FULL PAPER

Synthesis and Solution Structure of 1*H*-Benzo-1,5-diazepine Derivatives with a Perfluoroalkyl Side Chain

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Dedicated to Professor *Manfred Michalik* on the occasion of his 75th birthday

The reaction of perfluorinated 3,5-dioxoesters with 1,2-diaminobenzenes or 2,3-diaminonaphthalenes afforded two types of 1*H*-benzo-1,5-diazepine derivatives containing a perfluorinated side chain. 2,5-Dihydro-1*H*-benzo-1,5-diazepin-2-ones were formed by cyclocondensation *via* the central keto and the ester group, whereas 1*H*-benzo-1,5-diazepines resulted from cyclocondensation *via* the two keto groups. The tautomerism and isomerization of these compounds have been investigated by ^{1}H-, ^{13}C-, and ^{19}F-NMR spectroscopy. The 1,5-diazepines appear in $CDCl_3$ solution as mixtures of two tautomeric forms, the enaminoimine **I** and diaminodiene **II**. In DMSO solution, besides **I** and **II**, two further species, **III** and **IV**, are formed by (*E*/*Z*) isomerization on the exocyclic C=C bond.

Keywords: Cyclocondensation, *N*-Heterocycles, NMR Spectroscopy, Tautomerism, Isomerization, Fluoro compounds.

Introduction

1*H*-Benzo-1,4-diazepines are of considerable pharmacological relevance. They show an anxiolytic, tranquilizing, antiepileptic, and anticonvulsive activity [1]. In 1960, the first drug, chlordiazepoxide (Librium®), appeared on the market. Three years later, it was replaced by Diazepam (Valium®) (*Fig. 1*) [2][3]. The isomeric 1*H*-benzo-1,5-diazepines show a similar pattern of pharmacological activity. Examples include the drug clobazam. Syntheses of 1,5-diazepines and of benzo-1,5-diazepines rely on cyclocondensation reactions of 1,2-diaminoethanes or 1,2-diaminobenzenes with 1,3-dielectrophiles [3]. Organofluorine molecules are important lead structures in medicinal chemistry, due to the chemical and metabolic stability of the C–F bond and the lipophilicity of many fluorinated molecules [4].

Despite the pharmacological importance of diazepines on the one hand and of fluorinated heterocycles on the other hand, syntheses of fluorinated diazepine derivatives have only been scarcely reported so far. *Saloutin et al.* [5] reported the synthesis of fluorinated 1*H*-benzo-1,5-diazepines by cyclocondensation of fluorinated *β*-ketoesters with 1,2-diaminobenzene. *Yachevskii* and co-workers described the cyclocondensation of 1,2-diaminobenzene with unsymmetrical perfluorinated 1,3,5-triketones [6]. We have recently reported the synthesis of perfluorinated 3,5-dioxoesters and their application to the synthesis of

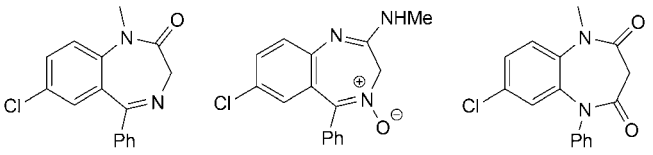

Fig. 1. Drugs with benzodiazepine core structures.

pyrazoles and isoxazoles [7][8]. Herein, we wish to present, to the best of our knowledge, the first cyclocondensation reactions of perfluorinated 3,5-dioxoesters with 1,2-diaminobenzenes. These reactions provide a convenient approach to 1*H*-benzo-1,5-diazepines containing a perfluorinated side chain.

Results and Discussion

Perfluorinated 3,5-dioxoesters **1a** – **f** were prepared, as previously reported [7], by reaction of the dianions of ethyl acetoacetate or ethyl 2-chloroacetoacetate with the corresponding perfluorinated esters (*Scheme 1*).

The cyclocondensation has been performed using two different procedures. The reaction of ethyl 6,6,6-trifluoro-3,5-dioxohexanoate (**1a**) with 1,2-diaminobenzene (**2a**), carried out in glacial AcOH at 80° (*Method A*), afforded a mixture of two compounds, which could be separated by column chromatography: 2,5-dihydro-1*H*-benzo-1,5-

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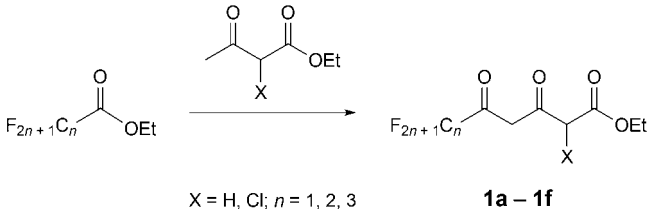
Scheme 1. Syntheses of compounds **1a** – **1f** according to [7].



diazepin-2-one (**3a**) (44% yield) and 1*H*-benzo-1,5-diazepine (**4a**) (29% yield) (*Scheme 2*, *Table 1*). The product **3a** was formed by cyclocondensation *via* the central keto and the ester group, whereas **4a** was formed by cyclocondensation *via* the two keto groups, in analogy to reactions with dialkyl 3,5-dioxopimelates [3e], while the ester group remained unattacked. To improve the yields, we also tested a different protocol. When the same substrates reacted in dry MeCN in the presence of trimethylchlorosilane as H_2O scavenger, the amount of **3a** increased up to 53%, while that of **4a** dropped down to 25% (*Method B*). Scope and limitations were studied for the reaction between different substituted 3,5-dioxoalkanoates (**1a** – **d**) and 1,2-diaminobenzenes **2a** and **2b** to obtain a series of compounds **3** and **4** (*Table 1*, *Scheme 2*). With regard to our intended NMR studies on the tautomerism, we were especially interested in the synthesis of the 1*H*-benzo-1,5-diazepines. Therefore, not in all cases the corresponding diazepinones have been isolated.

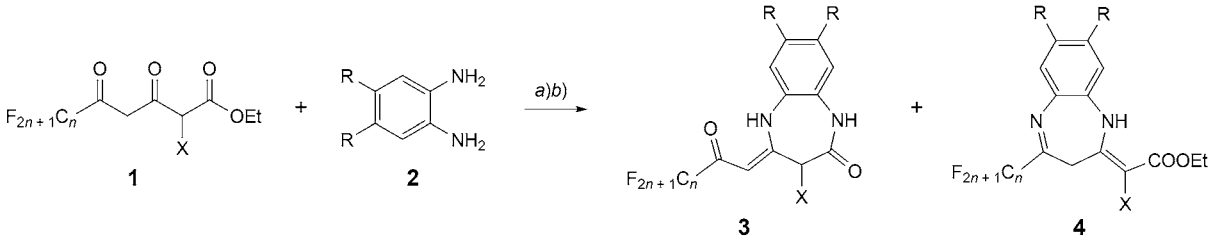
The reaction of ethyl 2-chloro-6,6,6-trifluoro-3,5-dioxohexanoate (**1d**) with 1,2-diaminobenzenes **2a**,**b** in glacial AcOH (*Method A*) afforded the 1*H*-benzo-1,5-diazepines **4g**,**h**. The chloride group proved to be compatible with this reaction and did not undergo a nucleophilic substitution reaction with the amine.

The reaction of 3,5-dioxoesters **1a** – **f** with 2,3-diaminonaphthalene (**2c**) afforded in the same way 1*H*-naphtho-1,5-diazepines **5a** – **f** (*Scheme 3*, *Table 2*). The corresponding 1*H*-naphtho-1,5-diazepin-2-ones were only formed in traces.

NMR Investigation

In the ^{1}H-NMR spectra of compounds **3** in $CDCl_3$ solution, characteristic signals for two NH groups (δ = 12.43 – 12.70 and 7.93 – 9.21) as well as an olefinic CH (δ = 5.67 – 5.77) and a CH_2 group (δ = 3.31 – 3.22) were observed. The NH signal at lower field should be assigned to an H-atom involved in an intramolecular hydrogen bond. In the ^{1}H,^{13}C-HMBC spectra recorded for **3d** and **3e**, cross peaks for each NH proton about three bonds with the C-atom of the CH_2 group were found, whereas only one NH (at lower field) correlated with the C-atom of the olefinic CH group. In addition, the olefinic CH proton correlated with C(1). These findings confirm that for compounds **3,** the tautomeric structure **3A** having a CH_2 group within the diazepine ring and therefore excluding the alternative structure **3A′** (*Fig. 2*).

Scheme 2. Syntheses of compounds **3** and **4**.



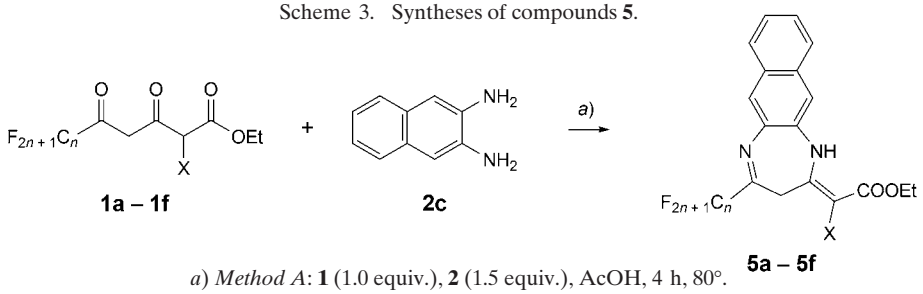
a) *Method A*: **1** (1.0 equiv.), **2** (1.5 equiv.), AcOH, 4 h, 80°. *b*) *Method B*: **1** (1.0 equiv.), **2** (1.3 equiv.), MeCN, Me_3SiCl, 4 h, 55°.

Table 1. Synthesis of **3** and **4**

1	**2**	**3**,**4**	C_nF_{2n+1}	R	X	*Method A*		*Method B*	
						3 [%][a])	**4** [%][a])	**3** [%][a])	**4** [%][a])
a	**a**	**a**	CF_3	H	H	44	29	53	25
a	**b**	**b**	CF_3	Cl	H	31	21	58	16
b	**a**	**c**	C_2F_5	H	H	58	16	[b])	38
b	**b**	**d**	C_2F_5	Cl	H	52	[c])		
c	**a**	**e**	C_3F_7	H	H	68	16	[b])	36
c	**b**	**f**	C_3F_7	Cl	H	64	[c])		
d	**a**	**g**	CF_3	H	Cl	[d])	37		
d	**b**	**h**	CF_3	Cl	Cl	[d])	54		

[a]) Yield of isolated product (for *Methods A* and *B*, see legend of *Scheme 2* and *Experimental Part*); [b]) Not isolated, ratio of **3**/**4** ≈ 1:1 (in the crude product); [c]) Not isolated, ratio of **3**/**4** ≈ 4:1 (in the crude product); [d]) Traces.

Scheme 3. Syntheses of compounds **5**.



a) *Method A*: **1** (1.0 equiv.), **2** (1.5 equiv.), AcOH, 4 h, 80°.

Table 2. Synthesis of **5a** – **5f**

1,**5**	C_nF_{2n+1}	X	**5** [%][a])
a	CF_3	H	45
b	C_2F_5	H	17
c	C_3F_7	H	34
d	CF_3	Cl	22
e	C_2F_5	Cl	43
f	C_3F_7	Cl	60

[a]) Yields of isolated products.

Compounds **4** and **5** exist both in $CDCl_3$ solution as mixtures of two species, which were proved by ^{1}H-, ^{13}C-, and ^{19}F-NMR spectra as enaminoimine form **I** and diaminodiene form **II** (*Scheme 4*). These tautomeric structures are similar to those of benzodiazepines containing polyfluoroalkyl and polyfluoroacyl groups reported by *Yachevskii et al.* [6]. Immediately after dissolving the compounds in $CDCl_3$, tautomers **I** were predominant (95 – 98%) over the tautomers **II**. Upon standing over a period of time between 2 h and up to 1 day, the tautomers **I** and **II** equilibrated to a ratio of 70 – 80% (**I**): 20 – 30% (**II**).

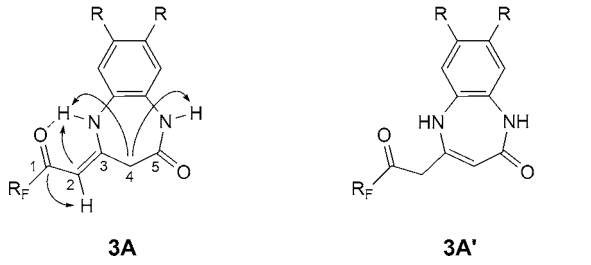
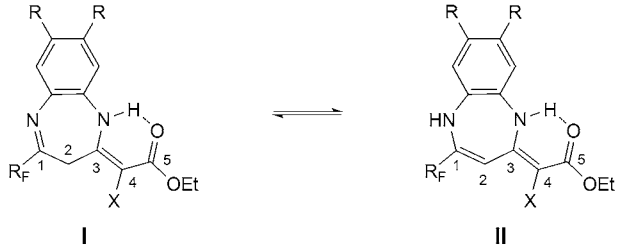


Fig. 2. Two possible tautomeric forms of **3** and characteristic HMBC (H → C) correlations of **3d** and **3e**.

Scheme 4. Tautomeric forms of **4** and **5** in $CDCl_3$ solution.

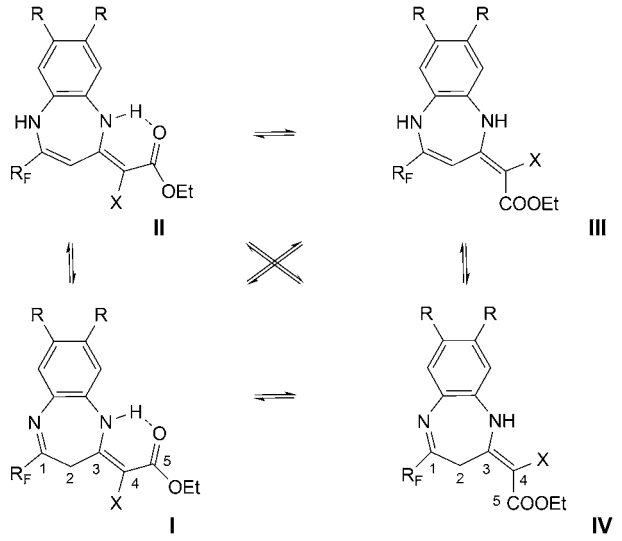


Typical signals for tautomers **I** in the ^{1}H-NMR spectra are those for the NH group (δ = 10.60 – 11.20), which is involved in an intramolecular hydrogen bond, the CH_2 at δ = 3.20 – 3.80 and the olefinic H(4) (for X = H; δ = 4.70 – 4.80). Typical signals for tautomers **II** (X = H) are those for both NH groups (δ(NH(1)) = 5.50 – 5.90, δ(NH(3)) = 10.10 – 10.70) and the signals for the olefinic H–C(2) (δ = 5.00 – 5.20) and H–C(4) (δ = 4.80 – 4.90); for the 4-Cl-substituted compounds (X = Cl), δ(H(2)) = 6.10 – 6.20, δ(NH(1)) = 5.60 – 6.00, and δ(NH(3)) = 10.60 – 11.15. The downfield shift of the NH(3) signal shows that this H-atom is involved in the intramolecular hydrogen bond of tautomer **II**. In some cases, the signal of H–C(2) is displayed as a triplet due to coupling over four bonds with both NH(1) and NH(3) ($^4J_{2,NH(1)} \approx {}^4J_{2,NH(3)} \approx 2.0$ Hz). These NMR data and the results from two-dimensional correlation spectra confirm the tautomeric structures given for **I** and **II**. For example, in the ^{1}H,^{13}C-HMBC spectrum recorded for **4a** and **4b**, cross peaks have been found for tautomer **I,** the NH with atoms C(2) and C(4), and for tautomer **II,** both NH with the olefinic C(2) and NH(3) also with the C(3) and C(4).

Since tautomeric equilibria can be influenced by polarity and basicity of the solvent [6][9], we have also recorded the spectra of some compounds **4** and **5** in (D_6) DMSO. Immediately after dissolving the compounds, only signals of tautomer **I** were observed in the ^{1}H-NMR spectra. Also, within 1 – 2 h, signals of tautomer **II** and two further species, **III** and **IV**, appeared, which were formed by (*E*/*Z*) isomerization about the exocyclic C=C bond (*Scheme 5*).

The state of equilibrium was achieved within 5 – 7 days. The equilibration proves to be a complex process, which includes two different reaction steps, tautomerization and rotation about the C=C bond. This process is catalyzed by the more polar and more basic solvent DMSO. In contrast to this, tautomerization resulted exceptionally in $CDCl_3$ solution. Furthermore, different to the $CDCl_3$ solution, in which tautomer **I** is predominant, in DMSO, the tautomer **II** was found to be the main component in the equilibrium mixtures, which might be explained by an additional stabilization of **II** due to

Scheme 5. Isomeric forms of **4** and **5** in (D_6)DMSO solution.



intermolecular interaction of the newly formed NH(1) group with the solvent molecules.

The dynamic behavior of compounds **4a** and **4g** in (D_6)DMSO solution was studied in detail, for which the ratio of isomers at the state of equilibrium was determined as 9% (**I**); 83% (**II**); 6% (**III**); and 2% (**IV**) for **4a**, and 11% (**I**); 54% (**II**); 18% (**III**); and 17% (**IV**) for **4g**. The ^{1}H-NMR spectra of **4g** (NH region) following the equilibration process are depicted in *Fig. 3*.

As for the tautomers **I** and **II** in $CDCl_3$ solution, the assignment of the resonances of the isomeric structures **I – IV** in DMSO solution was based on the signal intensities, chemical shifts, and ^{1}H,^{1}H- and ^{13}C,^{19}F- coupling constants, and the results of two–dimensional NMR measurements (^{1}H,^{1}H-COSY, ^{1}H,^{1}H-NOESY (EXSY), and ^{1}H,^{13}C-chemical shift correlation spectra (HSQC and HMBC)). For the purpose of comparison, significant ^{1}H- and ^{13}C-NMR data of isomers **I – IV** for **4a** and **4g** were collected in *Table 3*.

Typical signals for the newly formed tautomeric structure **III** in the ^{1}H-NMR spectra are those for the both NH groups and, as in **II**, the signals for the olefinic H–C(2) and H–C(4) (**4a**) or only H(2) (**4g**, X = Cl). Typical signals for **IV** are those for the NH group and, as in **I**, the signals for the CH_2 group and the olefinic H(4) (**4a**, X = H).

The NH groups of **III** and **IV** are not involved in intramolecular hydrogen bonds. In the mixture of the four species (**I – IV**), the differentiation between signals for the H-atoms, involved or not, have been made by recording the NMR spectra at higher temperature. The NH signals show characteristic high-field shifts (1 – 2 ppm) at increasing temperature (300 – 370 K), when they are not involved in an intramolecular hydrogen bond, while the others remain almost independently.

A characteristic for isomers **II** and **III**, the NH groups appear as doublets due to coupling about four bonds with H–C(2) (^4J = 1.5 – 2.0 Hz), which was confirmed by the corresponding COSY correlations. As expected, NH(1) of

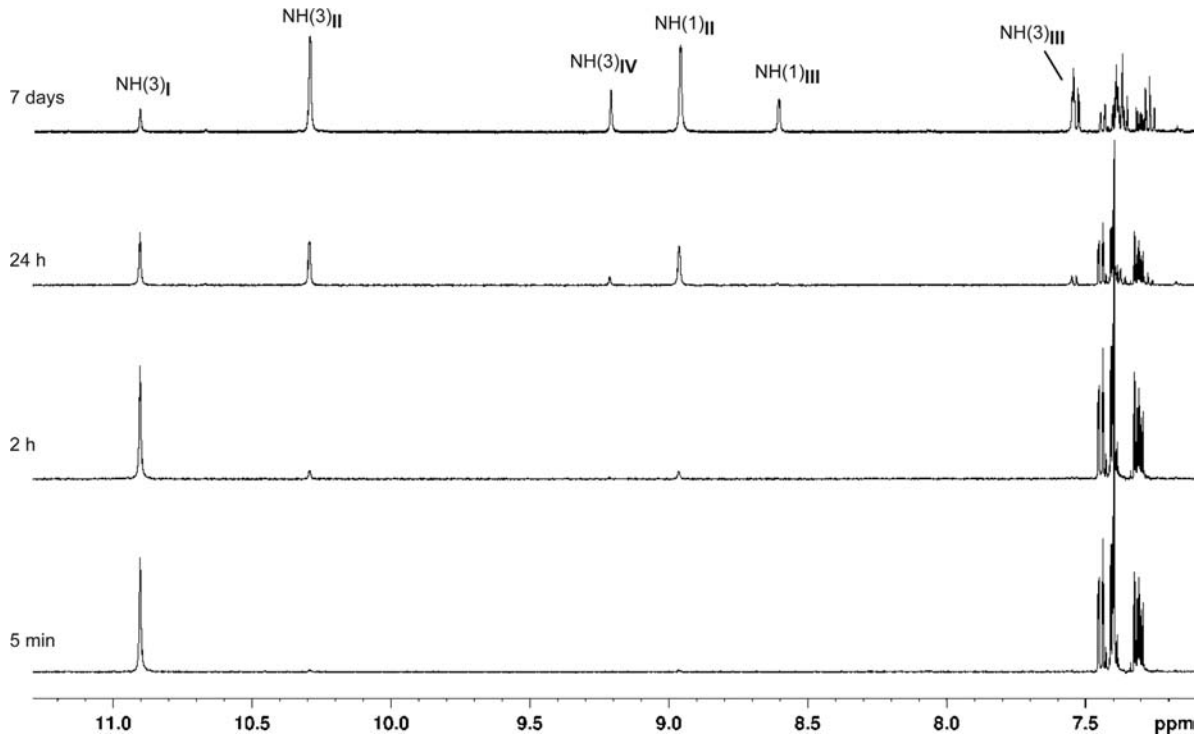


Fig. 3. ^{1}H-NMR spectra of **4g** (NH region) recorded at different times (500 MHz, (D_6)DMSO, 300 K).

Table 3. ^{1}H- and ^{13}C-NMR chemical shifts (δ, ppm) and coupling constants ($^{4}J_{H,H}$, $^{n}J_{C,F}$, in Hz, in Parentheses) for isomers **I** – **IV** of compounds **4a** and **4g** in (D_6)DMSO Solutions (for further NMR data, See *Experimental Part*)

	4a				**4g**			
	I	**II**	**III**	**IV**	**I**	**II**	**III**	**IV**
NH(1)	–	8.53 (*d*, *J* = 2.0)	8.50 (*d*, *J* = 2.0)	–	–	8.96 (*d*, *J* = 2.0)	8.61 (*d*, *J* = 2.0)	–
NH(3)	10.46	9.91 (*d*, *J* = 1.5)	8.21 (*d*, *J* = 2.0)	10.04	10.90	10.30 (*d*, *J* = 2.0)	7.55 (*d*, *J* = 2.0)	9.22
H(2)	3.51	5.20 (*t*', *J* = 2.0, 1.5)	7.01 (*t*', *J* = 2.0)	4.23	3.82	5.80 (*t*', *J* = 2.0)	7.08 (*t*', *J* = 2.0)	4.35
H(4)	4.84	5.00	5.21	5.16	–	–	–	–
C(1)	152.7 (*q*, *J* = 34.7)	135.1 (*q*, *J* = 31.2)	n.d.	n.d.	151.1 (*q*, *J* = 34.8)	138.4 (*q*, *J* = 31.1)	135.5 (*q*, *J* = 31.0)	153.0 (*q*, *J* = 34.5)
C(2)	33.6	96.9 (*q*, *J* = 5.0)	92.2 (*q*, *J* = 5.0)	27.6	30.9	92.7 (*q*, *J* = 5.2)	94.1 (*q*, *J* = 6.0)	28.5
C(3)	156.2	153.3	152.9	152.6	152.8	151.6	147.9	150.2
C(4)	85.6	93.0	95.1	87.8	91.9	97.2	99.8	93.6
C(5)	169.6	169.8	167.0	167.7	166.6	166.6	163.3	163.9

II showed in (D_6)DMSO solution a characteristic solvent shift to lower field (δ(NH(1)) = 8.50 – 9.40), compared with $CDCl_3$ solution (δ(NH(1)) = 5.50 – 6.00). Furthermore, it is worth mentioning the remarkable low-field shift of the H–C(2) signal of **III** compared with **II** and also the CH_2 resonance of **IV** compared with **I**, which can be attributed to the magnetic anisotropy effect of the ester C=O group, which is located in *syn*-position to the corresponding H-atom. In addition, also the ^{1}H,^{13}C-HMBC correlations correspond to the structures of isomers **I** – **IV**, which are given for **4g** in *Fig. 4*.

In conclusion, 1*H*-benzo-1,5-diazepine derivatives containing a perfluorinated side chain can be synthesized by cyclocondensation of perfluorinated 3,5-dioxoesters with 1,2-diaminobenzenes or 2,3-diaminonaphthalenes. With this reaction, mixtures of 1,5-diazepines formed by cyclocondensation *via* the two keto groups and 1,5-diazepin-2-ones resulted from cyclocondensation *via* the central keto and the ester group are accessible.

The diazepines showed different tautomeric behavior in solution, depending on the solvent. They exist as mixtures of only two tautomers in $CDCl_3$ solution. In DMSO solution, besides **I** and **II**, two additional species, **III** and **IV**, are formed by (*E*/*Z*) isomerization on the exocyclic C=C bonds.

Experimental Part

General

M.p.: *Boetius micro-heating plate BHMK 05* (*Rapido*, Dresden, Germany); uncorrected. ^{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.): *Bruker* spectrometers (Rheinstetten, Germany) *AVANCE 250*, *AVANCE 300*, and *AVANCE 500* in $CDCl_3$ and in (D_6) DMSO soln. at 300 K. The chemical shifts are referenced to solvent signals ($CDCl_3$: δ(H) = 7.26, δ(C) = 77.0; (D_6) DMSO: δ(H) = 2.50, δ(C) = 39.7). The assignment of

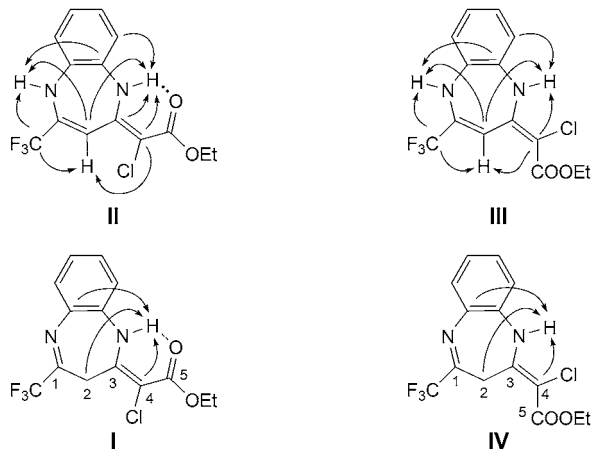
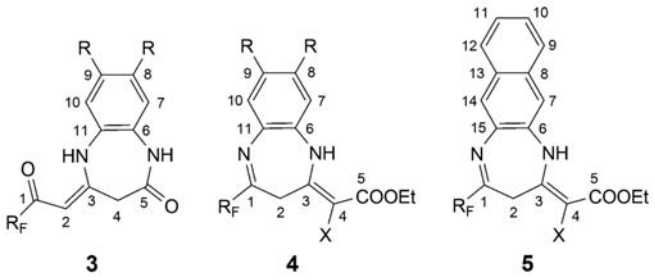


Fig. 4. Characteristic HMBC (H → C) correlations of **4g** in (D_6) DMSO solution.

NMR signals was supported by DEPT and two-dimensional ^{1}H,^{1}H-COSY, ^{1}H,^{1}H-NOESY (EXSY), and ^{1}H,^{13}C-correlation spectra (HSQC, HMBC) using standard pulse sequences (standard *Bruker* software). ^{19}F-NMR Spectra (282.4 MHz): *Bruker* spectrometer *AVANCE 300* and are referenced to $CFCl_3$. MS: *Finnigan MAT 95-XP* (*Thermo Electron*, Langenselbold, Germany); in *m*/*z*. Elemental analysis: *CHNS-Flash-EA-1112* instrument (*Thermoquest*, Austin, TX, USA).



*Synthesis of 1*H*-Benzo-1,5-diazepine Derivatives*

Method A. The 1,2-diaminobenzene **2** (1.5 equiv.) was dissolved in glacial AcOH (3 ml per 1.0 mmol of **1**) and 3,5-dioxoester **1** (1.0 equiv.) was added dropwise. The soln. was stirred at 80° for 4 h, then it was poured into H_2O (50 ml) and Na_2CO_3 was added until pH 7 was reached. The mixture was extracted with AcOEt (3 × 30 ml) and the combined org. layers were dried ($MgSO_4$). The mixture was filtered, the filtrate was concentrated *in vacuo*, and the residue was purified by CC (silica gel, cyclohexane/AcOEt or heptane/AcOEt).

*Synthesis of 1*H*-Benzo-1,5-diazepine Derivatives*

Method B. In a pressure tube, to a soln. of 1,2-diaminobenzene **2** (1.3 equiv.) in dry MeCN (9 ml per 1.0 mmol of **1**) was added 3,5-dioxoester **1** (1.0 equiv.) at 55°. The mixture was stirred for 10 min and subsequently trimethylchlorosilane (3.0 equiv) was added dropwise. The mixture was stirred at 55° for 4 h. Subsequently, the soln. was concentrated *in vacuo* and the residue was purified by CC (silica gel, cyclohexane/AcOEt or heptane/AcOEt).

(4*Z*)-1,3,4,5-Tetrahydro-4-(3,3,3-trifluoro-2-oxopropylidene)-2*H*-1,5-benzodiazepin-2-one (**3a**) and **Ethyl (2*Z*)-1,3-Dihydro-[4-(trifluoromethyl)-2*H*-1,5-benzodiazepin-2-ylidene]acetate** (**4a**). *Method A*: Starting with **1a** (0.248 g, 1.10 mmol), **2a** (0.165 g, 1.53 mmol), and AcOH (3 ml), **3a** was isolated as a white to yellow solid (0.13 g, 44%), m.p. = 243 – 245°, R_f = 0.27 (cyclohexane/AcOEt, 2:1) and **4a** as an orange solid (0.095 g, 29%), m.p. = 120 – 121°, R_f = 0.78 (cyclohexane/AcOEt, 2:1). *Method B:* Starting with **1a** (0.235 g, 1.04 mmol), **2a** (0.141 g, 1.3 mmol), MeCN (9 ml), and trimethylchlorosilane (0.326 g, 3.0 mmol), **3a** was isolated as a white to yellow solid (0.15 g, 53%) and **4a** as an orange solid (0.076 g, 25%).

3a: ^{1}H-NMR (500.13 MHz, $CDCl_3$): 3.31 (*s*, 2 H, H(4)); 5.67 (*q*, $^4J_{H,F}$ = 0.5, 1 H, H(2)); 7.10 (*dd*, $^3J_{7,8}$ = 7.8, $^4J_{7,9}$ = 1.5, 1 H, H(7)); 7.25 – 7.35 (*m*, 3 H, H(8,9,10)); 7.93 (*s*, 1 H, NHCO); 12.57 (*s*, 1 H, NH(3)). ^{19}F-NMR (282.4 MHz, $CDCl_3$): −76.9 (CF_3). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 41.5 (C(4)); 90.2 (*q*, $^3J_{C,F}$ = 1.5, C(2)); 117.0 (*q*, $^1J_{C,F}$ = 288, CF_3); 122.5 (C(7)); 123.7 (C(10)); 126.4 (C(9)); 127.5 (C(8)); 129.6, 129.9 (C(6, 11)); 160.2 (C(3)); 166.9 (CONH); 178.8 (*q*, $^2J_{C,F}$ = 34.4, C(1)). IR (ATR, cm^{-1}): 3340*w*, 3196*w*, 3118*w*, 3079*w*, 2979*w*, 2919*w*, 2853*w*, 1679*m*, 1598*m*, 1573*m*, 1524*m*, 1497*m*, 1424*m*, 1382*m*, 1328*m*, 1278*m*, 1245*m*, 1184*m*, 1146*m*, 1133*s*, 1110*s*, 1044*m*. MS (EI, 70 eV): 270 [M^+, (100)], 228 (12), 201 (88), 159 (73), 135 (11), 131 (15). HR-MS (EI, 70 eV): calc. for $C_{12}H_9F_3N_2O_2$ (M^+): 270.06100, found: 270.06106. Anal. calc. for $C_{12}H_9F_3N_2O_2$ (270.207): C 53.34, H 3.36, N 10.37, found: C 53.69, H 3.43, N 9.91.

4a: ^{1}H-NMR (300.13 MHz, $CDCl_3$) tautomer **I**: 1.29 (*t*, $^3J_{CH2,CH3}$ = 7.2, Me); 3.22 ('*t*', $^4J_{2,NH}$ = $^4J_{2,4}$ = 0.7, 2 H, H(2)); 4.16 (*q*, $^3J_{CH2,CH3}$ = 7.2, OCH_2); 4.69 (*t*, $^4J_{2,4}$ = 0.7, 1 H, H(4)); 7.08 (*dd*, ^3J = 7.9, ^4J = 1.4, 1 H, H(7)); 7.18 (*m*, ^4J = 1.4, 1 H, H(9)); 7.28 (*m*, ^4J = 1.7, 1 H, H(8)); 7.41 (*dd*, ^4J = 7.9, ^4J = 1.7, 1 H, H(10)); 10.61 (*s*, 1 H, NH); tautomer **II**: 1.29 (*t*, $^3J_{CH2,CH3}$ = 7.2, Me); 4.17 (*q*, $^3J_{CH2,CH3}$ = 7.2, OCH_2); 4.81 (br. *s*, 1 H, H(4)); 5.04 ('*t*', $^4J_{2,NH(1)}$ = $^4J_{2,NH(3)}$ = 2.0, 1 H, H(2)); 5.52 (br. *s*, 1 H, NH (1)); 6.56 (*dd*, ^3J = 7.7, ^4J = 1.5, 1 H, H(10)); 6.75 (*m*, ^4J = 1.7, 1 H, H(7)); 6.81 (*dd*, ^3J = 7.7, ^4J = 1.7, 1 H, H (9)); 6.87 (*m*, ^4J = 1.5, 1 H, H(8)); 10.07 (*s*, 1 H, NH(3)). ^{19}F-NMR (282.4 MHz, $CDCl_3$) tautomer **I**: −73.6 (CF_3); tautomer **II**: −71.0 (CF_3). ^{13}C-NMR (75.5 MHz, $CDCl_3$) tautomer **I**: 14.4 (CH_3); 34.1 (C(2)); 59.5 (OCH_2); 85.9 (C(4)); 119.4 (*q*, $^1J_{C,F}$ = 277, CF_3); 122.3 (C(7)); 124.2 (C(9)); 129.0 (C(8)); 130.0 (C(10)); 132.3 (C(6)); 136.6 (C(11)); 152.2 (*q*, $^2J_{C,F}$ = 35.5, C(1)); 155.5 (C(3)); 170.5 (C(5)); tautomer **II**: 14.4 (CH_3); 59.5 (OCH_2); 93.8 (C(4)); 99.0 (*q*, $^3J_{C,F}$ = 5.0, C(2)); 120.2 (C(10)); 121.6 (C(7)); 122.9 (C(9)); 124.5 (C(8)); 130.8, 131.3 (C(6, 11)); 131.0 (*q*, $^2J_{C,F}$ = 30.7, C(1)); 152.2 (C(3)); 170.2 (C(5)); CF_3 not determined.

^{1}H-NMR (500.13 MHz, ((D$_6$)DMSO) isomer **I**: 1.21 (*t*, $^3J_{CH2,CH3}$ = 7.1, Me); 3.51 (*s*, 2 H, H(2)); 4.09 (*q*, $^3J_{CH2,CH3}$ = 7.1, OCH_2); 4.84 (*s*, 1 H, H(4)); 7.25 (*ddd*, ^3J = 8.0, ^3J = 6.6, ^4J = 2.0, 1 H, H(9)); 7.32 – 7.37 (*m*, 2 H, H(7, 8)); 7.39 (*m*, 1 H, H(10)); 10.46 (*s*, 1 H, NH); isomer **II**: 1.21 (*t*, $^3J_{CH2,CH3}$ = 7.1, Me); 4.11 (*q*, $^3J_{CH2,CH3}$ = 7.1, OCH_2); 5.00 (*s*, 1 H, H(4)); 5.20 ('*t*', $^4J_{2,NH(1)}$ = 2.0, $^4J_{2,NH(3)}$ = 1.5, 1 H, H(2)); 6.65 (*dd*, $^3J_{7,8}$ = 7.6, $^4J_{7,9}$ = 1.7, 1 H, H(7)); 6.80 – 6.87 (*m*, 2 H, H(8,9)); 7.02 (*dd*, $^3J_{9,10}$ = 7.7, $^4J_{8,10}$ = 1.8, 1 H, H(10)); 8.53 (*d*, $^4J_{2,NH(1)}$ = 2.0, 1 H, NH (1)); 9.91 (*d*, $^4J_{2,NH(3)}$ = 1.5, 1 H, NH(3)); isomer **III**: 1.17 (*t*, $^3J_{CH2,CH3}$ = 7.1, Me); 4.01 (*q*, $^3J_{CH2,CH3}$ = 7.1, OCH_2);

5.21 (*s*, 1 H, H(4)); 7.01 ('*t*', $^4J_{2,NH(1)} = {}^4J_{2,NH(3)}$ = 2.0, 1 H, H(2)); 6.77 – 6.83 (*m*, 3 H), 6.99 (*m*, 1 H), (CH_{Ar}); 8.21 (*d*, $^4J_{2,NH(3)}$ = 2.0, 1 H, NH(3)); 8.50 (*d*, $^4J_{2,NH(1)}$ = 2.0, 1 H, NH(1)); isomer **IV**: 1.17 (*t*, $^3J_{CH2,CH3}$ = 7.1, Me); 4.03 (*q*, $^3J_{CH2,CH3}$ = 7.1, OCH_2); 4.23 (*s*, 2 H, H(2)); 5.16 (*s*, 1 H, H(4)); 7.15 – 7.20 (*m*, 2 H), 7.25 (*m*, 1 H), 7.33 (*m*, 1 H), (CH_{Ar}); 10.04 (*s*, 1 H, NH). ^{19}F-NMR (282.4 MHz, (D_6)DMSO) isomer **I**: −72.3 (CF_3); isomer **II**: −68.6 (CF_3); isomer **III**: −75.5 (CF_3); isomer **IV**: −72.2 (CF_3). ^{13}C-NMR (125.8 MHz, (D_6)DMSO) isomer **I**: 14.5 (CH_3); 33.6 (C(2)); 59.1 (OCH_2); 85.6 (C(4)); 121.7 (*q*, $^1J_{C,F}$ = 278, CF_3); 122.9 (C(7)); 124.4 (C(9)); 129.3 (C(8)); 129.5 (C(10)); 132.3 (C(6)); 136.2 (C(11)); 152.7 (*q*, $^2J_{C,F}$ = 34.7, C(1)); 156.2 (C(3)); 169.6 (C(5)); isomer **II**: 14.4 (CH_3); 59.2 (OCH_2); 93.0 (C(4)); 96.9 (*q*, $^3J_{C,F}$ = 5.0, C(2)); 120.9 (*q*, $^1J_{C,F}$ = 276, CF_3); 121.0 (C(7)); 121.4 (C(10)); 123.2 (C(9)); 124.4 (C(8)); 130.7 (C(6)); 132.5 (C(11)); 135.1 (*q*, $^2J_{C,F}$ = 31.2, C(1)); 153.3 (C(3)); 169.8 (C(5)); isomer **III**: 14.5 (CH_3); 58.6 (OCH_2); 92.2 (*q*, $^3J_{C,F}$ = 5.0, C(2)); 95.1 (C(4)); 120.9, 121.1, 122.4, 124.0 (CH_{Ar}); 152.9 (C(3)); 167.0 (C(5)); (C(1), CF_3, C_{Ar} not determined); isomer **IV**: 14.6 (CH_3); 27.6 (C(2)); 58.4 (OCH_2); 87.8 (C(4)); 122.0, 123.5, 129.1, 129.4 (CH_{Ar}); 152.6 (C(3)); 167.7 (C(5)); (C(1), CF_3, C_{Ar} not determined). IR (ATR, cm^{-1}): 3256*w*, 3209*w*, 3115*w*, 3075*w*, 2987*w*, 2945*w*, 2903*w*, 2871*w*, 1659*m*, 1614s, 1566*m*, 1495*w*, 1481*m*, 1440*m*, 1390*w*, 1361*m*, 1303*m*, 1275*s*, 1251*s*, 1238*m*, 1221*m*, 1184*s*, 1161*s*, 1108*s*, 1064*m*, 1044*s*, 1001*m*. MS (EI, 70 eV): 299 [$(M+H)^+$, (15)], 298 [M^+, (100)], 253 (33), 252 (98), 224 (49), 205 (10), 155 (57). HR-MS (ESI-TOF/MS): calc. for $C_{14}H_{14}F_3N_2O_2$ [$(M+H)^+$]: 299.1002, found: 299.1004. Anal. calc. for $C_{14}H_{13}F_3N_2O_2$ (298.260): C 56.38, H 4.39, N 9.39, found: C 56.50, H 4.31, N 9.14.

(4*Z*)-7,8-Dichloro-1,3,4,5-tetrahydro-4-(3,3,3-trifluoro-2-oxopropylidene)-2*H*-1,5-benzodiazepin-2-one (**3b**) and **Ethyl (2*Z*)-[7,8-Dichloro-1,3-dihydro-4-(trifluoromethyl)-2*H*-1,5-benzodiazepin-2-ylidene]acetate** (**4b**). *Method A*: Starting with **1a** (0.234 g, 1.04 mmol), **2b** (0.266 g, 1.5 mmol), and AcOH (3 ml), **3b** was isolated as an orange solid (0.117 g, 31%), m.p. = 245 – 247°, R_f = 0.47 (cyclohexane/AcOEt, 2:1) and **4b** as an orange solid (0.081 g, 21%), m.p. = 128 – 130°, R_f = 0.83 (cyclohexane/AcOEt, 2:1). *Method B*: Starting with **1a** (0.258 g, 1.14 mmol), **2b** (0.26 g, 1.47 mmol), MeCN (9 ml), and trimethylchlorosilane (0.338 g, 3.1 mmol), **3b** was isolated as an orange solid (0.224 g, 58%) and **4b** as an orange solid (0.067 g, 16%). **3b**: ^{1}H-NMR (500.13 MHz, $CDCl_3$): 3.32 (*s*, 2 H, H(4)); 5.71 (*q*, $^4J_{H,F}$ = 0.5, 1 H, H(2)); 7.25 (*s*, 1 H, H(7)); 7.38 (*s*, 1 H, H(10)); 8.43 (*s*, 1 H, NHCO); 12.43 (*s*, 1 H, NH(3)). ^{19}F-NMR (282.4 MHz, $CDCl_3$): −77.0 (CF_3). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 41.4 (C(4)); 91.0 (*q*, $^3J_{C,F}$ = 1.8, C(2)); 116.8 (*q*, $^1J_{C,F}$ = 289, CF_3); 123.8 (C(7)); 124.8 (C(10)); 128.2, 128.9 (C(6,11)); 130.2, 131.1 (C(8, 9)); 159.4 (C(3)); 166.8 (CONH); 179.5 (*q*, $^2J_{C,F}$ = 34.7, C(1)). IR (ATR, cm^{-1}): 3194*w*, 3110*w*, 3046*w*, 2955*w*, 2127*w*, 1683*m*, 1623*w*, 1591*m*, 1567*m*, 1519*m*, 1499*m*, 1473*m*, 1430*m*, 1378*m*, 1312*m*, 1294*m*, 1274*m*, 1242*m*, 1225*m*, 1192*m*, 1139*s*, 1107*s*, 1001*m*. MS (EI, 70 eV): 342 [M^+, $^{37}Cl_2$ (11)], 340 [M^+ $^{35}Cl^{37}Cl$ (64)], 338 [M^+, $^{35}Cl_2$ (100)], 298 [$^{37}Cl^{35}Cl$ (15)], 296 [$^{35}Cl_2$ (24)], 273 [$^{35}Cl_2$ (10)], 271 [$^{37}Cl^{35}Cl$ (60)], 269 [$^{35}Cl_2$ (90)], 227 [$^{37}Cl_2$ (10)], 229 [$^{37}Cl^{35}Cl$ (60)], 227 [$^{35}Cl_2$ (94)], 199 (15). HR-MS (EI, 70 eV): calc. for $C_{12}H_7{}^{35}Cl_2F_3N_2O_2$ (M^+): 337.98312, found: 337.992146; calc. for $C_{12}H_7{}^{35}Cl^{37}ClF_3N_2O_2$ (M^+): 339.98017, found: 339.979662; calc. for $C_{12}H_7{}^{37}Cl_2F_3N_2O_2$ (M^+): 341.97722, found: 341.977666. Anal. calc. for $C_{12}H_7Cl_2F_3N_2O_2$ (339.097): C 42.50, H 2.08, N 8.26, found: C 42.64, H 2.24, N 8.07.

4b: ^{1}H-NMR (500.13 MHz, $CDCl_3$) tautomer **I**: 1.30 (*t*, $^3J_{CH2,CH3}$ = 7.2, Me); 3.22 (*s*, 2 H, H(2)); 4.18 (*q*, $^3J_{CH2,CH3}$ = 7.2, OCH_2); 4.74 (*s*, 1 H, H(4)); 7.20 (*s*, 1 H, H(7)); 7.51 (*s*, 1 H, H(10)); 10.65 (*s*, 1 H, NH); tautomer **II**: 1.29 (*t*, $^3J_{CH2,CH3}$ = 7.2, Me); 4.17 (*q*, $^3J_{CH2,CH3}$ = 7.2, OCH_2); 4.89 (*s*, 1 H, H(4)); 5.10 ('*t*', $^4J_{2,NH(1)} = {}^4J_{2,NH(3)}$ = 1.8, 1 H, H(2)); 5.54 (*s*, 1 H, NH(1)); 6.85 (*s*, 1 H, H(7)); 6.71 (*s*, 1 H, H(10)); 10.18 (*s*, 1 H, NH(3)). ^{19}F-NMR (282.4 MHz, $CDCl_3$) tautomer **I**: −73.8 (CF_3); tautomer **II**: −70.8 (CF_3). ^{13}C-NMR (125.8 MHz, $CDCl_3$) tautomer **I**: 14.3 (CH_3); 34.2 (C(2)); 59.9 (OCH_2); 87.7 (C(4)); 119.2 (*q*, $^1J_{C,F}$ = 278, CF_3); 123.7 (C(7)); 127.7, 132.7 (C(8,9)); 131.1 (C(10)); 131.8 (C(6)); 135.7 (C(11)); 153.8 (*q*, $^2J_{C,F}$ = 35.9, C(1)); 154.2 (C(3)); 170.4 (C(5)); tautomer **II**: 14.3 (CH_3); 59.9 (OCH_2); 95.7 (C(4)); 99.5 (*q*, $^3J_{C,F}$ = 4.5, C(2)); 120.7 (*q*, $^1J_{C,F}$ = 276, CF_3); 121.1 (C(10)); 122.4 (C(7)); 125.4, 127.2 (C(8,9)); 130.3 (C(11)); 130.5 (C(6)); 133.5 (*q*, $^2J_{C,F}$ = 32.0, C(1)); 150.6 (C(3)); 170.1 (C(5)). HR-MS (ESI-TOF/MS, negative): calc. for $C_{14}H_{11}Cl_2F_3N_2O_2$ [$(M-H)^-$]: 365.0077, found: 365.0082.

(4*Z*)-1,3,4,5-Tetrahydro-4-(3,3,4,4,4-pentafluoro-2-oxobutylidene)-2*H*-1,5-benzodiazepin-2-one (**3c**) and **Ethyl (2*Z*)-1,3-Dihydro-[4-(pentafluoroethyl)-2*H*-1,5-benzodiazepin-2-ylidene]acetate** (**4c**). *Method A*: Starting with **1b** (0.275 g, 0.996 mmol) and **2a** (0.162 g, 1.5 mmol) in AcOH (3 ml), **3c** was isolated as a colorless solid (0.186 g, 58%), m.p. = 212 – 214° and **4c** as an orange solid (0.056 g, 16%), m.p. = 97 – 99°). *Method B*: Starting with **1b** (0.276 g, 1.0 mmol), **2a** (0.141 g, 1.3 mmol), MeCN (9 ml), and trimethylchlorosilane (0.326 g, 3.0 mmol), **4c** was isolated as an orange solid (0.132 g, 38%) (**3c** was not isolated, ratio of **3c**/**4c** in the crude product approx. 1:1).

3c: ^{1}H-NMR (500.13 MHz, $CDCl_3$): 3.31 (*s*, 2 H, H(4)); 5.74 (*t*, $^4J_{H,F}$ = 1.4, 1 H, H(2)); 7.14 (*dd*, $^3J_{7,8}$ = 7.8, $^4J_{7,9}$ = 1.5, 1 H, H(7)); 7.25 – 7.29 (*m*, 2 H, H(9,10)); 7.32 (*ddd*, $^3J_{7,8}$ = 7.8, $^3J_{8,9}$ = 6.6, $^4J_{8,10}$ = 2.3, 1 H, H(8)); 8.56 (*s*, 1H, NHCO); 12.70 (s, 1 H, NH(3)). ^{19}F-NMR (282.4 MHz, $CDCl_3$): −123.2 (CF_2); −82.4 (CF_3). ^{13}C–NMR (125.8 MHz, $CDCl_3$): 41.6 (C(4)); 91.3 (C(2)); 107.7 (*tq*, $^1J_{C,F}$ = 264, $^2J_{C,F}$ = 37.6, CF_2); 118.4 (*qt*, $^1J_{C,F}$ = 287, $^2J_{C,F}$ = 35.5, CF_3); 122.6 (C(7)); 123.7 (C(10)); 126.4 (C(9)); 127.6 (C(8)); 129.4, 130.1 (C(6,11)); 160.0 (C(3)); 167.4 (CONH); 180.0 (*t*, $^2J_{C,F}$ = 24.9, C(1)). IR (ATR, cm^{-1}): 3199*w*, 3129*w*, 3079*w*, 2981*w*, 2915*w*, 1681*m*,

1621*m*, 1598*m*, 1574s, 1519*m*, 1497*m*, 1429*w*, 1381*m*, 1326*m*, 1274*w*, 1241*w*, 1216*m*, 1183*s*, 1161*m*, 1142*m*, 1116*m*, 1046*w*, 1018*s*. MS (EI, 70 eV): 320 [M^+, (85)], 201 (100), 159 (58), 135 (12), 131 (13), 67 (16). HR-MS (EI, 70 eV): calc. for $C_{13}H_9F_5N_2O_2$ (M^+): 320.05787, found: 320.057928. Anal. calc. for $C_{13}H_9F_5N_2O_2$ (320.215): C 48.76, H 2.83, found: C 49.05, H 3.11.

4c: ^{1}H-NMR (300.13 MHz, $CDCl_3$) tautomer **I**: 1.30 (*t*, $^3J_{CH2,CH3}$ = 7.2, Me); 3.25 (*s*, 2 H, H(2)); 4.17 (*q*, $^3J_{CH2,CH3}$ = 7.2, OCH_2); 4.68 (*t*, $^4J_{2,4}$ = 0.6, 1 H, H(4)); 7.08 (*dd*, ^3J = 7.9, ^4J = 1.4, 1 H, H(7)); 7.18 (*m*, ^4J = 1.4, 1 H, H(9)); 7.28 (*m*, ^4J = 1.6, 1 H, H(8)); 7.40 (*dd*, ^4J = 7.9, ^4J = 1.6, 1 H, H(10)); 10.65 (*s*, 1 H, NH); tautomer **II**: 1.29 (*t*, $^3J_{CH2,CH3}$ = 7.2, Me); 4.18 (*q*, $^3J_{CH2,CH3}$ = 7.2, OCH_2); 4.82 (br. *s*, 1 H, H(4)); 5.00 (br. '*t*', $^4J_{2,NH}$ = 2.0, $^4J_{2,NH}$ = 1.5, 1 H, H(2)); 5.50 (br. *s*, 1 H, NH(1)); 6.55 (*dd*, ^3J = 7.7, ^4J = 1.5, 1 H, H_{Ar}); 6.76 (*dd*, ^3J = 7.7, ^4J = 1.7, 1 H, H_{Ar}); 6.81 (*m*, ^4J = 1.7, 1 H, H_{Ar}); 6.89 (*m*, ^4J = 1.5, 1 H, H_{Ar}); 10.09 (*s*, 1 H, NH(3)). ^{19}F-NMR (282.4 MHz, $CDCl_3$) tautomer **I**: −118.2 (*q*, $^3J_{F,F}$ = 2.0, CF_2); −81.4 (*t*, $^3J_{F,F}$ = 2.0, CF_3); tautomer **II**: −121.6 (*q*, $^3J_{F,F}$ = 2.0, CF_2); −84.0 (*t*, $^3J_{F,F}$ = 2.0, CF_3). ^{13}C-NMR (75.5 MHz, $CDCl_3$) tautomer **I**: 14.3 (CH_3); 34.2 (C(2)); 59.5 (OCH_2); 86.1 (C(4)); 110.0 (*tq*, $^1J_{C,F}$ = 256, $^2J_{C,F}$ = 37.4, CF_2); 118.5 (*qt*, $^1J_{C,F}$ = 287, $^2J_{C,F}$ = 35.8, CF_3); 122.3 (C(7)); 124.1 (C(9)); 129.1 (C(8)); 130.2 (C(10)); 132.2 (C(6)); 136.8 (C(11)); 152.8 (*t*, $^2J_{C,F}$ = 27.7, C(1)); 155.6 (C(3)); 170.6 (C(5)); tautomer **II**: 14.3 (CH_3); 59.5 (OCH_2); 94.0 (C(4)); 101.5 (*t*, $^3J_{C,F}$ = 5.0, C(2)); 120.3 (C(10)); 121.6 (C(7)); 123.1 (C(9)); 124.7 (C(8)); 131.2, 131.7 (C(6,11)); 133.6 (*t*, $^2J_{C,F}$ = 22.0, C(1)); 152.3 (C(3)); 170.2 (C(5)); CF_2CF_3 not determined. IR (ATR, cm^{-1}): 3443*w*, 3248*w*, 3196*w*, 3057*w*, 3023*w*, 2987*w*, 2943*w*, 2907*w*, 2874*w*, 1658*m*, 1616*s*, 1565*m*, 1494*w*, 1482*m*, 1447*w*, 1428*w*, 1376*w*, 1367*w*, 1325*w*, 1284*s*, 1274*s*, 1250*s*, 1229*m*, 1205*s*, 1176*s*, 1158*s*, 1142*s*, 1124*m*, 1117*m*, 1101*s*, 1087*s*, 1039*s*. MS (EI, 70 eV): 348 [M^+, (99)], 303 (34), 302 (89), 276 (17), 205 (20), 156 (21), 155 (100). HR-MS (ESI-TOF/MS): calc. for $C_{15}H_{14}F_5N_2O_2$ [(M+H)$^+$]: 349.097, found: 349.0975. Anal. calc. for $C_{15}H_{13}F_5N_2O_2$ (348.268): C 51.73, H 3.76, found: C 52.01, H 4.01.

(4*Z*)-7,8-Dichloro-1,3,4,5-tetrahydro-4-(3,3,4,4,4-pentafluoro-2-oxobutylidene)-2*H*-1,5-benzodiazepin-2-one (**3d**). *Method A*: Starting with **1b** (0.282 g, 1.021 mmol) and **2b** (0.266 g, 1.50 mmol) in AcOH (3 ml), **3d** was isolated as a colorless solid (0.206 g, 52%), m.p. = 243 – 245° (**4d** was not isolated, ratio of **3d**/**4d** in the crude product approx. 4:1). ^{1}H-NMR (500.13 MHz, $CDCl_3$): 3.32 (*s*, 2 H, H(4)); 5.77 (*t*, $^4J_{H,F}$ = 1.4, 1 H, H(2)); 7.24 (*s*, 1 H, H(7)); 7.39 (*s*, 1 H, H(10)); 8.21 (*s*, 1 H, NHCO); 12.58 (*s*, 1 H, NH(3)). ^{19}F-NMR (282.4 MHz, $CDCl_3$): −123.3 (*q*, $^3J_{F,F}$ = 1.5, CF_2); −82.3 (*t*, $^3J_{F,F}$ = 1.5, CF_3). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 41.5 (C(4)); 92.1 (C(2)); 123.8 (C(7)); 124.9 (C(10)); 128.9, 129.2 (C(6,11)); 130.2, 131.2 (C(8, 9)); 159.2 (C(3)); 166.6 (CONH); 180.9 (*t*, $^2J_{C,F}$ = 25.0, C(1)); C_2F_5 not determined. IR (ATR, cm^{-1}): 3245*w*, 3201*w*, 3158*w*, 3116*w*, 3045*w*, 295*w*, 1688*m*, 1683*m*, 1625*m*, 1589*m*, 1567*m*, 1556*m*, 1516*m*, 1498*m*, 1473*m*, 1430*m*, 1374*m*, 1353*m*, 1316*m*, 1293*m*, 1263*m*, 1191*s*, 1167*s*, 1139*s*, 1116*s*, 1019*s*. MS (EI, 70 eV): 392 [M^+, $^{37}Cl_2$ (7)], 390 [M^+, $^{35}Cl^{37}Cl$ (44)], 338 [M^+, $^{35}Cl_2$ (68)], 273 [$^{37}Cl_2$ (15)], 271 [$^{35}Cl^{37}Cl$ (66)], 269 [$^{35}Cl_2$ (100)], 231 [$^{37}Cl_2$ (7)], 229 [$^{37}Cl^{35}Cl$ (40)], 227 [$^{35}Cl_2$ (68)], 199 (13), 114 (13), 67 (24). HR-MS (ESI-TOF/MS): calc. for $C_{13}H_8{}^{35}Cl_2F_5N_2O_2$ [(M+H)$^+$]: 388.9878, found: 388.9883; calc. for $C_{13}H_8{}^{35}Cl^{37}ClF_5N_2O_2$ [(M + H)$^+$]: 390.985, found: 390.9855.

(4*Z*)-4-(3,3,4,4,5,5,5-Heptafluoro-2-oxopentylidene)-1,3,4,5-tetrahydro-2*H*-1,5-benzodiazepin-2-one (**3e**) and **Ethyl (2*Z*)-[4-(Heptafluoropropyl)-1,3-dihydro-2*H*-1,5-benzodiazepin-2-ylidene]acetate** (**4e**). *Method A*: Starting with **1c** (0.326 g, 0.999 mmol) and **2a** (0.162 g, 1.50 mmol) in AcOH (3 ml), **3e** was isolated as a colorless solid (0.253 g, 68%), m.p. = 182 – 183° and **4e** as an orange solid (0.064 g, 16%). *Method B*: Starting with **1c** (0.309 g, 0.95 mmol), **2a** (0.141 g, 1.30 mmol), MeCN (9 ml), and trimethylchlorosilane (0.326 g, 3.0 mmol), **4e** was isolated as an orange solid (0.137 g, 36%) (**3e** was not isolated, ratio of **3e**/**4e** in the crude product approx. 1:1).

3e: ^{1}H-NMR (300.13 MHz, $CDCl_3$): 3.31 (*s*, 2 H, H(4)); 5.72 (*t*, $^4J_{H,F}$ = 1.6, 1 H, H(2)); 7.17 (*m*, 1 H, H(7)); 7.25 – 7.35 (*m*, 3 H, H(8,9,10); 9.21 (*s*, 1 H, NHCO); 12.68 (*s*, 1 H, NH(3)). ^{19}F-NMR (282.4 MHz, $CDCl_3$): −126.7 (*s*, CF_2); −121.0 (*q*, $^3J_{F,F}$ = 9.0, CF_3CF_2); −80.5 (*t*, $^3J_{F,F}$ = 9.0, CF_3). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 41.6 (C(4)); 91.6 (C(2)); 122.7 (C(7)); 123.6 (C(10)); 126.3, 127.6 (C(8,9)); 129.3, 130.2 (C(6,11)); 159.9 (C(3)); 168.0 (CONH); 179.6 (*t*, $^2J_{C,F}$ = 24.7, C(1)); C_3F_7 not determined. IR (ATR, cm^{-1}): 3189*w*, 3118*w*, 3064*w*, 2982*w*, 2922*w*, 2871*w*, 1688*s*, 1600*s*, 1574*s*, 1519*m*, 1501*s*, 1428*m*, 1380*m*, 1335*s*, 1269*m*, 1260*m*, 1211*s*, 1180*s*, 1149*s*, 1116*s*, 1105*s*, 1072*s*. MS (EI, 70 eV): 371 (M+H$^+$ 20), 370 (76), 202 (26), 201 (100), 159 (53), 131 (12). HR-MS (EI, 70 eV): calcd. for $C_{14}H_9F_7N_2O_2$ (M^+): 370.05468, found: 370.054495.

4e: ^{1}H-NMR (300.13 MHz, $CDCl_3$) tautomer **I**: 1.30 (*t*, $^3J_{CH2,CH3}$ = 7.2, Me); 3.26 (*s*, 2 H, H(2)); 4.17 (*q*, $^3J_{CH2,CH3}$ = 7.2, OCH_2); 4.68 (*s*, 1 H, H(4)); 7.08 (*dd*, ^3J = 8.0, ^4J = 1.5, 1 H, H_{Ar}); 7.18 (*m*, ^4J = 1.5, 1 H, H_{Ar}); 7.28 (*m*, ^4J = 1.5, 1 H, H_{Ar}); 7.40 (*dd*, ^4J = 7.9, ^4J = 1.5, 1 H, H_{Ar}); 10.65 (*s*, 1 H, NH); tautomer **II**: 1.30 (*t*, $^3J_{CH2,CH3}$ = 7.2, Me); 4.18 (*q*, $^3J_{CH2,CH3}$ = 7.2, OCH_2); 4.83 (br. *s*, 1 H, H(4)); 5.01 ('*t*', $^4J_{2,NH(1)}$ = $^4J_{2,NH(3)}$ = 2.0, 1 H, H(2)); 5.49 (br. *s*, 1 H, NH(1)); 6.55 (*dd*, ^3J = 7.7, ^4J = 1.7, 1 H, H(10)); 6.77 (*dd*, ^3J = 7.7, ^4J = 1.5, 1 H, H(7)); 6.81 (*m*, ^4J = 1.7, 1 H, H(9)); 6.90 (*m*, ^4J = 1.5, 1 H, H(8)); 10.09 (*s*, 1 H, NH(3)). ^{19}F-NMR (282.4 MHz, $CDCl_3$) tautomer **I**: −125.5 (*s*, $CF_2CF_2CF_3$); −116.4 (*q*, $^3J_{F,F}$ = 9.2, CF_2CF_3); −80.1 (*t*, $^3J_{F,F}$ = 9.2, CF_3); tautomer **II**: −126.6 (*s*, $CF_2CF_2CF_3$); −118.6 (*q*, $^3J_{F,F}$ = 9.2, CF_2CF_3); −80.3 (*t*, $^3J_{F,F}$ = 9.2, CF_3). ^{13}C-NMR (75.5 MHz, $CDCl_3$) tautomer **I**: 14.4 (CH_3); 34.7 (C(2)); 59.5 (OCH_2); 86.3 (C(4)); 108 – 120 (*m*, $CF_2CF_2CF_3$); 122.3 (C(7)); 124.1 (C(9)); 129.2 (C(8)); 130.2 (C(10)); 132.3 (C(6)); 136.9 (C(11));

153.1 (*t*, $^2J_{C,F}$ = 25.6, C(1)); 155.6 (C(3)); 170.6 (C(5)); tautomer **II**: 14.4 (CH_3); 59.5 (OCH_2); 94.2 (C(4)); 102.2 (*t*, $^3J_{C,F}$ = 7.0, C(2)); 120.4 (C(10)); 121.6 (C(7)); 123.1 (C(9)); 124.7 (C(8)); 131.4, 131.8 (C(6,11)); 152.3 (C(3)); 170.3 (C(5)); C(1), $CF_2CF_2CF_3$ not determined. IR (ATR, cm^{-1}): 3255*w*, 3190*w*, 2991*w*, 2901*w*, 1655*m*, 1614*s*, 1566*m*, 1481*m*, 1435*w*, 1392*w*, 1354*w*, 1331*w*, 1306*m*, 1271*s*, 1237*m*, 1214*s*, 1183*s*, 1157*s*, 1128*s*, 1112*s*, 1091*s*, 1070*m*, 1039*s*, 1001*m*. MS (EI, 70 eV): 398 [M^+, (98)], 353 (33), 352 (88), 205 (21), 156 (21), 155 (100). HR-MS (ESI-TOF/MS, positiv): calc. for $C_{16}H_{14}F_5NaN_2O_2$ [$(M + Na)^+$]: 421.0757, found: 421.0761.

(4*Z*)-7,8-Dichloro-4-(3,3,4,4,5,5,5-heptafluoro-2-oxopentylidene)-1,3,4,5-tetrahydro-2*H*-1,5-benzodiazepin-2-one (**3f**). *Method A*: Starting with **1c** (0.326 g, 0.999 mmol) and **2b** (0.266 g, 1.50 mmol) in AcOH (3 ml), **3f** was isolated as a colorless solid (0.280 g, 64%), m.p. = 264 – 266° (**4f** was not isolated, ratio of **3f**/**4f** in the crude product approx. 4:1). ^{1}H-NMR (500.13 MHz, $CDCl_3$): 3.32 (*s*, 2 H, H(4)); 5.75 (*t*, $^4J_{H,F}$ = 1.5, 1 H, H(2)); 7.23 (*s*, 1 H, H(7)); 7.39 (*s*, 1 H, H(10)); 8.09 (*s*, 1 H, NHCO); 12.57 (*s*, 1 H, NH(3)). ^{19}F-NMR (282.4 MHz, $CDCl_3$): −126.6 (*s*, CF_2); −121.0 (*q*, $^3J_{F,F}$ = 9.1, CF_3CF_2); −80.5 (*t*, $^3J_{F,F}$ = 9.1, CF_3). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 41.5 (C(4)); 92.4 (C(2)); 123.7 (C(7)); 124.9 (C(10)); 128.9, 129.2 (C(6,11)); 130.2, 131.2 (C(8,9)); 159.1 (C(3)); 166.5 (CONH); 180.7 (*t*, $^2J_{C,F}$ = 25.3, C(1)); C_3F_7 not determined. IR (ATR, cm^{-1}): 3390*w*, 3237*m*, 3158*w*, 3119*w*, 3056*w*, 3016*w*, 2945*w*, 1696*s*, 1621*m*, 1585*m*, 1550*s*, 1517*m*, 1496*m*, 1481*s*, 1428*m*, 1374*m*, 1350*m*, 1331*m*, 1308*m*, 1293*m*, 1263*m*, 1204*s*, 1179*s*, 1160*m*, 1139*s*, 1121*s*, 1072*m*. MS (EI, 70 eV): 442 (M^+, $^{37}Cl_2$ (8)], 440 [M^+, $^{37}Cl^{35}Cl$ (44)], 438 (M^+, $^{35}Cl_2$ (68)], 273 [$^{37}Cl_2$ (11)], 271 [$^{37}Cl^{35}Cl$ (67)], 269 [$^{35}Cl_2$ (100)], 229 [$^{37}Cl^{35}Cl$ (55)], 227 [$^{35}Cl_2$ (55), 199 (10), 67 (14). HR-MS (EI, 70 eV): calc. for $C_{14}H_7{}^{35}Cl_2F_7N_2O_2$ (M^+): 437.97673, found: 437.975842.

Ethyl (2*E*)-2-Chloro[1,3-dihydro-4-(trifluoromethyl)-2*H*-1,5-benzodiazepin-2-ylidene]acetate (**4g**). *Method A*: Starting with **1d** (0.266 g, 1.021 mmol) and **2a** (0.162 g, 1.5 mmol) in AcOH (3 ml), **4g** was isolated as a yellow solid (0.126 g, 37%), m.p. = 111 – 113°. ^{1}H-NMR (300.13 MHz, $CDCl_3$) tautomer **I**: 1.37 (*t*, $^3J_{CH2,CH3}$ = 7.2, Me); 3.68 (*d*, $^4J_{2,NH}$ = 0.8, 2 H, H(2)); 4.28 (*q*, $^3J_{CH2,CH3}$ = 7.2, OCH_2); 7.10 (*dd*, ^3J = 7.9, ^4J = 1.5, 1 H, H(7)); 7.22 (*m*, ^4J = 1.5, 1 H, H(9)); 7.30 (*m*, ^4J = 1.7, 1 H, H(8)); 7.44 (*dd*, ^3J = 7.8, ^4J = 1.7, 1 H, H(10)); 11.10 (*s*, 1 H, NH); tautomer **II**: 1.37 (*t*, $^3J_{CH2,CH3}$ = 7.2, Me); 4.28 (*q*, $^3J_{CH2,CH3}$ = 7.2, OCH_2); 5.60 (br. *s*, 1 H, NH(1)); 6.09 (‘*t*’*q*, $^4J_{2,NH(1)} = {}^4J_{2,NH(3)}$ = 2.0, $^4J_{2,F}$ = 0.6, 1 H, H(2)); 6.57 (*dd*, ^3J = 7.7, ^4J = 1.5, 1 H, H(10)); 6.73 (*dd*, ^3J = 7.7, ^4J = 1.7, 1 H, H(7)); 6.84 (*m*, ^4J = 1.7, 1 H, H(9)); 6.90 (*m*, ^4J = 1.5, 1 H, H(8)); 10.55 (*s*, 1 H, NH(3)). ^{19}F-NMR (282.4 MHz, $CDCl_3$) tautomer **I**: −72.7 (CF_3); tautomer **II**: −71.0 (CF_3). ^{13}C-NMR (75.5 MHz, $CDCl_3$) tautomer **I**: 14.3 (CH_3); 30.5 (C(2)); 61.5 (OCH_2); 92.9 (C(4)); 119.2 (*q*, $^1J_{C,F}$ = 277, CF_3); 122.6 (C(7)); 124.6 (C(9)); 129.1 (C(8)); 130.0 (C(10)); 132.0 (C(6)); 136.6 (C(11)); 151.3 (*q*, $^2J_{C,F}$ = 36.3, C(1)); 152.3 (C(3)); 167.7 (C(5)); tautomer **II**: 14.3 (CH_3); 61.5 (OCH_2); 95.8 (C(4)); 96.3 (*q*, $^3J_{C,F}$ = 5.0, C(2)); 120.3 (C(10)); 122.3, 122.4 (C(7,9)); 123.8 (C(8)); 131.5, 131.9 (C(6,11)); 149.0 (C(3)); 167.3 (C(5)); C(1), CF_3 not determined.

^{1}H-NMR (500.13 MHz, (D_6)DMSO) isomer **I**: 1.27 (*t*, $^3J_{CH2,CH3}$ = 7.1, Me); 3.82 (*s*, 2 H, H(2)); 4.22 (*q*, $^3J_{CH2,CH3}$ = 7.1, OCH_2); 7.31 (*ddd*, ^3J = 8.0, ^3J = 6.0, ^4J = 2.7, 1 H, H(9)); 7.38 – 7.43 (*m*, 2 H, H(7, 8)); 7.44 (*m*, 1 H, H(10)); 10.90 (*s*, 1 H, NH); isomer **II**: 1.27 (*t*, $^3J_{CH2,CH3}$ = 7.1, Me); 4.23 (*q*, $^3J_{CH2,CH3}$ = 7.1, OCH_2); 5.80 (‘*t*’, $^4J_{2,NH(1)} = {}^4J_{2,NH(3)}$ = 2.0, 1 H, H(2)); 6.66 (*dd*, $^3J_{7,8}$ = 7.4, $^4J_{7,9}$ = 2.0, 1 H, H(7)); 6.87 – 6.93 (*m*, 2 H, H(8,9)); 7.01 (*dd*, $^3J_{9,10}$ = 7.5, $^4J_{8,10}$ = 2.1, 1 H, H(10)); 8.96 (*d*, $^4J_{2,NH(1)}$ = 2.0, 1 H, NH(1)); 10.30 (*d*, $^4J_{2,NH(3)}$ = 2.0, 1 H, NH(3)); isomer **III**: 1.23 (*t*, $^3J_{CH2,CH3}$ = 7.1, Me); 4.15 (*q*, $^3J_{CH2,CH3}$ = 7.1, OCH_2); 6.87 – 6.94 (*m*, 2 H), 7.00 – 7.04 (*m*, 2 H), (CH_{Ar}); 7.08 (‘*t*’, $^4J_{2,NH(1)} = {}^4J_{2,NH(3)}$ = 2.0, 1 H, H(2)); 7.55 (*d*, $^4J_{2,NH(3)}$ = 2.0, 1 H, NH(3)); 8.61 (*d*, $^4J_{2,NH(1)}$ = 2.0, 1 H, NH(1)); isomer **IV**: 1.24 (*t*, $^3J_{CH2,CH3}$ = 7.2, Me); 4.17 (*q*, $^3J_{CH2,CH3}$ = 7.2, OCH_2); 4.35 (br. *s*, 2 H, H(2)); 7.27 (*m*, 1 H, H(9)); 7.35 – 7.43 (*m*, 2 H, H(7, 8)); 7.54 (*m*, 1 H, H(10)); 9.22 (*s*, 1 H, NH). ^{19}F-NMR (282.4 MHz, (D_6)DMSO) isomer **I**: −71.3 (CF_3); isomer **II**: −69.0 (CF_3); isomer **III**: −68.7 (CF_3); isomer **IV**: −72.1 (CF_3). ^{13}C-NMR (125.8 MHz, (D_6) DMSO) isomer **I**: 14.3 (CH_3); 30.9 (C(2)); 61.3 (OCH_2); 91.9 (C(4)); 119.3 (*q*, $^1J_{C,F}$ = 277, CF_3); 123.3 (C(7)); 125.0 (C(9)); 129.5 (C(8)); 129.6 (C(10)); 131.9 (C(6)); 136.2 (C(11)); 151.1 (*q*, $^2J_{C,F}$ = 34.8, C(1)); 152.8 (C(3)); 166.6 (C(5)); isomer **II**: 14.2 (CH_3); 61.5 (OCH_2); 92.7 (*q*, $^3J_{C,F}$ = 5.2, C(2)); 97.2 (C(4)); 120.6 (*q*, $^1J_{C,F}$ = 278, CF_3); 121.6 (C(10)); 122.0 (C(7)); 124.2 (C(9)); 125.3 (C(8)); 132.0 (C(6)); 133.9 (C(11)); 138.4 (*q*, $^2J_{C,F}$ = 31.1, C(1)); 151.6 (C(3)); 166.6 (C(5)); isomer **III**: 14.2 (CH_3); 61.0 (OCH_2); 94.1 (*q*, $^3J_{C,F}$ = 6.0, C(2)); 99.8 (C(4)); 135.5 (*q*, $^2J_{C,F}$ = 31.0, C(1)); 147.9 (C(3)); 163.3 (C(5)); CF_3, CH_{Ar}, C_{Ar} not determined; isomer **IV**: 14.3 (CH_3); 28.5 (C(2)); 60.8 (OCH_2); 93.6 (C(4)); 150.2 (C(3)); 153.0 (*q*, $^2J_{C,F}$ = 34.5, C(1)); 163.9 (C(5)); CF_3, CH_{Ar}, C_{Ar} not determined. IR (ATR, cm^{-1}): 3241*w*, 3174*w*, 3147*w*, 3057*w*, 3029*w*, 2996*w*, 2979*w*, 2937*w*, 2905*w*, 2143*w*, 1959*w*, 1925*w*, 1641*m*, 1601*s*, 1561*m*, 1517*w*, 1480*m*, 1467*m*, 1456*m*, 1445*m*, 1423*m*, 1414*m*, 1360*m*, 1313*w*, 1293*m*, 1272*s*, 1254*s*, 1218*s*, 1199*s*, 1182*s*, 1118*s*, 1060*s*, 1043*s*, 1025*s*. MS (EI, 70 eV): 334 [M^+, ^{37}Cl (34)], 332 [M^+, ^{35}Cl (100)], 288 [^{37}Cl (30)], 286 [^{35}Cl (30), 223 (66), 189 (20). HR-MS (EI, 70 eV): calc. for $C_{14}H_{12}{}^{35}ClF_3N_2O_2$ (M^+): 332.05339, found: 332.054166. Anal. calc. for $C_{14}H_{12}ClF_3N_2O_2$ (332.705): C 50.54, H 3.64, N 8.42, found: C 50.96, H 3.71, N 8.10.

Ethyl (2*E*)-2-Chloro[7,8-dichloro-1,3-dihydro-4-(trifluoromethyl)-2*H*-1,5-benzodiazepin-2-ylidene]acetate (**4h**). *Method A*: Starting with **1d** (0.271 g, 1.040 mmol) and **2b** (0.230 g, 1.30 mmol) in AcOH (3 ml), **4h** was isolated as a red solid (0.226 g, 54%), m.p. = 131 – 133°. ^{1}H-NMR (300.13 MHz, $CDCl_3$) tautomer **I**: 1.36 (*t*, $^3J_{CH2,CH3}$ = 7.1, Me); 3.70 (*d*, $^4J_{2,NH}$ = 0.8, 2 H, H(2)); 4.28 (*q*,

$^3J_{CH2,CH3}$ = 7.1, OCH_2); 7.22 (*s*, 1 H, H(7)); 7.55 (*s*, 1 H, H(10)); 11.12 (*s*, 1 H, NH); tautomer **II**: 1.37 (*t*, $^3J_{CH2,CH3}$ = 7.1, Me); 4.29 (*q*, $^3J_{CH2,CH3}$ = 7.1, OCH_2); 5.62 (br. *s*, 1 H, NH(1)); 6.13 ('*t*'*q*, $^4J_{2,NH(1)}$ = $^4J_{2,NH(3)}$ = 2.0, $^4J_{2,F}$ = 0.6, 1 H, H(2)); 6.71 (*s*, 1 H, H(10)); 6.84 (*s*, 1 H, H (7)); 10.63 (*s*, 1 H, NH(3)). ^{19}F-NMR (282.4 MHz, $CDCl_3$) tautomer **I**: −72.9 (CF_3); tautomer **II**: −70.9 (CF_3). ^{13}C-NMR (75.5 MHz, $CDCl_3$) tautomer **I**: 14.2 (CH_3); 30.6 (C(2)); 61.8 (OCH_2); 94.5 (C(4)); 119.0 (*q*, $^1J_{C,F}$ = 278, CF_3); 123.6 (C(7)); 131.1 (C(10)); 128.1, 131.4, 132.8, 135.7 (C_{Ar}); 151.0 (C(3)); 152.9 (*q*, $^2J_{C,F}$ = 36.5, C (1)); 167.6 (C(5)); tautomer **II**: 14.2 (CH_3); 61.8 (OCH_2); 96.7 (*q*, $^3J_{C,F}$ = 5.0, C(2)); 97.4 (C(4)); 120.6 (*q*, $^1J_{C,F}$ = 276, CF_3); 121.1, 123.0 (CH_{Ar}); 126.2, 127.8, 131.3, 132.2 (C_{Ar}); 148.8 (C(3)); 167.3 (C(5)); C(1) not determined. IR (ATR, cm^{-1}): 3431*w*, 3217*w*, 3152*w*, 3090*w*, 3034*w*, 2985*w*, 2906*w*, 1651*m*, 1601*s*, 1539*m*, 1495*w*, 1464*m*, 1445*m*, 1421*w*, 1393*w*, 1366*m*, 1336*m*, 1296*m*, 1256*s*, 1243*s*, 1221*s*, 1180*s*, 1123*s*, 1068*s*, 1057*s*, 1024*s*. MS (EI, 70 eV): 406 [M^+, $^{37}Cl_3$ (3)], 404 [M^+, $^{37}Cl_2{}^{35}Cl$ (28)], 402 [M^+, $^{37}Cl^{35}Cl_2$ (79)], 400 [M^+, $^{35}Cl_3$ (79)], 360 [$^{37}Cl_3$ (4)], 358 [$^{37}Cl_2{}^{35}Cl$ (33)], 356 [$^{37}Cl^{35}Cl_2$ (98)], 354 [$^{35}Cl_3$ (100)], 322 (21), 320 (30), 295 [$^{37}Cl_2{}^{35}Cl$ (13)], 293 [$^{37}Cl^{35}Cl_2$ (49)], 291 [$^{35}Cl_3$ (57)], 257 (25), 223 (22). HR-MS (ESI-TOF/MS): calc. for $C_{14}H_{11}{}^{35}Cl_3F_3N_2O_2$ [(M+H)$^+$]: 400.9833, found: 400.9835; calc. for $C_{14}H_{11}{}^{37}Cl^{35}Cl_2F_3N_2O_2$ [(M+H)$^+$]: 402.9805, found: 402.9807.

Ethyl (2*Z*)-[1,3-Dihydro-4-(trifluoromethyl)-2*H*-naphtho[2,3-*b*][1,4]diazepin-2-ylidene]acetate (**5a**). *Method A*: Starting with **1a** (0.232 g, 1.026 mmol) and **2c** (0.238 g, 1.504 mmol) in AcOH (4 ml), **5a** was isolated as a yellow solid (0.161 g, 45%), m.p. 124-126°), R_f = 0.60 (heptane/AcOEt, 1:1). ^{1}H-NMR (300.13 MHz, $CDCl_3$) tautomer **I**: 1.32 (*t*, $^3J_{CH2,CH3}$ = 7.2, Me); 3.27 (*s*, 2 H, H(2)); 4.20 (*q*, $^3J_{CH2,CH3}$ = 7.2, OCH_2); 4.77 (*s*, 1 H, H(4)); 7.44 (*m*, 1 H, H(11)); 7.51 (*m*, 1 H, H(10)); 7.53 (*m*, 1 H, H(7)); 7.75 (br. *d*, ^3J = 8.0, 1 H, H(9)); 7.83 (br. *d*, ^3J = 8.0, 1 H, H (12)); 7.93 (*m*, 1 H, H(14)); 10.72 (*s*, 1H, NH); tautomer **II**: 1.32 (*t*, $^3J_{CH2,CH3}$ = 7.2, Me); 4.22 (*q*, $^3J_{CH2,CH3}$ = 7.2, OCH_2); 4.85 (*s*, 1 H, H(4)); 5.18 ('*t*', $^4J_{2,NH(1)}$ = $^4J_{2,NH(3)}$ = 2.0, 1 H, H(2)); 5.90 (*s*, 1 H, NH(1)); 7.04 (*s*, 1 H, H (14)); 7.22 (*s*, 1 H, H(7)); 7.23 – 7.32 (*m*, 2 H, H(10,11)); 7.51 – 7.58 (*m*, 2 H, H(9,12)); 10.67 (*s*, 1 H, NH(3)). ^{19}F-NMR (282.4 MHz, $CDCl_3$) tautomer **I**: −73.7 (CF_3); tautomer **II**: −70.7 (CF_3). ^{13}C-NMR (75.5 MHz, $CDCl_3$) tautomer **I**: 14.4 (CH_3); 33.7 (C(2)); 59.5 (OCH_2); 86.6 (C(4)); 119.1 (C(7)); 119.4 (*q*, $^1J_{C,F}$ = 277, CF_3); 125.8 (C(11)); 126.6 (C(9)); 127.6 (C(10)); 128.0 (C(12)); 129.0 (C(14)); 130.1, 130.8, 132.9, 136.1 (C_{Ar}); 153.5 (*q*, $^2J_{C,F}$ = 35.2, C(1)); 156.2 (C(3)); 170.2 (C(5)); tautomer **II**: 14.4 (CH_3); 59.5 (OCH_2); 92.7 (C(4)); 99.2 (*q*, $^3J_{C,F}$ = 4.4, C(2)); 116.4 (C(14)); 117.5 (C(7)); 125.3, 125.5, 126.0, 126.3 (CH_{Ar}); 129.8, 130.9, 131.0, 132.0 (C_{Ar}); 133.9 (*q*, $^2J_{C,F}$ = 31.4, C(1)); 152.1 (C(3)); 170.4 (C(5)); CF_3 not determined. IR (ATR, cm^{-1}): 3432*w*, 3241*w*, 3181*w*, 3055*w*, 3005*w*, 2983*w*, 2962*w*, 2940*w*, 2898*w*, 1738*w*, 1656*m*, 1613*s*, 1505*m*, 1484*m*, 1460*m*, 1444*m*, 1422*m*, 1366*m*, 1321*m*, 1299*m*, 1210*m*, 1194*m*, 1165*s*, 1153*s*, 1111*s*, 1054*m*, 1034*s*. MS (EI, 70 eV): 348 [M^+, (52)], 303 (22), 302 (100), 274 (14), 236 (7), 206 (10), 205 (41), 179 (8), 152 (7), 151 (6). Anal. calc. for $C_{18}H_{15}F_3N_2O_2$ (348.11): C 62.07, H 4.34, N 8.04, found: C 61.55, H 3.94, N 7.63.

Ethyl (2*Z*)-[1,3-Dihydro-4-(pentafluoroethyl)-2*H*-naphtho[2,3-*b*][1,4]diazepin-2-ylidene]acetate (**5b**). *Method A*: Starting with **1b** (0.282 g, 1.022 mmol) and **2c** (0.230 g, 1.454 mmol) in AcOH (4 ml), **5b** was isolated as a yellow solid (0.068 g, 17%); m.p. 136 – 138°. ^{1}H-NMR (300.13 MHz, $CDCl_3$) tautomer **I**: 1.32 (*t*, $^3J_{CH2,CH3}$ = 7.2, Me); 3.29 (*s*, 2 H, H(2)); 4.20 (*q*, $^3J_{CH2,CH3}$ = 7.2, OCH_2); 4.77 (*s*, 1 H, H(4)); 7.43 (*ddd*, ^3J = 8.2, ^3J = 6.8, ^4J = 1.5, 1 H, H(11)); 7.50 (*ddd*, ^3J = 8.2, ^3J = 6.8, ^4J = 1.5, 1 H, H (10)); 7.50 (*s*, 1 H, H(7)); 7.73 (br. *d*, ^3J = 8.2, 1 H, H(9)); 7.82 (br. *d*, ^3J = 8.2, 1 H, H(12)); 7.91 (*s*, 1 H, H(14)); 10.75 (*s*, 1 H, NH); tautomer **II**: 1.32 (*t*, $^3J_{CH2,CH3}$ = 7.2, Me); 4.22 (*q*, $^3J_{CH2,CH3}$ = 7.2, OCH_2); 4.86 (*s*, 1 H, H(4)); 5.14 (*s*, 1 H, H(2)); 5.92 (*s*, 1 H, NH(1)); 7.00 (*s*, 1 H, H (14)); 7.19 (*s*, 1 H, H(7)); 7.25 – 7.32 (*m*, 2 H, H(10,11)); 7.51 – 7.57 (*m*, 2 H, H(9,12)); 10.64 (*s*, 1 H, NH(3)). ^{19}F-NMR (282.4 MHz, $CDCl_3$) tautomer **I**: −118.1 (*q*, $^3J_{F,F}$ = 2.0, CF_2); −81.3 (*t*, $^3J_{F,F}$ = 2.0, CF_3); tautomer **II**: −121.3 (*q*, $^3J_{F,F}$ = 2.0, CF_2); −83.9 (*t*, $^3J_{F,F}$ = 2.0, CF_3). ^{13}C-NMR (75.5 MHz, $CDCl_3$) tautomer **I**: 14.4 (CH_3); 33.8 (C(2)); 59.5 (OCH_2); 86.8 (C(4)); 110.1 (*tq*, $^1J_{C,F}$ = 256, $^2J_{C,F}$ = 38.0, CF_2); 110.1 (*tq*, $^1J_{C,F}$ = 218, $^2J_{C,F}$ = 38.0, CF_2); 118.5 (*qt*, $^1J_{C,F}$ = 287, $^2J_{C,F}$ = 35.7, CF_3); 119.1 (C(7)); 125.9 (C(11)); 126.6 (C(9)); 127.7 (C(10)); 128.1 (C(12)); 129.3 (C(14)); 130.1, 130.8, 133.0, 136.3 (C_{Ar}); 154.3 (*t*, $^2J_{C,F}$ = 27.5, C(1)); 156.3 (C(3)); 170.3 (C (5)); tautomer **II**: 14.4 (CH_3); 59.5 (OCH_2); 93.1 (C(4)); 102.0 (*t*, $^3J_{C,F}$ = 6.0, C(2)); 110.7 (*tq*, $^1J_{C,F}$ = 258, $^2J_{C,F}$ = 38.7, CF_2); 116.6 (C(14)); 117.7 (C(7)); 118.5 (*qt*, $^1J_{C,F}$ = 288, $^2J_{C,F}$ = 38.8, CF_3); 125.4, 125.6, 126.1, 126.4 (CH_{Ar}); 129.9, 131.1, 131.2, 132.4 (C_{Ar}); 133.1 (*t*, $^2J_{C,F}$ = 23.0, C(1)); 152.1 (C(3)); 170.4 (C(5)). IR (ATR, cm^{-1}): 3301*w*, 3201*w*, 3054*w*, 2978*w*, 2937*w*, 1659*m*, 1614*s*, 1506*m*, 1485*m*, 1415*m*, 1366*m*, 1347*w*, 1326*m*, 1288*s*, 1254*m*, 1240*m*, 1189*s*, 1157*s*, 1084*s*, 1043*m*. MS (EI, 70 eV): 398 [M^+, (56)], 353 (24), 352 (100), 286 (8), 255 (7), 216 (5), 206 (13), 205 (53). HR-MS (ESI-TOF/MS): calc. for $C_{19}H_{16}F_5N_2O_2$ [(M+H)$^+$]: 399.11265, found: 399.11294. Anal. calc. for $C_{19}H_{15}F_5N_2O_2$ (398.312): C 57.29, H 3.79, N 7.03, found: C 56.84, H 3.39, N 6.54.

Ethyl (2*Z*)-[4-(Heptafluoropropyl)-1,3-dihydro-2*H*-naphtho[2,3-*b*][1,4]diazepin-2-ylidene]acetate (**5c**). *Method A*: Starting with **1c** (0.340 g, 1.042 mmol) and **2c** (0.240 g, 1.517 mmol) in AcOH (4 ml), **5c** was isolated as a yellow solid (0.159 g, 34%); m.p. 143 – 146°, R_f = 0.62 (heptane/AcOEt, 1:1). ^{1}H-NMR (300.13 MHz, $CDCl_3$) tautomer **I**: 1.32 (*t*, $^3J_{CH2,CH3}$ = 7.2, Me); 3.30 (*s*, 2 H, H(2)); 4.20 (*q*, $^3J_{CH2,CH3}$ = 7.2, OCH_2); 4.76 (*s*, 1 H, H(4)); 7.44 (*ddd*, ^3J = 8.2, ^3J = 6.8, ^4J = 1.5, 1 H, H(11)); 7.50 (*ddd*, ^3J = 8.2, ^3J = 6.8, ^4J = 1.5, 1 H, H(10)); 7.50 (*s*, 1 H, H

(7)); 7.74 (br. *d*, ^3J = 8.2, 1 H, H(9)); 7.83 (br. *d*, ^3J = 8.2, 1 H, H(12)); 7.92 (*s*, 1 H, H(14)); 10.76 (*s*, 1 H, NH); tautomer **II**: 1.32 (*t*, $^3J_{CH2,CH3}$ = 7.2, Me); 4.22 (*q*, $^3J_{CH2,CH3}$ = 7.2, OCH_2); 4.88 (*s*, 1 H, H(4)); 5.15 (br. *s*, 1 H, H (2)); 5.90 (*s*, 1 H, NH(1)); 7.00 (*s*, 1 H, H(14)); 7.21 (*s*, 1 H, H(7)); 7.25 – 7.33 (*m*, 2 H, H(10,11)); 7.52 – 7.59 (*m*, 2 H, H(9,12)); 10.65 (*s*, 1 H, NH(3)). ^{19}F-NMR (282.4 MHz, $CDCl_3$) tautomer **I**: −125.5 (*m*, CF_2); −116.3 (*m*, CF_2); −80.0 (*t*, $^3J_{F,F}$ = 9.2, CF_3); tautomer **II**: −126.5 (*m*, CF_2); −118.3 (*m*, CF_2); −80.2 (*t*, $^3J_{F,F}$ = 9.2, CF_3). IR (ATR, cm^{-1}): 3430*w*, 3195*w*, 3116*w*, 3053*w*, 2982*w*, 2929*w*, 2903*w*, 1659*m*, 1614*s*, 1504*m*, 1484*w*, 1471*w*, 1434*w*, 1409*w*, 1342*m*, 1323*w*, 1288*m*, 1276*m*, 1261*m*, 1227*s*, 1202*s*, 1158*s*, 1145*s*, 1105*s*, 1067*m*, 1043*s*. MS (EI, 70 eV): 448 [M^+, (68)], 403 (27), 402 (100), 376 (8), 255 (7) 206 (11), 205 (55). HR-MS (ESI-TOF/MS): Calc. for $C_{20}H_{15}F_7N_2O_2$: [(M+H)$^+$] 448.10163, found: 448.10163.

Ethyl (2*E*)-2-Chloro[1,3-dihydro-4-(trifluoromethyl)-2*H*-naphtho[2,3-*b*][1,4]diazepin-2-ylidene]acetate (5d). *Method A*: Starting with **1d** (0.265 g, 1.017 mmol) and **2c** (0.240 g, 1.517 mmol) in AcOH (4 ml), **5d** was isolated as a yellow solid (0.085 g, 22%), m.p. 129 – 130°, R_f = 0.56 (heptane/AcOEt, 1:1). ^{1}H-NMR (300.13 MHz, $CDCl_3$) tautomer **I**: 1.39 (*t*, $^3J_{CH2,CH3}$ = 7.2, Me); 3.74 (*d*, $^3J_{2,NH}$ = 0.8, 2 H, H (2)); 4.31 (*q*, $^3J_{CH2,CH3}$ = 7.2, OCH_2); 7.46 (*m*, 1 H, H(11)); 7.52 (*m*, 1 H, H(10)); 7.53 (*s*, 1 H, H(7)); 7.75 (br. *d*, ^3J = 8.0, 1 H, H(9)); 7.84 (br. *d*, ^3J = 8.0, 1 H, H(12)); 7.95 (*s*, 1 H, H(14)); 11.19 (*s*, 1 H, NH); tautomer **II**: 1.40 (*t*, $^3J_{CH2,CH3}$ = 7.2, Me); 4.32 (*q*, $^3J_{CH2,CH3}$ = 7.2, OCH_2); 6.01 (br. *s*, 1 H, NH(1)); 6.20 ('*t*'*q*, $^4J_{2,NH(1)}$ = $^4J_{2,NH(3)}$ = 2.0, $^4J_{2,F}$ = 0.5, 1 H, H(2)); 7.01 (*s*, 1 H, H(14)); 7.15 (*s*, 1 H, H(7)); 7.25 – 7.32 (*m*, 2 H, H(10,11)); 7.51 – 7.57 (*m*, 2 H, H(9,12)); 11.12 (*s*, 1 H, NH(3)). ^{19}F-NMR (282.4 MHz, $CDCl_3$) tautomer **I**: −73.0 (CF_3); tautomer **II**: −70.7 (CF_3). IR (ATR, cm^{-1}): 3218*w*, 3153*w*, 2985*w*, 2960*w*, 2905*w*, 1647*m*, 1628*w*, 1601*s*, 1565*w*, 1500*w*, 1474*w*, 1457*w*, 1423*w*, 1365*m*, 1329*w*, 1315*w*, 1295*m*, 1254*s*, 1240*s*, 1207*m*, 1176*s*, 1159*s*, 1125*s*, 1059*s*, 1020*m*. MS (EI, 70 eV): 384 [M^+, ^{37}Cl (26)], 382 [M^+, ^{35}Cl (82)], 348 (47), 339 [^{37}Cl (6)], 337 [^{35}Cl (17)], 338 [^{37}Cl (24)], 336 [^{35}Cl (74)], 303 (28), 302 (100), 276 [^{37}Cl (12)], 274 [^{35}Cl (31)], 273 (71), 239 (15), 236 (15), 205 (47), 152 (19), HR-MS (ESI-TOF/MS): Calc. for $C_{18}H_{14}{}^{35}ClF_3N_2O_2$ [(M+H)$^+$]: 382.06904, found: 382.068812.

Ethyl (2*E*)-2-Chloro[1,3-dihydro-4-(pentafluoroethyl)-2*H*-naphtho[2,3-*b*][1,4]diazepin-2-ylidene]acetate (5e). *Method A*: Starting with **1e** (0.370 g, 1.191 mmol) and **2c** (0.237 g, 1.498 mmol) in AcOH (4 ml), **5e** was isolated as a yellow solid (0.220 g, 43%), m.p. 133 – 135°. ^{1}H-NMR (300.13 MHz, $CDCl_3$) tautomer **I**: 1.39 (*t*, $^3J_{CH2,CH3}$ = 7.2, Me); 3.77 (*s*, 2 H, H(2)); 4.31 (*q*, $^3J_{CH2,CH3}$ = 7.2, OCH_2); 7.46 (*ddd*, ^3J = 8.2, ^3J = 6.8, ^4J = 1.5, 1 H, H(11)); 7.52 (*ddd*, ^3J = 8.2, ^3J = 6.8, ^4J = 1.5, 1 H, H(10)); 7.53 (*s*, 1 H, H(7)); 7.76 (br. *d*, ^3J = 8.2, 1 H, H(9)); 7.85 (br. *d*, ^3J = 8.2, 1 H, H(12)); 7.95 (*s*, 1 H, H(14)); 11.23 (*s*, 1H, NH); tautomer **II**: 1.40 (*t*, $^3J_{CH2,CH3}$ = 7.2, Me); 4.32 (*q*, $^3J_{CH2,CH3}$ = 7.2, OCH_2); 5.97 (*s*, 1 H, NH(1)); 6.18 ('*t*', $^4J_{2,NH(1)}$ = $^4J_{2,NH(3)}$ = 2.0, 1 H, H(2)); 7.01 (*s*, 1 H, H(14)); 7.20 (*s*, 1 H, H(7)); 7.27 – 7.35 (*m*, 2 H, H(10,11)); 7.52 – 7.61 (*m*, 2 H, H(9,12)); 11.14 (*s*, 1 H, NH(3)). ^{19}F-NMR (282.4 MHz, $CDCl_3$) tautomer **I**: −116.6 (*q*, $^3J_{F,F}$ = 2.0, CF_2); −81.2 (*t*, $^3J_{F,F}$ = 2.0, CF_3); tautomer **II**: −121.0 (*q*, $^3J_{F,F}$ = 2.0, CF_2); −83.7 (*t*, $^3J_{F,F}$ = 2.0, CF_3). ^{13}C-NMR (75.5 MHz, $CDCl_3$) tautomer **I**: 14.3 (CH_3); 30.2 (C(2)); 61.5 (OCH_2); 93.4 (C(4)); 119.6 (C(7)); 126.1 (C(11)); 126.7 (C(9)); 127.9 (C(10)); 128.1 (C(12)); 129.4 (C(14)); 130.3, 130.5, 133.0, 136.2 (C_{Ar}); 153.6 (C(3)); 154.1 (*t*, $^2J_{C,F}$ = 28.0, C(1)); C_2F_5 not determined; tautomer **II**: 14.2 (CH_3); 61.6 (OCH_2); 97.9 (C(4)); 99.4 (*m*, C(2)); 116.7 (C (14)); 118.7 (C(7)); 125.7, 125.9, 126.3, 126.5 (CH_{Ar}); 130.2, 131.4, 131.9, 133.8 (C_{Ar}); 135.8 (*t*, $^2J_{C,F}$ = 22.9, C(1)); 150.2 (C(3)); C_2F_5 not determined. IR (ATR, cm^{-1}): 3429*w*, 3151*w*, 3048*w*, 3003*w*, 2984*w*, 2939*w*, 1645*m*, 1603*s*, 1565*m*, 1498*m*, 1460*m*, 1443*m*, 1427*m*, 1388*w*, 1368*m*, 1329*m*, 1254*s*, 1237*m*, 1190*s*, 1162*s*, 1136*s*, 1084*s*, 1055*s*, 1018*s*. MS (EI, 70 eV): 434 [M^+, ^{37}Cl (26)], 432 [M^+, ^{35}Cl (72)], 398 (7), 389 [M^+, ^{37}Cl (9)], 387 [M^+, ^{35}Cl (27)], 388 (36), 386 (100), 362 [M^+, ^{37}Cl (5)], 360 [M^+, ^{35}Cl (15)], 353 (16), 352 (25), 324 (22), 323 (74), 311 (18), 286 (20), 255 (27), 254 (54), 241 (29), 240 (19), 239 (64), 219 [M^+, ^{37}Cl (5)], 217 [M^+, ^{35}Cl (12)]. HR-MS (ESI-TOF/MS, negative mode): Calc. for $C_{19}H_{13}{}^{37}ClF_5N_2O_2$ [(M−H)$^-$]: 433.05617, found: 433.05672; Calc. for $C_{19}H_{13}{}^{35}ClF_5N_2O_2$ [(M−H)$^-$]: 431.05912, found: 431.05951. Anal. calc. for $C_{19}H_{14}ClF_5N_2O_2$ (432.770): C 52.73, H 3.26, N 6.47, found: C 53.08, H 3.08, N 6.26.

Ethyl (2*E*)-2-Chloro[4-(heptafluoropropyl)-1,3-dihydro-2*H*-naphtho[2,3-*b*][1,4]diazepin-2-ylidene]acetate (5f). *Method A*: Starting with **1f** (0.354 g, 0.982 mmol) and **2c** (0.245 g, 1.549 mmol) in AcOH (4 ml), **5f** was isolated as a yellow solid (0.282 g, 60%), m.p. 148 – 151°. ^{1}H-NMR (300.13 MHz, $CDCl_3$) tautomer **I**: 1.40 (*t*, $^3J_{CH2,CH3}$ = 7.2, Me); 3.77 (*s*, 2 H, H(2)); 4.31 (*q*, $^3J_{CH2,CH3}$ = 7.2, OCH_2); 7.46 (*m*, 1 H), 7.52 (*m*, 1 H), (H(10,11)); 7.52 (*s*, 1 H, H (7)); 7.75 (br. *d*, ^3J = 8.2, 1 H, H(9)); 7.85 (br. *d*, ^3J = 8.2, 1 H, H(12)); 7.95 (*s*, 1 H, H(14)); 11.25 (*s*, 1 H, NH); tautomer **II**: 1.40 (*t*, $^3J_{CH2,CH3}$ = 7.2, Me); 4.31 (*q*, $^3J_{CH2,CH3}$ = 7.2, OCH_2); 5.98 (*s*, 1 H, NH(1)); 6.17 ('*t*', $^4J_{2,NH(1)}$ = $^4J_{2,NH(3)}$ = 2.0, 1 H, H(2)); 7.00 (*s*, 1 H, H(14)); 7.19 (*s*, 1 H, H(7)); 7.29 – 7.33 (*m*, 2 H, H(10,11)); 7.50 – 7.60 (*m*, 2 H, H(9,12)); 11.14 (*s*, 1 H, NH(3)). ^{19}F-NMR (282.4 MHz, $CDCl_3$) tautomer **I**: −126.3 (*s*, CF_2); −118.1 (*q*, $^3J_{F,F}$ = 9.5, CF_3CF_2); −80.2 (*t*, $^3J_{F,F}$ = 9.5, CF_3); tautomer **II**: −125.4 (*s*, CF_2); −114.7 (*q*, $^3J_{F,F}$ = 9.3, CF_3CF_2); −80.0 (*t*, $^3J_{F,F}$ = 9.3, CF_3). IR (ATR, cm^{-1}): 3427*w*, 3152*w*, 3053*w*, 2984*w*, 2963*w*, 2931*w*, 2905*w*, 1644*m*, 1603*s*, 1566*w*, 1515*m*, 1504*m*, 1474*w*, 1461*m*, 1427*w*, 1398*w*, 1360*m*, 1342*m*, 1319*w*, 1257*s*, 1224*s*, 1180*s*, 1152*s*, 1108*s*, 1056*m*, 1023*m*. MS (EI, 70 eV): 484 [M^+, ^{37}Cl (20)], 482 [M^+, ^{35}Cl (60)], 483 (13), 449 (11), 448 (53), 438 [M^+, ^{37}Cl (15)], 436 [M^+, ^{35}Cl (46)], 437 (12), 403 (27), 402 (100), 373 (18), 255 (13), 254 (19), 239 (16), 206 (12), 205 (50). HR-MS (ESI-TOF/MS): Calc. for $C_{20}H_{14}{}^{35}ClF_7N_2O_2$ [(M+H)$^+$]: 482.06265, found: 482.062735.

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