Electronic Supplementary Information

Metal-free regioselective C–C bond cleavage in 1,3,5-triazine derivatives of β-diketones

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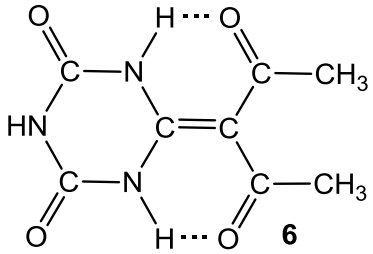
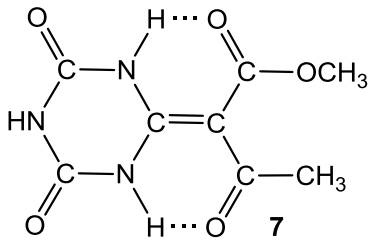
Analytical data for compounds 6−13



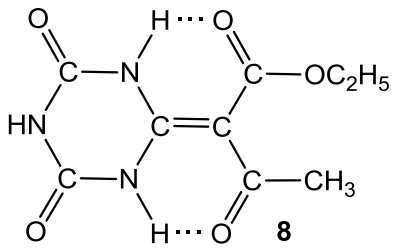
6

6. Yield 70 % (based on cyanuric chloride), light yellow, soluble in methanol, ethanol, DMSO. Anal. Calcd for $C_8H_9N_3O_4$ (M = 211.17): C, 45.50; H, 4.30; N, 19.90. Found: C, 45.50; H, 4.26; N, 19.76. MS (ESI): *m/z*: 212 $[M+H]^+$. IR (KBr, selected bands, cm^{-1}): 3462, 3453 and 3196 ν(NH), 1725 and 1623 ν(C=O). ^1H NMR (300.13 MHz, DMSO-d_6), δ: 2.37 (6H, $2CH_3$), 11.96 (1H, NH), 13.22 (2H, NH). $^{13}C\{^1H\}$ NMR (75.468 MHz, DMSO-d_6), 32.3 ($2CH_3$), 100.5 (C=C), 147.7 (C=C−NH), 155.8 (2C=O) and 199.9 (2C=O).



7

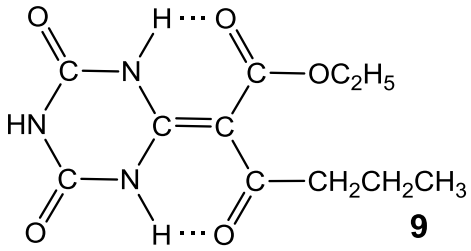
7. Yield 62 % (based on cyanuric chloride), light yellow, soluble in methanol, ethanol, DMSO. Anal. Calcd for $C_8H_9N_3O_5$ (M = 227.17): C, 42.30; H, 3.99; N, 18.50. Found: C, 42.67; H, 3.99; N, 18.47. MS (ESI): *m/z*: 226 $[M-H^+]$. IR (KBr, selected bands, cm^{-1}): 3483, 3030 and 2831 ν(NH), 1737 and 1634 ν(C=O). ^1H NMR (300.13 MHz, DMSO-d_6), δ: 2.37 (3H, CH_3), 3.77 (3H, OCH_3), 11.97 (1H, NH), 13.59 (2H, NH). $^{13}C\{^1H\}$ NMR (75.468 MHz, DMSO-d_6), 32.1 (CH_3), 52.0 (OCH_3), 88.5 (C=C), 147.5 (C=C−NH), 156.2 (2C=O), 169.1 and 198.8 (2C=O).



8

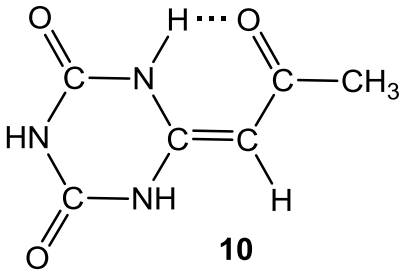
8. Yield 67 % (based on cyanuric chloride), light yellow, soluble in methanol, ethanol, DMSO. Anal. Calcd for $C_9H_{11}N_3O_5$ (M = 241.20): C, 44.82; H, 4.60; N, 17.42. Found: C, 44.85; H, 4.44; N, 16.67.

MS (ESI): *m/z*: 240 [M−H$^+$]. IR (KBr, selected bands, cm^{-1}): 3458, 3451 and 3195 *ν*(NH), 1743 and 1643 *ν*(C=O). ^{1}H NMR (300.13 MHz, DMSO-*d*$_6$), *δ*: 1.27−1.31 (3H, CH$_3$), 2.41 (3H, CH$_3$), 4.25 (2H, CH$_2$), 11.96 (1H, NH), 13.70 (2H, NH). ^{13}C{^{1}H} NMR (75.468 MHz, DMSO-*d*$_6$), 13.9 (CH$_3$), 32.3 (CH$_3$), 61.0 (CH$_2$), 88.5 (C=C), 147.5 (C=C−NH), 156.3 (2C=O), 168.8 and 198.8 (2C=O).



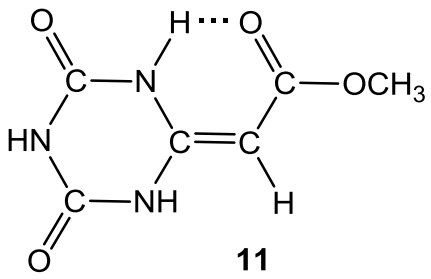
9

9. Yield 54 % (based on cyanuric chloride), light yellow, soluble in methanol, ethanol, DMSO. Anal. Calcd for C$_{11}$H$_{15}$N$_3$O$_5$ (*M* = 269.10): C, 49.07; H, 5.62; N, 15.61. Found: C, 48.99; H, 5.61; N, 15.48. MS (ESI): *m/z*: 268 [M−H$^+$]. IR (KBr, selected bands, cm^{-1}): 3202, 3116 and 2960 *ν*(NH), 1721 and 1648 *ν*(C=O). ^{1}H NMR (300.13 MHz, DMSO-*d*$_6$), *δ*: 0.88 and 0.90 (3H, CH$_3$), 1.28−1.31 (3H, CH$_3$), 1.54 and 1.55 (2H, CH$_2$), 2.74 (2H, CH$_2$), 4.25 and 4.27 (2H, CH$_2$), 11.93 (1H, NH), 13.70 (2H, NH). ^{13}C{^{1}H} NMR (75.468 MHz, DMSO-*d*$_6$), 13.7 (CH$_3$), 13.9 (CH$_3$), 18.5 (CH$_2$), 44.6 (CH$_2$), 61.0 (CH$_2$), 88.5 (C=C), 147.5 (C=C−NH), 156.0 (2C=O), 168.7 and 201.3 (2C=O).



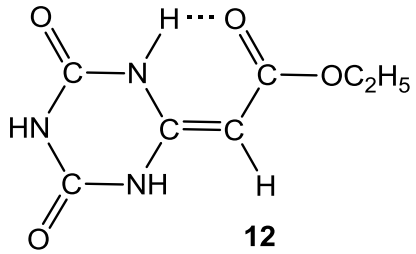
10

10. Yield 65 % (based on **1**), light orange crystals soluble in methanol, ethanol, DMSO. Anal. Calcd for C$_6$H$_7$N$_3$O$_3$ (*M* = 169.13): C, 42.61; H, 4.17; N, 24.84. Found: C, 42.41; H, 4.20; N, 24.61. MS (ESI): *m/z*: 170 [M+H]$^+$. IR (KBr, selected bands, cm^{-1}): 3496, 3429 and 3080 *ν*(NH), 1748, 1707, 1662 *ν*(C=O). ^{1}H NMR (300.13 MHz, DMSO-*d*$_6$), *δ*: 2.00 (3H, CH$_3$), 5.01 (1H, CH), 11.24 and 11.38 (2H, NH), 12.46 (1H, NH). ^{13}C{^{1}H} NMR (75.468 MHz, DMSO-*d*$_6$), 27.2 (CH$_3$), 82.3 (C=CH), 148.0 (C=C−NH), 149.0 and 149.7 (C=O), 196.4 (C=O).



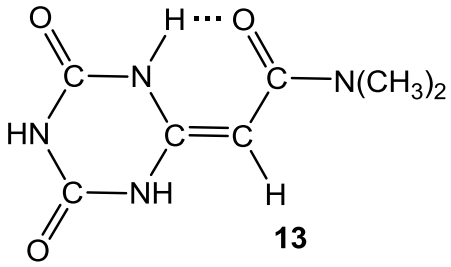
11

11. Yield 60 % (based on **2**), light orange crystals soluble in methanol, ethanol, DMSO. Anal. Calcd for $C_6H_7N_3O_4$ (M = 185.04): C, 38.92; H, 3.81; N, 22.70. Found: C, 38.87; H, 3.80; N, 22.63. MS (ESI): *m/z*: 184 [M−H$^+$]. IR (KBr, selected bands, cm^{-1}): 3410, 3176 and 2831 ν(NH), 1743, 1644 and 1632 ν(C=O). ^{1}H NMR (300.13 MHz, DMSO-d_6), δ: 3.58 (3H, OCH_3), 4.48 (1H, CH), 10.56 (1H, NH), 11.16 and 11.27 (2H, NH). ^{13}C{^{1}H} NMR (75.468 MHz, DMSO-d_6), 50.7 (OCH_3), (CH_2), 70.6 (C=<u>C</u>H), 147.8 (C=<u>C</u>−NH), 148.8 and 149.0 (C=O), 169.9 (C=O).



12

12. Yield 69 % (based on **3**), light orange crystals soluble in methanol, ethanol, DMSO. Anal. Calcd for $C_7H_9N_3O_4$ (M = 199.16): C, 42.21; H, 4.55; N, 21.10. Found: C, 41.66; H, 4.43; N, 20.89. MS (ESI): *m/z*: 198 [M−H$^+$]. IR (KBr, selected bands, cm^{-1}): 3432, 3191 and 3066 ν(NH), 1739, 1712 and 1682 ν(C=O). ^{1}H NMR (300.13 MHz, DMSO-d_6), δ: 1.15−1.19 (3H, CH_3), 4.06 (2H, CH_2), 4.46 (1H, CH), 10.59 (1H, NH), 11.13 and 11.25 (2H, NH). ^{13}C{^{1}H} NMR (75.468 MHz, DMSO-d_6), 14.3 (CH_3), 59.0 (CH_2), 70.9 (C=<u>C</u>H), 147.7 (C=<u>C</u>−NH), 148.8 and 148.9 (C=O), 169.5 (C=O).



13

13. Yield 64 % (cyanuric chloride), light orange crystals soluble in methanol, ethanol, DMSO. Anal. Calcd for $C_7H_{10}N_4O_3$ (M = 198.17): C, 42.42; H, 5.09; N, 28.27. Found: C, 42.43; H, 5.09; N, 27.99.

MS (ESI): *m/z*: 197 [M−H$^+$]. IR (KBr, selected bands, cm^{-1}): 3431, 3240 and 3088 *ν*(NH), 1733, 1712 and 1676 *ν*(C=O). ^{1}H NMR (300.13 MHz, DMSO-d_6), *δ*: 2.87 (6H, 2CH$_3$), 4.77 (1H, CH), 10.86 and 10.88 (2H, NH), 12.28 (1H, NH). ^{13}C{^{1}H} NMR (75.468 MHz, DMSO-d_6), overlapped by solvent (2CH$_3$), 70.4 (C=CH), 146.5 (C=C−NH), 149.0 and 149.9 (C=O), 169.0 (C=O).

2. X-ray analyses

Table S1. Crystal data and structure refinement for **6** and **10**.

Identification code	**6**	**10**
Empirical formula	$C_8H_9N_3O_4$	$C_6H_7N_3O_3$
Formula weight	211.18	169.15
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions	a = 10.765(7) Å b = 4.612(3) Å c = 17.297(11) Å α= 90° β= 97.133(13)° γ = 90°	a = 9.0878(6) Å b = 11.2798(8) Å c = 6.7696(5) Å α= 90° β= 92.969(3)° γ = 90°
Volume	852.1(10) Å^3	693.01(8) Å^3
Z	4	4
Density (calculated)	1.646 Mg/m^3	1.621 Mg/m^3
Absorption coefficient	0.134 mm^{-1}	0.133 mm^{-1}
F(000)	440	352
Crystal size	0.46 x 0.11 x 0.03 mm^3	0.23 x 0.16 x 0.08 mm^3
Theta range for data collection	1.91 to 25.25°.	2.24 to 28.00°.
Index ranges	-12<=h<=12, -5<=k<=5, -20<=l<=19	-11<=h<=11, -14<=k<=14, -8<=l<=8
Reflections collected	4187	7656
Independent reflections	1496 [R(int) = 0.0603]	1667 [R(int) = 0.0284]
Completeness to theta = 25.25°	96.9 %	99.9 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9954 and 0.9409	0.9891 and 0.9707
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	1496 / 0 / 138	1667 / 0 / 122
Goodness-of-fit on F^2	0.998	1.052
Final R indices [I>2sigma(I)]	R1 = 0.0529, wR2 = 0.1148	R1 = 0.0362, wR2 = 0.0943
R indices (all data)	R1 = 0.1068, wR2 = 0.1370	R1 = 0.0470, wR2 = 0.1009
Largest diff. peak and hole	0.214 and -0.343 e.Å^{-3}	0.341 and -0.226 e.Å^{-3}

Table S2. Bond lengths [Å] and angles [°] for **6** and **10**.

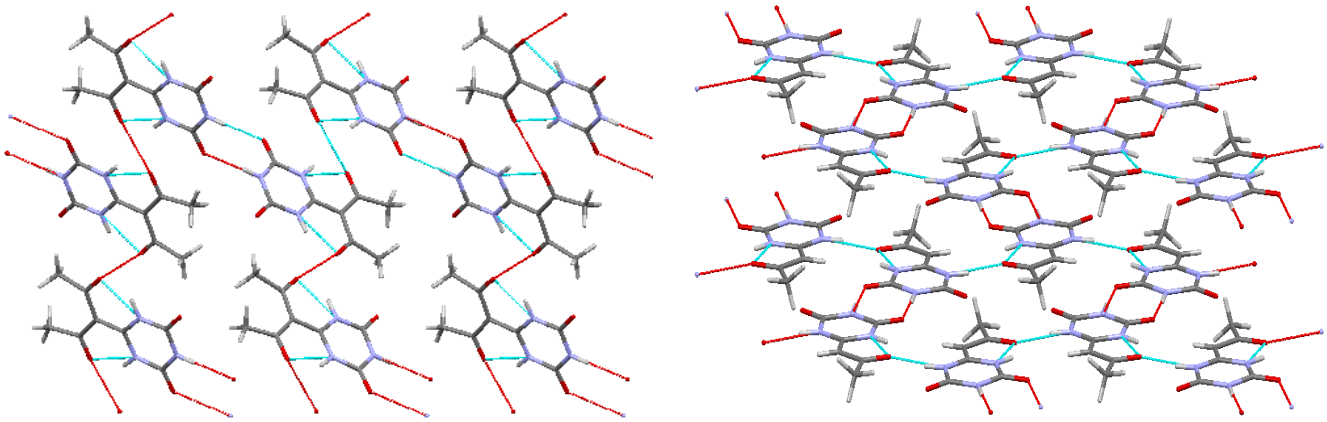
6		**10**	
O(1)-C(1)	1.215(4)	O(1)-C(1)	1.2172(15)
O(2)-C(2)	1.225(4)	O(2)-C(2)	1.2043(15)
O(3)-C(5)	1.257(4)	O(3)-C(5)	1.2610(15)
O(4)-C(7)	1.246(4)	N(1)-C(3)	1.3590(15)
N(1)-C(3)	1.358(4)	N(1)-C(1)	1.3703(15)
N(1)-C(1)	1.370(4)	N(1)-H(1)	0.91(2)
N(1)-H(1)	0.8754	N(2)-C(1)	1.3661(15)
N(2)-C(2)	1.363(4)	N(2)-C(2)	1.3795(16)
N(2)-C(1)	1.376(4)	N(2)-H(2)	0.910(19)
N(2)-H(2)	0.8598	N(3)-C(3)	1.3639(15)
N(3)-C(3)	1.359(4)	N(3)-C(2)	1.3795(16)
N(3)-C(2)	1.371(4)	N(3)-H(3)	0.897(17)
N(3)-H(3)	0.8579	C(3)-C(4)	1.3698(17)
C(3)-C(4)	1.418(4)	C(4)-C(5)	1.4268(17)
C(4)-C(5)	1.457(4)	C(5)-C(6)	1.4989(17)
C(4)-C(7)	1.465(4)	C(3)-N(1)-C(1)	125.03(11)
C(5)-C(6)	1.503(4)	C(1)-N(2)-C(2)	125.04(10)
C(7)-C(8)	1.502(4)	C(3)-N(3)-C(2)	124.30(11)
C(3)-N(1)-C(1)	124.5(3)	O(1)-C(1)-N(2)	123.60(11)
C(2)-N(2)-C(1)	125.0(3)	O(1)-C(1)-N(1)	121.53(11)
C(3)-N(3)-C(2)	124.8(3)	N(2)-C(1)-N(1)	114.87(10)
O(1)-C(1)-N(1)	122.6(3)	O(2)-C(2)-N(3)	122.40(11)
O(1)-C(1)-N(2)	122.5(3)	O(2)-C(2)-N(2)	122.87(11)
N(1)-C(1)-N(2)	114.9(3)	N(3)-C(2)-N(2)	114.72(11)
O(2)-C(2)-N(2)	122.7(3)	N(1)-C(3)-N(3)	115.90(11)
O(2)-C(2)-N(3)	122.5(3)	N(1)-C(3)-C(4)	121.12(11)
N(2)-C(2)-N(3)	114.8(3)	N(3)-C(3)-C(4)	122.97(10)
N(1)-C(3)-N(3)	115.9(3)	C(3)-C(4)-C(5)	123.00(11)
N(1)-C(3)-C(4)	121.8(3)	O(3)-C(5)-C(4)	122.04(11)
N(3)-C(3)-C(4)	122.3(3)	O(3)-C(5)-C(6)	119.92(11)
C(3)-C(4)-C(5)	117.9(3)	C(4)-C(5)-C(6)	118.04(11)
C(3)-C(4)-C(7)	117.3(3)		
C(5)-C(4)-C(7)	124.8(3)		
O(3)-C(5)-C(4)	121.3(3)		
O(3)-C(5)-C(6)	114.4(3)		
C(4)-C(5)-C(6)	124.2(3)		
O(4)-C(7)-C(4)	121.4(3)		
O(4)-C(7)-C(8)	114.9(3)		
C(4)-C(7)-C(8)	123.7(3)		

Symmetry transformations used to generate equivalent atoms:

Table S3. Hydrogen bonds [Å and °] for **6** and **10**.

Compound	D−H···A	d(D−H)	d(D···A)	d(H···A)	<(D−H···A)
	N(1)-H(1)···O(3)	0.88	2.490(3)	1.76	139.8
6[i]	N(2)-H(2)···O(2)#1	0.86	2.824(4)	1.98	167.6
	N(3)-H(3)···O(4)	0.86	2.486(3)	1.76	140.5
	N(1)-H(1)···O(3)	0.91(2)	2.5996(14)	1.873(19)	134.9(17)
10[ii]	N(3)-H(3)···O(3)#1	0.897(17)	2.7412(14)	1.852(18)	170.5(17)
	N(2)-H(2)···O(1)#2	0.910(19)	2.8167(14)	1.907(19)	177.6(16)

Symmetry transformations used to generate equivalent atoms: *i*) #1 -x,y-1/2,-z+3/2; *ii*) #1 -x+1,y+1/2,-z+1/2 #2 -x+2,-y,-z



6 **10**

Figure S1. Packing diagrams of **6** and **10** viewed down the crystallographic *b* and *a*-axis, respectively. The hydrogen bonds are shown as blue lines