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Interaction of 1,1,3,3-tetramethylguanidine with 3-acyl-4*H*-chromenes

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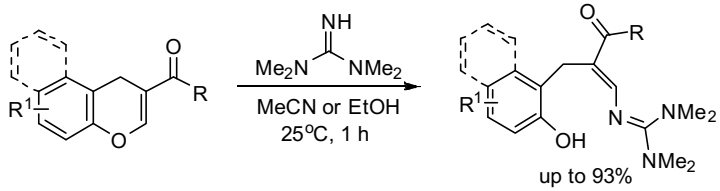
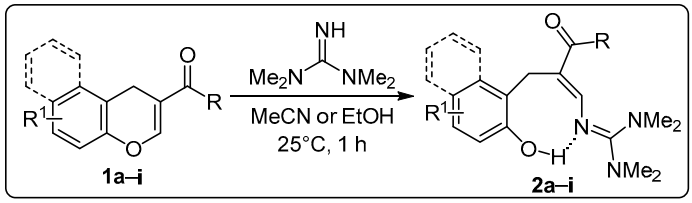


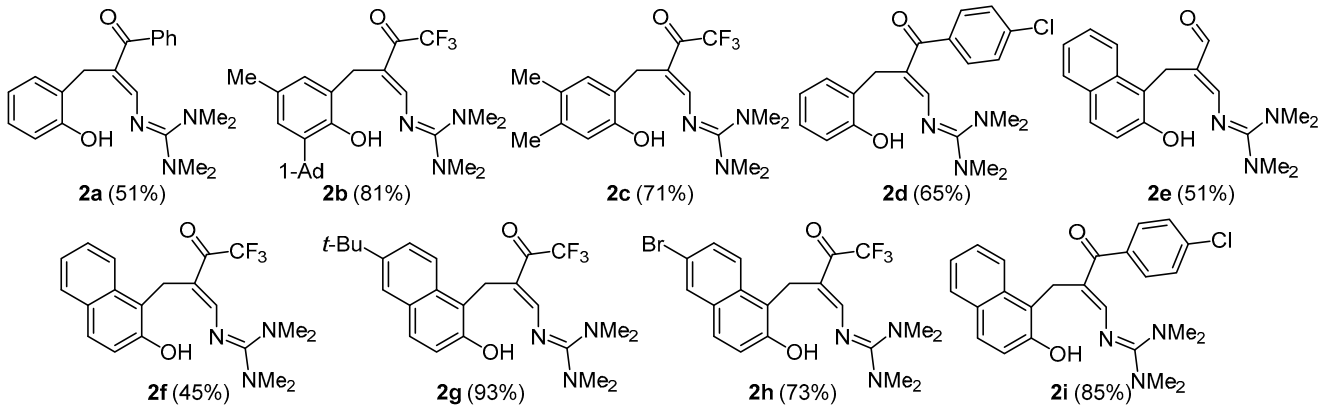
A series of substituted 2-(3-oxoprop-1-en-1-yl)guanidines was obtained *via* the interaction of 1,1,3,3-tetramethylguanidine with fused 4*H*-pyrans, containing a carbonyl group in the β-position to the oxygen atom. The proposed reaction mechanism includes a conjugate 1,4-addition with subsequent opening of the dihydropyran ring.

Keywords: 1,1,3,3-tetramethylguanidine, electron-deficient 4*H*-chromenes, push-pull 2-aza-1,3-dienes, Michael reaction.

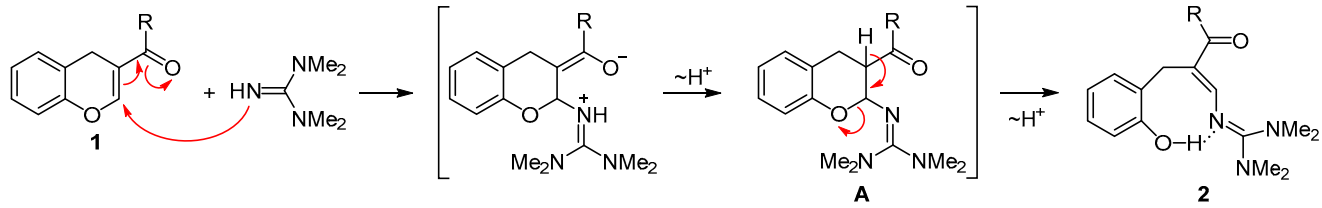
1,1,3,3-Tetramethylguanidine (TMG) finds wide use in organic synthesis as a strong (pK_a 13.6) non-nucleophilic base.[1] The presence of two non-equivalent nucleophilic centers within its structure (nitrogen atoms of the imino and dimethylamino groups) allows TMG to be considered capable of taking part in reactions with various electrophilic reagents. Literature provides several examples of reactions of TMG with C-electrophiles such as alkylating[2] or acylating[3] agents, aryl halides,[4] carbodiimides,[5] isothiocyanates,[6] isocyanates,[7] and certain other reagents.[8] However, instances where TMG would act as a Michael donor in reactions with α,β-unsaturated carbonyl compounds are virtually unknown.[9] We have shown that TMG reacts with fused 4*H*-pyrans **1a**–**i** containing a carbonyl group in the β-position to the oxygen atom with the formation of substituted 2-(3-oxoprop-1-en-1-yl)-guanidines **2a**–**i** in 45–93% yields (Scheme 1). Ethanol or acetonitrile was employed as the solvent.

Scheme 1





Scheme 2



Acyl chromenes may be regarded as Michael acceptors due to the high polarization of the double bond in the pyran ring. 1,4-Addition of TMG to them leads to an unstable adduct **A**, which is stabilized by opening of the dihydropyran ring and formation of a conjugated chain (Scheme 2). The structure of compound **2a**, the adduct of TMG and chromene **1a**, was confirmed by X-ray structural analysis (Fig. 1).

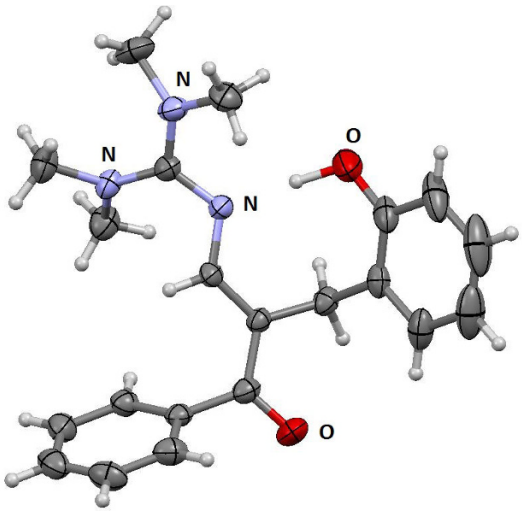


Figure 1. Molecular structure of compound **2a** with atoms represented as thermal vibration ellipsoids of 50% probability.

A characteristic of the structure of compound **2a** is the strong intramolecular hydrogen bond N···H in the eight-membered pseudo ring between the hydrogen atom of the hydroxyl group and the imine nitrogen atom, with a length of 1.601 Å and the corresponding angle O–H···N of 167.41°. Due to the high basicity of TMG one can assume that compound **2a** exists as a zwitterion in which the hydrogen atom is localized at the imine nitrogen atom. However, the length of the C–O bond in the phenoxide ion must be by about 0.1 Å shorter than in the non-ionized form due to the stronger coupling with the benzene ring, and equal about 1.27 Å.[10] In the case of compound **2a** the length of the C–O bond is 1.353 Å, which makes the bipolar structure unlikely (Fig. 2).

The obtained alkenyl guanidines **2a**–**i** may be regarded as push-pull azadienes[11] in which considerable polarization of the conjugated system exists owing to the presence of two donor dimethylamino groups at one end and an acceptor acyl group at the other. Such distribution of the electron density has an effect on bond lengths. In the structure of the compound the double bonds in this fragment are somewhat longer, whereas single bonds are shorter than typical, which indicates a certain contribution of the bipolar structure to the resonance hybrid.

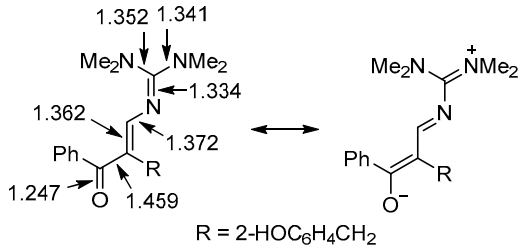


Figure 2. Bond lengths (Å) and resonance structures for compound **2a**.

The *E*-configuration has been attributed to every other product by analogy with compound **2a**. Protons of the dimethylamine and methylene groups appear in the ^{1}H NMR spectra of compounds **2a**–**i** as singlet signals in the 2.80–2.98 and 3.67–4.18 ppm ranges, respectively. In the ^{13}C NMR spectra, the carbon atoms of the dimethylamino group resonate in the range of 40.3–40.9 ppm. In the case of phenol derivatives **2a**–**d** the signals of the carbon atoms of the mehylene group appear at 25.1–26.3 ppm, whereas for naphthol derivatives **2e**–**i** they exhibit at 19.6–21.8 ppm. In the ^{1}H NMR spectra, the signal of the proton of the hydroxyl group is found at 9.98–11.81 ppm as a broad singlet. The carbon atom bonded with the guanidine moiety and the imine carbon atom resonate respectively at 156.4–162.2 and 165.1–166.9 ppm. In the ^{13}C NMR spectra of trifluoroacetyl derivatives **2b**,**c**,**f**–**h**, the signals of the trifluoromethyl and carbonyl carbon atoms are observed in the form of quartets at 118.1–118.9 ppm with $^{1}J_{CF}$ = 290.8 Hz and at 177.0–179.1 ppm with $^{2}J_{CF}$ = 31.5 Hz, respectively. In the DEPT spectra, the number of protons directly connected to the ^{13}C atoms is consistent with the proposed structures. In the IR spectra of compounds **2a**–**i** the absorption bands of the carbonyl group are observed in the 1610–1655 cm^{-1} range and have a moderate intensity.

To conclude, we have developed a method for the synthesis of novel push-pull type 2-aza-1,3-dienes containing carbonyl and dimethylamino groups at opposite ends of the diene moiety. The obtained alkenylguanidines are proposed for use as the dienes in the Diels–Alder reaction with highly polarized dienophiles.

Experimental

IR spectra were registered on a Shimadzu IR Affinity-1 spectrometer in KBr pellets. ^{1}H and ^{13}C NMR spectra (400 and 100 MHz, respectively), as well as DEPT spectra were

acquired on a JEOL JNM-ECX400 spectrometer, with TMS as internal standard. Elemental analysis was performed on a EuroVector EA-3000 CHNS-analyzer. Melting points were determined on a SRS OptiMelt MPA100 apparatus. TLC was performed on Silufol UV-254 plates, visualization with UV light or in an iodine chamber. The starting compounds **1a**–**i** were synthesized following previously published methods for similar heterocycles.[12]

Synthesis of 2-(3-oxoprop-1-en-1-yl)guanidines 2a,c–i (General method). TMG (0.63 ml, 0.58 g, 5 mmol) was added at room temperature to a suspension of acylchromene **1a**,**c**–**i** (1 mmol) in 95% ethanol (4 ml; compounds **1a**,**c**,**e**) or acetonitrile (4 ml; compounds **1c**,**d**,**f**–**i**). The obtained solution was kept at room temperature for 1 h until the disappearance of the starting chromene by TLC (eluent CH_2Cl_2), then water (0.5-1.0 ml) was added with stirring. If a crystalline precipitate formed, it was filtered off and washed with 70% aqueous acetonitrile or ethanol. Otherwise, additional cold water (15 ml) was added, the formed precipitate was filtered off, washed with cold water, dried in air, and further purified by recrystallization.

2-[(1*E*)-2-(2-Hydroxybenzyl)-3-oxo-3-phenylprop-1-en-1-yl]-1,1,3,3-tetramethylguanidine (2a). Yield 51%, colorless crystals, mp 159–160°C (EtOH). IR spectrum, ν, cm^{-1}: 3200–2400 (OH), 1612 (C=O), 1590, 1551, 1516, 1470, 1420, 1400, 1369, 1273, 1246, 1192, 1161, 1134, 1088, 1030, 949. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.82 (12H, s, $2N(CH_3)_2$); 3.86 (2H, s, CH_2); 6.73 (1H, td, *J* = 7.3, *J* = 1.2, H Ar); 6.82 (1H, dd, *J* = 8.0, *J* = 0.9, H Ar); 7.03 (1H, td, *J* = 8.0, *J* = 1.6, H Ar); 7.14 (1H, s, CHN); 7.28–7.39 (3H, m, H Ar); 7.41–7.43 (2H, m, H Ar); 7.46 (1H, dd, *J* = 7.6, *J* = 1.6, H Ar); 10.63 (1H, br. s, OH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 26.3 (CH_2); 40.3 ($2N(CH_3)_2$); 116.9 (CH); 119.4 (CH); 124.4 (C); 127.2 (CH); 127.7 (2CH); 128.5 (2CH, C); 129.8 (CH); 131.8 (CH); 141.3 (C); 155.8 (C–O); 156.4 (CHN); 165.1 (C=N); 197.2 (C=O). Found, %: C 71.70; H 7.21; N 11.89. $C_{21}H_{25}N_3O_2$. Calculated, %: C 71.77; H 7.17; N 11.96.

2-[(1*E*)-4,4,4-Trifluoro-2-(2-hydroxy-4,5-dimethylbenzyl)-3-oxobut-1-en-1-yl]-1,1,3,3-tetramethylguanidine (2c). Yield 71%, colorless crystals, mp 127–128°C (MeOH). IR spectrum, ν, cm^{-1}: 3400–2700 (OH), 1655 (C=O), 1589, 1547, 1512, 1477, 1462, 1404, 1315, 1285, 1223, 1188, 1123, 1080, 1030, 957. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.13 (3H, s, CH_3); 2.14 (3H, s, CH_3); 2.98 (12H, s, $2N(CH_3)_2$); 3.67 (2H, s, CH_2); 6.65 (1H, s) and 7.19 (1H, s, H Ar); 7.64 (1H, d, *J* = 1.6, CHN); 9.98 (1H, br. s, OH). ^{13}C NMR spectrum($CDCl_3$), δ, ppm: 18.7 (CH_3); 19.6 (CH_3); 25.1 (CH_2); 40.7 ($2N(CH_3)_2$); 118.0 (C); 118.1 (q, $^1J_{CF}$ = 290.8, CF_3); 118.2 (CH); 124.7 (C); 127.5 (C); 132.6 (CH); 135.7 (C); 152.9 (C–O); 157.4 (CHN); 166.3 (C=N); 179.0 (q, $^2J_{CF}$ = 31.5, C=O). Found, %: C 58.29; H 6.46; N 11.27. $C_{18}H_{24}F_3N_3O_2$. Calculated, %: C 58.21; H 6.51; N 11.31.

2-[(1*E*)-3-(4-Chlorophenyl)-2-(2-hydroxybenzyl)-3-oxoprop-1-en-1-yl]-1,1,3,3-tetramethylguanidine (2d). Yield 65%, colorless crystals, mp 171–172°C (EtOH). IR spectrum, ν, cm^{-1}: 3200–2400 (OH), 1610 (C=O), 1587, 1553, 1506, 1483, 1466, 1452, 1416, 1404, 1366, 1285, 1261, 1246, 1233, 1134, 1084, 1032, 951, 943, 841, 827, 787, 748. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.84 (12H, s, $2N(CH_3)_2$); 3.86 (2H, s, CH_2); 6.74 (1H, t, *J* = 7.3, H-5'); 6.83 (1H, d, *J* = 7.8, H-3'); 7.04 (1H, dd, *J* = 7.8, *J* = 7.3, H-4'); 7.12 (1H, s, CHN); 7.29 (2H, d, *J* = 8.2, H Ar); 7.39 (2H, d, *J* = 8.2, H Ar); 7.44 (1H, d, *J* = 7.3, H-6'); 10.55 (1H, br. s, OH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 26.3 (CH_2); 40.4 ($2N(CH_3)_2$); 116.9 (CH); 119.5 (CH); 124.3 (C); 127.3 (CH); 128.0 (2CH); 128.3 (C); 130.0 (2CH); 131.8 (CH); 135.9 (C); 139.6 (C); 155.7 (C–O); 156.4 (CHN); 165.2 (C=N); 195.7 (C=O). Found, %: C 65.29; H 6.22; N 10.97. $C_{21}H_{24}ClN_3O_2$. Calculated, %: C 65.36; H 6.27; N 10.89.

2-[(1*E*)-2-Formyl-3-(2-hydroxynaphthalen-1-yl)prop-1-en-1-yl]-1,1,3,3-tetramethylguanidine (2e). Yield 51%, colorless crystals, mp 84–86°C (EtOH). IR spectrum, ν, cm^{-1}: 3600–2400 (OH), 1643 (C=O), 1620, 1599, 1557, 1514, 1466, 1398, 1371, 1337, 1275, 1260, 1231, 1196, 1165, 1138, 1061, 1030, 995. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.92 (12H, s, $2N(CH_3)_2$); 4.05 (2H, s, CH_2); 7.12 (1H, s, CHN); 7.17 (1H, d, *J* = 8.7, H Ar); 7.25 (1H, dd., *J* = 7.8, *J* = 6.9, *J* = 0.9, H Ar); 7.44 (1H, ddd, *J* = 8.7, *J* = 6.9, *J* = 1.4, H Ar); 7.59 (1H, d, *J* = 8.7, H Ar); 7.68 (1H, d, *J* = 7.8, H Ar); 8.60 (1H, d, *J* = 8.7, H Ar); 9.21 (1H, s, CHO); 11.11 (1H, br. s, OH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 19.6 (CH_2); 40.5 ($2N(CH_3)_2$); 120.9 (CH); 121.0 (C); 122.7 (CH); 125.1 (CH); 126.0 (C, CH); 127.8 (CH); 128.0 (CH); 129.4 (C); 134.0 (C); 153.0 (C–O); 162.0 (CHN); 165.5 (C=N); 192.1 (C=O). Found, %: C 70.06; H 7.11; N 12.99. $C_{19}H_{23}N_3O_2$. Calculated, %: C 70.13; H 7.12; N 12.91.

2-{(1*E*)-4,4,4-Trifluoro-2-[(2-hydroxy-1-naphthyl)methyl]-3-oxobut-1-en-1-yl}-1,1,3,3-tetramethylguanidine (2f). Yield 45%, light-yellow crystals, mp 147–148°C (CH_3CN–H_2O, 5:1). IR spectrum, ν, cm^{-1}: 3600–2800 (OH), 1638 (C=O), 1618, 1597, 1560, 1508, 1468, 1422, 1402, 1319, 1248, 1231, 1186, 1165, 1132, 997, 908. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.95 (12H, s, $2N(CH_3)_2$); 4.18 (2H, s, CH_2); 7.11 (1H, d, *J* = 8.7, H Ar); 7.26 (1H, ddd, *J* = 8.0, *J* = 6.9, *J* = 0.9, H Ar); 7.46 (1H, ddd, *J* = 8.5, *J* = 6.9, *J* = 1.4, H Ar); 7.60 (1H, d, *J* = 8.7, H Ar); 7.69 (1H, d, *J* = 8.0, H Ar); 7.73 (1H, d, *J* = 1.6, CHN); 8.47 (1H, d, *J* = 8.5, H Ar); 11.17 (1H, br. s, OH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 21.2 (CH_2); 40.7 ($2N(CH_3)_2$); 116.9 (C); 118.4 (q, $^1J_{CF}$ = 290.8, CF_3); 120.6 (C); 120.7 (CH); 122.7 (CH); 125.1 (CH); 126.2 (CH); 128.07 (CH); 128.11 (CH); 129.4 (C); 134.2 (C); 153.2 (C–O); 159.3 (CHN); 166.6 (C=N); 179.1 (q, $^2J_{CF}$ = 31.5, C=O). Found, %: C 61.13; H 5.60; N 10.59. $C_{20}H_{22}F_3N_3O_2$. Calculated, %: C 61.06; H 5.64; N 10.68.

2-{(1*E*)-2-[(6-*tert*-Butyl-2-hydroxy-1-naphthyl)methyl]-4,4,4-trifluoro-3-oxobut-1-en-1-yl}-1,1,3,3-tetramethylguanidine (2g). Yield 93%, colorless crystals, mp 154–156°C (CH_3CN). IR spectrum, ν, cm^{-1}: 3200–2500 (OH), 2959 ($CH_{t\text{-}Bu}$), 1647 (C=O), 1597, 1558, 1508, 1466, 1404, 1369, 1319, 1246, 1231, 1188, 1157, 1138, 1123, 1061, 999, 910. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1.31 (9H, s, $(CH_3)_3C$); 2.90 (12H, s, $2N(CH_3)_2$); 3.99 (2H, s, CH_2); 6.99 (1H, d, *J* = 8.6, H Ar); 7.47 (1H, d, *J* = 8.9,

H Ar); 7.57 (1H, d, *J* = 8.6, H Ar); 7.61 (1H, s) and 7.80 (1H, s, H-5', CHN); 8.27 (1H, d, *J* = 8.9, H Ar); 11.13 (1H, br. s, OH). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 21.2 (CH_2); 31.6 ($(\underline{C}H_3)_3C$); 34.6 ($(CH_3)_3\underline{C}$); 40.8 ($2N(CH_3)_2$); 114.1 (C); 118.9 (q, $^1J_{CF}$ = 290.8, CF_3); 120.3 (C); 120.9 (CH); 123.5 (CH); 124.7 (CH); 125.0 (CH); 128.2 (CH); 129.1 (C); 132.4 (C); 144.9 (C); 153.3 (C–O); 161.9 (CHN); 166.9 (C=N); 177.0 (q, $^2J_{CF}$ = 31.5, C=O). Found, %: C 64.21; H 6.68; N 9.41. $C_{24}H_{30}F_3N_3O_2$. Calculated, %: C 64.13; H 6.73; N 9.35.

2-{(1*E*)-2-[(6-Bromo-2-hydroxy-1-naphthyl)methyl]-4,4,4-trifluoro-3-oxo-but-1-en-1-yl}-1,1,3,3-tetramethylguanidine (2h). Yield 73%, colorless crystals, mp 148–150°C (MeOH). IR spectrum, ν, cm^{-1}: 3200–2400 (OH), 1640 (C=O), 1616, 1585, 1558, 1501, 1470, 1396, 1342, 1327, 1285, 1242, 1204, 1192, 1157, 1136, 1123, 999. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 2.90 (12H, s, $2N(CH_3)_2$); 3.99 (2H, s, CH_2); 7.08 (1H, d, *J* = 8.9, H Ar); 7.46 (1H, d, *J* = 9.2, H Ar); 7.60 (1H, d, *J* = 8.9, H Ar); 7.82 (1H, s) and 7.96 (1H, s, H-5', CHN); 8.33 (1H, d, *J* = 9.2, H Ar); 11.38 (1H, br. s, OH). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 21.3 (CH_2); 40.9 ($2N(CH_3)_2$); 113.7 (C); 115.9 (C); 118.9 (q, $^1J_{CF}$ = 290.8, CF_3); 120.9 (C); 122.2 (CH); 127.3 (CH); 127.6 (CH); 129.0 (CH); 130.2 (CH); 130.5 (C); 132.8 (C); 154.4 (C–O); 162.2 (CHN); 166.9 (C=N); 177.1 (q, $^2J_{CF}$ = 31.5, C=O). Found, %: C 50.92; H 4.40; N 8.94. $C_{20}H_{21}BrF_3N_3O_2$. Calculated, %: C 50.86; H 4.48; N 8.90.

2-{(1*E*)-3-(4-Chlorophenyl)-2-[(2-hydroxy-1-naphthyl)-methyl]-3-oxoprop-1-en-1-yl}-1,1,3,3-tetramethylguanidine (2i). Yield 85%, light-yellow crystals, mp 158–160°C (DMF–MeOH, 1:2). IR spectrum, ν, cm^{-1}: 3200–2400 (OH), 1616 (C=O), 1601, 1587, 1547, 1512, 1470, 1420, 1366, 1312, 1288, 1238, 1229, 995. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 2.80 (12H, s, $2N(CH_3)_2$); 4.12 (2H, s, CH_2); 7.04 (1H, d, *J* = 8.7, H Ar); 7.18 (1H, t, *J* = 7.8, H Ar); 7.21 (1H, s, CHN); 7.31 (1H, dd, *J* = 8.5, *J* = 7.8, H Ar); 7.35 (2H, d, *J* = 8.4, H Ar); 7.39 (2H, d, *J* = 8.4, H Ar); 7.58 (1H, d, *J* = 8.7, H Ar); 7.69 (1H, d, *J* = 7.8, H Ar); 8.40 (1H, d, *J* = 8.5, H Ar); 11.81 (1H, br. s, OH). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 21.8 (CH_2); 40.5 ($2N(CH_3)_2$); 121.1 (CH); 121.3 (C); 121.4 (C); 122.7 (CH); 125.0 (CH); 126.2 (CH); 127.9 (CH); 128.5 (3CH); 129.1 (C); 130.6 (2CH); 134.4 (C); 135.2 (C); 140.1 (C); 154.1 (C–O); 159.3 (CHN); 165.7 (C=N); 194.9 (C=O). Found, %: C 68.94; H 5.93; N 9.72. $C_{25}H_{26}ClN_3O_2$. Calculated, %: C 68.88; H 6.01; N 9.64.

2-{(1*E*)-2-[3-(1-Adamantyl)-2-hydroxy-5-methylbenzyl]-4,4,4-trifluoro-3-oxobut-1-en-1-yl}-1,1,3,3-tetramethylguanidine (2b). TMG (0.32 ml, 0.29 g, 2.5 mmol) was added to a suspension of 2,2,2-trifluoro-1-(4*H*-chromen-3-yl)ethanone (**1b**) (0.20 g, 0.5 mmol) in 95% ethanol (4 ml). The mixture was heated to reflux, then the obtained solution was kept for 1 h at room temperature and for 12 h at –30°C. The formed precipitate was filtered off, washed with ice-cold methanol, and recrystallized from 95% ethanol. Yield 81%, light-yellow crystals, mp 209–211°C (EtOH). IR spectrum, ν, cm^{-1}: 3400–2400 (OH), 2901, 2843 (CH Ad), 1636 (C=O), 1593, 1562, 1512, 1458, 1404, 1327, 1285, 1254, 1238, 1219, 1180, 1165, 1130, 1061, 1030, 953. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.74 (6H, br. s, CH_2 Ad); 2.02 (3H, br. s, CH Ad); 2.13 (6H, br. s, CH_2 Ad); 2.21 (3H, s, CH_3); 2.96 (12H, s, $2N(CH_3)_2$); 3.71 (2H, s, CH_2); 6.83 (1H, d, *J* = 1.8) and 7.16 (1H, d, *J* = 1.8, H Ar); 7.63 (1H, s, CHN); 10.16 (1H, br. s, OH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 20.9 (CH_3); 25.5 (CH_2); 29.4 (3CH Ad); 37.0 (C Ad); 37.4 ($6CH_2$ Ad); 40.6 ($2N(CH_3)_2$); 118.2 (q, $^1J_{CF}$ = 290.8, CF_3); 118.4 (C); 125.4 (CH); 128.0 (C); 128.6 (C); 129.8 (CH); 137.3 (C); 151.7 (C–O); 158.0 (CHN); 166.3 (C=N); 179.0 (q, $^2J_{CF}$ = 31.5, C=O). Found, %: C 66.06; H 7.33; N 8.50. $C_{27}H_{36}F_3N_3O_2$. Calculated, %: C 65.97; H 7.38; N 8.55.

X-ray structural analysis of compound 2a was performed at 295(2) K on a Stoe STADI-VARI Pilatus-100K diffractometer. Crystals were grown from CH_3OH–CH_2Cl_2, 1:2 mixture by slow evaporation at room temperature. A single crystal with linear dimensions of 0.2 × 0.2 × 0.2 mm was selected for studies. The structure was solved with the direct method and refined by the least-squares technique in the anisotropic approximation, H atom positions were calculated geometrically and refined according to the "rider" model. All calculations were performed using the SHELXL software package.[13] Crystallographic data for structure **2a** and refinement parameters were deposited at Cambridge Crystallographic Data Center (deposit CCDC 1424954).

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