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Synthesis of γ-Azido-β-ureido Ketones and Their Transformation into Functionalized Pyrrolines and Pyrroles via Staudinger/aza-Wittig Reaction

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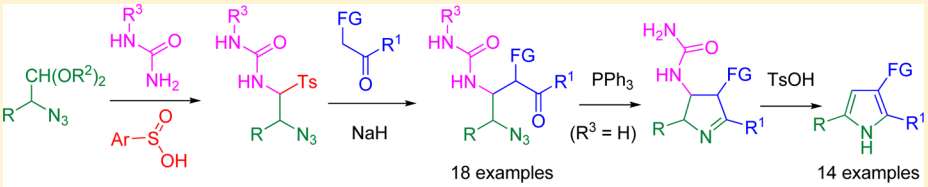
Supporting Information



ABSTRACT: A simple two-step procedure yielding γ-azido-β-ureido ketones or/and their cyclic isomers, 6-(1-azidoalkyl)-4-hydroxyhexahydropyrimidin-2-ones, has been developed. The synthesis includes three-component condensation of acetals of 2-azidoaldehydes with urea or methylurea and *p*-toluenesulfinic acid in aqueous formic acid followed by reaction of the obtained *N*-[(2-azido-1-tosyl)alkyl]ureas with sodium enolates of α-functionalized ketones. The azido ketones or their cyclic isomers are transformed into ureido-substituted Δ^1- or/and Δ^2-pyrrolines via Staudinger/aza-Wittig reaction promoted by PPh_3. The obtained pyrrolines are converted into 3-functionalized 1*H*-pyrroles via elimination of urea under acidic conditions. Convenient one-pot syntheses of 1*H*-pyrroles starting from *N*-[(2-azido-1-tosyl)alkyl]ureas or γ-azido-β-ureido ketones have been also developed.

INTRODUCTION

The ring system of pyrrole[1] occurs in many pharmacologically active natural compounds, including hemes and chlorophylls, bile pigments, alkaloids and antibiotics, etc.[2] Pyrroles, particularly 3-functionalized ones, have significant medicinal and agrochemical applications. For example, atorvastatin **1** is a top-selling synthetic drug that lowers blood contents of cholesterol and triglycerides, acting as an inhibitor of 3-hydroxy-3-methylglutaryl-coenzyme A (HMG-CoA) reductase (Figure 1).[3] Compound **2** shows dose-dependent antiproliferative and cytodifferentiation activities against human acute promyelocytic leukemia HL-60 cells.[4] Pyrrole **3** inhibits HIV-1 reverse transcriptase and is active against AZT-resistant HIV-1 (strain G9106).[5] 3-Aroyl-substituted pyrrole derivatives (e.g., **4**) are COX-1/COX-2 inhibitors with anti-inflammatory activity.[6] Chlorfenapyr **5** has been extremely effective against insects and mites in agriculture for over 15 years.[7]

Most pyrrole syntheses rely on classical condensation reactions, such as the Hantzsch reaction based on condensation of α-haloketones with 1,3-dicarbonyl compounds and amines,[8] the Paal–Knorr reaction involving cyclocondensation of 1,4-diketones with amines[9] or the Knorr reaction using condensation of α-aminoketones with β-keto esters or β-diketones.[10] In addition, other synthetic approaches have been developed.[1,2e,11,12] Staudinger/intramolecular aza-Wittig reaction provides an efficient approach to pyrrolines that can be converted into pyrroles.[13,14] This protocol uses γ-azido ketones as starting materials. The success of the method strongly depends on the availability of these compounds. γ-Azido ketones are prepared by reaction of γ-haloketones with sodium azide,[14a,e,f,15] oxidation of γ-azido alkohols,[14b,g,i,16] ozonolysis of γ-azido alkenes,[17] alkylation of ketone enolates with β-

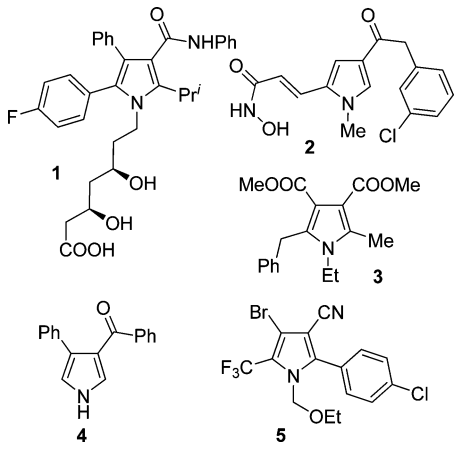


Figure 1. Selected examples of 3-funtionalized pyrroles with biological activity.

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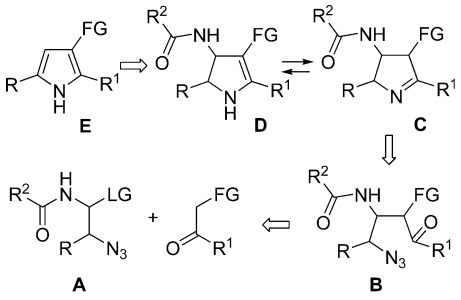
azidoalkyl halides,[14d,j] aldol reaction of ketones with α-azido ketones,[18] and reaction of silyl ethers with acetals of α-azido ketones.[18b,19] The drawbacks of these methods are low availability of starting compounds, multistep syntheses, small-scale preparations, harsh reaction conditions, long reaction times, poor yields, laborious procedures, etc. Thus, the development of a new effective approach to γ-azido ketones, especially with functional groups at the α- and β-positions, is highly desirable in the context of pyrrole synthesis.

We hypothesized that amidoalkylation of enolates of α-functionalized ketones with *N*-(β-azidoalkyl)amides **A** bearing a leaving group at the α-position to nitrogen could give γ-azido ketones **B** with an amido group at β-position, which significantly expands synthetic potential of these compounds (Scheme 1). They could be transformed into pyrrolines **C** or/and **D** using Staudinger/intramolecular aza-Wittig reaction. Subsequent elimination of amide group from compounds **C** and **D** would give 3-functionalized pyrroles **E**.

Scheme 1. Retrosynthesis of Pyrrolines and Pyrroles via Staudinger/aza-Wittig/Elimination Reactions



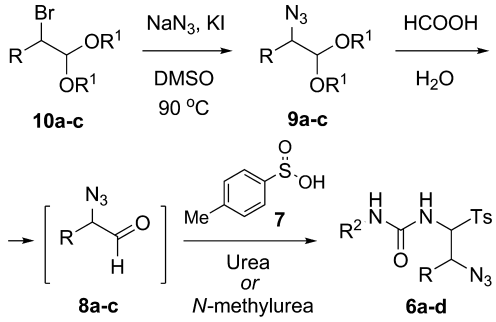
FG = functional group, LG = good leaving group

Recently we showed that readily available *N*-[(α-tosyl)alkyl]-ureas possess high amidoalkylation reactivity toward enolates of various ketones giving access to functionalized hexahydro-, 1,2,3,4-tetrahydro-, and 1,2-dihydropyrimidin-2-ones, tetrahydro-1*H*-1,3-diazepin-2-ones, 4,5-dihydrofurans, and 1-carbamoyl-1*H*-pyrroles.[20] Herein we report the synthesis of γ-azido-β-ureido ketones by the reaction of *N*-[(2-azido-1-tosyl)alkyl]-ureas with enolates of ethyl benzoyl acetate, dibenzoylmethane, α-arylsulfonyl, and α-phenylthio ketones and transformation of the obtained γ-azido-β-ureido ketones into functionalized pyrrolines and then into pyrroles using Staudinger/aza-Wittig/elimination sequence.

RESULTS AND DISCUSSION

Synthesis of α-Functionalized γ-Azido-β-ureido Ketones. β-Azidoalkyl-substituted ureas **6a–d** served as starting amidoalkylation reagents (Scheme 2). Previously we obtained *N*-[(α-tosyl)alkyl]ureas using three-component condensation of aldehyde, *p*-toluenesulfinic acid (**7**), and urea in water at room temperature.[20] Since 2-azidoaldehydes **8a–c** seem to be unstable (at least **8a**[21]), we used their acetals in the three-component condensation. Acetals **9a–c** were prepared according to the literature procedure described for **9a**[22] and based on the reaction of bromoacetals **10a–c** with NaN_3 (1.5 equiv) in the presence of KI (0.1 equiv) in DMSO at 90 °C. The progress of the reactions was monitored by ^{1}H NMR spectroscopy, allowing the reaction time to be decreased to 46–88.5 h compared with the reported procedure (5 days). Reduced reaction times led to increased product yields. Acetals **9a–c** were demonstrated to be stable upon distillation and were prepared with high purity in 64–85% yields.

Scheme 2. Synthesis of *N*-[(β-Azido-α-tosyl)alkyl]ureas



8a R = H, **b** R = Me, **c** R = Et.
9, 10 a R = H, R^1 = Et;
b R = R^1 = Me;
c R = Et, R^1 = Me.

6 a R = R^2 = H;
b R = H, R^2 = Me;
c R = Me, R^2 = H;
d R = Et, R^2 = H.

We found that the reaction between acetal **9a**, acid **7**, and urea in water at room temperature proceeded very slowly to give sulfone **6a** after 5 days in only 44% yield, presumably because of decreased rate of hydrolysis of **9a** into **8a** due to poor water solubility and low acidity of **7** (pK_a 2.80 in water at 25 °C).[23] The hydrolysis of acetal **9a** smoothly proceeded in 80% formic acid at room temperature for 4 h. Then sulfinic acid **7** and urea were subsequently added followed by the addition of water. The condensation completed in the resulting 25% formic acid after 21 h to give **6a** in 86% yield. Sulfone **6a** precipitated from the solution formed after the addition of all reagents and was isolated by filtration with 99% purity according to ^{1}H NMR data for isolated crude material. Analogously, *N*-methyl-substituted sulfone **6b** was synthesized from acetal **9a**, sulfinic acid **7**, and methylurea in 88% yield. When 2-azidopropanal dimethyl acetal (**9b**) was used in reaction with acid **7** and urea under the described conditions, the corresponding sulfone **6c** was isolated in only 18% yield, and about 70% of acetal **9b** was recovered by extraction of the filtrate, indicating a low rate of its hydrolysis (Table 1, entry 1).

Table 1. Dependence of the Yield of Sulfone 6c from 9b on the Conditions of the Hydrolytic Step

	hydrolytic conditions[a]		
entry	temp (°C)	time (h)	isolated yield of **6c** (%)
1	20	4	18
2	20	24	63
3	40	1.5	49
4	40	4	71
5	40	6	71

[a]Treatment of acetal **9b** with 80% aqueous HCOOH. Subsequent three-component condensation was carried out as described for sulfone **6a** (25% aqueous HCOOH, rt, 24 h).

The decrease in the rate of hydrolysis of 2-azidopropanal dimethyl acetal (**9b**) compared with acetal **9a** can be explained by steric hindrance caused by the methyl group at the α-position.

Prolongation of the hydrolytic step (24 h, rt) increased the yield of **6c** to 63% (entry 2). Table 1 shows that the optimal conditions for the preparation of sulfone **6c** include stirring of **9b** in 80% HCOOH for 4 h upon heating at 40 °C (water bath)

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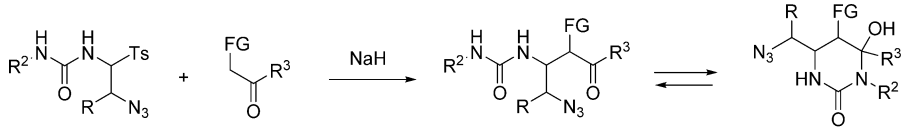
Table 2. Reaction of Sulfones 6a−d with Sodium Enolates of Ketones 11a−h; Synthesis of γ-Azido-β-ureido Ketones 12 or/and Their Cyclic Isomers 13



6a-d **11a-h** **12a-r** **13a-r**

entry	CH-acid	sulfone	R	R^2	R^3	FG	ratio NaH:**11**[a]	reaction conditions	product(s)	yield (%)[b]	dr[c]
1	**11a**	**6a**	H	H	Me	SO_2Ph	1.00:1.02	MeCN, 8 h, rt	**12a**	74	65:35
2	**11b**	**6a**	H	H	Me	Ts	1.00:1.01	MeCN, 8 h, rt	**13b**	84	90:10
3	**11b**	**6b**	H	Me	Me	Ts	1.00:1.01	MeCN, 8 h, rt	**12c**	84	63:37
4	**11b**	**6c**	Me	H	Me	Ts	1.00:1.01	THF, 8 h, rt	**12d**	61	62:20:14:4
5	**11b**	**6c**	Me	H	Me	Ts	1.00:1.00	MeCN, 8 h, rt	**12d**	60	62:21:13:4
6	**11b**	**6d**	Et	H	Me	Ts	1.00:1.01	MeCN, 8 h, rt	**12e**	71	69:19:9:3
7	**11b**	**6d**	Et	H	Me	Ts	1.00:1.02	MeCN, 24 h, rt	**12e**	69	74:20:5:1
8	**11c**	**6a**	H	H	Ph	SO_2Ph	1.01:1.03	THF, 8 h, rt	**12f**	92	55:45
9	**11d**	**6a**	H	H	Ph	Ts	1.00:1.01	MeCN, 8 h, rt	**12g**	94	60:40
10	**11d**	**6a**	H	H	Ph	Ts	1.01:1.02	THF, 8 h, rt	**12g**	96	60:40
11	**11d**	**6c**	Me	H	Ph	Ts	1.00:1.01	THF, 8 h, rt	**12h**	93	33:25:28:14
12	**11d**	**6c**	Me	H	Ph	Ts	1.00:1.01	MeCN, 9 h, rt	**12h**	86	35:32:20:13
13	**11d**	**6d**	Et	H	Ph	Ts	1.00:1.01	MeCN, 8 h, rt	**12i**	98	46:26:20:8
14	**11d**	**6d**	Et	H	Ph	Ts	1.00:1.01	THF, 9 h, rt	**12i**	98	48:25:19:8
15	**11e**	**6a**	H	H	Ph	SPh	1.00:1.02	MeCN, 8 h, rt	**12j** + **13j**	16	(35:23):(42:0)[d]
16	**11e**	**6a**	H	H	Ph	SPh	1.00:1.02	THF, 8 h, rt	**12j**	66	52:48
17	**11e**	**6a**	H	H	Ph	SPh	1.00:1.02	THF, 24 h, rt	**12j**	40	51:49
18	**11e**	**6b**	H	Me	Ph	SPh	1.00:1.02	THF, 8 h, rt	**12k**	73	72:28
19	**11e**	**6c**	Me	H	Ph	SPh	1.00:1.01	THF, 8 h, rt	**12l**	41	39:29:20:12
20	**11e**	**6c**	Me	H	Ph	SPh	1.00:1.02	THF, 8 h, 40 °C	**12l**	28	36:32:28:4
21	**11e**	**6c**	Me	H	Ph	SPh	1.10:1.12	THF, 8 h, rt	**12l** + **13l**	37	(12:5:18:3):(43:19)[d]
22	**11f**	**6a**	H	H	Me	SPh	1.00:1.02	MeCN, 8 h, rt	**13m**	54	48:41:11
23	**11f**	**6a**	H	H	Me	SPh	1.01:1.02	THF, 8 h, rt	**13m**	60	43:38:19
24	**11f**	**6a**	H	H	Me	SPh	1.01:1.04	THF, 24 h, rt	**13m**	53	46:37:17
25	**11f**	**6b**	H	Me	Me	SPh	1.00:1.02	THF, 8 h, rt	**12n** + **13n**	58	(74:8):(9:9)[d]
26	**11f**	**6c**	Me	H	Me	SPh	1.00:1.02	THF, 8 h, rt	**13o**	38	40:50:10
27	**11f**	**6c**	Me	H	Me	SPh	1.10:1.12	THF, 12 h, rt	**13o**	48	50:45:5
28	**11f**	**6c**	Me	H	Me	SPh	1.01:1.03	THF, 12 h, 40 °C	**13o**	27	48:42:10
29	**11f**	**6d**	Et	H	Me	SPh	1.00:1.01	THF, 8 h, rt	**12p** + **13p**	30	(44:0):(30:19:7)[d]
30	**11g**	**6a**	H	H	Ph	Bz	1.00:1.05	THF, 8 h, rt	**12q**	77	
31	**11h**	**6a**	H	H	Ph	CO_2Et	1.01:1.02	MeCN, 8 h, rt	**13r**	39	100:0

[a]The amount of the corresponding sulfone **6** is 1.00 equiv. [b]Isolated yield. [c]Determined by ^{1}H NMR of the crude isolated product. [d]The ratio in the first parentheses is for **12**, the ratio in the second parentheses is for **13**.

followed by condensation with urea and sulfinic acid **7** (entry 4). Prolongation of the hydrolytic step at 40 °C had no effect on the yield (entry 5). Under the described optimal conditions sulfone **6d** was obtained by the reaction of **9c** with acid **7** and urea in 80% yield. Compounds **6c,d** formed with high selectivity as mixtures of two diastereomers in 97:3 and 90:10 ratio, respectively.

Sulfones **6a−d** readily reacted with sodium enolates of α-functionalized ketones generated by treatment of CH-acids **11a−h** with NaH in dry solvent (MeCN or THF) to give products of nucleophilic substitution of the tosyl group, γ-azido-β-ureido ketones **12**, or/and their cyclic isomers, hydroxypyrimidinones **13**. Experimental data for this reaction are summarized in Table 2.

We focused our attention on the synthesis of γ-azido ketones bearing arylsulfonyl or arylthio groups, since they are the starting materials for pyrroles with sulfur-containing substituent at C-3. These pyrroles can be considered as useful building blocks for further functionalization allowing, for example, a regioselective synthesis of tetrasubstituted pyrroles.[24]

Thus, reactions of sulfones **6a−d** with sodium enolates of α-arylsulfonyl ketones **11a−d**, with the exception of the reaction of **6a** with the Na-enolate of **11b**, gave γ-azido ketones **12a,c−i** in 60−98% yields as mixtures of diastereomers (Table 2, entries 1, 3−14). The use of different solvents (entries 4, 9, 11, 13 vs entries 5, 10, 12, 14, respectively) and reaction time (entry 6 vs entry 7) had a slight effect on diastereoselectivity and yield of the final products.

The sodium enolate of tosylacetone (**11b**) reacted with urea **6a** in MeCN to give the corresponding γ-azido ketone **12b**, which spontaneously and completely cyclized into hydroxypyrimidinone **13b** under reaction conditions. Pyrimidine **13b** was isolated in 84% yield as a mixture of two diastereomers in a ratio of 90:10 (Table 2, entry 2). The pure major isomer of **13b** was isolated after crystallization of the crude product from EtOH. According to ^{1}H NMR data, the major diastereomer had (4*R**,5*R**,6*R**)-configuration with equatorial orientation of the

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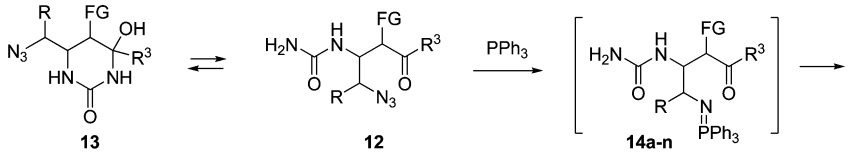
Scheme 3. Synthesis of Pyrrolines and Pyrroles via Staudinger/aza-Wittig Reaction



14-17	a	b	c	d	e	f	g	h	i	j	k	l	m	n
FG	SO_2Ph	Ts	Ts	Ts	SO_2Ph	Ts	Ts	Ts	SPh	SPh	SPh	COOEt	COOEt	Bz
R	H	H	Me	Et	H	H	Me	Et	H	H	Me	H	Me	H
R^3	Me	Me	Me	Me	Ph	Ph	Ph	Ph	Ph	Me	Me	Ph	Ph	Ph

substituents at C-5 and C-6 ($^3J_{H\text{-}5,H\text{-}6}$ = 9.7, $^3J_{N(1)H,H\text{-}6} \approx 0$ Hz)[25] and axial orientation of the hydroxyl group ($^4J_{H\text{-}5,OH}$ = 1.3 Hz) in DMSO-d_6. The relative configuration of the minor diastereomer was determined as (4*R**,5*S**,6*S**) with axial orientation of hydroxyl group and substituents at C-5 and C-6 ($^3J_{H\text{-}5,H\text{-}6}$ = 0.8, $^4J_{H\text{-}5,OH}$ = 0, $^3J_{N(1)H,H\text{-}6}$ = 4.6 Hz).[25,26] Thus, the diastereomers of **13b** differ only in configuration at C-4. A possible explanation of this result could lie in fully diastereoselective reaction of **6a** with the Na-enolate of **11b** to give (*R**,*R**)-**12b** followed by its cyclization to the isomeric mixture of **13b**. However, reaction of the same enolate with **6b** under the similar conditions proceeds with poor selectivity to provide a 63:37 diastereomeric mixture of **12c** (entry 3), which does not cyclize to **13c** due to steric hindrance caused by the *N*-Me group. Thus in the case of **6a**, poor selectivity of the amidoalkylation step should be also expected. We suppose that an initially formed diastereomeric mixture of **12b** cyclizes to a mixture of isomers of **13b** followed by base-promoted isomerization at C-5 to give the thermodynamically more stable isomers of **13b**. The different results of the reactions of **6a** with Na-enolates of **11a** and **11b** (entry 1 vs entry 2) can be explained by differences in thermodynamic stability of acyclic and cyclic forms of the obtained compounds.

The reaction between Na-enolates of phenylthioketones **11e**,**f** and sulfones **6a**−**d** proceeded in more complex fashion. The sodium enolate of phenylthioacetone (**11f**) reacted with **6a** to give hydroxypyrimidinone **13m** as a mixture of three diastereomers whose ratio slightly changed in different solvents (MeCN or THF), but the product yield slightly increased when THF was used (entry 22 vs entry 23). Extension of the reaction time from 8 to 24 h (THF, rt) had a small effect on the results obtained (entry 23 vs entry 24). The major diastereomer of phenylthio-substituted pyrimidine **13m** had (4*R**,5*S**,6*R**)-configuration with axial orientation of the phenylthio-group ($^3J_{H\text{-}5,H\text{-}6}$ = 2.8, $^4J_{H\text{-}5,N(1)H}$ = 1.3, $^4J_{H\text{-}5,N(3)H}$ = 1.3 Hz), equatorial orientation of the azidomethyl-group at C-6 ($^3J_{H\text{-}6,N(1)H} \approx 0$ Hz), and presumably axial orientation of the OH-group[27] in DMSO-d_6 solution. The first minor diastereomer (38%, entry 23) had (4*R**,5*R**,6*R**)-configuration with equatorial orientation of the substituents at C-5 and C-6 and axial orientation of the hydroxyl group ($^3J_{H\text{-}5,H\text{-}6}$ = 11.4, $^3J_{N(1)H,H\text{-}6} \approx 0$, $^4J_{5\text{-}H,OH}$ = 0.9 Hz). Configuration of the second minor diastereomer could not be unambiguously established from the ^{1}H NMR spectra. Only the orientation of the azidomethyl group could be determined as axial from the high value of coupling between $N_{(1)}H$ and H-6 (broadened unresolved multiplet for $N_{(1)}H$, half-height width = 7.1 Hz).[25] After crystallization of crude product from EtOH the ratio of (4*R**,5*R**,6*R**)- and (4*R**,5*S**,6*R**)-diastereomers changed to 70:30, the second minor diastereomer being completely removed.

The reaction of **6a** with the Na-enolate of **11e** smoothly proceeded in THF; however, in contrast to the reaction of **6a** with **11f** under the similar conditions, γ-azido ketone **12j** was exclusively obtained in 66% yield as a mixture of two diastereomers (entry 16). Prolongation of the reaction time decreased the yield of **12j** and had no effect on stereoselectivity (entry 16 vs entry 17). Notably, when MeCN was used instead of THF, the yield of the product was dramatically reduced, and the crude isolated material contained hydroxypyrimidine (4*R**,5*R**,6*R**)-**13j** (42%) along with two diastereomers of γ-azido ketone **12j** (entry 15). The relative configuration of **13j** was determined from the values of couplings in its ^{1}H NMR spectrum as described above for **13b**,**m**.

Since the use of THF compared with MeCN significantly increased the product yields, all reactions of **6b**−**d** with phenythioketones **11e**,**f** were carried out in THF. Sulfone **6b** reacted with the Na-enolate of **11e** to give γ-azido ketone **12k** as a mixture of two diastereomers in 73% yield (entry 18). Under the similar conditions, the product of the reaction between **11f** and **6b** partially cyclized, affording a mixture of pyrimidine **13n** (18%) along with azido ketone **12n** (entry 25). Reaction of **6c** with **11e** (THF, 8 h, rt) gave γ-azido ketone **12l** as diastereomeric mixture in relatively low yield (entry 19). Our attempts to increase the yield of **12l** using heating of the reaction mixture at 40 °C (entry 20) or 10% excess of the nucleophile (entry 21) failed. In the last case, a 38:62 mixture of γ-azido ketone **12l** and hydroxypyrimidine **13l** was obtained showing significant influence of the basicity of the medium on the cyclization of **12** into **13**. Treatment of **6c** with the Na-enolate of **11f** in THF under various conditions gave exclusively pyrimidine **13o** in 27−48% yields as mixtures of three diastereomers with similar ratios (entries 26−28). The reaction of **6d** with the Na-enolate of **11f** (THF, 8 h, rt) resulted in the formation of a 44:56 mixture of **12p** and **13p** in rather low yield (entry 29).

The reaction of sulfone **6a** with an equimolar amount of the Na-enolate of dibenzoylmethane (**11g**) in dry THF afforded γ-azido ketone **12q** along with 10% of *N*-[(1-azido-4-oxo-4-phenyl)but-2-yl]-*N*′-benzoylurea (^{1}H NMR data for isolated crude material). The latter resulted from base-promoted

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cleavage of the C(4)−C(5) bond in the corresponding hydroxypyrimidine **13q**. This type of cleavage was previously observed for 5-acyl-substituted hydroxypyrimidines.[28] When the basicity of the reaction medium was lowered by the addition of 5% excess of dibenzoylmethane (toward NaH), this side reaction did not proceed. Under these conditions pure γ-azido ketone **12q** was isolated in 77% yield (entry 30). When MeCN was used instead of THF, the completion of the reaction between dibenzoylmethane and NaH was hampered by formation of a dense suspension of the enolate, reducing the yield and purity of **12q**.

Sodium enolate of ethyl benzoyl acetate (**11h**) reacted with **6a** in MeCN to give 4-hydroxypyrimidine **13r**, which was isolated in 39% yield as a single diastereomer with (4*R**,5*S**,6*R**)-configuration (entry 31). The orientations of the substituents at C-6, C-5, and C-4 were analogous to those described for the major diastereomer of **13b**. A decrease in the yield of **13r** can be explained by partial loss of the product during aqueous workup because of high solubility of **13r** in water.

Synthesis of Functionalized Δ^1-Pyrrolines, Δ^2-Pyrrolines, and Pyrroles. γ-Azido ketones **12** and hydroxypyrimidines **13** were used as starting materials in the synthesis of functionalized pyrrolines via Staudinger/aza-Wittig reaction promoted by PPh_3 (1.2 equiv) in refluxing solvent (Scheme 3). Azido ketones **12f,g** reacted with PPh_3 in refluxing THF for 1 h 40 min to give iminophosphoranes **14e,f**, which spontaneously cyclized into the corresponding 4-ureido-substituted Δ^1-pyrrolines **15e,f** and precipitated from the reaction mixture. Due to low solubility in THF they were isolated by filtration in 89% yield completely free from $POPh_3$. Though starting ketones **12f,g** were mixtures of two diastereomers (Table 2), pyrrolines **15e,f** were obtained as a single *trans*-diastereomer, presumably due to base-promoted epimerization at the sulfur-bearing carbon during the reaction under the action of iminophosphoranes **14e,f**.[29] The *trans*-configuration of **15e,f** follows from the values of vicinal coupling constants between the protons at C-3, C-4, and C-5. Two of these constants were close to zero, confirming that the corresponding dihedral angles were about 90°. Calculations of the geometries of *cis*- and *trans*-**15e,f** using semiempirical methods AM1 and PM6[30] showed that these angles were in good agreement only with a *trans*-configuration of **15e,f**. The Δ^1-pyrroline ring of *trans*-**15e,f** adopts an envelope conformation (C-4 out of the plane) with pseudoaxial orientations of the ureido and arylsulfonyl groups. *trans*-Configuration of **15e** was confirmed in a $^1H,^1H$-NOESY experiment. Diagnostic NOEs were observed between the NH proton and pseudoequatorial H-3 and H-5 protons and between *ortho*-protons of the phenylsulfonyl group and the H-4 proton.

Analogously, reaction of **12h** with PPh_3 in refluxing THF for 2 h gave Δ^1-pyrroline **15g**, which was isolated by filtration of the precipitated solid in 74% yield. Compound **15g** was obtained as a mixture of two diastereomers in a ratio of 72:28, which differ only in the relative orientation of the methyl group at C-5. In contrast to **12f−h**, treatment of **12q** with PPh_3 (THF, reflux, 4.5 h) afforded 4-ureido-substituted Δ^2-pyrroline **16n** in 72% yield that formed as a result of imine-enamine tautomeric shift in the intermediate Δ^1-pyrroline **15n**.

We found that with the exception of **12f−h,q**, other γ-azido ketones **12** and hydroxypyrimidines **13** being reacted with PPh_3 afforded complex mixtures of products. Selected experimental data for this reaction are shown in Table 3.

Table 3. Functionalized Pyrroline Synthesis by PPh_3-Promoted Staudinger/aza-Wittig Reaction of γ-Azido Ketones 12 and Hydroxypyrimidines 13[a]

entry	starting material[b]	solvent	reaction time (h)	product(s)	ratio of products
1	**12a**	THF	1.7	*trans*-**15a** + **16a** + **17a**	28:69:3
2	**13b**	THF	2	*trans*-**15b** + **16b**	39:61
3	**13b**	MeCN	1.6	*trans*-**15b** + **16b**	39:61
4	**13b**	1,4-dioxane	3	*trans*-**15b** + **16b** + **17b**	31:55:14
5	**12j**	MeCN	4	*trans*-**15i** + *cis*-**15i**	80:20
6	**13m**	MeCN	5	*trans*-**15j** + *cis*-**15j** + **16j**	64:20:16
7	**13r**	MeCN	1	*trans*-**15l** + *cis*-**15l** + **16l**	59:13:28

[a]Reactions were carried out in refluxing solvent using 1.2 equiv of PPh_3. After their completion the solvent was removed under reduced pressure, and the resulting crude products were analyzed by ^1H NMR spectroscopy. [b]Diastereomer ratios of **12** and **13** are shown in Table 2.

Table 3 shows that reactions of **12a,j** and **13b,m,r** with PPh_3 gave mixtures of the corresponding Δ^1- and Δ^2-pyrrolines. Some of these mixtures also contained aromatic pyrroles (entries 1 and 4). No products precipitated from the reaction mixtures, and therefore their isolation required column chromatography to separate $POPh_3$. During chromatographic purification on silica gel, the 4-ureidopyrrolines partially decomposed (especially 3-phenylthio-substituted ones) and aromatized via elimination of urea. Our attempts to prepare pure ureidopyrrolines **15** and **16**, with the exception of **15e−g**, **16n**, failed.

The final step of the pyrrole synthesis involved conversion of the obtained ureidopyrrolines **15** or/and **16** into 3-functionalized aromatic pyrroles **17**. The experimental data for this transformation are shown in Table 4.

We developed three different synthetic procedures for the preparation of pyrroles **17**. Arylsulfonyl-substituted pyrroles **17a,c,d,h** were obtained using a one-pot procedure based on the reaction of the corresponding azido ketones **12a,d,e,i** with 1.2 equiv of PPh_3 (THF, reflux, 2−2.4 h) followed by the addition of 0.5 equiv of TsOH (THF, reflux, 10−30 min) (Table 4, entries 1, 4, 6, 10). Overall yields of **17a,c,d,h** after purification by column chromatography were 69−93%. Pyrrole **17c** was also prepared in 47% overall yield according to another one-pot synthesis starting from sulfone **6c** (entry 5). After the reaction between sulfone **6c** and the sodium enolate of tosylacetone in THF was complete, PPh_3 was added, the obtained reaction mixture was refluxed for 1 h, and then TsOH (0.5 equiv) was added followed by reflux for 1.25 h. The overall yield of pyrrole **17c** obtained from **6c** was higher than that from **12d**. Analogously, using the above described one-pot procedures, pyrrole **17l** was synthesized from pyrimidine **13r** (entry 14) and sulfone **6a** (entry 15) in 83% and 89% overall yields, respectively. Sulfones **6a,c** were used as starting materials for the one-pot preparation of pyrroles **17b,m** (entries 2, 3, 16). The yield of pyrrole **17b** increased when the reaction was carried out in MeCN (Table 4, entry 2 vs entry 3).

The pyrroline formation from hydroxypyrimidine **13m** using Staudinger/aza-Wittig sequence strongly depended on the reaction conditions. When **13m** was reacted with PPh_3 in refluxing THF for 1 h 10 min, TLC showed no starting

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Table 4. Synthesis of 3-Functionalized Pyrroles

entry	starting material	solvent	reaction conditions	product	isolated yield (%)
1	**12a**	THF	(i) PPh_3 (1.23 equiv), reflux, 2 h (ii) TsOH (0.50 equiv), reflux, 10 min	**17a**	93
2	**11b** + **6a**	THF	(i) **11b** (1.02 equiv), NaH (1.00 equiv), rt, 8 h (ii) PPh_3 (1.20 equiv), reflux, 1 h (iii) TsOH (0.51 equiv), reflux, 1 h	**17b**	61
3	**11b** + **6a**	MeCN	(i) **11b** (1.02 equiv), NaH (1.00 equiv), rt, 8 h (ii) PPh_3 (1.19 equiv), reflux, 1 h (iii) TsOH (0.50 equiv), reflux, 1 h	**17b**	71
4	**12d**	THF	(i) PPh_3 (1.19 equiv), reflux, 2.4 h (ii) TsOH (0.50 equiv), reflux, 15 min	**17c**	70
5	**11b** + **6c**	THF	(i) **11b** (1.04 equiv), NaH (1.00 equiv), rt, 8 h (ii) PPh_3 (1.13 equiv), reflux, 1 h (iii) TsOH (0.51 equiv), reflux, 1.25 h	**17c**	47
6	**12e**	THF	(i) PPh_3 (1.21 equiv), reflux, 2 h (ii) TsOH (0.50 equiv), reflux, 15 min	**17d**	74
7	**15e**	MeCN	TsOH (0.10 equiv), reflux, 30 min	**17e**	96
8	**15f**	MeCN	TsOH (0.10 equiv), reflux, 30 min	**17f**	93
9	**15g**	MeCN	TsOH (0.30 equiv), reflux, 20 min	**17g**	97
10	**12i**	THF	(i) PPh_3 (1.13 equiv), reflux, 2 h (ii) TsOH (0.50 equiv), reflux, 30 min	**17h**	69
11	**12j**	THF	(i) PPh_3 (1.19 equiv), reflux, 2 h (ii) TsOH (0.50 equiv), reflux, 15 min	**17i**	69
12	**13m**	MeCN	(i) PPh_3 (1.09 equiv), reflux, 5 h (ii) TsOH (0.50 equiv), reflux, 5 min	**17j**	77
13	**13o**	MeCN	(i) PPh_3 (1.20 equiv), reflux, 4.5 h (ii) TsOH (0.49 equiv), reflux, 15 min	**17k**	79
14	**13r**	MeCN	(i) PPh_3 (1.18 equiv), reflux, 1 h (ii) TsOH (0.10 equiv), reflux, 5 min	**17l**	83
15	**11h** + **6a**	MeCN	(i) **11h** (1.00 equiv), NaH (1.00 equiv), rt, 8 h (ii) PPh_3 (1.25 equiv), reflux, 1.17 h (iii) TsOH (0.20 equiv), reflux, 1 h	**17l**	89
16	**11h** + **6c**	MeCN	(i) **11h** (1.04 equiv), NaH (1.00 equiv), rt, 8 h (ii) PPh_3 (1.23 equiv), reflux, 1 h (iii) TsOH (0.20 equiv), reflux, 30 min	**17m**	85
17	**16n**	MeCN	TsOH (0.10 equiv), reflux, 10 min	**17n**	96

material. After removal of solvent, no signals of expected pyrrolines were observed in the ^{1}H NMR spectrum. Analogously we studied the mixture formed in the reaction of **13m** with PPh_3 in refluxing 1,4-dioxane for 3 h 50 min, but only unidentified products of decomposition were detected. However, reflux of **13m** with PPh_3 in MeCN for 5 h led to desired recyclization of **13m** into a mixture of *trans*-**15j**, *cis*-**15j**, and **16j** in a ratio of 64:20:16, respectively (Table 3, entry 6). The subsequent aromatization of this mixture under the action of TsOH gave pyrrole **17j** in 77% overall yield (Table 4, entry 12). The similar procedure was used for the one-pot preparation of **17k** in 79% yield from pyrimidine **13o** (entry 13).

Δ^1-Pyrroline **15i** was obtained as a mixture of *trans*- and *cis*-diastereomers in a ratio of 80:20 after reflux of **12j** in MeCN with PPh_3 for 4 h (Table 3, entry 5). However, after reflux of this mixture with 0.1 equiv of TsOH for 10 min, the resulting reaction mixture unexpectedly contained 4% of 2-phenyl-1*H*-pyrrole (according to ^{1}H NMR spectrum of crude isolated material[31]). The amount of this side product increased to 8% when the reflux with TsOH was continued for 2 h. We found that the formation of pyrrole **17i** in the reaction of **12j** with PPh_3 in THF (reflux, 2 h) followed by the treatment of the obtained mixture with 0.50 equiv of TsOH (reflux, 15 min) proceeded without any side processes. The overall yield of **17i** was 69% after column chromatography (Table 4, entry 11).

Pyrrolines **15e−g** and **16n** were readily aromatized to pyrroles **17e−g,n** via elimination of urea in refluxing MeCN in the presence of TsOH in 93−97% yields (Table 4, entries 7−9, 17). Greater amount of TsOH for 5-methyl-substituted **15g** was used to decrease the reaction time (Table 4, entry 9).

CONCLUSION

We have developed an efficient three-step protocol for preparation of γ-azido-β-ureido ketones bearing arylsulfonyl-, arylthio-, acyl-, and alkoxycarbonyl-substituents at the α-position to the carbonyl group or their cyclic isomers, 6-(1-azidoalkyl)-4-hydroxyhexahydropyrimidin-2-ones, involving amidoalkylation of α-functionalized ketone enolates with *N*-[(2-azido-1-tosyl)alkyl]ureas. Compared with the literature approaches to γ-azido ketones, advantages of our approach are high synthetic flexibility, high availability of starting materials and reagents, mild reaction conditions, and introduction of additional functionalities to the α- and β-positions of the target products. The obtained γ-azido-β-ureido ketones or their cyclic isomers are transformed into ureido-substituted Δ^1- or/and Δ^2-pyrrolines via intramolecular Staudinger/aza-Wittig reaction promoted by PPh_3. The pyrro-

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lines readily eliminate urea under acidic conditions to give 3-functionalized 1*H*-pyrroles. The latter can be readily prepared using convenient one-pot procedures starting from *N*-[(2-azido-1-tosyl)alkyl]ureas or *γ*-azido-*β*-ureido ketones. We believe that the synthesis of pyrroles described in this article is an attractive alternative to the classical pyrrole syntheses. This has been illustrated by the successful preparation of previously inaccessible pyrroles.

EXPERIMENTAL SECTION

General Procedures. All solvents were distilled prior to use; 95% EtOH was used unless otherwise indicated. Petroleum ether had a distillation range of 40−70 °C. Dry solvents (MeCN, THF, DMSO, 1,4-dioxane) were obtained according to standard procedures. *p*-Toluenesulfinic acid (**7**) was synthesized by treatment of a saturated aqueous solution of sodium *p*-toluenesulfinate[32] with hydrochloric acid at 0 °C, dried over P_2O_5, and stored at 0 °C. Sodium hydride (NaH) (60% suspension in mineral oil) was thoroughly washed with dry pentane and dried in a vacuum prior to use. NaN_3 and KI were finely powdered and dried in a vacuum desiccator over P_2O_5. All other reagents were purchased from commercial sources and used without additional purification. IR spectra (in Nujol) were recorded using a FT-IR spectrophotometer for crystallized compounds. Band characteristics in IR spectra are defined as very strong (vs), strong (s), medium (m), weak (w), and shoulder (sh). ^{1}H and proton-decoupled ^{13}C NMR spectra (solutions in DMSO-d_6 or $CDCl_3$) were acquired using a 300 or 600 MHz spectrometer. ^{1}H NMR chemical shifts are referenced to the residual proton signal in DMSO-d_6 (2.50 ppm) or $CDCl_3$ (7.25 ppm). In ^{13}C NMR spectra the DMSO-d_6 signal (39.50 ppm) was used as a reference. Multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q), and some combinations of these, multiplet (m). Selective ^{1}H−^{1}H decoupling, ^{1}H−^{1}H NOESY, and DEPT-135 experiments were used to aid in the assignment of ^{1}H and ^{13}C NMR signals. Thin-layer chromatography was carried out on silica gel 60 F_{254} aluminum backed plates in chloroform/methanol (9:1, v/v) and chloroform/methanol (5:1, v/v) as solvent systems. Spots were visualized with iodine vapors or UV light. Column chromatography was performed with silica gel 60 (0.04−0.063 mm). All yields refer to isolated, spectroscopically and TLC pure compounds. The color of substances was white, if not otherwise mentioned. Evaporation of solvent from all the reaction mixtures formed after the reactions of nucleophilic substitution and after one-pot syntheses of pyrroles (from **6**) was carried out, at the beginning, upon cooling (temperature of water bath about 5−10 °C) and low vacuum (about 100 mmHg), otherwise the vigorous foaming complicated the evaporation. It is important that pyrroles **17b,c** left the column during purification by chromatography after $POPh_3$ and contained the small amounts of $POPh_3$ (due to their close R_f values). To remove this impurity they were recrystallized from EtOH. In the case of pyrrole **17a**, which was highly soluble in EtOH, the column was eluted with less polar system (petroleum ether/$CHCl_3$, 1:1) until only the traces of $POPh_3$ were detected in the fractions (TLC). For pyrroles **17d,h** the eluting system was changed to petroleum ether/acetone and they left the column before $POPh_3$ (for **17a,b,c** it did not work). Other purifications had no difficulties.

***N*-[(2-Azido-1-tosyl)ethyl]urea (6a).** To a freshly distilled 2-azidoethanal diethyl acetal (**9a**) (7.879 g, 49.49 mmol) was added 80% formic acid (25 mL), the resulting colorless solution was stirred at room temperature for 5 h 30 min, and then *p*-toluenesulfinic acid (**7**) (7.737 g, 49.53 mmol) and H_2O (50 mL) were added. The mixture was stirred for 10 min, and to the formed clear solution were added urea (14.869 g, 247.57 mmol) and H_2O (25 mL). Urea dissolved in 5 min followed by precipitation of a fine heavy solid. The suspension was stirred for 21 h and cooled to 0 °C, and the precipitate was filtered, washed with ice-cold water (8 × 15 mL) so that the smell of formic acid disappeared and petroleum ether, and dried to give **6a** (12.096 g, 86%), which was used without further purification. Mp 125 °C (decomp, MeCN); IR (Nujol) ν_{max} 3458 (s), 3369 (s), 3358 (s), 3276 (m), 3212 (m) (NH), 3089 (w), 3065 (w), 3043 (m) (CH_{arom}), 2181 (m), 2111 (vs) (N_3), 1695 (s), 1667 (s) (amide-I), 1616 (m), 1599 (w) (CC_{arom}), 1516 (br s) (amide-II), 1308 (s), 1143 (s) (SO_2), 825 (m) (CH_{arom}) cm^{-1}; ^{1}H NMR (300.13 MHz, DMSO-d_6) δ 7.69−7.74 (m, 2H, ArH), 7.41−7.47 (m, 2H, ArH), 7.15 (d, ^3J = 10.3 Hz, 1H, NH), 5.84 (s, 2H, NH_2), 5.17 (ddd, ^3J = 10.3, ^3J = 7.4, ^3J = 4.3 Hz, 1H, CHN), 3.78 (dd, ^2J = 13.3, ^3J = 7.4 Hz, 1H, CH_AN_3), 3.76 (dd, ^2J = 13.3, ^3J = 4.3 Hz, 1H, CH_BN_3), 2.41 (s, 3H, CH_3); ^{13}C NMR (75.48 MHz, DMSO-d_6) δ 156.3 (C═O), 144.7 (C), 134.1 (C), 129.7 (2CH), 128.8 (2CH), 69.1 (CHN), 48.1 (CH_2N_3), 21.1 (CH_3). Anal. Calcd for $C_{10}H_{13}N_5O_3S$: C, 42.40; H, 4.63; N, 24.72. Found: C, 42.34; H, 4.70; N, 24.64.

***N*-[(2-Azido-1-tosyl)ethyl]-*N*′-methylurea (6b).** Compound **6b** (29.43 g, 88%) was prepared from acetal **9a** (17.97 g, 0.113 mol), sulfinic acid **7** (17.63 g, 0.113 mol), *N*-methylurea (12.54 g, 0.169 mol), 80% HCOOH (56 mL), and H_2O (168 mL) (rt, 24 h) as described for **6a**. Mp 114.5 °C (decomp, MeCN); IR (Nujol) ν_{max} 3376 (s), 3286 (s), 3195 (m) (NH), 3088 (w), 3067 (w) (CH_{arom}), 2210 (w), 2147 (w), 2108 (s) (N_3), 1673 (s) (amide-I), 1595 (m) (CC_{arom}), 1559 (br s), 1532 (m) (amide-II), 1492 (w) (CC_{arom}), 1293 (s), 1126 (s) (SO_2), 817 (m) (CH_{arom}) cm^{-1}; ^{1}H NMR (300.13 MHz, DMSO-d_6) δ 7.67−7.73 (m, 2H, ArH), 7.41−7.47 (m, 2H, ArH), 7.12 (d, ^3J = 10.3 Hz, 1H, NH), 6.02 (q, ^3J = 4.7 Hz, 1H, NH), 5.18 (ddd, ^3J = 10.3, ^3J = 6.5, ^3J = 5.4 Hz, 1H, CHN), 3.69−3.81 (m, 2H, CH_2N_3), 2.43 (d, ^3J = 4.7 Hz, 3H, NCH_3), 2.41 (s, 3H, CH_3 in Ts); ^{13}C NMR (75.48 MHz, DMSO-d_6) δ 156.4 (C═O), 144.8 (C), 134.1 (C), 129.7 (2CH), 128.8 (2CH), 69.6 (CHN), 48.1 (CH_2N_3), 26.3 (NCH_3), 21.1 (CH_3 in Ts). Anal. Calcd for $C_{11}H_{15}N_5O_3S$: C, 44.44; H, 5.09; N, 23.55. Found: C, 44.50; H, 5.23; N, 23.44.

***N*-[(2-Azido-1-tosyl)propyl]urea (6c).** To a freshly distilled 2-azidopropanal dimethyl acetal (**9b**) (16.23 g, 0.112 mol) was added 80% formic acid (56 mL), the resulting solution was stirred in a water bath (41 °C) for 4 h and cooled to room temperature, and *p*-toluenesulfinic acid (**7**) (17.47 g, 0.112 mol) and H_2O (112 mL) were added. The mixture was stirred for 30 min, and to the formed suspension were added urea (33.58 g, 0.559 mol) and H_2O (56 mL). The clear solution formed in 5 min followed by precipitation of a fine heavy solid. The suspension was stirred for 24 h and cooled to 0 °C, the precipitate was filtered, washed with ice-cold water (8 × 30 mL) so that the smell of formic acid disappeared and petroleum ether, and dried to give **6c** (23.73 g, 71%) as a mixture of two diastereomers (97:3), which was used without further purification. Crystallization from MeCN afforded the pure major isomer. Mp 126.5 °C (decomp, MeCN); IR (Nujol) ν_{max} 3450 (s), 3369 (s), 3334 (sh), 3315 (br m), 3273 (m), 3215 (m) (NH), 3066 (w), 3044 (w), 3031 (w) (CH_{arom}), 2130 (s), 2101 (s), 2087 (s) (N_3), 1699 (s), 1666 (s) (amide-I), 1624 (w), 1599 (w) (CC_{arom}), 1525 (s) (amide-II), 1496 (w) (CC_{arom}), 1303 (s), 1146 (s) (SO_2), 812 (m) (CH_{arom}) cm^{-1}; ^{1}H NMR of the major diastereomer (300.13 MHz, DMSO-d_6) δ 7.68−7.74 (m, 2H, ArH), 7.39−7.45 (m, 2H, ArH), 6.93 (d, ^3J = 10.6 Hz, 1H, NH), 5.90 (s, 2H, NH_2), 5.02 (dd, ^3J = 10.6, ^3J = 2.0 Hz, 1H, CHN), 4.54 (dq, ^3J = 6.6, ^3J = 2.0 Hz, 1H, CHN_3), 2.40 (s, 3H, CH_3 in Ts), 1.21 (d, ^3J = 6.6 Hz, 3H, CH_3); ^{1}H NMR the minor isomer (300.13 MHz, DMSO-d_6) δ 7.23 (d, ^3J = 10.8 Hz, 1H, NH), 5.82 (s, 2H, NH_2), 5.17 (dd, ^3J = 10.8, ^3J = 4.1 Hz, 1H, CHN), 4.14 (dq, ^3J = 6.7, ^3J = 4.1 Hz, 1H, CHN_3), 2.40 (s, 3H, CH_3 in Ts), 1.38 (d, ^3J = 6.7 Hz, 3H, CH_3), signals of other protons overlap with signals of analogous protons of the major isomer; ^{13}C NMR of the major diastereomer (75.48 MHz, DMSO-d_6) δ 156.7 (C═O), 144.5 (C), 134.8 (C), 129.6 (2CH), 128.7 (2CH), 71.9 (CHN), 54.8 (CHN_3), 21.1 (CH_3 in Ts), 17.3 (CH_3). Anal. Calcd for $C_{11}H_{15}N_5O_3S$: C, 44.44; H, 5.09; N, 23.55. Found: C, 44.44; H, 5.18; N, 23.45.

***N*-[(2-Azido-1-tosyl)butyl]urea (6d).** To a freshly distilled 2-azidobutanal dimethyl acetal (**9c**) (19.01 g, 0.119 mol) was added 80% formic acid (60 mL), resulting yellow solution was stirred in water bath (41 °C) for 4 h and cooled to room temperature, and *p*-toluenesulfinic acid (**7**) (18.66 g, 0.119 mol) and H_2O (120 mL) were added. The mixture was stirred for 20 min, and to the formed suspension were added urea (35.85 g, 0.597 mol) and H_2O (60 mL). After 5 min in the resulting clear solution formed a white oily

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precipitate. After 1 h the precipitate was triturated until the fine solid was obtained. The suspension was stirred for 23 h and cooled to 0 °C, and the precipitate was filtered, washed with ice-cold water (8 × 30 mL) so that the smell of formic acid disappeared and petroleum ether, and dried to give **6d** (29.64 g, 80%) as a mixture of two diastereomers (90:10), which was used without further purification. After crystallization from MeCN the diastereomeric ratio changed to 94:6. Mp 125.5 °C (decomp, MeCN); IR (Nujol) ν_{max} 3450 (s), 3365 (br s), 3277 (m), 3219 (m) (NH), 3096 (w), 3071 (w), 3052 (w), 3029 (w) (CH_{arom}), 2107 (s) (N_3), 1698 (s), 1666 (s) (amide-I), 1621 (m), 1599 (m) (CC_{arom}), 1520 (s) (amide-II), 1307 (s), 1144 (s) (SO_2), 810 (m) (CH_{arom}) cm^{-1}; ^1H NMR the major isomer (300.13 MHz, DMSO-d_6) δ 7.69−7.75 (m, 2H, ArH), 7.40−7.46 (m, 2H, ArH), 6.94 (d, ^3J = 10.6 Hz, 1H, NH), 5.89 (s, 2H, NH_2), 5.06 (dd, ^3J = 10.6, ^3J = 1.7 Hz, 1H, CHN), 4.30 (dt, ^3J = 7.1, ^3J = 1.7 Hz, 1H, CHN_3), 2.40 (s, 3H, CH_3 in Ts), 1.43−1.58 (m, 2H, CH_2), 0.94 (t, ^3J = 7.4 Hz, 3H, CH_3 in Et); ^1H NMR the minor isomer (300.13 MHz, DMSO-d_6) δ 7.21 (d, ^3J = 10.8 Hz, 1H, NH), 5.81 (s, 2H, NH_2), 5.15 (dd, ^3J = 10.8, ^3J = 5.5 Hz, 1H, CHN), 3.88 (ddd, ^3J = 10.1, ^3J = 5.5, ^3J = 3.3 Hz, 1H, CHN_3), 2.40 (s, 3H, CH_3 in Ts), 0.98 (t, ^3J = 7.4 Hz, 3H, CH_3 in Et), signals of other protons overlap with signals of analogous protons of the major isomer; ^{13}C NMR of the major isomer (75.48 MHz, DMSO-d_6) δ 156.5 (C═O), 144.5 (C), 134.6 (C), 129.6 (2CH), 128.7 (2CH), 70.6 (CHN), 60.8 (CHN_3), 25.2 (CH_2), 21.1 (CH_3 in Ts), 10.0 (CH_3). Anal. Calcd for $C_{12}H_{17}N_5O_3S$: C, 46.29; H, 5.50; N, 22.49. Found: C, 46.32; H, 5.69; N, 22.47.

2-Azidoethanal Diethyl Acetal (9a).[33] Acetal **9a** (42.33 g, 85%) was prepared from 2-bromoethanal diethyl acetal (**10a**)[34] (61.39 g, 0.311 mol), NaN_3 (30.39 g, 0.475 mol), and KI (5.17 g, 0.031 mol) in DMSO (232 mL) (90 °C, 88.5 h) as described for **9c**. Bp 74.5−76.5 °C/20 mmHg; ^1H NMR (300.13 MHz, CDCl3) δ 4.58 (t, ^3J = 5.3 Hz, 1H, CHO), 3.71 (dq, ^2J = 9.2, ^3J = 7.1 Hz, 2H, OCH_2), 3.57 (dq, ^2J = 9.2, ^3J = 7.1 Hz, 2H, OCH_2), 3.23 (d, ^3J = 5.4 Hz, 2H, CH_2N_3), 1.22 (t, ^3J = 7.1 Hz, 6H, CH_3 in OEt).

2-Azidopropanal Dimethyl Acetal (9b).[35] Acetal **9b** (24.48 g, 75%) was prepared from 2-bromopropanal dimethyl acetal (**10b**)[36] (41.14 g, 0.225 mol), NaN_3 (21.93 g, 0.337 mol), and KI (3.80 g, 0.023 mol) in DMSO (170 mL) (90 °C, 64 h) as described for **9c**. Bp 60.5−62.5 °C/20 mmHg; ^1H NMR (300.13 MHz, $CDCl_3$) δ 4.14 (d, ^3J = 5.8 Hz, 1H, CHO), 3.47 (dq, ^3J = 5.8, ^3J = 6.8 Hz, 1H, CHN_3), 3.43 (s, 3H, OCH_3), 3.40 (s, 3H, OCH_3), 1.18 (d, ^3J = 6.8 Hz, 3H, CH_3).

2-Azidobutanal Dimethyl Acetal (9c). To a stirred solution of freshly distilled 2-bromobutanal dimethyl acetal (**10c**)[36] (56.22 g, 0.285 mol) in dry DMSO (215 mL) were added NaN_3 (27.83 g, 0.428 mol) and KI (4.754 g, 0.029 mol), and the suspension was heated in an oil bath (90 °C) for 46 h. After 3 h from beginning of heating a dark solution formed. The progress of the reaction was monitored by ^1H NMR spectroscopy. After the reaction was complete the obtained black solution was cooled to room temperature. The resulting solid was dissolved in H_2O (325 mL), the solution was extracted with diethyl ether (250 mL, 2 × 200 mL, 2 × 150 mL), and the combined extracts were washed with brine (3 × 50 mL) and dried over Na_2SO_4 (transparent yellow liquid). After the solvent was removed in a vacuum the residue was distilled to give **9c** (29.12 g, 64%) as a colorless liquid. Bp 71−72.5 °C/20 mmHg; n^{20}_D 1.4321; IR (film) ν_{max} 2969 (m), 2938 (m), 2881 (m), 2835 (m) (CH_3, CH_2, CH), 2160 (sh), 2107 (s) (N_3), 1464 (m) (CH_3, CH_2), 1380 (m) (CH_3), 1104 (s), 1080 (s), 1063 (s) (C−O) cm^{-1}; ^1H NMR (300.13 MHz, DMSO-d_6) δ 4.29 (d, ^3J = 5.9 Hz, 1H, CHO), 3.41 (ddd, ^3J = 9.4, ^3J = 5.9, ^3J = 3.6 Hz, 1H, CHN_3), 3.38 (s, 3H, OCH_3), 3.35 (s, 3H, OCH_3), 1.58 (ddq, ^2J = 14.2, ^3J = 7.4, ^3J = 3.6 Hz, 1H, CH_A in CH_2), 1.34 (ddq, ^2J = 14.2, ^3J = 9.4, ^3J = 7.4 Hz, 1H, CH_B in CH_2), 0.93 (t, ^3J = 7.5 Hz, 3H, CH_3); ^{13}C NMR (75.48 MHz, DMSO-d_6) δ 105.5 (CHO), 63.8 (CHN_3), 54.8 (OCH_3), 54.4 (OCH_3), 22.0 (CH_2), 10.1 (CH_3 in Et). Anal. Calcd for $C_6H_{13}N_3O_2$: C, 45.27; H, 8.23; N, 26.40. Found: C, 44.80; H, 8.03; N, 26.76.[37]

***N*-[(1-Azido-4-oxo-3-phenylsulfonyl)but-2-yl]urea (12a).** To a mixture of phenylsulfonylacetone (**11a**) (0.710 g, 3.58 mmol) and NaH (0.084 g, 3.52 mmol) was added dry MeCN (7 mL), the mixture was stirred in an ice-cold bath for 15 min, and to the resulting solution were added sulfone **6a** (0.992 g, 3.50 mmol) and MeCN (4 mL). The suspension was stirred at room temperature for 8 h, and solvent was removed in a vacuum. To a solid residue were added saturated aq $NaHCO_3$ (2 mL) and petroleum ether (10 mL), the obtained mixture was triturated until complete crystallization, and the resulting suspension was left overnight at room temperature and cooled to 0 °C. The precipitate was filtered and washed with ice-cold water and petroleum ether. The obtained solid was dried in a vacuum desiccator (over P_2O_5) on the filter, cooled (−10 °C), washed with cold (−10 °C) diethyl ether (3 × 4 mL), and dried to give **12a** (0.839 g, 74%) as a mixture of two diastereomers (65:35). After crystallization from EtOH the diastereomeric ratio did not change. Mp 121−121.5 °C (decomp, EtOH); IR (Nujol) ν_{max} 3444 (br s), 3371 (s), 3315 (sh), 3218 (br m) (NH), 3069 (w) (CH_{arom}), 2198 (m), 2163 (m), 2098 (vs) (N_3), 1712 (s) (C═O), 1664 (s) (amide-I), 1610 (m) (CC_{arom}), 1542 (br s) (amide-II), 1300 (s), 1145 (s) (SO_2), 741 (s), 687 (s) (CH_{arom}) cm^{-1}; ^1H NMR of the major diastereomer (300.13 MHz, DMSO-d_6) δ 7.60−7.90 (m, 5H, ArH), 6.26 (d, ^3J = 9.1 Hz, 1H, NH), 5.76 (s, 2H, NH_2), 4.87 (d, ^3J = 7.6 Hz, 1H, $CHSO_2$), 4.47 (ddt, ^3J = 9.1, ^3J = 7.6, ^3J = 5.1 Hz, 1H, CHN), 3.50 (d, ^3J = 5.1 Hz, 2H, CH_2N_3), 2.20 (s, 3H, CH_3); ^1H NMR of the minor diastereomer (300.13 MHz, DMSO-d_6) δ 7.60−7.90 (m, 5H, ArH), 6.26 (d, ^3J = 8.6 Hz, 1H, NH), 5.64 (s, 2H, NH_2), 4.99 (d, ^3J = 7.7 Hz, 1H, $CHSO_2$), 4.23 (dddd, ^3J = 8.6, ^3J = 7.7, ^3J = 7.2, ^3J = 4.5 Hz, 1H, CHN), 3.44 (dd, ^2J = 12.8, ^3J = 7.2 Hz, 1H, CH_AN_3), 3.38 (dd, ^2J = 12.8, ^3J = 4.5 Hz, 1H, CH_BN_3), 2.27 (s, 3H, CH_3); ^{13}C NMR of the major diastereomer (75.48 MHz, DMSO-d_6) δ 199.5 (C═O), 157.29 (CONH), 137.6 (C), 134.7 (CH), 129.5 (2CH), 128.67 (2CH), 73.9 ($CHSO_2$), 53.5 (CH_2N_3), 48.2 (CHN), 31.6 (CH_3); ^{13}C NMR of the minor diastereomer (75.48 MHz, DMSO-d_6) δ 199.5 (C═O), 157.34 (CONH), 138.3 (C), 134.4 (CH), 129.3 (2CH), 128.64 (2CH), 74.2 ($CHSO_2$), 52.4 (CH_2N_3), 48.8 (CHN), 32.7 (CH_3). Anal. Calcd for $C_{12}H_{15}N_5O_4S$: C, 44.30; H, 4.65; N, 21.53. Found: C, 44.10; H, 4.68; N, 21.62.

6-(Azidomethyl)-4-hydroxy-4-methyl-5-tosylhexahydropyrimidin-2-one (13b). Compound **13b** (2.720 g, 84%) as a mixture of (4*R**,5*R**,6*R**)- and (4*R**,5*S**,6*S**)-diastereomers (90:10) was prepared from tosylacetone (**11b**) (2.051 g, 9.66 mmol), NaH (0.230 g, 9.57 mmol), and sulfone **6a** (2.699 g, 9.53 mmol) in dry MeCN (19 mL) (8 h, rt) as described for **12a**. After crystallization from EtOH, the major isomer was obtained. Mp 119.5−120 °C (decomp, EtOH); IR of the major isomer (Nujol) ν_{max} 3324 (s), 3298 (s), 3246 (m) (NH, OH), 3100 (w), 3060 (w), 3033 (w) (CH_{arom}), 2110 (s) (N_3), 1703 (s), 1656 (s) (amide-I), 1598 (m) (CC_{arom}), 1491 (s) (amide-II), 1301 (s), 1156 (s) (SO_2), 813 (m) (CH_{arom}) cm^{-1}; ^1H NMR of the major isomer (300.13 MHz, DMSO-d_6) δ 7.76−7.81 (m, 2H, ArH), 7.40−7.45 (m, 2H, ArH), 7.02 (d, ^4J = 2.1 Hz, 1H, $N_{(3)}H$), 6.69 (dd, ^4J = 2.1, ^3J = 1.0 Hz, 1H, $N_{(1)}H$), 5.98 (d, ^4J = 1.3 Hz, 1H, OH), 3.77 (dddd, ^3J = 9.7, ^3J = 3.3, ^3J = 2.6, ^3J = 1.0 Hz, 1H, H-6), 3.62 (dd, ^2J = 13.0, ^3J = 2.6 Hz, 1H, CH_AN_3), 3.57 (dd, ^2J = 13.0, ^3J = 3.3 Hz, 1H, CH_BN_3), 3.53 (dd, ^3J = 9.7, ^4J = 1.3 Hz, 1H, H-5), 2.40 (s, 3H, CH_3 in Ts), 1.66 (s, 3H, 4-CH_3); ^1H NMR of the minor isomer (300.13 MHz, DMSO-d_6) δ 7.74−7.81 (m, 2H, ArH), 7.42−7.50 (m, 2H, ArH), 7.18 (dd, ^4J = 1.8, ^4J = 0.8 Hz, 1H, $N_{(3)}H$), 6.74 (dd, ^3J = 4.6, ^4J = 1.8 Hz, 1H, $N_{(1)}H$), 5.99 (s, 1H, OH), 3.74 (ddt, ^3J = 7.2, ^3J = 4.6, ^3J = 0.8 Hz, 1H, H-6), 3.63 (unresolved m, half-height width =2.7 Hz, 1H, H-5), 3.56 (d, ^3J = 7.2 Hz, 2H, CH_2N_3), 2.41 (s, 3H, CH_3 in Ts), 1.57 (s, 3H, 4-CH_3); ^{13}C NMR of the major isomer (75.48 MHz, DMSO-d_6) δ 154.2 (C-2), 144.4 (C), 136.7 (C), 129.4 (2CH), 129.1 (2CH), 79.4 (C-4), 67.0 (C-5), 53.1 (CH_2N_3), 49.0 (C-6), 27.9 (4-CH_3), 21.0 (CH_3 in Ts). ^{13}C NMR of the minor isomer (75.48 MHz, DMSO-d_6) δ 153.0 (C-2), 144.5 (C), 135.8 (C), 129.8 (2CH), 128.2 (2CH), 79.1 (C-4), 64.0 (C-5), 55.6 (CH_2N_3), 49.3 (C-6), 28.2 (4-CH_3), 21.1 (CH_3 in Ts). Anal. Calcd for $C_{13}H_{17}N_5O_4S$: C, 46.01; H, 5.05; N, 20.64. Found: C, 46.07; H, 5.27; N, 20.41.

***N*-[(1-Azido-4-oxo-3-tosyl)pent-2-yl]-*N*′-methylurea (12c).** Compound **12c** (1.020 g, 84%) as a mixture of two diastereomers (63:37) was prepared from tosylacetone (**11b**) (0.738 g, 3.48 mmol),

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NaH (0.082 g, 3.43 mmol), and sulfone **6b** (1.020 g, 3.43 mmol) in dry MeCN (12 mL) (8 h, rt) as described for **12a**. After two crystallizations from EtOAc/petroleum ether (1:1) the diastereomeric ratio did not change. Mp 119−119.5 °C (decomp, EtOAc/petroleum ether, 1:1); IR (Nujol) ν_{max} 3403 (s), 3342 (br s), ∼3301 (sh) (NH), 2113 (s), 2093 (s) (N_3), 1717 (s) (C═O), 1667 (s), 1639 (s) (amide-I), 1595 (w) (CC_{arom}), 1562 (s) (amide-II), 1508 (m) (CC_{arom}), 1319 (s), 1144 (s) (SO_2), 817 (m) (CH_{arom}) cm^{-1}; ^1H NMR of the major diastereomer (300.13 MHz, DMSO-d_6) δ 7.70−7.75 (m, 2H, ArH), 7.44−7.49 (m, 2H, ArH), 6.18 (d, ^3J = 9.2 Hz, 1H, NH), 6.08 (q, ^3J = 4.6 Hz, 1H, NH), 4.82 (d, ^3J = 7.4 Hz, 1H, $CHSO_2$), 4.48 (ddt, ^3J = 9.2, ^3J = 7.4, ^3J = 5.0 Hz, 1H, CHN), 3.49 (d, ^3J = 5.0 Hz, 2H, CH_2N_3), 2.50 (d, ^3J = 4.6 Hz, 3H, NCH_3), 2.42 (s, 3H, CH_3 in Ts), 2.20 (s, 3H, CH_3 in Ac); ^1H NMR of the minor diastereomer (300.13 MHz, DMSO-d_6) δ 7.68−7.73 (m, 2H, ArH), 7.41−7.46 (m, 2H, ArH), 6.21 (d, ^3J = 8.5 Hz, 1H, NH), 5.82 (q, ^3J = 4.7 Hz, 1H, NH), 4.99 (d, ^3J = 7.9 Hz, 1H, $CHSO_2$), 4.19 (dddd, ^3J = 8.5, ^3J = 7.9, ^3J = 7.7, ^3J = 4.1 Hz, 1H, CHN), 3.45 (dd, ^2J = 12.7, ^3J = 7.7 Hz, 1H, H_A in CH_2N_3), 3.34 (dd, ^2J = 12.7, ^3J = 4.1 Hz, 1H, H_B in CH_2N_3), 2.44 (d, ^3J = 4.7 Hz, 3H, NCH_3), 2.42 (s, 3H, CH_3 in Ts), 2.28 (s, 3H, CH_3 in Ac); ^{13}C NMR of the major diastereomer (75.48 MHz, DMSO-d_6) δ 199.7 (C═O), 157.1 (CONH), 145.4 (C), 134.7 (C), 129.9 (2CH), 128.72 (2CH), 73.9 ($CHSO_2$), 53.5 (CH_2N_3), 48.4 (CHN), 31.7 (CH_3 in Ac), 26.21 (NCH_3), 21.12 (CH_3 in Ts); ^{13}C NMR of the minor diastereomer (75.48 MHz, DMSO-d_6) δ 199.6 (C═O), 157.1 (CONH), 144.9 (C), 135.5 (C), 129.6 (2CH), 128.66 (2CH), 74.2 ($CHSO_2$), 52.2 (CH_2N_3), 49.1 (CHN), 32.8 (CH_3 in Ac), 26.14 (NCH_3), 21.11 (CH_3 in Ts). Anal. Calcd for $C_{14}H_{19}N_5O_4S$: C, 47.58; H, 5.42; N, 19.82. Found: C, 47.55; H, 5.57; N, 19.87.

***N*-[(2-Azido-5-oxo-4-tosyl)hex-3-yl]urea (12d).** Compound **12d** (1.178 g, 61%) as a mixture of four diastereomers (62:20:14:4) was prepared from tosylacetone (**11b**) (1.182 g, 5.57 mmol), NaH (0.132 g, 5.49 mmol), and sulfone **6c** (1.632 g, 5.49 mmol) in dry THF (17 mL) (8 h, rt) as described for **12a**. After crystallization from EtOH the diastereomeric ratio changed to 71:23:4:2. Mp 107−110.5 °C (decomp, EtOH); IR (Nujol) ν_{max} 3483 (s), 3379 (br s), 3330 (br s), 3204 (m) (NH), 3055 (w) (CH_{arom}), 2125 (vs), 2092 (s) (N_3), 1720 (s) (C═O), 1677 (s), 1664 (s) (amide-I), 1607 (m), 1597 (m) (CC_{arom}), 1544 (s) (amide-II), 1493 (w) (CC_{arom}), 1320 (s), 1143 (s) (SO_2), 817 (m) (CH_{arom}) cm^{-1}; ^1H NMR of the major diastereomer (300.13 MHz, DMSO-d_6) δ 7.73−7.78 (m, 2H, ArH), 7.43−7.49 (m, 2H, ArH), 6.10 (d, ^3J = 9.8 Hz, 1H, NH), 5.73 (s, 2H, NH_2), 4.67 (d, ^3J = 7.8 Hz, 1H, $CHSO_2$), 4.50 (ddd, ^3J = 9.8, ^3J = 7.8, ^3J = 2.3 Hz, 1H, CHN), 3.99 (dq, ^3J = 6.5, ^3J = 2.3 Hz, 1H, CHN_3), 2.42 (s, 3H, CH_3 in Ts), 2.19 (s, 3H, CH_3 in Ac), 1.14 (d, ^3J = 6.5 Hz, 3H, CH_3); ^1H NMR of the first minor diastereomer (20%) (300.13 MHz, DMSO-d_6) δ 7.66−7.72 (m, 2H, ArH), 7.38−7.43 (m, 2H, ArH), 5.92 (d, ^3J = 10.0 Hz, 1H, NH), 5.59 (s, 2H, NH_2), 4.70 (d, ^3J = 9.7 Hz, 1H, $CHSO_2$), 4.35 (ddd, ^3J = 10.0, ^3J = 9.7, ^3J = 2.5 Hz, 1H, CHN), 3.59 (dq, ^3J = 6.5, ^3J = 2.5 Hz, 1H, CHN_3), 2.41 (s, 3H, CH_3 in Ts), 2.35 (s, 3H, CH_3 in Ac), 1.11 (d, ^3J = 6.5 Hz, 3H, CH_3); ^1H NMR of the second minor diastereomer (14%) (300.13 MHz, DMSO-d_6) δ 6.21 (d, ^3J = 9.4 Hz, 1H, NH), 5.77 (s, 2H, NH_2), 4.80 (d, ^3J = 5.8 Hz, 1H, $CHSO_2$), 4.43 (ddd, ^3J = 9.4, ^3J = 5.8, ^3J = 5.0 Hz, 1H, CHN), 3.65 (dq, ^3J = 6.5, ^3J = 5.0 Hz, 1H, CHN_3), 2.29 (s, 3H, CH_3 in Ac), signals of other protons overlap with proton signals of the other isomers; ^1H NMR of the third minor diastereomer (4%) (300.13 MHz, DMSO-d_6) δ 5.65 (s, 2H, NH_2), 4.93 (d, ^3J = 8.8 Hz, 1H, $CHSO_2$), 2.28 (s, 3H, CH_3 in Ac), signals of other protons overlap with proton signals of the other isomers; ^{13}C NMR of the major diastereomer (75.48 MHz, DMSO-d_6) δ 199.3 (C═O), 157.7 (CONH), 145.4 (C), 134.8 (C), 129.9 (2CH), 128.7 (2CH), 74.6 ($CHSO_2$), 59.31 (CHN_3), 51.2 (CHNH), 31.3 (CH_3 in Ac), 21.1 (CH_3 in Ts), 15.6 (CH_3); ^{13}C NMR of the first minor diastereomer (20%) (75.48 MHz, DMSO-d_6) δ 200.1 (C═O), 157.6 (CONH), 144.7 (C), 135.5 (C), 129.5 (2CH), 128.9 (2CH), 75.2 ($CHSO_2$), 58.4 (CHN_3), 51.2 (CHNH), 32.7 (CH_3 in Ac), 21.1 (CH_3 in Ts), 15.2 (CH_3); ^{13}C NMR of the second minor diastereomer (14%) (75.48 MHz, DMSO-d_6) δ 200.4 (C═O), 157.4 (CONH), 145.3 (C), 134.6 (C), 129.8 (2CH), 128.8 (2CH), 72.1 ($CHSO_2$), 59.25 (CHN_3), 51.9 (CHNH), 32.3 (CH_3 in Ac), 21.1 (CH_3 in Ts), 14.3 (CH_3). Anal. Calcd for $C_{14}H_{19}N_5O_4S$: C, 47.58; H, 5.42; N, 19.82. Found: C, 47.35; H, 5.52; N, 19.45.

Analogously, compound **12d** was prepared in MeCN as a mixture of four diastereomers (62:21:13:4) in 60% yield. In this case vigorous foaming occurred during evaporation of the solvent from the reaction mixture formed after completion of the reaction making the workup difficult.

***N*-[(5-Azido-2-oxo-3-tosyl)hept-4-yl]urea (12e).** Compound **12e** (1.400 g, 71%) as a mixture of four diastereomers (69:19:9:3) was prepared from tosylacetone (**11b**) (1.154 g, 5.43 mmol), NaH (0.129 g, 5.38 mmol), and sulfone **6d** (1.673 g, 5.37 mmol) in dry MeCN (17 mL) (8 h, rt) as described for **12a**. After crystallization from EtOH the diastereomeric ratio changed to 78:21:1:0. Mp 131.5−132 °C (decomp, EtOH); IR (Nujol) ν_{max} 3468 (s), 3378 (m), 3357 (br s), 3215 (br m), 3203 (sh) (NH), 3062 (w), 3049 (w) (CH_{arom}), 2111 (br vs) (N_3), 1716 (s) (C═O), 1665 (vs) (amide-I), 1613 (m), 1597 (m) (CC_{arom}), 1541 (vs) (amide-II), 1495 (w) (CC_{arom}), 1320 (s), 1144 (s) (SO_2), 818 (m) (CH_{arom}) cm^{-1}; ^1H NMR of the major diastereomer (300.13 MHz, DMSO-d_6) δ 7.74−7.79 (m, 2H, ArH), 7.44−7.50 (m, 2H, ArH), 6.08 (d, ^3J = 9.6 Hz, 1H, NH), 5.70 (s, 2H, NH_2), 4.69 (d, ^3J = 8.3 Hz, 1H, $CHSO_2$), 4.62 (ddd, ^3J = 9.6, ^3J = 8.3, ^3J = 1.8 Hz, 1H, CHN), 3.71 (dt, ^3J = 7.0, ^3J = 1.8 Hz, 1H, CHN_3), 2.42 (s, 3H, CH_3 in Ts), 2.18 (s, 3H, CH_3 in Ac), 1.39−1.62 (m, 2H, CH_2, signals overlap with signals of the CH_2 protons of the minor isomer), 0.94 (t, ^3J = 7.3 Hz, 3H, CH_3); ^1H NMR of the first minor diastereomer (19%) (300.13 MHz, DMSO-d_6) δ 7.69−7.74 (m, 2H, ArH), 7.38−7.44 (m, 2H, ArH), 5.90 (d, ^3J = 9.9 Hz, 1H, NH), 5.58 (s, 2H, NH_2), 4.76 (d, ^3J = 9.2 Hz, 1H, $CHSO_2$), 4.48 (ddd, ^3J = 9.9, ^3J = 9.2, ^3J = 2.1 Hz, 1H, CHN), 3.28−3.35 (m, 1H, CHN_3, signals overlap with HOD signal), 2.41 (s, 3H, CH_3 in Ts), 2.34 (s, 3H, CH_3 in Ac), 1.39−1.62 (m, 2H, CH_2, signals overlap with signals of the CH_2 protons of the major isomer), 0.89 (t, ^3J = 7.4 Hz, 3H, CH_3); ^1H NMR of the second minor diastereomer (9%) (300.13 MHz, DMSO-d_6) δ 6.22 (d, ^3J = 9.2 Hz, 1H, NH), 5.79 (s, 2H, NH_2), 4.81 (d, ^3J = 5.2 Hz, 1H, $CHSO_2$), 2.31 (s, 3H, CH_3 in Ac), 0.83 (t, ^3J = 7.4 Hz, 3H, CH_3), signals of other protons overlap with proton signals of the other isomers; ^1H NMR of the third minor diastereomer (3%) (300.13 MHz, DMSO-d_6) δ 5.65 (s, 2H, NH_2), 5.01 (d, ^3J = 8.6 Hz, 1H, $CHSO_2$), 2.25 (s, 3H, CH_3 in Ac), signals of other protons overlap with proton signals of the other isomers; ^{13}C NMR of the major diastereomer (75.48 MHz, DMSO-d_6) δ 199.2 (C═O), 157.5 (CONH), 145.4 (C), 134.8 (C), 129.9 (2CH), 128.7 (2CH), 74.8 ($CHSO_2$), 65.8 (CHN_3), 49.4 (CHNH), 31.2 (CH_3 in Ac), 23.8 (CH_2), 21.1 (CH_3 in Ts), 10.4 (CH_3); ^{13}C NMR of the first minor diastereomer (19%) (75.48 MHz, DMSO-d_6) δ 200.2 (C═O), 157.4 (CONH), 144.7 (C), 135.7 (C), 129.5 (2CH), 128.8 (2CH), 75.4 ($CHSO_2$), 64.9 (CHN_3), 49.7 (CHNH), 32.7 (CH_3 in Ac), 23.5 (CH_2), 21.1 (CH_3 in Ts), 10.3 (CH_3). Anal. Calcd for $C_{15}H_{21}N_5O_4S$: C, 49.03; H, 5.76; N, 19.06. Found: C, 48.80; H, 5.92; N, 18.90.

***N*-[(1-Azido-4-oxo-4-phenyl-3-phenylsulfonyl)but-2-yl]urea (12f).** To a mixture of phenylsulfonylacetophenone (**11c**) (2.084 g, 8.00 mmol) and NaH (0.189 g, 7.89 mmol) was added dry THF (22 mL), the mixture was stirred at room temperature for 13 min, and to the resulting dense suspension were added sulfone **6a** (2.222 g, 7.84 mmol) and THF (3 mL). The suspension was stirred at room temperature for 8 h, and solvent was removed in a vacuum. To a solid residue was added saturated aq $NaHCO_3$ (10 mL), the obtained mixture was triturated until complete crystallization, and the resulting suspension was left overnight at room temperature and cooled to 0 °C. The precipitate was filtered and washed with ice-cold water and petroleum ether. The obtained slightly yellow solid was dried in a vacuum desiccator (over P_2O_5) on the filter, cooled (−10 °C), washed with cold (−10 °C) diethyl ether (3 × 10 mL), and dried to give **12f** (2.787 g, 92%) as a mixture of two diastereomers (55:45). After crystallization from EtOH the diastereomeric ratio did not change. Mp 149.5 °C (decomp, EtOH); IR (Nujol) ν_{max} 3448 (m), 3427 (m), 3363 (s), 3225 (br m) (NH), 3066 (w) (CH_{arom}), 2188 (w), 2160 (w), 2099 (vs) (N_3), 1672 (vs), 1663 (sh) (C═O and amide-I), 1609 (w), 1595 (m), 1583 (w) (CC_{arom}), 1541 (br s), 1521 (sh) (amide-II), 1301 (s), 1144 (s) (SO_2), 750 (m), 739 (s), 682 (s) (CH_{arom}) cm^{-1};

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^{1}H NMR of the major diastereomer (300.13 MHz, DMSO-d_6) δ 7.43−7.94 (m, 10H, ArH), 6.35 (d, ^3J = 8.6 Hz, 1H, NH), 5.94 (d, ^3J = 6.0 Hz, 1H, $CHSO_2$), 5.78 (s, 2H, NH_2), 4.62 (dddd, ^3J = 8.6, ^3J = 6.0, ^3J = 6.0, ^3J = 4.5 Hz, 1H, CHN), 3.58 (dd, ^2J = 12.6, ^3J = 6.0 Hz, 1H, CH_AN_3), 3.54 (dd, ^2J = 12.6, ^3J = 4.5 Hz, 1H, CH_BN_3); ^{1}H NMR of the minor diastereomer (300.13 MHz, DMSO-d_6) δ 7.43−7.94 (m, 10H, ArH), 6.32 (d, ^3J = 8.3 Hz, 1H, NH), 5.93 (d, ^3J = 8.2 Hz, 1H, $CHSO_2$), 5.73 (s, 2H, NH_2), 4.42 (dddd, ^3J = 8.3, ^3J = 8.2, ^3J = 6.6, ^3J = 4.5 Hz, 1H, CHN), 3.46 (dd, ^2J = 12.9, ^3J = 4.5 Hz, 1H, CH_AN_3), 3.42 (dd, ^2J = 12.9, ^3J = 6.6 Hz, 1H, CH_BN_3); ^{13}C NMR of the major diastereomer (75.48 MHz, DMSO-d_6) δ 192.3 (C═O in Bz), 157.5 (CONH), 137.5 (C), 136.74 (C), 134.51 (CH), 134.2 (CH), 129.20 (2CH), 129.1 (2CH), 128.8 (2CH), 128.75 (2CH), 67.8 ($CHSO_2$), 53.5 (CH_2N_3), 49.5 (CHN); ^{13}C NMR of the minor diastereomer (75.48 MHz, DMSO-d_6) δ 191.7 (C═O in Bz), 157.5 (CONH), 138.0 (C), 136.70 (C), 134.45 (CH), 134.4 (CH), 129.23 (2CH), 129.0 (4CH), 128.76 (2CH), 69.0 ($CHSO_2$), 52.5 (CH_2N_3), 49.8 (CHN). Anal. Calcd for $C_{17}H_{17}N_5O_4S$: C 52.71; H, 4.42; N, 18.08. Found: C, 52.54; H, 4.55; N, 17.98.

***N*-[(1-Azido-4-oxo-4-phenyl-3-tosyl)but-2-yl]urea (12g).** Compound **12g** (2.437 g, 96%) as a mixture of two diastereomers (60:40) was prepared from tosylacetophenone (**11d**) (1.767 g, 6.44 mmol), NaH (0.153 g, 6.38 mmol), and sulfone **6a** (1.790 g, 6.31 mmol) in dry THF (25 mL) (8 h, rt) as described for **12f**. After crystallization from MeCN the diastereomeric ratio did not change. Mp 172 °C (decomp, MeCN); IR (Nujol) ν_{max} 3446 (s), 3369 (s), 3348 (sh), 3211 (br m) (NH), 3062 (w) (CH_{arom}), 2193 (w), 2166 (w), 2099 (s) (N_3), 1670 (s) (C═O), 1641 (s) (amide-I), 1608 (m), 1598 (m) (CC_{arom}), 1541 (s) (amide-II), 1296 (m), 1143 (s) (SO_2), 821 (m), 742 (s), 688 (m) (CH_{arom}) cm^{-1}; ^{1}H NMR of the major diastereomer (300.13 MHz, DMSO-d_6) δ 7.31−7.93 (m, 9H, ArH), 6.33 (d, ^3J = 8.7 Hz, 1H, NH), 5.88 (d, ^3J = 6.2 Hz, 1H, $CHSO_2$), 5.77 (s, 2H, NH_2), 4.56 (dddd, ^3J = 8.7, ^3J = 6.2, ^3J = 5.9, ^3J = 4.5 Hz, 1H, CHN), 3.57 (dd, ^2J = 12.6, ^3J = 5.9 Hz, 1H, CH_AN_3), 3.53 (dd, ^2J = 12.6, ^3J = 4.5 Hz, 1H, CH_BN_3), 2.34 (s, 3H, CH_3); ^{1}H NMR of the minor diastereomer (300.13 MHz, DMSO-d_6) δ 7.31−7.93 (m, 9H, ArH), 6.32 (d, ^3J = 8.4 Hz, 1H, NH), 5.88 (d, ^3J = 8.2 Hz, 1H, $CHSO_2$), 5.74 (s, 2H, NH_2), 4.37 (dddd, ^3J = 8.4, ^3J = 8.2, ^3J = 6.6, ^3J = 4.3 Hz, 1H, CHN), 3.45 (dd, ^2J = 12.8, ^3J = 4.3 Hz, 1H, CH_AN_3), 3.40 (dd, ^2J = 12.8, ^3J = 6.6 Hz, 1H, CH_BN_3), 2.36 (s, 3H, CH_3); ^{13}C NMR of the major diastereomer (75.48 MHz, DMSO-d_6) δ 192.2 (C═O in Bz), 157.38 (CONH), 145.1 (C), 136.81 (C), 134.6 (C), 134.0 (CH), 129.57 (2CH), 129.1 (2CH), 128.8 (2CH), 128.6 (2CH), 68.0 ($CHSO_2$), 53.4 (CH_2N_3), 49.5 (CHN), 21.05 (CH_3); ^{13}C NMR of the minor diastereomer (75.48 MHz, DMSO-d_6) δ 191.7 (C═O in Bz), 157.41 (CONH), 145.0 (C), 136.76 (C), 135.0 (C), 134.2 (CH), 129.60 (2CH), 129.0 (2CH), 128.9 (2CH), 128.7 (2CH), 69.1 ($CHSO_2$), 52.5 (CH_2N_3), 49.7 (CHN), 21.08 (CH_3). Anal. Calcd for $C_{18}H_{19}N_5O_4S$: C, 53.86; H, 4.77; N, 17.45. Found: C, 53.67; H, 4.87; N, 17.42.

***N*-[(4-Azido-1-oxo-1-phenyl-2-tosyl)pent-3-yl]urea (12h).** Compound **12h** (1.294 g, 93%) as a mixture of four diastereomers (33:25:28:14) was prepared from tosylacetophenone (**11d**) (0.928 g, 3.38 mmol), NaH (0.080 g, 3.35 mmol), and sulfone **6c** (0.995 g, 3.35 mmol) in dry THF (15 mL) (8 h, rt) as described for **12f**. Analogously, compound **12h** was prepared in MeCN as a mixture of four diastereomers (35:32:20:13) in 86% yield. After crystallization from EtOH the diastereomeric ratio changed to 34:35:22:9. Mp 158−158.5 °C (decomp, EtOH); IR (Nujol) ν_{max} 3449 (br s), 3379 (br s), 3320 (m), 3187 (br s) (NH), 3088 (w) (CH_{arom}), 2113 (br vs) (N_3), 1688 (vs), 1673 (br vs), 1663 (sh) (C═O and amide-I), 1595 (m), 1580 (w) (CC_{arom}), 1529 (s), 1519 (s) (amide-II), 1320 (s), 1150 (s) (SO_2), 817 (m), 755 (s), 685 (m) (CH_{arom}) cm^{-1}; ^{1}H NMR of the major diastereomer (300.13 MHz, DMSO-d_6) δ 7.31−8.02 (m, 9H, ArH, signals overlap with signals of the aromatic protons of other isomers), 6.30 (d, ^3J = 9.2 Hz, 1H, NH), 5.80 (s, 2H, NH_2), 5.72 (d, ^3J = 4.7 Hz, 1H, $CHSO_2$, signals overlap with signals of the CHN proton of the first minor isomer), 4.57 (ddd, ^3J = 9.2, ^3J = 5.7, ^3J = 4.7 Hz, 1H, CHN), 3.58 (dq, ^3J = 6.7, ^3J = 5.7 Hz, 1H, CHN_3), 2.36 (s, 3H, CH_3 in Ts), 1.17 (d, ^3J = 6.7 Hz, 3H, CH_3); ^{1}H NMR of the first minor diastereomer (32%) (300.13 MHz, DMSO-d_6) δ 7.31−8.02 (m, 9H, ArH, signals overlap with signals of the aromatic protons of other isomers), 6.09 (d, ^3J = 9.5 Hz, 1H, NH), 5.74 (s, 2H, NH_2), 5.72 (d, ^3J = 5.2 Hz, 1H, $CHSO_2$), 4.69 (ddd, ^3J = 9.5, ^3J = 5.2, ^3J = 2.4 Hz, 1H, CHN), 4.04 (dq, ^3J = 6.5, ^3J = 2.4 Hz, 1H, CHN_3), 2.36 (s, 3H, CH_3 in Ts), 1.13 (d, ^3J = 6.5 Hz, 3H, CH_3); ^{1}H NMR of the second minor diastereomer (20%) (300.13 MHz, DMSO-d_6) δ 7.31−8.02 (m, 9H, ArH, signals overlap with signals of the aromatic protons of other isomers), 6.09 (d, ^3J = 9.5 Hz, 1H, NH), 5.68 (s, 2H, NH_2), 5.60 (d, ^3J = 9.7 Hz, 1H, $CHSO_2$), 4.53 (ddd, ^3J = 9.7, ^3J = 9.5, ^3J = 2.4 Hz, 1H, CHN), 3.50 (dq, ^3J = 6.4, ^3J = 2.4 Hz, 1H, CHN_3), 2.38 (s, 3H, CH_3 in Ts), 1.10 (d, ^3J = 6.4 Hz, 3H, CH_3); ^{1}H NMR of the third minor diastereomer (13%) (300.13 MHz, DMSO-d_6) δ 5.84 (d, ^3J = 9.3 Hz, 1H, $CHSO_2$), 5.76 (s, 2H, NH_2), 1.07 (d, ^3J = 6.6 Hz, 3H, CH_3), signals of other protons overlap with signals of analogous protons of other isomers; ^{13}C NMR of the diastereomeric mixture (34:35:22:9) (75.48 MHz, DMSO-d_6) (shown only the nonaromatic carbon signals) δ 199.7, 192.21, 192.20, 190.8 (C═O), 157.8, 157.7, 157.4 (CONH), 70.3, 69.4, 68.1, 66.3 ($CHSO_2$), 60.0, 59.6, 58.8, 58.5 (CHN_3), 53.1, 52.9, 52.5, 52.3 (CHNH), 21.10, 21.08, 21.07 (CH_3 in Ts), 15.7, 15.22, 15.21, 15.1 (CH_3). Anal. Calcd for $C_{19}H_{21}N_5O_4S$: C, 54.93; H, 5.09; N, 16.86. Found: C, 54.80; H, 5.21; N, 16.65.

***N*-[(4-Azido-1-oxo-1-phenyl-2-tosyl)hex-3-yl]urea (12i).** Compound **12i** (2.581 g, 98%) as a mixture of four diastereomers (46:26:20:8) was prepared from tosylacetophenone (**11d**) (1.699 g, 6.19 mmol), NaH (0.147 g, 6.14 mmol), and sulfone **6d** (1.909 g, 6.13 mmol) in dry MeCN (20 mL) (8 h, rt) as described for **12f**. No washings of the crude product with diethyl ether were carried out (after addition of diethyl ether to the dried solid, it partially dissolved and turned into an oily substance). After crystallization from MeCN the diastereomeric ratio changed to 57:43:0:0, respectively. Mp 100−105 °C (MeCN); IR (Nujol) ν_{max} 3449 (s), 3399 (m), 3384 (m), 3313 (m), 3234 (m), 3201 (br s) (NH), 3043 (w), 3025 (w) (CH_{arom}), 2099 (s) (N_3), 1672 (vs) (C═O and amide-I), 1619 (m), 1596 (m), 1580 (w) (CC_{arom}), 1524 (s) (amide-II), 1494 (w) (CC_{arom}), 1333 (s), 1154 (s) (SO_2), 811 (m), 750 (s), 688 (m) (CH_{arom}) cm^{-1}; ^{1}H NMR of the major diastereomer (300.13 MHz, DMSO-d_6) δ 7.90−7.96 (m, 2H, ArH), 7.46−7.75 (m, 5H, ArH, signals overlap with signals of analogous protons of other isomers), 7.31−7.40 (m, 2H, ArH, signals overlap with signals of analogous protons of other isomers), 6.04 (d, ^3J = 9.5 Hz, 1H, NH), 5.73 (d, ^3J = 5.5 Hz, 1H, $CHSO_2$), 5.69 (s, 2H, NH_2), 4.80 (ddd, ^3J = 9.5, ^3J = 5.5, ^3J = 2.0 Hz, 1H, CHN), 3.78 (dt, ^3J = 7.0, ^3J = 2.0 Hz, 1H, CHN_3), 2.35 (s, 3H, CH_3 in Ts), 1.43−1.57 (m, 2H, CH_2, signals overlap with signals of analogous protons of other isomers), 0.93 (t, ^3J = 7.3 Hz, 3H, CH_3); ^{1}H NMR of the first minor diastereomer (26%) (300.13 MHz, DMSO-d_6) δ 7.96−8.03 (m, 2H, ArH), 7.46−7.75 (m, 5H, ArH, signals overlap with signals of analogous protons of other isomers), 7.31−7.40 (m, 2H, ArH, signals overlap with signals of analogous protons of other isomers), 6.04 (d, ^3J = 9.7 Hz, 1H, NH), 5.66 (d, ^3J = 9.2 Hz, 1H, $CHSO_2$), 5.66 (s, 2H, NH_2), 4.67 (ddd, ^3J = 9.7, ^3J = 9.2, ^3J = 2.0 Hz, 1H, CHN), 3.20 (dt, ^3J = 6.9, ^3J = 2.0 Hz, 1H, CHN_3), 2.38 (s, 3H, CH_3 in Ts), 1.43−1.57 (m, 2H, CH_2, signals overlap with signals of analogous protons of other isomers), 0.86 (t, ^3J = 7.3 Hz, 3H, CH_3); ^{1}H NMR of the second minor diastereomer (20%) (300.13 MHz, DMSO-d_6) δ 6.37 (d, ^3J = 9.0 Hz, 1H, NH), 5.85 (s, 2H, NH_2), 4.65 (ddd, ^3J = 9.0, ^3J = 5.4, ^3J = 4.3 Hz, 1H, CHN), 3.30−3.38 (m, 1H, CHN_3, signals overlap with HOD signal), 2.36 (s, 3H, CH_3 in Ts), 0.87 (t, ^3J = 7.3 Hz, 3H, CH_3), signals of other protons overlap with signals of analogous protons of other isomers; ^{1}H NMR of the third minor diastereomer (8%) (300.13 MHz, DMSO-d_6) δ 6.12 (d, ^3J = 9.6 Hz, 1H, NH), 5.75 (s, 2H, NH_2), 5.91 (d, ^3J = 9.1 Hz, 1H, $CHSO_2$), 4.49 (ddd, ^3J = 9.6, ^3J = 9.1, ^3J = 7.9 Hz, 1H, CHN), 2.40 (s, 3H, CH_3 in Ts), 0.79 (t, ^3J = 7.4 Hz, 3H, CH_3), signals of other protons overlap with signals of analogous protons of other isomers; ^{13}C NMR of the major diastereomer (75.48 MHz, DMSO-d_6) δ 199.1 (C═O), 157.57 (CONH), 145.0 (C), 137.1 (C), 134.6 (C), 133.7 (CH), 129.5 (2CH), 129.2 (2CH), 128.7 (2CH), 128.6 (2CH), 68.3 ($CHSO_2$), 66.5 (CHN_3), 51.1 (CHNH), 24.0 (CH_2), 21.06 (CH_3 in Ts), 10.5 (CH_3); ^{13}C NMR of the first minor diastereomer (26%) (75.48 MHz, DMSO-d_6) δ 199.3 (C═O),

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157.59 (CONH), 144.8 (C), 136.7 (C), 135.1 (C), 134.3 (CH), 129.4 (2CH), 129.2 (2CH), 128.9 (2CH), 128.8 (2CH), 70.5 ($CHSO_2$), 65.1 (CHN_3), 50.9 (CHNH), 23.6 (CH_2), 21.09 (CH_3 in Ts), 10.3 (CH_3). Anal. Calcd for $C_{20}H_{23}N_5O_4S$: C, 55.93; H, 5.40; N, 16.31. Found: C, 55.91; H, 5.50; N, 16.32.

***N*-[(1-Azido-4-oxo-4-phenyl-3-phenylthio)but-2-yl]urea (12j).** Compound **12j** (2.682 g, 66%) as a mixture of two diastereomers (52:48) was prepared from phenylthioacetophenone (**11e**) (2.619 g, 11.47 mmol), NaH (0.273 g, 11.38 mmol), and sulfone **6a** (3.218 g, 11.36 mmol) in dry THF (25 mL) (8 h, rt) as described for **12a**. After crystallization from EtOH the diastereomeric ratio did not change. Mp 114.5−115.5 °C (decomp, EtOH); IR (Nujol) ν_{max} 3441 (s), 3386 (m), 3363 (m), 3343 (m), 3203 (br s) (NH), 3073 (w), 3057 (w), 3025 (w) (CH_{arom}), 2161 (w), 2103 (vs) (N_3), 1664 (vs) (C═O and amide-I), 1605 (m), 1596 (m), 1579 (m) (CC_{arom}), 1528 (s) (amide-II), 755 (m), 740 (s), 690 (s) (CH_{arom}) cm^{-1}; ^1H NMR of the 52:48 diastereomeric mixture (300.13 MHz, DMSO-d_6) δ 7.25−7.93 (m, 10H, ArH in both isomers), 6.41 (d, ^3J = 8.6 Hz, 0.48H, NH in minor isomer), 6.39 (d, ^3J = 8.6 Hz, 0.52H, NH in major isomer), 5.75 (s, 0.96H, NH_2 in minor isomer), 5.61 (s, 1.04H, NH_2 in major isomer), 5.09 (d, ^3J = 8.4 Hz, 1H, CHS in both isomers), 4.18−4.29 (m, 1H, CHN in both isomers), 3.74 (dd, ^2J = 12.5, ^3J = 6.5 Hz, 0.52H, CH_AN_3 in major isomer), 3.68 (dd, ^2J = 12.5, ^3J = 4.3 Hz, 0.52H, CH_BN_3 in major isomer), 3.45 (dd, ^2J = 12.6, ^3J = 4.6 Hz, 0.48H, CH_AN_3 in minor isomer), 3.41 (dd, ^2J = 12.6, ^3J = 6.3 Hz, 0.48H, CH_BN_3 in minor isomer); ^{13}C NMR of the 52:48 diastereomeric mixture (75.48 MHz, DMSO-d_6) δ 194.6, 194.1 (C═O in Bz), 158.0, 157.8 (CONH), 135.8, 135.7 (C), 133.52, 133.49 (CH), 133.47 (2CH), 132.9 (2CH), 131.9, 131.5 (C), 129.3, 129.1, 128.8, 128.7, 128.5, 128.4, 128.2 (2CH), 53.1 (CHS), 53.0, 52.5 (CH_2N_3), 51.6 (CHS), 50.5, 49.9 (CHN). Anal. Calcd for $C_{17}H_{17}N_5O_2S$: C, 57.45; H, 4.82; N, 19.70. Found: C, 57.47; H, 4.97; N, 19.65.

***N*-[(1-Azido-4-oxo-4-phenyl-3-phenylthio)but-2-yl]-*N*′-methylurea (12k).** Compound **12k** (0.892 g, 73%) as a mixture of two diastereomers (72:28) was prepared from phenylthioacetophenone (**11e**) (0.770 g, 3.37 mmol), NaH (0.080 g, 3.32 mmol), and sulfone **6b** (0.985 g, 3.31 mmol) in dry THF (14 mL) (8 h, rt) as described for **12a**. Crystallization from EtOH afforded the pure major isomer. Mp 183.5−184 °C (decomp, EtOH); IR of the major isomer (Nujol) ν_{max} 3342 (br s), 3308 (br s) (NH), 3074 (w), 3056 (w) (CH_{arom}), 2106 (s) (N_3), 1662 (s) (amide-I), 1629 (s) (C═O), 1595 (w) (CC_{arom}), 1577 (br s) (amide-II), 1525 (w) (CC_{arom}), 751 (m), 689 (m) (CH_{arom}) cm^{-1}; ^1H NMR of the major diastereomer (300.13 MHz, DMSO-d_6) δ 7.84−7.89 (m, 2H, ArH), 7.61−7.68 (m, 1H, ArH), 7.48−7.55 (m, 2H, ArH), 7.26−7.39 (m, 5H, ArH), 6.35 (d, ^3J = 8.6 Hz, 1H, NH), 6.05 (q, ^3J = 4.7 Hz, 1H, NH), 5.11 (d, ^3J = 8.6 Hz, 1H, CHS), 4.26 (ddt, ^3J = 8.6, ^3J = 8.6, ^3J = 5.4 Hz, 1H, CHN), 3.43 (d, ^3J = 5.4 Hz, 2H, CH_2N_3), 2.60 (d, ^3J = 4.7 Hz, 3H, CH_3); ^1H NMR of the minor diastereomer (300.13 MHz, DMSO-d_6) δ 6.33 (d, ^3J = 8.4 Hz, 1H, NH), 5.91 (q, ^3J = 4.7 Hz, 1H, NH), 5.10 (d, ^3J = 8.2 Hz, 1H, CHS), 3.63−3.78 (m, 2H, CH_2N_3), 2.49 (d, ^3J = 4.7 Hz, 3H, CH_3), signals of other protons overlap with signals of analogous protons of the major diastereomer; ^{13}C NMR of the major diastereomer (75.48 MHz, DMSO-d_6) δ 194.2 (C═O), 158.0 (CONH), 135.7 (C), 133.5 (CH), 133.4 (2CH), 131.6 (C), 129.1 (2CH), 128.8 (2CH), 128.4 (CH), 128.2 (2CH), 53.0 ($CHSO_2$), 52.9 (CH_2N_3), 50.2 (CHN), 26.4 (NCH_3). Anal. Calcd for $C_{18}H_{19}N_5O_2S$: C, 58.52; H, 5.18; N, 18.96. Found: C, 58.46; H, 5.29; N, 18.98.

***N*-[(4-Azido-1-oxo-1-phenyl-2-phenylthio)pent-3-yl]urea (12l).** To a mixture of phenylthioacetophenone (**11e**) (1.257 g, 5.50 mmol) and NaH (0.130 g, 5.43 mmol) was added dry THF (15 mL), the mixture was stirred in an ice-cold bath for 15 min, and to the resulting solution were added sulfone **6c** (1.613 g, 5.42 mmol) and THF (5 mL). The suspension was stirred at room temperature for 8 h, and solvent was removed in a vacuum. The yellow oily residue was triturated with petroleum ether (3 × 15 mL), to the formed oil was added saturated aq $NaHCO_3$ (2.5 mL) and petroleum ether (15 mL), and the obtained mixture was left overnight at room temperature and cooled to 0 °C. The resulting oily material was transferred to the filter, triturated, washed with cold diethyl ether until crystallization was complete, washed with ice-cold water and petroleum ether, and dried to give **12l** (0.817 g, 41%) as a mixture of four diastereomers (39:29:20:12) (white solid). After crystallization from EtOH the diastereomeric ratio changed to 53:20:27:0, respectively. Mp 121.5−123 °C (decomp, EtOH)) (under slow heating; less than 1 °C/min) and 113−119 °C (decomp, EtOH) (under rapid heating; more than 1 °C/15 s); IR (Nujol) ν_{max} 3400 (br s), 3361 (m), 3204 (br s) (NH), 3020 (w) (CH_{arom}), 2118 (s), 2089 (s) (N_3), 1664 (br vs), 1626 (m) (C═O and amide-I), 1595 (w), 1578 (w) (CC_{arom}), 1538 (s) (amide-II), 752 (s), 742 (s), 690 (s) (CH_{arom}) cm^{-1}; ^1H NMR of the major diastereomer (300.13 MHz, DMSO-d_6) δ 7.23−7.93 (m, 10H, ArH, signals overlap with signals of the aromatic protons of other isomers), 6.29 (d, ^3J = 9.9 Hz, 1H, NH), 5.74 (s, 2H, NH_2), 5.10 (d, ^3J = 8.0 Hz, 1H, CHS), 4.33 (ddd, ^3J = 9.9, ^3J = 8.0, ^3J = 7.0 Hz, 1H, CHN), 3.49 (dq, ^3J = 7.0, ^3J = 6.6 Hz, 1H, CHN_3), 1.17 (d, ^3J = 6.6 Hz, 3H, CH_3); ^1H NMR of the first minor diastereomer (29%) (300.13 MHz, DMSO-d_6) δ 7.23−7.93 (m, 10H, ArH, signals overlap with signals of the aromatic protons of other isomers), 6.29 (d, ^3J = 9.9 Hz, 1H, NH), 5.75 (s, 2H, NH_2), 4.82 (d, ^3J = 10.3 Hz, 1H, CHS), 4.24 (ddd, ^3J = 10.3, ^3J = 9.9, ^3J = 2.5 Hz, 1H, CHN), 3.61 (dq, ^3J = 6.5, ^3J = 2.5 Hz, 1H, CHN_3), 1.21 (d, ^3J = 6.5 Hz, 3H, CH_3); ^1H NMR of the second minor diastereomer (20%); (300.13 MHz, DMSO-d_6) δ 7.23−7.93 (m, 10H, ArH, signals overlap with signals of the aromatic protons of other isomers), 6.18 (d, ^3J = 9.5 Hz, 1H, NH), 5.51 (s, 2H, NH_2), 4.83 (d, ^3J = 9.1 Hz, 1H, CHS), 4.38 (dq, ^3J = 6.6, ^3J = 2.4 Hz, 1H, CHN_3), 4.25 (ddd, ^3J = 9.5, ^3J = 9.1, ^3J = 2.4 Hz, 1H, CHN), 1.24 (d, ^3J = 6.6 Hz, 3H, CH_3); ^1H NMR of the third minor diastereomer (12%) (300.13 MHz, DMSO-d_6) δ 6.39 (d, ^3J = 10.1 Hz, 1H, NH), 5.72 (s, 2H, NH_2), 5.01 (d, ^3J = 6.4 Hz, 1H, CHS), 3.77 (dq, ^3J = 6.8, ^3J = 6.6 Hz, 1H, CHN_3), 1.25 (d, ^3J = 6.6 Hz, 3H, CH_3), signals of other protons overlap with signals of analogous protons of other isomers; ^{13}C NMR of the diastereomeric mixture (53:20:27) (75.48 MHz, DMSO-d_6) (shown only the nonaromatic carbon signals) δ 194.3, 193.7, 193.5 (C═O), 158.6, 158.0, 157.8 (CONH), 58.7, 58.6, 58.0 (CHN_3), 54.9, 54.3, 53.4, 52.3 (CHS, CHNH), 16.1, 16.0, 15.1 (CH_3). Anal. Calcd for $C_{18}H_{19}N_5O_2S$: C, 58.52; H, 5.18; N, 18.96. Found: C, 58.50; H, 5.23; N, 18.90.

A 38:62 mixture (0.387 g, 37%) of azido ketone **12l** (four diastereomers, 33:13:47:7) and hydroxypyrimidine **13l** (two diastereomers, 69:31) was obtained from phenylthioacetophenone (**11e**) (0.729 g, 3.19 mmol), NaH (0.075 g, 3.13 mmol), and sulfone **6c** (0.847 g, 2.85 mmol) in dry THF (12 mL) (8 h, rt) as described for **12l**. ^1H NMR of the major diastereomer of hydroxypyrimidine **13l** (300.13 MHz, DMSO-d_6) δ 7.19 (s, 1H, NH), 3.80 (dd, ^3J = 11.5, ^3J = 2.1 Hz, 1H, H-6), 2.92 (d, ^3J = 11.5 Hz, 1H, H-5), 0.83 (d, ^3J = 6.6 Hz, 3H, CH_3), signals of other protons overlap with proton signals of other isomers; ^1H NMR of the minor diastereomer of hydroxypyrimidine **13l** (300.13 MHz, DMSO-d_6) δ 6.48 (s, 1H, OH), 4.13 (q, ^3J = 7.0 Hz, 1H, CHN_3), 3.59 (d, ^3J = 11.1 Hz, 1H, H-6), 3.11 (d, ^3J = 11.1 Hz, 1H, H-5), 1.46 (d, ^3J = 7.0 Hz, 3H, CH_3), signals of other protons overlap with proton signals of other isomers.

6-(Azidomethyl)-4-hydroxy-4-methyl-5-phenylthiohexahydropyrimidin-2-one (13m). To a mixture of phenylthioacetone (**11f**) (1.252 g, 7.53 mmol) and NaH (0.179 g, 7.46 mmol) was added dry THF (11 mL), the mixture was stirred in an ice-cold bath for 20 min, and to the resulting solution were added sulfone **6a** (2.098 g, 7.41 mmol) and THF (7 mL). The suspension was stirred at room temperature for 8 h, and solvent was removed in a vacuum. The oily residue was triturated with petroleum ether (3 × 15 mL), to the formed yellow oil were added saturated aq $NaHCO_3$ (2.5 mL) and petroleum ether (15 mL), the obtained mixture was triturated until complete crystallization, and the resulting suspension was left overnight at room temperature and cooled to 0 °C. The precipitate was filtered and washed with ice-cold water and petroleum ether. The obtained slightly yellow solid was dried in a vacuum desiccator (over P_2O_5) on the filter, cooled (−10 °C), washed with cold (−10 °C) diethyl ether (3 × 10 mL), and dried to give **13m** (1.249 g, 60%) as a mixture of three diastereomers (43:38:19). Crystallization of this mixture from EtOH afforded only two major isomers in a ratio of

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30:70 with (4*R**,5*S**,6*R**)- and (4*R**,5*R**,6*R**)-configurations, respectively. Mp 154.5−155.5 °C (decomp, EtOH); IR (Nujol) ν_{max} 3275 (br vs), 3109 (m) (NH, OH), 2111 (s) (N_3), 1681 (vs) (amide-I), 1511 (s) (amide-II), 740 (s), 690 (m) (CH_{arom}) cm^{-1}; ^1H NMR of the 30:70 mixture of (4*R**,5*S**,6*R**)- and (4*R**,5*R**,6*R**)-diastereomers (300.13 MHz, DMSO-d_6) δ 7.19−7.51 (m, 5H, ArH in both isomers), 7.14 (d, ^4J = 2.2 Hz, 0.7H, $N_{(3)}H$ in major isomer), 7.09 (dd, ^4J = 2.0, ^4J = 1.3 Hz, 0.3H, $N_{(3)}H$ in minor isomer), 6.72 (d, ^4J = 2.2 Hz, 0.7H, $N_{(1)}H$ in major isomer), 6.53 (dd, ^4J = 2.0, ^4J = 1.3 Hz, 0.3H, $N_{(1)}H$ in minor isomer), 5.84 (d, ^4J = 0.9 Hz, 0.7H, OH in major isomer), 5.83 (s, 0.3H, OH in minor isomer), 4.13 (ddd, ^3J = 8.5, ^3J = 5.9, ^3J = 2.8 Hz, 0.3H, H-6 in minor isomer), 3.54−3.79 (m, 2.7H, CH_2N_3 in both isomers and H-6 in major isomer), 3.31 (ddd, ^3J = 2.8, ^4J = 1.3, ^4J = 1.3 Hz, 0.3H, H-5 in minor isomer), 3.12 (dd, ^3J = 11.4, ^4J = 0.9 Hz, 0.7H, H-5 in major isomer), 1.54 (s, 2.1H, CH_3 in major isomer), 1.48 (s, 0.9H, CH_3 in minor isomer); ^{13}C NMR of (4*R**,5*R**,6*R**)-diastereomer (75.48 MHz, DMSO-d_6) δ 154.5 (C-2), 135.7 (C), 130.23 (2CH), 129.2 (2CH), 126.7 (CH), 80.0 (C-4), 54.3 (C-6), 53.1 (C-5), 51.5 (CH_2N_3), 27.1 (CH_3); ^{13}C NMR of (4*R**,5*S**,6*R**)-diastereomer (75.48 MHz, DMSO-d_6) δ 154.6 (C-2), 136.0 (C), 130.18 (2CH), 129.3 (2CH), 126.6 (CH), 81.7 (C-4), 54.4 (C-6), 51.7 (CH_2N_3), 49.3 (C-5), 26.6 (CH_3). Anal. Calcd for $C_{12}H_{15}N_5O_2S$: C, 49.13; H, 5.15; N, 23.87. Found: C, 49.23; H, 5.36; N, 24.10.

***N*-[(1-Azido-4-oxo-3-phenylthio)pent-2-yl]-*N*′-methylurea (12n).** A 82:18 mixture (1.042 g, 58%) of azido ketone **12n** (two diastereomers, 90:10) and hydroxypyrimidine **13n** (two diastereomers, 50:50) was obtained from phenylthioacetone (**11f**) (0.997 g, 5.99 mmol), NaH (0.141 g, 5.90 mmol) and sulfone **6b** (1.752 g, 5.89 mmol) in dry THF (19 mL) (8 h, rt) as described for **12a**. After crystallization from EtOH, pure oxoalkylurea **12n** was obtained as a mixture of two diastereomers (78:22). Mp 116−117.5 °C (decomp, EtOH); IR (Nujol) ν_{max} 3359 (s), 3311 (s), 3183 (w), 3133 (w) (NH), 3058 (w), 3022 (w) (CH_{arom}), 2146 (m), 2103 (s) (N_3), 1699 (s) (C═O), 1636 (s) (amide-I), 1580 (s), 1533 (m) (amide-II), 757 (s), 692 (m) (CH_{arom}) cm^{-1}; ^1H NMR of the major diastereomer (300.13 MHz, DMSO-d_6) δ 7.29−7.47 (m, 5H, ArH), 6.26 (d, ^3J = 9.1 Hz, 1H, NH), 5.93 (q, ^3J = 4.6 Hz, 1H, NH), 4.21 (dddd, ^3J = 9.5, ^3J = 9.1, ^3J = 6.1, ^3J = 3.9 Hz, 1H, CHN), 3.92 (d, ^3J = 9.5 Hz, 1H, CHS), 3.65 (dd, ^2J = 12.6, ^3J = 6.1 Hz, 1H, CH_AN_3), 3.59 (dd, ^2J = 12.6, ^3J = 3.9 Hz, 1H, CH_BN_3), 2.53 (d, ^3J = 4.6 Hz, 3H, NCH_3), 2.18 (s, 3H, CH_3 in Ac); ^1H NMR of the minor diastereomer (300.13 MHz, DMSO-d_6) δ 7.29−7.47 (m, 5H, ArH, signals overlap with signals of the aromatic protons of the major isomer), 6.31 (d, ^3J = 8.3 Hz, 1H, NH), 5.96 (q, ^3J = 4.7 Hz, 1H, NH), 4.14−4.26 (m, 2H, NCH−CHS, signals overlap with signals of the CHN proton of the major isomer), 3.31 3.44 (m, 2H, CH_2N_3, signals partly overlap with the HOD signal), 2.58 (d, ^3J = 4.7 Hz, 3H, NCH_3), 2.23 (s, 3H, CH_3 in Ac); ^{13}C NMR of the major diastereomer (75.48 MHz, DMSO-d_6) δ 203.1 (C═O), 157.5 (CONH), 132.8 (C), 131.7 (2CH), 129.4 (2CH), 128.0 (CH), 58.3 ($CHSO_2$), 52.6 (CH_2N_3), 49.8 (CHN), 26.9 (CH_3 in Ac), 26.29 (NCH_3); ^{13}C NMR of the minor diastereomer (75.48 MHz, DMSO-d_6) δ 202.8 (C═O), 157.9 (CONH), 132.8 (C), 131.9 (2CH), 129.2 (2CH), 127.8 (CH), 59.7 ($CHSO_2$), 52.9 (CH_2N_3), 49.5 (CHN), 28.3 (CH_3 in Ac), 26.35 (NCH_3). Anal. Calcd for $C_{13}H_{17}N_5O_2S$: C, 50.80; H, 5.57; N, 22.78. Found: C, 50.93; H, 5.48; N, 22.84.

^1H NMR of hydroxypyrimidine **13n** (diastereomeric mixture, 50:50) (300.13 MHz, DMSO-d_6) δ 7.18−7.56 (m, 5H, ArH), 6.88 (br s, 0.5H, NH), 6.68 (br s, 0.5H, NH), 6.14 (s, 0.5H, OH), 6.12 (s, 0.5H, OH), 4.06−4.14 (m, 0.5H, H-6), 3.50−3.80 (m, 2.5H, CH_2N_3 and H-6), 3.40 (unresolved m, half-height width = 5.4 Hz, 0.5H, H-5), 3.27 (d, ^3J = 10.7 Hz, 0.5H, H-5), 2.85 (s, 1.5H, NCH_3), 2.80 (s, 1.5H, NCH_3), 1.70 (s, 1.5H, 4-CH_3), 1.58 (s, 1.5H, 4-CH_3).

6-(1-Azidoethyl)-4-hydroxy-4-methyl-5-phenylthiohexahydropyrimidin-2-one (13o). Compound **13o** (0.460 g, 48%) as a mixture of three diastereomers (50:45:5) was prepared from phenylthioacetone (**11f**) (0.580 g, 3.49 mmol), NaH (0.082 g, 3.43 mmol), and sulfone **6c** (0.924 g, 3.11 mmol) in dry THF (13 mL) (12 h, rt) as described for **12l**. After crystallization from EtOH the diastereomeric ratio changed to 53:47:0, respectively. Mp 148−148.5 °C (decomp, EtOH); IR (Nujol) ν_{max} 3289 (br s), 3131 (br m), 3100 (br m), 3073 (br m) (NH, OH), 3020 (w) (CH_{arom}), 2113 (s), ∼2098 (sh) (N_3), 1662 (br s) (amide-I), 1582 (w) (CC_{arom}), 1510 (s), 1497 (s) (amide-II), 742 (s), 690 (m) (CH_{arom}) cm^{-1}; ^1H NMR of the major diastereomer (300.13 MHz, DMSO-d_6) δ 7.19−7.51 (m, 5H, ArH, signals overlap with signals of the aromatic protons of other isomers), 7.19 (br s, 1H, NH), 6.54 (br s, 1H, NH), 5.86 (d, ^4J = 1.0 Hz, 1H, OH), 4.01 (dq, ^3J = 7.0, ^3J = 1.3 Hz, 1H, CHN_3), 3.43 (dd, ^3J = 11.2, ^3J = 1.3 Hz, 1H, H-6), 3.14 (dd, ^3J = 11.2, ^4J = 1.0 Hz, 1H, H-5), 1.56 (s, 3H, 4-CH_3), 1.41 (d, ^3J = 7.0 Hz, 3H, CH_3); ^1H NMR of the first minor diastereomer (45%) (300.13 MHz, DMSO-d_6) δ 7.19−7.51 (m, 5H, ArH, signals overlap with signals of the aromatic protons of other isomers), 7.16 (br s, 1H, NH), 6.45 (br s, 1H, NH), 5.78 (s, 1H, OH), 3.77−3.89 (m, 2H, H-6 and CHN_3), 3.43 (unresolved m, half-height width =3.9 Hz, 1H, H-5), 1.45 (s, 3H, 4-CH_3), 1.45 (d, ^3J = 5.7 Hz, 3H, CH_3); ^1H NMR of the second minor diastereomer (5%) (300.13 MHz, DMSO-d_6) δ 6.22 (br s, 1H, NH), 5.90 (s, 1H, OH), 4.25 (dq, ^3J = 6.6, ^3J = 2.0 Hz, 1H, CHN_3), 3.64 (dd, ^3J = 11.7, ^3J = 2.0 Hz, 1H, H-6), 2.99 (d, ^3J = 11.7 Hz, 1H, H-5), 1.60 (s, 3H, 4-CH_3), signals of other protons overlap with signals of analogous protons of other isomers; ^{13}C NMR of the major diastereomer (75.48 MHz, DMSO-d_6) δ 154.9 (C-2), 135.9 (C), 130.0 (2CH), 129.3 (2CH), 126.7 (CH), 79.9 (C-4), 57.4 (CHN_3), 56.1 (C-5), 54.5 (C-6), 27.2 (4-CH_3), 15.5 (CH_3); ^{13}C NMR of the first minor diastereomer (45%) (75.48 MHz, DMSO-d_6) δ 154.9 (C-2), 136.1 (C), 130.0 (2CH), 129.2 (2CH), 126.5 (CH), 81.6 (C-4), 57.5 (CHN_3), 55.5 (C-5), 54.3 (C-6), 26.6 (4-CH_3), 16.0 (CH_3). Anal. Calcd for $C_{13}H_{17}N_5O_2S$: C, 50.80; H, 5.57; N, 22.78. Found: C, 50.83; H, 5.66; N, 22.90.

6-(1-Azidopropyl)-4-hydroxy-4-methyl-5-phenylthiohexahydropyrimidin-2-one (13p). A 44:56 mixture (0.584 g, 30%) of azido ketone **12p** (a single diastereomer) and hydroxypyrimidine **13p** (three diastereomers, 54:33:13) was prepared from phenylthioacetone (**11f**) (1.015 g, 6.10 mmol), NaH (0.145 g, 6.03 mmol), and sulfone **6d** (1.872 g, 6.01 mmol) in dry THF (19 mL) (8 h, rt) as described for **12l**. After crystallization from EtOH, pure hydroxypyrimidine **13p** was obtained as a mixture of three diastereomers (52:43:5). Mp 149.5−150 °C (decomp, EtOH); IR (Nujol) ν_{max} 3289 (br s), 3114 (br m), 3085 (br m) (NH, OH), 2111 (s) (N_3), 1666 (sh), 1657 (br vs) (amide-I), 1580 (w) (CC_{arom}), 1510 (m), 1494 (s) (amide-II), 741 (s), 690 (m) (CH_{arom}) cm^{-1}; ^1H NMR of the major diastereomer (300.13 MHz, DMSO-d_6) δ 7.19−7.51 (m, 5H, ArH, signals overlap with signals of the aromatic protons of other isomers), 7.16 (br s, 1H, $N_{(3)}H$), 6.43 (br s, 1H, $N_{(1)}H$), 5.79 (s, 1H, OH), 3.90 (dd, ^3J = 10.1, ^3J = 2.5 Hz, 1H, H-6), 3.63−3.71 (m, 1H, CHN_3, signals overlap with the CHN_3 signals of the first minor isomer), 3.46 (unresolved m, half-height width =4.8 Hz, 1H, H-5), 1.61−2.14 (m, 2H, CH_2, signals overlap with the CH_2 signals of the first minor isomer), 1.44 (s, 3H, 4-CH_3), 0.96 (t, ^3J = 7.2 Hz, 3H, CH_3 in Et); ^1H NMR of the first minor diastereomer (33%) (300.13 MHz, DMSO-d_6) δ 7.19−7.51 (m, 5H, ArH, signals overlap with signals of the aromatic protons of other isomers), 7.19 (br s, 1H, $N_{(3)}H$), 6.47 (br s, 1H, $N_{(1)}H$), 5.87 (d, ^4J = 0.9 Hz, 1H, OH), 3.63−3.71 (m, 1H, CHN_3, signals overlap with the CHN_3 signals of the major isomer), 3.54 (dd, ^3J = 11.2, ^3J = 1.4 Hz, 1H, H-6), 3.18 (dd, ^3J = 11.2, ^4J = 0.9 Hz, 1H, H-5), 1.61−2.14 (m, 2H, CH_2, signals overlap with the CH_2 signals of the major isomer), 1.56 (s, 3H, 4-CH_3), 0.92 (t, ^3J = 7.3 Hz, 3H, CH_3 in Et); ^1H NMR of the second minor diastereomer (13%) (300.13 MHz, DMSO-d_6) δ 6.25 (br s, 1H, $N_{(1)}H$), 5.93 (s, 1H, OH), 3.11 (d, ^3J = 11.4 Hz, 1H, H-5), 1.62 (s, 3H, 4-CH_3), 0.47 (t, ^3J = 7.3 Hz, 3H, CH_3 in Et); signals of other protons overlap with proton signals of other isomers; ^{13}C NMR of the diastereomeric mixture (52:43:5) (75.48 MHz, DMSO-d_6) (shown only the signals of two major isomers) δ 154.91, 154.85 (C-2), 136.0, 135.8 (C), 129.9, 129.4, 129.33, 129.25 (2CH), 126.7, 126.3 (CH), 81.7, 79.9 (C-4), 63.7, 62.6 (CHN_3), 55.44, 55.38, 54.1, 51.9 (C-6 and C-5), 27.2, 26.5 (4-CH_3), 23.3, 23.0 (CH_2), 11.0, 9.6 (CH_3 in Et). Anal. Calcd for $C_{14}H_{19}N_5O_2S$: C, 52.32; H, 5.96; N, 21.79. Found: C, 52.25; H, 6.12; N, 22.07.

^1H NMR of oxoalkylurea **12p** (300.13 MHz, DMSO-d_6) δ 6.17 (d, ^3J = 9.9 Hz, 1H, NH), 5.64 (s, 2H, NH_2), 4.22 (ddd, ^3J = 10.8, ^3J = 9.9, ^3J = 1.9 Hz, 1H, CHN), 4.02 (dt, ^3J = 7.1, ^3J = 1.9 Hz, 1H, CHN_3),

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3.75 (d, ^3J = 10.8 Hz, 1H, CHS), 2.19 (s, 3H, CH_3 in Ac), 0.99 (t, ^3J = 7.1 Hz, 3H, CH_3 in Et), signals of other protons overlap with proton signals of cyclic isomers.

***N*-[(1-Azido-4-oxo-4-phenyl-3-benzoyl)but-2-yl]urea (12q).** Compound **12q** (3.044 g, 77%) was prepared from dibenzoylmethane (**11g**) (2.645 g, 11.79 mmol), NaH (0.270 g, 11.25 mmol), and sulfone **6a** (3.188 g, 11.25 mmol) in dry THF (25 mL) (8 h, rt) as described for **12a**. Compound **12q** formed a strong solvate (with EtOH) being crystallized from EtOH. Heating of this solvate in a vacuum at 56 °C for about 8 h led to partial decomposition of **12q** without complete removal of EtOH (^{1}H NMR data). Drying in high vacuum over P_2O_5 for 1 week at rt gave **12q** with 25% of EtOH (^{1}H NMR, elemental analysis). Purification of **12q** by crystallization from other solvents or their mixtures failed because of its high solubility or the tendency to transformations upon heating. Mp 83−85 °C (decomp, EtOH); IR (Nujol) ν_{max} 3511 (w), 3454 (br s), 3357 (br s), 3282 (br s), 3206 (m), 3069 (m) (NH), 2170 (m), 2107 (vs) (N_3), 1695 (s), 1685 (s), 1666 (s) (C═O and amide-I), 1594 (s), 1580 (m) (CC_{arom}), 1557 (s) (amide-II), 764 (s), 695 (s) (CH_{arom}) cm^{-1}; ^{1}H NMR (300.13 MHz, DMSO-d_6) δ 7.92−8.05 (m, 4H, ArH), 7.61−7.72 (m, 2H, ArH), 7.47−7.60 (m, 4H, ArH), 6.33 (d, ^3J = 9.5 Hz, 1H, NH), 6.08 (d, ^3J = 5.3 Hz, 1H, CHCOPh), 5.65 (s, 2H, NH_2), 4.61 (dddd, ^3J = 9.5, ^3J = 8.2, ^3J = 5.3, ^3J = 4.8 Hz, 1H, CHN), 3.58 (dd, ^2J = 12.4, ^3J = 8.2 Hz, 1H, H_A in CH_2N_3), 3.46 (dd, ^2J = 12.4, ^3J = 4.8 Hz, 1H, H_B in CH_2N_3); ^{13}C NMR (75.48 MHz, DMSO-d_6) δ 195.8 (C═O in Bz), 195.0 (C═O in Bz), 157.7 (CONH), 136.0 (C), 135.4 (C), 133.9 (CH), 133.8 (CH), 129.1 (2CH), 129.0 (2CH), 128.5 (2CH), 128.3 (2CH), 56.7 (CHBz), 53.1 (CH_2N_3), 49.8 (CHN). Anal. Calcd. for $C_{18}H_{17}N_5O_3 \times 0.25C_2H_5OH$: C, 61.23; H, 5.14; N, 19.30. Found: C, 61.18; H, 5.34; N, 19.20.

Ethyl 6-(Azidomethyl)-4-hydroxy-2-oxo-4-phenylhexahydropyrimidine-5-carboxylate (13r). To a stirred suspension of NaH (0.140 g, 5.82 mmol) in dry MeCN (6 mL) cooled in an ice-cold bath was added a solution of ethyl benzoyl acetate (**11h**) (1.162 g, 5.89 mmol) in MeCN (6 mL), and the resulting mixture was stirred for 12 min. The ice-bath was removed, and to the obtained solution were added sulfone **6a** (1.632 g, 5.76 mmol) and MeCN (5 mL). The suspension was stirred at room temperature for 8 h, and solvent was removed in a vacuum. The oily residue was triturated with petroleum ether (3 × 15 mL), to the formed oil were added saturated aq $NaHCO_3$ (2 mL) and petroleum ether (15 mL), and the obtained mixture was left overnight at room temperature and cooled to 0 °C. The oily substance was transferred on the filter, the liquids were filtered, and the substance was triturated on the filter and washed with small portions of cold (−10 °C) diethyl ether until crystallization was complete, washed with ice-cold water (2 × 3 mL) and petroleum ether, and dried to give **13r** (0.720 g, 39%) as a single (4*R**,5*S**,6*R**)-diastereomer. *Note*: the product is moderately soluble in diethyl ether and water. Mp 92.5−99 °C (decomp, EtOAc/petroleum ether, 2:1); IR (Nujol) ν_{max} 3480 (m), 3313 (s), 3235 (br s), 3089 (br m), 3073 (br m) (NH, OH), 2108 (vs) (N_3), 1725 (s) (C═O), 1676 (vs) (amide-I), 1492 (s) (amide-II), 1260 (s), 1157 (s) (C−O), 761 (s), 700 (s) (CH_{arom}) cm^{-1}; ^{1}H NMR (300.13 MHz, DMSO-d_6) δ 7.41−7.48 (m, 2H, ArH), 7.26−7.38 (m, 3H, ArH), 7.13 (d, ^4J = 1.8 Hz, 1H, $N_{(3)}H$), 6.85 (d, ^4J = 1.8 Hz, 1H, $N_{(1)}H$), 6.31 (d, ^4J = 0.8 Hz, 1H, OH), 4.04 (ddd, ^3J = 11.4, ^3J = 3.4, ^3J = 3.4 Hz, 1H, H-6), 3.62−3.77 (m, 2H, OCH_2), 3.65 (dd, ^2J = 13.1, ^3J = 3.4 Hz, 1H, H_A in CH_2N_3), 3.23 (dd, ^2J = 13.1, ^3J = 3.4 Hz, 1H, H_B in CH_2N_3), 2.75 (dd, ^3J = 11.4, ^4J = 0.8 Hz, 1H, H-5), 0.71 (t, ^3J = 7.1 Hz, 3H, CH_3); ^{13}C NMR (75.48 MHz, DMSO-d_6) δ 168.3 (C═O), 154.9 (C-2), 142.9 (C), 127.7 (CH), 127.6 (2CH), 126.2 (2CH), 81.8 (C-4), 59.7 (OCH_2), 52.6 (C-5), 52.2 (CH_2N_3), 49.1 (C-6), 13.4 (CH_3). Anal. Calcd for $C_{14}H_{17}N_5O_4$: C, 52.66; H, 5.37; N, 21.93. Found: C, 52.41; H, 5.48; N, 21.82.

***trans*-5-Phenyl-4-phenylsulfonyl-3-ureido-3,4-dihydro-2*H*-pyrrole (*trans*-15e).** To urea **12f** (2.338 g, 6.04 mmol) and PPh_3 (1.857 g, 7.08 mmol) was added dry THF (21 mL), and the obtained mixture was refluxed under stirring for 1 h 40 min. A clear solution formed at the beginning of reflux, and after 2 min the product precipitated to give a dense suspension. After the reaction was complete, the mixture was evaporated to half of its volume in a vacuum, the resulting suspension was cooled to −10 °C, the precipitate was filtered on a cold (−10 °C) filter and washed with THF (3 × 10 mL, −10 °C), diethyl ether (2 × 10 mL, −10 °C), and petroleum ether, and dried to give *trans*-**15e** (1.852 g, 89%). Mp 167.5−171 °C (decomp, EtOH); IR (Nujol) ν_{max} 3438 (s), 3339 (m), 3311 (w), 3213 (br s), 3068 (br s) (NH), 1664 (s) (amide-I), 1603 (s) (C═N), 1584 (s), 1573 (br s), 1562 (s) (amide-II), 1322 (vs), 1148 (vs) (SO_2), 767 (s), 750 (s), 697 (m), 687 (s) (CH_{arom}) cm^{-1}; ^{1}H NMR (600.13 MHz, DMSO-d_6) δ 7.82−7.85 (m, 2H, ArH), 7.77−7.80 (m, 2H, ArH), 7.68−7.72 (m, 1H, ArH), 7.53−7.58 (m, 2H, ArH), 7.42−7.46 (m, 1H, ArH), 7.34−7.38 (m, 2H, ArH), 6.59 (d, ^3J = 7.7 Hz, 1H, NH), 5.45 (s, 2H, NH_2), 5.35 (dd, ^4J = 1.5, ^3J = 1.1 Hz, 1H, H-4), 4.64 (dddd, ^3J = 7.7, ^3J = 5.8, ^3J = 1.1, ^3J = 1.1 Hz, 1H, H-3), 3.91 (ddd, ^2J = 17.2, ^3J = 5.8, ^4J = 1.5 Hz, 1H, H_A-2), 3.81 (dd, ^2J = 17.2, ^3J = 1.1 Hz, 1H, H_B-2); ^{13}C NMR (150.90 MHz, DMSO-d_6) δ 164.3 (C-5), 157.3 (C═O), 137.6 (C), 134.2 (CH), 133.1 (C), 130.5 (CH), 129.2 (2CH), 128.6 (2CH), 128.4 (2CH), 128.0 (2CH), 76.6 (C-4), 67.8 (C-2), 52.4 (C-3). Anal. Calcd for $C_{17}H_{17}N_3O_3S$: C, 59.46; H, 4.99; N, 12.24. Found: C, 59.44; H, 5.11; N, 12.46.

***trans*-5-Phenyl-4-tosyl-3-ureido-3,4-dihydro-2*H*-pyrrole (*trans*-15f).** Compound *trans*-**15f** (1.098 g, 89%) was prepared from urea **12g** (1.384 g, 3.45 mmol) and PPh_3 (1.055 g, 4.02 mmol) in dry THF (26 mL) (reflux, 1 h 40 min) as described for *trans*-**15e**. Mp 174.5−176 °C (decomp, EtOH); IR (Nujol) ν_{max} 3466 (s), 3361 (m), 3266 (br m), 3223 (br m), 3078 (br s) (NH), 1676 (m), 1656 (s) (amide-I), 1615 (m), 1596 (s), 1580 (m), 1570 (m) (amide-II and C═N), 1317 (s), 1132 (s) (SO_2), 817 (m), 769 (s), 697 (m) (CH_{arom}) cm^{-1}; ^{1}H NMR (300.13 MHz, DMSO-d_6) δ 7.80−7.86 (m, 2H, ArH), 7.62−7.68 (m, 2H, ArH), 7.41−7.48 (m, 1H, ArH), 7.32−7.40 (m, 4H, ArH), 6.60 (d, ^3J = 7.6 Hz, 1H, NH), 5.47 (s, 2H, NH_2), 5.31 (dd, ^4J = 1.1, ^3J = 1.1 Hz, 1H, H-4), 4.61 (dddd, ^3J = 7.6, ^3J = 5.2, ^3J = 1.5, ^3J = 1.1 Hz, 1H, H-3), 3.86 (ddd, ^2J = 17.2, ^3J = 5.2, ^4J = 1.1 Hz, 1H, H_A-2), 3.78 (dd, ^2J = 17.2, ^3J = 1.5 Hz, 1H, H_B-2), 2.38 (s, 3H, CH_3); ^{13}C NMR (75.48 MHz, DMSO-d_6) δ 164.4 (C-5), 157.4 (C═O), 144.9 (C), 134.7 (C), 133.2 (C), 130.5 (CH), 129.7 (2CH), 128.7 (2CH), 128.5 (2CH), 128.0 (2CH), 76.7 (C-4), 67.9 (C-2), 52.4 (C-3), 21.1 (CH_3). Anal. Calcd for $C_{18}H_{19}N_3O_3S$: C, 60.49; H, 5.36; N, 11.76. Found: C, 60.17; H, 5.56; N, 11.96.

2-Methyl-5-phenyl-4-tosyl-3-ureido-3,4-dihydro-2*H*-pyrrole (15g). To urea **12h** (1.270 g, 3.06 mmol) and PPh_3 (0.967 g, 3.69 mmol) was added dry THF (15 mL), and the obtained mixture was refluxed under stirring for 2 h. A clear solution formed at the beginning of reflux, and after 15 min the product precipitated to give a suspension. After the reaction was complete, the mixture was evaporated to a quarter of its volume in a vacuum, the resulting suspension was cooled to −10 °C and transferred on a cold (−10 °C) filter with cold diethyl ether, and the precipitate was filtered, washed with THF (2 mL, −10 °C), diethyl ether (2 × 5 mL, −10 °C), and petroleum ether, and dried to give **15g** (0.846 g, 74%) as a mixture of two diastereomers (72:28). After crystallization from EtOH the diastereomeric ratio changed to 73:27. Mp 191−193 °C (decomp, EtOH); IR (Nujol) ν_{max} 3407 (s), 3276 (s), 3202 (s), 3084 (s) (NH), 3029 (w) (CH_{arom}), 1655 (s) (amide-I), 1616 (s) (C═N), 1598 (w) (CC_{arom}), 1564 (s) (amide-II), 1494 (w) (CC_{arom}), 1318 (s), 1148 (s) (SO_2), 810 (m), 767 (s), 699 (s) (CH_{arom}) cm^{-1}; ^{1}H NMR of the major diastereomer (300.13 MHz, DMSO-d_6) δ 7.26−7.84 (m, 9H, ArH, signals overlap with signals of the aromatic protons of the minor isomer), 6.48 (d, ^3J = 9.6 Hz, 1H, NH), 5.44 (s, 2H, NH_2), 5.31 (dd, ^4J = 0.9, ^3J = 0.9 Hz, 1H, H-4), 4.79 (ddd, ^3J = 9.6, ^3J = 5.9, ^3J = 0.9 Hz, 1H, H-3), 4.03 (ddq, ^3J = 7.2, ^3J = 5.9, ^4J = 0.9 Hz, 1H, H-2), 2.37 (s, 3H, CH_3 in Ts), 1.17 (d, ^3J = 7.2 Hz, 3H, 2-CH_3); ^{1}H NMR of the minor diastereomer (300.13 MHz, DMSO-d_6) δ 7.26−7.69 (m, 9H, ArH, signals overlap with signals of the aromatic protons of the major isomer), 6.55 (d, ^3J = 7.6 Hz, 1H, NH), 5.54 (s, 2H, NH_2), 5.35 (d, ^3J = 2.9 Hz, 1H, H-4), 4.18 (ddd, ^3J = 7.6, ^3J = 2.9, ^3J = 2.6 Hz, 1H, H-3), 4.03 (dq, ^3J = 7.1, ^3J = 2.6 Hz, 1H, H-2), 2.37 (s, 3H, CH_3 in Ts), 1.18 (d, ^3J = 7.1 Hz, 3H, 2-CH_3); ^{13}C NMR of the major diastereomer (75.48 MHz, DMSO-d_6) δ 163.1 (C-5), 157.5 (C═O), 144.9 (C), 135.0 (C), 133.0 (C), 130.5 (CH), 129.7 (2CH), 128.6 (2CH), 128.4

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(2CH), 127.9 (2CH), 77.8 (C-4), 69.8 (C-2), 54.9 (C-3), 21.1 (CH_3 in Ts), 14.7 (2-CH_3); ^{13}C NMR of the minor diastereomer (75.48 MHz, DMSO-d_6) δ 162.5 (C-5), 157.6 (C═O), 144.7 (C), 134.9 (C), 133.5 (C), 130.1 (CH), 129.6 (2CH), 128.52 (2CH), 128.47 (2CH), 127.8 (2CH), 77.5 (C-2), 76.2 (C-2), 57.4 (C-3), 21.1 (CH_3 in Ts), 19.5 (2-CH_3). Anal. Calcd for $C_{19}H_{21}N_3O_3S$: C, 61.44; H, 5.70; N, 11.31. Found: C, 61.31; H, 5.90; N, 11.20.

4-Benzoyl-5-phenyl-3-ureido-2,3-dihydro-1*H*-pyrrole (16n). Compound **16n** (0.347 g, 72%) as a yellow solid was prepared from urea **12q** (0.552 g, 1.57 mmol) and PPh_3 (0.490 g, 1.87 mmol) in dry THF (8 mL) (reflux, 4 h 30 min) as described for **15g**. Mp 133−134 °C (decomp, EtOH) (rate of heating 1 °C per 11−13 s), mp 145−146 °C (decomp, EtOH) (rate of heating 1 °C per 1 min, decomposition before melting); IR (Nujol) ν_{max} 3428 (m), 3396 (br s), 3356 (m), 3210 (br s), 3170 (br s), 3146 (br s), 3084 (br m), 3069 (br m), 3060 (br m) (NH), 3027 (m), 3002 (w) (CH_{arom}), 1645 (s) (amide-I and C═O), 1621 (m) (C═C), 1581 (w) (CC_{arom}), 1524 (s) (amide-II), 725 (s), 697 (s) (CH_{arom}) cm^{-1}; ^{1}H NMR (300.13 MHz, DMSO-d_6) δ 7.91 (br s, 1H, H-1), 7.04−7.22 (m, 8H, ArH), 6.92−6.99 (m, 2H, ArH), 6.08 (d, ^3J = 5.1 Hz, 1H, NH), 5.49 (s, 2H, NH_2), 4.94 (ddd, ^3J = 8.3, ^3J = 5.1, ^3J = 2.5 Hz, 1H, H-3), 3.76 (dd, ^2J = 12.0, ^3J = 8.3 Hz, 1H, H_A-2), 3.40 (ddd, ^2J = 12.0, ^3J = 2.5, ^3J = 1.4 Hz, 1H, H_B-2); ^{13}C NMR (75.48 MHz, DMSO-d_6) δ 189.1 (C═O in Bz), 164.6 (C-5), 158.4 (CONH), 141.6 (C), 131.8 (C), 129.4 (CH), 128.8 (3CH), 127.9 (2CH), 127.5 (2CH), 126.9 (2CH), 107.9 (C-4), 53.9 (C-3), 53.8 (C-2). Anal. Calcd for $C_{18}H_{17}N_3O_2$: C, 70.34; H, 5.58; N, 13.67. Found: C, 70.35; H, 5.68; N, 13.50.

2-Methyl-3-phenylsulfonyl-1*H*-pyrrole (17a). A solution of **12a** (0.358 g, 1.10 mmol) and PPh_3 (0.355 g, 1.35 mmol) in dry THF (7 mL) was refluxed under stirring for 2 h, then TsOH·H_2O (0.105 g, 0.55 mmol) was added, and reflux was continued for 10 min. The solvent was removed in a vacuum, and the obtained residue was dissolved in $CHCl_3$ (15 mL), subsequently washed with saturated aq $NaHCO_3$ (10 mL), H_2O (3 × 10 mL), and brine (2 × 10 mL), and dried over Na_2SO_4. Then the solvent was removed in a vacuum, and the obtained residue was purified by column chromatography on silica gel 60 (16 g) eluting with petroleum ether/$CHCl_3$ (from 1:1 to 1:3). (*Note*: the fraction with the product came after $POPh_3$). The main fraction was concentrated in a vacuum, the solid residue was triturated with H_2O (2 mL) and cooled, and the precipitate was filtered and dried to give **17a** (0.225 g, 93%). Mp 112.5−113 °C (EtOAc/petroleum ether, 1:1); IR (Nujol) ν_{max} 3329 (vs), ∼3289 (sh) (NH), 3068 (w), 3056 (w) (CH_{arom}), 1560 (m) (CC_{arom}), 1297 (vs), 1137 (vs) (SO_2), 758 (s), 729 (vs), 686 (s) (CH_{arom}) cm^{-1}; ^{1}H NMR (300.13 MHz, DMSO-d_6) δ 11.53 (br s, 1H, NH), 7.77−7.88 (m, 2H, ArH), 7.50−7.64 (m, 3H, ArH), 6.72 (dd, ^3J = 3.1, ^3J = 2.0 Hz, 1H, H-5), 6.35 (dd, ^3J = 3.1, ^4J = 2.2 Hz, 1H, H-4), 2.36 (s, 3H, CH_3); ^{13}C NMR (75.48 MHz, DMSO-d_6) δ 144.2 (C), 132.33 (CH), 132.27 (C-2), 129.2 (2CH), 125.9 (2CH), 118.3 (C-3), 117.5 (C-5), 108.7 (C-4), 11.5 (CH_3). Anal. Calcd for $C_{11}H_{11}NO_2S$: C, 59.71; H, 5.01; N, 6.33. Found: C, 59.78; H, 5.14; N, 6.43.

2-Methyl-3-tosyl-1*H*-pyrrole (17b). *Method A.* To a mixture of tosylacetone (**11b**) (0.570 g, 2.69 mmol) and NaH (0.063 g, 2.63 mmol) was added dry THF (10 mL), the mixture was stirred in an ice-cold bath for 10 min, and to the resulting solution were added sulfone **6a** (0.744 g, 2.63 mmol) and dry THF (5 mL). The suspension was stirred at room temperature for 8 h, PPh_3 (0.826 g, 3.15 mmol) was added, and the reaction mixture was refluxed under stirring for 1 h 5 min. Vigorous foaming occurred during all of the refluxing time (use of a straight condenser and periodic shaking of the flask is recommended). Then TsOH·H_2O (0.256 g, 1.35 mmol) was added, and reflux was continued for 1 h 10 min (foaming slightly decreased but continued). The solvent was removed in a vacuum, the obtained residue was dissolved in $CHCl_3$ (25 mL), subsequently washed with saturated aq $NaHCO_3$ (20 mL), H_2O (5 × 20 mL), and brine (2 × 10 mL), and dried over Na_2SO_4. Then the solvent was removed in a vacuum, and the residue was purified by column chromatography on silica gel 60 (25 g) eluting with petroleum ether/$CHCl_3$ (from 1:1 to 1:5) (*Note*: the fraction with the product came after $POPh_3$). The main fraction was concentrated in a vacuum, and the solid residue was recrystallized from EtOH to give **17b** (0.395 g, 61%). The mother liquor was concentrated in a vacuum to afford 0.064 g of a 55:45 mixture of **17b** and $POPh_3$ (according to ^{1}H NMR spectrum). Mp 204.5−205.5 °C (EtOH); IR (Nujol) ν_{max} 3296 (br vs), 3126 (m) (NH), 3020 (w) (CH_{arom}), 1595 (m), 1563 (m), 1492 (m) (CC_{arom}), 1278 (s), 1137 (vs) (SO_2), 816 (m) (CH_{arom}) cm^{-1}; ^{1}H NMR (300.13 MHz, DMSO-d_6) δ 11.49 (br s, 1H, NH), 7.68−7.73 (m, 2H, ArH), 7.32−7.37 (m, 2H, ArH), 6.71 (dd, ^3J = 3.1, ^3J = 2.4 Hz, 1H, H-5), 6.33 (dd, ^3J = 3.1, ^4J = 2.6 Hz, 1H, H-4), 2.35 (s, 3H, CH_3 in Ts), 2.34 (s, 3H, 2-CH_3); ^{13}C NMR (75.48 MHz, DMSO-d_6) δ 142.6 (C), 141.5 (C), 132.0 (C-2), 129.6 (2CH), 126.0 (2CH), 118.8 (C-3), 117.3 (C-5), 108.6 (C-4), 20.9 (CH_3 in Ts), 11.4 (2-CH_3). Anal. Calcd for $C_{12}H_{13}NO_2S$: C, 61.25; H, 5.57; N, 5.95. Found: C, 61.27; H, 5.67; N, 5.98.

Method B. Pyrrole **17b** (0.453 g, 71%) was prepared from tosylacetone (**11b**) (0.590 g, 2.78 mmol), NaH (0.065 g, 2.73 mmol), and sulfone **6a** (0.773 g, 2.73 mmol) in MeCN (16 mL) (rt, 8 h), then PPh_3 (0.855 g, 3.25 mmol) (reflux, 1 h), and then TsOH·H_2O (0.260 g, 1.37 mmol) (reflux, 1 h) as described in Method A. The crude product was purified by column chromatography on silica gel 60 (25 g) eluting with petroleum ether/$CHCl_3$ (from 35:65 to 1:4) (*Note*: the fraction with the product came after $POPh_3$). The main fraction was concentrated in a vacuum, and the solid residue was recrystallized from EtOH.

2,5-Dimethyl-3-tosyl-1*H*-pyrrole (17c). *Method A.* Pyrrole **17c** (0.250 g, 47%) was prepared from tosylacetone (**11b**) (0.471 g, 2.21 mmol), NaH (0.051 g, 2.14 mmol), and sulfone **6c** (0.636 g, 2.14 mmol) in THF (13 mL) (rt, 8 h), then PPh_3 (0.634 g, 2.42 mmol) (reflux, 1 h), and then TsOH·H_2O (0.208 g, 1.09 mmol) (reflux, 1 h 10 min) as described in Method A for **17b**. The crude product was purified by column chromatography on silica gel 60 (20 g) eluting with petroleum ether/$CHCl_3$ (from 1:1 to 1:4) (*Note*: the fraction with the product came after $POPh_3$). The main fraction was concentrated in a vacuum, and the solid residue was recrystallized from EtOH. Mp 188.5−189.5 °C (EtOH); IR (Nujol) ν_{max} 3302 (br vs), 3186 (m) (NH), 3084 (w), 3032 (w) (CH_{arom}), 1596 (m), 1526 (m), 1495 (w) (CC_{arom}), 1282 (s), 1144 (s) (SO_2), 822 (m) (CH_{arom}) cm^{-1}; ^{1}H NMR (300.13 MHz, DMSO-d_6) δ 11.25 (br s, 1H, NH), 7.65−7.70 (m, 2H, ArH), 7.31−7.36 (m, 2H, ArH), 5.97 (dq, ^4J = 2.7, ^4J = 1.0 Hz, 1H, H-4), 2.34 (br s, 3H, 2-CH_3), 2.30 (s, 3H, CH_3 in Ts), 2.07 (d, ^4J = 1.0 Hz, 3H, 5-CH_3); ^{13}C NMR (75.48 MHz, DMSO-d_6) δ 142.4 (C), 141.7 (C), 130.8 (C-2), 129.6 (2CH), 126.7 (C-5), 125.9 (2CH), 118.1 (C-3), 105.7 (C-4), 20.9 (CH_3 in Ts), 12.1 (5-CH_3), 11.4 (2-CH_3). Anal. Calcd for $C_{13}H_{15}NO_2S$: C, 62.62; H, 6.06; N, 5.62. Found: C, 62.68; H, 6.27; N, 5.56.

Method B. Pyrrole **17c** (0.317 g, 70%) was prepared from urea **12d** (0.643 g, 1.82 mmol) and PPh_3 (0.572 g, 2.18 mmol) in THF (9 mL) (reflux, 2 h 25 min) and then TsOH·H_2O (0.174 g, 0.92 mmol) (reflux, 15 min) as described for **17a**. The crude product was purified by column chromatography on silica gel 60 (20 g) eluting with petroleum ether/$CHCl_3$ (from 1:3 to 1:5). The main fraction was concentrated in a vacuum, and the solid residue was recrystallized from EtOH.

5-Ethyl-2-methyl-3-tosyl-1*H*-pyrrole (17d). Pyrrole **17d** (0.346 g, 74%) was prepared from urea **12e** (0.667 g, 1.77 mmol) and PPh_3 (0.561 g, 2.14 mmol) in THF (9 mL) (reflux, 2 h) and then TsOH·H_2O (0.169 g, 0.89 mmol) (reflux, 15 min) as described for **17a**. The crude product was purified by column chromatography on silica gel 60 (25 g) eluting with petroleum ether/acetone (from 5:1 to 4.5:1). Mp 129−130.5 °C (EtOAc/petroleum ether, 1:3); IR (Nujol) ν_{max} 3269 (br vs), 3177 (m) (NH), 3100 (w), 3060 (w), 3030 (w) (CH_{arom}), 1594 (m), 1520 (m), 1492 (w) (CC_{arom}), 1284 (s), 1141 (s) (SO_2), 809 (s) (CH_{arom}) cm^{-1}; ^{1}H NMR (300.13 MHz, DMSO-d_6) δ 11.26 (br s, 1H, NH), 7.66−7.71 (m, 2H, ArH), 7.31−7.37 (m, 2H, ArH), 5.99 (dt, ^4J = 2.8, ^4J = 1.0 Hz, 1H, H-4), 2.43 (dq, ^3J = 7.5, ^4J = 1.0 Hz, 2H, CH_2 in Et), 2.34 (br s, 3H, 2-CH_3), 2.32 (s, 3H, CH_3 in Ts), 1.10 (t, ^3J = 7.5 Hz, 3H, CH_3 in Et); ^{13}C NMR (75.48 MHz, DMSO-d_6) δ 142.4 (C), 141.7 (C), 133.1 (C-5), 130.9 (C-2), 129.6 (2CH), 125.9 (2CH), 117.9 (C-3), 104.2 (C-4), 20.9 (CH_3 in Ts), 19.8 (CH_2), 13.3 (CH_3 in Et), 11.4 (2-CH_3). Anal. Calcd for

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$C_{14}H_{17}NO_2S$: C, 63.85; H, 6.51; N, 5.32. Found: C, 63.77; H, 6.59; N, 5.38.

2-Phenyl-3-phenylsulfonyl-1*H*-pyrrole (17e).[38] A solution of *trans*-**15e** (0.599 g, 1.75 mmol) and TsOH·H_2O (0.033 g, 0.17 mmol) in MeCN (7 mL) was refluxed for 30 min under stirring, and then the solvent was removed in a vacuum. The solid residue was triturated with saturated aq $NaHCO_3$ (2 mL) and petroleum ether (5 mL) and cooled (0 °C), and the precipitate was filtered, washed with ice-cold water and petroleum ether, and dried to give **17e** (0.475 g, 96%). Mp 156−157 °C (EtOAc/petroleum ether, 1:1); IR (Nujol) ν_{max} 3299 (br vs) (NH), 3029 (w), 3020 (w) (CH_{arom}), 1605 (m), 1584 (m), 1557 (m), 1499 (m) (CC_{arom}), 1298 (s), 1141 (s) (SO_2), 761 (s), 755 (s), 688 (s) (CH_{arom}) cm^{-1}; ^1H NMR (300.13 MHz, DMSO-d_6) δ 12.02 (br s, 1H, NH), 7.35−7.65 (m, 10H, ArH), 6.98 (d, ^3J = 3.0 Hz, 1H, H-5), 6.61 (d, ^3J = 3.0 Hz, 1H, H-4); ^{13}C NMR (75.48 MHz, DMSO-d_6) δ 143.6 (C), 134.2 (C-2), 132.5 (CH), 130.3 (C), 129.2 (2CH), 129.0 (2CH), 128.4 (CH), 128.0 (2CH), 126.1 (2CH), 119.8 (C-3), 119.0 (C-5), 111.0 (C-4). Anal. Calcd for $C_{16}H_{13}NO_2S$: C, 67.82; H, 4.62; N, 4.94. Found: C, 67.83; H, 4.88; N, 5.05.

2-Phenyl-3-tosyl-1*H*-pyrrole (17f). Pyrrole **17f** (0.436 g, 93%) was prepared from *trans*-**15f** (0.567 g, 1.57 mmol) and TsOH·H_2O (0.029 g, 0.15 mmol) in MeCN (10 mL) (reflux, 30 min) as described for **17e**. Mp 154−155 °C (EtOH); IR (Nujol) ν_{max} 3252 (br s) (NH), 3029 (m), 3019 (w) (CH_{arom}), 1592 (m), 1558 (m), 1498 (m) (CC_{arom}), 1309 (s), 1138 (s) (SO_2), 819 (m), 767 (s), 701 (s) (CH_{arom}) cm^{-1}; ^1H NMR (300.13 MHz, DMSO-d_6) δ 11.98 (br s, 1H, NH), 7.46−7.54 (m, 4H, ArH), 7.35−7.46 (m, 3H, ArH), 7.23−7.28 (m, 2H, ArH), 6.96 (d, ^3J = 3.0 Hz, 1H, H-5), 6.58 (d, ^3J = 3.0 Hz, 1H, H-4), 2.30 (s, 3H, CH_3); ^{13}C NMR (75.48 MHz, DMSO-d_6) δ 142.8 (C), 140.8 (C), 133.9 (C-2), 130.4 (C), 129.4 (2CH), 129.2 (2CH), 128.3 (CH), 128.0 (2CH), 126.1 (2CH), 120.2 (C-3), 118.9 (C-5), 111.0 (C-4), 20.9 (CH_3). Anal. Calcd for $C_{17}H_{15}NO_2S$: C, 68.66; H, 5.08; N, 4.71. Found: C, 68.53; H, 5.21; N, 4.75.

5-Methyl-2-phenyl-3-tosyl-1*H*-pyrrole (17g). Pyrrole **17g** (0.431 g, 97%) was prepared from **15g** (0.530 g, 1.43 mmol) and TsOH·H_2O (0.083 g, 0.43 mmol) in MeCN (8 mL) (reflux, 20 min) as described for **17e**. Mp 181−182 °C (MeCN); IR (Nujol) ν_{max} 3276 (vs), 3192 (w), 3168 (w), 3124 (w) (NH), 3069 (w), 3043 (w), 3029 (w) (CH_{arom}), 1594 (sh), 1587 (m), 1519 (w), 1492 (w) (CC_{arom}), 1283 (s), 1139 (s) (SO_2), 811 (br m), 768 (m), 760 (m), 728 (m), 699 (s) (CH_{arom}) cm^{-1}; ^1H NMR (300.13 MHz, DMSO-d_6) δ 11.69 (br s, 1H, NH), 7.46−7.52 (m, 4H, ArH), 7.33−7.44 (m, 3H, ArH), 7.23−7.28 (m, 2H, ArH), 6.25 (dq, ^4J = 2.7, ^4J = 0.9 Hz, 1H, H-4), 2.30 (s, 3H, CH_3 in Ts), 2.19 (d, ^4J = 0.9 Hz, 3H, 5-CH_3); ^{13}C NMR (75.48 MHz, DMSO-d_6) δ 142.7 (C), 141.0 (C), 132.7 (C-2), 130.6 (C), 129.4 (2CH), 129.0 (2CH), 128.5 (C-5), 128.0 (CH), 127.9 (2CH), 126.1 (2CH), 119.7 (C-3), 108.5 (C-4), 20.9 (CH_3 in Ts), 12.1 (5-CH_3). Anal. Calcd for $C_{18}H_{17}NO_2S$: C, 69.43; H, 5.50; N, 4.50. Found: C, 69.45; H, 5.65; N, 4.53.

5-Ethyl-2-phenyl-3-tosyl-1*H*-pyrrole (17h). Pyrrole **17h** (0.347 g, 69%) was prepared from urea **12i** (0.667 g, 1.55 mmol) and PPh_3 (0.486 g, 1.75 mmol) in THF (8 mL) (reflux, 2 h) and then TsOH·H_2O (0.147 g, 0.77 mmol) (reflux, 30 min) as described for **17a**. The crude product was purified by column chromatography on silica gel 60 (22 g) eluting with petroleum ether/acetone (from 7:1 to 6:1). Mp 174−175 °C (EtOAc/petroleum ether, 1:2); IR (Nujol) ν_{max} 3285 (vs), 3163 (w) (NH), 3059 (w), 3024 (w) (CH_{arom}), 1595 (w), 1584 (m), 1515 (w), 1492 (w) (CC_{arom}), 1280 (s), 1140 (s) (SO_2), 814 (s), 768 (m), 697 (s) (CH_{arom}) cm^{-1}; ^1H NMR (300.13 MHz, DMSO-d_6) δ 11.68 (br s, 1H, NH), 7.46−7.52 (m, 4H, ArH), 7.33−7.44 (m, 3H, ArH), 7.23−7.28 (m, 2H, ArH), 6.28 (dt, ^4J = 2.5, ^4J = 0.9 Hz, 1H, H-4), 2.55 (dq, ^3J = 7.6, ^4J = 0.9 Hz, 2H, CH_2 in Et), 2.30 (s, 3H, CH_3 in Ts), 1.18 (t, ^3J = 7.6 Hz, 3H, CH_3 in Et); ^{13}C NMR (75.48 MHz, DMSO-d_6) δ 142.7 (C), 141.0 (C), 134.9 (C-5), 132.8 (C-2), 130.6 (C), 129.4 (2CH), 129.1 (2CH), 128.1 (CH), 127.9 (2CH), 126.1 (2CH), 119.5 (C-3), 106.9 (C-4), 20.9 (CH_3 in Ts), 19.8 (CH_2), 13.3 (CH_3 in Et). Anal. Calcd for $C_{19}H_{19}NO_2S$: C, 70.13; H, 5.89; N, 4.30. Found: C, 70.05; H, 5.96; N, 4.30.

2-Phenyl-3-phenylthio-1*H*-pyrrole (17i). A solution of **12j** (0.436 g, 1.23 mmol) and PPh_3 (0.384 g, 1.46 mmol) in dry THF (7 mL) was refluxed under stirring for 2 h, then TsOH·H_2O (0.115 g, 0.61 mmol) was added, and reflux was continued for 15 min. The solvent was removed in a vacuum, the obtained residue was dissolved in $CHCl_3$ (20 mL), subsequently washed with saturated aq $NaHCO_3$ (10 mL), H_2O (3 × 10 mL), and brine (2 × 10 mL), and dried over Na_2SO_4. Then the solvent was removed in a vacuum, and the obtained residue was purified by column chromatography on silica gel 60 (15 g) eluting with petroleum ether/acetone (from 100:1 to 20:1). The main fraction was concentrated in a vacuum to give **17i** (0.213 g, 69%) as a slightly yellow oil. This oil crystallized upon prolonged trituration with water to give a slightly violet solid. Mp 58.5−59.5 °C; IR (Nujol) ν_{max} 3410 (br vs) (NH), 1600 (m), 1581 (s), 1546 (m), 1494 (s) (CC_{arom}), 772 (s), 742 (s), 689 (s) (CH_{arom}) cm^{-1}; ^1H NMR (300.13 MHz, DMSO-d_6) δ 11.72 (br s, 1H, NH), 7.63−7.68 (m, 2H, ArH), 7.32−7.39 (m, 2H, ArH), 7.19−7.27 (m, 3H, ArH), 7.00−7.09 (m, 3H, ArH), 7.03 (dd, ^3J = 2.8, ^3J = 2.8 Hz, H-5), 6.27 (dd, ^3J = 2.8, ^4J = 2.4 Hz, H-4); ^{13}C NMR (75.48 MHz, DMSO-d_6) δ 140.1 (C), 134.6 (C-2), 131.8 (C), 128.9 (2CH), 128.3 (2CH), 126.8 (CH), 126.6 (2CH), 124.8 (2CH), 124.5 (CH), 119.6 (C-5), 116.3 (C-4), 103.5 (C-3). Anal. Calcd for $C_{16}H_{13}NS$: C, 76.46; H, 5.21; N, 5.57. Found: C, 76.12; H, 5.48; N, 5.54.

2-Methyl-3-phenylthio-1*H*-pyrrole (17j).[39] A solution of pyrimidine **13m** (0.564 g, 1.92 mmol) and PPh_3 (0.608 g, 2.09 mmol) in dry MeCN (9 mL) was refluxed under stirring for 5 h, then TsOH·H_2O (0.037 g, 0.20 mmol) was added, and reflux was continued for 5 min. The solvent was removed in a vacuum, and the obtained residue was dissolved in $CHCl_3$ (20 mL), subsequently washed with saturated aq $NaHCO_3$ (10 mL), H_2O (5 × 10 mL), and brine (2 × 10 mL), and dried over Na_2SO_4. The solvent was removed in a vacuum, and the residue was purified by column chromatography on silica gel 60 (28 g) eluting with petroleum ether/$CHCl_3$ (from 4:1 to 1:2). The main fraction was concentrated in a vacuum, and the obtained oily substance was triturated with water (2 mL) until crystallization was complete (rapid crystallization). The precipitate was filtered and dried to give **17j** (0.281 g, 77%) as a slightly yellow solid. Mp 61−62.5 °C; IR (Nujol) ν_{max} 3327 (br vs) (NH), 3029 (w), 3020 (w) (CH_{arom}), 1579 (s), 1562 (m), 1488 (m) (CC_{arom}), 742 (s), 694 (s) (CH_{arom}) cm^{-1}; ^1H NMR (300.13 MHz, DMSO-d_6) δ 11.14 (br s, 1H, NH), 7.16−7.24 (m, 2H, ArH), 7.00−7.07 (m, 1H, ArH), 6.93−6.99 (m, 2H, ArH), 6.76 (dd, ^3J = 2.9, ^3J = 2.6 Hz, 1H, H-5), 6.06 (dd, ^3J = 2.9, ^4J = 2.5 Hz, 1H, H-4), 2.16 (s, 3H, CH_3); ^{13}C NMR (75.48 MHz, DMSO-d_6) δ 140.5 (C), 132.9 (C-2), 128.7 (2CH), 124.6 (2CH), 124.2 (CH), 117.1 (C-5), 113.4 (C-4), 102.5 (C-3), 10.8 (CH_3). Anal. Calcd for $C_{11}H_{11}NS$: C, 69.80; H, 5.86; N, 7.40. Found: C, 69.58; H, 6.06; N, 7.34.

2,5-Dimethyl-3-phenylthio-1*H*-pyrrole (17k).[40] Pyrrole **17k** (0.354 g, 79%) as a slightly yellow solid was prepared from pyrimidine **13o** (0.679 g, 2.21 mmol) and PPh_3 (0.697 g, 2.66 mmol) in MeCN (8 mL) (reflux, 4 h 30 min) followed by addition of TsOH·H_2O (0.208 g, 1.09 mmol) (reflux, 15 min) as described for **17j**. The crude product was purified twice by column chromatography: (1) silica gel 60 (20 g) eluting with petroleum ether/acetone (from 12:1 to 8:1); (2) silica gel 60 (5 g) eluting with petroleum ether/acetone (from 100:1 to 10:1). Crystallization from EtOAc/petroleum ether (1:9, v/v) gave **17k** as a white solid. Mp 121.5−122.5 °C (EtOAc/petroleum ether, 1:8); IR (Nujol) ν_{max} 3392 (vs) (NH), 3067 (w), 3056 (w), 3028 (w) (CH_{arom}), 1597 (w), 1581 (s), 1516 (m) (CC_{arom}), 744 (s), 692 (m) (CH_{arom}) cm^{-1}; ^1H NMR (300.13 MHz, DMSO-d_6) δ 10.87 (br s, 1H, NH), 7.16−7.23 (m, 2H, ArH), 6.99−7.06 (m, 1H, ArH), 6.94−6.99 (m, 2H, ArH), 5.72 (dq, ^4J = 2.7, ^4J = 1.0 Hz, 1H, H-4), 2.15 (d, ^4J = 1.0 Hz, 3H, 5-CH_3), 2.12 (s, 3H, 2-CH_3); ^{13}C NMR (75.48 MHz, DMSO-d_6) δ 140.7 (C), 131.6 (C-2), 128.7 (2CH), 126.3 (C-5), 124.6 (2CH), 124.1 (CH), 110.7 (C-4), 101.8 (C-3), 12.7 (5-CH_3), 10.8 (2-CH_3). Anal. Calcd for $C_{12}H_{13}NS$: C, 70.89; H, 6.45; N, 6.89. Found: C, 70.85; H, 6.63; N, 6.94.

Ethyl 2-Phenyl-1*H*-pyrrole-3-carboxylate (17l). *Method A.* A solution of pyrimidine **13r** (0.626 g, 1.96 mmol) and PPh_3 (0.607 g, 2.32 mmol) in dry MeCN (10 mL) was refluxed under stirring for 1 h, then TsOH·H_2O (0.037 g, 0.19 mmol) was added, and reflux was continued for 5 min. The solvent was removed in a vacuum, and the

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obtained residue was dissolved in $CHCl_3$ (30 mL), subsequently washed with saturated aq $NaHCO_3$ (10 mL), H_2O (3 × 10 mL), and brine (2 × 10 mL), and dried over Na_2SO_4. Then the solvent was removed in a vacuum, and the residue was purified by column chromatography on silica gel 60 (28 g) eluting with petroleum ether/$CHCl_3$ (from 3:1 to 3:2). The main fraction was concentrated in a vacuum, and the obtained oily substance was triturated with H_2O (2 mL) until rapid crystallization was complete. The precipitate was filtered and dried to give **17l** (0.353 g, 83%). Mp 73.5−75 °C (lit.[41] mp 68 °C); IR (Nujol) ν_{max} 3330 (s), 3266 (vs) (NH), 3055 (w), 3020 (w) (CH_{arom}), 1679 (vs) (C═O), 1607 (w), 1580 (m), 1563 (m) (CC_{arom}), 1292 (vs), 1143 (vs) (C−O), 764 (s), 697 (m) (CH_{arom}) cm^{-1}; ^1H NMR (300.13 MHz, DMSO-d_6) δ 11.62 (br s, 1H, NH), 7.56−7.61 (m, 2H, ArH), 7.31−7.44 (m, 3H, ArH), 6.85 (dd, ^3J = 2.9, ^3J = 2.5 Hz, 1H, H-5), 6.54 (dd, ^3J = 2.9, ^4J = 2.5 Hz, 1H, H-4), 4.11 (q, ^3J = 7.1 Hz, 2H, OCH_2), 1.18 (t, ^3J = 7.1 Hz, CH_3); ^{13}C NMR (75.48 MHz, DMSO-d_6) δ 164.2 (C═O), 136.2 (C-2), 132.0 (C), 129.0 (2CH), 127.7 (2CH), 127.6 (CH), 118.5 (C-5), 111.3 (C-4), 111.1 (C-3), 58.8 (OCH_2), 14.2 (CH_3).

Method B. To a stirred suspension of NaH (0.080 g, 3.33 mmol) in dry MeCN (6 mL) cooled in an ice-cold bath was added a solution of ethyl benzoyl acetate (**11h**) (0.677 g, 3.43 mmol) in MeCN (4 mL), and the resulting mixture was stirred for 8 min. The ice-bath was removed, and to the obtained solution were added sulfone **6a** (0.942 g, 3.33 mmol) and MeCN (3 mL). The suspension was stirred at room temperature for 8 h, PPh_3 (1.088 g, 4.15 mmol) was added, and the reaction mixture was refluxed under stirring for 1 h. Then TsOH·H_2O (0.129 g, 0.68 mmol) was added, and reflux was continued for 1 h (TLC control). The solvent was removed in a vacuum, and the obtained residue was dissolved in $CHCl_3$ (45 mL), subsequently washed with saturated aq $NaHCO_3$ (10 mL), H_2O (5 × 10 mL), and brine (2 × 10 mL), and dried over Na_2SO_4. Then the solvent was removed in a vacuum, and the residue was purified twice by column chromatography: (1) silica gel 60 (30 g) eluting with petroleum ether/$CHCl_3$ (from 3:1 to 2:1); (2) silica gel 60 (28 g) eluting with petroleum ether/$CHCl_3$ (from 3:1 to 3:2). The main fraction was concentrated in a vacuum, and the obtained oily substance was triturated with H_2O (2 mL) upon cooling until crystallization was complete (about 30 min). The precipitate was filtered, and dried to give **17l** (0.636 g, 89%).

Ethyl 5-Methyl-2-phenyl-1*H*-pyrrole-3-carboxylate (17m). To a stirred suspension of NaH (0.054 g, 2.25 mmol) in dry MeCN (4 mL) cooled in an ice-cold bath was added a solution of ethyl benzoyl acetate (**11h**) (0.459 g, 2.33 mmol) in MeCN (3.5 mL), and the resulting mixture was stirred for 10 min. The ice-bath was removed, and to the obtained solution were added sulfone **6c** (0.668 g, 2.25 mmol) and MeCN (4.5 mL). The suspension was stirred at room temperature for 8 h, PPh_3 (0.724 g, 2.76 mmol) was added, and the reaction mixture was refluxed under stirring for 1 h (pink coloring of reaction mixture appeared). Then TsOH·H_2O (0.217 g, 1.14 mmol) was added, and reflux was continued for 30 min (pink coloring changed to slightly yellow). The solvent was removed in a vacuum, and the obtained residue was dissolved in $CHCl_3$ (26 mL), subsequently washed with saturated aq $NaHCO_3$ (10 mL), H_2O (5 × 10 mL), and brine (2 × 10 mL), and dried over Na_2SO_4. Then the solvent was removed in a vacuum, and the residue was purified by column chromatography on silica gel 60 (22 g) eluting with petroleum ether/$CHCl_3$ (from 5:1 to 3:1). The main fraction was concentrated in a vacuum, and the obtained oily substance was triturated with water (2 mL) upon cooling until crystallization was complete (about 1.5−2 h). The precipitate was filtered and dried to give **17m** (0.439 g, 85%). Mp 77.5−78.5 °C (benzene/petroleum ether, 1:4) (lit.[42] mp 81 °C); IR (Nujol) ν_{max} 3306 (vs), 3267 (vs), 3198 (m), 3179 (m) (NH), 3077 (w), 3058 (w), 3029 (w) (CH_{arom}), 1689 (sh), 1672 (br vs) (C═O), 1613 (w), 1592 (m), 1576 (w), 1532 (m) (CC_{arom}), 1241 (s), 1161 (s), 1104 (s) (C−O), 761 (s), 693 (s) (CH_{arom}) cm^{-1}; ^1H NMR (300.13 MHz, DMSO-d_6) δ 11.34 (br s, 1H, NH), 7.54−7.60 (m, 2H, ArH), 7.28−7.42 (m, 3H, ArH), 6.22 (dq, ^4J = 2.7, ^4J = 1.0 Hz, 1H, H-4), 4.08 (q, ^3J = 7.1 Hz, 2H, OCH_2), 2.20 (d, ^4J = 1.0 Hz, 3H, 5-CH_3), 1.17 (t, ^3J = 7.1 Hz, CH_3 in OEt); ^{13}C NMR (75.48 MHz, DMSO-d_6) δ 164.2 (C═O), 135.1 (C-2), 132.2 (C), 128.8 (2CH), 127.9 (C-5), 127.6 (2CH), 127.3 (CH), 110.8 (C-3), 109.0 (C-4), 58.6 (OCH_2), 14.2 (CH_3 in OEt), 12.3 (5-CH_3).

3-Benzoyl-2-phenyl-1*H*-pyrrole (17n).[43] Pyrrole **17n** (0.193 g, 96%) as a slightly yellow solid was prepared from **16n** (0.252 g, 0.82 mmol) and TsOH·H_2O (0.016 g, 0.08 mmol) in MeCN (5 mL) (reflux, 10 min) as described for **17e**. After crystallization from EtOH the color of the product did not change. Mp 153−154 °C (EtOH); IR (Nujol) ν_{max} 3234 (br vs), 3185 (br vs) (NH), 3059 (m), 3020 (w) (CH_{arom}), 1626 (vs), 1610 (vs), 1595 (vs) (C═O and CC_{arom}), 1571 (vs), 1494 (s) (CC_{arom}), 754 (s), 701 (vs) (CH_{arom}) cm^{-1}; ^1H NMR (300.13 MHz, DMSO-d_6) δ 11.81 (br s, 1H, NH), 7.64−7.70 (m, 2H, ArH), 7.21−7.53 (m, 8H, ArH), 6.93 (dd, ^3J = 2.9, ^3J = 2.3 Hz, 1H, H-5), 6.38 (dd, ^3J = 2.9, ^4J = 2.0 Hz, 1H, H-4); ^{13}C NMR (75.48 MHz, DMSO-d_6) δ 191.3 (C═O), 139.6 (C), 136.2 (C-2), 132.1 (C), 131.5 (CH), 129.0 (2CH), 128.5 (2CH), 128.0 (2CH), 127.9 (2CH), 127.4 (CH), 119.7 (C-3), 118.6 (C-5), 112.7 (C-4). Anal. Calcd for $C_{17}H_{13}NO$: C, 82.57; H, 5.30; N, 5.66. Found: C, 82.43; H, 5.45; N, 5.59.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^1H and ^{13}C NMR and IR spectra of all the synthesized compounds; $^1H,^1H$-NOESY of *trans*-**15e**; ^1H NMR spectra of the reaction mixtures formed from **12a,j,13b,m,r** and PPh_3. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(39) Previously, pyrrole **17j** was prepared as a liquid.[48] We obtained it as a crystalline solid, and our IR and NMR data for this compound differs significantly from those described in ref 48.
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