HETEROCYCLES, Vol. 103, No. 2, 2021, pp. 790 - 808. © 2021 The Japan Institute of Heterocyclic Chemistry
Received, 9th October, 2020, Accepted, 6th November, 2020, Published online, 27th November, 2020
DOI: 10.3987/COM-20-S(K)39

INTRAMOLECULAR TRANSAMIDATION-CYCLIZATION OF *N*-(α-OXOACETYL) DIAMINE: INFLUENCE OF SOLVENT, ACIDITY AND SUBSTITUENTS

Takashi Kouko, Hiroaki Miyazawa, Hideki Hikita, Hiromi Totsuka, Kazuhiro Higuchi,* and Tomomi Kawasaki*

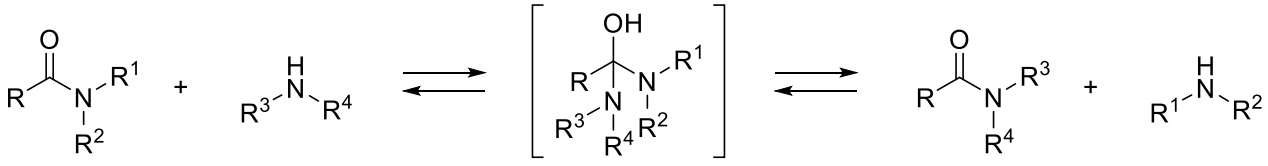
Meiji Pharmaceutical University, 2-522-1 Noshio, Kiyose, Tokyo 204-8588, Japan
khiguchi@my-pharm.ac.jp, kawasaki@my-pharm.ac.jp

This paper is dedicated to Professor Yasuyuki Kita on the occasion of his 77th birthday.

Abstract – We studied the selective formation of 3,5- and 2,5-pyrazinone via a transamidation-cyclization reaction. The equilibrium between acyl amides changed depending on the solvent, acidity, and substituents. Furthermore, selective transformation of 2,5-pyrazinone was accomplished by using a substrate with a secondary amine.

INTRODUCTION

Transamidation is the reaction of an amide and an amine to generate an amidal intermediate, followed by the elimination of another amine to give a new amide (Scheme 1).[1] The equilibrium between both amides exists in a simple reaction system. Numerous studies have been carried out to shift the equilibrium in the desired direction and thereby expand the practicality of the reaction.[2-7]



Scheme 1. Equilibrium in transamidation reaction between amides and amines

In particular, much research has been pursued on intermolecular transamidation reactions, and practical methods have recently been demonstrated.[2] In addition, a variety of intramolecular transamidations have

been reported and categorized based on the reaction driving forces: 1) release of strain on the β-lactam,[3] 2) conjugate base stability of amines vs. amides,[4] 3) nucleophilicity of amines vs. amides,[5] 4) competition between intra- and intermolecular transamidations,[6] and 5) transamidation, followed by cyclization to stable products.[7,8] Among them, transamidation-cyclization is a powerful method for small-ring synthesis. For instance, Beshore's group demonstrated the concise preparation of a series of substituted piperazinones via tandem reductive amination and transamidation-cyclization.[7a] We also accomplished the total synthesis of natural products, including hamacanthins, via a novel transamidation-cyclization as the key reaction (Figure 1).[8] Herein, we describe the effect of acidity, solvents, and substituents on the transamidation-cyclization reaction.

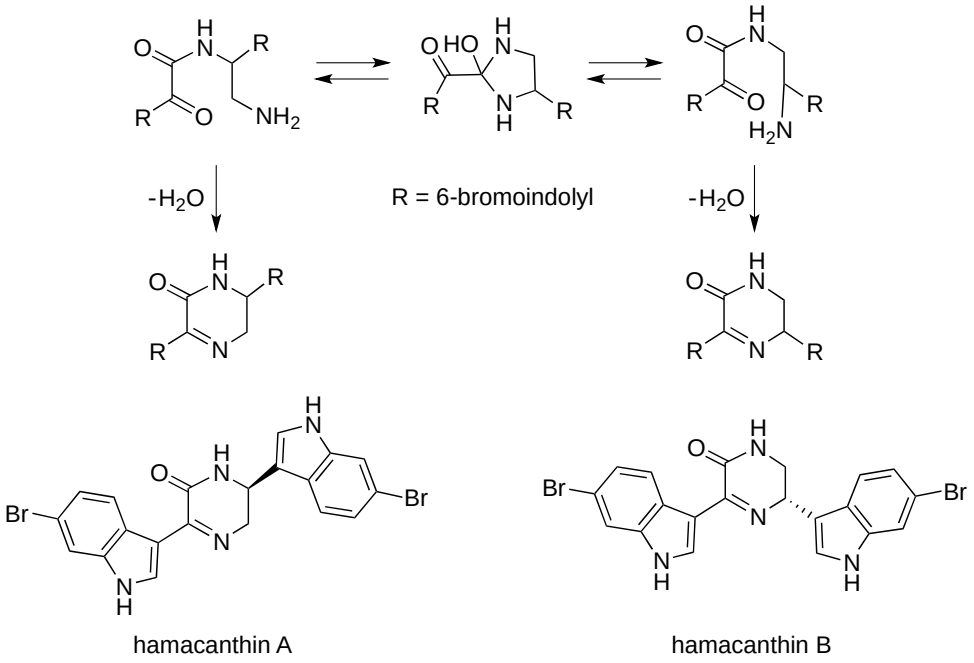
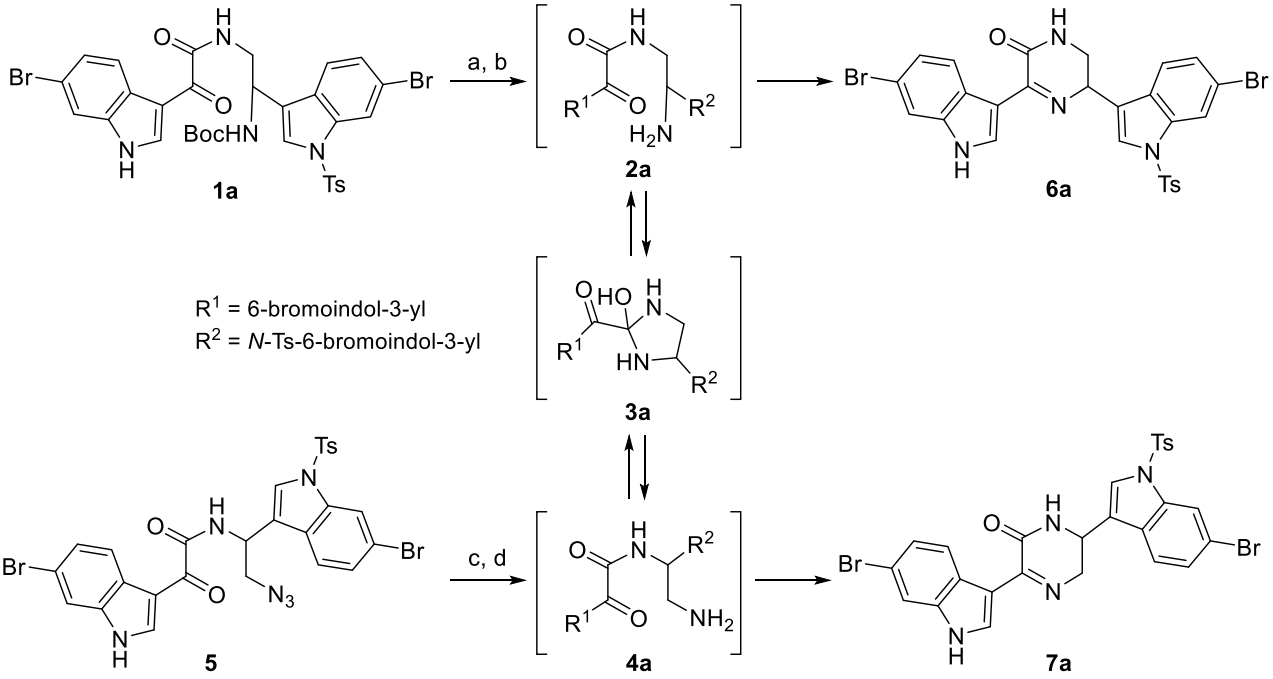


Figure 1. Synthesis of hamacanthins via transamidation-cyclization

RESULTS AND DISCUSSION

N-(α-Oxoacetyl)diamine **1a** as the reaction substrate was prepared from the readily available indolylglycine[9] using our previously reported method.[8b] Boc-deprotection of **1a** with HCO_2H at room temperature followed by heating intermediary amine **2a** in HCO_2H-containing 1,2-dichloroethane (0.14 μL/mL) proceeded with transamidation-cyclization to afford 3,5-bisindolylpyrazinone **6a** and 2,5-isomer **7a** in 35% and 42% yields, respectively (Scheme 2, Table 1, entry 4). On the other hand, after Staudinger reduction of *N*-(2-azidoethyl)-2-oxoethanamide **5**,[10] corresponding regio-isomer of **1a**, the same treatment of intermediary amine **4a** as above produced **6a** and **7a** in 21% and 47% yields, respectively. These results indicate the equilibrium for the transamidation between **2a** and **4a** via imidazolidine intermediate **3a**.

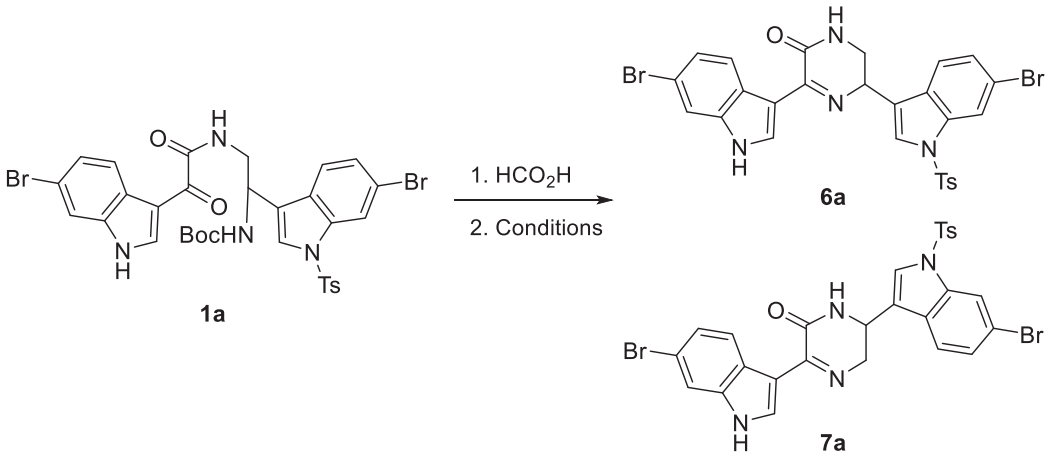


Reagents: (a) HCO_2H, CH_2Cl_2, rt; (b) HCO_2H, 1,2-dichloroethane, reflux, **6a**: 35% **7a**: 42% (2 steps), see also Table 1, entry 4; (c) Ph_3P, H_2O, THF, 40 °C; (d) HCO_2H, 1,2-dichloroethane, reflux, **6a**: 21% **7a**: 47% (2 steps).

Scheme 2. Equilibrium for transamidation between **2a** and **4a** via imidazolidine intermediate **3a**

The transamidation-cyclization was affected by amount of HCO_2H and solvent as shown in Table 1. The influence of varying amounts of HCO_2H on the transamidation-cyclization was examined (Table 1, entries 1-7). In the case of large amount of HCO_2H (entries 1 and 2), the direct cyclization of intermediary **2a** occurred in preference to transamidation to give mainly **6a** over **7a** (**6a**/**7a** = 2.1-2.2). The reactions in entries 3 and 5 denoted the same tendency in entry 4 (see also Scheme 1) to form **6a** and **7a** in nearly equal proportion (**6a**/**7a** = 0.83-1.0). The reaction with small amount of HCO_2H or without HCO_2H (entries 6 and 7) was carried out to indicate the similar selectivity (**6a**/**7a** = 1.5-2.2) to reactions in entries 1 and 2. Next, we attempted the transamidation-cyclization of **1a** in various solvents under the same conditions as entry 4 (entries 8-10).[8b] When 1,4-dioxane was used instead of 1,2-dichloroethane, **6a** was obtained in 38% yield in preference to **7a** (30%)(**6a**/**7a** = 1.3) (entry 8). When the reaction was performed with heating in either EtOH or DMF, more selective cyclization to **6a** was observed (**6a**/**7a** = 5.0−6.6; entries 9 and 10).

Table 1. Effect of acidity and solvents on transamidation-cyclization

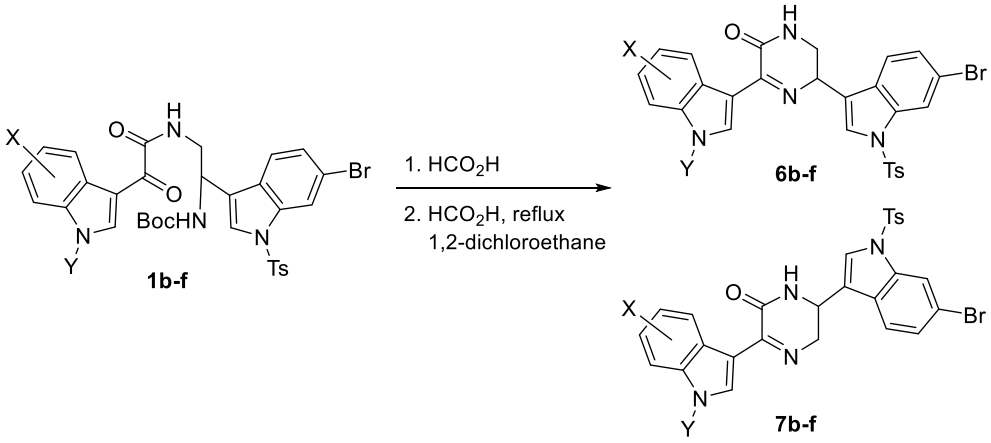


Entry	pH	Ratio of HCO_2H/Solvent (μL/mL)	Solvent	Temperature	Yields[a] **6a** (%)	**7a** (%)	Ratio **6a:7a**
1	1	3.5	1,2-DCE	reflux	55	26	2.1:1
2	2	1.4	1,2-DCE	reflux	50	23	2.2:1
3	3	0.45	1,2-DCE	reflux	50	48	1:1
4	4	0.14	1,2-DCE	reflux	35	42	1:1.2
5	5	0.07	1,2-DCE	reflux	36	41	1:1.1
6	6	0.03	1,2-DCE	reflux	41	27	1.5:1
7	7	0	1,2-DCE	reflux	53	24	2.2:1
8	4	0.14	1,4-dioxane	80 °C	38	30	1.3:1
9	4	0.14	EtOH	reflux	75	15	5:1
10	4	0.14	DMF	80 °C	46	7	6.6:1

[a]Isolate yields.

The transamidation-cyclization was also influenced by the substituent (X, Y) in the indolyl ketone moiety of **1**, as shown in Table 2. 5-Methoxyindole and *N*-methylindole derivatives **1b−c** were treated with HCO_2H under similar conditions (Table 1, entry 4) to furnish **6b−c** (45%, 39%) and **7b−c** (55%, 46%), respectively (Table 2, entries 1, 2). The trends observed in the transamidation-cyclization of **1b−c** were similar to those in the case of **1a**. The regioselectivity in the transamidation-cyclization reactions of **1d−f** bearing electron-withdrawing groups (Y = Ac, Ms, Ts; Table 2, entries 3−5) was opposite to that in the reactions of **1a−c**.[8b] For instance, the major product from *N*-acetyl derivative **1d** was **6d** (55%) together with regioisomer **7d** (42%), as shown in entry 3. In particular, a stronger electron-withdrawing group (Ts) led to the predominant formation of **6f** (68%) over **7f** (18%) (entry 5). This tendency is attributed to the electrophilicity of the carbonyl group adjacent to the indole ring, which is enhanced by electron-withdrawing groups (Y = Ac, Ms, Ts). When the electrophilicity of the carbonyl group increased, the direct cyclization was faster than the transamidation.

Table 2. Substituent effect on left-side indole

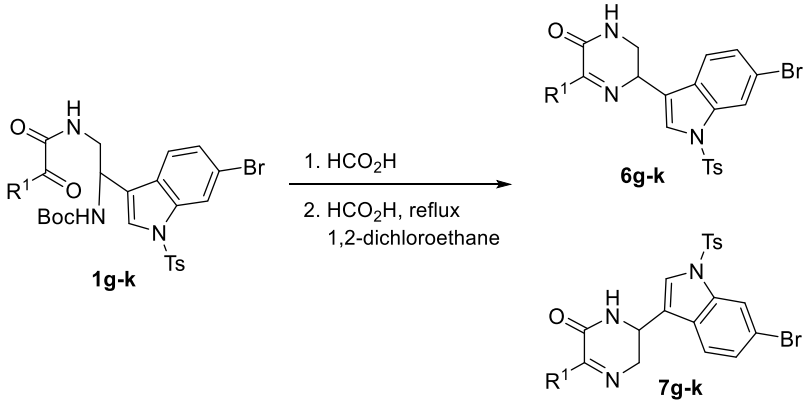


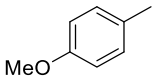
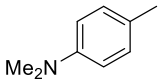
Entry	X	Y	Starting material	Yields[a]		Ratio
				6 (%)	**7** (%)	**6**:**7**
1	5-MeO	H	**1b**	45	55	1:1.2
2	6-Br	Me	**1c**	39	46	1:1.2
3	6-Br	Ac	**1d**	55	42	1.3:1
4	6-Br	Ms	**1e**	61	39	1.6:1
5	6-Br	Ts	**1f**	68	18	3.7:1

[a] Isolate yields.

Furthermore, we attempted the transamidation-cyclization of 2-oxoethanamides **1g−k** possessing other aromatic rings (R^1). The results are collated in Table 3. Pyrrole derivative **1g** gave an inseparable mixture of **6g** and **7g** (99%, 1.4:1[11]; entry 1) in the same treatment as Table 2. In contrast, the reactions of furyl, phenyl, 4-methoxy-, and 4-dimethylaminophenyl derivatives **1h−k** occurred regioselectively with direct cyclization to **6h−k** without notable transamidation to **7h−k** (**6**:**7** = 41−77:1) (entries 2−5). We clarified that this transamidation-cyclization was a characteristic reaction concerning the electron-donating indole and pyrrole nuclei.

Table 3. Effect of left units

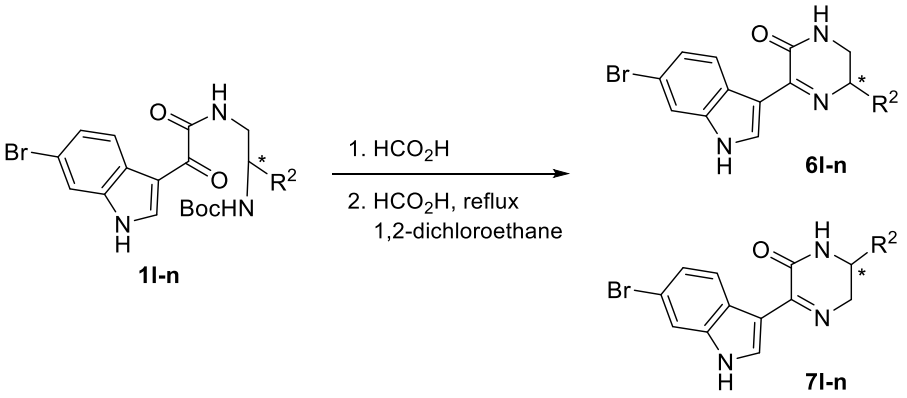


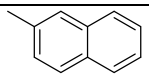
Entry	R^1	Starting material	Yields[a] **6** (%)	**7** (%)	Ratio **6**:**7**
1		**1g**	99[b]		1.4:1[c]
2		**1h**	82	2	41:1
3		**1i**	77	1	77:1
4		**1j**	80	8	10:1
5		**1k**	74[b]		11:1[c]

[a]Isolate yields. [b]A mixture of isomers. [c]The ratio was determined by HPLC.

We also investigated the effect of the substituent (R^2) on the transamidation-cyclization, as shown in Table 4. The same treatment of β-naphthyl, phenyl, and *tert*-butyl derivatives **1l−n** as Table 3 afforded **6l−n** and **7l−n** (1.1−1.8:1), respectively (Table 4, entries 1−3). Comparison of these results with the result for the reaction of **1a** (Table 1, entry 4) revealed that the transamidation-cyclization is also affected by the surrounding bulkiness of the amino group in intermediates **2** and **4** (Scheme 2).

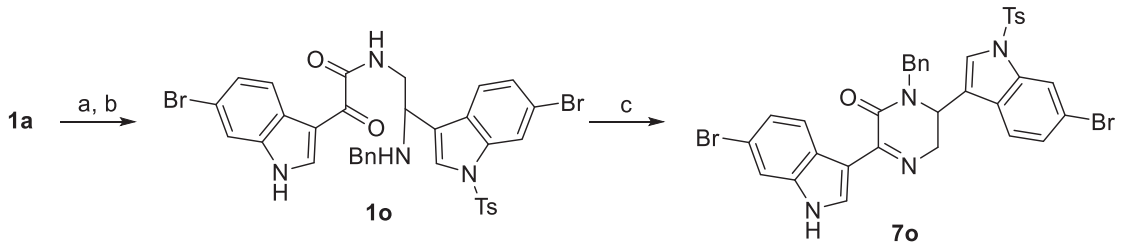
Table 4. Effect of right units



Entry	R^2	Starting material	Yields[a] **6** (%)	**7** (%)	Ratio **6**:**7**
1		*rac*-**1l**	44	40	1.1:1
2		(*R*)-**1m**	58	32	1.8:1
3		(*S*)-**1n**	51	39	1.3:1

[a]Isolate yields.

Finally, we attempted the transamidation-cyclization of secondary amine **1o** (Scheme 3).[8b] Benzylamine derivative **1o** was prepared in 71% two-step yield via the treatment of **1a** with HCO_2H to remove the Boc group, followed by reductive benzylation with benzaldehyde and $NaBH_3CN$. The transamidation-cyclization of **1o** in a similar manner proceeded smoothly to selectively afford 2,5-pyrazynone **7o** in 59% yield.



Reagents: (a) HCO_2H, CH_2Cl_2, rt; (b) PhCHO, $NaBH_3CN$, HCl, THF-MeOH (2:1), rt, 74% (2 steps); (c) HCO_2H, 1,2-dichloroethane, reflux, 59%.

Scheme 3. Transamidation-cyclization of a secondary amine **1o**

CONCLUSION

We demonstrated that the equilibrium of transamidation-cyclization is affected by the acidity, solvents, and substituents, and that it is possible to selectively construct 3,5-pyrazinone **6** and the 2,5-isomer **7**. We indicated that transamidation-cyclization is one of the useful methodologies for the natural product synthesis.[8]

EXPERIMENTAL

All melting points are uncorrected and were measured on a Yanagimoto micromelting point apparatus. Optical rotations were obtained on a JASCO DIP-140 digital polarimeter. Diastereomer ratio were determined on a HPLC (JASCO UV-975) instrument equipped with and Finepak SIL-5 column (JASCO corporation). IR spectra were recorded on a Shimadzu FTIR-8100 spectrophotometer or Shimadzu FTIR-8400s spectrophotometer. ^1H and ^{13}C NMR spectra were measured on a JEOL JNM-AL 300 (300 MHz), JEOL JNM-GSX 400 (400 MHz) or JEOL JNM-LA 500 (500 MHz) spectrometers with tetramethylsilane as an internal standard. *J*-Values are given in Hz. Mass spectra were recorded on a JEOL JMS-DX 302 or JEOL JMS 700 instrument with a direct inlet system operating at 70 eV. Elemental analyses were obtained using a Perkin-Elmer Model 240B elemental analyzer. Column chromatography was carried out on silica gel (Kanto Chemical Co. Inc., 230-400 mesh and Merck, 230-400 mesh). Hydrogen ion exponent (pH) was measured on a Horiba F-13 and electrode was used with Horiba 9677-10D. *N*-(α-Oxoacetyl)diamines **1** were prepared according to our previously reported procedure.[8]

Typical procedure for transamidation-cyclization to 3,5-pyrazinone (**6**) and 2,5-isomer (**7**). A solution of bisindole **1a** (122 mg, 0.16 mmol) and HCO_2H (4 mL) in CH_2Cl_2 (4 mL) was stirred at room temperature for 4.5 h. After removal of solvent and HCO_2H under a reduced pressure, the residue was diluted with 1,2-dichlorethane (9 mL) followed by the addition of with HCO_2H (1.26 mL). The solution was heated under reflux for 1 h, and the resulting mixture was concentrated under a reduced pressure to give a crude compound. The crude was purified by silica gel column chromatography with AcOEt-*n*-hexane (2 : 1) as an eluent to afford 3,5-pyrazinone **6a** (36 mg, 35%) and 2,5-isomer **7a** (43 mg, 42%), respectively. Other pyrazinones **6b-n**, **7b-o** were also obtained with the above method from the corresponding starting materials **1b-o**.

5-(6-Bromoindol-3-yl)-3-[6-bromo-1-{(4-methylphenyl)sulfonyl}indol-3-yl]-1*H*,2*H*,3*H*-1,4-diazin-6-one (**6a**)[8,11]: yield 35%; colorless powder; mp 261-262 °C (acetone/*n*-hexane); IR (KBr) 3399, 1690, 1624 cm^{-1}; ^1H NMR (acetone-d_6, 300 MHz) δ 2.34 (s, 3H), 3.64 (ddd, 1H, *J* = 12.8, 10.3, 2.3 Hz), 3.83 (dt, 1H, *J* = 12.8, 4.8 Hz), 5.29 (dd, 1H, *J* = 10.3, 4.8 Hz), 7.19 (dd, 1H, *J* = 8.5, 1.8 Hz), 7.39 (d, 2H, *J* = 8.6 Hz), 7.42 (dd, 1H, *J* = 8.5, 1.8 Hz), 7.63 (br, 1H), 7.66 (d, 1H, *J* = 1.8 Hz), 7.74 (d, 1H, *J* = 1.1 Hz), 7.80 (d, 1H, *J* = 8.5 Hz), 7.89 (d, 2H, *J* = 8.6 Hz), 8.18 (d, 1H, *J* = 1.8 Hz), 8.36 (d, 1H, *J* = 8.6 Hz), 8.55 (d, 1H, *J* = 2.9 Hz), 10.80 (br, 1H); ^{13}C NMR (acetone-d_6, 100 MHz) δ 21.5, 44.1, 54.6, 112.6, 115.1, 116.1, 117.1, 118.6, 123.0, 123.8, 124.4, 125.0, 125.2, 126.1, 127.1, 127.5, 129.4, 130.9, 134.0, 135.4, 136.8, 138.1, 146.5, 157.9, 158.5; MS (EI) *m/z* (%) 642 (M+4, 0.2), 640 (M+2, 0.4), 638 (M^+, 0.2), 445 (40), 443 (35), 290 (56), 288 (54), 262 (20), 260 (19), 197 (48), 195 (47), 156 (20), 139 (26), 116 (33), 92 (38), 91 (100), 89 (24), 65 (37), 63 (20), 39 (22); HRMS (EI) *m/z*: [M^+] calcd for $C_{27}H_{20}Br_2N_4O_3S$ 637.9623, found 637.9615; Anal. Calcd for $C_{27}H_{20}Br_2N_4O_3S$: C, 50.64; H, 3.15; N, 8.75. Found: C, 50.57; H, 3.38; N, 9.02.

5-(6-Bromoindol-3-yl)-2-[6-bromo-1-{(4-methylphenyl)sulfony}indol-3-yl]-1*H*,2*H*,3*H*-1,4-diazin-6-one (**7a**)[8,10]: yield 42%; colorless powder; mp >300 °C (THF/*n*-hexane), IR (KBr) 3399, 1673, 1595 cm^{-1}; ^1H NMR (acetone-d_6, 300 MHz) δ 2.22 (s, 3H), 4.25-4.28 (m, 2H), 5.07-5.21 (m, 1H), 6.93 (d, 2H, *J* = 8.6 Hz), 7.25 (dd, 1H, *J* = 8.6, 1.8 Hz), 7.45 (dd, 1H, *J* = 8.6, 1.8 Hz), 7.61 (d, 2H, *J* = 8.6 Hz), 7.65 (d, 1H, *J* = 0.9 Hz), 7.73 (d, 1H, *J* = 1.8 Hz), 7.78 (d, 1H, *J* = 8.6 Hz), 7.98 (br, 1H), 8.12 (d, 1H, *J* = 1.8 Hz), 8.36 (d, 1H, *J* = 8.6 Hz), 8.59 (d, 1H, *J* = 2.9 Hz), 10.82 (br, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 20.9, 45.4, 51.9, 110.6, 114.1, 114.7, 115.5, 117.6, 121.4, 122.2, 123.1, 124.0, 124.71, 124.74, 126.2, 126.3, 127.4, 129.8, 132.6, 133.2, 135.0, 136.9, 145.3, 157.0, 157.1; MS (EI) *m/z* (%) 642 (M+4, 18), 640 (M+2, 34), 638 (M^+, 18), 487 (52), 485 (97), 483 (51), 236 (96), 234 (100), 223 (20), 156 (46), 155 (36), 92 (25), 91

(69), 65 (23); HRMS (EI) *m/z*: [M^+] calcd for $C_{27}H_{20}Br_2N_4O_3S$ 637.9623, found 637.9619; Anal. Calcd for $C_{27}H_{20}Br_2N_4O_3S$: C, 50.64; H, 3.15; N, 8.75. Found: C, 50.88; H, 3.24; N, 8.61.

3-[6-Bromo-1-{(4-methylphenyl)sulfonyl}indol-3-yl]-5-(5-methoxyindol-3-yl)-1*H*,2*H*,3*H*-1,4-diazin-6-one (**6b**): yield 45%; colorless crystals; mp 180-182 °C (THF/*n*-hexane); IR (KBr) 3296, 1676, 1591, 1578, 1369, 1171, 1140 cm^{-1}; ^1H NMR (acetone-d_6, 300 MHz) δ 2.35 (s, 3H), 3.59 (ddd, 1H, *J* = 12.8, 11.2, 1.8 Hz), 3.62 (3H, s), 3.89 (dt, 1H, *J* = 12.8, 4.2 Hz), 5.27 (dd, 1H, *J* = 11.2, 4.2 Hz), 6.82 (dd, 1H, *J* = 8.8, 2.6 Hz), 7.37 (d, 1H, *J* = 8.8 Hz), 7.40 (d, 2H, *J* = 8.4 Hz), 7.46 (dd, 1H, *J* = 8.4, 1.5 Hz), 7.64 (br, 1H), 7.84 (d, 1H, *J* = 8.4 Hz), 7.88 (d, 1H, *J* = 1.3 Hz), 7.91 (d, 2H, *J* = 8.4 Hz), 8.09 (d, 1H, *J* = 2.6 Hz), 8.19 (d, 1H, *J* = 1.5 Hz), 8.55(d, 1H, *J* = 2.9 Hz), 10.60 (br, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz,) δ 21.0, 42.5, 53.1, 54.7, 103.8, 110.4, 111.9, 112.1, 115.6, 117.4, 122.6, 123.1, 123.9, 126.1, 126.2, 126.4, 128.2, 130.2, 130.8, 132.4, 133.6, 135.1, 145.5, 154.3, 157.2, 157.4; MS (EI) *m/z* (%) 592 (M+2, 3), 590 (M^+, 4), 445 (78), 443 (72), 291 (19), 288 (100), 262 (37), 260 (37), 147 (35), 132 (26), 127 (19), 104 (17), 91 (29); HRMS (EI) *m/z*: [M^+] calcd for $C_{28}H_{23}BrN_4O_4S$ 590.0623, found 590.0611.

2-[6-Bromo-1-{(4-methylphenyl)sulfonyl}indol-3-yl]-5-(5-methoxyindol-3-yl)-1*H*,2*H*,3*H*-1,4-diazin-6-one (**7b**): yield: 55%; yellow crystals; mp 278-280 °C (THF/*n*-hexane); IR (KBr) 3394, 1674, 1589, 1576, 1373, 1171, 1134 cm^{-1}; ^1H NMR (acetone-d_6, 300 MHz) δ 2.21 (s, 3H), 3.78 (s, 3H), 4.28 (t, 2H, *J* = 5.1 Hz), 5.18 (dd, 1H, *J* = 8.9, 5.1 Hz), 6.88 (dd, 1H, *J* = 8.8, 2.6 Hz), 6.92 (d, 2H, *J* = 8.3 Hz), 7.42 (d, 1H, *J* = 8.8 Hz), 7.46 (dd, 1H, *J* = 8.5, 1.8 Hz), 7.60 (d, 2H, *J* = 8.3 Hz), 7.67 (d, 1H, *J* = 1.1 Hz), 7.81 (d, 1H, *J* = 8.5 Hz), 7.95 (br, 1H), 8.07 (d, 1H, *J* = 2.6 Hz), 8.13 (d, 1H, *J* = 1.8 Hz), 8.54 (d, 1H, *J* = 3.1 Hz), 10.59 (br, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 20.9, 45.4, 51.9, 55.3, 104.5, 110.3, 111.6, 112.0. 115.5, 117.6, 121.4, 122.2, 124.8, 126.21, 126.28, 126.32, 127.5, 129.8, 130.9, 132.2, 133.1, 135.0, 145.2, 154.3, 157.2, 157.5; MS (EI) *m/z* (%) 592 (M+2, 36), 590 (M^+, 34), 437 (74), 435 (72), 186 (100), 91 (20); HRMS (EI) *m/z*: [M^+] calcd for $C_{28}H_{23}BrN_4O_4S$ 590.0623, found 590.0628; Anal. Calcd for $C_{28}H_{23}BrN_4O_4S$: C, 56.86; H, 3.92; N, 9.47. Found: C, 56.94; H, 4.06; N, 9.12.

5-(6-Bromo-1-methylindol-3-yl)-3-[6-bromo-1-{(4-methylphenyl)sulfonyl}indol-3-yl]-1*H*,2*H*,3*H*-1,4-diazin-6-one (**6c**): yield: 39%; yellow powder; mp 284-286 °C (CH_2Cl_2/*n*-hexane); IR (KBr) 3480, 1725, 1684, 1372, 1364 cm^{-1}; ^1H NMR (acetone-d_6, 300 MHz) δ 2.37 (s, 3H), 3.65 (ddd, 1H, *J* = 12.7, 10.3, 2.2 Hz), 3.85 (dt, 1H, *J* = 12.7, 4.8 Hz), 3.93 (s, 3H), 5.31 (dd, 1H, *J* = 10.3, 4.8 Hz), 7.23 (dd, 1H, *J* = 8.6, 1.8 Hz), 7.43 (d, 2H, *J* = 8.3 Hz), 7.44 (dd, 1H, *J* = 8.4, 1.8 Hz), 7.64 (br, 1H), 7.68 (d, 1H, *J* = 1.8 Hz), 7.74 (d, 1H, *J* = 1.1 Hz), 7.81 (d, 1H, *J* = 8.4 Hz), 7.90 (d, 2H, *J* = 8.3 Hz), 8.20 (d, 1H, *J* = 1.8 Hz), 8.37

(d, 1H, *J* = 8.6 Hz), 8.43 (s, 1H); ^{13}C NMR (acetone-d_6, 100 MHz) δ 21.5, 33.5, 44.1, 54.6, 111.5, 113.5, 116.2, 117.1, 118.6, 123.0, 123.8, 124.5, 125.1, 125.2, 126.6, 127.1, 127.5, 129.4, 130.9, 135.4, 136.8, 137.8, 138.8, 146.5, 157.8, 158.2; HRMS (FAB) *m/z*: [M+H$^+$] calcd for $C_{28}H_{23}Br_2N_4O_3S$ 652.9859, found 652.9837; Anal. Calcd for $C_{28}H_{22}Br_2N_4O_3S$: C, 51.39; H, 3.39; N, 8.56. Found: C, 51.39; H, 3.51; N, 8.32.

5-(6-Bromo-1-methylindol-3-yl)-2-[6-bromo-1-{(4-methylphenyl)sulfonyl}indol-3-yl]-1*H*,2*H*,3*H*-1,4-diazin-6-one (**7c**): yield: 46%; yellow powder; mp 280-282 °C (AcOEt/*n*-hexane); IR (KBr) 3650, 1678, 1597, 1458, 1373, 1173 cm^{-1}; ^{1}H NMR (acetone-d_6, 300 MHz) δ 2.23 (s, 3H), 3.95 (s, 3H), 4.23 (d, 2H, *J* = 5.7 Hz), 5.18 (dt, 1H, *J* = 5.7, 3.5 Hz), 6.95 (d, 2H, *J* = 7.9 Hz), 7.27 (dd, 1H, *J* = 8.6, 1.8 Hz), 7.45 (dd, 1H, *J* = 8.6, 1.8 Hz), 7.63 (d, 2H, *J* = 7.9 Hz), 7.69 (s, 1H), 7.72 (d, 1H, *J* = 1.8 Hz), 7.79 (d, 1H, *J* = 8.6 Hz), 7.98 (br, 1H), 8.12 (d, 1H, *J* = 1.8 Hz), 8.35, (d, 1H, *J* = 8.6 Hz), 8.45 (s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 20.9, 33.0, 45.5, 51.9, 109.7, 112.8, 115.0, 115.4, 117.6, 121.3, 122.2, 123.4, 124.1, 124.7, 125.1, 126.2, 126.3, 127.4, 129.8, 133.2, 135.0, 136.3, 137.4, 145.3, 156.9, 156.9; MS (EI) *m/z* (%) 656 (M+4, 21), 654 (M+2, 37), 652 (M$^+$, 19), 501 (51), 499 (100), 497 (51), 250 (86), 248 (88), 235 (16), 156 (23), 91 (27); HRMS (EI) *m/z*: [M$^+$] calcd for $C_{28}H_{22}Br_2N_4O_3S$ 651.9779, found 651.9775.

5-(1-Acetyl-6-bromoindol-3-yl)-3-[6-bromo-1-{(4-methylphenyl)sulfonyl}indol-3-yl]-1*H*,2*H*,3*H*-1,4-diazin-6-one (**6d**): yield: 55%; yellow powder; mp >300 °C (THF/*n*-hexane); IR (KBr) 3485, 1727, 1678, 1603, 1422, 1375 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 2.32 (s, 3H), 2.70 (s, 3H), 3.55-3.68 (m, 2H), 5.36 (dd, 1H, *J* = 9.6, 5.0 Hz), 7.415 (d, 2H, *J* = 8.3 Hz), 7.419 (dd, 1H, *J* = 8.5, 1.7 Hz), 7.47 (dd, 1H, *J* = 8.6, 1.8 Hz), 7.756 (d, 1H, *J* = 8.5 Hz), 7.758 (d, 1H, *J* = 0.9 Hz), 7.89 (d, 2H, *J* = 8.3 Hz), 8.07 (d, 1H, *J* = 1.7 Hz), 8.21 (d, 1H, *J* = 8.6 Hz), 8.52 (d, 1H, *J* = 1.8 Hz), 8.76 (s, 1H), 8.47 (br, 1H); MS (EI) *m/z* (%) 684 (M+4, 12), 682 (M+2, 22), 680 (M$^+$, 14), 528 (22), 526 (24), 484 (20), 445 (21), 290 (30), 288 (28), 197 (22), 156 (36), 139 (24), 118 (29), 92 (53), 92 (100), 65 (44), 43 (52); HRMS (EI) *m/z*: [M$^+$] calcd for $C_{29}H_{22}Br_2N_4O_4S$ 679.9728, found 679.9728; Anal. Calcd for $C_{29}H_{22}Br_2N_4O_4S$: C, 51.04; H, 3.25; N, 8.21. Found: C, 51.15; H, 3.48; N, 8.12.

5-(1-Acetyl-6-bromoindol-3-yl)-2-[6-bromo-1-{(4-methylphenyl)sulfonyl}indol-3-yl]-1*H*,2*H*,3*H*-1,4-diazin-6-one (**7d**): yield 42%; yellow powder; mp >300 °C (THF/*n*-hexane); IR (KBr) 3480, 1715, 1692, 1590, 1582, 1460, 1422, 1375 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 2.17 (s, 3H), 2.73 (s, 3H), 4.23 (br, 2H), 5.08 (br, 1H), 7.02 (d, 2H, *J* = 8.1 Hz), 7.48 (dd, 1H, *J* = 8.7, 1.8 Hz), 7.49 (dd, 1H, *J* = 8.5, 1.8 Hz), 7.69 (s, 1H), 7.70 (d, 2H, *J* = 8.1 Hz), 7.80 (d, 1H, *J* = 8.7 Hz), 8.02 (d, 1H, *J* = 1.8 Hz), 8.30 (d, 1H, *J* =

8.5 Hz), 8.57 (d, 1H, *J* = 1.8 Hz), 8.79 (s, 1H), 9.20 (br, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 20.9, 23.8, 45.3, 52.1, 114.7, 115.5, 117.7, 117.8, 118.0, 120.8, 122.2, 124.3, 124.8, 126.28, 126.32, 126.7, 126.9, 127.3, 129.8, 132.5, 133.3, 135.0, 135.3, 145.3, 156.1, 156.5, 169.8; MS (EI) *m/z* (%) 684 (M+4, 12), 682 (M+2, 22), 680 (M+, 11), 529 (21), 527 (40), 525 (20), 485 (23), 278 (31), 276 (27), 236 (40), 234 (40), 222 (22), 156 (43), 155 (30), 139 (24), 92 (48), 91 (100), 65 (39), 43 (32); HRMS (EI) *m/z*: [M^+] calcd for $C_{29}H_{22}Br_2N_4O_4S$ 679.9728, found 679.9729; Anal. Calcd for $C_{29}H_{22}Br_2N_4O_4S$: C; 51.04, H, 3.25; N, 8.21. Found: C, 51.03; H, 3.40; N, 7.89.

3-[6-Bromo-1-{(4-methylphenyl)sulfonyl}indol-3-yl]-5-{6-bromo-1-(methylsulfonyl)indol-3-yl}-1*H*,2*H*,3*H*-1,4-diazin-6-one (**6e**): yield 61%; colorless powder; mp 272-275 °C (THF/*n*-hexane); IR (KBr) 3006, 2924, 1740, 1688, 1597, 1374, 1173, 1163, 1138 cm^{-1}; ^{1}H NMR (acetone-d_6, 300 MHz) δ 2.37 (s, 3H), 3.58 (s, 3H), 3.77 (ddd, 1H, *J* = 12.8, 10.5, 2.2 Hz), 3.90 (dt, 1H, *J* = 12.8, 4.8 Hz), 5.43 (dd, 1H, *J* = 10.5, 4.8 Hz), 7.42 (d, 2H, *J* = 8.6 Hz), 7.44 (dd, 1H, *J* = 8.6, 1.7 Hz), 7.46 (dd, 1H, *J* = 8.4, 1.7 Hz), 7.78 (d, 1H, *J* = 1.1 Hz), 7.82 (d, 1H, *J* = 8.4 Hz), 7.83 (br, 1H), 7.92 (d, 2H, *J* = 8.6 Hz), 8.11 (d, 1H, *J* = 1.7 Hz), 8.20 (d, 1H, *J* = 1.7 Hz), 8.42 (d, 1H, *J* = 8.6 Hz), 8.76 (s, 1H); ^{13}C NMR (acetone-d_6, 100 MHz) δ 21.5, 42.0, 43.7, 55.0, 116.2, 116.4, 117.1, 118.7, 118.8, 122.9, 123.0, 125.3, 125.8, 127.1, 127.6, 127.7, 128.3, 129.3, 130.9, 133.5, 135.4, 136.1, 136.7, 146.6, 157.0, 157.6; MS (EI) *m/z* (%) 720 (M+4, 2), 718 (M+2, 4), 716 (M^+, 1), 156 (37), 139 (24), 108 (15), 92 (64), 91 (100), 65 (66), 64 (89), 63 (25), 48 (60), 39 (28); Anal. Calcd for $C_{28}H_{22}Br_2N_4O_5S_2$: C, 46.81; H, 3.09; N, 7.80. Found: C, 46.53; H, 3.17; N, 7.64.

2-[6-Bromo-1-{(4-methylphenyl)sulfonyl}indol-3-yl]-5-{6-bromo-1-(methylsulfonyl)indol-3-yl}-1*H*,2*H*,3*H*-1,4-diazin-6-one (**7e**): yield 39%; colorless powder; mp 186-189 °C (THF/*n*-hexane); IR (KBr) 2924, 1688, 1601, 1374, 1175, 1138 cm^{-1}; ^{1}H NMR (acetone-d_6, 300 MHz) δ 2.27 (s, 3H), 3.58 (s, 3H), 4.35 (d, 2H, *J* = 6.3 Hz), 5.25 (br, 1H), 7.10 (d, 2H, *J* = 8.5 Hz), 7.46 (dd, 1H, *J* = 8.5, 1.7 Hz), 7.50 (dd, 1H, *J* = 8.6, 1.7 Hz), 7.739 (d, 2H, *J* = 8.5 Hz), 7.743 (s, 1H), 7.75 (d, 1H, *J* = 1.7 Hz), 7.80 (d, 1H, *J* = 8.5 Hz), 8.13 (br, 1H), 8.15 (d, 1H, *J* = 1.7 Hz), 8.44 (d, 1H, *J* = 8.6 Hz), 8.78 (s, 1H); Anal. Calcd for $C_{28}H_{22}Br_2N_4O_5S_2$: C, 46.81; H, 3.09; N, 7.80. Found: C, 46.53; H, 3.10; N, 7.57.

3,5-Bis[6-bromo-1-{(4-methylphenyl)sulfonyl}indol-3-yl]-1*H*,2*H*,3*H*-1,4-diazin-6-one (**6f**): yield 68%; colorless powder; mp 156-159 °C (THF/*n*-hexane); IR (KBr) 2924, 1686, 1597, 1383, 1175, 1136, 1092 cm^{-1}; ^{1}H NMR (acetone-d_6, 300 MHz) δ 2.36 (s, 3H), 2.39 (s, 3H), 3.71-3.80 (m, 1H), 3.83-3.91 (m, 1H), 5.39 (dd, 1H, *J* = 10.7, 5.0 Hz), 7.39 (dd, 1H, *J* = 8.5, 1.8 Hz), 7.41 (d, 2H, *J* = 8.5 Hz), 7.43 (dd, 1H, *J* =

8.5, 1.8 Hz), 7.46 (d, 2H, *J* = 8.5 Hz), 7.77 (d, 1H, *J* = 1.1 Hz), 7.78 (d, 1H, *J* = 8.5 Hz), 7.84 (br, 1H), 7.91 (d, 2H, *J* = 8.5 Hz), 7.97 (d, 2H, *J* = 8.5 Hz), 8.18 (d, 1H, *J* = 1.8 Hz), 8.19 (d, 1H, *J* = 1.8 Hz), 8.33 (d, 1H, *J* = 8.5 Hz), 8.90 (s, 1H); Anal. Calcd for $C_{34}H_{26}Br_2N_4O_5S_2$: C, 51.40; H, 3.30; N, 7.05. Found: C, 51.24; H, 3.44; N, 6.84.

2,5-Bis[6-bromo-1-{(4-methylphenyl)sulfonyl}indol-3-yl]-1*H*,2*H*,3*H*-1,4-diazin-6-one (**7f**): yield: 18%; colorless powder; mp >300 °C (THF/*n*-hexane); IR (KBr) 2924, 1686, 1597, 1379, 1175, 1138, 1090 cm^{-1}; ^1H NMR (acetone-d_6, 300 MHz) δ 2.13 (s, 3H), 2.23 (s, 3H), 4.30 (dd, 2H, *J* = 6.1, 2.6 Hz), 5.23 (br, 1H), 6.72 (d, 2H, *J* = 8.3 Hz), 7.36 (d, 2H, *J* = 8.3 Hz), 7.40 (dd, 1H, *J* = 8.6, 1.8 Hz), 7.42 (dd, 1H, *J* = 8.6, 1.8 Hz), 7.50 (d, 2H, *J* = 8.3 Hz), 7.65 (s, 1H), 7.75 (d, 1H, *J* = 8.6 Hz), 7.96 (d, 2H, *J* = 8.3 Hz), 8.08 (d, 1H, *J* = 1.8 Hz), 8.13 (br, 1H), 8.21 (d, 1H, *J* = 1.8 Hz), 8.27 (d, 1H, *J* = 8.6 Hz), 8.91 (s, 1H); MS (EI) *m/z* (%) 796 (M+4, 1), 794 (M+2, 2), 792 (M^+, 1), 278 (22), 156 (48), 155 (17), 138 (61), 123 (17), 107 (16), 92 (54), 90 (100), 65 (37), 39 (18); Anal. Calcd for $C_{34}H_{26}Br_2N_4O_5S_2$: C, 51.40; H, 3.30; N, 7.05. Found: C, 51.17; H, 3.42; N, 6.85.

3-[6-Bromo-1-{(4-methylphenyl)sulfonyl}indol-3-yl]-5-(1-phenylpyrrol-2-yl)-1*H*,2*H*,3*H*-1,4-diazin-6-one (**6g**) and 2-[6-Bromo-1-{(4-methylphenyl)sulfonyl}indol-3-yl]-5-(1-phenylpyrrol-2-yl)-1*H*,2*H*,3*H*-1,4-diazin-6-one (**7g**): yield 99% (regioisomer mixture, HPLC conditions; AcOEt/*n*-hexane = 1 : 1, flow 1.0 mL/min, Rt (min) 27.7/22.5, area ratio = 1.4 : 1); ^1H NMR (acetone-d_6, 300 MHz) δ 2.24 (s, 3H x 0.4), 2.37 (s, 3H x 0.6), 3.45 (ddd, 1H x 0.6, *J* = 12.8, 10.5, 2.2 Hz), 3.88 (dt, 1H x 0.6, *J* = 12.8, 4.8 Hz), 4.14-4.16 (dd, 2H x 0.4, *J* = 7.3, 5.5 Hz), 4.95 (dd, 1H x 0.6, *J* = 10.5, 4.8 Hz), 5.14 (br, 1H x 0.4), 6.29 (dd, 1H x 0.6, *J* = 3.9, 2.8 Hz), 6.32 (dd, 1H x 0.4, *J* = 3.8, 2.8 Hz), 6.92-8.20 (m, 16H); HRMS (FAB) *m/z*: [$M+H^+$] calcd for $C_{29}H_{24}BrN_4O_3S$ 587.0752, found 587.0744.

3-[6-Bromo-1-{(4-methylphenyl)sulfonyl}indol-3-yl]-5-furan-2-yl-1*H*,2*H*,3*H*-1,4-diazin-6-one (**6h**): yield 82%; green powder; mp 276-283 °C (AcOEt/*n*-hexane); IR (KBr) 3405, 1690, 1595, 1373, 1173, 1132 cm^{-1}; ^1H NMR (acetone-d_6, 300 MHz) δ 2.32 (s, 3H), 3.64 (ddd, 1H, *J* = 12.8, 10.5, 2.0 Hz), 3.84 (dt, 1H, *J* = 12.8, 5.0 Hz), 5.26 (dd, 1H, *J* = 10.5, 5.0 Hz), 6.55 (dd, 1H, *J* = 3.5, 1.8 Hz), 7.37 (d, 2H, *J* = 8.4 Hz), 7.40 (dd, 1H, *J* = 8.4, 1.8 Hz), 7.47 (d, 1H, *J* = 3.5 Hz), 7.65 (br, 1H), 7.67 (d, 1H, *J* = 1.8 Hz), 7.70 (d, 1H, *J* = 1.1 Hz), 7.76 (d, 1H, *J* = 8.4 Hz), 7.85 (d, 2H, *J* = 8.4 Hz), 8.13 (d, 1H, *J* = 1.8 Hz); ^{13}C NMR (acetone-d_6, 100 MHz) δ 21.5, 43.9, 54.9, 112.4, 117.0, 118.4, 118.6, 122.8, 123.2, 125.3, 127.1, 127.5, 130.9, 135.4, 136.7, 145.9, 146.5, 150.0, 152.4, 156.2, 178.0; MS (EI) *m/z* (%) 513 (M+2, 84), 511 (M^+, 97), 509 (24), 377 (15), 360 (24), 358 (96), 356 (100), 354 (26), 330 (22), 328 (39), 326 (18), 303

(18), 301 (58), 299 (42), 222 (19), 220 (38), 155 (21), 96 (17), 91 (53); HRMS (EI) *m/z*: [M^+] calcd for $C_{23}H_{18}BrN_3O_4S$ 511.0201, found 511.0196.

2-[6-Bromo-1-{(4-methylphenyl)sulfonyl}indol-3-yl]-5-furan-2-yl-1*H*,2*H*,3*H*-1,4-diazin-6-one (**7h**): yield 2%; colorless powder; mp 237-239 °C (acetone); IR (KBr) 3505, 1680, 1595, 1373, 1171, 1140 cm^{-1}; ^1H NMR (acetone-d_6, 300 MHz) δ 2.35 (s, 3H), 4.16 (dd, 1H, *J* = 17.0, 8.3 Hz), 4.24 (dd, 1H, *J* = 17.0, 4.8 Hz), 5.18 (ddd, 1H, *J* = 8.1, 5.5, 2.8 Hz), 6.60 (dd, 1H, *J* = 3.4, 1.7 Hz), 7.33 (d, 2H, *J* = 8.4 Hz), 7.45 (dd, 1H, *J* = 8.5, 1.7 Hz), 7.50 (d, 1H, *J* = 3.4 Hz), 7.745 (d, 1H, *J* = 1.7 Hz), 7.746 (d, 1H, *J* = 0.7 Hz), 7.78 (d, 1H, *J* = 8.5 Hz), 7.83 (d, 2H, *J* = 8.4 Hz), 7.94 (br, 1H), 8.15 (d, 1H, *J* = 1.7 Hz); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 21.0, 45.4, 51.9, 111.7, 115.4, 116.8, 117.6, 120.5, 122.2, 124.9, 126.2, 126.4, 127.3, 130.0, 133.3, 134.9, 145.2, 145.5, 148,5, 151.2, 155.4; MS (EI) *m/z* (%) 513 (M+2, 36), 511 (M^+, 36), 359 (22), 258 (96), 357 (28), 256 (100), 107 (47), 91 (25); HRMS (EI) *m/z*: [M^+] calcd for $C_{23}H_{18}BrN_3O_4S$ 511.0201, found 511.0193.

3-[6-Bromo-1-{(4-methylphenyl)sulfonyl}indol-3-yl]-5-phenyl-1*H*,2*H*,3*H*-1,4-diazin-6-one (**6i**): yield 77%; colorless powder; mp 215-218 °C (AcOEt/*n*-hexane); IR (KBr) 1684, 1599, 1173 cm^{-1}; ^1H NMR (acetone-d_6, 300 MHz) δ 2.36 (s, 3H), 3.72 (ddd, 1H, *J* = 13.0, 10.1, 2.4 Hz), 3.90 (dt, 1H, *J* = 13.0, 4.8 Hz), 5.31 (dd, 1H, *J* = 10.1, 4.8 Hz), 7.39-7.49 (m, 6H), 7.72 (br, 1H), 7.74 (d, 1H, *J* = 1.1 Hz), 7.80 (d, 1H, *J* = 8.4 Hz), 7.90 (d, 2H, *J* = 8.4 Hz), 8.03-8.08 (m, 2H), 8.18 (d, 1H, *J* = 1.8 Hz); MS (EI) *m/z* (%) 523 (M+2, 40), 521 (M^+, 38), 369 (81), 367 (100), 365 (23), 340 (19), 338 (20), 311 (54), 309 (51), 289 (28), 222 (25), 220 (22), 155 (29), 141 (21), 129 (21), 118 (23), 104 (55), 91 (68), 89 (22); HRMS (EI) *m/z*: [M^+] calcd for $C_{25}H_{20}BrN_3O_3S$, 521.0409, found 521.0409; Anal. Calcd for $C_{25}H_{20}BrN_3O_3S$: C, 57.48; H, 3.86; N, 8.04. Found: C, 57.59; H, 4.11; N, 7.92.

2-[6-Bromo-1-{(4-methylphenyl)sulfonyl}indol-3-yl]-5-phenyl-1*H*,2*H*,3*H*-1,4-diazin-6-one (**7i**): yield 1%; colorless powder; mp 247-248 °C (THF/*n*-hexane); IR (KBr) 1674, 1611, 1372, 1252, 1173, 1138, 1094 cm^{-1}; ^1H NMR (acetone-d_6, 300 MHz) δ 2.32 (s, 3H), 4.24-4.27 (m, 2H), 5.19-5.25 (m, 1H), 7.25 (d, 2H, *J* = 7.9 Hz), 7.39-7.49 (m, 4H), 7.63-7.73 (m, 4H), 7.97-8.03 (m, 3H), 8.15 (d, 1H, *J* = 1.3 Hz); MS (EI) *m/z* (%) 523 (M+2, 55), 521 (M^+, 52), 369 (47), 368 (93), 367 (53), 366 (87), 156 (15), 117 (100), 91 (27); HRMS (EI) *m/z*: [M^+] calcd for $C_{25}H_{20}BrN_3O_3S$ 521.0409, found 521.0411; Anal. Calcd for $C_{25}H_{20}BrN_3O_3S$: C, 57.48; H, 3.86; N, 8.04. Found: C, 57.56; H, 3.91; N, 7.80.

3-[6-Bromo-1-{(4-methylphenyl)sulfonyl}indol-3-yl]-5-(4-methoxyphenyl)-1*H*,2*H*,3*H*-1,4-diazin-6-one (**6j**): yield 80%; colorless powder; mp 127-129 °C (AcOEt/*n*-hexane); IR (KBr) 2926, 1680, 1597, 1262, 1173, 1123, 1094 cm^{-1}; ^1H NMR (acetone-d_6, 300 MHz) δ 2.35 (s, 3H), 3.65 (dd, 1H, *J* = 12.9, 10.3 Hz), 3.84 (s, 3H), 3.86 (ddd, 1H, *J* = 12.9, 4.6, 3.5 Hz), 5.25 (dd, 1H, *J* = 10.3, 4.6 Hz), 6.94 (d, 2H, *J* = 9.0 Hz), 7.39 (d, 2H, *J* = 8.4 Hz), 7.44 (dd, 1H, *J* = 8.4, 1.7 Hz), 7.70 (br, 1H), 7.72 (d, 1H, *J* = 0.9 Hz), 7.78 (d, 1H, *J* = 8.4 Hz), 7.89 (d, 2H, *J* = 8.4 Hz), 8.09 (d, 2H, *J* = 9.0 Hz), 8.17 (d, 1H, *J* = 1.7 Hz); HRMS (FAB) *m/z*: [M+H$^+$] calcd for $C_{26}H_{23}BrN_3O_4S$ 552.0593, found 552.0588; Anal. Calcd for $C_{26}H_{22}BrN_3O_4S$: C, 56.53; H, 4.01; N, 7.61. Found: C, 56.47; H, 4.30; N, 7.44.

2-[6-Bromo-1-{(4-methylphenyl)sulfonyl}indol-3-yl]-5-(4-methoxyphenyl)-1*H*,2*H*,3*H*-1,4-diazin-6-one (**7j**): yield 8%; colorless crystals; mp 234-236 °C (AcOEt/*n*-hexane); IR (KBr) 2926, 2851, 1742, 1671, 1260, 1171 cm^{-1}; ^1H NMR (acetone-d_6, 300 MHz) δ 2.34 (s, 3H), 3.87 (s, 3H), 4.20 (d, 2H, *J* = 6.4 Hz), 5.17-5.22 (m, 1H), 6.98 (d, 2H, *J* = 9.0 Hz), 7.26 (d, 2H, *J* = 8.4 Hz), 7.46 (dd, 1H, *J* = 8.4, 1.7 Hz), 7.73 (d, 1H, *J* = 0.9 Hz), 7.79 (d, 1H, *J* = 8.4 Hz), 7.80 (d, 2H, *J* = 8.4 Hz), 7.96 (br, 1H), 8.06 (d, 2H, *J* = 9.0 Hz), 8.15 (d, 1H, *J* = 1.7 Hz); ^{13}C NMR (acetone-d_6, 100 MHz) δ 21.5, 47.5, 53.4, 55.6, 113.7, 117.1, 118.8, 121.9, 122.2, 122.5, 125.8, 127.2, 127.5, 130.8, 131.2, 135.2, 136.7, 146.5, 157.6, 160.9, 162.1; HRMS (FAB) *m/z*: [M+H$^+$] calcd for $C_{26}H_{23}BrN_3O_4S$ 552.0593, found 552.0598.

3-[6-Bromo-1-{(4-methylphenyl)sulfonyl}indol-3-yl]-5-(4-dimethylaminophenyl)-1*H*,2*H*,3*H*-1,4-diazin-6-one (**6k**) and 2-[6-Bromo-1-{(4-methylphenyl)sulfonyl}indol-3-yl]-5-(4-dimethylaminophenyl)-1*H*,2*H*,3*H*-1,4-diazin-6-one (**7k**): yield 74% (11 : 1, regioisomer mixture, the ratio was determined by HPLC) (regioisomer mixture, HPLC conditions; AcOEt/*n*-hexane = 1 : 1, flow 1.0 mL/min, Rt (min) 69.6/62.6, area ratio = 11 : 1); major product **6k** ^1H NMR (acetone-d_6, 300 MHz) δ 2.35 (s, 3H), 3.03 (s, 6H), 3.60 (ddd, 1H, *J* = 12.7, 10.1, 2.6 Hz), 3.84 (dt, 1H, *J* = 12.7, 4.7 Hz), 5.19 (dd, 1H, *J* = 10.1, 4.7 Hz), 6.71 (d, 2H, *J* = 9.2 Hz), 7.40 (d, 2H, *J* = 8.5 Hz), 7.44 (dd, 1H, *J* = 8.4, 1.7 Hz), 7.58 (br, 1H), 7.71 (d, 1H, *J* = 1.1 Hz), 7.77 (d, 1H, *J* = 8.4 Hz), 7.89 (d, 2H, *J* = 8.5 Hz), 8.06 (d, 2H, *J* = 9.2 Hz), 8.17 (d, 1H, *J* = 1.7 Hz); minor product **7k** ^1H NMR (acetone-d_6, 300 MHz) δ 2.31 (s, 3H), 3.04 (s, 6H), 4.14-4.16 (m, 2H), 5.14 (br, 1H), 6.75 (d, 2H, *J* = 9.0 Hz), 7.21 (d, 2H, *J* = 8.4 Hz), 7.45 (dd, 1H, *J* = 8.4, 1.7 Hz), 7.68 (s, 1H), 7.75 (d, 2H, *J* = 8.4 Hz), 7.77 (d, 1H, *J* = 8.4 Hz), 7.80 (d, 2H, *J* = 8.4 Hz), 7.89 (br, 1H), 8.03 (d, 2H, *J* = 9.0 Hz), 8.14 (d, 1H, *J* = 1.7 Hz); HRMS (EI) *m/z*: [M$^+$] calcd for $C_{27}H_{25}BrN_4O_3S$ 564.0831, found 564.0822.

5-(6-Bromoindol-3-yl)-3-naphthyl-1*H*,2*H*,3*H*-1,4-diazin-6-one (**6l**): yield 44%; yellow powder; mp 242 °C (AcOEt/*n*-hexane); IR (KBr) 3401, 1674, 1580 cm^{-1}; ^1H NMR (acetone-d_6, 300 MHz) δ 3.54 (ddd, 1H, *J* = 13.0, 11.4, 1.8 Hz), 3.83 (dt, 1H, *J* = 13.0, 4.9 Hz), 5.24 (dd, 1H, *J* = 11.4, 4.9 Hz), 7.28 (dd, 1H, *J* = 8.6, 1.8 Hz), 7.46-7.57 (m, 2H), 7.65 (br, 1H), 7.71 (d, 1H, *J* = 1.8 Hz), 7.72 (dd, 1H, *J* = 8.4, 1.7 Hz), 7.87-7.97 (m, 2H), 7.97 (d, 1H, *J* = 8.4 Hz), 8.11 (d, 1H, *J* = 1.7 Hz), 8.58 (d, 1H, *J* = 8.6 Hz), 8.63 (d, 1H, *J* = 2.7 Hz), 10.82 (br, 1H); ^{13}C NMR (acetone-d_6, 100 MHz) δ 46.3, 61.5, 112.9, 115.0, 116.1, 124.4, 125.3, 126.26, 126.29, 126.4, 126.5, 126.7, 128.2, 128.6, 128.7, 132.4, 133.5, 133.8, 134.2, 139.9, 158.0, 158.2; MS (EI) *m/z* (%) 419 (M+2, 86), 417 (M^+, 88), 236 (98), 234 (100), 155 (28), 154 (56); HRMS (EI) *m/z*: [M^+] calcd for $C_{22}H_{16}BrN_3O$ 417.0477, found 417.0473; Anal. Calcd for $C_{22}H_{16}BrN_3O$: C, 63.17; H, 3.86; N, 10.05. Found: C, 63.41; H, 4.08; N, 9.77.

5-(6-Bromoindol-3-yl)-2-naphthyl-1*H*,2*H*,3*H*-1,4-diazin-6-one (**7l**): yield 40%; colorless powder; mp: 209 °C (THF/*n*-hexane); IR (KBr) 3453, 1672, 1584 cm^{-1}; ^1H NMR (acetone-d_6, 300 MHz) δ 4.08 (dd, 1H, *J* = 16.5, 9.3 Hz), 4.31 (ddd, 1H, *J* = 16.4, 4.8, 1.1 Hz), 5.03 (ddd, 1H, *J* = 9.3, 4.8, 2.0 Hz), 7.24 (dd, 1H, *J* = 8.6, 1.8 Hz), 7.40-7.55 (m, 2H), 7.63 (dd, 1H, *J* = 8.6, 1.8 Hz), 7.67 (d, 1H, *J* = 1.8 Hz), 7.84 (br, 1H), 7.86-8.05 (m, 4H), 8.42 (d, 1H, *J* = 8.6 Hz), 8.62 (d, 1H, *J* = 1.8 Hz), 10.76 (br, 1H); ^{13}C NMR (acetone-d_6, 100 MHz) δ 54.9, 55.6, 112.6, 114.9, 116.0, 124.2, 125.2, 125.5, 126.2, 126.4, 126.7, 126.9, 128.2, 128.5, 129.0, 133.3, 133.8, 134.0, 137.8, 138.0, 158.0, 158.3; MS (EI) *m/z* (%) 419 (M+2, 71), 417 (M^+, 78), 362 (72), 360 (72), 154 (100); HRMS (EI) *m/z*: [M^+] calcd for $C_{22}H_{16}BrN_3O$ 417.0477, found 417.0468; Anal. Calcd for $C_{22}H_{16}BrN_3O$: C, 63.17; H, 3.86; N, 10.05. Found: C, 62.98; H, 3.83; N, 10.23.

(*R*)-5-(6-Bromoindol-3-yl)-3-phenyl-1*H*,2*H*,3*H*-1,4-diazin-6-one (**6m**): yield 58%; yellow powder; mp 207-209 °C (AcOEt/*n*-hexane); $[\alpha]_D^{22}$ –375.7 (*c* 0.98, acetone); IR (KBr) 3378, 1673, 1574, 1561, 1441, 1408, 1329 cm^{-1}; ^1H NMR (acetone-d_6, 300 MHz) δ 3.42 (ddd, 1H, *J* = 12.7, 11.3, 2.5 Hz), 3.72 (dt, 1H, *J* = 12.7, 5.0, Hz), 5.06 (dd, 1H, *J* = 11.3, 5.0 Hz), 7.25 (dd, 1H, *J* = 8.5, 1.8 Hz), 7.33 (t, 1H, *J* = 7.4 Hz), 7.42 (t, 2H, *J* = 7.4 Hz), 7.56 (br, 1H), 7.60 (d, 2H, *J* = 7.4 Hz), 7.69 (d, 1H, *J* = 1.8 Hz), 8.51 (d, 1H, *J* = 8.5 Hz), 8.59 (s, 1H), 10.76 (br, 1H); ^{13}C NMR (acetone-d_6, 100 MHz) δ 46.5, 61.4, 112.8, 115.0, 116.0, 124.4, 125.2, 126.2, 127.7, 127.8, 129.0, 133.7, 138.1, 142.3, 157.9, 158.1; MS (EI) *m/z* (%) 369 (M+2, 97), 367 (M^+, 100), 312 (93), 310 (95), 231 (23), 222 (58), 141 (17), 118 (15), 104 (43), 89 (19); HRMS (EI) *m/z*: [M^+] calcd for $C_{18}H_{14}BrN_3O$ 367.0320, found 367.0327; Anal. Calcd for $C_{18}H_{14}BrN_3O$: C, 58.71; H, 3.83; N, 11.41. Found: C, 58.61; H, 4.13; N, 11.08.

(*R*)-5-(6-Bromoindol-3-yl)-2-phenyl-1*H*,2*H*,3*H*-1,4-diazin-6-one (**7m**): yield 32%; yellow crystals; mp 211-214 °C (AcOEt/*n*-hexane); $[\alpha]_D^{22}$ –81.4 (*c* 1.03, acetone); IR (KBr) 3418, 1676, 1610, 1588, 1447, 1391, 1331, 1117 cm^{-1}; ^1H NMR (acetone-d_6, 300 MHz) δ 3.96 (dd, 1H, *J* = 16.3, 9.2 Hz), 4.22 (dd, 1H, *J* = 16.3, 4.8 Hz), 4.84 (ddd, 1H, *J* = 9.2, 4.8, 1.9 Hz), 7.24 (dd, 1H, *J* = 8.5, 1.8 Hz), 7.30 (t, 1H, *J* = 7.1 Hz), 7.37 (t, 2H, *J* = 7.1 Hz), 7.45 (d, 2H, *J* = 7.1 Hz), 7.66 (d, 1H, *J* = 1.8 Hz), 7.77 (br, 1H), 8.40 (d, 1H, *J* = 8.5 Hz), 8.59 (d, 1H, *J* = 2.8 Hz), 10.75 (br, 1H); MS (EI) *m/z* (%) 369 (M+2, 82), 367 (M^+, 83), 236 (98), 235 (19), 234 (100), 222 (23), 220 (23), 155 (21), 104 (19); HRMS (EI) *m/z*: [M^+] calcd for $C_{18}H_{14}BrN_3O$ 367.0320, found 367.0318; Anal. Calcd for $C_{18}H_{14}BrN_3O$: C, 58.71; H, 3.83; N, 11.41. Found: C, 58.63; H, 3.73; N, 11.41.

(*S*)-5-(6-Bromoindol-3-yl)-3-*tert*-butyl-1*H*,2*H*,3*H*-1,4-diazin-6-one (**6n**): yield 51%; colorless powder; mp 289-291 °C (AcOEt/*n*-hexane); $[\alpha]_D^{22}$ +324.8 (*c* 0.93, acetone); IR (KBr) 3254, 2949, 1655, 1585, 1566, 1447 cm^{-1}; ^1H NMR (acetone-d_6, 300 MHz) δ 1.17 (s, 9H), 3.28 (ddd, 1H, *J* = 12.8, 11.4, 1.0 Hz), 3.41 (dd, 1H, *J* = 12.8, 4.2 Hz), 3.51 (ddd, 1H, *J* = 11.4, 5.7, 4.2 Hz), 7.29 (dd, 1H, *J* = 8.4, 1.8 Hz), 7.42 (br, 1H), 7.67 (d, 1H, *J* = 1.8 Hz), 8.52 (d, 1H, *J* = 8.4 Hz), 8.53 (d, 1H, *J* = 3.1 Hz), 10.72 (br, 1H); ^{13}C NMR (acetone-d_6, 100 MHz) δ 27.2, 34.3, 40.1, 66.3, 113.1, 114.9, 115.9, 124.2, 125.0, 126.2, 133.2, 138.1, 157.0, 158.2; MS (EI) *m/z* (%) 349 (M+2, 35), 347 (M^+, 36), 292 (100), 290 (95), 264 (50), 262 (52), 222 (19), 220 (17), 183 (45), 142 (15); HRMS (EI) *m/z*: [M^+] calcd for $C_{16}H_{18}BrN_3O$ 347.0633, found 347.0627.

(*S*)-5-(6-Bromoindol-3-yl)-2-*tert*-butyl-1*H*,2*H*,3*H*-1,4-diazin-6-one (**7n**): yield 39%; yellow crystals; mp 232-245 °C (AcOEt/*n*-hexane); $[\alpha]_D^{22}$ +13.6 (*c* 1.25, acetone); IR (KBr) 3406, 3192, 1678, 1593, 1393 cm^{-1}; ^1H NMR (acetone-d_6, 400 MHz) δ 3.38 (ddd, 1H, *J* = 8.5, 5.0, 2.7 Hz), 3.84 (dd, 1H, *J* = 16.6, 8.5 Hz), 4.10 (dd, 1H, *J* = 16.6, 5.0 Hz), 7.27 (dd, 1H, *J* = 8.5, 2.0 Hz), 7.28 (br, 1H), 7.68 (d, 1H, *J* = 2.0 Hz), 8.45 (d, 1H, *J* = 8.5 Hz), 8.53 (d, 1H, *J* = 2.9 Hz), 10.71 (br, 1H); ^{13}C NMR (acetone-d_6, 100 MHz) δ 26.6, 34.0, 49.3, 59.2, 112.7, 114.8, 115.9, 124.1, 125.1, 126.2, 132.9, 138.0, 157.9, 158.5; MS (EI) *m/z* (%) 349 (M+2, 99), 347 (M^+, 100), 236 (98), 292 (35), 290 (33), 264 (56), 262 (57), 236 (60), 234 (60), 222 (61), 220 (61), 183 (55), 155 (18), 141 (21), 114 (15); HRMS (EI) *m/z*: [M^+] calcd for $C_{16}H_{18}BrN_3O$ 347.0633, found 347.0632; Anal. Calcd for $C_{16}H_{18}BrN_3O$: C, 55.18; H, 5.21; N, 12.07. Found: C, 55.38; H, 5.41; N, 11.96.

1-Benzyl-5-(6-bromoindol-3-yl)-2-[6-bromo-1-{(4-methylphenyl)sulfonyl}indol-3-yl]-1*H*,2*H*,3*H*-1,4-diazin-6-one (**7o**): yield: 59%; colorless powder; 257-258 °C (AcOEt/*n*-hexane); IR (KBr) 3405, 1655,

1590, 1448, 1420, 1375 cm^{-1}; ^1H NMR (acetone-d_6, 300 MHz) δ 2.12 (3H, s), 4.13 (dd, 1H, *J* = 16.7, 5.2 Hz), 4.20 (d, 1H, *J* = 15.0 Hz), 4.40 (dd, 1H, *J* = 16.7, 2.2 Hz), 5.18 (ddd, 1H, *J* = 5.2, 2.2, 1.3 Hz), 5.52 (d, 1H, *J* = 15.0 Hz), 6.58 (d, 2H, *J* = 8.6 Hz), 7.20 (dd, 1H, *J* = 8.6, 1.8 Hz), 7.26-7.44 (m, 9H), 7.68 (d, 1H, *J* = 8.6 Hz), 7.79 (d, 1H, *J* = 1.8 Hz), 8.08 (d, 1H, *J* = 1.8 Hz), 8.19 (d, 1H, *J* = 8.6 Hz), 8.74 (d, 1H, *J* = 2.8 Hz), 10.92 (br, 1H); ^{13}C NMR (acetone-d_6, 100 MHz) δ 21.3, 49.1, 51.6, 52.5, 112.4, 115.1, 116.2, 117.1, 118.9, 121.6, 122.4, 124.4, 125.5, 125.7, 126.2, 126.9, 127.3, 128.1, 128.6, 128.7, 129.2, 130.5, 133.8, 134.7, 136.9, 138.21, 138.24, 146.1, 157.7, 158.1; MS (EI) *m/z* (%) 732 (M+4, 49), 730 (M+2, 89), 728 (M^+, 49), 469 (86), 467 (81), 380 (19), 378 (20), 236 (62), 234 (62), 155 (25), 91 (100); HRMS (EI) *m/z*: [M^+] calcd for $C_{34}H_{26}Br_2N_4O_3S$ 728.0092, found 728,0080; Anal. Calcd for $C_{34}H_{26}Br_2N_4O_3S$: C, 55.90; H, 3.59; N, 7.67. Found: C, 56.02; H, 3.71; N, 7.53.

ACKNOWLEDGEMENTS

We thank N. Eguchi, T. Suzuki, T. Koseki, and S. Yamada in the Analytical Center from our University for microanalysis and spectral measurements.

REFERENCES AND NOTES

1. For review of transamidation reaction: (a) M. K. Marković, D. Marković, and S. Laclef, *Synthesis*, 2020, **52**, 3231; (b) P. Acosta-Guzmán, A. Mateus-Gómez, and D. Gamba-Sánchez, *Molecules*, 2018, **23**, 2382; (c) R. M. Lanigan and T. D. Sheppard, *Eur. J. Org. Chem.*, 2013, 7453; (d) M. E. González-Rosende, E. Castillo, J. Lasri, and J. Sepúlveda-Arques, *Prog. React. Kinet. Mech.*, 2004, **29**, 311.
2. For selected references about intermolecular transamidation reaction: (a) M. Fairley, L. J. Bole, F. F. Mulks, L. Main, A. R. Kennedy, C. T. O'Hara, J. García-Alvarez, and E. Hevia, *Chem. Sci.*, 2020, **11**, 6500; (b) Y. Shimizu, H. Morimoto, M. Zhang, and T. Ohshima, *Angew. Chem. Int. Ed.*, 2012, **51**, 8564; (c) N. A. Stephenson, J. Zhu, S. H. Gellman, and S. S. Stahl, *J. Am. Chem. Soc.*, 2009, **131**, 10003; (d) E. Bon, D. C. H. Bigg, and G. Bertrand, *J. Org. Chem.*, 1994, **59**, 4035.
3. (a) M. Alajarín, A. Vidal, and F. Tovar, *Tetrahedron*, 2005, **61**, 1531; (b) A. Klapars, S. Parris, K. W. Anderson, and S. L. Buchwald, *J. Am. Chem. Soc.*, 2004, **126**, 3529; (c) A. Vasudevan, C. I. Villamil, and S. W. Djuric, *Org. Lett.*, 2004, **6**, 3361; (d) B. K. Banik, S. Samajdar, and I. Banik, *Tetrahedron Lett.*, 2003, **44**, 1699; (e) L. Banfi, G. Guanti, and M. Rasparini, *Eur. J. Org. Chem.*, 2003, 1319; (f) H. H. Wasserman, H. Matsuyama, and R. Robinson, *Tetrahedron*, 2002, **58**, 7177; (g) K. Papadopoulos and D. W. Young, *Tetrahedron Lett.*, 2002, **43**, 3951; (h) L. Banfi, G. Guanti, and M. Rasparini, *Tetrahedron Lett.*, 1998, **39**, 9539; (i) L. Crombie, D. Haigh, R. C. F. Jones, and A. R. Mat-Zin, *J. Chem. Soc., Perkin Trans. 1*, 1993, 2055; (j) L. Crombie, D. Haigh, R. C. F. Jones, and

A. R. Mat-Zin, *J. Chem. Soc., Perkin Trans. 1*, 1993, 2047; (k) M. J. Begley, L. Crombie, D. Haigh, R. C. F. Jones, S. Osborne, and R. A. B. Webster, *J. Chem. Soc., Perkin Trans. 1*, 1993, 2027; (l) L. Crombie, R. C. F. Jones, and D. Haigh, *Tetrahedron Lett.*, 1986, **27**, 5151; (m) L. Crombie, R. C. F. Jones, and D. Haigh, *Tetrahedron Lett.*, 1986, **27**, 5147; (n) H. H. Wasserman and R. P. Robinson, *Heterocycles*, 1984, **21**, 279; (o) L. Crombie, R. C. F. Jones, Ab. R. Mat-Zin, and S. Osborne, *J. Chem. Soc., Chem. Commun.*, 1983, 959; (p) L. Crombie, R. C. F. Jones, S. Osborne, and A. R. Mat-Zin, *J. Chem. Soc., Chem. Commun.*, 1983, 959; (q) H. H. Wasserman and G. D. Berger, *Tetrahedron*, 1983, **39**, 2459; (r) H. H. Wasserman and J. S. Wu, *Heterocycles*, 1982, **17**, 581; (s) M. S. Manhas, S. G. Amin, and A. K. Bose, *Heterocycles*, 1976, **5**, 669; (t) H. Peter, B. Müller, and H. Bickel, *Helv. Chim. Acta*, 1975, **58**, 2450; (u) B. J. R. Nicolaus, E. Bellasio, G. Pagani, L. Mariani, and E. Testa, *Helv. Chim. Acta*, 1965, **48**, 1867.

4. (a) T. C. Stephens and W. P. Unsworth, *Synlett*, 2020, **31**, 133; (b) A. R. Maddirala and P. R. Andreana, *Eur. J. Org. Chem.*, 2016, 196; (c) J.-F. Zheng, L.-R. Jin, and P.-Q. Huang, *Org Lett.*, 2004, **6**, 1139; (d) C. Jentgens, R. Hofmann, A. Guggisberg, S. Bienz, and M. Hesse, *Helv. Chim. Acta*, 1997, **80**, 966; (e) U. A. Häusermann, A. Linden, J. Song, and M. Hesse, *Helv. Chim. Acta*, 1996, **79**, 1995; (f) P. Kuehne, A. Linden, and M. Hesse, *Helv. Chim. Acta*, 1996, **79**, 1085; (g) M. K.-H. Doll, A. Guggisberg, and M. Hesse, *Helv. Chim. Acta*, 1996, **79**, 541; (h) N. Itoh, H. Matsuyama, M. Yoshida, N. Kamigata, and M. Iyoda, *Heterocycles*, 1995, **41**, 415; (i) B. F. Tawil, A. Guggisberg, and M. Hesse, *Tetrahedron*, 1992, **48**, 3775; (j) E. Stephanou, A. Guggisberg, and M. Hesse, *Helv. Chim. Acta*, 1979, **62**, 1932; (k) U. Kramer, H. Schmid, A. Guggisberg, and M. Hesse, *Helv. Chim. Acta*, 1979, **62**, 811; (l) U. Kramer, A. Guggisberg, M. Hesse, and H. Schmid, *Helv. Chim. Acta*, 1978, **61**, 1342; (m) A. Guggisberg, U. Kramer, C. Heidelberger, R. Charubala, E. Stephanou, M. Hesse, and H. Schmid, *Helv. Chim. Acta*, 1978, **61**, 1050; (n) A. Guggisberg, B. Dabrowski, U. Kramer, C. Heidelberger, E. Stephanou, M. Hesse, and H. Schmid, *Helv. Chim. Acta*, 1978, **61**, 1039; (o) U. Kramer, A. Guggisberg, M. Hesse, and H. Schmid, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 200; (p) U. Kramer, A. Guggisberg, M. Hesse, and H. Schmid, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 861; (q) G. I Glover, R. B. Smith, and H. Rapoport, *J. Am. Chem. Soc.*, 1965, **87**, 2003.

5. (a) Y. A. Kovygin, K. S. Shikhaliev, M. Y. Krysin, A. Y. Potapov, I. V. Ledenyova, Y. A. Kosheleva, and D. Y. Vandyshev, *Chem. Heterocycl. Compd.*, 2019, **55**, 748; (b) K.-I. Tanaka, T. Maesoba, and H. Sawanishi, *Heterocycles*, 2006, **68**, 183; (c) K.-I. Tanaka, H. Nemoto, and H. Sawanishi, *Tetrahedron: Asymmetry*, 2005, **16**, 1989; (d) K.-I. Tanaka, H. Nemoto, and H. Sawanishi, *Tetrahedron: Asymmetry*, 2005, **16**, 809; (e) M. Bella, S. Kobbelgaard, and K. A. Jørgensen, *J. Am. Chem. Soc.*, 2005, **127**, 3670; (f) N. Langlois, *Tetrahedron Lett.*, 2002, **43**, 9531;

(g) N. Langlois, *Org. Lett.*, 2002, **4**, 185; (h) A. Dinsmore, P. M. Doyle, P. B. Hithcock, and D. W. Young, *Tetrahedron Lett.*, 2000, **41**, 10153; (i) P. J. Murray, I. D. Starkey, and J. E. Davies, *Tetrahedron Lett.*, 1998, **39**, 6721; (j) A. N. Bowler, A. Dinsmore, P. M. Doyle, and D. W. Young, *J. Chem. Soc., Perkin Trans. 1*, 1997, 1297; (k) A. Dinsmore, P. M. Doyle, and D. W. Young, *Tetrahedron Lett.*, 1995, **36**, 7503; (l) J. Bohrisch, H. Faltz, M. Pätzel, and J. Liebscher, *Tetrahedron*, 1994, **50**, 10701; (m) A. N. Bowler, P. M. Doyle, and D. W. Young, *J. Chem. Soc., Chem. Comm.*, 1991, 314.

6. (a) L. Tang, X.-M. Li, J. H. Matuska, Y.-H. He, and Z. Guan, *Org. Lett.*, 2018, **20**, 5618; (b) T. J. Potter and J. A. Ellman, *Org. Lett.*, 2017, **19**, 2985; (c) N. Hoshiya, K. Noda, Y. Mihara, N. Kawai, and J.-i. Uenishi, *J. Org. Chem.*, 2015, **80**, 7790; (d) K. Kim and S. H. Hong, *J. Org. Chem.*, 2015, **80**, 4152; (e) D. Gahtory, M. Chouhan, R. Sharma, and V. A. Nair, *Org. Lett.*, 2013, **15**, 3942; (f) M. E. González-Rosende, E. Castillo, B. Asíns, R. Mamouni, and J. Sepúlveda-Arques, *Tetrahedron*, 2007, **63**, 8709; (g) R. K. Grover, A. P. Kesarwani, G. K. Srivastava, B. Kundub, and R. Roy, *Tetrahedron*, 2005, **61**, 5011; (h) Y. Jiang, J. Zhao, and L. Hu, *Tetrahedron Lett.*, 2002, **43**, 4589; (i) F. Johnson, I. Havus, R. G. Gentles, S. Sibutani, H.-C. Lee, C. R. Iden, and R. Rieger, *J. Am. Chem. Soc.*, 1992, **114**, 4923; (j) T.-L. Ho, *Synth. Commun.*, 1980, **10**, 469; (k) I. D. Entwistle, *Tetrahedron Lett.*, 1979, **20**, 555; (l) G. Just and G. Rosebery, *Synth. Commun.*, 1973, **3**, 447; (m) K. Undheim and P. E. Fjeldstad, *J. Chem. Soc.*, *Perkin Trans. 1,* 1973, 829; (n) K. L. Kirk and L. A. Cohen, *J. Am. Chem. Soc.*, 1972, **38**, 8142; (o) C. Panetta, *J. Org. Chem.*, 1969, **34**, 2773; (p) M. Masaki, T. Kitahara, H. Kurita, and M. Ohta, *J. Am. Chem. Soc.*, 1968, **90**, 4508; (q) R. W. Holly and A. D. Holly, *J. Am. Chem. Soc.*, 1952, **74**, 3069.
7. (a) D. C. Beshore and J. C. Dinsmore, *Org. Lett.*, 2002, **4**, 1201; (b) D. C. Beshore and C. J. Dinsmore, *Tetrahedron Lett.*, 2000, **41**, 6309.
8. (a) T. Kouko, K. Matsumura, and T. Kawasaki, *Tetrahedron*, 2005, **61**, 2309; (b) T. Kawasaki, T. Kouko, H. Totsuka, and K. Hiramatsu, *Tetrahedron Lett.*, 2003, **44**, 8849.
9. T. Kawasaki, H. Enoki, K. Matsumura, M. Ohyama, M. Inagawa, and M. Sakamoto, *Org. Lett.*, 2000, **2**, 3027.
10. B. Jiang, C.-G. Yang, and J. Wang, *J. Org. Chem.*, 2001, **66**, 4865.
11. As the behavior of **6g** and **7g** on HPLC experiment is similar to that of **6a** and **7a**, the major product was decided to be **7g**.