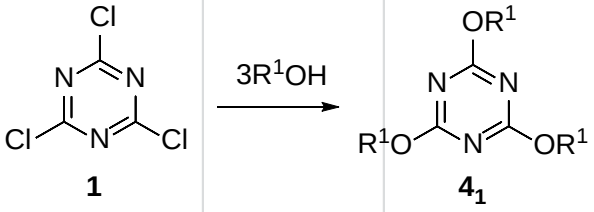
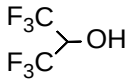
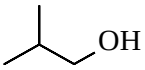
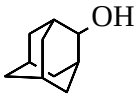
Table S1. Synthesis of C_3-Symmetrical Trialkoxy-Substituted TAZ Derivatives (**4**)

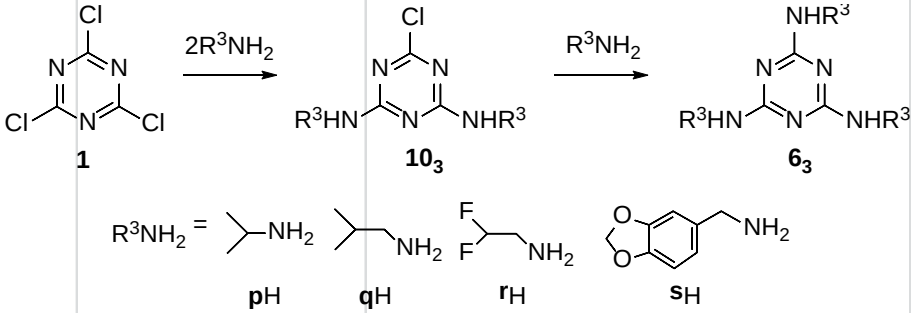


1 **4_1**

Entry	**R^{1}O**H	Base	Ratio of **1** : **R^{1}O**H : Base or **1** : **R^{1}O**K	Conditions[a]	Product (yield %)
1	 **c**H	NaH	1 : 3.2 : 3.2	1) rt 15 min to reflux 1 h 2) rt 15 min to reflux 1 h	**4c** (73)
2	 **d**H	NaH	1 : 3 : 3	1) rt 10 min to reflux 10 min 2) rt 10 min to reflux 2 h	**4d** (69)
3	 **e**H	*t*-BuOK	1 : 3	0℃ 10 min to rt 1 h	**4e** (72)
4	 **h**H	NaH	1 : 3 : 3	1) rt 10 min to reflux 10 min 2) rt 10 min to reflux 2 h	**4h** (35)[b]

a) Under an N_2 (Entries 1, 3) or Ar (Entries 2, 4) atmosphere. *b*) Yield after recrystalization.

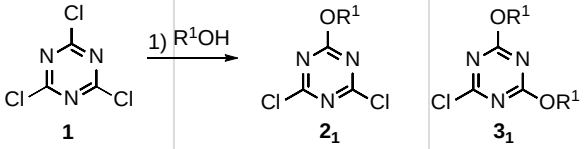
Table S2. Synthesis of C_3-Symmetrical Trialkylamino-TAZ Derivatives (**6**)



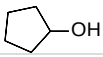
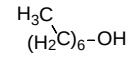
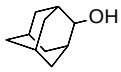
Entry	R^3NH_2	Ratio of **1** : R^3NH_2 (: DIPA)[a)]	Conditions[b)]	Products (yield %)
1	**p**H	1 : 12	MW 1.5 h	**6p** (67), **10p** (7)
2	**q**H	1 : 3.3 : 3.3	reflux 22 h	**6q** (45), **10q** (13)
3	**q**H	1 : 3.3 : 3.3	MW 40 min	**6q** (74), **10q** (20)
4	**q**H	1 : 10	0℃ 25 min to rt 1 h, then MW 25 min	**6q** (92)
5	**r**H	1 : 3.3 : 3.3	reflux 3.5 h	**10r** (86)
6	**r**H	1 : 10	0℃ 20 min to rt 1 h, then MW 80 min	**6r** (88)
7	**s**H	1 : 10	0℃ 15 min to rt 1 h, then MW 80 min	**6s** (85)

a) DIPA stands for di-isopropylamine. *b)* MW means irradiation of microwave (100W, 100℃) in dioxane. To reflux was conducted in THF.

Table S3. Synthesis of Mono- or Di- alkoxy-Substituted TAZ Indermediates (**2**, **3**)

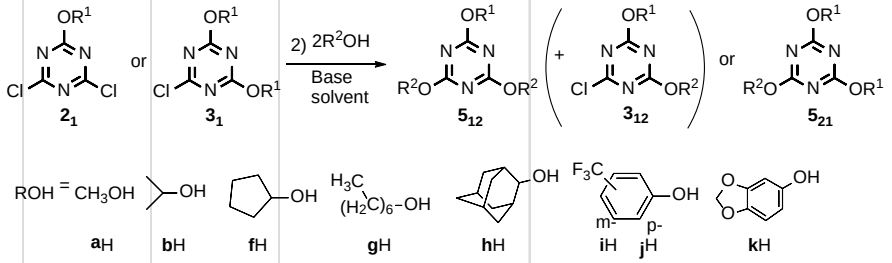


1 **2$_1$** **3$_1$**

Entry	**R^{1}O**H	Method	Ratio of **1** : **R^{1}O**H : Base	Conditions[a]	Products (yield %)
1	**b**H 	collidine/acetone	1 : 2 : 7	rt 3.5 h	**2b**[b] (85)
2	**b**H	NaH/THF	1 : 2 : 3	1) 0℃ 1.5 h 2) -77℃ 10 min to rt 18 h	**3b**[b] (62)
3	**d**H 	collidine/acetone	1 : 1.1 : 1.1	rt 3 h	**2d** (79)
4	**d**H	NaH/benzene	1 : 2 : 2	1) reflux 2 h 2) reflux 1 h	**3d** (59)
5	**f**H 	collidine/acetone	1 : 2.6 : 1.5	rt 2 h	**2f** (46)
6	**f**H	NaH/THF	1 : 2 : 3	1) 0℃ 4 h 2) -78℃ 30 min to 10℃ rt 18 h	**2f** (10), **3f** (59)
7[c]	**g**H 	collidine/acetone	1 : 1.3 : 1	0 ℃ 1 h	**2g** (70)
8	**h**H 	collidine/THF	1 : 1.2 : 1.2	rt 2.5 h	**2h** (63)
9	**j**H	collidine/acetone	1 : 1 : 1	rt 16 h	**2j** (30), **3j** (35)

a) Under a N_2 (Entry 6) or an Ar (Entries 2, 4, 7, 8) atmosphere. *b*) A part of data about compounds **2b** and **3b** were reported in reference 5. *c*) Data were taken from referemce 6.

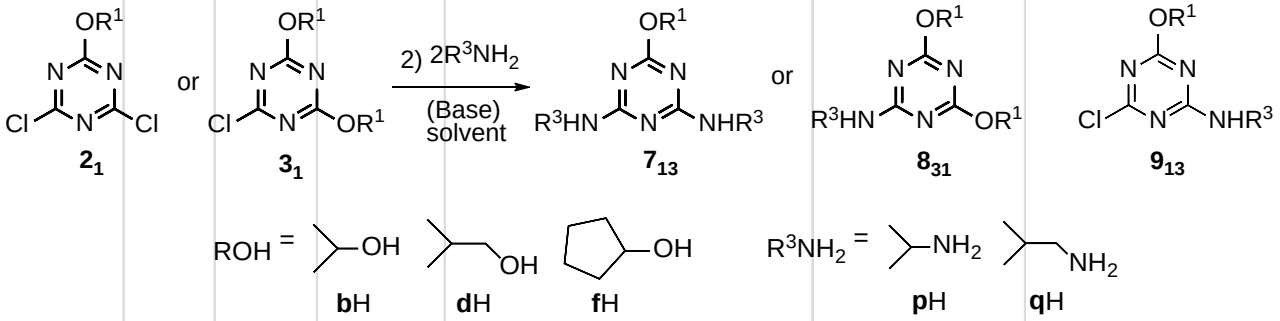
Table S4. Synthesis of C_S-Symmetrical Trialkoxy-Substituted TAZ Derivatives (**5**)



Entry	**2** or **3**	$\mathbf{R^2OH}$	Base/ solvent	Ratio of **2** or **3** : $\mathbf{R^2OH}$: (Base)	Conditions[a)]	Products (yield %)
1	**2a**	**b**H	NaH/ THF	1 : 2.5 : 2.1	1) **b**H + NaH, rt 10 min to reflux 30 min 2) + **2a**, rt 15 min to reflux 2 h	**5ab** (27)
2	**2a**	**k**H	collidine/ acetone-THF	1 : 2.05 : 2.05	rt 1 day to reflux 1 h, acetone-THF	**5ak** (51),[c)] **3ak** (28)
3	**2b**	**h**H	NaH/ THF	1 : 2.5 : 2.1	1) **h**H + NaH, rt 30 min to reflux 30 min 2) + **2b**, rt 10 min to reflux 2 h	**5bh** (60)
4	**2b**	**i**H	collidine/ acetone	1 : 2 : 2	rt 18 h, acetone	**5bi** (77)
5	**2b**	**j**H	collidine/ dioxnae	1 : 3 : 3	MW[b)] 300 W, 40 min, 160℃, dioxane	**5bj** (50), **3bj** (21)
6	**2b**	**k**H	collidine/ acetone	1 : 2.05 : 2.05	rt 17 h, acetone	**5bk** (33), **3bk** (54)
7	**2f**	**i**H	collidine/ acetone	1 : 2 : 2	rt 30 min to reflux 1 h, acetone	**5fi** (71)
8	**2f**	**j**H	collidine/ acetone	1 : 2 : 2	rt 30 min to reflux 2 h, acetone	**5fj**·(**3fj**)$_2$ (29)
9	**2f**	**k**H	collidine/ acetone	1 : 2.05 : 2.05	rt 19 h, acetone	**5fk** (14)[d)]
10	**2g**	**i**H	collidine/ acetone	1 : 2.15 : 2.15	rt 30 min to reflux 1 h, acetone	**5gi** (93)
11	**2g**	**j**H	Et_3N/ acetone	1 : 3 : 2	rt 40 min to reflux 2 d, acetone	**5gj** (58)
12	**2h**	**b**H	NaH/ THF	1 : 2.5 : 2.1	1) **b**H + NaH, rt 10 min to reflux 30 min 2) + **2h**, rt 15 min to reflux 2 h	**5hb** (57)
13	**2j**	**g**H	collidine/ acetone	1 : 2 : 2	rt 19 h to reflux 2.5h, acetone	**3jg** (90)
14	**2j**	**g**H	NaH/ THF	1 : 5 : 4	1) **g**H and NaH, rt 1.5 h 2) + **2j** reflux 1 h	**5jg** (36)
15	**2k**	**b**H	Et_3N/ THF	1 : 1.1 : 1.7	rt 3 d	**5kb** (85)
16	**3a**	**k**H	Et_3N/ THF	1 : 1.1 : 1.1	rt 20 h	**5ka** (67)
17	**3b**	**j**H	collidine/ acetone to dioxnae	1 : 2 : 2	rt 40 min to reflux 3.5 h, acetone, then MW[b)] 50-300 W, 85 min, 160℃, dioxane	**5jb** (42)

a) Reactions using NaH was conducted under an Ar atmosphere. *b*) MW stands for microwave irradiation. *c*) Compound **5ak** has been reported in reference 6. *d*)Yield after recrystallization.

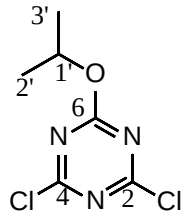
Table S5. Synthesis of C_S-Symmetrical Alkoxy-alkylamino-trisubstituted TAZ Derivatives (**7**, **8**) and Byproduct (**9**)



Entry	**2** or **3**	R^3NH_2	Base	Ratio of **1** : R^3NH_2 : (Base)	Conditions[a)]	Products (yield %)
1	**2b**	**p**H	DIPEA	1 : 4 : 2	reflux 17 h	**7bp** (85)[c)]
2		**q**H	DIPEA	1 : 4 : 2	reflux 3.5 h	**7bq** (47), **9bq** (12)
3	**2d**	**p**H	—	1 : 10	MW 60 min	**7dp** (65)
4		**q**H	—	1 : 6.7	MW 25 min	**7dq** (67)
5	**2f**	**q**H	DIPEA	1 : 2.5 : 2.5	reflux 2 h	**9fq** (73)
6		**q**H	DIPEA	1 : 1.9 : 2	reflux 20 h	**7fq** (29)
7	**3b**	**p**H	—	1 : 3	MW 30 min	**8pb** (69)[c)]
8		**q**H	DIPEA	1 : 1 : 1.25	reflux 17.5 h	**8qb** (24)[c)]
9	**3d**	**p**H	DIPEA	1 : 1.1 : 1.1	reflux 22 h	**8pd** (52)
10		**q**H	—	1 : 3	MW 30 min	**8qd** (85)

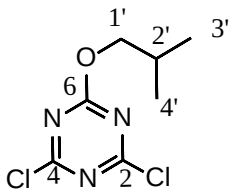
a) DIPEA stands for di-isopropylethylamine. *b)* MW means irradiation of microwave (100W, 100℃) in dioxane. To reflux was conducted in THF. *c*) Yields after recrystallization.

Compounds list



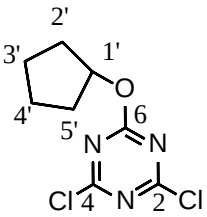
2b

Formula: $C_6H_7Cl_2N_3O$
Mol Wt: 208.04



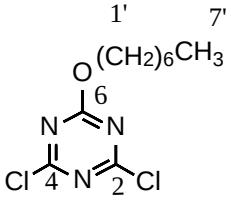
2d

Formula: $C_7H_9Cl_2N_3O$
Mol Wt: 222.07



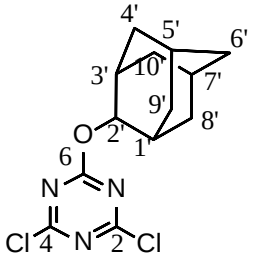
2f

Formula: $C_8H_9Cl_2N_3O$
Mol Wt: 234.08



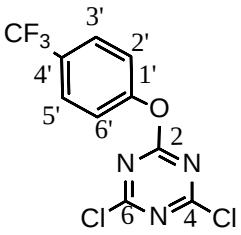
2g

Formula: $C_{10}H_{15}Cl_2N_3O$
Mol Wt: 264.15



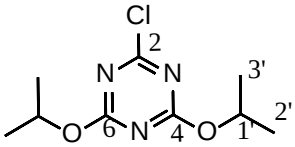
2h

Formula: $C_{13}H_{15}Cl_2N_3O$
Mol Wt: 300.18



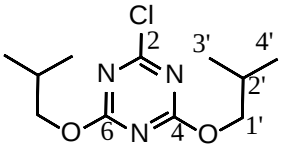
2j

Formula: $C_{10}H_4Cl_2F_3N_3O$
Mol Wt: 310.06



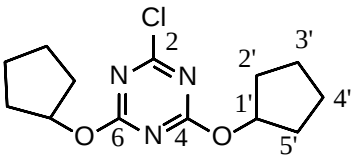
3b

Formula: $C_9H_{14}ClN_3O_2$
Mol Wt: 231.68
Log P: 3.02



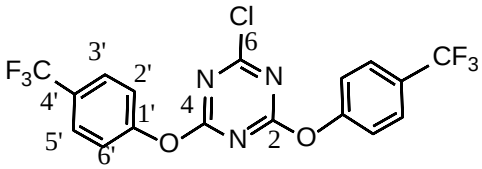
3d

Formula: $C_{11}H_{18}ClN_3O_2$
Mol Wt: 259.73
Log P: 4.15



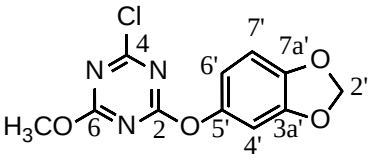
3f

Formula: $C_{13}H_{18}ClN_3O_2$
Mol Wt: 283.76
Log P: 3.97



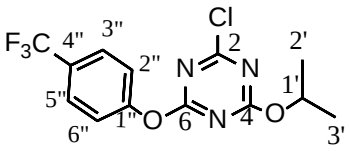
3j

Formula: $C_{17}H_8ClF_6N_3O_2$
Mol Wt: 435.71
Log P: 6.87



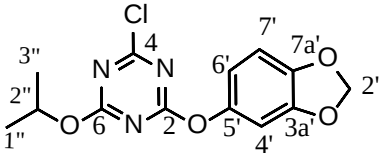
3ak

Formula: $C_{11}H_8ClN_3O_4$
Mol Wt: 281.65
Log P: 3.15



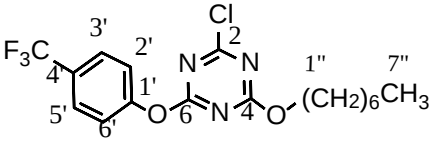
3bj

Formula: $C_{13}H_{11}ClF_3N_3O_2$
Mol Wt: 333.70
Log P: 4.95



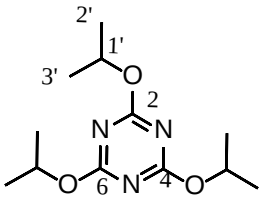
3bk

Formula: $C_{13}H_{12}ClN_3O_4$
Mol Wt: 309.71
Log P: 3.8



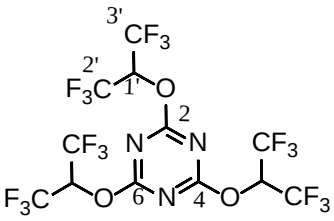
3jg

Formula: $C_{17}H_{19}ClF_3N_3O_2$
Mol Wt: 389.80
Log P: 6.78



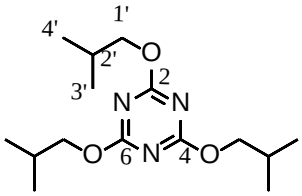
4b

Formula: $C_{12}H_{21}N_3O_3$
Mol Wt: 255.32
Log P: 3.36



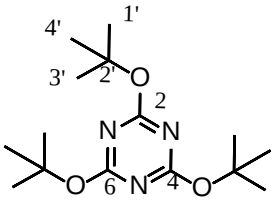
4c

Formula: $C_{12}H_3F_{18}N_3O_3$
Mol Wt: 579.15
Log P: 7.21



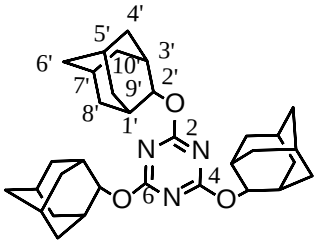
4d

Formula: $C_{15}H_{27}N_3O_3$
Mol Wt: 297.40
Log P: 5.06



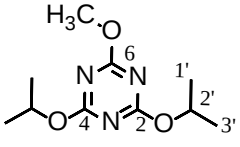
4e

Formula: $C_{15}H_{27}N_3O_3$
Mol Wt: 297.40
Log P: 4.02



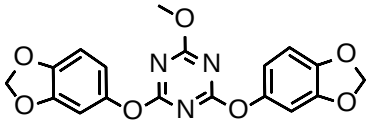
4h

Formula: $C_{33}H_{45}N_3O_3$
Mol Wt: 531.74
Log P: 7.42



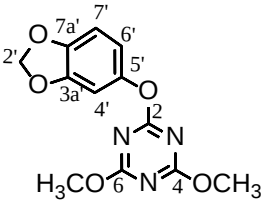
5ab

Formula: $C_{10}H_{17}N_3O_3$
Mol Wt: 227.264
Log P: 2.71



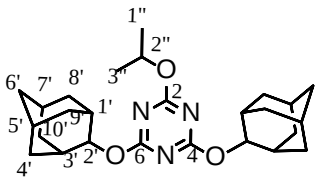
5ak

Formula: $C_{18}H_{13}N_3O_7$
Mol Wt: 383.316
Log P: 4.28



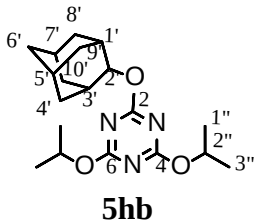
5ka

Formula: $C_{12}H_{11}N_3O_5$
Mol Wt: 277.236
Log P: 2.84



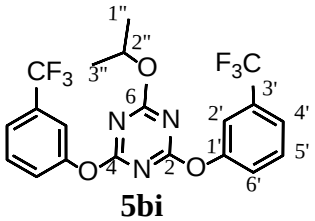
5bh

Formula: $C_{26}H_{37}N_3O_3$
Mol Wt: 439.600
Log P: 6.07



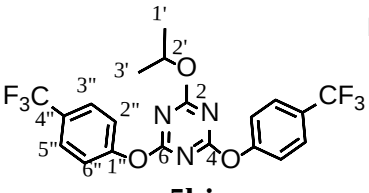
5hb

Formula: $C_{19}H_{29}N_3O_3$
Mol Wt: 347.459
Log P: 4.72



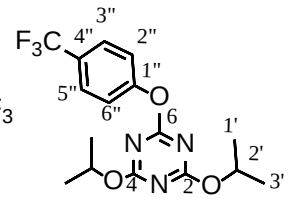
5bi

Formula: $C_{20}H_{15}F_6N_3O_3$
Mol Wt: 459.348
Log P: 7.22



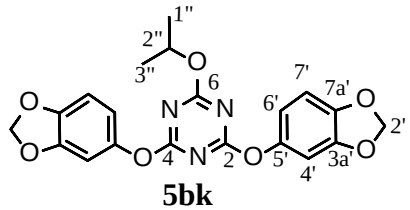
5bj

Formula: $C_{20}H_{15}F_6N_3O_3$
Mol Wt: 459.348
Log P: 7.22



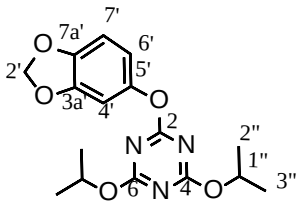
5jb

Formula: $C_{16}H_{18}F_3N_3O_3$
Mol Wt: 357.333
Log P: 5.29



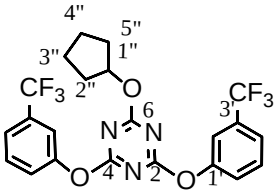
5bk

Formula: $C_{20}H_{17}N_3O_7$
Mol Wt: 411.370
Log P: 4.94



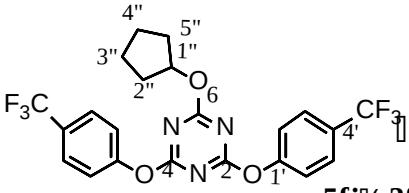
5kb

Formula: $C_{16}H_{19}N_3O_5$
Mol Wt: 333.344
Log P: 4.15



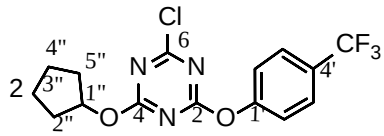
5fi

Formula: $C_{22}H_{17}F_6N_3O_3$
Mol Wt: 485.386
Log P: 7.69

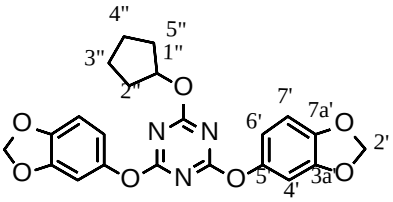


5fj (3fj)$_2$

Formula: $C_{22}H_{17}F_6N_3O_3$
Mol Wt: 485.386
Log P: 7.69

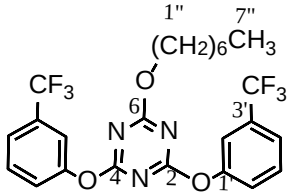


Formula: $C_{15}H_{13}ClF_3N_3O_2$
Mol Wt: 359.733
Log P: 5.42



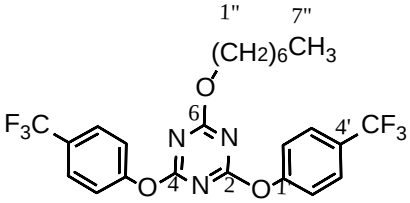
5fk

Formula: $C_{22}H_{19}N_3O_7$
Mol Wt: 437.408
Log P: 5.41



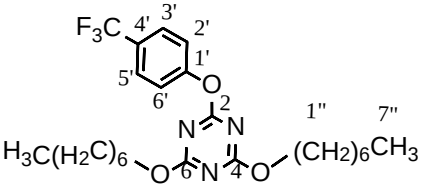
5gi

Formula: $C_{24}H_{23}F_6N_3O_3$
Mol Wt: 515.456
Log P: 9.06



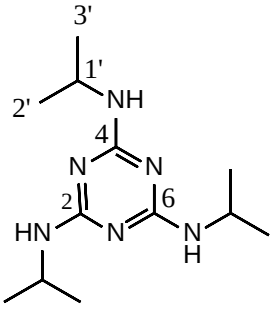
5gj

Formula: $C_{24}H_{23}F_6N_3O_3$
Mol Wt: 515.456
Log P: 9.06



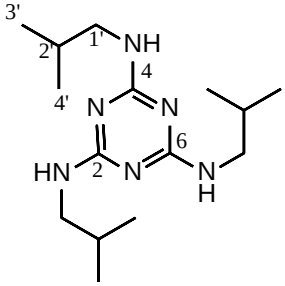
5jg

Formula: $C_{24}H_{34}F_3N_3O_3$
Mol Wt: 469.549
Log P: 8.97



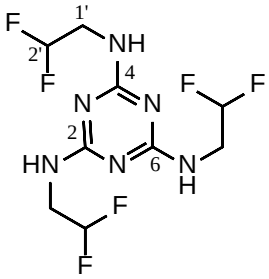
6p

Formula: $C_{12}H_{24}N_6$
Mol Wt: 252.37
Log P: 2.23



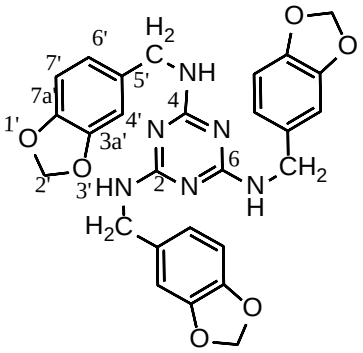
6q

Formula: $C_{15}H_{30}N_6$
Mol Wt: 294.45
Log P: 3.93



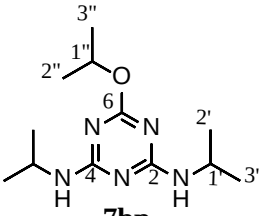
6r

Formula: $C_9H_{12}F_6N_6$
Mol Wt: 318.23
Log P: 1.23



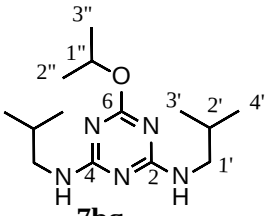
6s

Formula: $C_{27}H_{24}N_6O_6$
Mol Wt: 528.53
Log P: 4.8



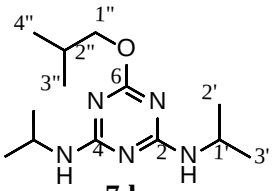
7bp

Formula: $C_{12}H_{23}N_5O$
Mol Wt: 253.350
Log P: 2.61



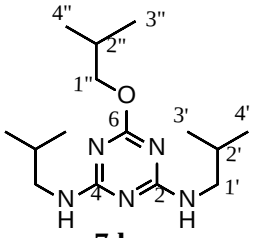
7bq

Formula: $C_{14}H_{27}N_5O$
Mol Wt: 281.404
Log P: 3.74



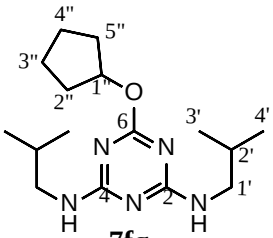
7dp

Formula: $C_{13}H_{25}N_5O$
Mol Wt: 267.377
Log P: 3.18



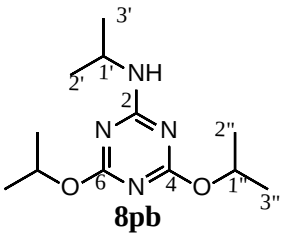
7dq

Formula: $C_{15}H_{29}N_5O$
Mol Wt: 295.431
Log P: 4.31



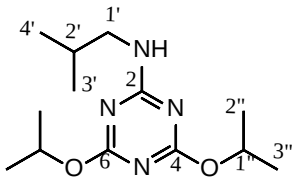
7fq

Formula: $C_{16}H_{29}N_5O$
Mol Wt: 307.442
Log P: 4.22



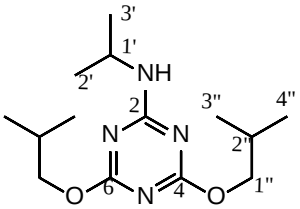
8pb

Formula: $C_{12}H_{22}N_4O_2$
Mol Wt: 254.334
Log P: 2.99



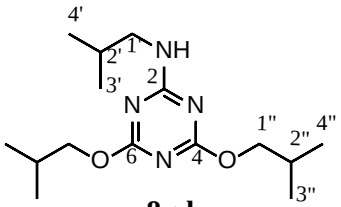
8qb

Formula: $C_{13}H_{24}N_4O_2$
Mol Wt: 268.361
Log P: 3.55



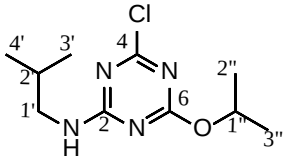
8pd

Formula: $C_{14}H_{26}N_4O_2$
Mol Wt: 282.388
Log P: 4.12



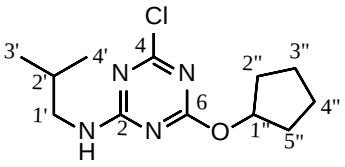
8qd

Formula: $C_{15}H_{28}N_4O_2$
Mol Wt: 296.415
Log P: 4.69



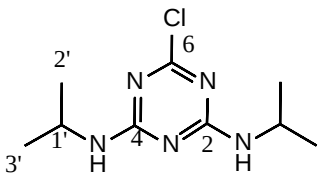
9bq

Formula: $C_{10}H_{17}ClN_4O$
Mol Wt: 244.723
Log P: 3.21



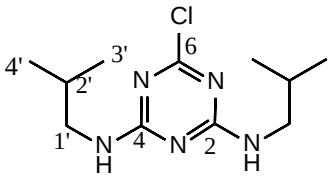
9fq

Formula: $C_{12}H_{19}ClN_4O$
Mol Wt: 270.761
Log P: 3.68



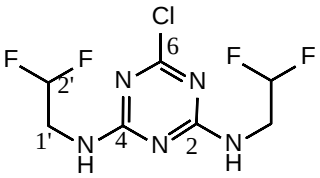
10p

Chemical Formula: $C_9H_{16}ClN_5$
Molecular Weight: 229.71
Log P: 2.26



10q

Chemical Formula: $C_{11}H_{20}ClN_5$
Molecular Weight: 257.77
Log P: 3.4



10r

Chemical Formula: $C_7H_8ClF_4N_5$
Molecular Weight: 273.62
Log P: 1.6