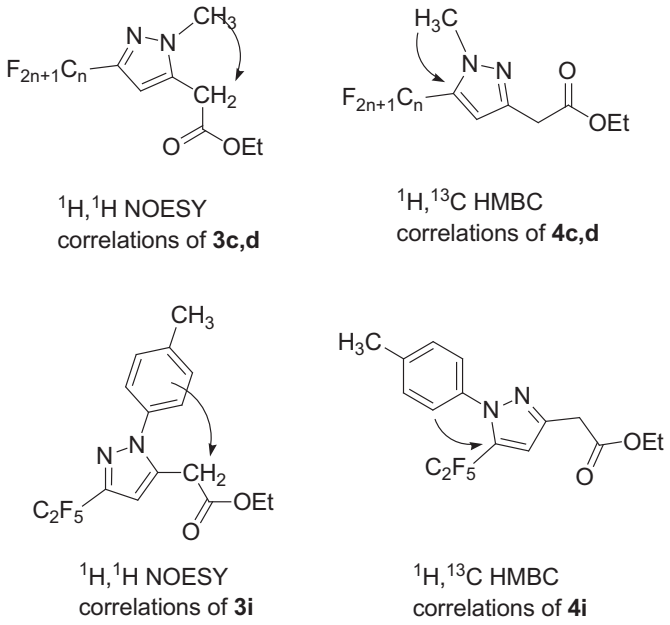
pyrazoles **3c** and **3d**, respectively, along with small amounts of regioisomers **4c** and **4d**, which could be separated by chromatography. The predominant formation of products **3c** and **3d** can be explained by protonation of the (more basic) nitrogen atom attached to the methyl group and subsequent regioselective attack of the non-protonated $NH_2$ group to the keto group neighbouring to the perfluoroalkyl group. This keto group is more electrophilic than the central keto group because of the strong electron withdrawing effect of the perfluoroalkyl group. The cyclization of 3,5-dioxoalkanoates **1a**–**c** with *p*-nitrophenyl hydrazine afforded pyrazoles **3e**–**g**. The moderate yields can be explained by formation of the corresponding hydrates as by-products. In case of the reaction of **1a**, product **5** could be isolated in 31% yield (Scheme 3). This type of hydrates should be intermediates during the formation of all pyrazoles. In general, it can be expected that the elimination of water is more difficult for the




**Scheme 3.** Compound **5**.

perfluoroalkylated derivatives studied in the present manuscript as compared to non-fluorinated pyrazoles, because of the strong electron withdrawing effect of the perfluoroalkyl groups and thus low stability of a cationic intermediate. In case of the *p*-nitrophenyl substituted molecules the elimination is particularly difficult because of the additional electron withdrawing effect of the aryl group. In addition, the formation of regioisomers might account to the moderate yields. The yields could not be improved by elevation of the temperature. The cyclization of **1a**–**c** with *p*-methylphenyl hydrazine (**2d**) resulted in the formation of pyrazoles **3h**–**j**. While $CF_3$-substituted pyrazole **3h** was isolated in good yield, the isolated yield of **3i** was rather low, which can be explained by the formation of regioisomer **4i** and by the low solubility of the 3,5-dioxoalkanoate. In case of **3j**, the regioisomeric side-product could not be completely separated by chromatography. 3,5-Dioxoalkanoates **1d**–**f** contain an additional chloro substituent and were prepared by condensation of the dianion of ethyl 2-chloroacetoacetate with the corresponding perfluoroalkanoates.[11] The cyclization of ethyl 6,6,6-trifluoro-3,5-dioxohexanoate (**1a**) with **2d**, carried out in glacial acetic acid at 25 °C for 2 h, afforded pyrazole **3k** in good yield and with excellent regioselectivity.

The structures of compounds **3** and **4** were confirmed by NMR spectroscopy. For instance, in the NOESY spectra of **3c**, **3d** and **3i** correlations were found between the protons of the *N*-methyl groups (**3c**, **3d**) and the *ortho*-aromatic protons (**3i**), respectively, with the protons of the neighbouring methylene group (Scheme 4). Such NOESY correlations have not been observed for compounds **4c**, **4d** and **4i**. Typically for these compounds, $^1H$,$^{13}C$ correlations of the *N*-methyl (**3c**, **3d**) and the *ortho*-aromatic (**3i**) protons to the carbon atom $F_2CC$ were observed in the $^1H$,$^{13}C$ HMBC spectra. The structure of **5** was independently confirmed by X-ray crystal structure analysis (Fig. 1).[14]




**Scheme 4.** Significant NOESY and HMBC correlations of selected compounds **3** and **4**.

The cyclization of **1d** with parent hydrazine (**2a**), carried out in glacial acetic acid, afforded product **6**, containing an exocyclic double bond, in 58% yield (Scheme 5). The chloride group was cleaved during the reaction, which might be explained by nucleophilic displacement of the chloride by the hydrazine and subsequent extrusion of nitrogen by a process related to the Wolff–Kishner reaction or by another type of reduction.

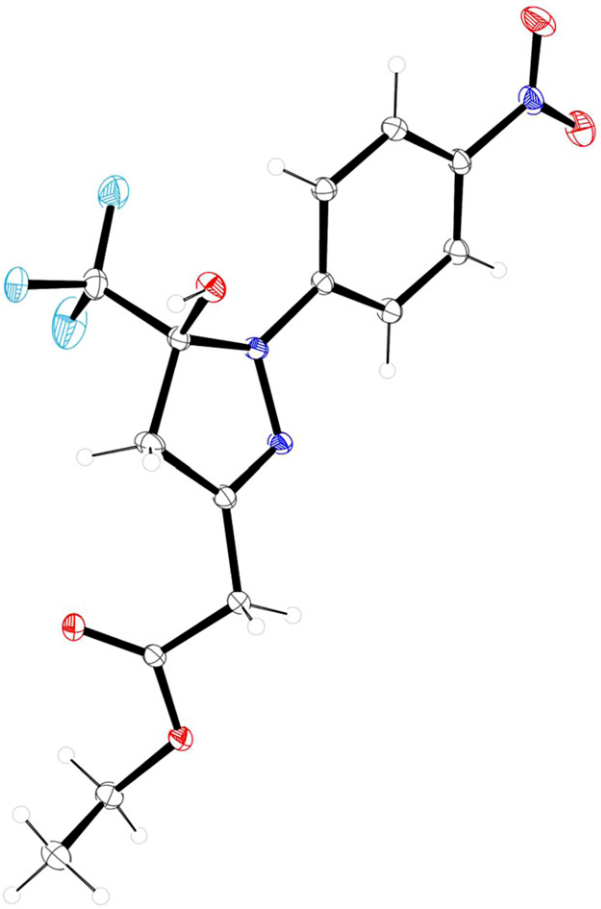
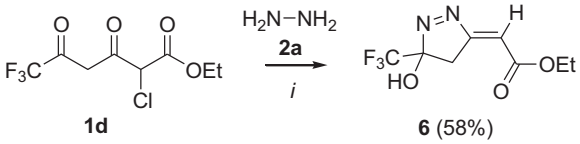


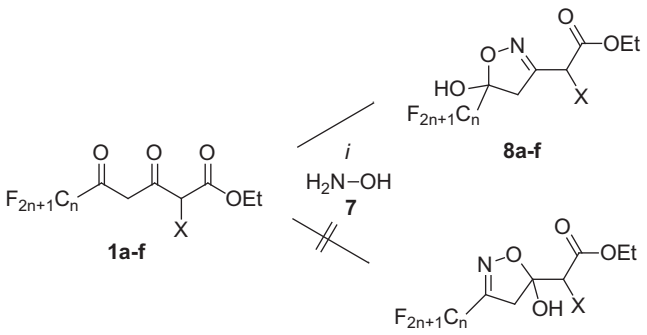
**Fig. 1.** Ortep plot of **5** (50% probability level).




**Scheme 5.** Synthesis of **6**; *conditions*: *i*, HOAc, 25 °C, 2 h.

The structure of compound **6** was confirmed by the NMR data. One of the non-equivalent methylene protons resonating as doubled multiplet at 2.81 ppm shows a coupling to the trifluoromethyl group ($^4J_{H,F}$=1.5 Hz). The second methylene proton resonates as a doublet of a doublet at 3.10 ppm. Except the geminal coupling of $^2J$=19.5 Hz, a coupling about four bonds to the olefinic hydrogen atom ($^4J_{H,H}$=2.5 Hz) was found. The olefinic hydrogen atom appears at 6.98 ppm as a triplet with the same coupling constant of 2.5 Hz. The hydroxyl proton resonates at 4.91 ppm. A $^1$H,$^1$H NOESY spectrum revealed a correlation between the olefinic hydrogen atom and the methylene protons of the ester group and between the hydroxyl group and the methylene proton at 2.81 ppm.

The cyclization of 3,5-dioxoalkanoates **1a**–**f** with hydroxylamine (**7**), carried out in glacial acetic acid (25 °C, 2 h), afforded the hydroxylated dihydroisoxazoles **8a**–**f** (Scheme 6, Table 2). It is important to note that, under the reaction conditions, extrusion of water and formation of the corresponding isoxazoles was not observed. Extended reaction times resulted in decomposition. Products **8a**–**f** were formed with very good regioselectivity. This might be explained by protonation of the amino group of **7**, attack of the (non-protonated) hydroxyl group to the more electrophilic keto group attached to the perfluoroalkyl group and subsequent cyclization. In the $^1$H NMR spectra of compounds **8** the non-equivalent $CH_2$ protons appear as AB spectra with geminal coupling constants $^2J$=18.5–19.5 Hz. For compounds **8d**–**f**, doubled sets of signals are observed, because diastereomers are formed due to the presence of a second asymmetric carbon atom. The structures of **8** were confirmed by the $^{13}$C NMR spectra, in which a coupling was observed between the fluorine atoms and the sp$^3$ hybridized carbon atom attached to the hydroxyl group. For instance, a coupling constant $J_{C,F}$=34.3 Hz, found in case of **8a**, is characteristic for a $^{13}$C,$^{19}$F coupling about two bonds, by which the alternative regioisomer can be excluded.




**Scheme 6.** Synthesis of **8a**–**f**; *conditions*: *i*, HOAc, 25 °C, 2 h.

**Table 2**
Synthesis of **8a**–**f**

| 8 | $C_nF_{2n+1}$ | X | % (**8**)[a] |
|---|---|---|---|
| **a** | $CF_3$ | H | 57 |
| **b** | $C_2F_5$ | H | 46 |
| **c** | $C_3F_7$ | H | 51 |
| **d** | $CF_3$ | Cl | 45 |
| **e** | $C_2F_5$ | Cl | 31 |
| **f** | $C_3F_7$ | Cl | 26 |

[a] Yields of isolated products.

In conclusion, we have reported the synthesis of pyrazines, containing a fluoroalkylated side-chain, by cyclization of fluoroalkylated 3,5-dioxoesters with hydrazines. The cyclization of 3,5-dioxoesters with hydroxylamine afforded hydroxylated fluoroalkylated dihydroisoxazoles. All reactions, which were carried out in glacial acetic acid, proceeded with good to very good regioselectivity.

## 3. Experimental section

### 3.1. General

$^1$H NMR spectra (250.13, 300.13 and 500.13 MHz, resp.) and $^{13}$C NMR spectra (62.9, 75.5 and 125.8 MHz, resp.) were recorded on Bruker spectrometers AVANCE 250, AVANCE 300 and AVANCE 500. The chemical shifts are referenced to solvent signals ($CDCl_3$: $\delta^1$H=7.26, $\delta^{13}$C=77.0; DMSO-$d_6$: $\delta^1$H=2.50, $\delta^{13}$C=39.7). The NMR signals were assigned by DEPT and two-dimensional $^1$H,$^1$H COSY, $^1$H,$^1$H NOESY and $^1$H,$^{13}$C correlation spectra (HSQC, HETCOR, HMBC) using standard pulse sequences (standard Bruker software).$^{19}$F NMR spectra (282.4 MHz) were recorded on Bruker spectrometer AVANCE 300 and $^{19}$F chemical shifts are referenced to $CFCl_3$.

### 3.2. Ethyl 2-(3-(perfluoroethyl)-1*H*-pyrazol-5-yl)acetate (3a)

$^1$H NMR (300.13 MHz, $CDCl_3$): $\delta$=1.29 (t, $^3J_{H,H}$=7.2 Hz, 3H, $OCH_2CH_3$), 3.79 (s, 2H, $CH_2$), 4.23 (q, $^3J_{H,H}$=7.2 Hz, $OCH_2$), 6.46 (s, 1H,

CH), 11.72 (br s, 1H, NH). $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$=−84.6 ($CF_3$), −113.0 ($CF_2$). $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$=14.0 ($CH_3$), 31.1 ($CH_2$), 62.0 ($OCH_2$), 104.7 (CH), 110.7 (tq, $^1J_{C,F}$=250 Hz, $^2J_{C,F}$=39.3 Hz, $CF_2$), 118.8 (qt, $^1J_{C,F}$=286 Hz, $^2J_{C,F}$=38.0 Hz, $CF_3$), 137.1 (CN), 141.5 (t, $^2J_{C,F}$=28.6 Hz, $F_2CC$), 169.5 (CO).

### 3.3. Ethyl 2-(3-(perfluoropropyl)-1*H*-pyrazol-5-yl)acetate (3b)

$^1$H NMR (300.13 MHz, $CDCl_3$): $\delta$=1.31 (t, $^3J_{H,H}$=7.2 Hz, 3H, $OCH_2CH_3$), 3.81 (s, 2H, $CH_2$), 4.25 (q, $^3J_{H,H}$=7.2 Hz, $OCH_2$), 6.45 (s, 1H, CH), 7.73 (br s, 1H, NH). $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$=−80.2 (t, $^3J_{F,F}$=9.7 Hz, $CF_3$), −110.9 ($CF_2$), −127.1 ($CF_2$). $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$=13.9 ($CH_3$), 31.1 ($CH_2$), 61.9 ($OCH_2$), 104–120 ppm (multiplets of $C_3F_7$), 105.1 (CH), 137.2 (CN), 141.4 (t, $^2J_{C,F}$=28.2 Hz, $F_2CC$), 169.5 (CO).

### 3.4. Ethyl 2-(1-methyl-3-(perfluoroethyl)-1*H*-pyrazol-5-yl)acetate (3c)

$^1$H NMR (300.13 MHz, $CDCl_3$): $\delta$=1.28 (t, $^3J_{H,H}$=7.2 Hz, 3H, $OCH_2CH_3$), 3.69 (s, 2H, $CH_2$), 3.89 (s, 3H, $NCH_3$), 4.20 (q, $^3J_{H,H}$=7.2 Hz, $OCH_2$), 6.47 (s, 1H, CH). $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$=−84.6 ($CF_3$), −113.0 ($CF_2$). $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$=14.0 ($OCH_2CH_3$), 31.7 ($CH_2$), 37.3 ($NCH_3$), 61.7 ($OCH_2$), 106.3 (m, CH), 110.7 (tq, $^1J_{C,F}$=250 Hz, $^2J_{C,F}$=38.9 Hz, $CF_2$), 118.8 (qt, $^1J_{C,F}$=286 Hz, $^2J_{C,F}$=38.0 Hz, $CF_3$), 136.9 (CN), 139.7 (t, $^2J_{C,F}$=28.8 Hz, $F_2CC$), 168.2 (CO).

### 3.5. Ethyl 2-(1-methyl-5-(perfluoroethyl)-1*H*-pyrazol-3-yl)acetate (4c)

$^1$H NMR (300.13 MHz, $CDCl_3$): $\delta$=1.26 (t, $^3J_{H,H}$=7.2 Hz, 3H, $OCH_2CH_3$), 3.65 (s, 2H, $CH_2$), 3.96 (s, 3H, $NCH_3$), 4.18 (q, $^3J_{H,H}$=7.2 Hz, $OCH_2$), 6.59 (s, 1H, CH). $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$=−83.9 ($CF_3$), −110.3 ($CF_2$). $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$=14.1 ($OCH_2CH_3$), 33.9 ($CH_2$), 38.7 (m, $NCH_3$), 61.1 ($OCH_2$), 109.1 (m, CH), 110.1 (tq, $^1J_{C,F}$=252 Hz, $^2J_{C,F}$=39.8 Hz, $CF_2$), 118.5 (qt, $^1J_{C,F}$=286 Hz, $^2J_{C,F}$=37.5 Hz, $CF_3$), 130.4 (t, $^2J_{C,F}$=28.8 Hz, $F_2CC$), 144.7 (CN), 170.1 (CO).

### 3.6. Ethyl 2-(1-methyl-3-(perfluoropropyl)-1*H*-pyrazol-5-yl) acetate (3d)

$^1$H NMR (300.13 MHz, $CDCl_3$): $\delta$=1.28 (t, $^3J_{H,H}$=7.2 Hz, 3H, $OCH_2CH_3$), 3.70 (s, 2H, $CH_2$), 3.90 (s, 3H, $NCH_3$), 4.20 (q, $^3J_{H,H}$=7.2 Hz, $OCH_2$), 6.47 (s, 1H, CH). $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$=−80.2 ($CF_3$), −110.8 ($CF_2$), −127.0 ($CF_2$). $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$=14.0 ($OCH_2CH_3$), 31.7 ($CH_2$), 37.3 ($NCH_3$), 61.7 ($OCH_2$), 104–120 ppm (multiplets of $C_3F_7$), 106.6 (CH), 136.8 (CN), 139.7 (t, $^2J_{C,F}$=28.3 Hz, $F_2CC$), 168.1 (CO).

### 3.7. Ethyl 2-(1-methyl-5-(perfluoropropyl)-1*H*-pyrazol-3-yl) acetate (4d)

$^1$H NMR (300.13 MHz, $CDCl_3$): $\delta$=1.26 (t, $^3J_{H,H}$=7.2 Hz, 3H, $OCH_2CH_3$), 3.66 (s, 2H, $CH_2$), 3.95 (s, 3H, $NCH_3$), 4.17 (q, $^3J_{H,H}$=7.2 Hz, $OCH_2$), 6.60 (s, 1H, CH). $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$=−80.1 ($CF_3$), −108.0 ($CF_2$), −125.7 ($CF_2$). $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$=14.0 ($OCH_2CH_3$), 33.9 ($CH_2$), 38.8 (m, $NCH_3$), 61.1 ($OCH_2$), 104–120 ppm (multiplets of $C_3F_7$), 109.6 (m, CH), 130.5 (t, $^2J_{C,F}$=29.0 Hz, $F_2CC$), 144.8 (CN), 170.1 (CO).

### 3.8. Ethyl 2-(1-(4-nitrophenyl)-3-(trifluoromethyl)-1*H*-pyrazol-5-yl)acetate (3e)

$^1$H NMR (300.13 MHz, DMSO-$d_6$): $\delta$=1.24 (t, $^3J_{H,H}$=7.2 Hz, 3H, $OCH_2CH_3$), 3.97 (q, $^3J_{H,H}$=7.2 Hz, 2H, $OCH_2$), 4.12 (s, 2H, $CH_2$), 7.00 (s, 1H, CH), 7.88 (m, 2H, Ar), 8.40 (m, 2H, Ar). $^{19}$F NMR (282 MHz, DMSO-$d_6$): $\delta$=−61.1 ($CF_3$). $^{13}$C NMR (62.9 MHz, DMSO-$d_6$): $\delta$=13.7 ($CH_3$), 31.6 ($CH_2$), 61.0 ($OCH_2$), 107.3 (CH), 121.1 (q, $^2J_{C,F}$=269 Hz, $CF_3$), 124.9, 125.9 ($CH_{Ar}$), 139.6 ($C_q$), 142.2 (q, $^2J_{C,F}$=37.8 Hz, $F_3CC$), 143.3, 147.1 ($C_q$), 168.2 (CO).

### 3.9. Ethyl 2-(5-hydroxy-1-(4-nitrophenyl)-5-(trifluoromethyl)-4,5-dihydro-1*H*-pyrazol-3-yl) acetate (5)

$^1$H NMR (300.13 MHz, DMSO-$d_6$): $\delta$=1.22 (t, $^3J_{H,H}$=7.2 Hz, 3H, $OCH_2CH_3$), 3.41, 3.62 (2d, $^2J_{H,H}$=19.5 Hz, 2H, $CH_2$), 3.62 (s, 2H, $CH_2$), 4.14 (q, $^3J_{H,H}$=7.2 Hz, 2H, $OCH_2$), 7.51 (m, 2H, Ar), 8.16 (m, 2H, Ar), 8.70 (s, 1H, OH). $^{19}$F NMR (282 MHz, DMSO-$d_6$): $\delta$=−80.1 ($CF_3$). $^{13}$C NMR (62.9 MHz, DMSO-$d_6$): $\delta$=13.9 ($CH_3$), 35.6 ($CH_2COO$), 46.1 ($CH_2$), 60.9 ($OCH_2$), 92.7 (q, $^2J_{C,F}$=32.3 Hz, $F_3CC$), 114.7 ($CH_{Ar}$), 123.8 (q, $^1J_{C,F}$=288 Hz, $CF_3$), 124.9 ($CH_{Ar}$), 139.7, 147.7, 149.6 ($C_q$), 168.4 (CO).

### 3.10. Ethyl 2-(1-(4-nitrophenyl)-3-(perfluoroethyl)-1*H*-pyrazol-5-yl)acetate (3f)

$^1$H NMR (300.13 MHz, $CDCl_3$): $\delta$=1.24 (t, $^3J_{H,H}$=7.2 Hz, 3H, $OCH_2CH_3$), 3.79 (s, 2H, $CH_2$), 4.17 (q, $^3J_{H,H}$=7.2 Hz, 2H, $OCH_2$), 6.76 (s, 1H, CH), 7.73 (m, 2H, Ar), 8.38 (m, 2H, Ar). $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$=−84.3 ($CF_3$), −113.4 ($CF_2$). $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$=14.0 ($CH_3$), 32.2 ($CH_2$), 62.0 ($OCH_2$), 108.5 (CH), 110.9 (tq, $^1J_{C,F}$=251 Hz, $^2J_{C,F}$=39.0 Hz, $CF_2$), 118.9 (qt, $^1J_{C,F}$=286 Hz, $^2J_{C,F}$=38.0 Hz, $CF_3$), 124.9, 126.0 ($CH_{Ar}$), 138.0 ($C_q$), 142.9 (t, $^2J_{C,F}$=29.2 Hz, $F_2CC$), 143.4, 147.6 ($C_q$), 168.0 (CO).

### 3.11. Ethyl 2-(1-(4-nitrophenyl)-3-(perfluoropropyl)-1*H*-pyrazol-5-yl)acetate (3g)

$^1$H NMR (300.13 MHz, $CDCl_3$): $\delta$=1.24 (t, $^3J_{H,H}$=7.2 Hz, 3H, $OCH_2CH_3$), 3.79 (s, 2H, $CH_2$), 4.17 (q, $^3J_{H,H}$=7.2 Hz, 2H, $OCH_2$), 6.75 (s, 1H, CH), 7.73 (m, 2H, Ar), 8.39 (m, 2H, Ar). $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$=−80.1 ($CF_3$), −111.3 ($CF_2$), −126.9 ($CF_2$). $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$=14.0 ($CH_3$), 32.2 ($CH_2$), 62.0 ($OCH_2$), 104–120 ppm (multiplets of $C_3F_7$), 108.7 (CH), 124.9, 126.0 ($CH_{Ar}$), 138.0 ($C_q$), 142.9 (t, $^2J_{C,F}$=28.8 Hz, $F_2CC$), 143.4, 147.6 ($C_q$), 168.0 (CO).

### 3.12. Ethyl 2-(5-hydroxy-5-(trifluoromethyl)-4,5-dihydro-3*H*-pyrazol-3-ylidene)acetate (6)

$^1$H NMR (500.13 MHz, $CDCl_3$): $\delta$=1.35 (t, $^3J_{H,H}$=7.2 Hz, 3H, $OCH_2CH_3$), 2.81 (dm, $^2J_{H,H}$=19.5 Hz, $^4J_{H,F}$=1.5 Hz, 1H), 3.10 (dd, $^2J_{H,H}$=19.5 Hz, $^4J_{H,H}$=2.5 Hz, 1H, $CH_2$), 4.30 (q, $^3J_{H,H}$=7.2 Hz, 2H, $OCH_2$), 4.91 (s, 1H, OH), 6.98 ('t', $^4J_{H,H}$=2.5 Hz, 1H, CH). $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$=−80.8 ($CF_3$). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta$=14.1 ($CH_3$), 30.1 ($CH_2$), 61.8 ($OCH_2$), 109.4 (q, $^2J_{C,F}$=31.0 Hz, $F_3CC$), 122.1 (CH), 122.4 (q, $^1J_{C,F}$=285 Hz, $CF_3$), 165.8 (CO), 170.0 ($C_q$).

### 3.13. Ethyl(2-*p*-tolyl-5-trifluoromethyl-2*H*-pyrazol-3-yl)acetate (3h)

$^1$H NMR (300.13 MHz, $CDCl_3$): $\delta$=1.22 (t, $^3J_{H,H}$=7.2 Hz, 3H, $OCH_2CH_3$), 2.42 (s, 3H, $CH_3$), 3.61 (s, 2H, $CH_2$), 4.13 (q, $^3J_{H,H}$=7.2 Hz, 2H, $OCH_2$), 6.65 (s, 1H, CH), 7.29–7.33 (m, 4H, Ar). $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$=−62.5 ($CF_3$). $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$=14.0 ($OCH_2CH_3$), 21.1 ($CH_3$), 32.1 ($CH_2$), 61.5 ($OCH_2$), 105.6 (q, $^3J_{C,F}$=2.2 Hz, CH), 121.2 (q, $^1J_{C,F}$=269 Hz, $CF_3$), 125.6, 129.9 ($CH_{Ar}$), 135.9, 137.4, 139.5 ($C_q$), 142.8 (q, $^2J_{C,F}$=38.3 Hz, $F_3CC$), 168.2 (CO).

### 3.14. Ethyl (5-pentafluorethyl-2-*p*-tolyl-2*H*-pyrazol-3-yl)acetate (3i)

$^1$H NMR (300.13 MHz, $CDCl_3$): $\delta$=1.22 (t, $^3J_{H,H}$=7.2 Hz, 3H, $OCH_2CH_3$), 2.42 (s, 3H, $CH_3$), 3.61 (s, 2H, $CH_2$), 4.14 (q, $^3J_{H,H}$=7.2 Hz,

2H, $OCH_2$), 6.68 (s, 1H, CH), 7.30–7.33 (m, 4H, Ar). $^{19}F$ NMR (282 MHz, $CDCl_3$): $\delta$=−84.4 ($CF_3$), −113.0 ($CF_2$). $^{13}C$ NMR (75.5 MHz, $CDCl_3$): $\delta$=14.0 ($OCH_2CH_3$), 21.1 ($CH_3$), 32.1 ($CH_2$), 61.6 ($OCH_2$), 106.8 (t, $^3J_{C,F}$=2.8 Hz, CH), 110.9 (tq, $^1J_{C,F}$=251 Hz, $^2J_{C,F}$=39.0 Hz, $CF_2$), 118.9 (qt, $^1J_{C,F}$=286 Hz, $^2J_{C,F}$=38.0 Hz, $CF_3$), 125.6, 129.9 ($CH_{Ar}$), 135.9, 137.6, 139.5 ($C_q$), 141.3 (t, $^2J_{C,F}$=28.6 Hz, $F_2CC$), 168.5 (CO).

### 3.15. Ethyl (3-pentafluoroethyl-2-*p*-tolyl-2*H*-pyrazol-5-yl)acetate (4i)

$^1H$ NMR (300.13 MHz, $CDCl_3$): $\delta$=1.29 (t, $^3J_{H,H}$=7.2 Hz, 3H, $OCH_2CH_3$), 2.41 (s, 3H, $CH_3$), 3.76 (s, 2H, $CH_2$), 4.26 (q, $^3J_{H,H}$=7.2 Hz, 2H, $OCH_2$), 6.81 (s, 1H, CH), 7.29–7.32 (m, 4H, Ar). $^{19}F$ NMR (282 MHz, $CDCl_3$): $\delta$=−83.4 ($CF_3$), −106.3 ($CF_2$). $^{13}C$ NMR (75.5 MHz, $CDCl_3$): $\delta$=14.1 ($OCH_2CH_3$), 21.2 ($CH_3$), 33.9 ($CH_2$), 61.5 ($OCH_2$), 109.8 (CH), 126.4, 129.4 ($CH_{Ar}$), 137.0, 139.6, 146.0 ($C_q$), 170.0 (CO), signals not given for $C_2F_5$ and $F_2CC$.

### 3.16. Ethyl (5-heptafluoropropyl-2-*p*-tolyl-2*H*-pyrazol-3-yl) acetate (3j)

$^1H$ NMR (300.13 MHz, $CDCl_3$): $\delta$=1.22 (t, $^3J_{H,H}$=7.2 Hz, 3H, $OCH_2CH_3$), 2.42 (s, 3H, $CH_3$), 3.68 (s, 2H, $CH_2$), 4.14 (q, $^3J_{H,H}$=7.2 Hz, 2H, $OCH_2$), 6.67 (s, 1H, CH), 7.25–7.33 (m, 4H, Ar). $^{19}F$ NMR (282 MHz, $CDCl_3$): $\delta$=−80.2 ($CF_3$), −111.0, −126.9 ($CF_2$). $^{13}C$ NMR (75.5 MHz, $CDCl_3$): $\delta$=14.0 ($OCH_2CH_3$), 21.1 ($CH_3$), 32.1 ($CH_2$), 61.6 ($OCH_2$), 107.1 (CH), 108–120 (ppm multiplets of $C_3F_7$), 125.6, 129.9 ($CH_{Ar}$), 135.9, 137.6, 139.5 ($C_q$), 141.3 (t, $^2J_{C,F}$=28.6 Hz, $F_2CC$), 168.4 (CO).

### 3.17. Ethyl (3-heptafluoropropyl-2-*p*-tolyl-2*H*-pyrazol-5-yl) acetate (4j)

$^1H$ NMR (300.13 MHz, $CDCl_3$): $\delta$=1.28 (t, $^3J_{H,H}$=7.2 Hz, 3H, $OCH_2CH_3$), 2.42 (s, 3H, $CH_3$), 3.76 (s, 2H, $CH_2$), 4.23 (q, $^3J_{H,H}$=7.2 Hz, 2H, $OCH_2$), 6.82 (s, 1H, CH), 7.25–7.33 (m, 4H, Ar). $^{19}F$ NMR (282 MHz, $CDCl_3$): $\delta$=−80.1 ($CF_3$), −104.1, −125.0 ($CF_2$). $^{13}C$ NMR (75.5 MHz, $CDCl_3$): $\delta$=14.1 ($OCH_2CH_3$), 21.2 ($CH_3$), 34.0 ($CH_2$), 61.1 ($OCH_2$), 108–120 ppm (multiplets of $C_3F_7$), 110.2 (CH), 126.5, 129.3 ($CH_{Ar}$), 131.5 (t, $^2J_{C,F}$=28.2 Hz, $F_2CC$), 137.0, 139.6, 146.0 ($C_q$), 170.0 (CO).

### 3.18. Ethyl 2-chloro-2-(2-*p*-tolyl-5-trifluoromethyl-2*H*-pyrazol-3-yl)acetate (3k)

$^1H$ NMR (300.13 MHz, $CDCl_3$): $\delta$=1.29 (t, $^3J_{H,H}$=7.2 Hz, 3H, $OCH_2CH_3$), 2.45 (s, 3H, $CH_3$), 4.26 (m, $ABX_3$, $^3J_{H,H}$=7.2 Hz, 2H, $OCH_2$), 5.30 (s, 1H, CHCl), 6.93 (s, 1H, CH), 7.31–7.42 (m, 4H, Ar). $^{19}F$ NMR (282 MHz, $CDCl_3$): $\delta$=−62.2 ($CF_3$). $^{13}C$ NMR (75.5 MHz, $CDCl_3$): $\delta$=14.0 ($OCH_2CH_3$), 21.1 ($CH_3$), 48.8 (CHCl), 61.6 ($OCH_2$), 105.6 (q, $^3J_{C,F}$=2.0 Hz, CH), 121.3 (q, $^1J_{C,F}$=268 Hz, $CF_3$), 125.7, 129.9 ($CH_{Ar}$), 135.9, 137.4, 139.5 ($C_q$), 142.8 (q, $^2J_{C,F}$=38.3 Hz, $F_3CC$), 168.5 (CO).

### 3.19. Ethyl 2-chloro-2-(5-pentafluoroethyl-2-*p*-tolyl-2*H*-pyrazol-3-yl)acetate (3l)

$^1H$ NMR (300.13 MHz, $CDCl_3$): $\delta$=1.28 (t, $^3J_{H,H}$=7.2 Hz, 3H, $OCH_2CH_3$), 2.45 (s, 3H, $CH_3$), 4.26 (m, $ABX_3$, $^3J_{H,H}$=7.2 Hz, 2H, $OCH_2$), 5.31 (s, 1H, CHCl) 6.96 (s, 1H, CH), 7.32–7.42 (m, 4H, Ar). $^{19}F$ NMR (282 MHz, $CDCl_3$): $\delta$=−84.3 ($CF_3$), −113.0 ($CF_2$). $^{13}C$ NMR (75.5 MHz, $CDCl_3$): $\delta$=13.8 ($OCH_2CH_3$), 21.2 ($CH_3$), 48.7 (CHCl), 63.3 ($OCH_2$), 107.2 (CH), 110.5 (tq, $^1J_{C,F}$=251 Hz, $^2J_{C,F}$=39.4 Hz, $CF_2$), 118.5 (qt, $^1J_{C,F}$=286 Hz, $^2J_{C,F}$=37.5 Hz, $CF_3$), 125.7, 130.2 ($CH_{Ar}$), 135.1, 139.6, 140.3 ($C_q$), 141.8 (t, $^2J_{C,F}$=29.1 Hz, $F_2CC$), 165.9 (CO).

### 3.20. Ethyl 2-chloro-2-(3-pentafluoroethyl-2-*p*-tolyl-2*H*-pyrazol-5-yl)acetate (4l)

$^1H$ NMR (300.13 MHz, $CDCl_3$): $\delta$=1.32 (t, $^3J_{H,H}$=7.2 Hz, 3H, $OCH_2CH_3$), 2.43 (s, 3H, $CH_3$), 4.31 (m, $^3J_{H,H}$=7.2 Hz, 2H, $OCH_2$), 5.51 (s, 1H, CHCl), 7.01 (m, 1H, CH), 7.29–7.33 (m, 4H, Ar). $^{19}F$ NMR (282 MHz, $CDCl_3$): $\delta$=−83.4 ($CF_3$), −106.5 ($CF_2$). $^{13}C$ NMR (75.5 MHz, $CDCl_3$): $\delta$=13.9 ($OCH_2CH_3$), 21.2 ($CH_3$), 51.8 (CHCl), 62.8 ($OCH_2$), 126.4, 129.5 ($CH_{Ar}$), 140.1 ($C_q$), 167.2 (CO), not all signals are given.

### 3.21. Ethyl 2-chloro-2-(5-heptafluoropropyl-2-*p*-tolyl-2*H*-pyrazol-3-yl)acetate (3m)

$^1H$ NMR (300.13 MHz, $CDCl_3$): $\delta$=1.27 (t, $^3J_{H,H}$=7.2 Hz, 3H, $OCH_2CH_3$), 2.45 (s, 3H, $CH_3$), 4.26 (m, $ABX_3$, $^3J_{H,H}$=7.2 Hz, 2H, $OCH_2$), 5.31 (s, 1H, CHCl), 6.95 (s, 1H, CH), 7.32–7.41 (m, 4H, Ar). $^{19}F$ NMR (282 MHz, $CDCl_3$): $\delta$=−80.2 ($CF_3$), −110.9 ($CF_2$), −126.8 ($CF_2$). $^{13}C$ NMR (75.5 MHz, $CDCl_3$): $\delta$=13.8 ($OCH_2CH_3$), 21.2 ($CH_3$), 48.8 (CHCl), 63.3 ($OCH_2$), 104–126 ppm (multiplets of $C_3F_7$), 107.4 (t, $^3J_{C,F}$=3.0 Hz, CH), 125.7, 130.2 ($CH_{Ar}$), 135.1, 139.7, 140.3 ($C_q$), 141.8 (t, $^2J_{C,F}$=29.0 Hz, $F_2CC$), 165.9 (CO).

### 3.22. Ethyl 2-chloro-2-(3-heptafluoropropyl-2-*p*-tolyl-2*H*-pyrazol-5-yl)acetate (4m)

$^1H$ NMR (300.13 MHz, $CDCl_3$): $\delta$=1.32 (t, $^3J_{H,H}$=7.2 Hz, 3H, $OCH_2CH_3$), 2.42 (s, 3H, $CH_3$), 4.30 (m, $ABX_3$, $^3J_{H,H}$=7.2 Hz, 2H, $OCH_2$), 5.51 (s, 1H, CHCl), 7.03 (s, 1H, CH), 7.24–7.34 (m, 4H, Ar). $^{19}F$ NMR (282 MHz, $CDCl_3$): $\delta$=−80.1 ($CF_3$), −104.2 ($CF_2$), −124.9 ($CF_2$). $^{13}C$ NMR (75.5 MHz, $CDCl_3$): $\delta$=13.9 ($OCH_2CH_3$), 21.2 ($CH_3$), 51.8 (CHCl), 62.8 ($OCH_2$), 104–126 ppm (multiplets of $C_3F_7$), 109.6 (m, CH), 126.5, 129.4 ($CH_{Ar}$), 132.3 (t, $^2J_{C,F}$=29.0 Hz, $F_2CC$), 136.7, 140.1, 148.1 ($C_q$), 167.1 (CO).

### 3.23. Ethyl (5-hydroxy-5-trifluoromethyl-4,5-dihydroisoxazol-3-yl)acetate (8a)

$^1H$ NMR (300.13 MHz, $CDCl_3$): $\delta$=1.30 (t, $^3J_{H,H}$=7.2 Hz, 3H, $OCH_2CH_3$), 3.24, 3.52 (2d, $^2J_{H,H}$=19.2 Hz, 2H, $CH_2$), 3.50 (s, 2H, $CH_2COO$), 4.21 (q, $^3J_{H,H}$=7.2 Hz, 2H, $OCH_2$), 5.20 (s, 1H, OH). $^{19}F$ NMR (282 MHz, $CDCl_3$): $\delta$=−83.0 ($CF_3$). $^{13}C$ NMR (75.5 MHz, $CDCl_3$): $\delta$=13.5 ($OCH_2CH_3$), 32.7 ($CH_2COO$), 44.3 ($CH_2$), 62.0 ($OCH_2$), 103.5 (q, $^2J_{C,F}$=34.3 Hz, $F_3CC$), 121.8 (q, $^1J_{C,F}$=283 Hz, $CF_3$), 154.0 (CN), 168.4 (CO).

### 3.24. Ethyl (5-hydroxy-5-pentafluoroethyl-4,5-dihydroisoxazol-3-yl)acetate (8b)

$^1H$ NMR (300.13 MHz, $CDCl_3$): $\delta$=1.29 (t, $^3J_{H,H}$=7.2 Hz, 3H, $OCH_2CH_3$), 3.24, 3.58 (2 d, $^2J_{H,H}$=18.8 Hz, 2H, $CH_2$), 3.50 (s, 2H, $CH_2COO$), 4.21 (q, $^3J_{H,H}$=7.2 Hz, 2H, $OCH_2$), 6.27 (s, 1H, OH). $^{19}F$ NMR (282 MHz, $CDCl_3$): $\delta$=−80.0 ($CF_3$), −123.4 (d, $^2J_{F,F}$=278 Hz, 1F, $CF_2$), −127.9 (d, $^2J_{F,F}$=278 Hz, 1F, $CF_2$). $^{13}C$ NMR (75.5 MHz, $CDCl_3$): $\delta$=13.7 ($OCH_2CH_3$), 32.8 ($CH_2COO$), 45.1 ($CH_2$), 62.0 ($OCH_2$), 104.7 (dd, $^2J_{C,F}$=27.0 Hz, $^2J_{C,F}$=25.5 Hz, $F_2CC$), 111.1 (tq, $^1J_{C,F}$=261 Hz, $^2J_{C,F}$=36.5 Hz, $CF_2$), 118.3 (qt, $^1J_{C,F}$=287 Hz, $^2J_{C,F}$=35.2 Hz, $CF_3$), 154.0 (CN), 168.5 (CO).

### 3.25. Ethyl (5-hydroxy-5-heptafluoropropyl-4,5-dihydroisoxazol-3-yl)acetate (8c)

$^1H$ NMR (300.13 MHz, $CDCl_3$): $\delta$=1.29 (t, $^3J_{H,H}$=7.2 Hz, 3H, $OCH_2CH_3$), 3.27 (d, $^2J_{H,H}$=18.8 Hz, 1H, $CH_2$), 3.51 (s, 2H, $CH_2COO$), 3.60 (d, $^2J_{H,H}$=18.8 Hz, 1H, $CH_2$), 3.81 (s, 1H, OH), 4.22 (q, $^3J_{H,H}$=7.2 Hz, 2H, $OCH_2$). $^{19}F$ NMR (282 MHz, $CDCl_3$): $\delta$=−81.0 ('t', $CF_3$), −120.2, −124.1 (2m, 2F, $CF_2$), −123.9, −125.2 (2m, 2F, $CF_2$). $^{13}C$

NMR (75.5 MHz, $CDCl_3$): $\delta$=13.8 ($OCH_2CH_3$), 32.9 ($CH_2COO$), 45.4 ($CH_2$), 62.1 ($OCH_2$), 105–114 ppm (multiplets of $CF_2$), 105.2 ('t', $^2J_{C,F}$=27.0 Hz, $F_2CC$), 112.8 (tt, $^1J_{C,F}$=262 Hz, $^2J_{C,F}$=29.8 Hz, $CF_3CF_2CF_2$), 117.6 (qt, $^1J_{C,F}$=288 Hz, $^2J_{C,F}$=33.5 Hz, $CF_3$), 154.0 (CN), 168.4 (CO).

### 3.26. Ethyl 2-chloro(5-hydroxy-5-trifluoromethyl-4,5-dihydroisoxazol-3-yl)acetate (8d)

$^1$H NMR (300.13 MHz, $CDCl_3$): $\delta$=1.33 (t, $^3J_{H,H}$=7.2 Hz, 3H, $OCH_2CH_3$), 1.34 (t, $^3J_{H,H}$=7.2 Hz, 3H, $OCH_2CH_3$), 3.37 (dm, $^2J_{H,H}$=18.5 Hz, 2H, $CH_2$), 3.57 (d, $^2J_{H,H}$=18.5 Hz, 1H, $CH_2$), 3.61 (d, $^2J_{H,H}$=18.5 Hz, 1H, $CH_2$), 4.31 (q, $^3J_{H,H}$=7.2 Hz, 2H, $OCH_2$), 4.32 (q, $^3J_{H,H}$=7.2 Hz, 2H, $OCH_2$), 5.20 (br, 2H, OH), 5.28 (s, 1H, CHCl), 5.29 (s, 1H, CHCl). $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$=−83.2, −83.0 ($CF_3$). $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$=13.5, 13.5 ($OCH_2CH_3$), 40.8, 40.8 ($CH_2$), 50.2, 50.3 (CH), 63.7, 63.8 ($OCH_2$), 104.2, 104.3 (q, $^2J_{C,F}$=34.7 Hz, $F_3CC$), 121.5 (q, $^1J_{C,F}$=284 Hz, $2CF_3$), 154.8, 155.0 (CN), 165.6, 165.8 (CO).

### 3.27. Ethyl 2-chloro(5-hydroxy-5-pentafluoroethyl)-4,5-(dihydroisoxazol-3-yl)acetate (8e)

$^1$H NMR (300.13 MHz, $CDCl_3$): $\delta$=1.33 (t, $^3J_{H,H}$=7.2 Hz, 3H, $OCH_2CH_3$), 1.34 (t, $^3J_{H,H}$=7.2 Hz, 3H, $OCH_2CH_3$), 3.36 (d, $^2J_{H,H}$=18.5 Hz, 2H, $CH_2$), 3.64 (d, $^2J_{H,H}$=18.5 Hz, 1H, $CH_2$), 3.68 (d, $^2J_{H,H}$=18.5 Hz, 1H, $CH_2$), 4.31 (q, $^3J_{H,H}$=7.2 Hz, 2H, $OCH_2$), 4.32 (q, $^3J_{H,H}$=7.2 Hz, 2H, $OCH_2$), 5.30 (s, 2H, 2CHCl), 7.30 (br, 2H, OH). $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$=−79.9, −80.0 (2 $CF_3$), −123.5, −128.0 (2d, AB, $^2J_{F,F}$=280 Hz, 2F, $CF_2$), −123.7, −128.1 (2d, AB, $^2J_{F,F}$=280 Hz, 2F, $CF_2$). $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$=13.6, 13.6 ($OCH_2CH_3$), 41.6, 41.7 ($CH_2$), 50.2, 50.2 (CHCl), 63.8, 63.9 ($OCH_2$), 105.3 (dd, $^2J_{C,F}$=27.5 Hz, $^2J_{C,F}$=25.3 Hz, $F_2CC$), 118.3, 118.3 (qt, $^1J_{C,F}$=287 Hz, $^2J_{C,F}$=35.2 Hz, $2CF_3$), 110.9, 110.9 (tq, $^1J_{C,F}$=262 Hz, $^2J_{C,F}$=36.9 Hz, $2CF_2$), 155.0, 155.3 (CN), 165.5, 165.9 (CO).

### 3.28. Ethyl 2-chloro-(5-hydroxy-5-heptafluoropropyl-4,5-dihydroisoxazol-3-yl)acetate (8f)

$^1$H NMR (300.13 MHz, $CDCl_3$): $\delta$=1.33 (t, $^3J_{H,H}$=7.2 Hz, 3H, $OCH_2CH_3$), 1.35 (t, $^3J_{H,H}$=7.2 Hz, 3H, $OCH_2CH_3$), 3.39 (d, $^2J_{H,H}$=18.8 Hz, 2H, $CH_2$), 3.67 (d, $^2J_{H,H}$=18.8 Hz, 1H, $CH_2$), 3.68 (d, $^2J_{H,H}$=18.8 Hz, 1H, $CH_2$), 4.31 (q, $^3J_{H,H}$=7.2 Hz, 2H, $OCH_2$), 4.31 (q, $^3J_{H,H}$=7.2 Hz, 2H, $OCH_2$), 5.29 (s, 1H, CHCl), 5.29 (s, 1H, CHCl), 5.55 (br, 2H, OH). $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$=−80.9 (dd, $CF_3$), −80.9 (dd, $CF_3$), −120.4 (m, 1F), −124.2 (m, 1F), ($CF_2$), −120.6 (m, 1F), −124.2 (m, 1F), ($CF_2$), −124.0 (m, 2F, $CF_2$), −124.9 (m, 2F, $CF_2$). $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$=13.6, 13.6 ($OCH_2CH_3$), 41.8 (m, $CH_2$), 41.9 (m, $CH_2$), 50.2, 50.2 (CHCl), 63.8, 63.9 ($OCH_2$), 105–117 ppm (multiplets of $CF_2CF_2$), 105.9 ('t', $^2J_{C,F}$=27.0 Hz, $F_2CC$), 117.6 (qt, $^1J_{C,F}$=288 Hz, $^2J_{C,F}$=33.6 Hz, $2CF_3$), 155.0, 155.3 (CN), 165.5, 165.9 (CO).

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