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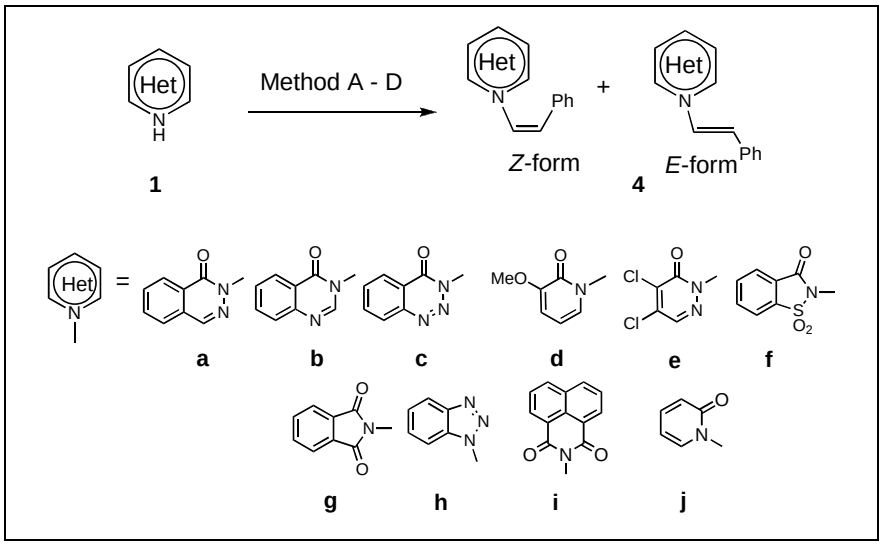

N-Styrylazinones and 1-styrylbenzotriazine were synthesized, and their photophysical properties were investigated. (*Z*)- and/or (*E*)-*N*-Styrylazinones (or azine) **4** were prepared from the corresponding heterocycles **1** and benzaldehyde (**3**) by four methods. The absorption maxima of (*Z*)- and/or (*E*)-**4a** – **4j** were measured in four solvents. Their absorption maxima showed a moderate dependence upon solvents. The absorption maxima of (*Z*)-isomers were blue-shifted as compared the corresponding (*E*)-isomers. Emission maxima, fluorescence band half-widths, 0,0 transition energies, Stokes shifts, and quantum yields of (*Z*)- and/or (*E*)-**4a, 4b, 4d, 4e** and **4j** were measured in organic solvents. The fluorescence spectra show moderate solvatochroism. The fluorescence properties of *N*-styrylheterocycles vary with every heterocycles.

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INTRODUCTION

The development of luminescent molecules is an active field of research in supramolecular chemistry [1-8]. An important area within this field is the development of luminescent chemosensors [6-8] because those sensors have the advantage of possessing high sensitivity and selectivity, as well as providing on-line and real time analysis thus revolutionizing the field of chemical analysis [9-25]. However, the development of useful fluorescent probe is difficult because of the lack of flexible design strategies. At present, design is largely empirical.

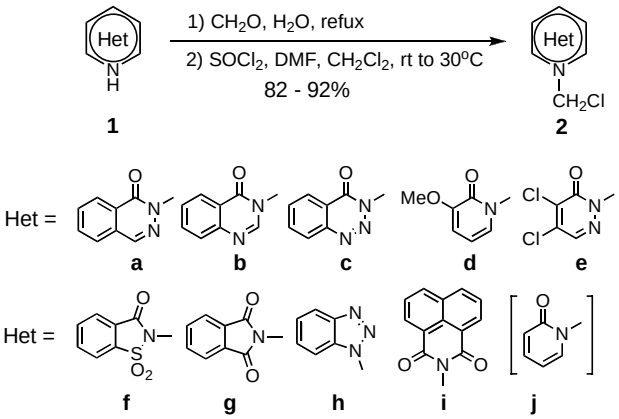
Organic molecules that contain styryl moiety are an important class of fluorescent molecules, which show a number of attractive photochemical and electro-optical properties [20,26-36]. The substitution of one phenyl ring of stilbene with a heterocyclic acceptor (pyridine) significantly affected the photophysical and photochemical behavior of these systems, because of the involvement of the (nπ*) excited state [28,37]. Thus, compounds such as *N*-styrylazines and *N*-styrylazinones containing Het-N-CH=CH-Ar moiety may possess photophysical properties suitable for fluorescent probe and sensor molecules. Also the derivatization of *N*-styrylazinones to useful derivatives containing various substituents on the phenyl ring and/or heterocycles is easy. The fluorescent properties of *N*-styrylazinones have not been reported, although some fluorescent probes not been reported, although some fluorescent probes containing styryl moiety have been synthesized [20-29].

Here we report on the synthesis and photophysical properties of some *N*-styrylazinones, focusing on the photophysical properties and potent fluorescent probes.

RESULTS AND DISCUSSION

As part of our research program for the search of novel fluorescent molecules, we attempted to synthesize some *N*-styrylheteocycles. Although synthetic methods leading

Scheme 1

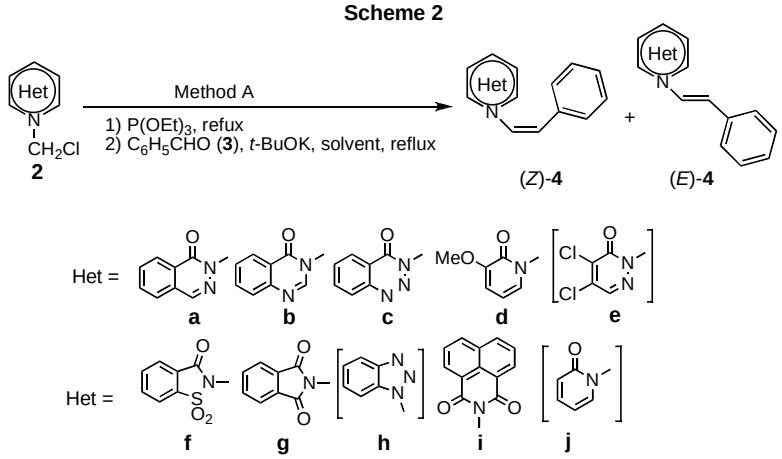


to some styryldiazines and few styrylazinones have been reported [38-51], they have some disadvantages such as low selectivity and low yield. Therefore, we tried synthesis of *N*-styrylazinones according to the synthetic sequence outlines depicted in Schemes 2-4.

N-Chloromethylheterocycles **2a** - **2i** were firstly prepared from heterocycles **1a** – **1i** in 82 – 92% yields according to the method described in the literature (Scheme 1) [52,53], whereas *N*-chloromethyl-2-pyridone (**1j**) could not be prepared from 2-pyridone by the same method.

2-chloromethyl-4,5-dichloropyridazin-3(2*H*)-one (**2e**) and benzaldehyde (**3**) according to Method B gave isomeric compounds (*Z*)-**4e** (5%) and (*E*)-**4e** (55%) (Scheme 3). However, **4h** and **4j** could also not synthesized by Method B. On the other hand, isomerizations of (*Z*)-isomers to the corresponding (*E*)-isomers on TLC were detected. In order to synthesize selectively (*E*)-**4a**, **4b**, **4d**, **4h** and **4j** isomers, therefore, we tried the synthesis by Method C [47]. Direct reaction of azinones **1a, 1b, 1d** and **1j** except for benzotriazole (**1h**) with (*E*)-β-bromostylene (**5**) in the

Scheme 2

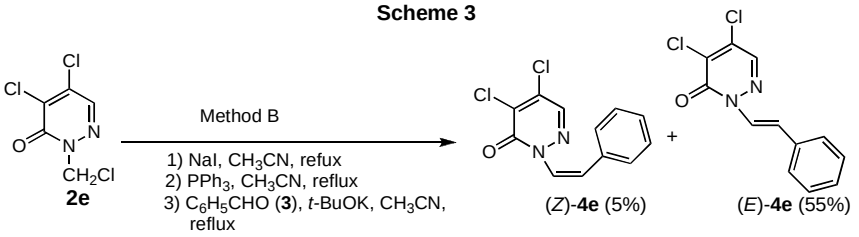


(*Z*)-and/or (*E*)-*N*-Styrylheterocycles for **4a–4d, 4f, 4g** and **4i** were synthesized from the corresponding *N*-chloromethyl derivatives **2** and benzaldehyde (**3**) by Method A (Table 1), whereas 2-styryl-4,5-dichloropyridazin-3(2*H*)-one (**4e**), 1-styrylbenzotriazole (**4h**) and *N*-styryl-2-pyridone (**4j**) could not be prepared by this Method. The main products in the Method A were the (*E*)-isomers.

Therefore, we attempted the synthesis of (*Z*)- and/or (*E*)-**4e**, **4h** and **4j** by using Method B. Coupling of

presence of potassium carbonate gave selectively the corresponding (*E*)-*N*-styrylazinones **4a** (89%), **4b** (82%), **4d** (79%) and **4j** (94%) (Scheme 4). On the other hand, coupling of benzotriazole (**1h**) with compound **5** by Method C gave (*E*)-1-styrylbenzotriazole (**4h**, 10%) and (*E*)-2-styrylbenzotriazole (5%), whereas compound (*E*)-**4h** was synthesized selectively from {[1*H*-benzo[*d*][1,2,3]triazol-1-yl]methyl}triphenylphosphonium chloride and benzaldehyde (**3**) in 67% yield by Method D (Scheme 4).

Scheme 3



Scheme 4

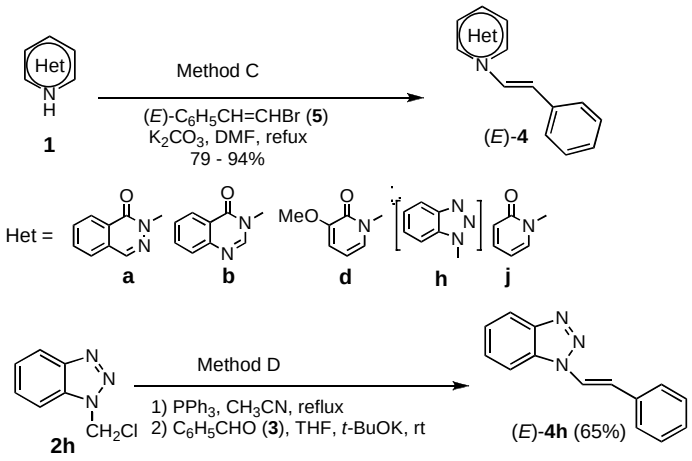


Table 1

Synthesis of (*Z*)-and/or (*E*)-*N*-Styrylheterocycles **4a**~**4j**

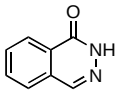
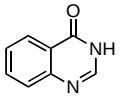
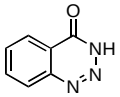
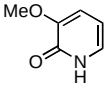
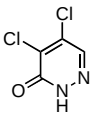
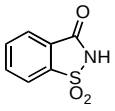
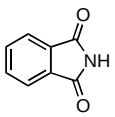
Entry	Heterocycles (**1**)	Method	Time (h)	Products (**4**)	
				(*Z*)-isomer (%)[a]	(*E*)-isomer (%)[a]
1		A	2	(*Z*)-**4a** (4)	(*E*)-**4a** (43)
2		C	23	—	(*E*)-**4a** (89)
3		A	2.5	(*Z*)-**4b** (trace)	(*E*)-**4b** (55)
4		C	24	—	(*E*)-**4b** (82)
5		A	1.5	(*Z*)-**4c** (5)	(*E*)-**4c** (44)
6		A	1	(*Z*)-**4d** (3)	(*E*)-**4d** (47)
7		C	24	—	(*E*)-**4d** (79)
8		B	2	(*Z*)-**4e** (5)	(*E*)-**4e** (55)
9		A	5	—	(*E*)-**4f** (42)
10		A	1	(*Z*)-**4g** (10)	(*E*)-**4g** (56)

Table 1

Synthesis of (*Z*)-and/or (*E*)-*N*-Styrylheterocycles **4a**~**4j**

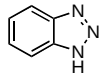
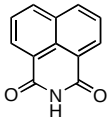
Entry	Heterocycles (**1**)	Method	Time (h)	Products (**4**) (*Z*)-isomer (%)[a]	(*E*)-isomer (%)[a]
11		C	38	—	(*E*)-**4h** (10)[c]
12		D	48	—[b]	(*E*)-**4h** (67)
13		A	0.5	—[b]	(*E*)-**4i**(65)
14		C	25	—[b]	(*E*)-**4j** (94)

Table 2

Long Wavelength Absorption Maxima for (*Z*)- and/or (*E*)-**4a~4j** at Room Temperature[a]

Compound	λ_{abs}^{max}(ε, $M^{-1}cm^{-1}$)			
	THF	CH_2Cl_2	CH_3CN	MeOH
(*Z*)-**4a**	325.5(12702)	316.5(8601)	319.5(4791)	317.0(10219)
(*E*)-**4a**	350.0(19852)	348.5(12977)	343.5(16585)	342.5(17964)
(*E*)-**4b**	324.0(12369)	322.0(14320)	321.0(12396)	319.5(14761)
(*Z*)-**4c**	352.0(2295)	352.5(3125)	346.5(3965)	348.0(4039)
(*E*)-**4c**	310.0(8056)	297.5(9126)	305.0(8151)	305.0(10316)
(*Z*)-**4d**	322.0(12618)	317.0(8755)	315.5(9389)	310.5(9048)
(*E*)-**4d**	343.5(9878)	338.5(11188)	338.0(7698)	332.0(14074)
(*Z*)-**4e**	338.0(8110)	332.5(6074)	328.0(5962)	326.5(8167)
(*E*)-**4e**	371.5(8515)	371.0(6283)	365.0(5978)	365.0(14556)
(*Z*)-**4f**	305.0(15483)	305.0(13577)	304.5(15061)	305.0(18793)
(*E*)-**4f**	300.0(8140)	300.0(10179)	298.5(8423)	268.0(21709)
(*Z*)-**4g**	261.0(14053)	261.5(15578)	258.5(14976)	266.5(18143)
(*E*)-**4g**	283.0(28628)	284.0(27204)	281.5(29090)	281.0(22546)
(*E*)-**4h**	316.0(16461)	299.5(14593)	311.5(7325)	305.0(10520)
(*E*)-**4i**	331.0(15850)	334.0(16720)	331.0(16950)	332.0(13710)
(*E*)-**4j**	348.5(16509)	345.0(14850)	344.0(16610)	336.5(12927)

[a]Data were collected from sample solution prepared under atmosphere without degassing or inert gas bubbling. The unit of λ_{abs}^{max} is nm.

All the compounds in this report gave satisfactory analytical and spectroscopic data in full accordance with the assigned structures. The (*Z*)- and (*E*)- isomers were easily distinguished by the coupling constants of the vinyl protons ($^3J_{(Z)}$ = 8.43 – 9.47 Hz; $^3J_{(E)}$ = 14.18 – 15.26 Hz).

The ultraviolet spectra of (*Z*)- and (*E*)-*N*-styrylazinones were measured in methylene chloride, tetrahydrofuran, acetonitrile and methanol. All the compounds in four solvents display a single, intense and long-wavelength absorption band. The corresponding absorption maxima (λ_{abs}) for (*Z*)- and/or (*E*)-**4a**–**4j** are reported in Table 2. The characteristic features of these compounds are that (*E*)-isomers absorb at longer wavelength than their corresponding (*Z*)-isomers for *N*-styryldiazinones (**4a** and **4e**) and *N*-styrylazinones (**4d** and **4g**), whereas *N*-styryltriazinone, (*Z*)-**4c** absorb at longer wavelength than their corresponding (*E*)-isomers.

The ultraviolet maximum for the (*Z*)-isomers of **4a**, **4d**, **4e** and **4g** are blue-shifted as compared to the corresponding (*E*)-isomers, a change consistent with deconjugation of heterocycles, carbon-carbon double bond and phenyl chromophores. This deconjugation may arise from twisting about the C-N bond between the heterocycle and vinyl group [27], and it may also depend on the kind of heterocycles for *N*-styrylheterocycles. Their absorption maxima showed moderate dependence on solvents, but they did not show regularity on the dielectric constants of solvents. Among all the compounds, (*E*)-2-styrylpyridazin-3(2*H*)-one [(*E*)-**4e**] showed the longest wavelength absorbance maxima at *ca* 365.0-371.0 nm in four solvents. The fluorescence spectra for (*Z*)- and/or (*E*)-*N*-styrylazinones were measured in methylene chlorides, tetrahydrofuran, acetonitrile, and methanol under neutral conditions. The corresponding fluorescence maxima (λ_f^{max}) for (*Z*)- and/or (*E*)-**4a**, **4b**, **4d**, **4e** and **4j** are reported in Table 3.

The kind of nitrogen-heterocycles affects the fluorescence properties of *N*-styrylazinones. *N*-Styryldiazinones

Table 3

Emission Maxima, Fluorescence Band Half-width ($\Delta\nu_{1/2}$), 0,0 Transition ($\lambda_{0,0}$), Stokes ($\Delta\nu_{st}$) and Quantum yield (Φ) for (*Z*)- and/or (*E*)- **4a**, **4b**, **4d**, **4e** and **4j**[a]

Entry	Compound	λ_f^{max}				$\Delta\nu_{1/2}$	$\lambda_{0,0}$	$\Delta\nu_{st}$	Quantum
		THF	CH_2Cl_2	CH_3CN	MeOH	(cm^{-1})	(nm)[c]	(cm^{-1})[d]	Yield(Φ)[e]
1	(*Z*)-**4a**	460.5	460.0	460.5	461.5	3956	388	9583	0.7034
2	(*E*)-**4a**	457.5	457.5	458.0	456.5	3928	398	7278	0.5229
3	(*E*)-**4b**	406.5	410.5	407.5	412.5	4637	359	6613	0.7914
4	(*Z*)-**4d**	430.0	420.5	417.0	407.5	4090	369	7715	0.8963
5	(*E*)-**4d**	425.0	413.0	428.0	418.0	4356	379	6221	0.4842
6	(*Z*)-**4e**	499.0	497.0	507.0	501.0	3642	395	10764	0.2566
7	(*E*)-**4e**	489.0	491.0	494.0	488.0	3465	429	7154	0.2610
8	(*E*)-**4j**	418.0	417.5	414.5	413.0	3301	386	4944	0.6059

[a]Data were collected from sample solution prepared under atmosphere without degassing or inert gas bubbling at room temperature. The unit of λ_{abs}^{max} is nm. Fluorescence band half-width ($\Delta\nu_{1/2}$), 0,0 transition ($\lambda_{0,0}$), and Stokes shifts ($\Delta\nu_{st}$) were measured in acetonitrile at room temperature. [b]Not available. [c]The value of $\lambda_{0,0}$ was obtained from the intersection of normalized absorption and fluorescence spectra. [d]$\Delta\nu_{st} = \nu_{sabs} - \nu_{f.}$ [e]Quantum yield of the emission is evaluated in acetonitrile at 25°C, the quantum yield values is that relative to 9,10-diphenylanthracene (1.00 x 10^{-4}M) in acetonitrile (from 352 nm excitation wavelength, $\Phi = 0.95$).

[(*Z*)-**4a**, (*E*)-**4a**, (*E*)-**4b**, (*Z*)-**4e** and (*E*)-**4e**] and *N*-styrylpyridones [(*Z*)-**4d**, (*E*)-**4d** and (*E*)-**4j**] showed the available emission spectra (Table 4), whereas the remaining compounds **4c**, and **4f**-**4i** did not give an available emission spectrum. The relationship between structure and fluorescence for **4a**-**4j** is show in Figure 1. Six membered-azinone derivatives containing one or two N_{sp2} atoms at α- or β-position of amide nitrogen such as **4a**, **4b**, **4d**, **4e** and **4j** are fluorescent, whereas *N*-styryl-azinones containing 1,2,3-triazine (**4c, 4h**) and azin-1,3-diones (**4g, 4i**) and *N*-styrylsaccharin (**4f**) are not fluorescent. Their emission maxima showed moderate solvatochroism, but they did not show regularity on the dielectric constants of solvents. The maxima of fluorescence of (*Z*)-**4a**, (*Z*)-**4d**, (*E*)-**4a**, (*E*)-**4b**, (*E*)-**4d** and (*E*)-**4j** appeared at 406.5-461.5 nm in four solvents, whereas the maxima of fluorescence of pyridazinone derivatives (*Z*)- and (*E*)-**4e** appeared at 488.0-507.0 nm in the same solvents. Fluorescence band half-width ($\Delta\nu_{1/2}$), 0,0 transition ($\lambda_{0,0}$), Stokes shifts ($\Delta\nu_{st}$) and

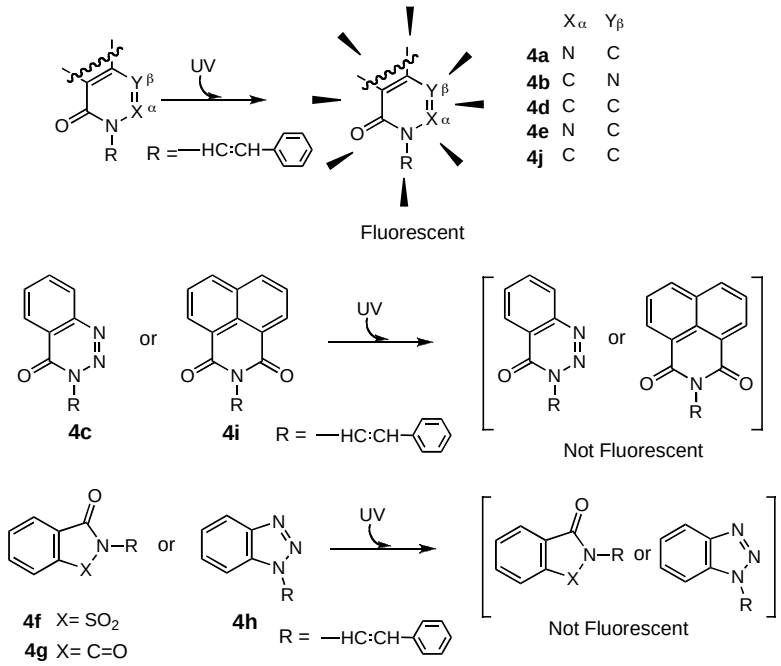


Figure 1. Relationship between the structures and the fluorescence.

quantum yield (Φ_f) of fluorescence for (*Z*)- and/or (*E*)-isomers **4a**, **4b**, **4d, 4e** and **4j** are presented in Table 3. Among the eight compounds, the value of $\lambda_{0,0}$ for (*E*)-**4e** is the largest. Compared with three isomeric pairs of (*Z*)-/(*E*)-**4a**, (*Z*)-/(*E*)-**4d** and (*Z*)-/(*E*)-**4e**, the Stokes shifts of (*Z*)-isomers are larger than the corresponding (*E*)-isomers. The Stokes shifts of (*Z*)-**4e** is the largest. The quantum yields (Φ_f) of (*Z*)-**4a** and (*Z*)-**4d** also are larger than those of their (*E*)- **4a** and (*E*)-**4d**, whereas the quantum yield (Φ_f) of (*Z*)-**4e** is smaller than that of (*E*)-**4e**.

This paper described the synthesis of nine isomeric *N*-styrylazinones and the investigation results of their optical spectroscopic properties. Nine *N*-chloromethylazinones except for 2-pyridone was prepared from the corresponding azinones in good to excellent yields. (*Z*)-and/or (*E*)-*N*-Styrylazinones (or azine) for **4a–4d, 4f, 4g** and **4i** were prepared from the corresponding *N*-chloromethyl derivatives and benzaldehyde. Also, compounds (*E*)-**4a**, **4b**, **4d** and **4j** synthesized selectively from the corresponding nitrogen-heterocylces and (*E*)-β-bromostylene (**5**) in good to excellent yields. Compound (*E*)-**4h** was synthesized selectively from {[1*H*-benzo[*d*][1,2,3]triazol-1-yl]methyl}triphenylphosphonium chloride and benzaldehyde (**3**) in 67% yield.

All the compounds in four solvents displayed a single intense long-wavelength absorption band. Their absorption maxima showed moderate dependence upon solvents. The absorption maxima of (*Z*)-isomers are blue-shifted as compared to the corresponding (*E*)-isomers. This blue shift is attributed to the deconjugation that twisted the C-N bond between the heterocycle and the vinyl group. The decojugation depends on the kind of heterocycles. The fluorescence spectra are in a normal Gaussisan shape except for (*E*)-**4d** and (*E*)-**4j**, showing moderate solvatochroism. The kind of heterocycle affects the fluorescence properties of *N*-styrylheterocycles. According to the relationship between structure and fluorescence for **4a**-**4j,** six membered-azinone derivatives containing one or two N_{sp2} atoms at α- or β-position of amide nitrogen such as **4a**, **4b**, **4d, 4e** and **4j** are fluorescent, whereas *N*-styrylazinones containing 1,2,3-triazine (**4c, 4h**) and azin-1,3-diones (**4g, 4i**) and *N*-styrylsaccharin (**4f**) are not fluorescent. These results may be a guide-line for the development of fluorescent molecules containing styryl moiety. *N*-Styryldiazinones **4a**, **4b** and **4e** and *N*-styrylpyridones **4d** and **4j** may be show potential for application as spectroscopic or fluorescent probes. Further work including the tuning of photophysical properties, the photoisomerization and application as fluorescence sensor are under way in our laboratory.

EXPERIMENTAL

General. Melting points were determined with a capillary apparatus and are uncorrected. ^{1}H and ^{13}C nmr spectra were recorded on a 300 MHz spectrometer with chemical shift values reported in δ (ppm) relative to an internal standard (TMS). Infrared spectra were obtained on an infrared spectrophotometer. Elemental analyses were performed with a Perkin Elmer 240 C. Open-bed chromatography was carried out on silica gel (70 – 230 mesh, Merck) using gravity flow. The column was packed as slurries with the elution solvent. UV spectra were measured on a Shimadzu PC-2401 double beam spectrophotometer. Fluorescence spectra were recorded on a PerkinElmer LS50B spectrofluorometer at room temperature. Quantum yield of the emission is evaluated in acetonitrile at 25°C, the quantum yield values are that relative to 9,10-diphenylanthrancene (1.00 x 10^{-4} *M*) in acetonitrile (from 352 nm extraction wavelength, $\Phi = 0.95$).

Typical process of *N*-chlormethylheterocycles. A mixture of nitrogen heterocycles **1** (340 mmol) and distilled water (350 ml) was stirred for 10 minutes at room temperature. After adding formaldehyde solution (36%, 70 ml), the solution was refluxed for 1.5 hours. After cooling to 5 – 10 °C, the resulting precipitate was collected by filtration, washed with cold water (0 – 5 °C, 200 ml) and dried in air to give the corresponding *N*-hydroxymethylheterocycles **2**. A solution of thionyl chloride (357 mmol) in methylene chloride (50 ml) was added slowly to the mixture of the resulting *N*-hydroxymethylheterocycle, methylene chloride (550 ml) and dimethylformamide (360 ml) for 30 minutes at room temperature with stirring. The resulting mixture was stirred for 2 hours at room temperature. After cooling to 0 °C, water (200 ml) was added slowly. And the solution was neutralized to pH 6.7 – 7.4 by using saturated solution of $NaHCO_3$ (50 ml). The organic layer was separated and then dried over anhydrous magnesium sulfate. The resulting organic solution was evaporated under reduced pressure. The residue was washed with *n*-hexane (100 ml) to give *N*-chloromethylheterocycles **2**.

***N*-Chloromethylphthalazin-1(2*H*)-one (2a).** Yield 87%. White crystal (diethyl ether/*n*-hexane = 1:2, v/v). mp 146 -147 °C (lit.[54] mp 146 -147 °C); tlc (CH_2Cl_2) R_f = 0.5; ir (KBr) 3100, 1700, 1600, 1580, 1360, 1260, 1180, 1160, 960 cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 7.76 ppm (s, 1H); ^{13}C nmr ($CDCl_3$) δ 134.8, 137.0, 137.5, 153.8 ppm. *Anal.* Calcd. for $C_4HCl_3N_2O$: C 24.09, H 0.51, N 14.05; Found: C 24.10, H 0.53, N 14.07.

***N*-Chloromethylquinazolin-4(3*H*)-one (2b).** Yield 89%. White crystal (diethyl ether/*n*-hexane = 1:2, v/v). mp 114 -115 °C (lit.[55] mp 119 °C); tlc (CH_2Cl_2) R_f = 0.29; ir (KBr) 3102, 2968, 1708, 1636, 1490, 1312, 1280, 1200, 1174, 790 cm^{-1}; ^{1}H nmr (DMSO-d_6): δ 5.99 (s, 2H), 7.60 – 7.67 (m, 1H), 7.72 – 7.75 (m, 1H), 7.88 – 7.96 (m, 1H), 8.20 – 8.24 (m, 1H), 8.65 ppm (s, 1H); ^{13}C nmr (DMSO-d_6) δ 54.23, 121.48, 126.80, 127.82, 128.35, 135.71, 147.39, 147.58, 159.55 ppm. *Anal.* Calcd. for $C_4HCl_3N_2O$: C 24.09, H 0.51, N 14.05; Found: C 24.07, H 0.49, N 14.06.

3-Chloromethyl-1,2,3-benzotriazin-4(3*H*)-one (2c). Yield 86%. White crystal (diethyl ether/*n*-hexane = 1:2, v/v). mp 127 -128 °C (lit.[56] mp 125 °C); tlc (CH_2Cl_2) R_f = 0.5; ir (KBr) 3082, 3014, 2988, 1700, 1464, 1306, 1060, 922, 780 cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 6.18 (s, 2H), 7.82 – 7.88 (m, 1H), 7.98 – 8.03 (m, 1H), 8.17 – 8.20 (m, 1H), 8.36 – 8.39 ppm (m, 1H); ^{13}C nmr ($CDCl_3$) δ 55.66, 119.56, 125.38, 128.91, 133.12, 135.59, 143.81, 154.60 ppm. *Anal.* Calcd. for $C_8H_6ClN_3O$: C 49.12, H 3.09, N 21.48; Found: C 49.10, H 3.06, N 21.50.

***N*-Chloromethyl-3-methoxypyrid-2(1*H*)-one (2d).** Yield 82%. White crystal (diethyl ether/*n*-hexane = 1:3, v/v). mp 108 -109 °C; tlc (EtOAc/CH_2Cl_2=1:1, v/v) R_f = 0.43; ir (KBr) 3102, 2984, 1680, 1620, 1274, 1240, 760, 696 cm^{-1}; ^{1}H nmr ($CDCl_3$): δ

3.93 (s, 3H), 5.73 (s, 2H), 6.19 (t, J = 7.19 Hz, 1H), 6.58 (dd, J = 1.57, 7.4 Hz, 1H), 7.01 (dd, J = 1.62, 7.03 Hz, 1H) ppm; ^{13}C nmr ($CDCl_3$) δ 55.47, 55.97, 106.17, 112.44, 126.95, 150.09, 157.41 ppm. *Anal.* Calcd. for $C_7H_8ClNO_2$: C 48.43, H 4.64, N 8.07; Found: C 48.40, H 4.62, N 8.06.

4,5-Dichloro-2-chloromethylpyridazin-3(2H)-one (2e). Yield 92%. White crystal (diethyl ether/*n*-hexane = 1:5, v/v). mp 69 - 70 °C (lit. [54] mp 70 - 71 °C); tlc (CH_2Cl_2) R_f = 0.65; ir (KBr) 3046, 2984, 1670, 1292, 1122, 964 cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 5.83 (s, 2H), 7.88 ppm (s, 1H); ^{13}C nmr ($CDCl_3$) δ 58.40, 134.87, 137.23, 137.34, 155.58 ppm. *Anal.* Calcd. for $C_5H_3Cl_3N_3O$: C 28.13, H 1.42, N 13.12; Found: C 28.10, H 1.41, N 13.09.

***N*-Chloromethylsaccharin (2f).** Yield 89%. White crystal (diethyl ether/*n*-hexane = 1:1, v/v). mp 146 -147 °C (lit. [57] mp 145-146 °C); tlc (CH_2Cl_2) R_f = 0.41; ir (KBr) 3062, 1736, 1286, 1202 cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 5.58 (s, 2H), 7.79 – 8.15 ppm (m, 4H); ^{13}C nmr ($CDCl_3$) δ 45.32, 121.26, 125.70, 126.30, 134.75, 135.65, 137.48, 157.48 ppm. *Anal.* Calcd. for $C_8H_6ClNO_3S$: C 41.48, H 2.61, N 6.05; Found: C 41.45, H 2.60, N 6.01.

***N*-Chloromethylphthalimide (2g).** Yield 90%. White crystal (diethyl ether/*n*-hexane = 1:2, v/v). mp 131 -133 °C (lit. [57] mp 130 -132 °C); tlc (CH_2Cl_2) R_f = 0.73; ir (KBr) 3058, 1762, 1466, 1428, 1382, 1308, 936, 730 cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 5.49 (s, 2H), 7.78 – 7.83 (m, 2H), 7.91 – 7.95 ppm (m, 2H); ^{13}C nmr ($CDCl_3$) δ 44.80, 124.24, 131.81, 134.83, 166.14 ppm. *Anal.* Calcd. for $C_9H_6ClNO_2$: C 55.26, H 3.09, N 7.16; Found: C 55.23, H 3.08, N 7.14.

1-Chloromethylbenzotriazole (2h). Yield 92%. White crystal (diethyl ether/*n*-hexane = 1:1, v/v). mp 136 -137 °C (lit. [58] mp 136 -139 °C); tlc (CH_2Cl_2) R_f = 0.51; ir (KBr) 3050, 2984, 1624, 1506, 1460, 1296, 1238, 1080, 754, 700 cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 6.41 (s, 2H), 7.42 – 7.47 (m, 1H), 7.56 – 7.61 (m, 1H), 7.66 – 7.69 (m, 1H), 8.08 – 8.11 ppm (m, 1H); ^{13}C nmr ($CDCl_3$) δ 53.45, 109.57, 120.51, 124.87, 128.60, 132.05, 146.53 ppm. *Anal.* Calcd. for $C_7H_6ClN_3$: C 50.17, H 3.61, N 25.07; Found: C 50.16, H 3.58, N 25.08.

***N*-Chloromethyl-1,8-naphthalimide (2i).** Yield 91%. White crystal (diethyl ether/*n*-hexane = 1:2, v/v). mp 215-216 °C; tlc (CH_2Cl_2) R_f = 0.64; ir (KBr) 3074, 3008, 1708, 1678, 1585, 1359, 1308, 1232, 1170, 946, 781 cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 6.00 (s, 2H), 7.77 (t, J = 8.04 Hz, 2H), 8.24 (d, J = 8.26 Hz, 2H), 8.62 ppm (d, J = 7.32 Hz, 2H); ^{13}C nmr ($CDCl_3$) δ 47.63, 121.79, 127.08, 131.69, 131.91, 134.77 ppm. *Anal.* Calcd. for $C_9H_6ClNO_2$: C 63.56, H 3.28, N 5.70; Found: C 63.53, H 3.27, N 5.69.

Typical Process of *N*-styrylheterocycles.

***Method A*.** A mixture of *N*-chloromethylheterocycles (204.5 mmol) and triethylphosphate (215 mmol) was refluxed for 3 hours. After cooling to room temperature, excess triethylphosphate was evaporated under reduced pressure to give crude product. A solution of the crude product and toluene (50 ml) for *N*-chloromethylphthalimide or tetrahydrofuran (50 ml) for *N*-chloromethylphthalazin-1(2*H*)-one, *N*-chloromethylquinazolin-4(3*H*)-one, 3-chloromethyl-1,2,3-benzotriazin-4(3*H*)-one, *N*-chloromethyl-3-methoxy-2(1*H*)-pyridone and *N*-chloromethylsaccharin was stirred for 30 minutes at room temperature. After adding slowly *t*-butoxide (1.3 g, 11.6 mmol) at room temperature, the mixture was refluxed for 3 hours. The solvent was evaporated. The residue was applied to the top of an open-bed silica gel column (10 x 2.5 cm). The column was eluted with ethyl acetate/methylene chloride (1:10, v/v). Fractions containing (*Z*)-isomer or (*E*)-isomer were combined and evaporated to give (*Z*)-and/or (*E*)-**4a**–**4d**, **4f, 4g** and **4i**, respectively.

***(Z)*-2-Styrylphthalazin-1(2*H*)-one [(*Z*)-4a].** Pale yellow crystal (diethyl ether/*n*-hexane = 1:2, v/v). mp 133 -134 °C; tlc (CH_2Cl_2) R_f = 0.41; ir (KBr) 3100, 3050, 1660, 1500, 1460, 1420, 1360, 1340, 1260, 1180, 1140, 1040, 960, 920, 780, 740, 700, 600 cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 6.49 (d, J = 9.47 Hz, 1H), 7.18 – 7.23 (m, 6H), 7.66 – 7.69 (m, 1H), 7.75 – 7.85 (m, 2H), 8.08 (s, 1H), 8.46 – 8.49 ppm (m, 1H); ^{13}C nmr ($CDCl_3$) δ 124.19, 126.32, 127.03, 127.59, 127.93, 127.98, 129.22, 129.59, 131.89, 133.53, 134.46, 138.28, 158.85 ppm. *Anal.* Calcd. for $C_{16}H_{12}N_2O$: C 77.40, H 4.87, N 11.28; Found: C 77.42, H 4.91, N 11.30.

***(Z)*-3-Styryl-1,2,3-benzotriazin-4(3*H*)-one [(*Z*)-4c].** White crystal (diethyl ether/*n*-hexane = 1:2, v/v). mp 164 -165 °C; tlc (CH_2Cl_2) R_f = 0.68; ir (KBr) 3134, 2968, 1718, 1472, 1322, 1104, 1080, 980, 794, 706 cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 7.26 – 7.32 (m, 1H), 7.35 – 7.40 (m, 2H), 7.53 – 7.59 (m, 3H), 7.78 – 7.83 (m, 1H), 7.91 – 7.97 (m, 1H), 8.17 – 8.23 (m, 2H), 8.39 ppm (dd, J = 1.39, 7.90 Hz, 1H); ^{13}C nmr ($CDCl_3$) δ 119.52, 121.51, 122.73, 125.61, 126.61, 126.94, 128.26, 128.78, 128.85, 132.76, 134.95, 135.06, 143.27, 153.74 ppm. *Anal.* Calcd. for $C_{15}H_{11}N_3O$: C 72.28, H 4.45, N 16.86; Found: C 72.20, H 4.43, N 16.84.

***(Z)*-3-Methoxy-1-styrylpyrid-2(1*H*)-one [(*Z*)-4d].** Pale yellow crystal (diethyl ether/*n*-hexane = 1:2, v/v) mp 164 -165 °C; tlc (CH_2Cl_2/ethyl acetate = 20:1, v/v) R_f = 0.17; ir (KBr) 3100, 3050, 2980, 1680, 1620, 1570, 1500, 1480, 1460, 1420, 1340, 1280, 1240, 1190, 1160, 1060, 960, 950, 890, 870, 800, 740, 700 cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 3.84 (s, 3H), 5.96 (t, J = 7.21 Hz, 2H), 6.50 (d, J = 9.26 Hz, 3H), 6.59 (dd, J = 1.59, 7.02 Hz, 1H), 6.70 (dd, J = 1.61, 7.02 Hz, 1H), 6.97 (d, J = 9.26 Hz, 1H), 7.12 – 7.16 (m, 2H), 7.22 – 7.26 ppm (m, 3H); ^{13}C nmr ($CDCl_3$) δ 55.87, 105.07, 112.35, 124.77, 126.93, 128.15, 128.15, 128.20, 128.56, 128.86, 133.04, 150.21, 157.91 ppm. *Anal.* Calcd. for $C_{14}H_{13}NO_2$: C 73.99, H 5.77, N 6.16; Found: C 73.97, H 5.74, N 6.15.

***(Z)*-*N*-Styrylphthalimide [(*Z*)-4g]**. Yellow crystal (diethyl ether/*n*-hexane = 1:2, v/v). mp 121 -122 °C; tlc (CH_2Cl_2) R_f = 0.67; ir (KBr) 3150, 3090, 1720, 1680, 1620, 1500, 1480, 1460, 1400, 1305, 1260, 1180, 1120, 1080, 1020, 980, 920, 800, 780, 740, 720, 700 cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 6.31 (d, J = 9.12 Hz, 1H), 6.68 (d, J = 9.12 Hz, 1H), 7.21 – 7.26 (m, 5H), 7.71 – 7.74 (m, 2H), 7.83 – 7.86 ppm (m, 2H); ^{13}C nmr ($CDCl_3$) δ 116.32, 123.73, 128.01, 128.24, 130.06, 132.16, 134.32, 135,06, 166.34 ppm. *Anal.* Calcd. for $C_{16}H_{11}NO_2$: C 77.10, H 4.45, N 5.62; Found: C 77.08, H 4.44, N 5.59.

***(E)*-2-Styrylphthalazin-1(2*H*)-one [(*E*)-4a].** Pale yellow crystal (diethyl ether/*n*-hexane = 1:2, v/v). mp 138 -139 °C; tlc (CH_2Cl_2) R_f = 0.72; ir (KBr) 3100, 3050, 1730, 1680, 1660, 1620, 1500, 1460, 1400, 1360, 1320, 1280, 1190, 1140, 1120, 1080, 1040, 960, 900, 800, 760, 750, 700 cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 7.23 – 7.27 (m, 2H), 7.33 – 7.38 (m, 2H), 7.52 – 7.54 (m, 2H), 7.70 – 7.73 (m, 1H), 7.75 – 7.82 (m, 2H), 8.27 (s, 1H), 8.36 (dd, J = 14.37 Hz, 1H), 8.46 – 8.49 ppm (m, 1H); ^{13}C nmr ($CDCl_3$) δ 118.49, 124.70, 126.45, 126.63, 127.33, 127.46, 127.88, 128.72, 129.02, 132.06, 133.44, 135.88, 137.72, 157.53 ppm. *Anal.* Calcd. for $C_{16}H_{12}N_2O$: C 77.40, H 4.87, N 11.28; Found: C 77.37, H 4.85, N 11.26.

***(E)*-3-Styrylquinazolin-4(3*H*)-one [(*E*)-4b].** Light yellow crystal (diethyl ether/*n*-hexane = 1:3, v/v). mp 159 -160 °C; tlc (CH_2Cl_2) R_f = 0.46; ir (KBr) 3100, 3050, 1680, 1610, 1570, 1480, 1460, 1440, 1360, 1320, 1300, 1280, 1240, 1180, 1160, 1100, 1020, 980, 950, 880, 780, 750, 690 cm^{-1}; ^{1}H nmr (CD_3OD +

$CDCl_3$): δ 7.24 (d, J = 14.81 Hz, 1H), 7.28 – 7.42 (m, 3H), 7.53 – 7.61 (m, 3H), 7.73 – 7.87 (m, 3H), 8.30 (dd, J = 1.14 Hz, 8.00 Hz, 1H), 8.54 ppm (s, 1H); ^{13}C nmr (CD_3OD + $CDCl_3$) δ 121.26, 122.87, 124.07, 126.60, 127.00, 127.81, 128.40, 128.69, 134.34, 134.78, 143.77, 146.99, 160.20 ppm. *Anal.* Calcd. for $C_{16}H_{12}N_2O$: C 77.40, H 4.87, N 11.28; Found: C 77.38, H 4.83, N 11.27.

***(E)*-3-Styryl-1,2,3-benzotriazin-4(3*H*)-one [(*E*)-4c].** Yellow crystal (diethyl ether/*n*-hexane = 1:4, v/v). mp 175 -176 °C; tlc (CH_2Cl_2) R_f = 0.45; ir (KBr) 3100, 3050, 1705, 1690, 1660, 1620, 1600, 1500, 1480, 1460, 1340, 1320, 1280, 1220, 1200, 1120, 1100, 1080, 1040, 1000, 980, 900, 860, 780, 760, 700, 620 cm^{-1}; ^{1}H nmr (DMSO-d_6 + $CDCl_3$): δ 6.38 (d, J = 14.69 Hz, 1H), 7.15 – 7.22 (m, 1H), 7.27 – 7.32 (m, 2H), 7.36 – 7.39 (m, 2H), 7.44 – 7.49 (m, 2H), 7.51 – 7.57 (m, 1H), 7.72 (d, J = 14.07 Hz, 1H), 7.90 ppm (d, J = 7.13 Hz, 2H); ^{13}C nmr (DMSO-d_6 + $CDCl_3$) δ 117.99, 127.25, 129.46, 130.49, 131.27, 132.44, 132.51, 135.86, 137.40, 140.35, 169.60 ppm. *Anal.* Calcd. for $C_{15}H_{11}N_3O$: C 72.28, H 4.45, N 16.86; Found: C 72.27, H 4.41, N 16.85.

***(E)*-3-Methoxy-1-styrylpyridin-2(1*H*)-one [(*E*)-4d].** Pale yellow crystal (diethyl ether/*n*-hexane = 1:3, v/v). mp 165 -166 °C; tlc (CH_2Cl_2/ethyl acetate = 20:1, v/v) R_f = 0.29; ir (KBr) 3105, 3080, 3000, 2950, 1680, 1620, 1570, 1520, 1480, 1400, 1280, 1220, 1085, 1000, 880, 780, 760, 720, 680 cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 3.83 (s, 3H), 6.19 (t, J = 7.28 Hz, 1H), 6.60 (d, J = 7.37 Hz, 1H), 6.65 (d, J = 14.85 Hz, 1H), 7.25 – 7.30 (m, 2H), 7.32 – 7.37 (m, 2H), 7.46 (d, J = 7.95 Hz, 2H), 8.04 ppm (d, J = 14.85 Hz, 1H); ^{13}C nmr ($CDCl_3$) δ 55.97, 105.62, 111.61, 120.66, 123.59, 125.80, 126.69, 128.09, 128.78, 134.82, 150.36, 157.07 ppm. *Anal.* Calcd. for $C_{14}H_{13}NO_2$: C 73.99, H 5.77, N 6.16; Found: C 73.96, H 5.75, N 6.13.

***(E)*-2-Styrylsaccharine [(*E*)-4f].** White crystal (diethyl ether: *n*-hexane = 1:2, v/v). mp 163 -164 °C; tlc (CH_2Cl_2) R_f = 0.78; ir (KBr) 3095, 3010, 1740, 1642, 1600, 1485, 1450, 1350, 1300, 1285, 1180, 1120, 1090, 1060, 940, 840, 800, 750, 650 cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 7.10 (d, J = 15.19 Hz, 1H), 7.20 – 7.48 (m, 7H), 7.84 – 7.98 (m, 3H), 8.11 – 8.14 ppm (m, 1H); ^{13}C nmr ($CDCl_3$) δ 115.35, 121.08, 121.34, 125.61, 126.51, 126.67, 128.26, 128.81, 134.64, 134.69, 135.14, 137.59, 156.67 ppm. *Anal.* Calcd. for $C_{15}H_{11}NSO_3$: C 63.14, H 3.89, N 4.91; Found: C 63.12, H 3.86, N 4.90.

***(E)*-*N*-Styrylphthalimide [(*E*)-4g].** Yellow crystal (diethyl ether: *n*-hexane = 1:2 v/v). mp 187 -188 °C; tlc (CH_2Cl_2) R_f = 0.80; ir (KBr) 3150, 3090, 1740, 1680, 1630, 1490, 1480, 1405, 1240, 1200, 1140, 1050, 1040, 980, 920, 820, 780, 740, 705 cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 7.25 – 7.30 (m, 1H), 7.34 – 7.39 (m, 3H), 7.48 – 7.50 (m, 2H), 7.66 (d, J = 15. 16 Hz, 1H), 7.75 – 7.79 (m, 2H), 7.88 – 7.92 ppm (m, 2H); ^{13}C nmr ($CDCl_3$) δ 105.62, 111.61, 120.66, 123.59, 125.80, 126.69, 128.09, 128.78, 134.82, 150.36, 157.07 ppm. *Anal.* Calcd. for $C_{16}H_{11}NO_2$: C 77.10, H 4.45, N 5.62; Found: C 77.10, H 4.41, N 5.57.

***(E)*-*N*-Styryl-1,8-naphthalimide [(*E*)-4i].** Thin yellow crystal (diethyl ether/*n*-hexane = 1:1 v/v). mp 168-169 °C; tlc (CH_2Cl_2) R_f = 0.56; ir (KBr) 3060, 3028, 1705, 1671, 1666, 1582, 1369, 1352, 1304, 1231, 1178, 940, 893, 778 cm^{-1}; ^{1}H nmr (DMSO-d_6): δ 7.32 (d, J = 15.05 Hz, 1H), 7.33 – 7.35 (m, 1H), 7.39 – 7.44 (m, 2H), 7.45 (d, J = 14.94 Hz, 1H), 7.55 (d, J = 7.44 Hz, 2H), 7.85 (t, J = 7.47 Hz, 2H), 8.43 (d, J = 8.26 Hz, 2H), 8.47 ppm (d, J = 7.25 Hz, 2H); ^{13}C nmr ($CDCl_3$) δ 120.71, 122.50, 126.69, 127.07, 127.88, 127.93, 128.67, 131.52, 131.66, 134.14, 136.05 ppm. *Anal.* Calcd. for $C_{20}H_{13}NO_2$: C 80.25, H 4.38, N 4.68; Found: C 80.19, H 4.36, N 4.68.

***Method B*.** A mixture of 2-chloromethyl-4,5-dichloropyridazin-3(2*H*)-one (3 g, 14.055 mmol), sodium iodide (2.45 g, 14.76 mmol) and acetonitrile (50 ml) was refluxed for 2 hours. After cooling to 30–40 °C, triphenylphosphine (4.07 g, 15.51 mmol) was added to the reaction solution. And the mixture was then refluxed for 2 hours. Benzaldehyde (1.5 g, 14.10 mmol) and potassium *t*-butoxide (2.05 g, 95%, 17.21 mmol) were added to the reaction solution. The resulting mixture was refluxed for additional 1 hour. After evaporating the solvent was stirred for 20 minutes, then filtered by using Celite 545 and washed with methylene chloride (50 ml). The organic layer was separated and dried over anhydrous magnesium sulfate. The organic solution was evaporated under reduced pressure and the resulting residue was applied to the top of an open-bed silica gel. The column was eluted with methylene chloride/*n*-hexane (1: 5, v/v). Fractions containing (*Z*)- **4e** or (*E*)- **4e** were combined and evaporated to give (*Z*)- **4e** or (*E*)- **4e**, respectively.

***(Z)*-4,5-Dichloro-2-styrylpyridazin-3(2*H*)-one [(*Z*)-4e].** Pale yellow crystal (diethyl ether/*n*-hexane = 1:2, v/v). mp 110 -111 °C; tlc (CH_2Cl_2) R_f = 0.58; ir (KBr) 3100, 3060, 3000, 1660, 1580, 1500, 1460, 1400, 1370, 1340, 1305, 1280, 1220, 1180, 1165, 1140, 980, 900, 840, 800, 780, 760, 700, 640 cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 6.58 (d, J = 9.43 Hz, 1H), 7.00 (d, J = 9.43 Hz, 1H), 7.11 – 7.16 (m, 2H), 7.22 – 7.31 (m, 3H), 7.67 ppm (s, 1H); ^{13}C nmr ($CDCl_3$) δ 125.46, 126.72, 128.19, 128.27, 128.90, 133.41, 134.53, 135.85, 136.60, 155.83 ppm. *Anal.* Calcd. for $C_{12}H_8N_2Cl_2O$: C 53.96, H 3.02, N 10.49; Found: C 53.93, H 3.00, N 10.41.

***(E)*-4,5-Dichloro-2-styrylpyridazin-3(2*H*)-one [(*E*)-4e].** Pale yellow crystal (diethyl ether/*n*-hexane = 1:2, v/v). mp 161 -162 °C; tlc (CH_2Cl_2) R_f = 0.74; ir (KBr) 3108, 1664, 1592, 1300, 1238, 1134, 958, 898, 742, 696 cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 7.26 (d, J = 14.18 Hz, 1H), 7.28 – 7.38 (m, 3H), 7.47 – 7.50 (m, 2H), 7.86 (s, 1H), 8.10 ppm (d, J = 14.35 Hz, 1H); ^{13}C nmr ($CDCl_3$) δ 122.21, 124.13, 127.02, 128.49, 128.88, 134.49, 134.56, 135.94, 136.04, 154.68 ppm. *Anal.* Calcd. for $C_{12}H_8N_2Cl_2O$: C 53.96, H 3.02, N 10.49; Found: C 53.93, H 3.00, N 10.41.

***Method C*.** A mixture of heterocycles **1** (0.011 mol), (*E*)-β-bromostyrene (1.94 g, 0.013 mol), anhydrous potassium carbonate (3.34 g, 0.024 mol) and anhydrous dimethylformamaide (20 ml) was refluxed for 23–38 h under nitrogen. After cooling to room temperature, the reaction mixture was poured into ice water with stirring. The precipitate was collected by filtration, dried in air and recrystallized in suitable solvent to give (*E*)-**4a** (89%), (*E*)-**4b** (82%), (*E*)-**4d** (79%), (*E*)-**4h** (10%) and (*E*)-**4j** (94%).

***(E)*-1-Styrylpyridin-2(1*H*)-one [(*E*)-4j].** Pale yellow crystal (diethyl ether/*n*-hexane = 1:2, v/v). mp 150-151 °C; tlc (CH_2Cl_2) R_f = 0.15; ir (KBr) 3132, 2986, 1680, 1608, 1544, 1408, 1360, 1282, 1152, 976, 770, 706 cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 6.24 (t, J = 6.96 Hz, 1H), 6.59 (d, J = 8.84 Hz, 1H), 6.67 (d, J = 14.84 Hz, 1H), 7.26 – 7.38 (m, 4H), 7.46 – 7.48 (m, 2H) 7.61 (dd, J = 1.78, 7.04 Hz, 1H), 7.98 ppm (d, J = 14.84 Hz, 1H); ^{13}C nmr ($CDCl_3$) δ 105.62, 111.61, 120.66, 123.59, 125.80, 126.69, 128.09, 128.78, 134.82, 150.36, 157.07 ppm. *Anal.* Calcd. for $C_{13}H_{11}NO$: C 79.16, H 5.62, N 7.10; Found: C 79.13, H 5.58, N 7.11.

Method D. A mixture of *N*-chloromethylbenzotriazole (**2h**, 15.0 mmol), triphenylphosphine (16.5 mmol) and acetonitrile (60 ml) was refluxed for 48 hours. After cooling to 20~30 °C, The ((1*H*-benzo[*d*][1,2,3]triazol-1-yl)methyl)triphenylphosphonium chloride was collected by filtration, washed with dichloromethane(30ml x 2) and dried at room temperature. To a solution

of the crude product and tetrahydrofuran (50 ml or toluene) was added a benzaldehyde(15.1 mmol). The mixture was stirred for 30 minutes at room temperature. After adding slowly *t*-butoxide (1.3 g, 11.6 mmol) at room temperature, the mixture was stirred for 2 hours. The solvent was evaporated. The residue was applied to the top of an open-bed silica gel column (12 x 3.5 cm). The column was eluted with ethyl acetate/methylene chloride (1:10, v/v). Fractions containing (*Z*)-isomer or (*E*)-isomer were combined and evaporated to give (*E*)-**4h**.

(*E*)-1-Styrylbenzotiriazole [(*E*)-4h]. White crystal (diethyl ether /*n*-hexane = 1:5, v/v). mp 115 -116 °C (lit. [59] mp 116-117 °C); tlc (CH_2Cl_2/*n*-hexane = 2:1, v/v) R_f = 0.16. IR (KBr) 3062, 3024, 1652, 1486, 1452, 1163, 1056, 941, 744, 690 cm^{-1}; ^1H nmr ($CDCl_3$): δ 7.29 – 7.58 (m, 8 H), 7.71 – 7.58(m, 1H), 7.89(d, J = 14.64 Hz, 1H), 8.07 – 8.10 ppm (m, 1H); ^{13}C nmr ($CDCl_3$): δ 110.10, 120.41, 121.04, 121.77, 124.64, 126.59, 128.29, 128.48, 129.01, 131.50, 134.34, 146.34 ppm. *Anal.* Calcd. for $C_{14}H_{11}N_3$: C 76.00, H 5.01, N 18.99; Found: C 75.98, H 5.01, N 18.97.

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