Electronic Supporting Information

1*H*-1,3-diazepines, 5*H*-1,3-diazepines, 1,3-diazepin-ones, and 2,4-diazabicyclo[3.2.0]heptenes (Diazepines Part 3)

Ales Reisinger,[a] Rainer Koch,[b] Paul V. Bernhardt[a] and Curt Wentrup[a,]*

[a]*Department of Chemistry, School of Molecular and Microbial Sciences, The University of Queensland, Brisbane, Qld 4072, Australia. E-mail: wentrup@uq.edu.au*

[b]*Institut fürReine und Angewandte Chemie, Carl von Ossietetzky Universität, D-26111 Oldenburg, Germany*

NMR spectral and kinetic data (p S2)

Fig. S1. ^{1}H NMR spectrum of **4a** in DMSO-d_6 as a function of temperature.

Fig. S2. ^{1}H NMR spectrum of **4c** in acetone/D_2O as a function of temperature.

Fig. S3. ^{13}C NMR spectra showing the reaction **19v** -> **20**

Fig. S4. ^{1}H NMR spectra showing the reaction **19a** -> **25a**,

Fig. S5. ^{13}C NMR spectra showing the reaction **19a** -> **25a**

Fig. S6. ^{1}H NMR spectra showing the reaction **19g** -> **25g**

Fig, S7. Arrhenius and Eyring plots for **4b** and **4c**.

X-ray crystal data (p S8)

Fig. S8. ORTEP view of compound **22bB** (30% ellipsoids)

Fig. S9. ORTEP view of compound **26** (racemic)(30% ellipsoids)

Tables S1 – S3: bond lengths and angles for **4k**, **22bB** and **26**

Preparative and characterization data (p S14)

Diazepines, diazepinones and diazabicyclo[3.2.0]heptenes

Computational data (p S45)

Tables S4 –S10: Cartesian coordinates, ^{1}H and ^{13}C NMR spectra and absolute energies for **20a-c, 21a-b, 22aA-F** and **22aB** dimer, and IR spectra for **22aA-F** and **22aB** dimer.

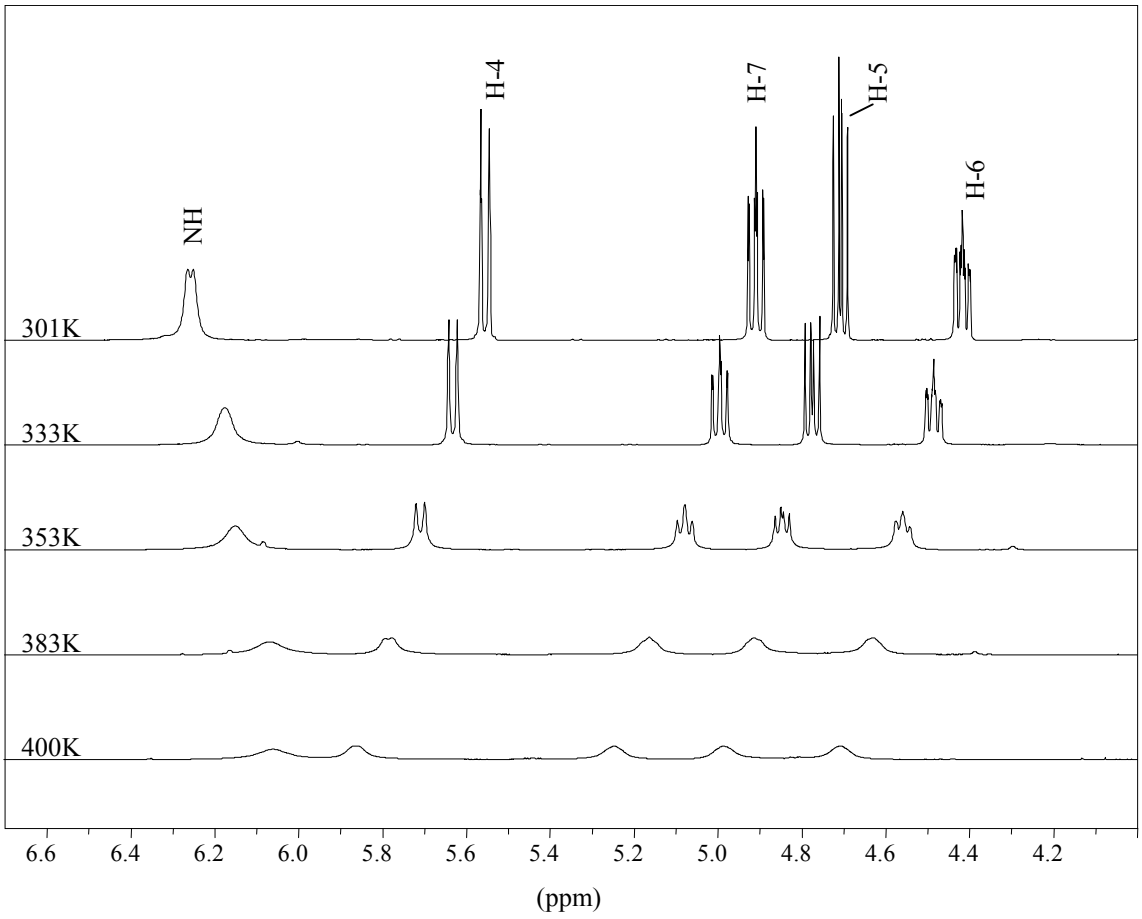

Figure S1. ^{1}H NMR spectra (400 MHz) of 1-methoxy-1H-1,3-diazepine **4a** in DMSO-d_6 solution as a function of temperature. The signal for the methoxy protons resonating at 3.54 ppm is not shown.

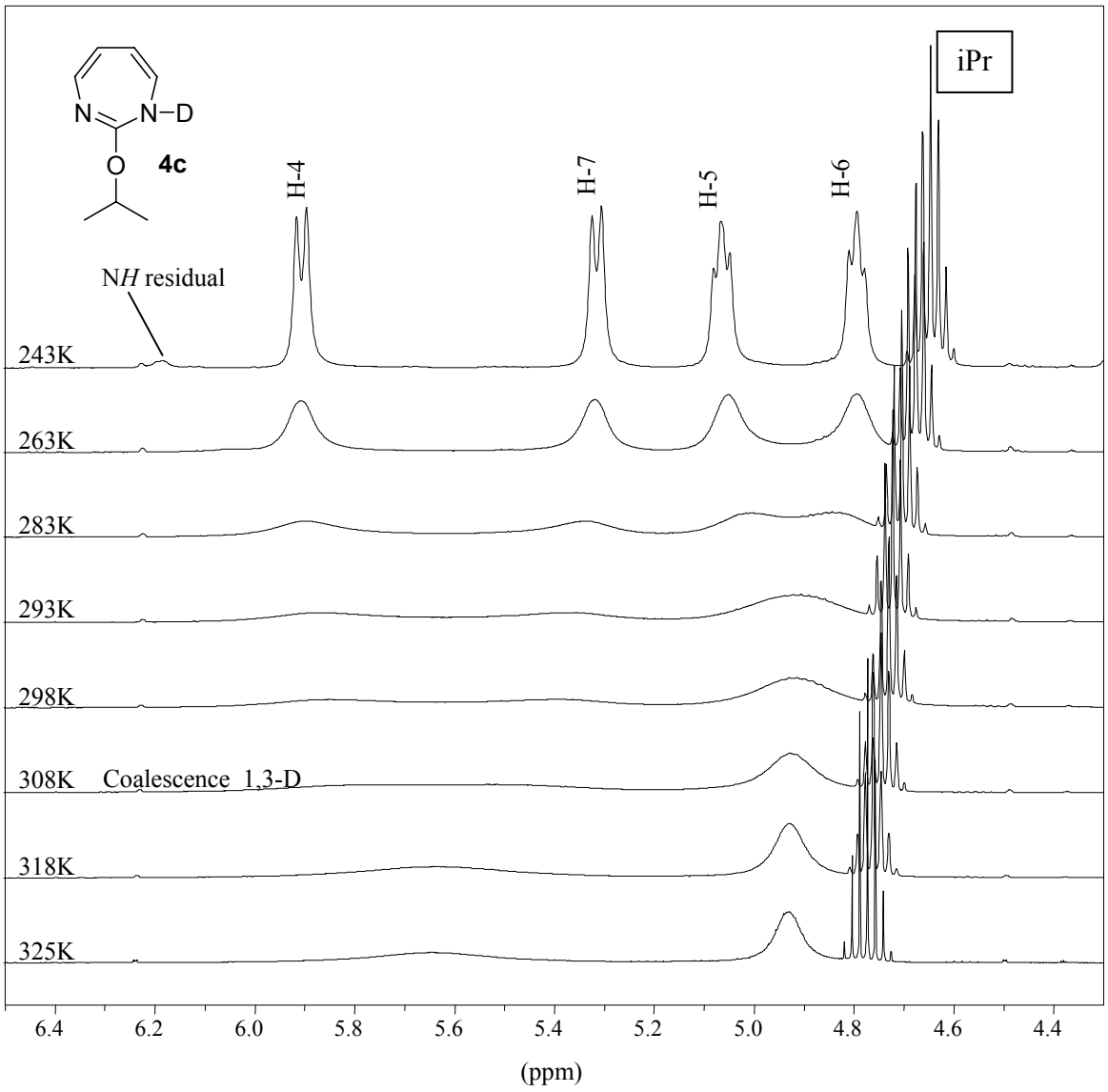

Fig. S2. Coalescence experiment on **4c** in acetone/D_2O as a function of temperature. Coalescence temperature 308 K for H4/H7. Note: H7 has been simplified to a doublet due to the exchange of H for D on N1.

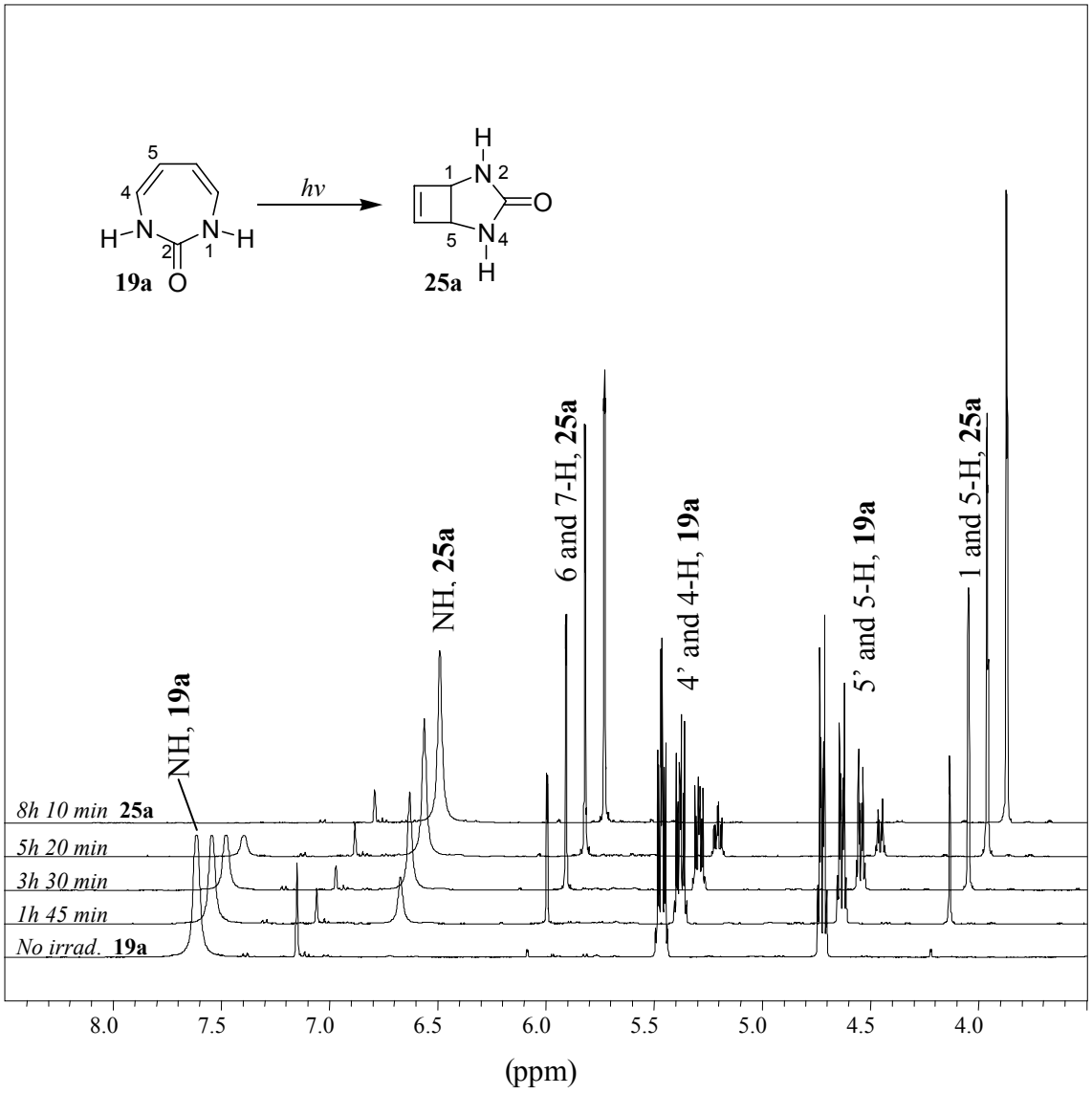

Fig. S3. ^{1}H NMR spectra of the conversion of **19a** to **25a** (400 MHz, benzene-d_6/DMSO-d_6)

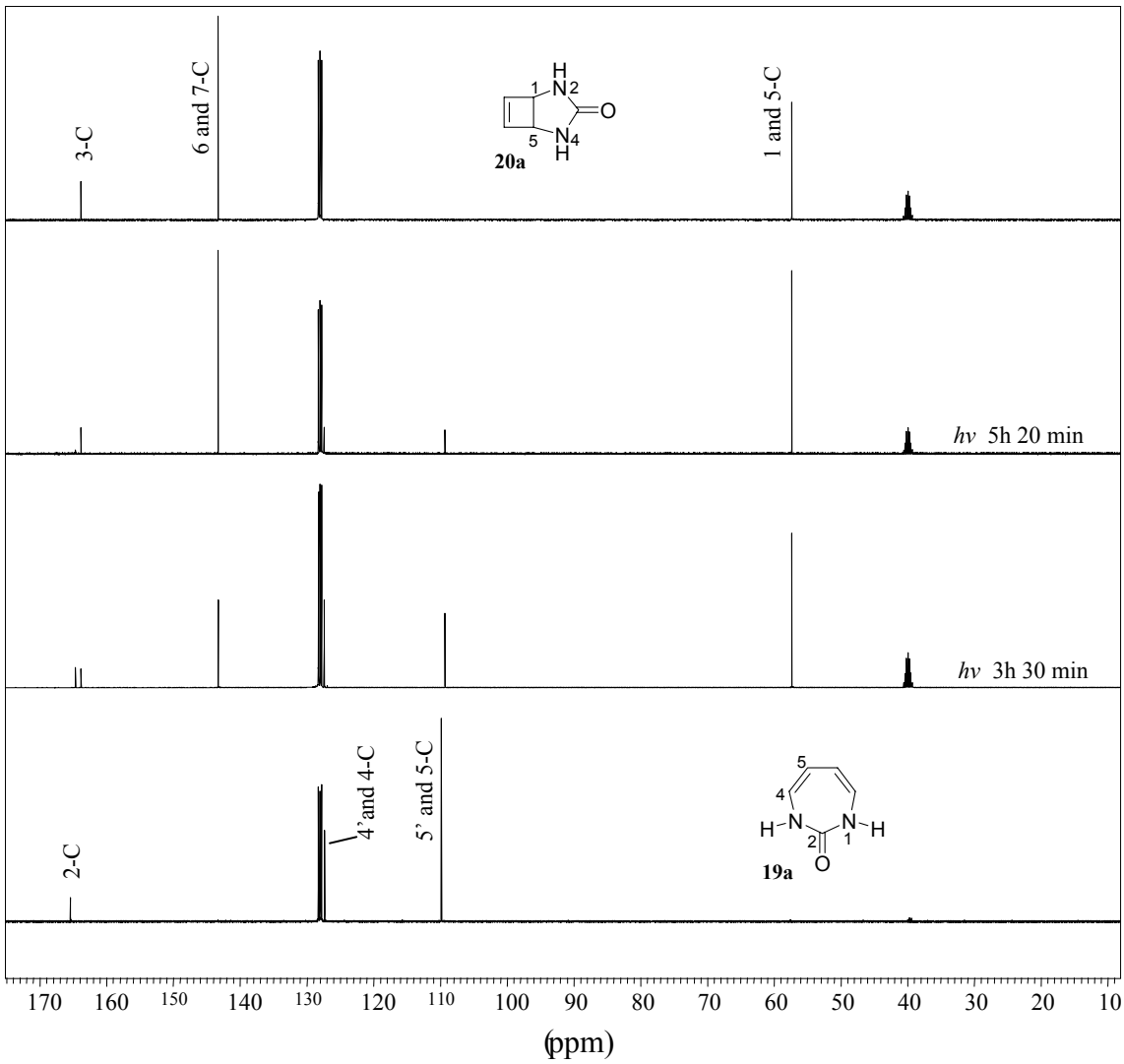

Fig. S4. ^{13}C NMR spectra of the phototransformation of **19a** (bottom) to **20a** (top) (100 MHz, benzene-d_6/DMSO-d_6)

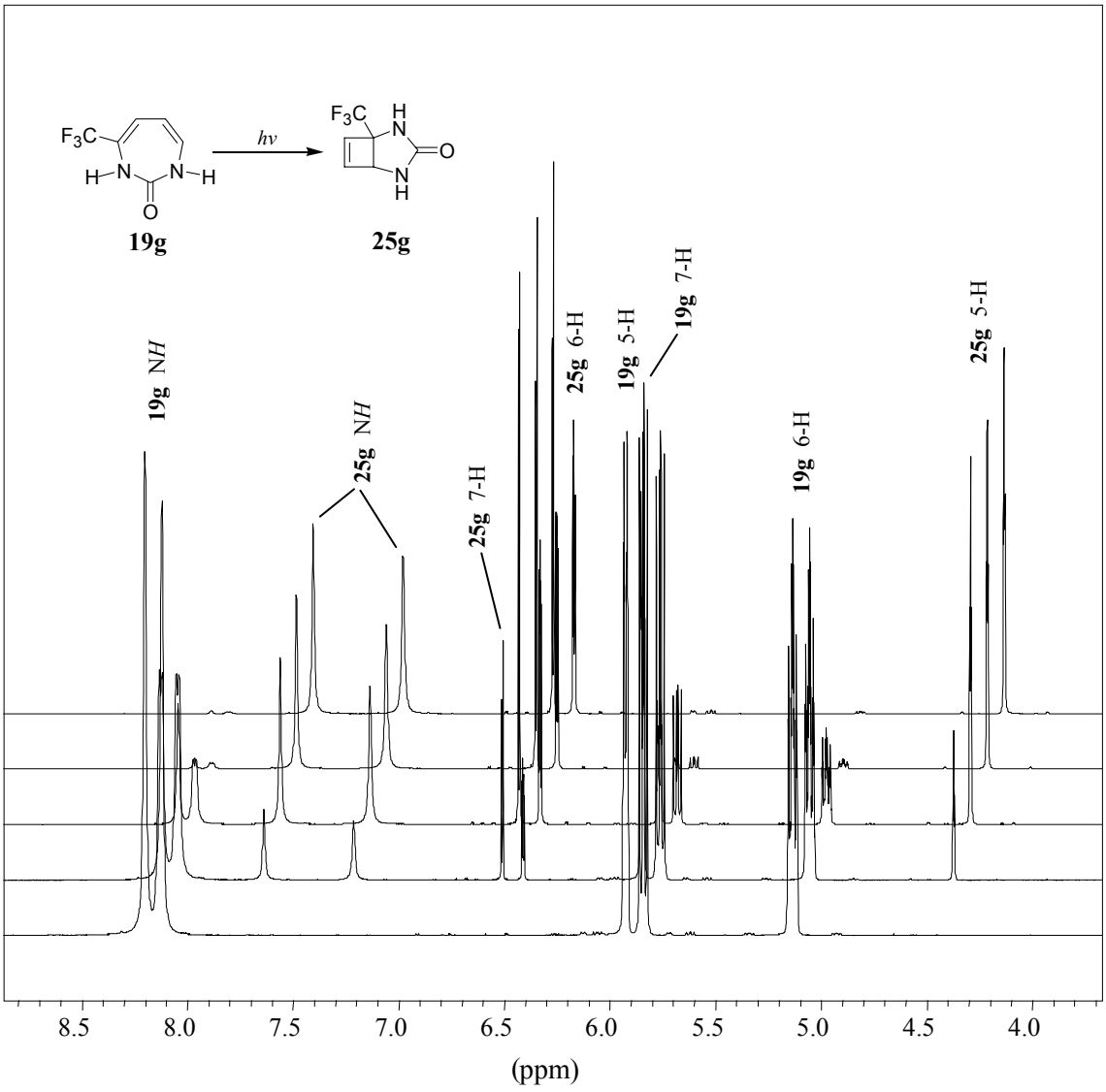

Fig. S5. ^{1}H NMR spectra showing phototransformation of **19g** to **25g** (400 MHz, DMSO-d_6).

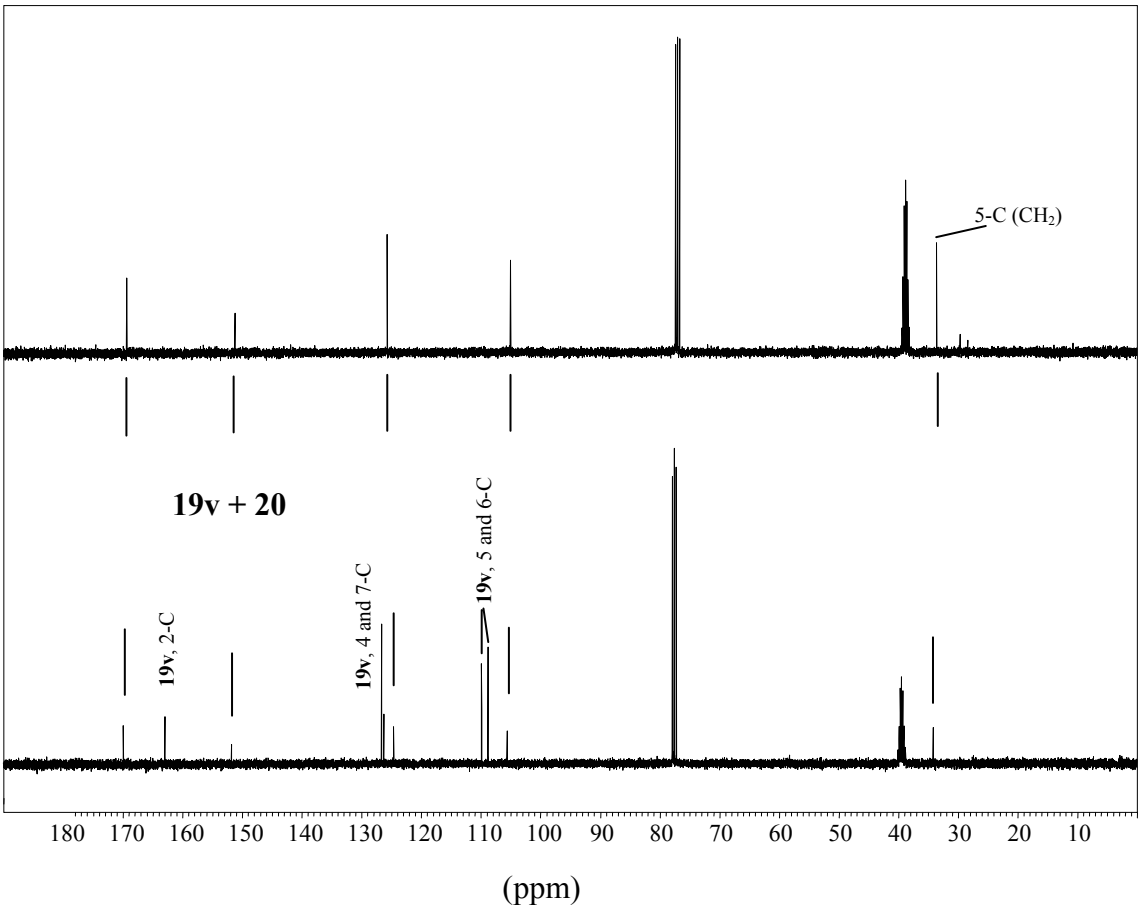

Fig. S6. ^{13}C NMR spectra of the conversion of **19v** to **20** (100 MHz, $CDCl_3$/DMSO-d_6/D_2O). Bottom: **19v** and **20** after 3 h in the NMR tube. Top: **20** as the only product after an additional 2 h.

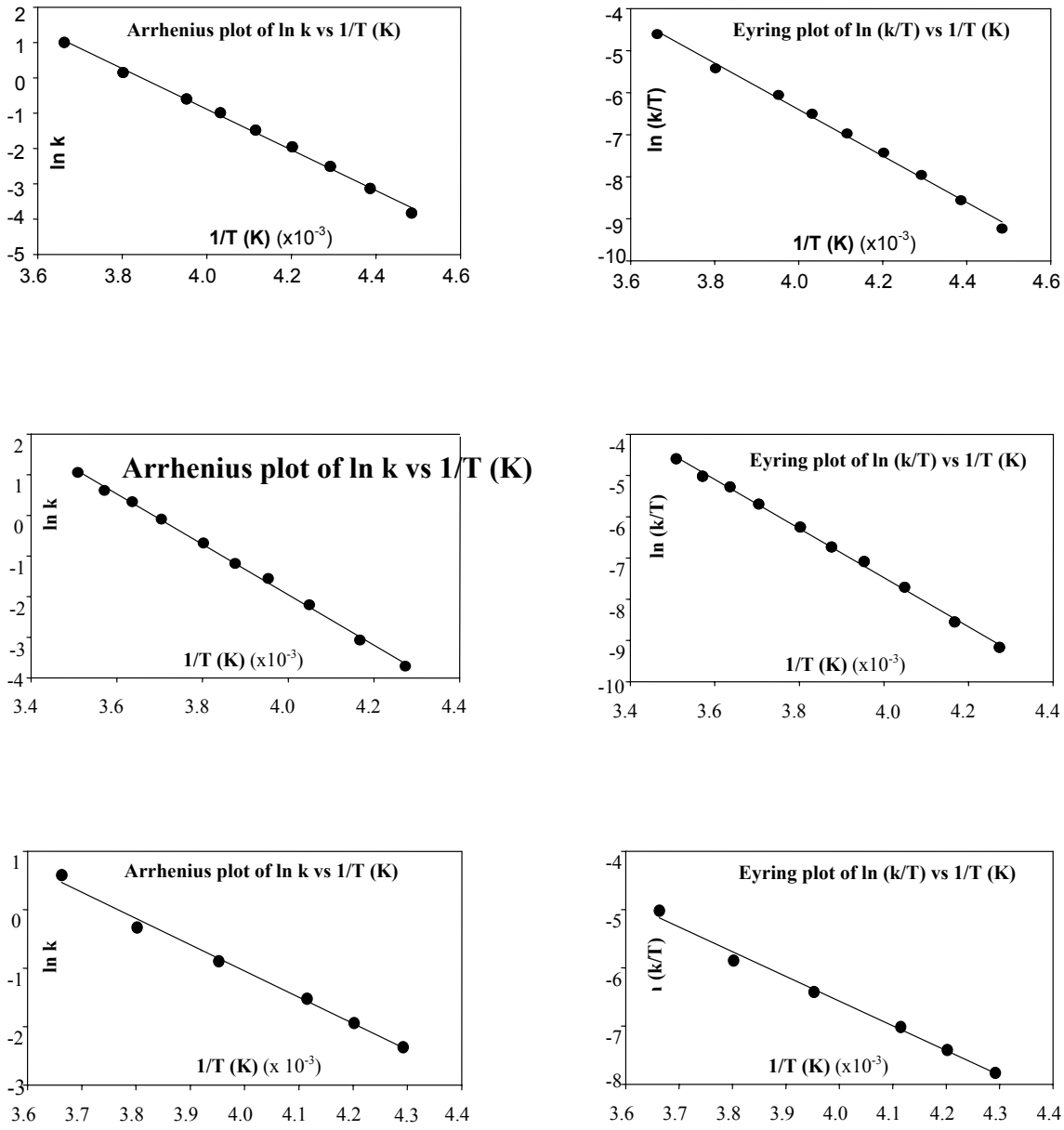

Fig. S7 Top: Arrhenius and Eyring plots for 2-isopropoxy-1*H*-1,3-diazepine **4c** in acetone–d_6. Intercept, slope: (left) 22.13, -5.75x10^3, (right) 15.71, -5.53x10^3. Middle: plots for **4c** in methanol–d_4. Intercept, slope: (left) 22.88, -6.21x10^3, (right) 16.33, -5.95x10^3. Bottom: plots for 2-ethoxy-1*H*-1,3-diazepine **4b** in acetone-d_6. Intercept, slope: (left) 16.94, -4.49x10^3, (right) 10.41, -4.24x10^3.

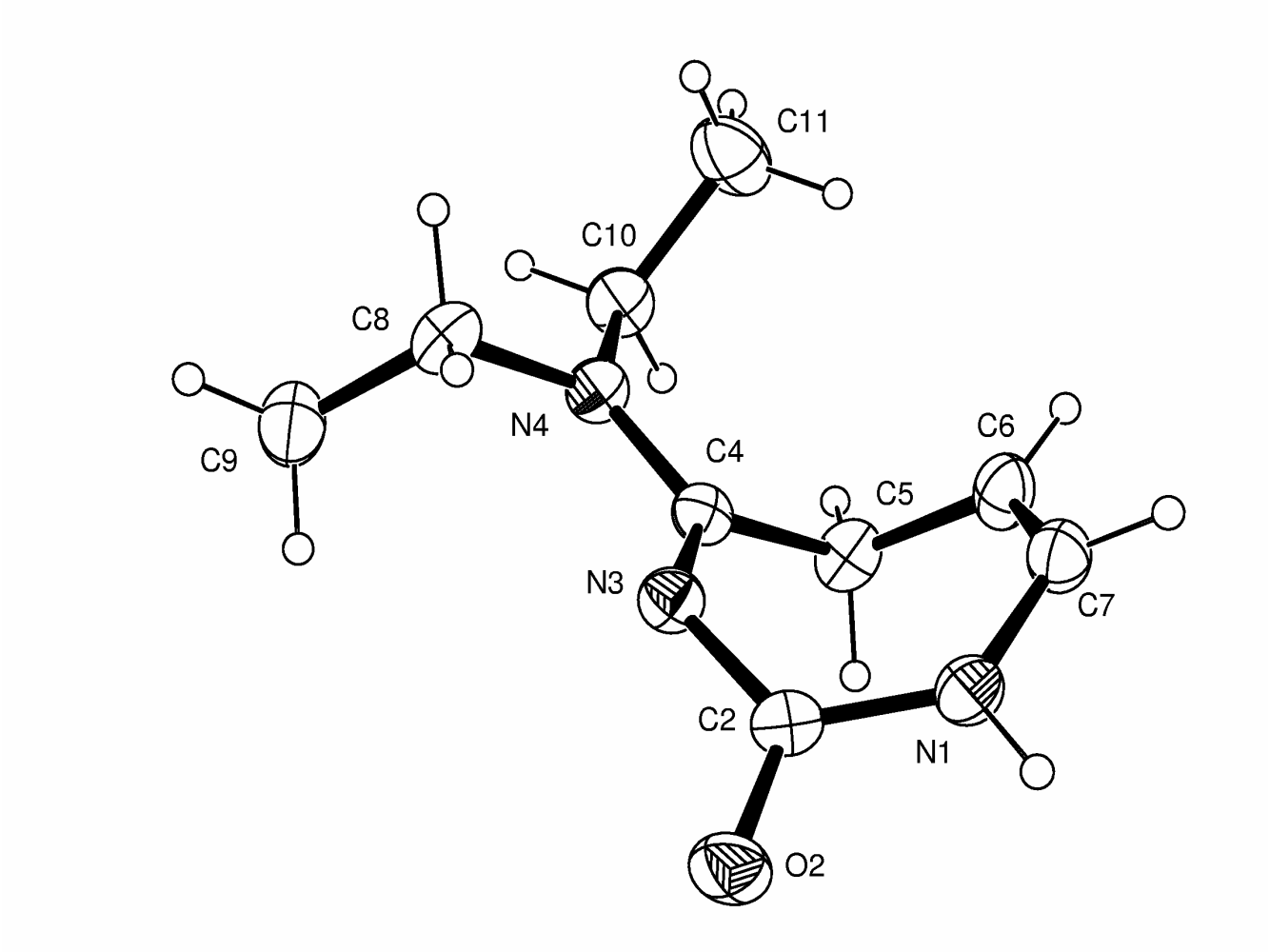

Fig. S8. ORTEP view of compound **22bB** (30% ellipsoids)

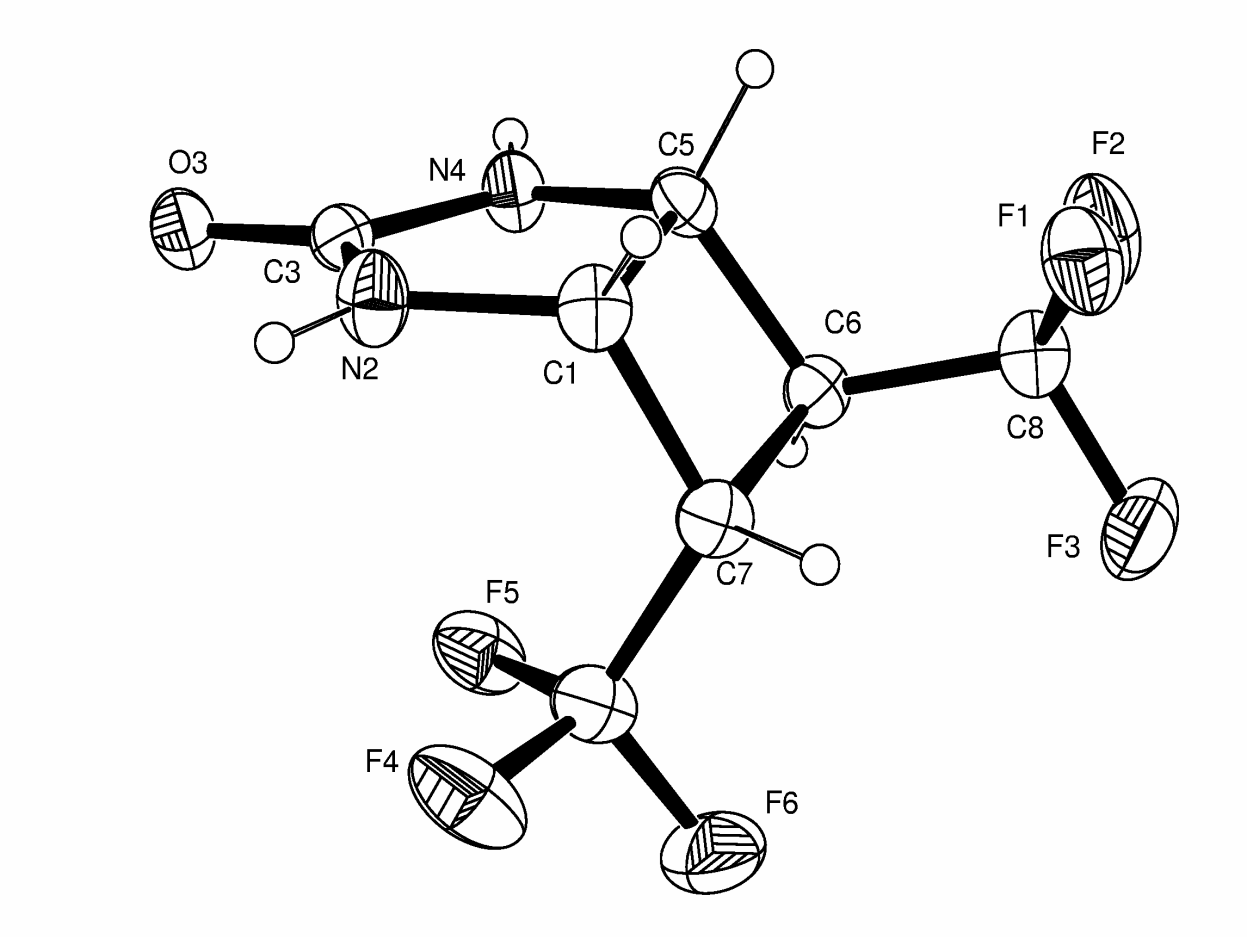

Fig. S9 ORTEP view of compound **26** (racemic)(30% ellipsoids)

Table S1. Bond lengths [Å] and angles [°] for **4k**.

C(2)-N(3)	1.275(3)
C(2)-O(2)	1.327(3)
C(2)-N(1)	1.382(3)
C(4)-C(5)	1.325(4)
C(4)-N(3)	1.396(3)
C(5)-C(9)	1.486(4)
C(5)-C(6)	1.487(4)
C(6)-C(7)	1.328(4)
C(6)-C(10)	1.488(4)
C(7)-N(1)	1.395(3)
C(8)-O(2)	1.444(3)
C(9)-F(2)	1.325(4)
C(9)-F(3)	1.330(4)
C(9)-F(1)	1.332(4)
C(10)-F(4)	1.317(4)
C(10)-F(5)	1.320(4)
C(10)-F(6)	1.333(4)

N(3)-C(2)-O(2)	122.7(2)
N(3)-C(2)-N(1)	127.0(2)
O(2)-C(2)-N(1)	110.30(19)
C(5)-C(4)-N(3)	130.0(2)
C(4)-C(5)-C(9)	118.6(3)
C(4)-C(5)-C(6)	121.7(2)
C(9)-C(5)-C(6)	119.4(3)
C(7)-C(6)-C(5)	121.3(2)
C(7)-C(6)-C(10)	118.0(3)
C(5)-C(6)-C(10)	120.7(2)
C(6)-C(7)-N(1)	124.0(2)
F(2)-C(9)-F(3)	105.8(3)
F(2)-C(9)-F(1)	105.7(3)
F(3)-C(9)-F(1)	105.8(3)
F(2)-C(9)-C(5)	114.2(3)
F(3)-C(9)-C(5)	111.8(3)
F(1)-C(9)-C(5)	112.9(3)

F(4)-C(10)-F(5)	105.7(3)
F(4)-C(10)-F(6)	107.3(3)
F(5)-C(10)-F(6)	104.1(3)
F(4)-C(10)-C(6)	112.7(2)
F(5)-C(10)-C(6)	113.9(3)
F(6)-C(10)-C(6)	112.5(3)
C(2)-N(1)-C(7)	117.42(19)
C(2)-N(3)-C(4)	119.2(2)
C(2)-O(2)-C(8)	117.7(2)

Table S2. Bond lengths [Å] and angles [°] for **26**

C(1)-N(2)	1.429(4)
C(1)-C(5)	1.551(4)
C(1)-C(7)	1.555(4)
C(3)-O(3)	1.231(4)
C(3)-N(4)	1.344(4)
C(3)-N(2)	1.351(4)
C(5)-N(4)	1.442(4)
C(5)-C(6)	1.543(4)
C(6)-C(8)	1.489(5)
C(6)-C(7)	1.549(4)
C(7)-C(9)	1.488(5)
C(8)-F(2)	1.325(4)
C(8)-F(3)	1.331(4)
C(8)-F(1)	1.339(4)
C(9)-F(4)	1.328(4)
C(9)-F(6)	1.331(4)
C(9)-F(5)	1.339(4)

N(2)-C(1)-C(5)	103.5(2)
N(2)-C(1)-C(7)	119.3(3)
C(5)-C(1)-C(7)	89.5(2)
O(3)-C(3)-N(4)	125.8(3)
O(3)-C(3)-N(2)	125.6(3)
N(4)-C(3)-N(2)	108.6(3)
N(4)-C(5)-C(6)	116.2(3)

N(4)-C(5)-C(1)	101.5(2)
C(6)-C(5)-C(1)	89.9(2)
C(8)-C(6)-C(5)	113.9(3)
C(8)-C(6)-C(7)	112.5(3)
C(5)-C(6)-C(7)	90.1(2)
C(9)-C(7)-C(6)	116.1(3)
C(9)-C(7)-C(1)	118.3(3)
C(6)-C(7)-C(1)	89.5(2)
F(2)-C(8)-F(3)	107.4(3)
F(2)-C(8)-F(1)	106.3(3)
F(3)-C(8)-F(1)	106.4(3)
F(2)-C(8)-C(6)	112.9(3)
F(3)-C(8)-C(6)	112.2(3)
F(1)-C(8)-C(6)	111.2(3)
F(4)-C(9)-F(6)	107.5(3)
F(4)-C(9)-F(5)	106.5(3)
F(6)-C(9)-F(5)	105.3(3)
F(4)-C(9)-C(7)	112.2(3)
F(6)-C(9)-C(7)	111.4(3)
F(5)-C(9)-C(7)	113.5(3)
C(3)-N(2)-C(1)	112.1(3)
C(3)-N(4)-C(5)	113.1(3)

Table S3. . Bond lengths [Å] and angles [°] for **22bB**

C(2)-O(2)	1.245(2)
C(2)-N(3)	1.360(2)
C(2)-N(1)	1.371(3)
C(4)-N(3)	1.307(2)
C(4)-N(4)	1.340(2)
C(4)-C(5)	1.494(3)
C(5)-C(6)	1.496(3)
C(6)-C(7)	1.315(3)
C(7)-N(1)	1.390(3)
C(8)-N(4)	1.459(3)
C(8)-C(9)	1.506(3)
C(10)-N(4)	1.466(2)

C(10)-C(11)	1.511(3)

O(2)-C(2)-N(3)	120.35(18)
O(2)-C(2)-N(1)	117.08(17)
N(3)-C(2)-N(1)	122.17(17)
N(3)-C(4)-N(4)	118.73(18)
N(3)-C(4)-C(5)	121.41(17)
N(4)-C(4)-C(5)	119.86(16)
C(4)-C(5)-C(6)	107.85(16)
C(7)-C(6)-C(5)	120.42(19)
C(6)-C(7)-N(1)	124.84(19)
N(4)-C(8)-C(9)	112.07(18)
N(4)-C(10)-C(11)	111.99(17)
C(2)-N(1)-C(7)	128.84(17)
C(4)-N(3)-C(2)	124.50(17)
C(4)-N(4)-C(8)	121.20(16)
C(4)-N(4)-C(10)	123.65(17)
C(8)-N(4)-C(10)	115.15(16)

Hydrogen bonds [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(2)#1	0.87(2)	2.04(2)	2.906(2)	174(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+2,-z+1

Preparative and compound characterization data

3,6-Bis(trifluoromethyl)-2-hydrazinopyridine

A 2.5 g (0.01 mol) portion of 3,6-bis(trifluoromethyl)-2-chloropyridine was dissolved in 15 ml of ethanol and hydrazine hydrate was added dropwise with stirring. The reaction was exothermic, and the solution turned yellow after addition of the first few drops. After a large excess of hydrazine had been added (*ca*. 15 ml), the mixture was gently heated (70 - 80 ^{o}C)

until no starting material was detected on a tlc plate (silica gel, dichloromethane, *ca*. 1 h). The reaction was then worked up in a usual way[2] to give 2.5 g of the hydrazinopyridine as white solid, mp 95 –96 °C, yield 98 %. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.87 (d, 1 H, 5-H, $J_{4,5}$ = 7.6 Hz), 7.08 (d, 1 H, 4-H, $J_{4,5}$ = 7.6 Hz), 6.68 (br s, 1 H, N*H*), 4.10 (br s, 2 H, NH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 156.1 (2-C), 149.5 (q, 6-C, $J_{C,F}$ = 34.8 Hz), 136.6 (q, 5-C, $J_{C,F}$ = 5.2 Hz), 123.2 (q, CF_3, $J_{C,F}$ = 270.3 Hz), 120.7 (q, CF_3, $J_{C,F}$ = 272.7 Hz), 111.5 (q, 3-C, $J_{C,F}$ = 33.2 Hz), 108.9 (q, 4-C, $J_{C,F}$ = 3.2 Hz); IR (KBr) 3344.9 and 3328.0 br (N*H*), 1619.2 s, 1593.0 m, 1517.9 m, 1457.3 m, 1384.5 w, 1365.9 m, 1315.9 s, 1285.5 m, 1257.8 w, 1196.6 m, 1179.4 m, 1162.2 m, 1115.3 vs, 1033.9 s, 999.6 w, 967.1 w, 928.3 w, 826.1 s, 788.8 w, 748.9 w cm^{-1}. Anal. calcd. for $C_7H_5F_6N_3$: C, 34.30; H, 2.06; N, 17.14 %. Found: C, 33.29; H, 1.90; N, 16.80 %. Despite repeated recrystallization and microanalyses this compound gave low carbon results. However, the compound appeared to be pure when examined by other spectroscopic methods (NMR, IR).

2-Azido-3,6-bis(trifluoromethyl)pyridine 1Aq

This compound was prepared according to the general procedure in ref. 2 and purified by distillation (rt., 0.5 –0.1 mbar), the compound exists largely in the azido form; clear oil; yield 73 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, 1 H, 5-H, $J_{4,5}$ = 7.9 Hz), 7.50 (d, 1 H, 4-H, $J_{4,5}$ = 7.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3 (2-C), 150.1 (q, 6-C, $J_{C,F}$ = 36.0 Hz), 138.1 (q, 5-C, $J_{C,F}$ = 4.0 Hz), 121.7 (q, CF_3, $J_{C,F}$ = 272.0 Hz), 120.3 (q, CF_3, $J_{C,F}$ = 273.1 Hz), 118.6 (q, 3-C, $J_{C,F}$ = 36.0 Hz), 115.7 (q, 4-C, $J_{C,F}$ = 3.3 Hz); IR (neat) 2145.3 vs , 1598.4 s, 1474.4 m, 1407.0 s, 1400.0 s, 1349.3 m, 1316.1 s, 1293.3 m, 1266.1 w, 1156.0 s, 1149.5 vs, 1129.2 vs, 1115.4 s, 1064.4 w, 1037.7 s, 925.0 w, 847.0 m, 787.6 w, 752.0 m, 706.1 w, 657.7 w cm^{-1}. Anal. calcd. for $C_7H_2F_6N_4$: C, 32.83; H, 0.79; N, 21.88 %. Found: C, 32.72; H, 0.85; N, 21.86 %.

2-Methoxy-1*H*-1,3-diazepine 4a. All data have been published.[1a] For the calculated ^{1}H and ^{13}C NMR data see ref. 12.

2-Ethoxy-1*H*-1,3-diazepine 4b

Purified either by flash column chromatography (silica gel 100, ethyl acetate / hexane, 10:1) or distillation (Kugelrohr, 50-70 ^{o}C, 0.5 mbar). Bright yellow crystalline solid, decomposes rapidly in air at room temperature, mp 37-38 ^{o}C. Yield: 72 %; ^{1}H NMR (acetone-d_6, 301 K, 400 MHz) δ 5.96 (d, 1 H, 4-H, $J_{4,5}$ = 8.00), 5.36 (dd, 1 H, 7-H, $J_{6,7}$ = 7.62, $J_{1,7}$ = 5.88 Hz), 5.10 (dd, 1 H, 5-H, $J_{4,5}$ = 8.00, $J_{5,6}$ = 5.12 Hz), 4.80 (dd, 1 H, 6-H, $J_{5,6}$ = 5.12, $J_{6,7}$ = 7.62), 5.80 br (1 H, NH), 3.95 (q, 2 H, O$CH_2$$CH_3$, ^{3}J = 7.08 Hz), 0.92 (t, 3 H, O$CH_2$$CH_3$, ^{3}J = 7.08 Hz); all protons were identified by homonuclear decoupling experiments; ^{13}C (acetone-d_6, 301 K, 100 MHz) δ 155.8 (2-C), 139.0 (4-C), 132.3 (7-C), 116.6 (5-C), 108.9 (6-C), 63.3 (OCH_2CH_3), 14.1 (OCH_2CH_3); all ^{13}C nuclei were identified from 2-D HMBC experiments; IR (KBr) 3379.2 br, 3032.0 w, 2982.9 w, 1673.1 vs, 1632.0 br vs, 1448.9 m, 1429.1 m, 1384.7 m, 1367.8 m, 1357.3 m, 1236.9 vs, 1137.0 w, 1093.7 w, 1048.4 m, 1017.2 m, 891.0 w, 780.3 w, 720.5 m, 695.4 m cm^{-1}; MS (EI) *m/z* 138 (M^{+}, 50 %), 124 (14), 110 (100),109 (14), 82 (43), 81 (41), 67 (34), 66 (16), 55 (25), 48 (13), 28 (49), 27 (17). HRMS, calcd. for $^{12}C_7H_{10}N_2O$: 138.078764; found: 138.079131. Anal. calcd. for $C_7H_{10}N_2O$: C, 60.83; H, 7.30; N, 20.28 %. Found: C, 60.63; H, 7.34; N, 20.10 %.

2-Propoxy-1*H*-1,3-diazepine 4c

Purified by distillation (Kugelrohr, 50-70 ^{o}C / 0.5 mbar). Yellow crystalline solid, unstable, rapidly decomposes in air at room temperature, mp 38-39 ^{o}C. Yield: 53 %; ^{1}H NMR (acetone-d_6, 301 K, 400 MHz) δ 5.97 (d, 1 H, 4-H, $J_{4,5}$ 8.08), 5.70 br (1 H, NH), 5.36 (ddd, 1 H, 7-H, $J_{6,7}$ 6.68, $J_{1,7}$ 6.70, $J_{5,7}$ 0.88 Hz), 5.08 (dd, 1 H, 5-H, $J_{4,5}$ 8.08, $J_{5,6}$ 8.04 Hz), 4.81 (m,

1 H, 6-H, $J_{5,6}$ 8.04, $J_{6,7}$ 6.68,), 4.80 (sep, 1 H, O*i*Pr, *J* 6.20 Hz), 1.16 (d, 6 H, O*i*Pr, *J* 6.20 Hz); ^{13}C NMR (acetone-d_6, 301 K, 100 MHz) δ 155.7 (2-C), 140.3 (4-C), 132.4 (7-C), 117.1 (5-C), 112.3 (6-C), 71.2 (O*i*Pr), 21.9 (O*i*Pr); IR (KBr) 3361.1 br, 2981.7 m, 1672.4 vs, 1630.7 vs, 1468.4 m, 1448.4 m, 1426.0 m, 1384.7 m, 1372.9 m, 1237.1 vs, 1180.6 w, 1145.3 w, 1110.1 s, 962.1 w, 918.2 w, 846.0 w, 777.7 w, 694.4 m cm^{-1}; MS (EI) *m/z* 152 (M^+, 54 %), 110 (100), 82 (34), 81 (17), 67 (18), 66 (5), 55 (16), 54 (5), 27 (2). HRMS, calcd. for $^{12}C_8H_{12}N_2O$: 152.094414; found: 152.094390. Anal. calcd. for $C_8H_{12}N_2O$: C, 63.13; H, 7.95; N, 18.41 %. Found: C, 62.96; H, 8.10; N, 18.33 %.

2-Methoxy-4-trifluoromethyl-1*H*-1,3-diazepine 4(5)e

Purified by Kugelrohr distillation (40-50 °C, 10^{-4} mbar); orange-red oil. Yield: 92 % from **7A**, 47 % from **6T**. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.84 (d, 1 H, 5-H, $J_{5,6}$ = 5.4 Hz), 5.45 (dd, 1 H, 7-H, $J_{1,6}$ = 5.1 Hz, $J_{6,7}$ = 7.8 Hz), 4.94 (dd, 1 H, 6-H, $J_{5,6}$ = 5.4 Hz, $J_{6,7}$ = 7.8 Hz), 4.80 (br, 1 H, N-H), 3.73 (s, 3 H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0 (2-C), 138.4 (q, 4-C, $J_{C,F}$ = 31.6 Hz), 132.9 (7-C), 121.2 (q, CF_3, $J_{C,F}$ = 272.2 Hz), 117.3 (5-C), 109.8 (6-C), 56.1 (OCH_3); the assignments were confirmed by a 2-D HMBC spectrum; for the calculated ^{1}H and ^{13}C NMR spectra see ref. 12; IR (CCl_4) 3409 m, 2997 m, 2976 w, 2953 w, 1688 vs, 1654 m, 1625 w, 1598 w, 1567 w, 1460 m, 1433 w, 1407 m, 1372 m, 1348 w, 1309 vs, 1251 vs, 1232 m, 1179 vs, 1134 vs, 1059 m, 1014 m, 963 m, 863 w, 786 w cm^{-1}; MS (EI) *m/z* 192 (M^+, 100 %), 178 (7), 177 (18), 173 (5), 165 (5), 160 (6), 157 (12), 150 (14), 149 (9), 141 (6), 136 (6), 135 (52), 116 (14), 115 (16), 108 (56), 107 (9), 100 (11), 95 (7), 80 (19), 77 (12), 69 (24), 58 (12), 53 (10), 52 (9), 39 (7). HRMS, calcd. for $^{12}C_7H_7F_3N_2O$: 192.05105; found: 192.05122. Anal. calcd. for $C_7H_7F_3N_2O$: C, 43.76; H, 3.67; N, 14.58 %. Found: C, 43.81; H, 3.65; N, 14.29 %.

2-Methoxy-4-trifluoromethyl-1*H*-1,3-diazepine 4(5)f

Purified by Kugelrohr distillation (40-50 ^{o}C, 10^{-4} mbar); orange-red oil. Yield: 89 % from **7A**. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.87 (d, 1 H, 5-H, $J_{5,6}$ = 5.8 Hz), 5.41 (dd, 1 H, 7-H, $J_{1,6}$ = 5.1 Hz, $J_{6,7}$ = 7.4 Hz), 4.97 (dd, 1 H, 6-H, $J_{5,6}$ = 5.8 Hz, $J_{6,7}$ = 7.4 Hz), 4.98 (br, 1 H, N-H), 4.15 (q, 2 H, O*CH*$_2$CH$_3$, $J_{CH2,CH3}$ = 7.0 Hz), 1.12 (t, 3 H, OCH$_2$*CH*$_3$, $J_{CH2,CH3}$ = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7 (2-C), 138.9 (q, 4-C, $J_{C,F}$ = 33.3 Hz), 132.2 (7-C), 123.1 (q, CF_3, $J_{C,F}$ = 273.0 Hz), 118.1 (5-C), 111.2 (6-C), 66.3 (O*CH*$_2$CH$_3$), 12.7 (OCH$_2$*CH*$_3$); IR (neat film) 3408 m, 2981 m, 2956 w, 1683 vs, 1653 s, 1624 m, 1581 w, 1462 s, 1423 w, 1407 s, 1371 m, 1344 w, 1308 vs, 1257 vs, 1173 vs, 1124 vs, 1059 m, 1015 s, 961 m, 893 w, 866 w, 822 w, 779 w cm^{-1}; MS (EI) *m/z* 206 (M^+, 100 %), 191 (5), 177 (18), 156 (12), 150 (18), 149 (10), 135 (52), 115 (17), 114 (19), 109 (56), 107 (9), 80 (22), 77 (14), 70 (24), 69 (13), 57 (10), 52 (14), 51 (7). HRMS, calcd. for $^{12}C_8H_9F_3N_2O$: 206.0667; found: 206.0665. Anal. calcd. for $C_8H_9F_3N_2O$: C, 46.61; H, 4.40; N, 13.59 %. Found: C, 46.87; H, 4.15; N, 13.29 %.

2-*tert*-Butoxy-4-trifluoromethyl-1*H*-1,3-diazepine 4(5)g

Purified by Kugelrohr distillation (40-50 ^{o}C, 10^{-4} mbar); as orange-red solid, mp 108-109 ^{o}C. Yield: 94 % from **7A**; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.84 (dq, 1 H, 5-H, $J_{5,6}$ = 5.8, $J_{H,F}$ = 1.1 Hz), 5.47 (dd, 1 H, 7-H, $J_{6,7}$ = 7.6, $J_{1,7}$ = 4.7 Hz), 4.98 (tm, 1 H, 6-H, $J_{5,6}$ = 5.8, $J_{6,7}$ = 7.6 Hz), 4.67 (br s, 1 H, N-H), 1.46 (s, 9 H, 3 x CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.2 (2-C), 139.3 (q, 4-C, $J_{C,F}$ = 34 Hz), 132.1 (7-C), 121.7 (CF_3, $J_{C,F}$ = 272 Hz), 116.8 (5-C), 109.5 (6-C), 86.3 (*t*-butoxy), 26.2 (3 x CH_3); MS (EI) *m/z* 234 (M^+, 6%), 178 (100), 159 (6), 135 (9), 108 (4), 81 (19), 57 (38), 41 (36), 39 (13). HRMS, calcd. for $^{12}C_{10}H_{13}F_3N_2O$: 234.09790; found: 234.09795. Anal. calcd. for $C_{10}H_{13}F_3N_2O$: C, 51.28; H, 5.59; N, 11.96 %. Found: C, 51.24; H, 5.66; N, 11.72 %.

5(6)-Trifluoromethyl-2-methoxy-1*H*-1,3-diazepine 4(5)h

Purified by distillation (Kugelrohr, ~100 ^{o}C / 0.1 – 0.5 mbar) or flash column chromatography (silica gel 100, hexane/ethyl acetate, 80 : 20). Red oil, yield 72 % from **8T**, 69 % from **9T**. ^{1}H NMR ($CDCl_3$, 200 MHz): isomer ratio **4h/5h** = 2:1; major isomer **4h** (5-CF_3): δ 6.72 (s, 1 H, 4-H), 5.51 (t, 1 H, 7-H, $J_{1,7}$ = 6.4, $J_{6,7}$ = 8.1 Hz), 5.06 (d, 1 H, 6-H, $J_{6,7}$ = 8.1 Hz), 4.80 (br, 1 H, N-H), 3.74 (s, 3 H, OCH_3); minor isomer **5h** (6-CF_3): δ 6.22 (d, 1 H, 4-H, $J_{4,5}$ = 8.3 Hz), 5.96 (d, 1 H, 7-H, $J_{1,7}$ = 7.3 Hz), 5.27 (d, 1 H, 5-H, $J_{4,5}$ = 8.3 Hz), 4.80 (br, 1 H, N-H), 3.71 (s, 3 H, OCH_3); all protons were identified by homonuclear decoupling experiments; ^{13}C NMR ($CDCl_3$, 50 MHz) both isomers: δ 156.1, 154. 4 (2-C), 143.2 br, 141.4 (q, $J_{C,F}$ = 3.1 Hz), 132.3, 134.7 (q, $J_{C,F}$ = 3.2 Hz), 121.7 (q, CF_3, $J_{C,F}$ = 272 Hz), 121.3 (q, CF_3, $J_{C,F}$ = 273 Hz), 118.7 (q, $J_{C,F}$ = 34 Hz), 116.3 (q, $J_{C,F}$ = 34 Hz), 111.1 br, 107.7 (q, 6-C, $J_{C,F}$ = 3.6 Hz), 57.8, 58.1 (OCH_3); IR (neat) 3261 br, 2996 w, 1680 vs, 1641 vs, 1613 vs, 1508 m, 1462 s, 1371 m, 1317 vs, 1282 vs, 1152 vs, 1114 vs, 1065 s, 1013 m, 936 w, 914 w, 891 w , 802 w cm^{-1}; MS (EI) *m/z* 192 (M^+, 100 %), 171 (5), 178 (6), 177 (22), 164 (5), 160 (6), 155 (12), 151 (18), 149 (7), 138 (13), 137 (54), 118 (11), 116 (11), 108 (24), 105 (52), 101 (7), 95 (9), 84 (27), 74 (12), 70 (14), 56 (6), 54 (10), 52 (5), 41 (7). HRMS, calcd. for $^{12}C_7H_7F_3N_2O$: 192.05105; found: 192.0511. Anal. calcd. for $C_7H_7F_3N_2O$: C, 43.76; H, 3.67; N, 14.58 %. Found: C, 43.52; H, 3.49; N, 14.32 %.

5(6)-Trifluoromethyl-2-ethoxy-1*H*-1,3-diazepine 4(5)i

Purified by distillation (Kugelrohr, ~100 ^{o}C / 0.1 – 0.5 mbar) or by flash column chromatography (silica gel 100, hexane/ethyl acetate 80 ; 20). Red oil, yield 74 % from **8T**. ^{1}H NMR ($CDCl_3$, 200 MHz) major isomer **4i**: δ 6.85 (s, 1 H, 4-H), 5.55 (dd, 1 H, 7-H, $J_{1,7}$ = 7.3, $J_{6,7}$ = 8.1 Hz), 5.10 (d, 1 H, 6-H, $J_{6,7}$ = 8.1 Hz), 4.80 (br, 1 H, N-H), 4.22 (q, 2 H, OCH_2CH_3), 1.31 (t, 3 H, OCH_2CH_3); minor isomer **5i**: δ 6.18 (d, 1 H, 4-H, $J_{4,5}$ = 8.2 Hz),

5.96 (d, 1 H, 7-H, $J_{1,7}$ = 7.2 Hz), 5.33 (d, 1 H, 5-H, $J_{4,5}$ = 8.2 Hz), 4.80 (br, 1 H, N-H); 4.18 (q, 2 H, O*CH*$_2$CH$_3$), 1.29 (t, 3 H, OCH$_2$*CH*$_3$); ^{13}C NMR ($CDCl_3$, 50 MHz) both isomers: δ 157.2, 154. 8 (2-C), 142.4 br, 142.1 (q, $J_{C,F}$ = 3.7 Hz), 133.7, 134.3 (q, $J_{C,F}$ = 3.5 Hz), 122.8 (q, CF_3, $J_{C,F}$ = 274 Hz), 122.2 (q, CF_3, $J_{C,F}$ = 274 Hz), 117.9 (q, $J_{C,F}$ = 32 Hz), 116.1 (q, $J_{C,F}$ = 33 Hz), 110.5 br, 108.9 (q, 6-C, $J_{C,F}$ = 4.7 Hz), 65.3, 64.9 (O*CH*$_2$CH$_3$), 14.2, 14.9 (OCH$_2$*CH*$_3$); IR (neat film) 3265 br, 2992 w, 2965 w, 2954 w, 1682 vs, 1640 vs, 1613 vs, 1505 m, 1497 m, 1464 s, 1412 w, 1370 m, 1318 vs, 1282 vs, 1150 vs, 1117 vs, 1072 s, 1021 s, 1015 m, 967 w, 938 w, 918 w, 878 w , 812 w cm^{-1}; MS (EI) *m/z* 206 (M^+, 46 %), 192 (14), 178 (100), 177 (18), 164 (5), 163 (7), 157 (6), 150 (18), 149 (20), 148 (26), 136 (34), 135 (64), 130 (20), 123 (44), 116 (47), 108 (37), 104 (14), 102 (12), 95 (9), 89 (10), 84 (21), 75 (15), 69 (21), 54 (20), 52 (10), 44 (7). HRMS, calcd. for $^{12}C_8H_9F_3N_2O$: 206.06670; found: 192.0511. Anal. calcd. for $C_8H_9F_3N_2O$: C, 46.61; H, 4.40; N, 13.59 %. Found: C, 46.79; H, 4.38; N, 14.56 %. Despite repeated Kugelrohr distillation this compound gave low / high nitrogen analyses (*ca*. 1 % deviation). However, this compound appears to be pure by spectroscopic criteria (NMR, IR, MS).

5,6-Bis(trifluoromethyl)-2-ethoxy-1*H*-1,3-diazepine 4l

Purified by Kugelrohr distillation (50-60 ^{o}C, 0.1 –0.5 mbar). Orange crystalline solid, mp 80 – 81 ^{o}C. Yield: 60 %. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.11 (q, 1 H, 4-H, $J_{H,F}$ = 1.70 Hz), 6.42 (br d, 1 H, 7-H, $J_{1,7}$ = 6.80 Hz) 5.33 (br, 1 H, N-*H*), 4.25 (q, 2 H, O*CH*$_2$CH$_3$, $J_{CH2,CH3}$ = 7.1 Hz);), 1.29 (t, 3 H, OCH$_2$*CH*$_3$, $J_{CH2,CH3}$ = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 158.2 (2-C), 144.4 (q, 4-C, $J_{C,F}$ = 6.6 Hz), 138.8 (q, 7-C, $J_{C,F}$ = 6.2 Hz), 121.5 (q, CF_3, $J_{C,F}$ = 272 Hz), 121 (q, CF_3, $J_{C,F}$ = 272 Hz), 115.3 (q, 5-C or 6-C $J_{C,F}$ = 31.2 Hz), 114.2 (q, 6-C or 5-C, $J_{C,F}$ = 32 Hz), 63.0 (O*CH*$_2$CH$_3$), 13.2 (OCH$_2$*CH*$_3$); MS (EI) *m/z* 274 (M^+, 59 %), 255 (M-F, 9), 247 (6), 246 (73), 227 (16), 226 (12), 212 (6), 209 (6), 207 (17), 204 (8), 203 (63), 199 (15), 191 (14), 184 (100), 176 (24), 171 (14), 164 (7), 153 (9), 149 (17), 148 (9), 122 (16), 121 (10),

114 (9), 112 (27), 84 (55), 69 (23), 56 (13). HRMS, calcd. for $^{12}C_9H_8N_2F_6O$: 274. 0559; found: 274.0535. Anal. calcd. for $C_9H_8N_2F_6O$: C, 39.43; H, 2.94; N, 10.22 %. Found: C, 39.77; H, 3.04; N, 10.13 %.

4,6-Bis(trifluoromethyl)-2-methoxy-1*H*-1,3-diazepine 4(5)m

Purified by distillation (Kugelrohr, 40-60 ^{o}C, 0.5-0.1 mbar). Soft, orange crystalline solid, mp 39-40 ^{o}C, unstable in air, stable in solutions. Yield: 95%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.04 (d, 1 H, 7-H, $J_{1,7}$= 7.3), 5.79 (s, 1 H, 5-H), 5.13 (br s, 1 H, N-*H*; vanishes on addition of D_2O), 3.76 (s, 3 H, OCH_3); the assignments were confirmed by homonuclear decoupling experiments; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.3 (2-C), 139.5 (q, 4-C, $J_{C,F}$ = 32.3 Hz), 136.5 (q, 7-C, $J_{C,F}$ = 6.7 Hz), 122.8 (q, CF_3, $J_{C,F}$ = 270.9 Hz), 120.6 (q, CF_3, $J_{C,F}$ = 272.9 Hz), 112.8 (q, 6-C, $J_{C,F}$ = 31.6 Hz), 112.6 (m, 5-C); 57.2 (OCH_3); IR (KBr) 3241.4 br (N*H*), 3108.8 w, 2965.8 w, 1703.3 s, 1665.3 m, 1642.6 m,1495.3 m, 1467.3 w, 1452.7 w, 1444.5 w, 1402.6 m, 1373.2 w, 1283 vs, 1219.8 w, 1199.1 m, 1181.6 m, 1148.6 vs, 1122.8 vs, 1106.5 vs, 1053.0 w, 1009.4 s, 906.4 m, 885.7 w, 843.5 m, 744.4 w, 723.5 m, 712.3 m, 675.7 w, 637.8 w, 627.3 w cm^{-1}; HRMS, calcd. for $^{12}C_8H_6N_2F_6O$: 260.0384; found: 260.0384. Anal. calcd. for $C_8H_6N_2F_6O$: C, 36.94; H, 2.32; N, 10.77 %. Found: C, 36.76; H, 2.32; N, 10.71 %.

4,6-Bis(trifluoromethyl)-2-ethoxy-1*H*-1,3-diazepine 4(5)n

Purified by distillation (Kugelrohr, 40-60 ^{o}C, 0.5-0.1 mbar). Soft, yellow-orange crystalline solid, unstable in air, stable in solutions. Yield 93 %, mp 42-43 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.04 (d, 1 H, 7-H, $J_{1,7}$= 7.3; collapses to s on addition of D_2O), 5.80 (s, 1 H, 5-H), 5.03 (br s, 1 H, N-*H*, disappears on addition of D_2O), 4.19 (q, 2 H, O*CH*$_2$CH$_3$ $J_{CH2,CH3}$ = 6.98 Hz), (t, 3 H, OCH$_2$*CH*$_3$ $J_{CH2,CH3}$ = 6.98 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.6 (2-C), 139.7 (q, 4-C, $J_{C,F}$ = 32.3 Hz), 136.4 (q, 7-C, $J_{C,F}$ = 6.7 Hz), 123.0 (q, CF_3, $J_{C,F}$ = 270.9 Hz),

121.5 (q, CF_3, $J_{C,F}$ = 272.9 Hz), 112.9 (q, 6-C, $J_{C,F}$ = 30.9 Hz), 112.6 (m, 5-C); IR (KBr) 3220.9 br (N*H*), 3092.1 w, 3001.3 w, 2954.7 w, 1697.1 s, 1667.2 m, 1628.9 m, 1480.6 m, 1404.8 w, 1395.5 w, 1372.8 w, 1291.8 vs, 1218.8 w, 1181.1 vs, 1166.6 vs, 1141.2 s, 1111.1 vs, 1084.9 w, 1048.7 w, 1013.7 m, 990.1 m, 923.3 m, 903.1 m, 884.4 w, 856.5 m, 844.9 m, 748.5 w, 727.4 m, 677.5 m, 641.0 w, 625.3 w cm^{-1}; HRMS, calcd. for $^{12}C_9H_8N_2F_6O$: 274.0524; found: 274.0547. Anal. calcd. for $C_9H_8N_2F_6O$: C, 39.43; H, 2.94; N, 10.22 %. Found: C, 39.43; H, 2.97; N, 10.06 %.

4,6-Bis(trifluoromethyl)-2-*iso*propoxy-1*H*-1,3-diazepine 4(5)o

Purified by distillation (Kugelrohr, 40-60 ^oC, 0.5-0.1 mbar). Soft, yellow-orange crystalline solid, mp 46-47 ^oC, unstable in air, stable in solutions. Yield 95 %. ^1H NMR (DMSO-d_6, 400 MHz) δ 7.93(d, 1 H, 1-H, $J_{1,7}$= 7.2), 6.07 (d, 1 H, 7-H, $J_{1,7}$ = 7.2), 5.62 (s, 1 H, 5-H), 4.81 (sep, 1 H, O*CH*$(CH_3)_2$ $J_{CH,CH3}$ = 6.16 Hz), 1.21(d, 6 H, OCH(*CH₃)₂* $J_{CH,CH3}$ = 6.16 Hz); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 158.3 (2-C), 140.5 (q, 7-C, $J_{C,F}$ = 6.0 Hz), 138.5 (q, 4-C, $J_{C,F}$ = 31.0 Hz), 123.5 (q, CF_3, $J_{C,F}$ = 271.0 Hz), 120.5 (q, CF_3, $J_{C,F}$ = 268 Hz), 111.7 (q, 5-C, $J_{C,F}$ = 2.0 Hz), 109.0 (q, 6-C, $J_{C,F}$ = 30.0 Hz), 71.4 (*i*Pr), 22.3 (*i*Pr); IR (KBr) 3210.1 br (N*H*), 3086 w, 2990.7 w, 2946.3 w, 1697.6 s, 1668.7 m, 1639.0 m, 1477.6 m, 1403.9 w, 1394.1 w, 1377.3 w, 1343.1 s, 1292.2 vs, 1273.8 s, 1219.2 w, 1187.9 s, 1180.4 s, 1164.7 s, 1138.5 s, 1112.4 vs, 1040.9 m, 992.6 m, 928.5 m, 905.0 m, 855.2 m, 831.5 w, 749.5 w, 727.3 m, 678.9 m, 641.1 w, 625.8 w cm^{-1}; HRMS, calcd. for $^{12}C_{10}H_{10}N_2F_6O$: 288.0695; found: 288.0698. Anal. calcd. for $C_{10}H_{10}N_2F_6O$: C, 41.68; H, 3.50; N, 9.72 %. Found: C, 41.49; H, 3.60; N, 9.72 %.

4,6-Bis(trifluoromethyl)-2-*tert*-butoxy-1*H*-1,3-diazepine 4(5)p

Purified by distillation (Kugelrohr, 40-50 ^{o}C, 0.5-0.1 mbar). Soft, yellow-orange crystalline solid, unstable in air, stable in solutions. Yield 89 %, mp 64-65 ^{o}C. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.51 (br, 1 H, 1-H), 6.09 (d, 1 H, 7-H, $J_{1,7}$ = 7.1 Hz), 5.60 (s, 1 H, 5-H), 1.45 (s, 9 H, O(CH_3)$_3$); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 158.1 (2-C), 140.5 (q, 7-C, $J_{C,F}$ = 5.8 Hz), 138.5 (q, 4-C, $J_{C,F}$ = 31.3 Hz), 123.0 (q, CF_3, $J_{C,F}$ = 272.0 Hz), 121.5 (q, CF_3, $J_{C,F}$ = 269 Hz), 111.5 (q, 5-C, $J_{C,F}$ = 2.6 Hz), 109.0 (q, 6-C, $J_{C,F}$ = 31.1 Hz), 85.8 (*t*-butoxy), 26.4 (*t*-butoxy); IR (KBr) 3214 br (N*H*), 3084 w, 2990 w, 2942w, 1695 s, 1668 m, 1637 w, 1534 w, 1474 m, 1403 w, 1397 w, 1465 w, 1342 s, 1291 vs, 1274 s, 1263 s, 1219 w, 1188 s, 1182 s, 1165 s, 1154 m, 1137 s, 1115 vs, 1042 m, 928 m, 917 w, 902 m, 855 m, 833 w, 753 w, 734 m, 656 m, 632 w cm^{-1}. HRMS, calcd. for $^{12}C_{11}H_{12}N_2F_6O$: 302.08538; found: 302.08524. Anal. calcd. for $C_{11}H_{12}N_2F_6O$: C, 43.72; H, 4.00; N, 9.27 %. Found: C, 43.44; H, 3.68; N, 8.92 %.

4,7-Bis(trifluoromethyl)-2-methoxy-1*H*-1,3-diazepine 4q

Purified by distillation (Kugelrohr, 80-100 ^{o}C / 0.1 – 0.5 mbar). Red-orange oil, yield 93 %. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.97 (d m, 1 H, 5-H, $J_{5,6}$ 5.9 Hz), 5.79 (m, 1 H, 6-H), 5.12 (br, 1 H, N*H*), 3.87 (s, 3 H, OCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 156.5 (2-C), 142.4 (q, 4-C, $J_{C,F}$ = 31 Hz), 130.3 (q, 7-C, $J_{C,F}$ = 32 Hz), 121.1 (q, CF_3, $J_{C,F}$ = 273 Hz), 119.2 (q, CF_3, $J_{C,F}$ = 273 Hz), 113.5 (q, 5-C, $J_{C,F}$ = 5 Hz), 113.1 (q, 6-C, $J_{C,F}$ = 4 Hz), 56.3 (OCH_3); IR (neat) 3400 br, 2985 w, 1682 m, 1662 vs, 1622 s, 1453 m, 1374 m, 1351 m, 1327 m, 1308 s, 1259 vs, 1203 vs, 1135 s, 1077 s, 1060 m, 1021 m, 962 w, 956 w, 840 w , 811 w, 787 w, 712 w, 691 w, cm^{-1}; MS (EI) *m/z* 260 (M^+, 21 %), 245 (52), 230 (8), 220 (5), 211 (6), 187 (17), 183 (6), 175 (18), 162 (14), 150 (11), 149 (40), 104 (15), 95 (11), 90 (18), 88 (33), 86 (10), 78 (27), 77 (12), 75 (12), 74 (19), 73 (100), 69 (34) 64 (8), 50 (11). HRMS, calcd. for $^{12}C_8H_6N_2F_6O$: 260.0384; found: 260.0386. Anal. calcd. for $C_8H_6N_2F_6O$: C, 36.94; H, 2.32; N, 10.77 %. Found: C, 36.62; H, 2.16; N, 10.94 %.

4,7-Bis(trifluoromethyl)-2-ethoxy-1*H*-1,3-diazepine 4r

Purified by distillation (Kugelrohr, 80-100 ^{o}C / 0.1 – 0.5 mbar). Red-orange oil, yield 90 %. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.99 (d m, 1 H, 5-H, $J_{5,6}$ 5.9 Hz), 5.77 (m, 1 H, 6-H, couples to N*H*), 5.02 (br, 1 H, N*H*, vanishes on addition of D_2O, couples to 6-H), 4.25 (q, 2 H, O*CH*$_2$CH$_3$, $J_{CH2,CH3}$ = 7.1 Hz), 1.29 (t, 3 H, OCH$_2$*CH*$_3$, $J_{CH2,CH3}$ = 7.1 Hz); the assignments were confirmed by homonuclear decoupling experiments; ^{13}C NMR ($CDCl_3$, 50 MHz) δ 156.7 (2-C), 142.0 (q, 4-C, $J_{C,F}$ = 30.5 Hz), 130.5 (q, 7-C, $J_{C,F}$ = 32.3 Hz), 120.7 (q, CF_3, $J_{C,F}$ = 273 Hz), 118.5 (q, CF_3, $J_{C,F}$ = 273 Hz), 113.5 (q, 5-C, $J_{C,F}$ = 4.5 Hz), 113.1 (q, 6-C, $J_{C,F}$ = 4.5 Hz), 66.4 (O*CH*$_2$CH$_3$), 13.8 (OCH$_2$*CH*$_3$); IR (neat) 3403 br, 2989 w, 1685 m, 1658 vs, 1458 m, 1368 m, 1340 m, 1306 vs, 1256 vs, 1198 vs, 1130 vs, 1072 s, 1047 m, 1022 m, 966 w, 937 w, 831 w cm^{-1}; MS (EI) *m/z* 274 (M^+, 13 %), 246 (52), 239 (4), 231 (8), 227 (5), 219 (6), 207 (7), 203 (17), 184 (12), 183 (10), 176 (13), 164 (12), 151 (7), 150 (13), 149 (45), 103 (14), 102 (10), 96 (9), 90 (10), 88 (8), 87 (30), 86 (13), 79 (27), 75 (12), 74 (10), 73 (100), 69 (46) 64 (7), 62 (8), 61 (6). HRMS, calcd. for $^{12}C_9H_8N_2F_6O$: 274. 0559; found: 274.0533. Anal. calcd. for $C_9H_8N_2F_6O$: C, 39.43; H, 2.94; N, 10.22 %. Found: C, 39.55; H, 2.98; N, 10.00 %.

4,7-Bis(trifluoromethyl)-2-*t*butoxy-1*H*-1,3-diazepine 4s

Purified by distillation (ca 30-40 ^{o}C, 0.5-0.1 mbar) to afford **127c** as orange needles, mp 40-41 ^{o}C. Yield: 420 mg, 67 %; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.95 (dq, 1 H, 5-H, $J_{5,6}$ = 5.8, $J_{CF3,5}$ = 1.1 Hz), 5.78 (m, 1 H, 6-H, $J_{5,6}$ = 5.8, $J_{CF3,6}$ = 1.2 Hz, this proton was identified as 6-H, since the multiplet at 5.78 ppm simplified to doublet of quintets on irradiation of the N*H* proton at 4.85 ppm), 4.85 (br s, 1 H, N*H*), 0.91 (s, 9 H, 3 x CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.3 (2-C), 142.2 (q, 7-C, $J_{CF3,7-C}$ 32 Hz), 130 (q, 4-C, $J_{CF3,4-C}$ 33 Hz), 120.8 and

119.2 (2 x CF_3), 113 (m, 5- and 6-C), 85.1 (*t*-butoxy), 27.6 (3 x CH_3); IR (CCl_4) 3396.9 w, 2984.0 w, 1683.8 w, 1652.1 s, 1549.0 m, 1446.5 w, 1369.6 m, 1339.8 m, 1304.0 vs, 1267.3 m, 1199.0 vs, 1182.2 m, 1140.5 vs, 1075.3 m, 1041.5 m, 968.8 m, 937.9 m cm^{-1}; MS: due to facile elimination of *iso*butene, either in the neutral or the cation, the mass spectrum was identical with that of **19s**. Anal. calcd. for $C_{11}H_{12}F_6N_2O$: C, 43.72; H, 4.00; N, 9.27 %. Found: C, 43.10; H, 3.95; N, 9.11 %. Despite repeated Kugelrohr distillations this compound gave low carbon analyses (ca. 1 % deviation), presumably due to its thermal sensitivity. However, this compound appears to be pure by spectroscopic criteria (NMR, IR).

1-Benzoyl-2-ethoxy-1*H*-1,3-diazepine 12b

50 mg (0.4 mmol) of the 2-ethoxy-1*H*-1,3-diazepine **4(5)b** was dissolved in 2 ml of dry dichloromethane, cooled in an ice bath, and 40 mg (1.2 molar equiv.) of dry pyridine was added dropwise while stirring. To this mixture, 1.1 molar equiv. of freshly distilled benzoyl chloride was slowly added while the temperature of the solution was kept below +5 ^oC. The resulting reaction mixture was stirred for one hour at zero to +5 ^oC and then stored in a fridge overnight. Work up: 20 ml of ice water was added to the reaction mixture, which was then extracted with diethyl ether (3 x 20 ml). The ether layer was washed with brine, dried with $MgSO_4$, and evaporated to dryness. The crude product was purified by preparative TLC, followed by sublimation (90 ^oC, 0.5-0.1 mbar) to obtain 40 mg of **122a** as a white solid, mp 70-71 ^oC; yield: 51%. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.6-7.2 (m, 5 H, benz H), 6.77 (d, 1 H, 7-H, $J_{6,7}$ 8.0 Hz), 6.30 (d, 1 H, 4-H, $J_{4,5}$ 6.7 Hz), 5.9-5.9 (m, 2 H, 5 and 6-H), 3.84 (q, 2 H, OCH_2CH_3, $J_{CH2,CH3}$ 6.9 Hz), 0.75 (t, 3 H, OCH_2CH_3, $J_{CH2\,CH3}$ 6.9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.2 (CO), 145.2 (2-C), 137.8 (7-C), 134.9, 131.4, 128.3, 127.2 (benz-C), 125.6 (4-C), 120.8 (5 or 6-C), 116.0 (6 or 5-C), 65.7 (OEt), 13.1 (OEt). The proton and carbon-13 resonances were assigned using additional data obtained from DEPT-135 and 2D-HSQC

experiments. IR (KBr) 1687 vs, 1640 vs, 1618 vs, 1574 s, 1373 m, 1339 vs, 1264 m, 1217 m, 1115 w, 1067 m, 910 w, 792 w, 775 w, 717 m, 694 w, 677 m cm^{-1}; MS (EI) *m/z* (M^+, 22%), 137 (23), 109 (40), 105 (100), 81 (9), 77 (39), 67 (4), 66 (10), 51 (9). HRMS, calcd. for $^{12}C_{14}H_{14}N_2O_2$: 242.104979; found: 242.104225. Anal. calcd. for $C_{14}H_{14}N_2O_2$: C, 69.41; H, 5.83; N, 11.56. Found: C, 69.56; H, 5.87, N, 11.40 %.

1-Benzoyl-2-methoxy-4-trifluoromethyl-1*H*-1,3-diazepine 12e

950 mg (5.0 mmol) of the 2-methoxy-4(7)-trifluoromethyl-1*H*-1,3-diazepine **4(5)e** was dissolved in *ca*. 25 ml of dry THF in a 100 ml three neck round bottom flask and cooled to -75 to -80 ^oC. At this temperature, n-BuLi was added dropwise to the solution while stirring. To this mixture, freshly distilled benzoyl chloride (5.0 mmol; 0.7 g) in 15 ml of dry THF was slowly added. The resulting solution was stirred at this temperature for 1 h and then slowly allowed to warm to room temperature overnight. The volume of the crude reaction mixture was reduced under vacuum, ice water was added, and the residue extracted with diethyl ether (3 x 30 ml). After solvent evaporation, a pale yellow solid was collected and recrystallised from petroleum ether to afford clear plates, mp 58-59 ^oC, yield: 87%. ^1H NMR ($CDCl_3$, 200 MHz) δ 7.62-7.39 (m, 5 H, benz H), 6.50 (d, 1 H, 7-H, $J_{6,7}$ 7.1, $J_{5,7}$ 0.4 Hz), 6.48 (dq, 1 H, 5-H, $J_{5,6}$ 5.7, $J_{H,F}$ 1.1 Hz), 5.98 (tm, 1 H, 6-H), 3.52 (s, 3 H, OCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 167 (CO), 149 (2-C), 138 (q, 4-C, $J_{C,F}$ 32.9 Hz), 134, 132 (benz-C), 129 7 (7-C), 129, 127 (benz-C), 121 9 (q, CF_3, $J_{C,F}$ 273 Hz), 119 (6-C), 115 (q, 5-C, $J_{C,F}$ 4 Hz), 57.3 (OCH_3); IR (KBr) 2957 w, 1691 vs (CO), 1670 m, 1648 vs, 1631 vs, 1602 m, 1580 w, 1459 m, 1443 m, 1402 m, 1344 vs, 1306 vs, 1276 vs, 1229 s, 1187 s, 1157 s, 1126 vs, 1085 vs, 1029 m, 1019 m, 1002 m, 977 m, 943 m, 912 m, 868 m cm^{-1}; MS (EI) *m/z* (M^+, 5%), 191 (1), 122 (2), 107(2), 106 (8), 105 (100), 78 (3), 77 (35), 51 (8), 50 3). HRMS, calcd. for

$^{12}C_{14}H_{11}F_3N_2O_2$: 296.0759; found: 296.0778. Anal. calcd. for $C_{14}H_{11}F_3N_2O_2$: C, 56.76; H, 3.74; N, 9.45 %. Found: C, 56.96; H, 3.66; N, 9.29 %.

X-ray crystallographic data have been published.[1b]

1-Benzoyl-2-methoxy-5-trifluoromethyl-1*H*-1,3-diazepine 12h

5(6)-Trifluoromethyl-1*H*-1,3-diazepines **4(5)h** was treated with benzoyl chloride as described for **12e**. The crude product was purified by chromatography (silica gel 100, CH_2Cl_2 : hexane, 1:1) to obtain **12h** as a clear oil. Yield: 33 %. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.71-7.34 (m, 5 H, benz-H), 7.04 (s, 1 H, 4-H), 6.87 (d, 1 H, 7-H, $J_{6,7}$ 8.3 Hz), 5.94 (d, 1 H, 6-H, $J_{6,7}$ 8.3 Hz), 3.56 (s, 3 H, OC*H*$_3$); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 169.1 (CO), 151.2 (2-C), 139.8 (7-C), 133.9, 131.8, 128.1 and 127.4 (benz-C), 128.9 (q, 4-C, $J_{C,F}$ 6.2 Hz), 123.1 (q, 5-C, $J_{C,F}$ 32.8 Hz), 120.7 (CF_3, $J_{C,F}$ 271 Hz), 111.1 (q, 6-C, $J_{C,F}$ 2.9 Hz), 57.8 (O*C*H$_3$); IR (neat film) 3029 m, 2966 w, 1689 vs, 1644 vs, 1640 m, 1605 m, 1576 w, 1462 m, 1451 m, 1414 m, 1387 m, 1342 vs, 1327 vs, 1306 s, 1281 vs, 1226 s, 1191 s, 1161 s, 1129 vs, 1092 vs, 1027 m, 1021 m, 1009 w, 974 w, 922 m, 901 w, 867 m, 841 w, 797 m cm^{-1}; MS *m/z* 296 (M^+, 6 %), 281 (2), 123 (2), 106 (10), 105 (100), 78 (2), 77 (37), 51 (6), 50 (2); HRMS calcd. for $^{12}C_{14}H_{11}F_3N_2O_2$: 296.0759; found: 296.0764. Anal. calcd for $C_{14}H_{11}F_3N_2O_2$: C, 56.76; H, 3.74; N, 9.45 %. Found: C, 56.87; H, 3.49; N, 9.69 %.

1-Benzoyl-2-ethoxy-5-trifluoromethyl-1*H*-1,3-diazepine 12i

Yield: 27 %. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.65-7.39 (m, 5 H, benz-H), 7.00 (s, 1 H, 4-H), 6.91 (d, 1 H, 7-H, $J_{6,7}$ = 8.4 Hz), 5.91 (d, 1 H, 6-H, $J_{6,7}$ = 8.4 Hz), 3.89 (q, 2 H, OC*H*$_2$CH$_3$, $J_{CH2,CH3}$ = 7.0 Hz), 0.75 (t, 3 H, OCH$_2$*CH*$_3$, $J_{CH2,CH3}$ = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 168.2 (CO), 150.7 (2-C), 140.3 (7-C), 134.1, 130.8, 128.8 and 127.1 (benz-C), 128.5 (q, 4-C, $J_{C,F}$ = 6.4 Hz), 123.3 (q, 5-C, $J_{C,F}$ = 31.2 Hz), 120.4 (CF_3, $J_{C,F}$ = 271 Hz), 110.6 (q, 6-C, $J_{C,F}$ =

2.0 Hz), 66.1 (O*CH*$_2$CH$_3$), 13.4 (OCH$_2$*CH$_3$*); IR (neat film) 3031 m, 2984 m, 2961 w, 1697 vs, 1669 vs, 1629 m, 1602 w, 1584 m, 1553 w, 1471 m, 1448 m, 1410 m, 1384 w, 1357 vs, 1330 vs, 1303 s, 1287 vs, 1224 s, 1188 vs, 1158 s, 1129 vs, 1107 m, 1090 vs, 1033 m, 1019 m, 1001 m, 969 w, 957 w, 927 m, 906 w, 881 m, 857 w, 818 w, 778 m cm^{-1}; MS (EI) *m/z* 310 (M$^+$, 3%), 291 (1), 177 (2), 157 (2), 108 (5), 106 (7), 105 (100), 78 (2.1), 77 (30), 51 (4). Anal. calcd. for $C_{15}H_{13}F_3N_2O_2$: C, 58.07; H, 4.22; N, 9.03 %. Found: C, 58.21; H, 4.38; N, 9.02 %.

1-Benzoyl-4,6-bis(trifluoromethyl)-2-methoxy-1*H*-1,3-diazepine 12m

This compound was prepared from 4,6-bis(trifluoromethyl)-2-methoxy-1*H*-1,3-diazepine **4(5)m** following the procedure described for **12e**. Clear oil, purified by distillation (120 ^{o}C, 0.5-0.1 mbar). Yield: 20 %. ^{1}H NMR ($CDCl_3$ 200 MHz) δ 7.65-7.45 (m, 5 H, benz-H), 7.22 (q, 1 H, 7-H, $J_{H,F}$ = 1.5 Hz), 6.49 (s, 1 H, 5-H), 3.83 (s, 3 H, O*CH$_3$*); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 167.4 (CO), 150.6 (2-C), 140.5 (q, 4-C, $J_{C,F}$ = 33 Hz), 133.1 and 132.7 (benz-C), 132 2 (q, 7-C, $J_{C,F}$ = 5.4 Hz), 128.9 and 127.1 (benz-C), 122.5 (q, 7-C, $J_{C,F}$ = 32.2 Hz), 122.1 (q, CF_3, $J_{C,F}$ = 270 Hz), 120.7 (q, CF_3, $J_{C,F}$ = 271.3 Hz), 110.9 (m, 5-C), 58.1 (O*CH$_3$*); IR (KBr) 3032 m, 2989 w, 2932 w, 1702 vs, 1673 vs, 1652 vs, 1613 m, 1553 m, 1502 m, 1449 m, 1412 w, 1376 m, 1348 vs, 1322 s, 1304 s, 1260 vs, 1186 vs, 1132 s, 1169 m, 1154 s, 1078 m, 1034 w, 1010 m, 954 w, 921 m, 898 w, 876 m, 822 w, 782 w, 675 w cm^{-1}; MS (EI) *m/z* 364 (M$^+$, 49 %), 345 (5), 314 (11), 259 (26), 177 (8), 148 (10), 142 (12), 114 (14), 106 (43), 105 (100), 78 (8), 77 (57), 76 (5), 68 (9), 52 (5), 51 (19), 50 (5), 44 (7). HRMS, calcd. for $^{12}C_{15}H_{10}F_6N_2O_2$: 364.06465; found: 364.0643. Anal. calcd. for $C_{15}H_{10}F_6N_2O_2$: C, 49.46; H, 2.77; N, 7.69 %. Found: C, 49.67; H, 3.01; N, 7.87 %.

1-Benzoyl-6-chloro-2-ethoxy-4-trifluoromethyl-1*H*-1,3-diazepine 12x

This compound was prepared by benzoylation of the 6-chloro-2-ethoxy-4-trifluoromethyl-1*H*-1,3-diazepine **4(5)x** using the same procedure as applied for **12e**; yield: 31 %, mp 111-112 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.56-7.41 (m, 5 H, benz H), 6.66 (s, 1 H, 7-H), 6.45 (s, 1 H, 5-H), 4.00 (q, 2 H, OC*H*$_2$CH$_3$, $J_{CH2,CH3}$ 7.0 Hz), 0.77 (t, 3 H, OCH$_2$C*H*$_3$, $J_{CH2,CH3}$ 7.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.5 (CO), 150.1 (2-C), 139.0 (q, 4-C, $J_{C,F}$ 33 Hz), 133.8, 132.2 128.7 and 127.2 (benz.C), 125.7 (7-C), 125.3 (6-C), 120.8 (q, CF_3, $J_{C,F}$ 270 Hz), 116.7 (q, 5-C, $J_{C,F}$ 4.0 Hz), 65.8 (O*CH*$_2$CH$_3$), 13.1 (OCH$_2$*CH*$_3$); IR (KBr) 3064 m, 1678 vs, 1637 vs, 1603 w, 1473 w, 1449 m, 1410 w, 1369 m, 1342 vs, 1326 s, 1302 s, 1265 vs, 1192 vs, 1163 m, 1133 vs, 1089 m, 1029 w, 1012 m, 967 w, 916 m, 873 w, 843 m, 794 w cm^{-1}; MS (EI) *m/z* (M$^+$, 2%), 211(1), 176 (2), 148 (1), 142 (2), 114 (1), 106 (12), 105 (100), 78 (4), 77 (49), 76 (2), 69 (2), 52 (1), 51 (11), 50 (3). HRMS, calcd. for $^{12}C_{15}H_{12}ClF_3N_2O_2$: 344.0539; found: 344.0539. Anal. calcd. for $C_{15}H_{12}ClF_3N_2O_2$: C, 53.87; H, 3.39; N, 7.85 %. Found: C, 53.57; H, 3.61; N, 7.85 %.

1-Acetyl-2-ethoxy-1*H*-1,3-diazepine 13b

The same experimental procedure as for **12b** was used to obtain the 1-acetyl derivative **13b**. In this case, 140 mg (1.01 mmol) of **4(5)b** was treated with acetyl chloride to afford 120 mg of a clear oil (distilled at 80-90 °C/0.5-0.1 mbar). Yield: 66%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.68 (d, 1 H, 7-H, $J_{6,7}$ 8.2 Hz), 6.04 (d, 1 H, 4-H, $J_{4,5}$ 6.7 Hz), 5.95 (br, 1 H, 5-H), 5.79 (dd, 1 H, 6-H, $J_{6,7}$ 8.2 Hz) 4.26 (q, 2 H, OC*H*$_2$CH$_3$, $J_{CH2,CH3}$ 7.1 Hz), 2.04 (s, 3 H, CH_3), 1.30 (t, 3 H, OCH$_2$C*H*$_3$, $J_{CH2\ CH3}$ 7.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.4 (CO), 145.1 (2-C), 138.1 (7-C), 125.3 (4-C), 119.2 (5 or 6-C), 117.3 (6 or 5-C), 65.4 (OEt), 24.8 (CH_3), 13.3 (OEt). The proton and carbon-13 resonances were assigned using additional data obtained from DEPT-135 and 2D-HSQC experiments. IR (KBr) 2983 w, 1699 vs, 1639 vs, 1622 s, 1569 m, 1373 s, 1326 s, 1278 vs, 1214 s, 1116 w, 1081 m, 1051 m, 956 w, 885 w, 754 m,

668 w, 652 m cm^{-1}; MS (EI) *m/z* (M^+, 5%), 138 (11), 110 (15), 109 (8), 82 (6), 81 (8), 67 (9), 66 (7), 55 (4) 54 (3), 43 (100), 39 (3), 36 (22). HRMS, calcd. for $^{12}C_9H_{12}N_2O_2$: 180.089329; found: 180.090073. Anal. calcd for $C_9H_{12}N_2O_2$: C, 59.98; H, 6.71; N, 15.54 %. Found: C, 59.38; H, 6.63, N, 15.83 %.

1-Benzoyl-2-methoxy-4-trifluoromethyl-4,5,6,7-tetrahydro-1*H*-1,3-diazepine 14

Catalytic hydrogenation of **12e**: palladium was added into a pressure vessel containing 100 ml of absolute methanol and activated under hydrogen pressure (*ca*. 2 atm) for 25 minutes. **12e** (510 mg; 1.7 mmol) was then added to this solution, and the mixture was kept under pressure of hydrogen for 14 h while shaking. The resulting solution was filtered, and the volume was reduced in vacuum. The solid residue was crystallized from petroleum ether/diethyl ether (1:1) to afford 450 mg of **14** as clear, white cubes, mp 102-103 ^oC; yield: 87%. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.55-7.40 (m, 5 H, benz-H), 4.53 (m, 1 H, 7-H), 3.93 (m, 1 H, 4-H), 3.30 (s, 3 H, OCH_3), 2.95 (m, 1 H, 7-H), 2.10 (m, 1 H, 5-H), 1.95 (m, 1 H, 6-H), 1.85 (m, 1 H, 6-H), 1.58 (m, 1 H, 5-H); ^{13}C NMR ($CDCl_3$, δ MHz) δ 169.2 (CO), 156.3 (2-C), 135.7, 131.1, 128.3 and 126.5 (benz-C), 125.8 (q, CF_3, $J_{C,F}$ 278.3 Hz), 60.0 (q, 4-C, $J_{C,F}$ 29.6 Hz), 54.9 (OCH_3), 42.9 (7-C), 29.8 (q, 5-C, $J_{C,F}$ 1.3 Hz), 25.8 (6-C); IR (KBr) 2949 w, 1692 s, 1659 vs, 1578 w, 1507 w, 1438 m, 1381 m, 1358 m, 1328 s, 1283 s, 1263 m, 1241 m, 1212 m, 1174 s, 1145 m, 1118 s, 1055 w, 1028 w, 992 w, 953 w, 926 w, 873 w cm^{-1}; MS (EI) *m/z* (M^+, 2 %), 299 (1), 231 (2), 224 (1), 223 (13), 209 (1), 195 (6), 166 (4), 138 (2), 128 (1), 123 (1), 118 (14), 105 (8), 105 (100), 92 (2), 91 (2), 78 (3), 77 (36), 76 (2), 74 (2), 58 (2), 56 (2), 51 (7), 50 (2), 41 (2). HRMS, calcd. for $^{12}C_{14}H_{15}F_3N_2O_2$: 300.1085; found: 300.1086. Anal. calcd. for $C_{14}H_{15}F_3N_2O_2$: C, 56.00; H, 5.06; N, 9.33 %; found: C, 55.86; H, 5.06; N, 9.23 %.

2-Dimethylamino-4-methyl-5*H*-1,3-diazepine 16t

Purified by flash column chromatography (deactivated Al_2O_3 90 neutral, ether) or by distillation (~ 80 ^oC/0.5 mm Hg), decomposes on silica gel. Yellow oil, yield: 67 % by photolysis of **17T**, 63 % by photolysis of **18T**. ^1H NMR (400 MHz, $CDCl_3$) δ 6.67 (d, 1 H, 7-H, $J_{6,7}$ = 6.6 Hz), 4.66 (apparent q, 1 H, 6-H, $J_{6,7}$ = 6.3 Hz, $J_{5,6}$ = 6.3 Hz), 2.97 (s, 6 H, NMe_2), 2.32 (br, 2 H, 5-H, $J_{5,6}$ = 6.3 Hz), 2.17 (s, 3 H, Me); the assignments were confirmed by homonuclear decoupling experiments; ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4 (2-C), 158.4 (4-C), 140.1 (7-C), 99.1 (6-C), 36.4 (NMe_2), 36.0 (5-C), 25.0 (Me); IR (neat) 2963 s, 2931 m, 2924 w, 1622 vs, 1573 vs, 1561 vs, 1511 w, 1497 m, 1447 m, 1398 m, 1384 m, 1372 m, 1356 m, 1321 m, 1301 m, 1289 w, 1256 m, 1211 m, 1190 w, 1154 w, 1113 m, 1054 w, 1002 w, 968 w, 923 w, 902 w, 842 w, 767 m, 652 w cm^{-1}. MS (EI) *m/z* 151 (M^+, 76 %), 136 (42), 122 (79), 109 (15), 108 (9), 95 (100), 93 (6), 82 (11), 80 (21), 71 (5), 68 (38), 67 (26), 55 (11), 53 (7), 44 (14), 42 (76). HRMS, calcd. for $^{12}C_8H_{13}N_3$: 151.1109; found: 151. 1111. Anal. calcd. for $C_8H_{13}N_3$: C, 63.54; H, 8.67; N, 27.79 %. Found: C, 63.31; H, 9.01; N, 27.58 %.

2-Diethylamino-4-methyl-5*H*-1,3-diazepine 16u

Purified by flash column chromatography (deactivated Al_2O_3 90 neutral, ether) or by distillation (~ 80 ^oC/0.5 mm Hg), decomposes on silica gel. Yellow oil, yield: 64 % from photolysis of **17T**, 68 % from photolysis of **18T**. ^1H NMR (400 MHz, $CDCl_3$) δ 6.67 (d, 1 H, 7-H, $J_{6,7}$ = 6.7 Hz), 4.66 (apparent q, 1 H, 6-H, $J_{6,7}$ = 6.7 Hz, $J_{5,6}$ = 6.6 Hz), 3.41 (q, 4 H, NEt_2), 2.41 (br, 2 H, 5-H, $J_{5,6}$ = 6.6 Hz), 2.16 (s, 3 H, Me), 1.12 (t, 6 H, Net_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0 (2-C), 157.3 (4-C), 140.3 (7-C), 98.5 (6-C), 40.5 (NEt_2), 35.9 (5-C), 25.0 (Me), 13.6 (NEt_2); IR (neat) 2964 s, 2931 m, 2923 m, 2898 w, 1627 vs, 1577 vs, 1562 vs, 1505 w, 1478 s, 1465 s, 1448 s, 1396 s, 1385 m, 1377 m, 1354 m, 1321 m, 1303 w, 1289 m, 1256 m, 1211 w, 1198 w, 1167 m, 1115 m, 1057 w, 1002 w, 968 w, 943 w, 914 w, 854 w, 839 w, 761 m cm^{-1}. MS (EI) *m/z* 179 (M^+, 89 %), 164 (55), 150 (49), 136 (26), 123 (16), 109

(59), 107 (28), 95 (26), 83 (52), 81 (100), 72 (33), 67 (26), 56 (21), 54 (39), 42 (38). HRMS, calcd. for $^{12}C_{10}H_{17}N_3$: 179.1422; found: 179.1422. Anal. calcd for $C_{10}H_{17}N_3$: C, 67.00; H, 9.56; N, 23.44 %. Found: C, 67.31; H, 9.39; N, 23.76 %.

2-Di*iso*propylamino-4-methyl-5*H*-1,3-diazepine 16ua. Spectroscopic data have been published.[1a] Anal. calcd. for $C_8H_{13}N_3$: C, 69.52; H, 10.21; N, 20.27 %. Found: C, 69.37; H, 10.03; N, 20.47 %.

1,2-Dihydro-4-dimethylamino-5*H*-1,3-diazepin-2-one 22aB

To 150 mg (1.04 mmol) of **19v** in dioxane (100 ml) was added 10 ml of dimethylamine in dioxane, and the resulting solution was stirred at room temperature for 30 min, evaporated, and the product was crystallized from ether–dichloromethane (10:1). Yield: 61 %; mp 109-110 ^{o}C, decomp. ^{1}H NMR (400 MHz, acetone-d_6) δ 8.62 (br s, 1 H, O*H* or N*H*), 6.23 (d, 1 H, 7-H, $J_{6,7}$ = 7.2 Hz), 5.00 (q, 1 H, 6-H, $J_{6,7}$ = 7.2 Hz), 3.00 (d, 2 H, 5-H, $J_{5,6}$ = 7.5 Hz), 3.11 and 2.95 (br s, 3 H, $N(CH_3)_2$); all proton signals were identified from homonuclear decoupling experiments; ^{13}C NMR (100 MHz, acetone-d_6) δ 160.3 (2-C), 159.8 (4-C), 130.2 (7-C), 102.3 (6-C), 38.7 and 38.3 ($N(CH_3)_2$), 29.1 (5-C); IR (KBr) 3600-2800 s, v.br. (ν_{max} 3430), 3013 w, 2920 w, 1650 w sh, 1621 s, 1579 vs, 1445 w, 1406 m, 1386 m, 1340 m-s cm^{-1}; IR (Ar matrix, 20 K) 3444 (NH), 1690 s (C=O), 1654 m, 1608 s, 1501 w, 1445, w, 1413 w, 1407 w, 1386 w, 1354 vw, 1340 vw, 1315 w cm^{-1}. Anal. calcd. for $C_{11}H_{19}N_3O$: C, 54.89; H, 7.24; N, 27.43 %. Found: C, 54.52; H, 7.51; N, 26.23 %. Despite repeated recrystallization this compound gave a low nitrogen analysis (*ca*. 1 % deviation). However, the compound appears to be pure by spectroscopic criteria (NMR, IR).

1,2-Dihydro-4-diisopropylamino-5*H*-1,3-diazepin-2-one 22cB

150 mg (0.97 mmol) of 6-chlorotetrazolo[1,5-*a*]pyridine was photolyzed in a dioxane/*tert*-butanol solution (100/15 ml) without cooling the mixture in an ice-bath, thereby generating **19v**. When the reaction was completed (*ca*. 2 h), approximately 10 ml of di*iso*propylamine was added, and the resulting solution was stirred at room temperature for 30 min. The reaction was worked up as described for **22a**, and the product was crystallized from dichloromethane/diethyl ether (1:5) by slow addition of a few drops of hexane; mp 187-188 ^{o}C (decomp). The compound crystallizes with a molecule of water, which is liberated by sublimation (95 ^{o}C/10^{-3} torr/Ar) followed by deposition in an Ar matrix at 20 K (see IR spectrum below). Yield: 120 mg (54 %). ^{1}H NMR (400 MHz, acetone-d_6) δ 6.25 (d, 1 H, 7-H, $J_{6,7}$ = 7.2 Hz), 4.93 (q, 1 H, 6-H, $J_{6,7}$ = 7.2 Hz), 4.1 (br, 2 H, N*i*Pr$_2$), 3.03 (d, 2 H, 5-H, $J_{5,6}$ = 7.1 Hz), 1.25 (br d, 12 H, N*i*Pr$_2$, $J_{CH,CH3}$ = 5.8 Hz); all proton signals were identified from homonuclear decoupling experiments; ^{13}C NMR (100 MHz, acetone-d_6) δ 159.8 (2-C), 157.5 (4-C), 129.9 (7-C), 103.1 (6-C), 69.2 (*i*Pr), 31.7 (5-C), 21.8 and 20.2 (*i*Pr); IR (KBr) 3600-2800 s, v.br. (ν_{max} 3383), 3010 w, 2995 w, 2965 w, 2931 w, 1645 w sh, 1598 vs, 1566 vs, 1440 s, 1397 w, 1384 w, 1369 w, 1349 m, 1331 s, 1279 w, 1244 w, 1206 w, 1186 w, 1159 m, 1120 m cm^{-1}; IR (Ar matrix, 20 K) peaks at 3778, 3765, 3700, 3574, 3516, 3438 and 3355 cm^{-1} are due to H_2O monomer and dimer liberated from the crystalline sample; 3445 m (NH), 1688 s (C=O), 1652 s, 1590 vs, 1586 vs cm$^{—1}$. Anal. calcd. for $C_{11}H_{19}N_3O$•H_2O: C, 58.12; H, 9.31; N, 18.49 %. Found: C, 58.32; H, 9.60; N, 18.20 %. Apart from containing crystal water, the compound appears to be pure by spectroscopic criteria (NMR, IR).

5,7-Bis(trifluoromethyl)-2-ethoxy-5*H*-1,3-diazepin-4-one 24

This compound was obtained by photolysis of 2-azido-3,5-bis(trifluoromethyl)-6-chloropyridine[2] **1Ay** in ethanol/dioxane followed by aqueous workup. The intermediate products **4y/5y** were not isolated. Compound **24** was purified by sublimation (80 ^{o}C, 10^{-2} mm

Hg). White solid, mp. 119-120 °C; yield 57 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (br, 1 H), 5.80 (d, 1 H, 6-H, $J_{5,6}$ = 4.8 Hz), 4.33 (m, 2 H, O*CH*$_2$CH$_3$, ^3J = 7.12 Hz), 3.58 (br m, 1 H, 5-H), 1.36 (t, 3 H, OCH$_2$*CH*$_3$, ^3J = 7.12 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (C-4), 148.5 (C-2), 139.0 (q, C-7, $J_{C,F}$ = 34 Hz), 123.4 (q, CF_3, $J_{C,F}$ = 277 Hz), 123.2 (q, CF_3, $J_{C,F}$ = 273 Hz), 105.2 (q, C-6, $J_{C,F}$ = 3 Hz), 65.4 (O*CH*$_2$CH$_3$), 47.9 (q, C-5, $J_{C,F}$ = 29 Hz), 13.8 (OCH$_2$*CH*$_3$). IR (KBr) 3437 br, 3213 br, 2986 w, 2942 w, 1705 vs, 1647 vs, 1587 m, 1496 w, 1451 w, 1412 w, 1384 m, 1369 w, 1299 m, 1257.5 vs, 1233 m, 1193 m, 1177 m, 1139 vs, 1127 s, 1030.4 m, 966.1 m; MS (EI) *m/z* 290 (M^+, 32 %), 263 (7), 262 (60), 247 (25), 246 (25), 243 (10), 220 (9), 219 (71), 218 (11), 200 (11), 199 (67), 198 (17), 193 (15), 192 (19), 191 (17), 180 (11), 172 (9), 171 (39), 165 (12), 150 (100), 149 (27), 133 (14), 123 (25), 122 (48), 102 (26), 95 (11), 91 (12), 76 (27), 75 (10), 69 (14), 67 (47), 52 (13), 44 (27). HRMS, calcd. for: $^{12}C_9H_8N_2O_2F_6$: 290. 048447; found: 290.048740. Anal. calcd. for: $C_9H_8N_2O_2F_6$: C, 37.25; H, 2.78; N, 9.65 %. Found: C, 37.17; H, 2.83; N, 9.46 %.

1,3-Dihydro-1,3-diazepin-2-one 19a

Purified by sublimation at 70-90 °C/0.5-0.1 mbar. Pale yellow solid, mp139-140 °C. Yield: 48% (from photolysis of tetrazolo[1,5-*a*]pyridine **1Ta** in dioxane/*tert*-butanol mixture), or 76% (from photolysis of **1Ta** in dioxane/H_2O mixture); ^{1}H NMR (benzene-d_6/DMSO-d_6, 400 MHz) δ 7.35 (br s, 2 H, N*H*, exchanging with D_2O, and resonating at δ 5.75 in $CDCl_3$), 5.41 (m, 2 H, 4-H and 7-H), 4.74 (m, 2 H, 5-H and 6-H); the assignments were confirmed by homonuclear decoupling experiments; ^{13}C NMR (benzene-d_6/DMSO-d_6, 100 MHz) δ 165.4 (C-2), 127.3 (C-4 and C-7), 109.8 (C-5 and C-6); IR (KBr) 3267.0 vs (NH), 3164 s, 3056 m, 2972.5 m, 1745.1 vs (CO), 1646.5 vs, 1434 m, 1420.7 vs, 1314.4 s, 1272.6 m, 1232.2 s, 1146.8m, 1038.4 w, 928.0 w, 790.1 m, 750.9 m, 697.0 w, 687.7 w cm^{-1}; MS (EI) *m/z* 110 (M^+,100%), 82 (28), 81 (14), 67 (21), 55 (83), 54 (57), 52 (14), 41 (12), 39 (27), 38 (12).

HRMS calcd. for $^{12}C_5H_6N_2O$: 110.0475; found: 110.0479. Anal. calcd for : C, 54.54; H, 5.49; N, 25.44 %. Found: C, 54.85; H, 5.50; N, 25.22 %.

2,4-Diazabicyclo[3.2.0]hept-6-en-3-one 25a

Purified by sublimation at 90-110 ^{o}C, 0.5-0.1 mbar. White solid, mp 176-177 ^{o}C, yield: 98%; ^{1}H NMR (benzene-d_6/DMSO-d_6, 400 MHz) δ 6.84 (br s, 2 H, N*H*), 6.08 (m, 2 H, 6-H and 7-H), 4.22 (m, 2 H, 1-H and 5-H); ^{13}C NMR (benzene-d_6/DMSO-d_6, 100 MHz) δ 163.9 (C-3), 143.3 (C-6 and C-7), 57.3 (C-1 and C-5); IR (KBr) 3235.0 s (NH), 3164 s, 2959 w, 1669 vs, 1451 m, 1384 m, 1316 m, 1301 w, 1249 s, 1194 m, 1176 w, 1122 w, 1059 m, 991 w, 842 w, 804 m, 793 m, 763 w, 728 w, 693 w cm^{-1}; MS (EI) *m/z* (M^+, 14 %), 84 (100), 56 (14), 55 (15), 54 (12). HRMS calcd. for $^{12}C_5H_6N_2O$: 110.0481; found: 110.0480. Anal. calcd. for $C_5H_6N_2O$: C, 54.54; H, 5.49; N, 25.44 %. Found: C, 55.13; H, 5.62; N, 24.93 %.

4-Trifluoromethyl-1,3-dihydro-1,3-diazepin-2-one 19g

100 mg of neat **4(5)g** was heated to 100-120 ^{o}C for *ca*. 30 min and then sublimed at 80 ^{o}C/0.5-0.1 mbar to obtain 90 mg (98 %) of **19g** as pale yellow solid, mp 120-121 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.60 (br s, 1 H, N-H), 6.60 (br s, 1 H, N-H), 5.82 (dq, 1 H, 5-H, $J_{5,6}$ 5.8, $J_{CF3,5}$ 1.2 Hz), 5.76 (dd, 1 H,7-H, $J_{6,7}$ 8.6, $J_{1,7}$ 8.6 Hz), 5.15 (tm, 1 H, 6-H, $J_{5,6}$ 5.8, $J_{6,7}$ 8.6 Hz); all protons were identified from homonuclear decoupling experiments; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.5 (2-C), 130.0 (7-C), 126 (q, 4-C $J_{CF3,4-C}$ 33 Hz), 120 (q, CF_3, $J_{C,F}$ 272 Hz), 114.9 (q, 5-C, $J_{CF3,5-C}$ 4 Hz), 108 (6-C); IR (KBr) 3228 m br, 3083 m, 1723 s, 1705 vs, 1564 w, 1413 w, 1384 w, 1342 m, 1277 m, 1177 s, 1162 vs, 1076 w, 1054 w, 1013 w, 994 w, 899 w, 821 m, 763 w, 736 w, 691 w cm^{-1}; MS (EI) *m/z* 178 (M^+, 100%), 159 (6), 135 (9), 108 (4), 81 (19), 57 (36), 41 (35), 39 (11). HRMS, calcd. for $^{12}C_6H_5F_3N_2O$: 178.0353; found:

178.0359. Anal. calcd. for $C_6H_5F_3N_2O$: C, 40.46; H, 2.83; N, 15.73 %. Found: C, 40.39; H, 2.78; N, 15.66 %.

1-Trifluoromethyl-2,4-diazabicyclo[3.2.0]hept-6-en-3-one 25g

Purified by sublimation (90 ^{o}C/0.5-0.1mbar). White solid, mp 220-221 ^{o}C, yield: 98%; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.72 (br s, 1 H, N-H), 7.30 (br s, 1 H, N-H), 6.59 (d, 1 H, 7-H, $J_{6,7}$ = 2.9 Hz), 6.49 (dd, 1 H, 6-H, $J_{6,7}$ = 2.9, $J_{5,6}$ = 2.6 Hz), 4.45 (t, 1 H, 5-H, $J_{5,6}$ = 2.6, $J_{4,5}$ = 1.7 Hz); all protons were identified from homonuclear decoupling experiments; ^{13}C NMR (DMSO-d_6, 100 MHz) δ 161.5 (3-C), 145.3 (6-C), 138.0 (q, 7-C $J_{C,F}$ = 1.0 Hz), 124 (q, CF_3, $J_{C,F}$ = 277 Hz), 65.7 (q, 1-C, $J_{C,F}$ = 34 Hz), 56.0 (q, 5-C, $J_{C,F}$ = 3 Hz); IR (KBr) 3217 br, 3091 m, 1705 vs, 1561 m, 1414 w, 1348 w, 1345m, 1274 w, 1166 vs, 1074 w, 1054 w, 1013 w, 818 m cm^{-1}; MS (EI) *m/z* (M^+, 19 %) 153 (5), 152 (δ), 124 (8), 97 (11), 81 (8), 69 (7), 55 (9), 54 (7), 39 (7). HRMS, calcd. for $^{12}C_6H_5F_3N_2O$: 178.0355; found: 178.0349. Anal. calcd. for $C_6H_5F_3N_2O$: C, 40.46; H, 2.83; N, 15.73 %. Found: C, 40.42; H, 2.74; N, 15.61 %.

5-Trifluoromethyl-1,3-dihydro-1,3-diazepin-2-one 19j

100 mg of 6-trifluoromethyltetrazolo[1,5-*a*]pyridine **9T** was added to a degassed mixture of dry dioxane and *tert*-butanol (90/30 ml) and irradiated for 2 h. The solvent was removed in vacuum, and the crude residue was sublimed (100 ^{o}C/0.5-0.1 mbar) to afford 60 mg (61 %) of **19j** as a white solid, mp 127-128 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.49 (br s, 1 H, 3-NH), 6.25 (br s, 1 H, 1-NH), 6.09 (d, 1 H, 4-H, $J_{3,4}$ = 6.0 Hz), 5.61 (dd, 1 H, 7-H, $J_{1,7}$ = 8.7, $J_{6,7}$ = 8.8 Hz), 5.08 (d, 1 H, 6-H, $J_{6,7}$ = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 162 (2-C), 128 (q, 4-C, $J_{C,F}$ 6.5 Hz), 127 (7-C), 123 (q, CF_3, $J_{C,F}$ 269 Hz), 113 (q, 5-C, $J_{C,F}$ 31 Hz), 105 (q, 6-C, $J_{C,F}$ 2 Hz); MS (EI) *m/z* (M^+, 53%), 159 (13), 135 (21), 130 (19), 123 (34), 116 (35), 103 (13), 81 (21), 75 (11), 54 (70), 44 (19), 39 (18). HRMS, calcd. for $^{12}C_6H_5F_3N_2O$: 178.034848;

found: 178.035539. Anal. calcd. for $C_6H_5F_3N_2O$: C, 40.44; H, 2.83; N, 15.73 %. Found: C, 39.97; H, 2.77; N, 15.80 %.

6-Trifluoromethyl-2,4-diazabicyclo[3,2,0]hept-6-en-2-one 25j

30 mg of **19j** was dissloved in 1 ml of DMSO-d_6 in a 5 mm NMR tube and the resulting solution was photolysed for approximately 8 h. The reaction was followed by ^{1}H NMR spectroscopy. After no starting material was observed, the solvent was evaporated to afford 30 mg (98 %) of **25j**, mp 218-219 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.2 (br s, 1 H, 3-H), 7.0 (br s, 1 H, 1-H,) 6.9 (quintet, 1 H, 6-H, $J_{1,7}$ = 4.6, $J_{7,F}$ = 2.8 Hz), 4.72 (m, 1 H, 7-H, $J_{1,7}$ = 4.6, $J_{1,5}$ = 4.8 Hz), 4.49 (m, 1 H, 5-H, $J_{1,5}$ = 4.8, $J_{5,F}$ = 1.7 Hz); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 162.5 (3-C) 145 (q, 7-C, $J_{C,F}$ = 6 Hz), 141 (q, 6-C, $J_{C,F}$ = 36 Hz), 119 (q, CF_3, $J_{C,F}$ = 270 Hz) 55 (q, 5-C, $J_{C,F}$ = 2 Hz), 54 (1-C); IR (KBr) 3221 br, 1703 vs, 1644 m, 1572 m, 1446 w, 1414 w, 1384 w, 1329 m, 1276 w, 1227 m, 1197 w, 1164 s, 1116 vs, 1050 w, 951 w, 936 w, 874 m, 762 w cm^{-1}; MS (EI) *m/z*

(M^+, 6%), 159 (2), 139 (4), 123 (6), 116 (8), 103 (4), 84 (100), 69 (7), 56 (25), 54 (19), 39 (11). HRMS, calcd. for $^{12}C_6H_5N_2F_3O$: 178. 034848; found: 178.043095. Anal. calcd. for $C_6H_5N_2F_3O$: C, 40.41; H, 2.83; N, 15.73 %. Found: C, 40.21; H, 2.74; N, 15.80 %.

4,6-Bis(trifluoromethyl)-1,3-dihydro-1,3-diazepin-2-one 19p

100 mg of neat **4(5)p** was heated to *ca.* 100 ^{o}C for about 30 minutes to give 85 mg (98 %) of **162d**, mp 171-172 ^{o}C. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.97 (br, 1 H, N-H), 8.88 (br, 1 H, N-H), 6.49 (d, 1 H, 7-H, $J_{1,7}$ = 5.9 Hz), 5.92 (s, 1 H, 5-H); ^{13}C NMR (DMSO-d_6 100 MHz) δ 160.6 (2-C), 135.0 (q, 7-C, $J_{C,F}$ = 4.7 Hz), 126.6 (q, 4-C, $J_{C,F}$ = 34 Hz), 123 (q, CF_3, $J_{C,F}$ = 272 Hz), 121 (q, CF_3, $J_{C,F}$ = 273 Hz) 109.4 (m, 5-C), 107.7 (q, 6-C, $J_{C,F}$ = 32 Hz) ; IR (KBr) 3301 br, 3162 m, 2987 w, 2911 w, 1736 s, 1665 s, 1578 w, 1531 w, 1445 w, 1367 m, 1288

vs, 1206 vs, 1172 s, 1130 vs, 1034 m, 996 m, 941 w, 902 w, 845 m, 754 w cm^{-1}; MS (EI) *m/z* 246 (M^+, 100 %), 227 (8), 220 (21), 203 (11), 201 (18), 200 (49), 188 (7), 187 (23), 184 (64), 173 (26), 172 (4), 163 (19), 149 (34), 132 (15), 131 (61), 104 (11), 103 (9), 98 (27), 97 (11) 66 (18), 49 (6). HRMS, calcd. for $^{12}C_7H_4F_6N_2O$: 246.022232; found: 246.022359. Anal. calcd. for $C_7H_4F_6N_2O$: C, 34.16; H, 1.64; N, 11.38 %. Found: C, 34.45; H, 1.71; N, 11.27 %.

1,6-Bis(trifluoromethyl)-2,4-diazabicyclo[3.2.0]hept-6-en-3-one 25p

40 mg of **19p** was dissolved in 1 ml of DMSO-d_6 in a 5 mm NMR tube and irradiated until no **19p** could be detected by ^{1}H NMR spectroscopy (8 h). Solvent was removed in vacuum and the residue sublimed at 130-140 ^{o}C/0.5-0.1 mbar to yield 40 mg (98 %) of **25p** as a white solid, mp 234-235 ^{o}C. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.15 (br s, 1 H, N-H), 7.83 (br s, 1 H, N-H), 7.31 (s, 1 H, 7-H), 4.96 (s, 1 H 5-H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 160.7 (3-C), 142.5 (q, 6-C, $J_{C,F}$ = 33 Hz), 140.7 (7-C), 123.0 (q, CF_3, $J_{C,F}$ = 275 Hz), 119 (q, CF_3, $J_{C,F}$ = 272 Hz), 63.2 (5-C), 55.0 (q, 1-C, $J_{C,F}$ 28 Hz); IR (KBr) 3215 br, 3087 m, 2991 w, 1728 s, 1652 w, 1522 w, 1465 m, 1378 w, 1312 m, 1291 w, 1249 s, 1203 vs, 1187 s, 1151 vs, 1078 m, 1069 w, 1007 w, 942 m, 902 w, 828 w, 732 w cm^{-1}; MS (EI) *m/z* 246 (M^+, 39 %), 227 (7), 207 (11), 204 (6), 203 (22), 185 (9), 184 (32), 177 (15), 152 (100), 147 (21), 112 (25), 107 (9), 106 (34), 97 (13), 81 (10), 80 (34), 70 (11), 56 (6), 44 (5). HRMS, calcd. for $^{12}C_7H_4F_6N_2O$: 246.022232; found: 246.022641. Anal. calcd. for $C_7H_4F_6N_2O$: C, 34.16; H, 1.64; N, 11.38 %. Found: C, 34.24; H, 1.67; N, 11.67 %.

4,7-Bis(trifluoromethyl)-1,3-dihydro-1,3-diazepin-2-one 19s

All data have been published.[1a]

1,5-Bis(trifluoromethyl)-2,4-diazabicyclo[3.2.0]hept-6-en-3-one 25s

All data have been published.[1a]

4-Methyl-1,3-dihydro-1,3-diazepin-2-one 19t

120 mg (0.9 mmol) of 8-methyltetrazolo[1,5-*a*]pyridine **1Tt** was dissolved in a mixture of 100 ml of dioxane and *ca*. 45 ml of H_2O. The mixture was purged for 1 h with N_2, and then irradiated for 3 h and 30min. The solvent was removed under vacuum, and the resulting yellow-brown precipitate sublimed (70-80 ^oC/0.5-0.1 mbar) to give 90 mg (81 %) of **19t** as a pale yellow solid, mp 158-159 ^oC (discolours on melting, and re-melts at the same temperature). ^1H NMR (acetone-d_6/DMSO-d_6, 200 MHz) δ 7.23 (br s, 1 H, NH), 7.05 (br s, 1 H, NH), 5.47 (dd, 1 H, 7-H, $J_{6,7}$ 6.7, $J_{1,7}$ 5.9 Hz), 4.82 (m, 2 H, 5- and 6-H), 1.71 (s, CH_3); ^{13}C NMR (acetone-d_6/DMSO-d_6, 100 MHz) δ 164.1 (2-C), 136.6 (4-C), 125.7 (7-C), 110 (6-C), 107.2 (5-C), 22.3 (CH_3); IR (KBr) 3265 br, 3114 m, 2943 w, 1708 vs, 1677 s, 1637 vs, 1472 w, 1431 s, 1385 s, 1376 m, 1315 m, 1251 m, 1168 m, 1127 m, 1051 w, 1039 w, 929 w, 828 m, 771 cm^{-1}. HRMS, calcd. for $^{12}C_6H_8N_2O$: 124.06366; found: 124.06358. Anal. calcd. for $C_6H_8N_2O$: C, 58.05; H, 6.50; N, 22.57 %. found: C, 58.20; H, 6.58; N, 22.68 %.

1-Methyl-2,4-diazabicyclo[3,2,0]hept-6-en-2-one 25t

60 mg of the 2-diazepinone **19t** (in an NMR tube) was dissolved in 1ml of acetone-d_6 and a few drops of DMSO-d_6 was added due to low solubility of the formed product in acetone. The solution was then irradiated for 24 h. The solvent was removed under vacuum to yield 60 mg (98 %) of pure **25t**. Sublimation at 70 ^oC/0.5-0.1 mbar afforded **25t** as a white solid, mp 139-140 ^oC. ^1H NMR (actone-d_6/DMSO-d_6, 200 MHz) δ 6.73 (br s, 1 H, NH), 6.65 (br s, 1 H, NH), 6.38 (t, 1 H, 6-H, $J_{5,6}$ = 2.5, $J_{6,7}$ = 2.5 Hz), 6.23 (d, 1 H, 7-H, $J_{6,7}$ = 2.5 Hz), 4.05 (m, 1 H, 5-H), 1.68 (s, 3 H, CH_3); ^{13}C NMR (actone-d_6/DMSO-d_6, 50 MHz) δ 162.9 (3-C), 146.3 (6 or 7-C), 139.4 (7 or 6-C), 64.9 (1-C), 62.0 (5-C) 21.7 (CH_3); IR (KBr) 3202 br, 3056 m,

2983 w, 2961 w, 2936 w, 2924 w, 1691 vs, 1688 vs, 1444 m, 1409 w, 1375 w, 1292 m, 1219 w, 1192 m, 1135 w, 1126 w, 1108 w, 1055 w, 1013 w, 961 w, 893 w, 870 w, 799 s, 764 m, 738 m, 721 m, 618 w cm^{-1}. HRMS, calcd. for $^{12}C_6H_8N_2O$: 124.06366; found: 124.06361. Anal. calcd for $C_6H_8N_2O$: C, 58.05; H, 6.50; N, 22.57 %. Found: C, 58.31; H, 6.67; N, 22.75 %.

4-Chloro-1,3-dihydro-1,3-diazepin-2-one 19v

Purified by sublimation at 90 ^oC. Discolours on heating above 100-120 ^oC, decomposing above 150 ^oC without melting. Yield: 80% (from photolysis of 5-chlorotetrazolo[1,5-*a*]pyridine **1Tv** in the dioxane/ *tert*-butanol mixture); 75% (from photolysis of **1Tv** in dioxane/H_2O mixture); ^1H NMR ($CDCl_3$/DMSO-d_6, 400 MHz) δ 7.62 and 7.57 (br s, 2 H, N*H*), 5.58 (dd, 1 H, 7-H, $J_{6,7}$ = 8.12, $J_{1,7}$ = 5.44 Hz), 5.25 (dd, 1 H, 5-H, $J_{5,6}$ = 5.68, $J_{3,5}$ = 1.8 Hz), 4.94 (ddd, 1 H, 6-H, $J_{6,7}$ = 8.12, $J_{5,6}$ = 5.68, $J_{1,6}$ = 0.96 Hz); all protons were identified from homonuclear decoupling experiments; ^{13}C NMR ($CDCl_3$/DMSO-d_6, 100 MHz) δ 163 (2-C), 126.6 (7-C), 124.6 (4-C), 109.9 (5- or 6-C), 108.8 (6- or 5-C); IR (KBr) 3267 br, 3098 m, 2959 w, 1730 vs, 1678 m, 1543 m, 1479 w, 1345 m, 1225 w, 1167 m, 1042 w, 1002 w, 962 w, 912 w, 846 m, 801 w, 762 s, 711 w, 646 w cm^{-1}; MS (EI) *m/z* 144 (M^+, 74%), 116 (11), 101 (26), 89 (24), 81 (100), 63 (11), 54 (60), 53 (55), 52 (56), 39 (23), 38 (19), 37 (11). HRMS, calcd. for $^{12}C_5H_5ClN_2O$: 144.00904; found: 144.00682. Anal. calcd. for $C_5H_5ClN_2O$: C, 41.54; H, 3.49; N, 19.38 %. Found: C, 41.59; H, 3.55; N, 19.82 %.

6-Chloro-4-trifluoromethyl-1,3-dihydro-1,3-diazepin-2-one 19x

100 mg of 6-chloro-8-trifluoromethyltetrazolo[1,5-*a*]pyridine **1Tx** was added to a degassed mixture of dry dioxane and *tert*-butanol (90/30 ml), and irradiated for 3.5 h. The solvent was removed in vacuum, and the crude residue sublimed (100-120 ^oC/0.5-0.1 mbar) to afford 72

mg (73 %) of **19x** as a white solid, mp 141-142 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.71 (br, 1 H, N-H), 8.47 (br, 1 H, N-H), 6.17 (d, 1 H, 7-H, $J_{1,7}$ = 5.2 Hz), 6.03 (s, 1 H, 5-H); ^{13}C NMR (DMSO-d_6 100 MHz) δ 162.8 (2-C), 129.3 (7-C), 126.5 (q, 4-C, $J_{C,F}$ = 33 Hz), 120.0 (q, CF_3, $J_{C,F}$ = 273 Hz), 115.6 (6-C), 113.0 (5-C); IR (KBr) 3275 br, 3098 m, 2995 w, 2941 w, 1723 vs, 1679 m, 1647 s, 1589 m, 1523 m, 1501 w, 1467 m, 1397 w, 1323 s, 1274 vs, 1216 vs, 1165 s, 1121 vs, 1064 m, 1008 m, 965 m, 885 w, 821 w, 797 w, 765 w cm^{-1}; MS (EI) *m/z* 212 (M^+, 36 %), 193 (12), 177 (26), 173 (4), 161 (9), 151 (34), 142 (17), 115 (100), 105 (11), 104 (9), 78 (13), 56 (15), 43 (5). HRMS, calcd. for $^{12}C_6H_4ClF_3N_2O$: 211.99642; found: 211.99635. Anal. calcd. for $C_6H_4ClF_3N_2O$: C, 33.90; H, 1.90; N, 13.18 %. Found: C, 34.14; H, 1.67; N, 13.39 %.

6-Chloro-1-trifluoromethyl-2,4-diazabicyclo[3.2.0]hept-6-en-3-one 25x

40 mg of **19x** was dissolved in 1 ml of DMSO-d_6 in a 5 mm NMR tube and irradiated until no **19x** could be detected by ^{1}H NMR spectroscopy (7 h). Solvent was removed in vacuum and the residue sublimed at 100-120 ^{o}C/0.5-0.1 mbar to yield 40 mg (98 %) of **25x** as a white solid, mp 208-209 ^{o}C. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.05 (br s, 1 H, N-H), 7.76 (br s, 1 H, N-H), 6.70 (s, 1 H, 7-H), 4.80 (s, 1 H 5-H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 161.1 (3-C), 138.1 (6-C), 134.0 (7-C), 123.0 (q, CF_3, $J_{C,F}$ = 273 Hz), 62.9 (q, 1-C, $J_{C,F}$ = 31 Hz), 61.0 (5-C); IR (KBr) 3270 br, 3078 m, 2889 w, 1730 vs, 1715 vs, 1641 m, 1582 vs, 1434 m, 1344 w, 1309 s, 1272 vs, 1229 s, 1184 vs, 1182 s, 1056 m, 1003 w, 912 m, 848 w, 754 w, 689 w cm^{-1}; MS (EI) *m/z* 212 (M^+, 57 %), 177 (19), 152 (100), 135 (11), 116 (29), 106 (5), 98 (33), 97 (11), 80 (13), 75 (14), 69 (7), 54 (9), 43 (6). HRMS, calcd. for $^{12}C_6H_4ClF_3N_2O$: 211.99642; found: 211.99623. Anal. calcd. for $C_6H_4ClF_3N_2O$: C, 33.90; H, 1.90; N, 13.18 %. Found: C, 33.74; H, 2.17; N, 13.04 %.

7-Chloro-4,6-bis(trifluoromethyl)-1,3-dihydro-1,3-diazepin-2-one 19z

70 mg of 6,8-bis(trifluoromethyl)-5-chlorotetrazolo[1,5-*a*]pyridine **1Tz** was added to a degassed mixture of dry dioxane and *tert*-butanol (70/20 ml), and irradiated for 3 h. The solvent was removed in vacuum, and the crude residue sublimed (100-120 ^{o}C/0.5-0.1 mbar) to afford 35 mg (53 %) of **19z** as a white solid, mp 113-114 ^{o}C. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 9.80 (br, 1 H, N-H), 9.60 (br, 1 H, N-H), 6.29 (m, 1 H, 7-H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 161.1 (2-C), 135.0 (q, 4-C, $J_{C,F}$ = 33 Hz), 127.0 (7-C), 123 (q, CF_3, $J_{C,F}$ = 271 Hz), 120 (q, CF_3, $J_{C,F}$ = 273 Hz) 112.4 (q, 6-C, $J_{C,F}$ = 32 Hz), 108.7 (m, 5-C); IR (KBr) 3289 br, 3144 m, 2934 m, 2896 w, 1724 s, 1676 s, 1589 m, 1551 w, 1387 m, 1331 s, 1267 vs, 1226 vs, 1165 vs, 1112 s, 1064 m, 1003 w, 951 w, 911 m, 834 w, 761 w, 683 w cm^{-1}; MS (EI) *m/z* 279 (M^+, 100 %), 260 (12), 244 (64), 217 (18), 210 (6), 191 (29), 156 (14), 141 (27), 129 (33), 103 (8), 88 (22), 70 (18), 69 (6), 44 (9). HRMS, calcd. for $^{12}C_7H_3ClF_6N_2O$: 279.98381; found: 279.98366. Anal. calcd. for $C_7H_3ClF_6N_2O$: C, 29.97; H, 1.08; N, 9.99 %. Found: C, 29.65; H, 1.21; N, 9.74 %.

5-Chloro-1,6-bis(trifluoromethyl)-2,4-diazabicyclo[3.2.0]hept-6-en-3-one 25z

20 mg of **19z** was dissolved in 1 ml of DMSO-d_6 in a 5 mm NMR tube and irradiated until no **19z** could be detected by ^{1}H NMR spectroscopy (7 h). Solvent was removed in vacuum and the residue sublimed at 120-130 ^{o}C/0.5-0.1 mbar to yield 20 mg (98 %) of **25z** as a white solid, mp 192-193 ^{o}C (decomp). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 9.60 (br s, 1 H, N-H), 9.00 (br s, 1 H, N-H), 7.50 (s, 1 H, 7-H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 158.0 (3-C), 143.5 (q, 6-C, $J_{C,F}$ = 32 Hz), 137.8 (m, 7-C), 122.0 (q, CF_3, $J_{C,F}$ = 274 Hz), 118 (q, CF_3, $J_{C,F}$ = 272 Hz), 78.0 (5-C), 69.5 (q, 1-C, $J_{C,F}$ = 29 Hz); IR (KBr) 3259 br, 3107 m, 2984 w, 1723 vs, 1671 s, 1614 m, 1512 m, 1475 w, 1319 m, 1251 vs, 1209 vs, 1167 vs, 1101 vs, 1048 m, 956 m, 887 w, 822 w, 756 w, 675 w cm^{-1}; MS (EI) *m/z* 279 (M^+, 29 %), 260 (7), 251 (64),

237 (100), 236 (34), 202 (9), 159 (24), 147 (21), 122 (31), 101 (9), 78 (14), 54 (5), 43 (9), 42 (33). HRMS, calcd. for $^{12}C_7H_3ClF_6N_2O$: 279.98381; found: 279.98394. Anal. calcd. for $C_7H_3ClF_6N_2O$: C, 29.97; H, 1.08; N, 9.99 %. Found: C, 30.15; H, 0.92; N, 10.23 %.

5-Methyl-1,3-dihydro-1,3-diazepin-2-one 19aa

130 mg (1.0 mmol) of 6-methyltetrazolo[1,5-*a*]pyridine **1Taa** was treated in a similar manner as was **1Tt** and photolysed for 4 h to yield 100 mg of crude **19aa** as a pale yellow solid. Sublimation (70-80 ^{o}C/0.5-0.1 mbar) of the crude product afforded 80 mg (67%) of pure **19aa**; mp 117-118 ^{o}C. ^{1}H NMR (actone-d_6 / DMSO-d_6, 200 MHz) δ 7.69 (br s, 1 H, NH), 7.55 (br s, 1 H, NH), 6.12 (dd, 1 H, 7-H, $J_{1,7}$ = 8.6, $J_{6,7}$ = 8.6 Hz), 5.92 (m, 1 H, 4-H), 5.39 (d, 1 H, 6-H, $J_{6,7}$ = 8.6 Hz), 1.73 (s, 3 H, CH_3); ^{13}C NMR (actone-d_6 / DMSO-d_6, 50 MHz) δ 165.8 (2-C), 127.2 (7 or 4-C), 123.1 (4 or 7-C), 119.5 (5-C), 113.7 (6-C), 19.5 (CH_3); IR (KBr) 3271 br, 2977 w, 2937 w, 1702 vs, 1681 s, 1640 vs, 1468 w, 1435 m, 1404 m, 1384 w, 1308 m, 1261 m, 1238 w, 1205 m, 1175 m, 1091 w, 1075 w, 935 w, 842 m, 802 w, 763 m cm^{-1}. HRMS, calcd. for $^{12}C_6H_8N_2O$: 124.06366; found: 124.06349. Anal. calcd. for $C_6H_8N_2O$: C, 58.05; H, 6.50; N, 22.57. Found: C, 58.33; H, 6.68; N, 22.72.

6-Methyl-2,4-diazabicyclo[3,2,0]hept-6-en-2-one 25aa

30 mg of the 2-diazepinone **19aa** was irradiated in an NMR tube for *ca.* 8 h to give 30 mg (98 %) of **25aa** as a white solid, mp 137 –138 ^{o}C. ^{1}H NMR (actone-d_6/DMSO-d_6, 200 MHz) δ 6.60 (br s, 1 H, NH), 6.45 (br s, 1 H, NH), 6.00 (m, 1 H, 7-H), 4.32 (m, 2 H, 1 and 5-H), 1.70 (s, 3 H, CH_3); ^{13}C NMR (actone-d_6/DMSO-d_6, 50 MHz) δ 164.4 (3-C), 154.2 (6-C), 135.8 (7-C), 58.8 (1 or 5-C), 54.1 (5 or 1-C), 23.8 (CH_3); IR (KBr) 3198 br (N-*H*), 3059.0 m, 2984.7 w, 2959.1 w, 2941 w, 2924.5 w, 2831.8 w, 1688.0 vs, 1598.9 m, 1441.0 m, 1384 w, 1377.9 m, 1290 m, 1223.0 w, 1192.2 m, 1137.5 w, 1126.5 w, 1104.6 w, 1053.4 w, 1021.4 w,

963.6 w, 896.3 w, 872.1 w, 801.8 m, 730.5 m br, 616.0 w cm^{-1}. HRMS, calcd. for $^{12}C_6H_8N_2O$: 124.06366; found: 124.06351. Anal. calcd. for $C_6H_8N_2O$: C, 58.05; H, 6.50; N, 22.57. Found: C, 58.11; H, 6.55; N, 22.60.

3-Dimethylamino-2*H*-2,4-diazabicyclohepta-3,6-diene 27a

A solution of tetrazolo[1,5-*a*]pyridine **1Ta** (100 mg; 0.83 mmol) in 100 ml of dioxan/ dimethylamine was photolysed for 12 h. Evaporation of the solvent and chromatography on alumina, eluting with hexane-ethyl acetate 9:1, afforded a white solid, which was purified by sublimation at 70 °C/0.5 mbar; mp 136-137 °C; yield 20%; ^{1}H NMR (acetone-d_6) δ 6.21 (m, 2 H, H-6,7), 4.48 (m, 2 H, H-1,5), 2.81 (s, 6 H, CH_3); ^{13}C NMR (acetone-d_6) δ 164.5 (C=N), 143.1 (C-6,7), 67.9 (C-1,5), 378 (CH_3); IR (KBr) 3438 s, br., 1587 vs cm^{-1}; MS *m/z* 137 (M^+, 90%), 122 (55), 108 (95), 95 (100).

3-Di*iso*propylamino-6-trifluoromethyl-2*H*-2,4-diazabicyclohepta-3,6-diene 27i

Prepared from 6-trifluoromethyltetrazolo[1,5-*a*]pyridine **9T** and diisopropylamine as described for **27a**. Evaporation of the solvent gave a brown oil containing several compounds according to TLC. Chromatography on alumina, eluting with hexane-ethyl acetate 9:1 afforded 11 mg (8%) of a yellow oil; ^{1}H NMR ($CDCl_3$) δ 6.79 (m, 1 H, 7-H), 4.57 (m, 1 H, 1-H), 4.03 (m, 1 H, 5-H), 4.45 (br s, 1 H, 2-H), 4.06 (septet, 2 H, iPr), 1.30 (d, 12 H, CH_3); MS *m/z* 261 (M^+).

Computational data

Table S4: Cartesian coordinates of MP2/6-31G*-optimised geometries of tautomers **20a-c**, **21a-b**, **22aA-F** and the H-bonded dimeric **22aB** (B3LYP/6-31G*).

20a

N 1.6204243623 0.1517524542 -0.188325319
C 0.9485876529 -1.0486550069 -0.0267035011
C 1.1330423074 1.3319925332 -0.7766829331
C -0.0383980267 1.8752100688 -0.4173170739
C -0.8402657317 1.2788942951 0.7003902093
N -0.4507648202 -1.0197373648 -0.0948043248
C -1.3973255945 -0.0676503615 0.3030605138
O 1.5494431201 -2.1066391416 0.1302641878
O -2.5852638957 -0.359902897 0.319441554
H 2.6209069144 -0.0143849816 -0.2327839169
H 1.7723263614 1.769166444 -1.5394580312
H -0.406410089 2.750384947 -0.9419925697
H -1.6875400169 1.9046157772 0.983161679
H -0.1946709227 1.1378982257 1.5792982736
H -0.8395064825 -1.958198902 -0.1604471517

20b

N 1.6093511962 0.0759451307 -0.3686016673
C 0.9330562242 -1.0605003902 0.0827591697
C 1.1217472303 1.3238685175 -0.7588640279
C -0.0078456718 1.8706897703 -0.2724702021
C -0.7913030185 1.1593928292 0.7972981348
N -0.4508609417 -1.1140732301 -0.1443760918
C -1.2189084397 -0.142763926 0.1879785748
O 1.5625844259 -2.0099497207 0.5331114694
O -2.5406385569 -0.2172886823 -0.0749814214
H 2.613245856 -0.0751591512 -0.3954632376
H 1.7331403102 1.838226826 -1.4959391215
H -0.3630009831 2.813717097 -0.6732456083
H -1.6616518418 1.7302087642 1.1236506491
H -0.1530808173 0.9546877629 1.6671613127
H -2.6741292054 -1.0809981837 -0.5205699603

20c

N 1.5617401983 0.0989538279 -0.3191676371
C 0.8009998957 -0.9673921043 0.0723821992
C 1.0727988852 1.3262082643 -0.7824399151
C -0.0698276402 1.8770059558 -0.337415276
C -0.8843591392 1.2505626649 0.7541066677
N -0.4746546577 -1.1193490435 0.1758703306
C -1.4016801339 -0.0752430144 0.1949663597

O 1.6167644214 -2.0264634944 0.3295861015
O -2.5566821729 -0.2206058768 -0.1824696949
H 2.5419222509 -0.1172099877 -0.464666293
H 1.6874871271 1.7957040953 -1.5446458646
H -0.4266789065 2.7803822467 -0.8214677077
H -1.7389679879 1.8726145161 1.023483079
H -0.2695606113 1.0712043919 1.6445044261
H 1.0079501496 -2.7502243823 0.5793420399

21a

N 1.6055306836 0.2154089873 0.0161816031
C 0.8725125179 -1.1332873988 -0.2033457851
C 1.0891363729 1.3337842491 -0.8009898457
C -0.0901947477 1.8543022464 -0.4640121796
C -0.8934195019 1.33922057 0.6979380644
N -0.4481828165 -1.0949769186 0.1027390437
C -1.393403999 -0.0767585654 0.4848972411
O 1.5420242659 -2.0533963154 -0.5934839015
O -2.5434521122 -0.4235512689 0.6335444211
H 2.5851345304 -0.0039856366 -0.22487925
H 1.5936887723 0.4584181341 1.0210301275
H 1.7211684995 1.6207473711 -1.6325053194
H -0.4823290476 2.6712580846 -1.0624539419
H -1.7869192788 1.9439525773 0.8602184929
H -0.3200465411 1.3774978097 1.6380225476
H -0.908493087 -1.9988987541 -0.0392863118

21b

N 1.6737666507 0.1446287392 -0.2213941937
C 1.0430906294 -1.0291709811 0.056416518
C 1.1664619217 1.3391954942 -0.7717949742
C -0.0057368181 1.8717536035 -0.3985444734
C -0.803227133 1.2430901617 0.7176245234
N -0.4247083848 -1.0201818471 -0.0946998406
C -1.2799684892 -0.0735043742 0.2277842155
O 1.5566753598 -2.085002704 0.3541898931
O -2.573844995 -0.2229661683 0.1194997321
H 2.687041898 0.032028249 -0.1973027796
H 1.8123806171 1.8046468819 -1.5099258264
H -0.377453231 2.7676332985 -0.8825383114
H -1.6666642047 1.8436405427 1.0054593761
H -0.1672108158 1.0822352233 1.599596353
H -0.7557692812 -1.961291544 -0.3238675388
H -2.8620964255 -1.0844533424 -0.2571948893

22aA

N -0.6910732773 1.4424369955 -1.774282083

C -1.2185303464 0.3657339948 -1.2668640561
C 0.436157322 2.0013618539 -1.2059550828
C 1.4603508371 1.322075045 -0.6330041689
C 1.4109218787 -0.1742117164 -0.5939742334
N -0.9761012071 -0.2956421099 -0.0848470533
C 0.2568793321 -0.4581585457 0.3349621834
O -2.3173024232 -0.111130739 -1.9199844084
N 0.4631812444 -0.8260307926 1.6274664176
C 1.7219414707 -1.412919843 2.0684190354
C -0.7075494679 -1.0322130354 2.4722516229
H 0.4942908511 3.0843600775 -1.3070913553
H 2.3039206613 1.8535571483 -0.2013048979
H 2.355365003 -0.6192892689 -0.2825411053
H 1.1488214093 -0.575978818 -1.582039154
H -2.6317940985 -0.8591295364 -1.3782219439
H 1.7007305304 -1.4774728852 3.1570773858
H 2.5653368512 -0.7784265216 1.792452234
H 1.8813988466 -2.4207191369 1.6653024661
H -0.395338846 -0.9828991937 3.5171918939
H -1.1827564412 -2.0020154029 2.2803566087
H -1.4346288603 -0.2482957202 2.2653203619

22aB

N -0.8506444745 1.3990986271 -1.6259580428
C -1.3445661887 0.1281323578 -1.2841978868
C 0.2357293254 2.1024480236 -1.117988436
C 1.3141239186 1.5046594757 -0.5746936635
C 1.3995023943 0.0057483745 -0.5626976702
N -0.9666455168 -0.4019126856 -0.0554646589
C 0.2717830624 -0.4534984887 0.3372073906
O -2.196842683 -0.3885516841 -2.0028824035
N 0.5303169427 -0.8197469125 1.6306249711
C 1.8125878675 -1.3910905827 2.0226494602
C -0.6195695436 -1.2216758328 2.4355462096
H -1.3823151226 1.8130310323 -2.3856812535
H 0.1571290931 3.1844758752 -1.1931699905
H 2.0929820419 2.1064086936 -0.1181373538
H 2.3850320994 -0.3433853682 -0.25733161
H 1.2040880105 -0.390145365 -1.5680781865
H 1.8416805785 -1.4369065413 3.1126218277
H 2.6400243144 -0.7589384707 1.701197959
H 1.9608993645 -2.4061566878 1.6304344196
H -0.3133559362 -1.2471550305 3.4832051719
H -1.0000241833 -2.2067729206 2.1385020148
H -1.4201324715 -0.4964549117 2.3001279198

22aC

N -0.9132529882 1.7677875588 -0.8369213888

C -1.4098048142 0.8443176839 0.0872227726
C 0.214387265 2.4928412639 -0.3311715631
C 1.3363217047 1.8553369086 0.0479547042
C 1.5123762089 0.4163021961 -0.0045222136
N -0.8003605926 -0.1500086331 0.614320854
C 0.5129981383 -0.4858748161 0.2287815572
O -2.7124032023 1.0838824345 0.3967546027
N 0.7166581278 -1.8703656945 0.2853105119
C 2.0460753528 -2.3473465433 -0.0457325782
C -0.3452353982 -2.6963535178 -0.2819932909
H -1.6598683901 2.3807172531 -1.1547820671
H 0.0963656649 3.5708439111 -0.2465177642
H 2.1640569621 2.4666215479 0.4028514875
H 2.5171297026 0.056426758 -0.1941673748
H -2.9738426637 0.3482501713 0.9870839187
H 2.0682145754 -3.4295425903 0.1004949638
H 2.7784404181 -1.89630451 0.6275352964
H 2.3384640349 -2.1265702852 -1.0854728574
H -0.1832350672 -3.732218113 0.0272664119
H -0.3643543892 -2.6565538718 -1.3829436106
H -1.3061678024 -2.3599614182 0.1024086058

22aD

N -0.7527404183 1.3238883431 -1.8047089704
C -1.093171298 0.0187996832 -1.4794205411
C 0.2931130268 1.9993515134 -1.0379703116
C 1.5225166576 1.1341400636 -0.9239602722
C 1.4735901109 -0.0190035943 -0.229723476
N -0.9699034109 -0.3078037307 -0.110948495
C 0.2090806498 -0.4182681605 0.4323911095
O -1.5904524706 -0.7494756881 -2.2956461824
N 0.3105485906 -0.9916449064 1.6786983806
C 1.3596458522 -0.5730521287 2.597923275
C -0.9293039219 -1.4068623224 2.3196714908
H -0.7529846677 1.4676306962 -2.8109076569
H 0.512695015 2.9472328277 -1.5346433356
H -0.1053737811 2.2311965567 -0.0437834242
H 2.4311404278 1.4174133632 -1.4517192946
H 2.3317407465 -0.6857160881 -0.1775152067
H 1.0488007194 0.2957619781 3.1956539324
H 2.2647563773 -0.3092050555 2.0523631579
H 1.5894304802 -1.3975816959 3.2781399635
H -0.6773487102 -2.0752358748 3.1467057706
H -1.5491409412 -1.9266612043 1.5904543141
H -1.4982556951 -0.5507382669 2.7056671857

22aE

N -0.6409955834 1.9385926587 -0.8973060394

C -1.3153394484 0.872961085 -0.3529992074
C 0.4340500037 2.3474336516 -0.301736266
C 0.8540148961 1.8613938207 1.0508799522
C 1.3920836991 0.5117847164 0.6914753589
N -0.8201335003 -0.2657074832 0.0535449032
C 0.5397739859 -0.4493892544 0.2364420517
O -2.6589236642 0.9931325174 -0.4621460877
N 1.0357821052 -1.7702865414 0.0182616019
C 0.5880130199 -2.3134082065 -1.2645303768
C 0.6625748314 -2.6589386245 1.1209763965
H 1.0749771019 3.0399919155 -0.850179382
H 1.6092777865 2.5047987541 1.5062986138
H -0.0178291869 1.7894327889 1.7155871988
H 2.4501140631 0.2826670485 0.7716780772
H -3.01210219 0.1280425924 -0.169318826
H 1.1008021064 -3.2645010174 -1.436187317
H 0.8677286151 -1.620506633 -2.0621138109
H -0.4984022937 -2.480344441 -1.3052427866
H 1.1359802038 -3.6327910466 0.9634059659
H -0.4264189698 -2.8030838985 1.2002705192
H 1.0336650003 -2.2379797705 2.0584197349

22aF

N -1.0544016357 1.4417196799 -1.2669749462
C -1.6251631187 0.3244574206 -0.6714776706
C -0.3507624048 2.4402378869 -0.555372317
C 0.7198718279 2.1959504389 0.2258399397
C 1.2592222395 0.8684627541 0.453661712
N -0.9461792078 -0.1308831881 0.4596430396
C 0.4647670045 -0.2262576218 0.5362694478
O -2.6454078591 -0.2092900132 -1.0937272008
N 0.8831923811 -1.5386677255 0.8292533341
C 2.2473528725 -1.6681622981 1.3175588252
C 0.5971940071 -2.5040913914 -0.238290805
H -1.6459679582 1.7716541982 -2.0229873992
H -0.7157555991 3.4535090251 -0.7093082223
H 1.2059476123 3.05042873 0.6917489898
H 2.3360664032 0.751923862 0.518420219
H -1.4239844005 -0.9286111495 0.8706338292
H 2.3893916483 -2.6932568012 1.6692712332
H 2.3977120216 -0.9824444644 2.1534001173
H 3.0035604513 -1.4608496704 0.5431230391
H 0.7147568485 -3.5161063479 0.1581665123
H 1.2770740317 -2.3758945225 -1.0949003005
H -0.4287135168 -2.3847972528 -0.5903351975

dimeric 22aB

N -1.5575795413 0.9836938375 0.1236917683

C -2.0573966136 -0.3129329562 0.030163758
C -2.2448981195 2.1806884258 0.2365377212
C -3.4620168401 2.324745662 0.7892857486
C -4.1667694194 1.1390860398 1.401274516
N -3.3899934953 -0.5183117693 -0.2410089354
C -4.3833159605 0.127914156 0.284730378
O -1.2600656358 -1.2630787409 0.0524144788
N -5.6449460521 -0.0904068308 -0.193355346
C -6.7931777958 0.693847349 0.2446667275
C -5.8190964707 -0.9084484188 -1.3914983506
H -0.5308343122 1.0462507205 0.026203463
H -1.6901587711 3.037790622 -0.1366251636
H -3.9452814021 3.2957790068 0.7821523854
H -5.0860257046 1.4380707118 1.9045258724
H -3.5222412332 0.6609597235 2.1519346195
H -7.6856723132 0.2935151469 -0.240380885
H -6.707662439 1.7547421823 -0.0297794987
H -6.9474002984 0.6224733777 1.3257766226
H -5.8254569476 -0.2938375932 -2.3029669109
H -6.7671098947 -1.4510277007 -1.3239638542
H -4.991549355 -1.6135145027 -1.4553417775
N 1.5663601402 -0.9691930998 0.1342456434
C 2.0534574393 0.3057761623 -0.143255742
C 2.2647933483 -2.1472283527 0.3400851397
C 3.5168060987 -2.229997267 0.8230646197
C 4.2560123241 -0.9834671744 1.2434613321
N 3.3639023123 0.4729093242 -0.5258210483
C 4.3929965838 -0.1107559025 0.004227793
O 1.2556739306 1.2551275355 -0.1781815926
N 5.618805908 0.0455747617 -0.5796519658
C 6.7970461383 -0.686464233 -0.1310694
C 5.7085835462 0.71709572 -1.8742776765
H 0.5357330601 -1.0389934793 0.1137255011
H 1.6900084604 -3.0401098944 0.1077354495
H 4.0026210578 -3.1969470907 0.8972036458
H 5.2081713864 -1.2249054161 1.7154594043
H 3.6612553761 -0.4183835753 1.9745232307
H 7.6533488763 -0.3488955817 -0.7183312582
H 6.6976832927 -1.7718292795 -0.2733516945
H 7.0231223121 -0.4898554598 0.9215032021
H 5.655190164 0.0001530121 -2.7059653974
H 6.6571561435 1.2594923971 -1.9349847272
H 4.8762457258 1.4136634911 -1.9639955204

Table S5: B3LYP/6-31G*-calculated frequencies (scaled by 0.9613) and intensities of tautomers **22aA-F** and dimeric **22aB**.

A		**B**		**C**		**D**		**E**		**F**		**Dimeric B**		continued	
freq.	int.	freq.	int.	freq.	int.	freq.	int.	freq.	int.	freq.	int.	freq.	int.	freq.	int.
45,6	0	49,0	1	59,6	2	76,9	2	42,4	1	59,4	0	13,3	5	1119,9	1
75,2	2	68,6	3	74,6	1	80,5	2	98,8	2	88,9	4	25,1	1	1121,8	116
95,8	0	87,9	3	124,7	9	119,9	1	130,9	1	101,3	4	36,3	6	1121,9	9
120,4	0	98,5	1	170,1	2	126,1	7	150,6	5	174,2	2	51,6	0	1135,0	4
156,0	1	120,4	3	175,8	2	144,3	1	179,0	3	210,4	3	53,4	2	1135,7	4
199,7	6	154,4	1	207,6	7	206,4	1	227,8	3	228,7	0	61,1	2	1189,7	9
244,0	4	228,7	12	236,4	3	224,6	12	244,4	3	276,2	1	74,1	3	1190,9	203
276,8	1	261,7	2	272,0	3	243,7	4	282,8	5	295,9	3	76,6	2	1215,7	0
348,7	6	345,8	2	361,5	1	330,0	1	310,1	18	332,1	3	81,6	0	1216,9	80
375,1	1	365,9	2	378,8	2	383,0	4	377,3	0	366,1	8	95,4	0	1260,1	44
414,0	4	428,8	5	399,8	6	402,7	2	384,6	10	406,4	3	102,2	5	1263,5	12
435,4	5	433,8	14	438,3	4	426,2	8	410,0	6	417,6	2	104,6	0	1283,1	18
481,1	6	485,8	9	484,8	22	444,5	8	474,7	10	506,8	13	112,6	3	1283,5	1
497,8	98	543,6	22	527,9	58	488,1	97	532,6	26	524,8	5	125,6	0	1307,1	508
559,2	12	563,6	23	539,9	71	546,5	4	561,2	82	553,4	17	141,8	0	1309,8	102
563,0	15	579,1	48	577,3	12	595,7	2	572,9	8	611,3	48	147,7	23	1373,4	134
625,4	2	637,5	5	630,1	6	628,3	28	625,4	11	631,1	6	169,6	1	1373,9	18
683,0	37	679,2	49	649,2	8	696,6	6	661,0	10	655,0	11	173,0	2	1397,5	173
730,2	3	721,6	13	673,6	129	729,4	34	713,8	23	724,9	194	232,8	1	1397,5	20
764,6	25	787,2	3	713,3	5	789,8	39	730,7	24	740,4	11	234,5	49	1408,1	3
801,0	3	810,1	14	749,4	27	834,4	8	834,1	3	786,9	23	276,7	1	1408,5	89
872,2	26	833,3	14	810,6	30	853,8	1	873,4	4	817,1	4	277,0	26	1444,5	12
930,2	1	900,2	5	853,5	14	911,3	26	884,8	11	887,6	7	350,1	2	1444,5	12
937,3	4	931,5	10	877,3	20	952,0	29	938,6	21	892,1	4	360,4	0	1457,0	41
961,4	19	959,2	52	915,9	23	963,3	5	945,1	26	905,1	30	373,0	1	1457,0	19
989,5	46	992,2	12	962,4	31	1032,4	3	1038,6	45	968,5	15	373,6	2	1464,2	1
1049,5	31	1049,6	27	993,5	4	1048,9	7	1048,4	21	999,9	24	430,1	0	1464,3	4
1089,1	4	1092,5	1	1047,8	23	1080,9	20	1067,2	22	1043,2	12	438,2	18	1468,9	13
1109,7	25	1098,0	20	1088,1	38	1092,3	5	1097,4	4	1087,3	24	441,5	11	1468,9	16
1126,6	49	1120,7	41	1094,1	3	1135,0	47	1125,2	98	1098,1	13	444,0	14	1478,9	22
1140,7	22	1131,8	10	1115,2	188	1139,4	121	1142,3	69	1117,3	82	491,2	6	1479,0	0
1173,2	43	1176,3	162	1136,9	54	1168,2	11	1184,6	49	1143,4	15	495,6	22	1497,8	5
1220,8	9	1204,9	37	1195,3	159	1220,7	92	1224,2	15	1196,3	25	558,2	0	1498,0	161
1251,8	109	1241,6	19	1217,9	16	1253,8	30	1245,9	179	1218,0	46	559,1	5	1507,1	79
1276,6	26	1279,7	116	1238,0	56	1275,9	158	1262,3	43	1280,0	59	573,2	4	1519,5	1
1282,4	70	1288,6	111	1302,5	12	1338,1	66	1312,9	45	1309,5	76	586,6	16	1606,5	997
1333,6	569	1372,1	52	1333,1	62	1367,8	11	1340,1	11	1342,4	33	639,0	6	1609,4	10
1377,0	5	1396,3	81	1361,3	77	1400,2	91	1365,0	65	1406,4	40	639,2	9	1650,9	1297
1398,7	22	1407,1	21	1383,8	14	1402,4	36	1402,8	51	1411,7	1	678,4	6	1652,5	3
1416,6	72	1424,7	13	1409,0	16	1412,6	33	1412,9	78	1417,7	24	679,0	41	1669,3	1
1445,0	44	1445,2	20	1437,3	1	1438,2	13	1442,7	13	1436,3	9	724,1	3	1677,2	957
1453,3	42	1455,8	26	1457,7	14	1450,7	2	1446,9	5	1447,7	43	726,5	8	2911,9	42
1465,7	10	1464,2	2	1465,7	6	1457,2	16	1456,3	9	1454,7	3	784,8	4	2911,9	42
1473,3	2	1469,0	14	1467,7	118	1460,3	3	1461,8	37	1467,3	28	785,4	35	2918,0	116
1476,8	23	1478,8	7	1479,2	25	1475,4	13	1480,7	8	1474,3	7	806,5	67	2918,2	55
1494,3	3	1498,3	49	1493,5	21	1501,9	13	1491,2	45	1491,6	15	807,9	1	2923,1	9
1537,5	344	1611,9	383	1591,4	355	1587,6	376	1516,3	73	1644,2	265	826,3	12	2923,1	18
1598,1	402	1657,4	165	1660,2	206	1646,6	109	1574,3	474	1663,8	69	844,3	19	2983,3	22

1603,9	92	1717,6	581	1692,9	259	1724,5	449	1621,0	215	1745,8	456	849,0	4	2983,3	24
2913,8	34	2912,5	43	2863,7	56	2897,7	60	2870,0	50	2862,9	55	882,0	188	2986,8	56
2920,2	43	2919,0	67	2871,2	131	2912,3	72	2878,1	124	2877,1	91	912,0	19	2986,9	20
2921,0	47	2925,2	11	2969,2	18	2929,7	29	2901,8	35	2972,8	30	913,6	11	3028,3	70
2976,6	33	2981,9	23	2971,2	65	2962,6	36	2961,4	32	2977,3	46	934,9	32	3028,4	2
2994,8	19	2988,8	33	3014,0	26	2980,5	36	2977,4	42	3024,0	17	935,5	3	3036,0	18
3027,1	16	3029,4	24	3042,6	18	3006,3	22	3004,4	12	3031,9	14	968,1	50	3036,1	24
3030,2	35	3036,6	16	3064,0	7	3049,2	19	3019,4	28	3050,0	8	971,2	12	3068,1	1
3037,5	19	3062,9	14	3078,6	27	3054,6	0	3028,3	40	3072,9	37	994,6	85	3068,2	1
3078,2	24	3067,8	1	3097,4	18	3061,1	3	3065,4	8	3090,0	12	996,1	2	3071,1	13
3079,9	1	3096,4	15	3452,0	28	3072,4	22	3120,3	13	3464,7	34	1050,3	50	3071,3	0
3591,9	51	3457,6	37	3567,1	52	3458,8	22	3560,7	47	3473,9	37	1050,4	6	3096,5	1
												1092,0	1	3096,7	47
												1092,0	1	3098,5	3
												1119,6	10	3141,6	3693

Table S6: B3LYP/6-31+G**//MP2/6-31G*-calculated ^{13}C chemical shifts (ppm) of tautomers **22aA-F** relative to TMS. The second set is the assignment of experimental data, together with the sums of deviation.

	C2	C4	C5	C6	C7	C10	C11	
A	154.6	147.8	32.5	94.2	141.0	38.1	39.9	
B	152.9	155.1	31.3	101.1	127.1	38.8	40.1	
C	149.6	154.9	89.5	115.5	117.8	39.5	39.8	
D	160.1	154.4	126.1	138.4	42.0	39.1	37.4	
E	158.2	160.0	89.0	35.1	139.4	43.4	48.1	
F	164.6	146.4	93.1	113.7	122.3	40.9	42.0	
A	160.3	159.8	29.1	102.3	130.2	38.3	38.7	41.4
B	**159.8**	**160.3**	**29.1**	**102.3**	**130.2**	**38.3**	**38.7**	**20.4**
C	159.8	160.3	29.1	102.3	130.2	38.3	38.7	103.8
D	160.3	159.8	102.3	130.2	29.1	38.7	38.3	51.8
E	159.8	160.3	102.3	29.1	130.2	38.3	38.7	45.0
F	160.3	159.8	29.1	102.3	130.2	38.3	38.7	107.0

Table S7: B3LYP/6-31+G**//MP2/6-31G*-calculated ^{1}H chemical shifts (ppm) of tautomers **22aA-F** relative to TMS. The second set is the assignment of experimental data, together with the sums of deviation.

	OH	NH	H5	H6	H7	methyl groups protons							
A	5.03		3.36/1.82	4.71	7.20	2.35	3.40	2.95	2.03	2.79	3.73		
B		6.14	3.18/2.58	5.03	6.41	2.46	3.31	2.85	1.97	2.81	3.76		
C	5.59	4.34	4.65	5.55	5.44	2.35	2.71	2.36	2.08	1.96	3.71		
D		4.73	6.47	6.69	2.91/3.60	2.49	3.13	2.62	2.11	3.97	2.40		
E	5.63		4.88	3.00/1.01	6.74	2.14	1.90	2.55	2.55	2.92	2.64		
F	5.09*	4.81	4.77	5.67	5.93	2.46	2.59	2.27	2.38	1.89	3.20		
												1-5	all
A	8.62		3.00	5.00	6.23	3.11	3.11	3.11	2.95	2.95	2.95	6.38	9.44
B		**8.62**	**3.00**	**5.00**	**6.23**	**3.11**	**3.11**	**3.11**	**2.95**	**2.95**	**2.95**	**3.29**	**6.34**
C			wrong coupling										
D		8.62	6.23	5.00	3.00	3.11	3.11	3.11	2.95	2.95	2.95	6.51	10.05
E			wrong coupling			3.11	3.11	3.11	2.95	2.95	2.95		
F			wrong coupling			3.11	3.11	3.11	2.95	2.95	2.95		

* second NH signal

Table S8: Calculated absolute energies (kcal/mol, 0K) and zero-point vibrational energies of structures **20a-c**, **21a-b** and tautomers **22aA-F** at various levels of theory.

	HF/6-31G*		B3LYP/6-31G*		MP2/6-31G*
	Energy a.u.	ZPVE kcal/mol	Energy a.u.	ZPVE kcal/mol	Energy a.u.
A	-509.65471	124.22	-512.81468	115.26	-511.21113
B	-509.67320	124.26	-512.83129	115.38	-511.22686
C	-509.63689	124.37	-512.79556	115.22	-511.19041
D	-509.66895	124.40	-512.82406	115.48	-511.22196
E	-509.63732	123.86	-512.80039	114.95	-511.19576
F	-509.67059	124.86	-512.82545	115.87	-511.22131
20a	-451.48336	78.69			-452.78035
20b	-451.45380	78.43			-452.75419
20c	-451.45068	78.29			-452.74993
21a	-451.78829	87.40			-453.10328
21b	-451.81217	87.05			-453.08976

Table S9: B3LYP/6-31+G**//MP2/6-31G*-calculated ^{13}C chemical shifts (ppm) of structures **20a-c** and **21a-b** relative to TMS.

	C2	C4	C5	C6	C7
20a	146.9	166.6	36.9	109.0	124.6
20b	151.3	160.2	31.6	103.2	126.9
20c	143.0	160.1	42.4	109.0	119.9
21a	137.5	174.9	31.8	108.4	129.8
21b	136.0	156.7	35.8	132.0	117.5

Table S10: B3LYP/6-31+G**//MP2/6-31G*-calculated ^{1}H chemical shifts (ppm) of structures **20a-c** and **21a-b** relative to TMS.

	H1	H3/H9/H8		H5	H5	H6	H7
20a	5.98	6.90		2.95	3.22	5.59	6.35
20b	6.26	5.81		2.95	2.87	5.25	6.34
20c	6.41	5.22		3.19	2.70	5.45	6.21
	H1	H1/H9	H3	H5	H5	H6	H7
21a	6.42	7.15	7.68	4.22	3.57	7.29	6.85
21b	7.20	7.30	7.44	3.67	3.72	6.05	6.93