Supporting Information for:

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1,4-Thiazepines, 1,4-Benzothiazepin-5-ones and 1,4-Benzothioxepin Orthoamides via Multicomponent Reactions of Isocyanides

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General Procedure for the Synthesis of Ketoacids 1-2 and 8-9

The corresponding 2-chloroketone (30 mmol) was added to a solution of 3-mercaptopropionic acid (3.2 g, 30 mmol) or thiosalicylic acid (4.6 g, 30 mmol) and KOH (3.4 g, 60 mmol) in methanol (50 ml). The mixture was refluxed for 1 hour and then the solvent was evaporated under reduced pressure. The residue was stirred with water (50 ml) and ether (10 ml). The organic layer was discarded and the aqueous layer was acidified with an aqueous solution of HCl (37% w/v) until pH = 1. The resulting suspension was extracted with diethyl ether (2 x 40 ml). The organic extracts were dried and the solvent evaporated under reduced pressure to give the corresponding ketoacids which were recrystallized from Hexane/AcOEt.

6-Oxo-4-thiaheptanoic acid 1: White solid, 4.4 g (91%), m.p. 150-152 °C; IR (NaCl, cm^{-1}) ν 3600-3010 (OH), 1708 (CO); ^1H NMR (CDCl_3 , 200 MHz) δ 2.22 (s, 3H), 2.53-2.72 (m, 2H), 3.20 (s, 2H), 7.80 (s, br, 1H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 26.6 (CH_3), 27.8 (CH_2), 33.9 (CH_2), 41.7 (CH_2), 176.0 (CO), 204.9 (CO); MS (EI, m/z , %) 162 (M^+ , 64), 89 (100), 43 (90).

3-(2-Oxocyclohexylmercapto)propionic acid 2¹: White solid, 5.4 g (89%), mp 82-84°C (lit. 82-83 °C). IR (KBr, cm^{-1}) ν 2500-3300 (OH), 1703 (CO), 1693 (CO); ^1H NMR (CDCl_3 , 200 MHz) δ 1.61-1.84 (m, 3H), 1.92-2.04 (m, 2H), 2.12-2.26 (m, 2H), 2.61-2.64 (m, 2H), 2.70-2.74 (m, 2H), 2.90-2.98 (m, 1H), 3.35 (t, J = 4.6 Hz, 1H), 10.2 (s, br, 1H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 21.9 (CH_2), 26.3 (CH_2), 27.0 (CH_2), 33.1 (CH_2), 34.3 (CH_2), 37.7 (CH_2), 52.1 (CH), 177.8 (CO), 208.6 (CO).

2-(2-Oxopropylmercapto)benzoic acid 8²: White solid, 5.7 g (91%), mp 154-156 °C (lit. 153-154 °C). IR (KBr, cm^{-1}) ν 3250-2400 (OH), 1708 (CO), 1674 (CO); ^1H NMR (CDCl_3 , 200 MHz) δ 2.32 (s, 3 H), 3.74 (s, 2 H), 7.21-7.51 (m, 3 H, H_{Ar}), 8.11-8.14 (m, 1 H, H_{Ar}); ^{13}C NMR (CDCl_3 , 50 MHz) δ 28.3 (CH_3), 43.5 (CH_2), 125.1 (CH_{Ar}), 126.1 (CH_{Ar}), 132.8 (CH_{Ar}), 133.9 (CH_{Ar}), 140.8 (C_{Ar}), 171.1 (CO), 204.6 (CO).

2-(2-Oxocyclohexylmercapto)benzoic acid 9: White solid, 6.9 g (92%), mp 124-126°C. IR (KBr, cm^{-1}) ν 3600-2939 (OH), 1708 (CO); ^1H NMR (CDCl_3 , 200 MHz) δ 1.62-2.40 (m, 7 H), 2.89-3.07 (m, 1

H), 4.00 (t, $J = 5.2$ Hz, 1 H), 7.14-7.50 (m, 3 H, H_{Ar}), 8.03-8.07 (m, 1 H, H_{Ar}), 8.78 (s, br, 1 H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 22.7 (CH_2), 27.7 (CH_2), 33.9 (CH_2), 39.1 (CH_2), 53.9 (CH), 125.3 (CH_{Ar}), 128.5 (C_{Ar}), 132.2 (CH_{Ar}), 133.2 (CH_{Ar}), 139.4 (C_{Ar}), 171.1 (CO), 208.8 (CO).

General Procedure for the Synthesis of Hexahydro-1,4-thiazepines 7a-c: Aluminum trichloride (0.40 g, 3 mmol) was added in small portions to a stirred suspension of LiAlH_4 (0.38 g, 10 mmol) in THF (15 ml) at -10°C . The resulting mixture was stirred for 10 min and then a solution of **5a-c** (1 mmol) in THF (10 ml) was added at -10°C . The cooling bath was removed and the reaction mixture was stirred at room temperature for 2 h. The mixture was treated with an aqueous solution of NaOH (15% w/v, 20ml) and filtered. The solvent was removed under reduced pressure and the residue was extracted with ethyl acetate (3 x 10 ml). The organic layer was washed with brine and dried (Na_2SO_4). Removal of the solvent left a residue which was purified by column chromatography (SiO_2 , Hexane/AcOEt 6:1).

5-Benzyl-2,3,4,5,5a,6,7,8,8a,9-decahydrobenzo[1,5]thiazepin-5a-(N-cyclohexylcarboxamide) 7a: Sticky solid, 0.35 g (91%). IR (KBr, cm^{-1}) ν 3339 (NH), 1661 (CO); ^1H NMR (CDCl_3 , 400 MHz) δ 1.12-1.98 (m, 18 H), 2.28-2.41 (m, 2 H), 2.43-2.58 (m, 2 H), 2.61-2.70 (m, 2 H) 2.76 (dd, $J = 14.9$ Hz, $J = 11.1$ Hz, 1 H), 3.40 (d, $J = 13.5$ Hz, 1 H), 3.74 (d, $J = 13.5$ Hz, 1 H), 3.75-3.83 (m, 1 H), 7.18-7.39 (m, 5 H), 8.09 (d, $J = 8.0$ Hz, 1 H, NH); ^{13}C NMR (CDCl_3 , 100 MHz) δ 23.1 (CH_2), 25.1 (CH_2), 25.9 (CH_2), 27.9 (CH_2), 28.1 (CH_2), 32.6 (CH_2), 33.2 (CH_2), 33.5 (CH_2), 35.0 (CH_2), 35.1 (CH_2), 46.1 (CH_2), 48.1 (CH), 56.4 (CH_2), 56.6 (CH), 69.8 (Cq), 127.1 (CH_{Ar}), 128.3 (2 x CH_{Ar}), 128.9 (2 x CH_{Ar}), 140.2 (C_{Ar}), 172.8 (CO); MS (EI, m/z , %) 386 (M^+ , 1), 260 (100), 91 (74). HRMS (EI) $\text{M}^+_{\text{found}} = 386.2398$ $\text{C}_{23}\text{H}_{34}\text{N}_2\text{OS}$ requires 386.2392. Anal. calcd for $\text{C}_{23}\text{H}_{34}\text{N}_2\text{OS}$: C, 71.46; H, 8.86; N, 7.25. Found: C, 71.22; H, 8.73; N, 7.02.

5-(4-Chlorobenzyl)-2,3,4,5,5a,6,7,8,8a,9-decahydrobenzo[1,5]thiazepin-5a-(N-cyclohexylcarboxamide) 7b: Sticky solid, 0.39 g (93%). IR (KBr, cm^{-1}) ν 3337 (NH), 1660 (CO); ^1H NMR (CDCl_3 , 400 MHz) δ 1.14-1.99 (m, 18 H), 2.22-2.81 (m, 7 H), 3.37(d, $J = 13.8$ Hz, 1 H), 3.67 (d, $J = 13.8$ Hz, 1

H), 3.74-3.80 (m, 1 H), 7.21-7.32 (m, 5 H), 8.06 (d, $J = 8.4$ Hz, 1 H, NH); ^{13}C NMR (CDCl_3 , 100 MHz) δ 23.0 (CH_2), 25.1 (CH_2), 25.9 (CH_2), 27.8 (CH_2), 28.0 (CH_2), 32.6 (CH_2), 33.2 (CH_2), 33.5 (CH_2), 34.9 (CH_2), 35.2 (CH_2), 46.3 (CH_2), 48.1 (CH), 55.8 (CH_2), 56.4 (CH), 69.8 (Cq), 128.4 (2 x CH_{Ar}), 130.2 (2 x CH_{Ar}), 132.7 (C_{Ar}), 138.8 (C_{Ar}), 172.7 (CO). Anal. calcd for $\text{C}_{23}\text{H}_{33}\text{ClN}_2\text{OS}$: C, 65.61; H, 7.90; N, 6.65. Found: C, 65.78; H, 8.03; N, 6.85.

5-(3,4-Methylenedioxybenzyl)-2,3,4,5,5a,6,7,8,8a,9-decahydrobenzo[1,5]thiazepin-5a-(*N*-cyclohexylcarboxamide) 7c: White solid, 0.39 g (91%), mp 136-137 °C. IR (KBr, cm^{-1}) ν 3339 (NH), 1663 (CO); ^1H NMR (CDCl_3 , 400 MHz) δ 1.17-1.95 (m, 18 H), 2.28-2.76 (m, 7 H), 3.3 (d, $J = 13.5$ Hz, 1 H), 3.62 (d, $J = 13.5$ Hz, 1 H), 3.76-3.82 (m, 1 H), 5.92 (s, 2 H), 6.69-6.74 (m, 2 H), 6.88 (s, 1 H), 8.06 (d, $J = 8.4$ Hz, 1 H, NH); ^{13}C NMR (CDCl_3 , 100 MHz) δ 23.0 (CH_2), 25.1 (CH_2), 25.9 (CH_2), 27.9 (CH_2), 28.0 (CH_2), 32.6 (CH_2), 33.2 (CH_2), 33.5 (CH_2), 35.0 (CH_2), 35.3 (CH_2), 45.8 (CH_2), 48.2 (CH), 56.1 (CH_2), 56.5 (CH), 69.7 (Cq), 101.1 (CH_2), 107.9 (CH_{Ar}), 109.3 (CH_{Ar}), 121.9 (CH_{Ar}), 134.3 (C_{Ar}), 146.7 (C_{Ar}), 147.7 (C_{Ar}), 172.8 (CO). Anal. calcd for $\text{C}_{24}\text{H}_{34}\text{N}_2\text{O}_3\text{S}$: C, 66.94; H, 7.96; N, 6.51. Found: C, 67.06; H, 8.08; N, 6.50.

7-Aza-7-cyclohexyl-6-hydroxy-9-oxa-8-oxo-1,2-(tetramethylene)-3-thiabicyclo[4.2.1]nonane 14: White solid, 0.05 g (17%), mp 180-181 °C. IR(KBr, cm^{-1}) ν 3447 (OH), 1740 (CO); ^1H NMR (CDCl_3 , 400 MHz) δ 1.16-2.91 (m, 18 H), 3.19 (s, br, 1 H), 4.78 (s, br, 1 H), 5.91 (s, br, 1 H, OH), ^{13}C -NMR (CDCl_3 , 100 MHz) δ 22.3, 25.0, 25.2, 28.1, 29.8, 33.1 and 36.0 (7 x CH_2 , DEPT), 48.9 (CH, DEPT), 83.8 and 104.9 (2 x Cq), 170.4 (CO). MS (EI, m/z , %) 311 (M^+ , 2), 312 (M^++1 , 52), 240 (54), 205 (79), 97 (80), 79 (99), 67 (100). HRMS (EI) $\text{M}^+_{\text{found}} = 311.1554$ $\text{C}_{16}\text{H}_{25}\text{NO}_3\text{S}$ requires 311.1555. Anal. calcd for $\text{C}_{16}\text{H}_{25}\text{NO}_3\text{S}$: C, 61.70; H, 8.09; N, 4.50. Found: C, 61.77; H, 8.00; N, 4.47.

Crystal Structure Determination for 12a·MeOH: A crystal was attached to a glass fibre and transferred to a Bruker AXS SMART 1000 diffractometer with graphite monochromatized Mo $\text{K}\alpha$ X-radiation and a CCD area detector. A full sphere of the reciprocal space was collected up to $2\theta = 48.6^\circ$. Raw frame data

were integrated with the SAINT³ program. The structure was solved by direct methods with SHELXTL.⁴ An empirical absorption correction was applied with the program SADABS.⁵ After isotropic refinement difference maps showed the presence of one molecule of methanol in the asymmetric unit, and it was included in subsequent refinements. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms, with a common thermal parameter. All calculations were made with SHELXTL. Additional material is available from the Cambridge Crystallographic Data Centre, including atomic coordinates, thermal parameters, and a full list of bond lengths and angles (CCDC 202033).

Figure S 1: Molecular structure of 12a·MeOH.

Figure S 2: Crystal packing of **12a** and methanol.

Table 1. Crystal data and structure refinement for **12a·MeOH**.

Identification code	c7pasm	
Empirical formula	C ₂₀ H ₂₅ N O ₃ S. CH ₃ OH	
Formula weight	391.51	
Temperature	299(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 10.4558(16) Å	α = 90°.
	b = 18.361(3) Å	β = 98.457(3)°.
	c = 10.7947(17) Å	γ = 90°.
Volume	2049.8(6) Å ³	
Z	4	
Density (calculated)	1.269 Mg/m ³	
Absorption coefficient	0.184 mm ⁻¹	
F(000)	840	
Crystal size	0.27 x 0.31 x 0.39 mm ³	
Theta range for data collection	2.21 to 23.28°.	
Index ranges	-11 ≤ h ≤ 11, -20 ≤ k ≤ 20, -11 ≤ l ≤ 11	
Reflections collected	12972	
Independent reflections	2952 [R(int) = 0.0260]	
Completeness to theta = 23.28°	99.9 %	
Absorption correction	SADABS	
Max. and min. transmission	1.000000 and 0.733796	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2952 / 0 / 248	
Goodness-of-fit on F ²	1.011	
Final R indices [I > 2σ(I)]	R1 = 0.0333, wR2 = 0.0934	
R indices (all data)	R1 = 0.0380, wR2 = 0.0981	
Extinction coefficient	0.0143(12)	
Largest diff. peak and hole	0.164 and -0.162 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **12a·MeOH**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
S(1)	6570(1)	10010(1)	3699(1)	51(1)
O(1)	9683(1)	8446(1)	2593(1)	49(1)
O(2)	9536(1)	9549(1)	3535(1)	40(1)
O(3)	8077(1)	10508(1)	904(1)	50(1)
N(1)	8235(1)	9342(1)	1702(1)	39(1)
C(1)	7863(2)	8650(1)	3609(2)	42(1)
C(2)	7930(2)	7914(1)	3913(2)	53(1)
C(3)	7081(2)	7598(1)	4619(2)	66(1)
C(4)	6150(2)	8016(1)	5044(2)	71(1)
C(5)	6072(2)	8750(1)	4776(2)	62(1)
C(6)	6920(2)	9081(1)	4059(2)	47(1)
C(7)	8837(2)	8978(1)	2851(2)	40(1)
C(8)	8411(2)	10064(1)	1745(2)	39(1)
C(11)	8083(2)	10521(1)	3878(2)	43(1)
C(12)	9067(2)	10247(1)	3063(1)	39(1)
C(13)	10222(2)	10758(1)	3147(2)	47(1)
C(14)	9844(2)	11552(1)	2909(2)	57(1)
C(15)	8885(2)	11799(1)	3745(2)	61(1)
C(16)	7697(2)	11314(1)	3594(2)	53(1)
C(21)	7429(2)	8911(1)	731(2)	44(1)
C(22)	6064(2)	9196(1)	456(2)	58(1)
C(23)	5228(2)	8716(1)	-486(2)	61(1)
C(24)	5816(2)	8602(1)	-1647(2)	75(1)
C(25)	7191(2)	8330(2)	-1368(2)	76(1)
C(26)	8031(2)	8820(1)	-438(2)	66(1)
O(51)	1627(2)	9051(1)	1519(1)	82(1)
C(51)	2815(3)	9075(2)	2292(3)	112(1)

Table 3. Bond lengths [Å] and angles [°] for **12a·MeOH**.

S(1)-C(6)	1.7753(19)
S(1)-C(11)	1.8255(17)
O(1)-C(7)	1.3745(19)
O(2)-C(7)	1.4210(19)
O(2)-C(12)	1.4392(19)
O(3)-C(8)	1.2304(19)
N(1)-C(8)	1.339(2)
N(1)-C(7)	1.467(2)
N(1)-C(21)	1.475(2)
C(1)-C(2)	1.390(2)
C(1)-C(6)	1.405(2)
C(1)-C(7)	1.521(2)
C(2)-C(3)	1.380(3)
C(3)-C(4)	1.370(3)
C(4)-C(5)	1.379(3)
C(5)-C(6)	1.397(3)
C(8)-C(12)	1.523(2)
C(11)-C(16)	1.530(2)
C(11)-C(12)	1.534(2)
C(12)-C(13)	1.522(2)
C(13)-C(14)	1.522(2)
C(14)-C(15)	1.515(3)
C(15)-C(16)	1.517(3)
C(21)-C(26)	1.500(3)
C(21)-C(22)	1.508(2)
C(22)-C(23)	1.522(3)
C(23)-C(24)	1.490(3)
C(24)-C(25)	1.510(3)
C(25)-C(26)	1.526(3)
O(51)-C(51)	1.392(3)
C(6)-S(1)-C(11)	108.89(8)
C(7)-O(2)-C(12)	110.51(11)
C(8)-N(1)-C(7)	112.48(13)
C(8)-N(1)-C(21)	128.13(13)
C(7)-N(1)-C(21)	119.06(13)

C(2)-C(1)-C(6)	118.61(16)
C(2)-C(1)-C(7)	119.81(15)
C(6)-C(1)-C(7)	121.53(14)
C(3)-C(2)-C(1)	121.65(19)
C(4)-C(3)-C(2)	119.72(19)
C(3)-C(4)-C(5)	120.01(19)
C(4)-C(5)-C(6)	121.2(2)
C(5)-C(6)-C(1)	118.78(17)
C(5)-C(6)-S(1)	114.30(15)
C(1)-C(6)-S(1)	126.66(13)
O(1)-C(7)-O(2)	109.39(12)
O(1)-C(7)-N(1)	111.23(13)
O(2)-C(7)-N(1)	103.15(12)
O(1)-C(7)-C(1)	109.22(13)
O(2)-C(7)-C(1)	110.25(13)
N(1)-C(7)-C(1)	113.43(13)
O(3)-C(8)-N(1)	127.38(15)
O(3)-C(8)-C(12)	125.63(15)
N(1)-C(8)-C(12)	106.95(13)
C(16)-C(11)-C(12)	112.11(14)
C(16)-C(11)-S(1)	105.67(12)
C(12)-C(11)-S(1)	114.48(11)
O(2)-C(12)-C(13)	107.55(13)
O(2)-C(12)-C(8)	102.55(12)
C(13)-C(12)-C(8)	115.83(14)
O(2)-C(12)-C(11)	108.18(13)
C(13)-C(12)-C(11)	110.94(13)
C(8)-C(12)-C(11)	111.14(13)
C(12)-C(13)-C(14)	113.33(14)
C(15)-C(14)-C(13)	111.43(16)
C(14)-C(15)-C(16)	111.30(15)
C(15)-C(16)-C(11)	110.48(15)
N(1)-C(21)-C(26)	113.02(14)
N(1)-C(21)-C(22)	112.30(14)
C(26)-C(21)-C(22)	112.02(16)
C(21)-C(22)-C(23)	111.37(15)
C(24)-C(23)-C(22)	112.11(17)

C(23)-C(24)-C(25)	112.15(17)
C(24)-C(25)-C(26)	112.06(19)
C(21)-C(26)-C(25)	110.36(16)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **12a·MeOH**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
S(1)	42(1)	54(1)	58(1)	-4(1)	10(1)	4(1)
O(1)	46(1)	45(1)	54(1)	2(1)	5(1)	10(1)
O(2)	39(1)	42(1)	37(1)	2(1)	-5(1)	2(1)
O(3)	60(1)	50(1)	37(1)	7(1)	-4(1)	3(1)
N(1)	40(1)	42(1)	33(1)	-2(1)	-1(1)	3(1)
C(1)	44(1)	46(1)	34(1)	1(1)	-5(1)	-4(1)
C(2)	59(1)	50(1)	45(1)	3(1)	-6(1)	-4(1)
C(3)	85(2)	56(1)	54(1)	9(1)	1(1)	-20(1)
C(4)	83(2)	75(2)	56(1)	3(1)	18(1)	-29(1)
C(5)	62(1)	72(1)	54(1)	-8(1)	18(1)	-13(1)
C(6)	47(1)	55(1)	39(1)	-4(1)	3(1)	-7(1)
C(7)	40(1)	40(1)	37(1)	0(1)	-3(1)	5(1)
C(8)	35(1)	46(1)	35(1)	1(1)	3(1)	4(1)
C(11)	43(1)	47(1)	35(1)	-3(1)	-1(1)	3(1)
C(12)	40(1)	39(1)	35(1)	3(1)	-1(1)	3(1)
C(13)	45(1)	49(1)	44(1)	0(1)	0(1)	-4(1)
C(14)	59(1)	47(1)	64(1)	3(1)	1(1)	-7(1)
C(15)	69(1)	44(1)	65(1)	-7(1)	-6(1)	2(1)
C(16)	55(1)	49(1)	53(1)	-7(1)	-1(1)	10(1)
C(21)	45(1)	46(1)	39(1)	-5(1)	-2(1)	0(1)
C(22)	45(1)	67(1)	58(1)	-16(1)	-4(1)	4(1)
C(23)	47(1)	70(1)	62(1)	-13(1)	-10(1)	1(1)
C(24)	70(1)	100(2)	51(1)	-13(1)	-8(1)	-17(1)
C(25)	67(1)	109(2)	55(1)	-37(1)	13(1)	-14(1)
C(26)	54(1)	95(2)	49(1)	-22(1)	8(1)	-9(1)
O(51)	69(1)	121(1)	57(1)	17(1)	15(1)	-3(1)
C(51)	78(2)	166(3)	88(2)	31(2)	1(2)	-12(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **12a·MeOH**.

	x	y	z	U(eq)
H(1)	10243	8627	2232	73
H(2)	8562	7627	3633	63
H(3)	7140	7104	4805	79
H(4)	5572	7805	5515	85
H(5)	5444	9031	5077	74
H(11)	8481	10490	4757	51
H(13A)	10768	10607	2540	56
H(13B)	10725	10716	3973	56
H(14A)	10612	11854	3062	69
H(14B)	9467	11612	2039	69
H(15A)	8625	12297	3537	73
H(15B)	9294	11790	4612	73
H(16A)	7248	11352	2744	64
H(16B)	7114	11475	4159	64
H(21)	7368	8422	1081	53
H(22A)	6077	9687	126	69
H(22B)	5692	9216	1227	69
H(23A)	5107	8247	-105	74
H(23B)	4385	8939	-704	74
H(24A)	5802	9057	-2103	90
H(24B)	5301	8251	-2178	90
H(25A)	7559	8308	-2141	92
H(25B)	7192	7841	-1029	92
H(26A)	8884	8606	-229	79
H(26B)	8126	9292	-816	79
H(51)	1712	9198	818	122
H(51A)	3195	9548	2237	168
H(51B)	3379	8712	2030	168
H(51C)	2692	8983	3141	168

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