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REACTIONS OF 2-TRIPHENYLPHOSPHOIMINO-1-AZAAZULENES WITH ARYL ISOCYANATES AND ARYL ISOTHIOCYANATES †

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Abstract – Reaction of 2-triphenylphosphoimino-1-azaazulenes (**4a-c**), prepared from 2-amino-1-azaazulenes, with some aryl isocyanates gave 2-arylimino-3-aryl-2,3,4,4a-tetrahydro-1,3,4a-triazabenz[*a*]azulen-4-one (**6**) as major products. Reaction of aryl isothiocyanates gave 2-arylimino-3-aryl-2,3,4,4a-tetrahydro-1,3,4a-triazabenz[*a*]azulene-4-thiones (**10**).

INTRODUCTION

It is well known that iminophosphoranes are excellent sources for the forming of carbon-nitrogen double bond by aza-Wittig reaction. Especially for synthetic strategy of fused heterocycles, the aza-Wittig reaction of aryl iminophosphoranes with heterocumulenes such as aryl isocyanates followed by electrocyclization reaction[1-4] as well as the cycloaddition reaction of heterocycles[5-9] with heterocumulenes such as aryl isocyanates[10-12] or carbodiimide[13] is served as excellent methods.

The azaazulene chemistry has been attracted for attentions regarding the interesting chemical and physical natures as well as their physiological properties of azaazulenes as non-alternant heteroaromatics.[14-17] In the line of our investigation of azaazulene chemistry[14-16] and a construction of novel fused heterocycles, we recently reported the synthesis and some reactions of the 3-phenyl-8-tri-

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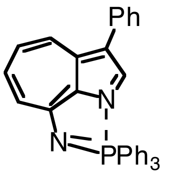
† Dedicated to Professor Barry M. Trost on occasion of his 65th birthday.

phenylphosphoimino-1-azaazulene (**1**), where the reactions of **1** with aryl aldehydes, aryl isocyanates, and dimethyl acetylenedicarboxylate gave some variety of fused heterocycles such as **2** and **3**.[18-20] Although it is considered that 2-phosphoimino-1-azaazulenes (**4**)[21] would also have potentialities for construction of novel fused heterocycles, related investigations were few. One interest report was appeared, where the reaction of 2-tributylphosphoimino-1-azaazulene with 2-bromotropone gave 6,7-diazaazuleno[1,2-*a*]azulene in low yield.[21] We previously communicated about the reaction of 2-triphenylphosphoimino-1-azaazulene with aryl isocyanates.[22] Recently, Nitta *et al.* reported the similar results of the reaction of 2-triphenylphosphoimino-1-azaazulenes.[23,24] We advanced the reactions from the view point of synthesis of azaazulene fused heterocycles, and now report full details of the synthesis of 2-triphenylphosphoimino-1-azaazulenes (**4a-c**) and some reactions of **4a-c** with aryl isocyanates and aryl isothiocyanates.

RESULTS AND DISCUSSION

Reaction with aryl isocyanates. As starting materials for heterocyclization by aza-Wittig reaction, 2-triphenylphosphoimino-1-azaazulenes (**4a-c**) were prepared in good yields in two ways as follows; Procedure A) reactions of 2-amino-1-azaazulenes (**5a-c**) with dibromotriphenylphosphorane and Procedure B) reactions of **5a-c** with triphenylphosphine and hexachloroethane in the presence of triethylamine (Scheme 1). Obtained **4a** as above was accord with reported one,[21] which was prepared by Staudinger reaction.



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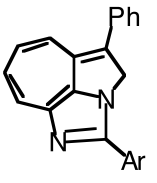

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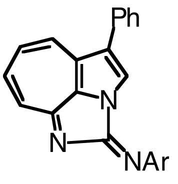

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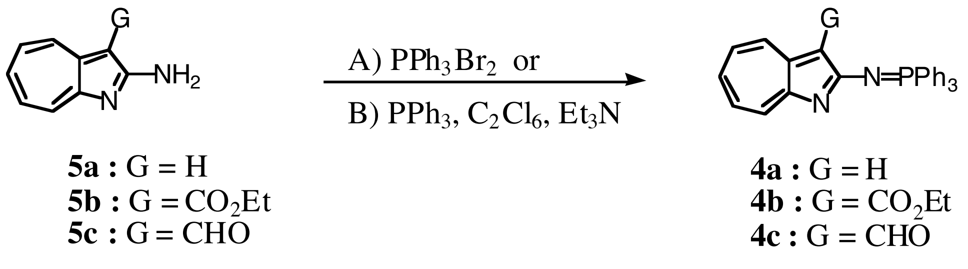
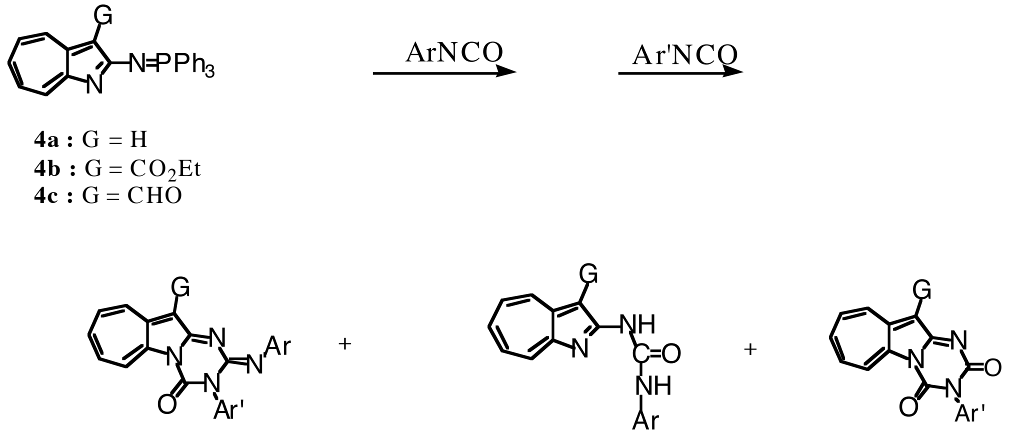


Scheme 1

Treatment of **4a** with an equivalent molar of phenyl isocyanate at room temperature for 24 h gave a mixture of 2-phenylimino-3-phenyl-2,3,4,4a-tetrahydro-1,3,4a-triazabenz[*a*]azulen-4-one (**6aa**) (20%), being as an aza-Wittig-electrocyclization product, together with **7aa** (14%) and recovered (**4a**) (52%) (Run 1). Treatment of **4a** with excess molar of phenyl isocyanate gave **6aa** in 70% yield, exclusively (Run 2). Under heating condition at 60 ℃, the yield was improved. But when more elevated temperature was adopted (over 80 ℃), as an abnormal aza-Wittig reaction[25] would be caused. Indeed, when the reaction was performed under reflux in xylene, 3-phenyl-2,3,4,4a-tetrahydro-1,3,4a-triazabenz[*a*]azulene-2,4-dione[26] (**8aa**) was obtained in 17% together with **6aa** (49%) and **7aa** (37%) (Run 4). Although Nitta *et al.* reported similar results,[23,24] they could not alluded about the reason of the abnormal aza-Wittig reaction.

The similar treatments of **4a-c** with some aryl isocyanates (*p*-methylphenyl isocyanate, *p*-methoxyphenyl isocyanate, and *p*-acetylphenyl isocyanate) were carried out and the results were listed in Table 1. On the reaction of **4a** with aryl isocyanate, it seems that the electron-withdrawing groups of aryl isocyanates facilitated the reaction and excellent yields of normal aza-Wittig reaction products were achieved (Runs 5-11).



4a : G = H
4b : G = CO_2Et
4c : G = CHO

6aa : G = H, Ar = Ar' = Ph
6ab : G = H, Ar = Ar' = *p*-Tol
6ac : G = H, Ar = Ar' = *p*-C_6H_4OMe
6ad : G = H, Ar = Ar' = *p*-C_6H_4Ac
6ae : G = H, Ar = Ph, Ar' = *p*-Tol
6ba : G = CO_2Et, Ar = Ar' = Ph
6bb : G = CO_2Et, Ar = Ar' = *p*-Tol
6ca : G = CHO, Ar = Ar' = Ph
6cb : G = CHO, Ar = Ar' = *p*-Tol
6cc : G = CHO, Ar = Ar' = *p*-C_6H_4OMe
6cd : G = CHO, Ar = Ar' = *p*-C_6H_4Ac

7aa : G = H, Ar = Ph
7ab : G = H, Ar = *p*-Tol
7ac : G = H, Ar = *p*-C_6H_4OMe
7ad : G = H, Ar = *p*-C_6H_4Ac
7ba : G = CO_2Et, Ar = Ph
7bb : G = CO_2Et, Ar = *p*-Tol
7ca : G = CHO, Ar = Ph
7cb : G = CHO, Ar = *p*-Tol
7cc : G = CHO, Ar = *p*-C_6H_4OMe
7cd : G = CHO, Ar = *p*-C_6H_4Ac

8aa : G = H, Ar' = Ph
8ab : G = H, Ar' = *p*-Tol
8ac : G = H, Ar' = *p*-C_6H_4OMe
8ad : G = H, Ar' = *p*-C_6H_4Ac
8ba : G = CO_2Et, Ar' = Ph
8bb : G = CO_2Et, Ar' = *p*-Tol
8ca : G = CHO, Ar' = Ph
8cb : G = CHO, Ar' = *p*-Tol
8cc : G = CHO, Ar' = *p*-C_6H_4OMe
8cd : G = CHO, Ar' = *p*-C_6H_4Ac

Scheme 2

For investigation of substitution effects and participation of substituents on 1-azaazulene nuclei, the reactions of ethyl 2-phosphoimino-1-azaazulene-3-carboxylate (**4b**) and 2-phosphoimino-1-azaazulene-3-carbaldehyde (**4c**) with aryl isocyanates were examined. It is expected that the cyclization would occur between ester group and carbodiimide, an aza-Wittig product. Thus the reaction of **4b** with aryl isocyanate was performed in a sealed tube under heating. Similar results as for **4a** was obtained; a slightly depression of the cylclization was observed and a few of **4b** was recovered (Runs 12, 13).

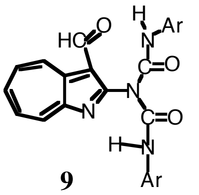
It is known that the reaction of 3-phosphoiminothiazole-4-carbaldehyde with aryl isocyanate underwent electrocyclic ring closure followed by Dimroth-type rearrangement and gave thiazolo[4,5-*d*]pyrimidines. Therefore we next examined the reaction of **4c** with aryl isocyanates (Runs 14-20). Treatment of **4c** with excess molar of phenyl isocyanate at room temperature for 56 h gave **9** (17%) together with **7ca** (15%), and a cyclization product was not obtained. For excepting to produce Dimroth-type products, elevated reaction temperature was adopted. But no Dimroth-type product was obtained, and **6**, **7**, and **8** were obtained. It seems that prolonged heating brought a depression of the yield of **8**. Compound (**8**) would react with excess molar of aryl isocyanate to give polymeric products. In the reaction, 2-(*N'*-arylureido)-1-azaazulenes (**7**) were obtained as major products. This shows that strong electron-withdrawing substituent on 1-azaazulene nuclei decreases the nucleophilicity of *N*-1 of (1-azaazulen-2-

Table 1. Reactions of **4** with aryl isocyanates.

Run	Reactants	Reagents	Conditions				Puroducts
			Solvents	Ratio	Temp/℃	Time / h	(Yield / %)
1	**4a**	PhNCO	Benzene	1:1	rt	24	**6aa** (20)**7aa**(14)**4a** (52)
2	**4a**	PhNCO	Benzene	1:3	rt	24	**6aa** (70)
3	**4a**	PhNCO	Benzene	1:3	60	3	**6aa** (84)
4	**4a**	PhNCO	Xylene	1:3	reflux	0.5	**6aa**(49)**7aa**(37)**8aa**(17)
5	**4a**	*p*-MeC$_6$H$_4$NCO	Benzene	1:1	rt	24	**6ab** (33)**4a** (48)
6	**4a**	*p*-MeC$_6$H$_4$NCO	Benzene	1:3	rt	24	**6ab** (72)
7	**4a**	*p*-MeC$_6$H$_4$NCO	Benzene	1:3	60	3	**6ab** (84)
8	**4a**	*p*-MeOC$_6$H$_4$NCO	Benzene	1:3	rt	24	**6ac** (61)
9	**4a**	*p*-MeOC$_6$H$_4$NCO	Benzene	1:3	60	3	**6ac** (73)
10	**4a**	*p*-AcC$_6$H$_4$NCO	Benzene	1:3	rt	8	**6ad** (95)
11	**4a**	*p*-AcC$_6$H$_4$NCO	Benzene	1:3	60	3	**6ad** (86)
12[a)]	**4b**	PhNCO	Benzene	1:3	60	4	**6ba** (45)**4b** (10)
13[a)]	**4b**	*p*-AcC$_6$H$_4$NCO	Benzene	1:3	60	4	**6bb** (75)**4b** (12)
14	**4c**	PhNCO	Benzene	1:3	rt	56	**7ca** (15)**9** (17)
15	**4c**	PhNCO	Xylene	1:3	120	2	**6ca** (20)**7ca** (16)**8ca**(1)
16	**4c**	*p*-MeC$_6$H$_4$NCO	Xylene	1:3	120	2.5	**6cb** (12)**7cb** (15)
17[a)]	**4c**	*p*-MeC$_6$H$_4$NCO	Xylene	1:3	120	0.5	**6cb**(49)**7cb**(15)**8cb**(19)
18	**4c**	*p*-MeOC$_6$H$_4$NCO	Xylene	1:3	120	2.5	**6cc** (1)**7cc** (37)
19[a)]	**4c**	*p*-MeOC$_6$H$_4$NCO	Xylene	1:3	120	1	**6cc**(4)**7cc** (34)**8cc** (30)
20	**4c**	*p*-AcC$_6$H$_4$NCO	Xylene	1:3	120	4	**6cb** (2)**7cb** (58)

a) Reacted in a sealed tube.

yl)carbodiimides, and subsequent attack of another molar of aryl isocyanate to the carbodiimide would became difficult. As the result, the intermediate carbodiimides were stabilized, and hydrolysis of the carbodiimides on work-up produces the 2-(*N*'-arylureido)-1-azaazulenes (**7**).



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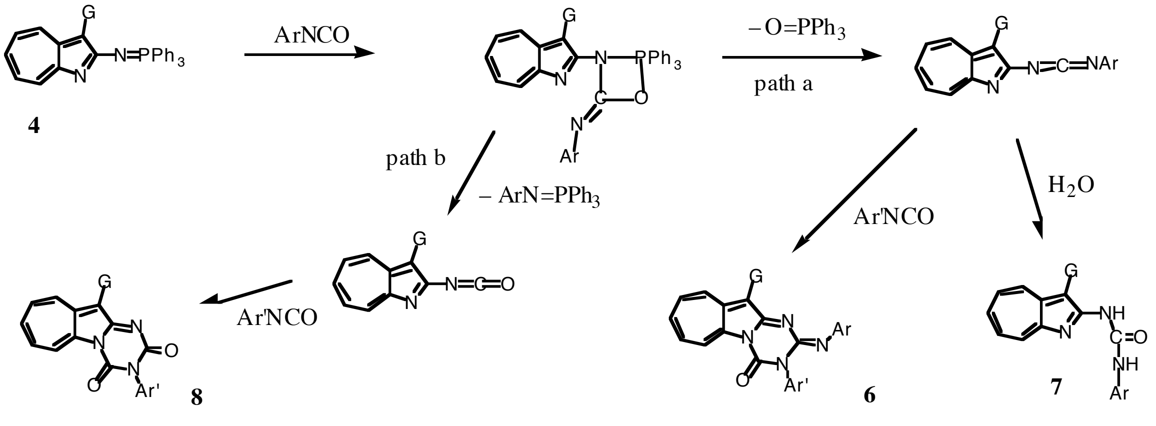
For clarification of reaction mechanism, a cross-reaction was performed. A mixture of **4a** with an equivalent molar of phenyl isocyanate in benzene was stirred for 24 h at room temperature. Then *p*-methylphenyl isocyanate was added to the mixture and stirring was continued for 24 h at room temperature. After separation by silica gel chromatography, the reaction mixture of **6aa** (22%), **7aa** (4%), **6ae** (10%), and **4a** (18%) was obtained and the structures and yields were decided by ^{1}HNMR spectrum. The result shows that the reaction proceeded *via* (1-azaazulen-2-yl)carbodiimide as an intermediate. Plausible mechanism is shown in Scheme 3. A normal aza-Wittig reaction affords a carbodiimide derivative (path a), and successive cycloaddition reaction with aryl isocyanate produces **6**. Hydrolysis of the carbodiimide on work-up gives **7**. An abnormal aza-Wittig reaction gives 1-azaazulen-2-yl isocyanate (path b), and a successive reaction with aryl isocyanate to gives **8**.



Scheme 3

These structures were deduced by spectroscopic data as well as by elemental analyses, and the structure of **6aa** was decided by X-Ray crystal structure analysis.

ORTEP drawing[28] of **6aa** is shown in Figure 1. Bond alternation is clearly observed, and the coupling constants of seven-membered ring protons existed in *J* = 11.4-11.5 Hz and *J* = 9.4-9.6 Hz in the ^{1}H NMR spectrum of **6aa** and the results consisted with the observation of X-Ray structure analysis. From the results, it is considered that compound (**6aa**) would have inherently extended 8-azaheptafulvene character.

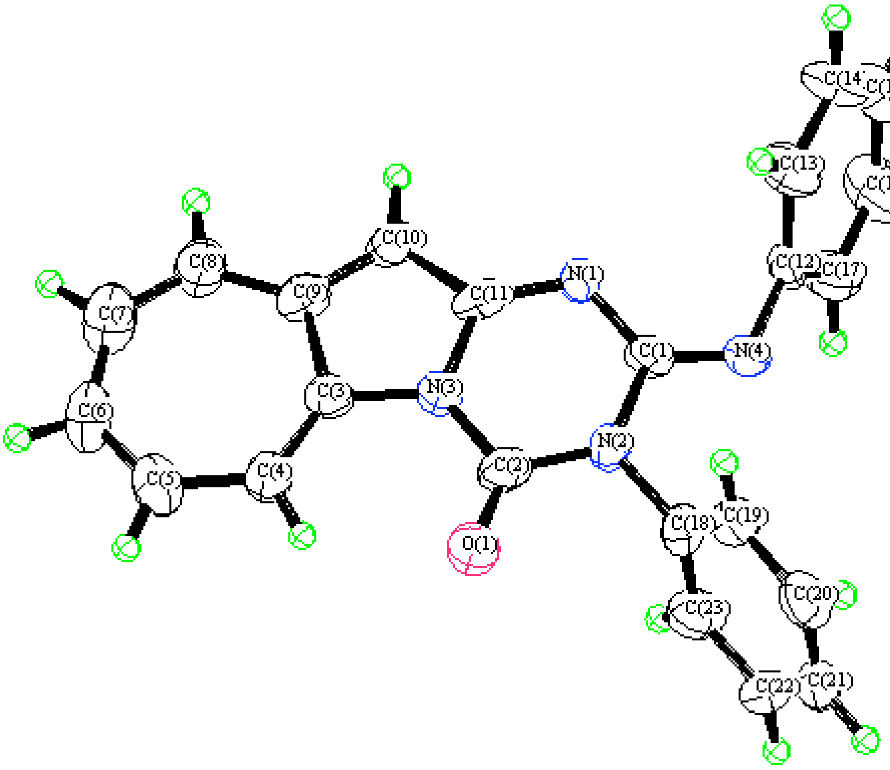
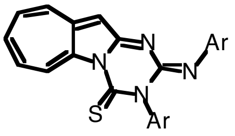


Figure 1. ORTEP drawing of **6aa** with thermal ellipsoids (50% probability).

Selective bond length (Å): N(1)−C(1) 1.41(1), N(1)−C(11) 1.300(9), N(2)−C(1) 1.447(9), N(2)−C(2) 1.394(9), N(3)−C(2) 1.390(9), N(3)−C(3) 1.421(9), N(3)−C(11) 1.414(9), N(4)−C(1) 1.272(9), C(3)−C(4) 1.35(1), C(3)−C(9) 1.47(1), C(4)−C(5) 1.43(1), C(5)−C(6) 1.36(1), C(6)−C(7) 1.41(1), C(7)−C(8) 1.35(1), C(8)−C(9) 1.44(1), C(9)−C(10) 1.35(1), C(10)−C(11) 1.41(4).

Reaction with isothiocyanates. We next examined the reaction with aryl isothiocyanates. Treatment of **4a** with excess molar phenyl isothiocyanate in benzene in a sealed tube at room temperature did not proceed, but when the reaction was performed at elevated temperature at 60 ℃ for 20 h, two products was obtained. Two cycloadducts, dark red prisms (**10a**) in 39% and red needles (**6aa**) in 14%, were isolated. Compound (**10a**), which was assigned as 2-phenylimino-3-phenyl-2,3,4,4a-tetrahydro-1,3,4a-triazabenz[*a*]azulene-4-thione, had components of $C_{23}H_{16}N_4S$ from MS spectrum [*m/z* 380 (M^+)] and elemental analysis. In the ^1H NMR spectrum of **10a**, the seven-membered protons resonated at δ 9.92 (1H, d, *J* 9.5), 7.33 (1H, d, *J* 10.6), 7.00 (1H, dd, *J* 10.8 and 9.5), 6.94 (1H, dd, *J* 10.6 and 9.4) and 6.90 (1H, ddd, *J* 10.8, 9.4 and 1.2) and this consisted the structure. The structure of compound (**10a**) was finally decided by X-Ray crystal structure analysis. Similar treatment of **4a** with excess molar of *p*-fluorophenyl isothiocyanate at 60 ℃ for 20 h, two products was obtained. Although the one product, being dark red prisms and yielded in 39%, was identified as a cycloadduct (**10b**), the other one could not be identified. In the reaction, the compound (**6af**) was not obtained.



10a : Ar = Ph
10b : Ar = *p*-FC_6H_4

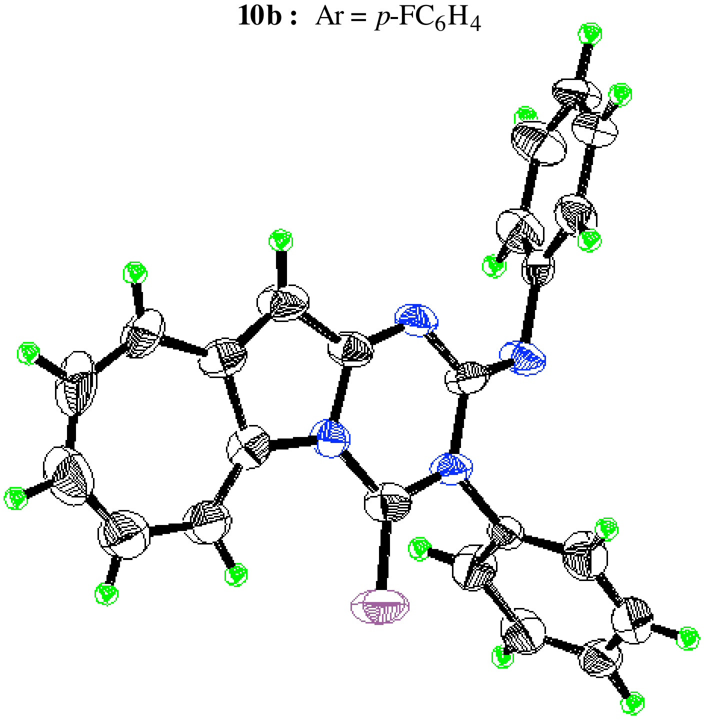


Figure 2. ORTEP drawing of **10a** with thermal ellipsoids (50% probability).

CONCLUSION

Synthesis and some reactions of 2-phosphoimino-1-azaazulene derivatives (**4a-c**) with aryl isocyanates were performed. 2-Arylimino-3-aryl-2,3,4,4a-tetrahydro-1,3,4a-triazabenz[*a*]azulen-4-one and 2-(*N'*-phenylureido)-1-azaazulenes were obtained as the normal aza-Wittig reaction products and 3-phenyl-2,3,4,4a-tetrahydro-1,3,4a-triazabenz[*a*]azulene-2,4-dione yielded as the abnormal aza-Wittig reaction products, in moderate to good yields. It is proved that abnormal aza-Wittig reaction influenced by the reaction temperature, and the reaction of higher temperature (over 80 ℃) preferred to produce abnormal aza-Wittig products. Reaction of **4a** with aryl isothiocyanates gave 2-arylimino-3-aryl-2,3,4,4a-tetrahydro-1,3,4a-triazabenz[*a*]azulene-4-thiones.

EXPERIMENTAL

Mps are measured using Yanagimoto micro-melting apparatus and uncorrected. ^{1}H NMR spectra (including HH-COSY and CH-COSY NMR) were recorded on a Bruker AVANCE 400S (400 MHz) and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400S (100.6 MHz) using deuteriochloroform as a solvent with tetramethylsilane as an internal standard unless otherwise stated; *J* value are recorded in Hz. IR spectra were recorded for KBr pellets on a Nicolet FT-IR Impact 410 unless otherwise started. MS spectra were taken with on a LC-MS Waters Integrity System. Elemental analyses were taken with a Perkin Elmer 2400II. Kiselgel 60 was used for column chromatography and Kiselgel 60G was used for thin-layer chromatography.

Synthesis of 2-triphenylphosphoimino-1-azaazulenes

Typical procedure A - Under argon atmosphere, a mixture of 2-amino-1-azaazulene (**5a**) (0.144 g, 1.00 mmol), dibromotriphenylphosphorane (0.591 g, 1.40 mmol), triethyl amine (0.3 mL, 2.8 mmol) in dry benzene (5.0 mL) was stirred for 24 h at rt. To the mixture, dry benzene (10 mL) was added, and the precipitate was filtered off. The filtrate was evaporated, and the residue was recrystallized from hexane-chloroform to give 2-triphenylphosphoimino-1-azaazulene (**4a**) as orange needles (0.214 g, 53%).

Typical procedure B - Under argon atmosphere, to a solution of 2-amino-1-azaazulene (**5a**) (0.144 g, 1.00 mmol) in dry benzene (10.0 mL) were added consecutively triethylamine (0.5 mL, 4.2 mmol), triphenylphosphorane (0.340 g, 1.30 mmol) and hexachloroethane (0.307 g, 1.3 mmol). After refluxed for 3 h, the precipitate was filtered off. The filtrate was evaporated, and the residue was chromatographed with hexane-ethyl acetate (4:1) to give **4a** (0.384 g, 95%).

4a: Orange prisms (from hexane-chloroform), mp 129-130 ℃ (lit.,[21] mp 129-130 ℃); δ_H 6.49 (1H, s), 7.09 (1H, dd, *J* 10.1 and 9.7), 7.19-7.23 (3H, m), 7.18 (1H, dd, *J* 10.3 and 9.6), 7.32 (1H, dd, *J* 10.3 and 9.7), 7.44-7.48 (5H, m), 7.53-7.57 (3H, m), 7.66-7.69 (1H, m), 7.71 (1H, d, *J* 10.1), 7.75 (1H, d, *J* 9.6), and 7.82-7.89 (6H, m); δ_C 106.30 (d, *J* 16.2), 124.28, 125.92, 127.61, 128.08, 128.12, 128.63, 129.09, 129.62, 131.87 (d, *J* 12.3), 132.85 (d, *J* 9.9), 147.58, 158.50, and 174.66 (d, *J* 1.3); δ_P 19.62; ν_{max} / cm^{-1} 1491 (P-Ph); *m*/z (rel intensity) 404 (M$^+$, 32), 403 (71), 277 (100), 262 (10), and 183 (67). *Anal.* Calcd for $C_{27}H_{21}N_2P$: C, 80.18; H, 5.23; N, 6.93. Found C, 79.55; H, 5.15; N, 6.52.

Synthesis of ethyl 2-triphenylphosphoimino-1-azaazulene-3-carboxylate

Under argon atmosphere, to a solution of ethyl 2-amino-1-azaazulene-3-carboxylate (**5b**) (0.432 g, 2.00 mmol) in dry benzene (20.0 mL) were added consecutively triethylamine (0.6 mL, 5.6 mmol), triphenylphosphine (0.628 g, 1.40 mmol) and hexachloethane (0.607 g, 1.44 mmol). After refluxed for 3 h, the precipitate was filtered off. The filtrate was evaporated, and the residue was chromatographed with hexane-ethyl acetate (4:1) to give **4b** (0.893 g, 94%).

4b: Yellow prisms (from hexane), mp 205.5-206 ℃; δ_H 1.57 (3H, t, *J* 7.1), 4.51 (2H, q, *J* 7.1), 7.26 (1H, like t, *J* 9.7), 7.40-7.50 (8H, m,), 7.53 (3H, ttd, *J* 7.4, 2.0, and 1.4), 7.73 (1H, d, *J* 9.9), 7.99 (6H, dddd, *J* 12.3, 8.5, 1.5, and 1.0), and 8.96 (1H, d, *J* 10.3); δ_C 30.09, 59.81, 105.22 (d, *J* 20.7), 128.14, 128.43, 128.73 (d, *J* 24.1), 129.39, 130.39, 130.60, 132.18, 132.25, 132.28, 132.42, 133.95 (d, *J* 10.0), 150.01, 160.87, 166.84, and 174.52 (d, *J* 6.9); ν_{max} / cm^{-1} 1658 (C=O) and 1490 (P-Ph); *m*/z (rel intensity) 476 (M$^+$, 5), 447 (12), 403 (10), 277 (100), 262 (8), 216 (31) and 183 (45). *Anal.* Calcd for $C_{30}H_{25}N_2O_2P$: C, 75.62; H, 5.29; N, 5.88. Found C, 75.27; H, 5.11; N, 6.08.

Synthesis of 2-triphenylphosphoimino-1-azaazulene-3-carboaldehyde

Under argon atmosphere, to a solution of 2-amino-1-azaazulene-3-carboaldehyde (**5c**) (0.172 g, 1.00 mmol) in dry benzene (20.0 mL) were added consecutively triethylamine (0.6 mL, 5.6 mmol), triphenylphosphorane (0.340 g, 1.30 mmol) and hexachloethane (0.306 g, 1.30 mmol). After refluxed for 0.5 h, and the precipitate was filtered off. The filtrate was evaporated, and the residue was chromatographed with hexane-ethyl acetate (4:1) to give **4c** (0.344 g, 80%).

4c: Orange prisms (from hexane-dichrolomethane), mp 225-228 ℃; δ_H 7.31 (1H, t, *J* 9.8), 7.45 (1H, dd, *J* 10.0 and 9.8), 7.46-7.49 (6H, m), 7.51 (1H, dd, *J* 9.9 and 9.4), 7.56 (3H, tdd, *J* 7.2, 2.0, and 1.5), 7.79 (1H, d, *J* 10.0), 7.91 (6H, dddd, *J* 12.4, 8.5, 1.5, and 1.0), 9.07 (1H, d, *J* 9.9), and 10.65 (1H, s); δ_C 113.60, 113.79, 128.72, 128.86, 128.90, 129.03, 129.71, 129.86, 132.03, 132.58 (d, *J* 2.9), 133.65, 133.75, 133.93, 134.55, 147.89, 162.99, 177.84, 177.92 and 188.65; ν_{max} / cm^{-1} 1475 (P-Ph). *Anal.* Calcd for $C_{28}H_{21}N_2OP$: C, 77.77; H, 4.89; N, 6.48. Found C, 77.73; H, 4.70; N, 6.54.

Reaction of 4a with aryl isocyanates

Typical procedure A - Under argon atmosphere, a mixture of 2-amino-1-azaazulene (**5a**) (0.036 g, 0.25 mmol), dibromotriphenylphosphorane (0.1525 g, 0.36 mmol) and triethylamine (0.15 mL, 1.4 mmol) in dry benzene (5.0 mL) in a sealed tube was stirred for 24 h at rt. Precipitated triethylamine hydrogenbromide was filtered off, and the filtrate was evaporated to give **4a**. The crude **4a** was dissolved to dry benzene (20 mL) under argon atmosphere, and phenyl isocyanate (0.0839 g, 0.75 mmol) was added to the solution. The mixture was stirred for 24 h at rt, then the precipitate was filtered off. The filtrate was evaporated, and chromatography of the residue with hexane-ethyl acetate (4:1) gave **6aa** (0.0634 g, 70%) as red crystals.

Typical procedure B - Under argon atmosphere, to a solution of **5a** (0.0576 g, 0.40 mmol) in dry benzene (10.0 mL) were added consecutively triethylamine (1.0 mL, 8.4 mmol), triphenylphosphine (0.136 g, 0.52 mmol) and hexachloroethane (0.126 g, 0.52 mmol). After refluxed for 2 h, and the precipitate was filtered off and the filtrate was evaporated to give **4a**. The crude **4a** was dissolved to dry benzene (20 mL) under argon atmosphere, and phenyl isocyanate (0.1429 g, 1.20 mmol) was added to the solution. The mixture was heated at 60 ℃ and stirred for 3 h, then the precipitate was filtered off. The filtrate was evaporated, and chromatography of the residue with hexane-ethyl acetate (4:1) gave **6aa** (0.1227 g, 84%), exclusively.

Typical procedure C - Under argon atmosphere, to a solution of **5a** (0.0576 g, 0.40 mmol) in dry benzene (10.0 mL) were added consecutively triethylamine (1.0 mL, 8.4 mmol), triphenylphosphine (0.136 g, 0.52 mmol) and hexachloroethane (0.126 g, 0.52 mmol). After refluxed for 2 h, the precipitate was filtered off and the filtrate was evaporated to give **4a**. The crude **4a** was dissolved to dry xylene (20 mL) under argon atmosphere, and phenyl isocyanate (0.1429 g, 1.20 mmol) was added to the solution. The mixture was heated under reflux and stirred for 0.5 h, then the precipitate was filtered off. The filtrate was evaporated, and chromatography of the residue with hexane-ethyl acetate (4:1) gave **6aa** (0.0713 g, 49%), **7aa** (0.0265 g, 25%) and **8aa**[26] (0.0035 g, 3%).

6aa: Red prisms (from acetonitrile), mp 283-284 ℃; δ_H 6.25 (1H, s), 6.88 (1H, dd, *J* 11.4 and 9.4), 6.96 (2H, d, *J* 7.8), 6.97 (1H, dd, *J* 11.4 and 9.6), 6.98 (1H, t, *J* 6.8), 7.00 (1H, dd, *J* 11.5 and 9.6), 7.23 (2H, like t, *J* 7.2), 7.37 (1H, d, *J* 11.5), 7.40 (2H, d, *J* 7.2), 7.42 (1H, t, *J* 7.4), 7.52 (2H, like t, *J* 7.4), and 8.61 (1H, d, *J* 9.4); δ_C 107.05, 121.05, 123.20, 128.74, 129.16, 132.14, 133.55, 133.93, 134.89, 136.97, 143.72, 148.88, 148.91, 149.62, and 157.49; ν_{max} / cm^{-1} 1716 (C=O) and 1633 (C=N); *m*/z (rel intensity) 365 (M$^+$+1, 44), 364 (M$^+$, 100), 129 (11), and 77 (16). *Anal.* Calcd for $C_{23}H_{16}N_4O$: C, 75.81; H, 4.43; N, 15.38. Found C, 75.50; H, 4.24; N, 15.23.

7aa: Orange prisms (from hexane-dichloromethane), mp 197-200 ℃; δ_H 6.85 (1H, s), 7.12 (1H, t, *J* 7.9), 7.37 (1H, dd, *J* 10.4 and 9.8), 7.39 (2H, t, *J* 7.9), 7.57 (1H, dd, *J* 10.4 and 9.8), 7.61 (1H, dd, *J* 10.4 and 9.8), 7.70 (2H, d, *J* 7.9), 8.22 (1H, d, *J* 10.4), 8.29 (1H, d, *J* 9.8), 8.6-9.2 (1H, br), and 11.9-12.3 (1H, br); ν_{max} / cm^{-1} 3392, 3255 (N-H), and 1706 (C=O). *Anal.* Calcd for $C_{16}H_{13}N_3O$: C, 72.99; H, 4.98; N, 15.96. Found C, 72.95; H, 5.16; N, 15.62.

8aa: Orange needles (from acetonitrile), mp 255 ℃ (decomp) (lit.,[26] mp 255 ℃ (decomp)); δ_H 6.57 (1H, s), 7.20-7.38 (5H, m), 7.40-7.60 (3H, m), 7.75 (1H, d, *J* 10.7), and 9.04 (1H, d, *J* 9.2); ν_{max} / cm^{-1} 1728 and 1668 (C=O). *Anal.* Calcd for $C_{17}H_{11}N_3O_2$: C, 70.58; H, 3.80; N, 14.40. Found C, 70.56; H, 3.99; N, 14.52.

6ab: Dark red needles (from acetonitrile), mp 237-238 ℃; δ_H 2.27 (3H, s), 2.40 (3H, s), 6.24 (1H, s), 6.85 (1H, dd, *J* 10.4 and 9.4), 6.86 (2H, d, *J* 8.0), 6.94 (1H, dd, *J* 10.4 and 9.4), 6.98 (1H, dd, *J* 11.2 and 9.4), 7.03 (2H, d, *J* 8.0), 7.27 (2H, d, *J* 8.0), 7.31 (2H, d, *J* 8.0), 7.34 (1H, d, *J* 11.2), and 8.57 (1H, d, *J* 9.4); δ_C 19.08, 19.45, 104.85, 114.50, 118.52, 120.72, 126.52, 127.06, 128.27, 129.94, 131.07, 131.63, 132.03, 132.50, 135.22, 141.49, 144.05, 146.68, 147.24, and 155.06; ν_{max} / cm^{-1} 1715 (C=O) and 1624 (C=N); *m*/z (rel intensity) 393 (M$^+$+1, 27), 392 (M$^+$, 67), 364 (16), 259 (100), 245 (38), 218 (18), 129 (86), 119 (38), 79 (17), 78 (35), 77 (15), and 70 (54). *Anal.* Calcd for $C_{25}H_{20}N_4O$: C, 76.51; H, 5.14; N, 14.26. Found C, 75.75; H, 5.13; N, 14.76.

6ac: Dark red needles (from acetonitrile), mp 233.5-235 ℃; δ_H 3.76 (3H, s), 3.85 (3H, s), 6.25 (1H, s), 6.80 (2H, d, *J* 8.0), 6.86 (1H, dddd, *J* 11.1, 9.6, 0.8, and 0.7), 6.95 (1H, dd, *J* 11.1 and 9.4), 6.96 (2H, d, *J*

8.9), 6.98 (1H, dd, *J* 11.2 and 9.6), 7.03 (2H, d, *J* 8.9), 7.30 (2H, d, *J* 8.9), 7.36 (1H, br d, *J* 11.2), and 8.58 (1H, br d, *J* 9.4); δ_C 55.66, 106.92, 113.92, 114.99, 120.68, 124.18, 129.34, 129.90, 131.89, 133.21, 133.79, 134.66, 141.87, 143.64, 148.82, 148.99, 149.90, 155.66, 157.07, and 159.41; ν_{max} / cm^{-1} 1711 (C=O) and 1630 (C=N); *m*/z (rel intensity) 425 (M^++1, 23), 424 (M^+, 7), 275 (100), 260 (48), 232 (28), 212 (11), 129 (12), and 77 (22). *Anal.* Calcd for $C_{25}H_{20}N_4O_3$: C, 70.74; H, 4.75; N, 13.20. Found C, 70.94; H, 4.66; N, 12.92.

6ad: Red fine needles (from acetonitrile), mp 256.5-258 ℃; δ_H 2.54 (3H, s), 2.65 (3H, s), 6.30 (1H, s), 7.00 (1H, dd, *J* 10.7 and 9.4), 7.01 (2H, d, *J* 8.7), 7.09 (1H, dd, *J* 11.2, and 7.6), 7.11 (1H, dd, *J* 10.7 and 7.6), 7.48 (1H, d, *J* 11.2), 7.53 (2H, d, *J* 8.6), 7.87 (2H, d, *J* 8.7), 8.13 (2H, d, *J* 8.6), and 8.68 (1H, d, *J* 9.4); δ_C 24.83, 27.80, 104.39, 119.39, 121.00, 127.32, 127.35, 129.96, 130.31, 131.85, 132.16, 133.14, 135.00, 138.77, 141.18, 146.09, 146.83, 147.71, 151.50, 155.47, 195.29, and 195.49; ν_{max} / cm^{-1} 1713, 1678 (C=O) and 1630 (C=N). *Anal.* Calcd for $C_{27}H_{20}N_4O_3$: C, 72.31; H, 4.49; N, 12.49. Found C, 72.74; H, 4.72; N, 12.09.

Reaction of 4b with aryl isocyanates

Under argon atmosphere, **4b** (0.1192 g, 0.25 mmol) was dissolved to dry benzene (20 mL), and phenyl isocyanate (0.0893 g, 0.75 mmol) was added to the solution in a sealed tube. The mixture was heated at 60 ℃ and stirred for 4 h, then the precipitate was filtered off. The filtrate was evaporated, and chromatography of the residue with hexane-ethyl acetate (4:1) gave **6ba** (0.0486 g, 45%), exclusively.

6ba: Red needles (from acetonitrile), mp 257.5-259 ℃; δ_H 1.20 (3H, t, *J* 7.2), 4.29 (2H, q, *J* 7.2), 6.97 (1H, dddd, *J* 10.5, 9.7, 1.2, and 0.8), 7.15 (2H, dd, *J* 8.4 and 1.3), 7.22 (2H, tm, *J* 8.3), 7.32 (1H, dddd, *J* 10.8, 9.7, 2.0, and 0.8), 7.38 (2H, dd, *J* 8.6 and 1.4), 7.44 (1H, dm, *J* 7.4), 7.47-7.57 (4H, m), 9.08 (1H, br d, *J* 11.4), and 9.18 (1H, dd, *J* 9.7 and 0.8); δ_C 14.45, 61.30, 104.04, 123.26, 123.88, 124.63, 128.52, 128.87, 129.03, 129.86, 133.54, 136.46, 136.76, 136.90, 139.08, 144.27, 147.90, 148.35, 148.93, 151.89, 154.26, and 163.91; ν_{max} / cm^{-1} 1714, 1673 (C=O) and 1640 (C=N); *m*/z (rel intensity) 437 (M^++1, 49), 436 (M^+, 70), 363 (13), 272 (72), 197 (100), 170 (83), 141 (35), 129 (11), 119 (50), 91 (43), and 77 (28). *Anal.* Calcd for $C_{26}H_{20}N_4O_3$: C, 71.55; H, 4.62; N, 12.84. Found C, 71.43; H, 4.43; N, 12.36.

6bd: Red prisms (from hexane-dichloromethane), mp 260.5-262 ℃; δ_H 1.17 (3H, t, *J* 7.2), 2.55 (3H, s), 2.66 (3H, s) 4.28 (2H, q, *J* 7.2), 7.19 (2H, ddd, *J* 8.6, 2.3, and 1.9), 7.42 (1H, dd, *J* 10.5 and 8.6), 7.51 (2H, ddd, *J* 8.6, 2.2, and 1.9), 7.52 (1H, dd, *J* 10.5 and 9.7), 7.61 (1H, ddd, *J* 11.4, 8.6, and 1.2), 7.87 (2H, ddd, *J* 8.6, 2.3, and 1.9), 8.15 (2H, ddd, *J* 8.6, 2.2, and 1.9), 9.16 (1H, d, *J* 11.4), and 9.24 (1H, dd, *J* 9.7 and 0.9); δ_C 14.38, 26.81, 27.14, 61.41, 103.95, 123.93, 125.43, 129.35, 129.49, 130.01, 132.39, 134.12, 137.07, 137.31, 137.39, 139.48, 140.82, 143.97, 148.39, 151.92, 153.37, 154.64, 163.62, 197.51 and 197.81; ν_{max} / cm^{-1} 1712, 1679 (C=O) and 1608 (C=N). *Anal.* Calcd for $C_{30}H_{24}N_4O_5$: C, 69.22; H, 4.65; N, 10.76. Found C, 69.64; H, 4.32; N, 10.52.

Reaction of 4c with aryl isocyanates

Typical procedure A - Under argon atmosphere, **4c** (0.1092 g, 0.25 mmol) was dissolved to dry benzene (20 mL), and phenyl isocyanate (0.0893 g, 0.75 mmol) was added to the solution. The mixture was stirred at rt for 56 h, then the precipitate was filtered off. The filtrate was evaporated, and chromatography of the residue with hexane-ethyl acetate (4:1) gave **7ca** (0.0123 g, 17%) together with **9** (0.0152 g, 15%).

Typical procedure B - Under argon atmosphere, **4c** (0.1732 g, 0.40 mmol) was dissolved to dry xylene (5 mL), and *p*-methylphenyl isocyanate (0.0159 g, 1.20 mmol) was added to the solution in a sealed tube. The mixture was heated at 120 ℃ and stirred for 1 h, then the precipitate was filtered off. The filtrate was evaporated, and chromatography of the residue with hexane-ethyl acetate (4:1) gave **6cb** (0.0815 g, 49%) together with **7cb** (0.0185 g, 15%) and **8cb** (0.0246 g, 18%).

6ca: Red needled (from acetonitrile), mp 245-246 ℃; δ_H 7.00 (1H, t, *J* 7.4), 7.06 (2H, dd, *J* 7.4 and 1.0), 7.25 (2H, t, *J* 7.4), 7.40-7.48 (4H, m), 7.54-7.60 (3H, m), 7.66 (1H, ddd, *J* 11.1, 8.8, and 1.0), 9.20 (1H, d, *J* 11.1), 9.26 (1H, d, *J* 9.7), and 10.17 (1H, s); δ_C 108.94, 120.16, 123.45, 123.69, 126.29, 128.58, 129.03, 129.91, 132.50, 134.13, 136.59, 137.86, 138.32, 141.43, 144.26, 148.04, 148.78, 149.42, 156.84, and 186.44; ν_{max} / cm^{-1} 1730, 1655 (C=O), 1613, and 1573 (C=N). *Anal.* Calcd for $C_{24}H_{16}N_4O_2$: C, 73.46; H, 4.11; N, 14.28. Found C, 73.71; H, 3.78; N, 13.80.

7ca: Yellow powders (from acetonitrile), mp 210 ℃ (decomp); δ_H 7.14 (1H, t, *J* 7.4), 7.38 (2H, dd, *J* 7.8 and 7.4), 7.67 (2H, d, *J* 7.8), 7.79 (2H, m), 7.96 (1H, dd, *J* 9.7 and 1.7), 8.48 (1H, d, *J* 9.7), 8.72 (1H, dd, *J* 8.7 and 2.0), 9.75 (1H, br s), 10.45 (1H, s), and 11.82 (1H, br s); δ_C 108.63, 120.52, 124.16, 129.40, 129.52, 134.38, 134.85, 135.65, 136.87, 138.70, 148.17, 151.49, 158.77, 162.52, and 183.97; ν_{max} / cm^{-1} 1712, 1635 (C=O). *Anal.* Calcd for $C_{17}H_{13}N_3O_2$: C, 70.09; H, 4.50; N, 14.42. Found C, 70.61; H, 4.43; N, 13.73.

8ca: Red powders (from dichloromethane-hexane); mp 245 ℃ (decomp.); δ_H 7.37 (2H, dd, *J* 7.3 and 1.5), 7.50 (1H, td, *J* 7.3 and 1.5), 7.56 (2H, t, *J* 7.3), 7.79 (1H, ddd, *J* 10.8, 10.1, and 1.5), 7.84 (1H, dd, *J* 10.8 and 9.2), 7.93 (1H, dd, *J* 11.0 and 10.1), 9.56 (1H, d, *J* 11.0), 9.64 (1H, dd, *J* 9.2, and 1.5), and 10.52 (1H, s) ; ν_{max} / cm^{-1} 1735, 1682, and 1657 (C=O). *Anal.* Calcd for $C_{18}H_{11}N_3O_3$: C, 68.14; H, 3.49; N, 13.24. Found C, 68.21; H, 3.23; N, 13.45.

9: Orange needles (from acetonitrile), mp 225-226 ℃; δ_H 7.12 (1H, t, *J* 7.9), 7.24-7.29 (1H, m), 7.34 (2H, dm, *J* 8.1), 7.39 (2H, t, *J* 7.9), 7.44 (2H, t, *J* 8.1), 7.76-7.71 (4H, m), 7.84 (1H, tm, *J* 9.5), 8.49 (1H, d, *J* 9.5), 8.45 (1H, dm, J 9.0), 9.10 (1H, s), 11.04 (1H, br s), and 12.07 (1H, br s); ν_{max} / cm^{-1} 1697 (C=O). *Anal.* Calcd for $C_{24}H_{18}N_4O_3$: C, 70.23; H, 4.42; N, 13.65. Found C, 70.80; H, 4.24; N, 13.23.

6cb: Red needles (from acetonitrile), mp 264-265 ℃; δ_H 2.29 (3H, s), 2.42 (3H, s), 6.97 (2H, d, *J* 8.3), 7.04 (2H, d, *J* 8.2), 7.27 (2H, d, *J* 10.3), 7.34 (2H, d, *J* 8.2), 7.43 (1H, dd, *J* 9.8 and 8.8), 7.55 (1H, dd, *J* 10.3 and 9.8), 7.63 (1H, ddd, *J* 11.1, 8.8, and 1.0), 9.17 (1H, d, *J* 11.1), 9.23 (1H, d, *J* 9.2), and 10.17 (1H, s); δ_C 21.35, 21.76, 108.96, 123.60, 126.10, 128.67, 129.14, 130.64, 132.78, 133.91, 137.65, 138.31, 138.78, 141.34, 145.34, 145.43, 147.75, 148.78, 149.39, 156.52, and 186.51; ν_{max} / cm^{-1} 1713 and 1635 (C=O). *Anal.* Calcd for $C_{26}H_{20}N_4O_2$: C, 74.27; H, 4.79; N, 13.33. Found C, 74.62; H, 4.44; N, 13.07.

7cb: Yellow powders (from acetonitrile), mp 167-168 ℃; δ_H 2.35 (3H, s), 7.18 (2H, d, *J* 8.2), 7.56 (2H, d, *J* 8.2), 7.87 (1H, dd, *J* 10.9 and 9.7), 7.89 (1H, dd, *J* 11.2 and 9.7), 7.93 (1H, dd, *J* 11.2 and 9.7), 8.46 (1H, d, *J* 9.7), 8.70 (1H, d, *J* 10.9), 9.72 (1H, br s), 10.44 (1H, s), and 11.72 (1H, br s) ; ν_{max} / cm^{-1} 1720, 1662 (C=O), 1648, and 1635 (C=N). *Anal.* Calcd for $C_{18}H_{15}N_3O_2 \cdot 1/2C_6H_6$: C, 73.24; H, 5.27; N, 12.20. Found C, 72.74; H, 5.01; N, 12.14.

8cb: Orange powders (from dichloromethane-hexane); mp 250 ℃ (decomp); δ_H 2.44 (3H, s) 7.24 (2H, d, *J* 8.1), 7.37 (2H, d, *J* 8.1), 7.78 (1H, dd, *J* 10.5 and 9.2), 7.81 (1H, dd, *J* 10.5 and 9.5), 7.93 (1H, ddd, *J* 11.0, 9.5, and 1.8), 9.55 (1H, d, *J* 11.0), 9.63 (1H, dd, *J* 9.2, and 1.5), and 10.51 (1H, s). *Anal.* Calcd for $C_{19}H_{13}N_3O_4$: C, 65.70; H, 3.77; N, 12.10. Found C, 66.21; H, 3.23; N, 11.75.

6cc: Red oil, δ_H 3.78 (3H, s), 3.85 (3H, s), 6.80 (2H, d, *J* 8.8), 7.05 (2H, d, *J* 8.9), 7.09 (2H, d, *J* 8.9), 7.31 (2H, d, *J* 8.6), 7.43 (1H, dd, *J* 10.7 and 9.9), 7.54 (1H, dd, *J* 10.2 and 9.8), 7.61 (1H, ddd, *J* 10.2, 9.9, and 1.5), 9.17 (1H, d, *J* 10.7), 9.23 (1H, d, *J* 9.7), and 10.21 (1H, s).

7cc: Yellow powders (from acetonitrile), mp 212-215 ℃; δ_H 3.83 (3H,s), 6.93 (2H, d, *J* 9.0), 7.58 (2H, d, *J* 9.0), 7.88 (1H, dd, *J* 11.0 and 9.7), 7.90 (1H, dd, *J* 10.9 and 9.2), 7.95 (1H, ddd, *J* 11.0, 9.7, and 1.5), 8.47 (1H, d, *J* 9.7), 8.72 (1H, d, *J* 11.0), 9.76 (1H, br s), 10.46 (1H, s), and 11.66 (1H, br s). *Anal.* Calcd for $C_{18}H_{15}N_3O_3$: C, 67.28; H, 4.71; N, 13.08. Found C, 67.45; H, 4.59; N, 13.22.

8cc: Orange powders (from dichloromethane-hexane); mp 250 ℃ (decomp); δ_H 3.87 (3H, s) 7.07 (2H, dd, *J* 8.9 and 2.1), 7.27 (2H, dd, *J* 8.9 and 2.1), 7.78 (1H, dd, *J* 10.5 and 9.2), 7.83 (1H, dd, *J* 10.5 and 9.3), 7.93 (1H, ddd, *J* 11.0, 9.3, and 1.8), 9.55 (1H, d, *J* 11.0), 9.64 (1H, dd, *J* 9.2 and 1.5), and 10.50 (1H, s), δ_H(DMSO) 3.82 (3H, s) 7.06 (2H, d, *J* 8.6), 7.28 (2H, d, *J* 8.6), 8.01 (1H, dd, *J* 10.9 and 9.3), 8.13 (1H, dd, *J* 10.2 and 9.5), 8.20 (1H, dd, *J* 10.9 and 9.3), 9.37 (1H, d, *J* 10.9), 9.55 (1H, d, *J* 9.5), and 10.27 (1H, s); δ_C (DMSO) 107.40, 114.56, 128.41, 130.04, 134.36, 139.61, 140.82, 143.11, 144.11, 148.00, 154.27, 159.31, and 160.36; ν_{max} / cm^{-1} 1745, 1680, and 1650 (C=O) 1616, 1579, and 1571 (C=N). *Anal.* Calcd for $C_{19}H_{13}N_3O_4$: C, 65.70; H, 3.77; N, 12.10. Found C, 66.21; H, 3.23; N, 11.75.

6cd: Red oil δ_H 2.57 (3H, s), 2.67 (3H, s), 7.08 (2H, d, *J* 8.6), 7.52 (2H, d, *J* 8.6), 7.54 (1H, dd, *J* 11.2 and 8.7), 7.67 (1H, dd, *J* 11.2 and 9.7), 7.75 (1H, ddd, *J* 11.2, 8.7, and 1.2), 7.88 (2H, d, *J* 8.6), 9.28 (1H, d, *J* 8.6), 9.31 (1H, dd, *J* 11.2 and 9.7), and 10.16 (1H, s).

7cd: Yellow powders (from acetonitrile), mp 206-208 ℃; δ_H 2.61 (3H, s), 7.80 (2H, d, *J* 8.6), 7.93-7.96 (2H, m), 8.00 (2H, d, *J* 8.6), 8.02-8.04 (1H, m), 8.55 (1H, d, *J* 9.6), 8.77 (1H, d, *J* 9.6), 9.87 (1H, br s), 10.48 (1H, s), and 12.22 (1H, br s); ν_{max} / cm^{-1} 1706, 1680, and 1630 (C=O) 1596 (C=N). *Anal.* Calcd for $C_{19}H_{15}N_3O_3$: C, 68.96; H, 4.54; N, 12.61. Found C, 68.64; H, 4.13; N, 12.20.

Reaction of 4a with aryl isothiocyanates.

Under argon atmosphere, **4a** (0.101 g, 0.25 mmol) was dissolved to dry benzene (20 mL), and phenyl isothiocyanate (0.101 g, 0.75 mmol) was added to the solution. The mixture was heated at 60 ℃ and stirred for 20 h, then the precipitate was filtered off. Then the filtrate was evaporated, and chromatography of the residue with hexane-ethyl acetate (4:1) gave **10a** (0.0367 g, 39%) together with **6aa** (0.0131 g, 14%).

10a: Red prisms (from acetonitrile), mp 196-197 ℃; δ_H 6.21 (1H, s), 6.90 (1H, ddd, *J* 10.8, 9.4, and 1.2), 6.94 (1H, dd, *J* 10.6 and 9.4), 6.96-6.98 (1H, m), 7.00 (1H, dd, *J* 10.8 and 9.5), 7.23 (1H, dd, *J* 8.4 and 7.9), 7.31 (1H, dd, *J* 7.9 and 1.0), 7.33 (1H, d, *J* 10.6), 7.42 (2H, t, *J* 7.4), 7.54 (1H, dd, *J* 7.9 and 7.4), and 9.92 (1H, d, *J* 9.5); δ_C 106.37, 122.89, 123.06, 128.49, 128.76, 129.09, 130.02, 132.23, 133.50, 134.62, 135.02, 141.65, 145.42, 146.84, 148.31, 150.85, 156.33, and 175.46; ν_{max} / cm^{-1} 1641, 1608 and

1579; *m*/z (rel intensity) 381 (M^++1, 3), 380 (M^+, 21), 379 (M^+-1, 18), 245 (72), 135 (95), and 77 (100). *Anal.* Calcd for $C_{23}H_{16}N_4S$: C, 72.61; H, 4.24; N, 14.73. Found C, 73.26; H, 4.10; N, 14.46.

In a similar manner, treatment of **4a** with *p*-fulorophenyl isothiocyanate at 60 ℃ for 20 h gave **10b** in a 39% yield.

10b: Red prisms (from acetonotrile-hexane), mp 120-123 ℃; δ_H 6.21 (1H, s), 6.92-6.95 (1H, m), 6.92-6.94 (4H, m), 6.96-7.01 (1H, dm, *J* 10.7 and 9.5), 7.04 (1H, dd, *J* 10.7 and 9.7), 7.18-7.25 (4H, m), 7.37 (1H, d, *J* 10.7), and 9.93 (1H, d, *J* 9.5); ν_{max} / cm^{-1} 1620 and 1591. *Anal.* Calcd for $C_{23}H_{14}N_4F_2S$: C, 66.33; H, 3.39; N, 13.45. Found C, 66.10; H, 3.60; N, 13.46.

X-Ray structure determination

Crystal data of 6aa: red prism, $C_{23}H_{16}N_4O$, *M* = 364.41, monoclinic, space group $P2_1/c$, *a* = 5.578(3) Å, *b* = 16.988(3) Å, *c* = 19.239(2) Å, β = 97.36(3)°, *V* = 1808.1(8) $Å^3$, *Z* = 4, D_{calc} = 1.339 g/cm^3, crystal dimension 0.12 x 0.28 x 0.88 mm. Data were measured on a Rigaku AFC 5S radiation diffractmeter with graphite-monochromated Mo-Kα radiation. Total 3970 reflections (3542 unique) were collected using ω-2θ scan technique with in a 2θ range of 55.0°. The structure was solved by direct methods (SIR92),[29] and refined a full-matrix least squares methods using TEXAN structure analysis software[30] with 253 variables and 1125 observed reflections [$I > 2\sigma(I)$]. The final refinement converged to *R* = 0.067 and *Rw* = 0.058.

Crystal data of 10a: red prisms, $C_{23}H_{16}N_4S$, *M* = 380.47, monoclinic, space group $P2_1/a$, *a* = 19.664(4) Å, *b* = 17.091(3) Å, *c* = 5.606(4) Å, β = 97.28(4)°, *V* = 1869(1) $Å^3$, *Z* = 4, D_{calc} = 1.352 g/cm^3, crystal dimension 0.08 x 0.46 x 1.00 mm. Data were measured on a Rigaku AFC 5S radiation diffractmeter with graphitemonochromated Mo-Kα radiation. Total 4246 reflections (3878 unique) were collected using ω-2θ scan technique with 2θ range of 55.0°. The structure was solved by direct methods (SAPI91)[31], and refined a full-matrix least squares methods using TEXAN structure analysis software[30] with 253 variables and 1376 observed reflections [$I > 2\sigma(I)$]. The final refinement converged to *R* = 0.071 and *Rw* = 0.067.

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