PREPARATION OF NEW NITROGEN-BRIDGED HETEROCYCLES. 62.[1] REACTION OF POTASSIUM PYRAZOLO[1,5-*a*]PYRIDINE-2-THIOLATES WITH ELECTRON-POOR ALKYNES

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Abstract : The reactions of potassium 3-cyano- and 3-(ethoxycarbonyl)pyrazolo[1,5-*a*]pyridine-2-thiolates, readily generated by the treatment of the corresponding 2-[(2-ethoxycarbonylethyl)-thio]pyrazolo[1,5-*a*]pyridines with potassium *tert*-butoxide in dimethylformamide, with electron deficient acetylenes such as ethyl propiolate and methyl phenylpropiolate were investigated. In these reactions intramolecular nucleophilic addition of initially formed anion intermediates onto the 3-cyano or 3-ethoxycarbonyl group was not observed, but the Michael-type adducts, ethyl or methyl 3-[(pyrazolo[1,5-*a*]pyridin-2-yl)thio]acrylates, were obtained in low to good yields. The stereochemistry of the acrylate moiety in these products was determined by ^{1}H-NMR spectroscopy and X-ray analysis, and the predominant *trans* mode of the addition was confirmed.

Introduction

The Michael addition is a conjugated addition of carbanion species to electron-poor alkenes and alkynes and is an useful method for stretching carbon-carbon bonds.[2] The hetero-versions using amines or hydroxy compounds as a nucleophile are also a convenient method for introducing a new carbon-heteroatom bond at a specific position.[3-5] Of the latter reactions, those using electron-poor propiolates afford the corresponding push-pull type of alkene derivatives which are not easily available by other methods. However, the primary adducts generated in these reactions are generally unstable because of their polarized carbon-carbon double bonds. Especially, when an intramolecular hydrogen bonding or steric hindrance is present, the smooth *cis-trans* isomerization of the double bond can occur and hence the addition mode of the nucleophile onto the triple bond tends to obscure. On the other hand, the double bond in vinylic thioethers is more stable and not susceptible to such *cis-trans* isomerization because of the dramatic relief of steric hindrance by the long carbon-sulfur bond and of the considerably weak ability for a hydrogen-bonding. According to the Woodward-Hoffmann rule[6] a Michael addition will become a *trans* mode as shown in Scheme 1 unless the carbon–oxygen bond of the allenyl alcoholate **B** rotates (see Figure 1). An alternative possibility of the inversion of the vinylic anion **C** to the corresponding **D** will be negligible because of the requirement for large movement of a substituent (alkoxycarbonyl group) on the anionic carbon.

Previously we have reported that the reactions of potassium 1,3-bis(ethoxycarbonyl)indolizine-2-thiolates with dimethyl acetylenedicarboxylate gave the corresponding Michael adducts *via* the

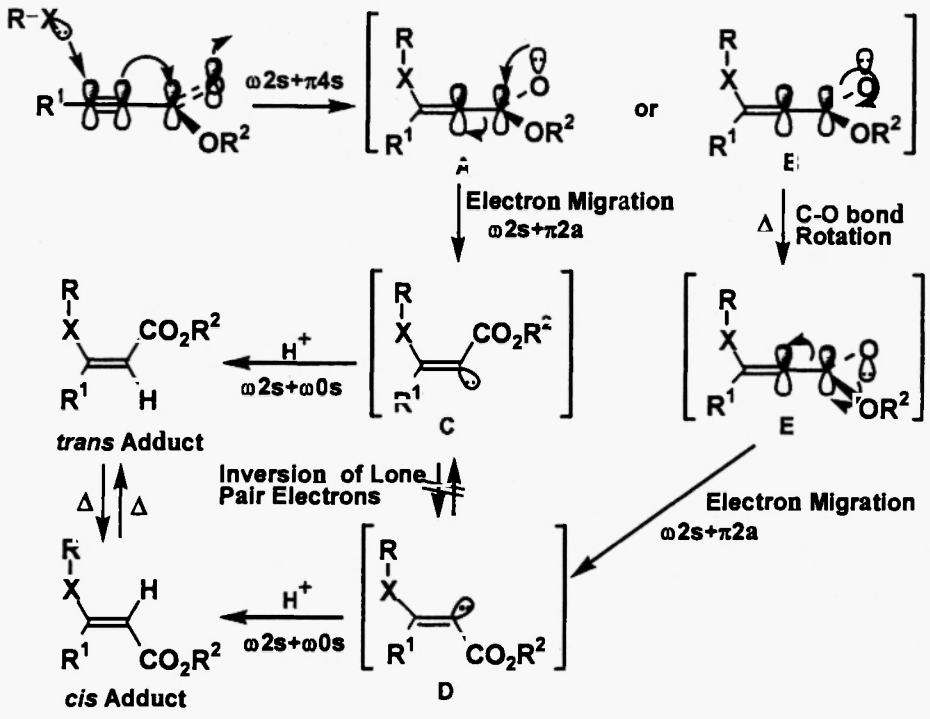


Figure-1

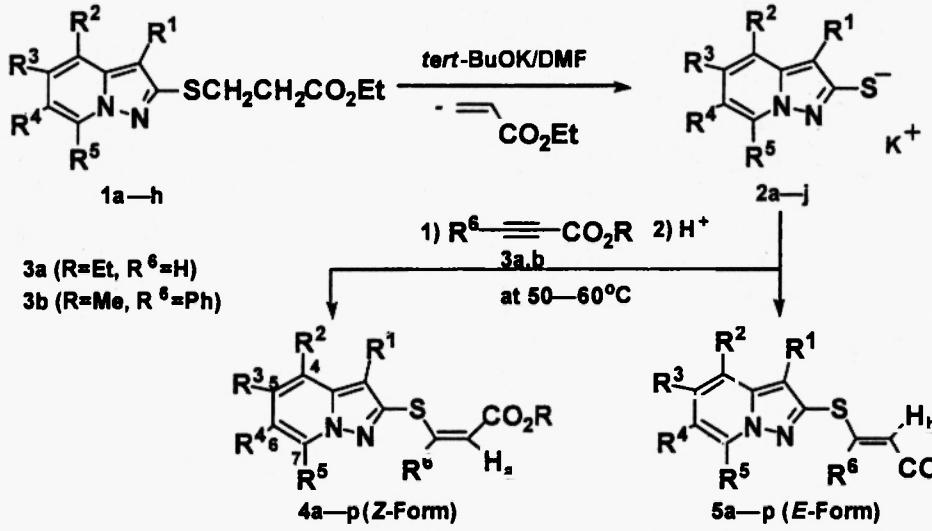
trans addition mode at a lower temperature (60 °C) and at a higher temperature (80 °C) provided thiino[2,3-*b*]indolizin-4-one derivatives *via* the intramolecular nucleophilic addition of a *cis*-mode intermediate such as **D** to the 3-ester carbonyl group.[7] Similar reactions with ethyl propiolate gave only the corresponding acrylates in low yields *via* the *trans* addition. In our effort to establish the mode of a Michael addition, we were interested in the reactions of pyrazolo[1,5-*a*]pyridine-2-thiolates with the electron poor alkynes. In this paper we report the Michael addition of some potassium pyrazolo[1,5-*a*]pyridine-2-thiolates onto ethyl propiolate and methyl 3-phenylpropiolate.

Results and Discussion

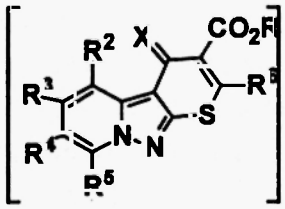
Reactions of Potassium Pyrazolo[1,5-*a*]pyridine-2-thiolates with Propiolates. When the reactions of potassium pyrazolo[1,5-*a*]pyridine-2-thiolates (**2a–h**), generated in situ from the treatment of 2-[(2-ethoxycarbonylethyl)thio]pyrazolo[1,5-*a*]pyridines (**1a–h**)[8] with potassium *tert*-butoxide in dimethylformamide (DMF), with ethyl propiolate (**3a**) at 50–60 °C in a water bath were performed, the corresponding Michael adducts, ethyl 3-[(pyrazolo[1,5-*a*]pyridin-2-yl)thio]acrylate derivatives (**4a–h** and **5a–h**) were formed in low to moderate yields(16–82%) as the *E*- and *Z*-mixtures. The preferred formation of *Z*-forms (**4a–h**) over *E*-forms (**5a–h**) in all reactions was observed. Similar reactions of thiolates **2a–d,g,h** with methyl 3-phenylpropiolate (**3b**) provided only the *Z*-form adducts **4i–l,o,p**, but those of **2e,f** with the same reagent afforded the *E*- and *Z*-mixtures in which **4m,n** (*Z*-form) were also predominant. When these reactions of pyrazolo[1,5-*a*]pyridine-2-thiolates (**2a–h**) with propiolates **3a,b** were carried out at room temperature, however, the expected Michael adducts **4** and **5** could be obtained only in low yields, and, instead of them,

the considerable amounts of corresponding pyrazolo[1,5-*a*]pyridine-2-thiols were formed.[6] In these reactions the tricyclic thiino[2',3':3,4]pyrazolo[1,5-*a*]pyridine derivatives such as **6** which might be formed from the intramolecular nucleophilic additions of initially formed carbanion intermediates onto the 3-ester carbonyl or the 3-cyano group was not detected at all. These results are summarized in Scheme-1.

The structural assignments for ethyl 3-[(pyrazolo[1,5-*a*]pyridin-2-yl)thio]acrylate derivatives (**4a–p** and **5a–h,m,n**) were mainly accomplished by elemental and spectral analyses. For example,



1,2	R^1	R^2	R^3	R^4	R^5
a	CN	H	H	H	H
b	CN	H	H	H	Me
c	CN	H	Me	H	H
d	CN	Me	H	Me	H
e	CO_2Et	H	H	H	H
f	CO_2Et	H	H	H	Me
g	CO_2Et	H	Me	H	H
h	CO_2Et	Me	H	Me	H



6 (X=O or NH)

React.	Prod.(Ratio)	Yield[a] (%)	R^1	R^2	R^3	R^4	R^5	R^6	R
2a+3a	4a+5a(10:1)	46	CN	H	H	H	H	H	Et
2b+3a	4b+5b (9:1)	26	CN	H	H	H	Me	H	Et
2c+3a	4c+5c (9:1)	61	CN	H	Me	H	H	H	Et
2d+3a	4d+5d (40:1)	16	CN	Me	H	Me	H	H	Et
2e+3a	4e+5e (9:1)	29	CO_2Et	H	H	H	H	H	Et
2f+3a	4f+5f (7:3)	52	CO_2Et	H	H	H	Me	H	Et
2g+3a	4g+5g (9:1)	52	CO_2Et	H	Me	H	H	H	Et
2h+3a	4h+5h (4:1)	47	CO_2Et	Me	H	Me	H	H	Et
2a+3b	4i	75	CN	H	H	H	H	Ph	Me
2b+3b	4j	82	CN	H	H	H	Me	Ph	Me
2c+3b	4k	68	CN	H	H	Me	H	Ph	Me
2d+3b	4l	80	CN	Me	H	Me	H	Ph	Me
2e+3b	4m+5m(97:3)	17	CO_2Et	H	H	H	H	Ph	Me
2f+3b	4n+5n(10:1)	56	CO_2Et	H	H	H	Me	Ph	Me
2g+3b	4o	56	CO_2Et	H	Me	H	H	Ph	Me
2h+3b	4p	54	CO_2Et	Me	H	Me	H	Ph	Me

a) Yield from 1.

Scheme-1

Table-1 : ^{1}H-NMR Spectral data of acrylate derivatives 4a–p and 5a–h,m,n.

No.[a)]	C-4	C-5	C-6	C-7	H_a or H_b	R^6	R^1	R
4a	7.70	7.48	7.02	8.50	6.14	7.96		1.35 4.29
4b	7.58	7.41	6.87	2.80	6.14	8.03		1.35 4.29
4c	7.45	2.48	6.83	8.35	6.12	7.93		1.34 4.29
4d	2.68	7.03	2.35	8.12	6.11	7.99		1.34 4.28
4e	8.12	7.41	6.94	8.44	6.10	8.48	1.46 4.43	1.35 4.28
4f	8.02	7.35	6.79	2.78	6.10	8.60	1.46 4.42	1.36 4.29
4g	7.89	2.46	6.76	8.30	6.08	8.46	1.46 4.42	1.35 4.28
4h	2.71	6.99	2.32	8.11	6.06	8.45	1.47 4.39	1.34 4.27
4i	7.47	7.34	6.93	8.36	6.25	7.0-7.2 7.3-7.4		3.85
4j	b)	7.27	6.75	2.62	6.23	7.0-7.1 7.3-7.4		3.84
4k	7.22	2.38	6.73	8.22	6.23	7.0-7.2 7.3-7.4		3.84
4l	2.49	6.89	2.27	8.00	6.21	7.0-7.5		3.84
4m	7.94	7.28	6.83	8.26	6.26	7.0-7.1 7.3-7.4	1.42 4.37	3.82
4n	7.85	7.21	6.64	2.47	6.27	7.0-7.1 7.3-7.5	1.44 4.39	3.82
4o	7.71	2.37	6.65	8.13	6.23	7.0-7.1 7.3-7.4	1.42 4.36	3.82
4p	2.52	6.84	2.22	7.87	6.21	7.0-7.1 7.3-7.4	1.43 4.37	3.81
5a	7.54	7.36	6.87	8.33	6.12	8.11		1.26 4.24
5b	b)	7.46	6.98	2.81	6.09	8.13		1.30 4.22
5c	7.46	2.50	6.87	8.40	6.10	8.08		1.30 4.22
5d	b)	b)	b)	b)	6.09	8.03		1.29 4.21
5e	8.06	b)	6.37	b)	6.23	8.67	1.42 4.35	1.30 4.23
5f	b)	b)	b)	2.80	6.24	8.78	b)	b)
5g	7.82	2.46	b)	8.35	6.23	8.65	1.44 4.42	1.34 4.24
5h	b)	7.00	b)	8.17	6.20	8.63	b)	b)
5m	8.14	7.43	6.98	8.46	6.07	7.0-7.1 7.3-7.6	1.34 4.29	3.51
5n	8.01	b)	6.79	2.71	6.18	7.0-7.1 7.3-7.6	1.35 4.29	3.53

a) The coupling constants are as follows; $J_{4,5}$=8.8–8.9 Hz, $J_{5,6}$=6.9–7.1 Hz, $J_{6,7}$=6.9–7.1 Hz, $J_{4,6}$=0.7–1.9 Hz, $J_{5,7}$=0.8–1.1 Hz, J_{Et}=7.1–7.2 Hz, $J_{vinyl\text{-}cis}$=9.8–10.4 Hz, $J_{vinyl\text{-}trans}$= 15.4–16.0 Hz. b) Overlapped with the proton signals of major product.

their elemental analyses coincided with the compositions for our proposed structures and IR spectra revealed the presence of an α,β-unsaturated cyano (2206–2220 cm^{-1}) and/or carbonyl groups (1678–1721 cm^{-1}). The remarkable characteristics in ^{1}H-NMR spectra (Table 1) of these acrylates are that they have the AB type signals for the vinyl protons at δ 6.06–6.14 and 7.93–8.60 (**4a–h**, its coupling constant is ca. 10.0 Hz) and at δ 6.09–6.24 and δ 8.03–8.78 (**5a–h**, its coupling constant is 15.4–16.0 Hz) respectively. The values of the coupling constants(ca. 10.0 Hz) for **4a–h** clearly demonstrated the *cis*-configuration and those (15.4–16.0 Hz) for **5a–h** showed the *trans*-configuration. Interestingly, a significant low-field shift (0.46–0.65 ppm) for the vinylic β-proton in ethyl 3-[[3-(ethoxycarbonyl)pyrazolo[1,5-*a*]pyridin-2-yl]thio]acrylates (**4e–h** and **5e–h**) was also observed, compared to the 3-[[3-cyanopyrazolo-[1,5-*a*]pyridin-2-yl]thio]acrylates (**4a–d** and **5a–d**). This effect strongly suggested the proximity between the 3-ethoxycarbonyl group and the acrylate moiety in **4e–h** and **5e–h**. On the other hand, the structural assignment for **4i–p** and **5m,n**, which have only one vinylic proton, was carried out by the comparison of the chemical shifts for each vinylic proton and X-ray analysis of one

compound **4j**. The chemical shifts for the H_a-protons in *Z*-forms **4i–p** appeared at a higher region than for the H_b-protons in *E*-forms **5m,n**, indicating the deshielding effect of the β-phenyl group in the former. Furthermore, the proton signals for the α-methoxycarbonyl group in E-forms **5m,n**, appeared near δ=3.5 ppm considerably higher than for the Z-forms (near δ=3.8). This high-field shift must be caused by the shielding effect of the β-phenyl group in **5m,n**. The final structural assignment for products **4i–p** and **5m,n** was accomplished by the X-ray analysis of one major compound **4j**. The ORTEP drawing[9] for **4j** is shown in Figure 2. From this drawing the *E*-form at the acrylate moiety and the deshielding effect of the β-phenyl group on the H_a-proton for major products **4i–p** can be easily visualized.

In summary, we examined Michael additions of some potassium pyrazolo[1,5-*a*]pyridine-2-thiolates with ethyl propiolate and methyl 3-phenylpropiolate and found a predominant or exclusive *trans* addition mode in these reactions.

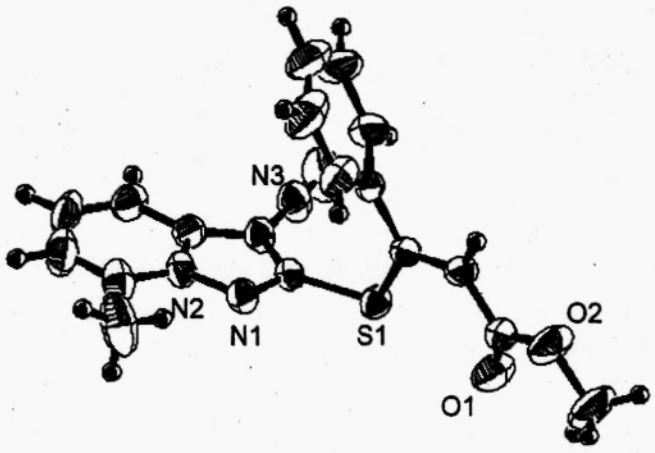


Figure-2 : ORTEP Drawing of compound **4j**.

Experimental

Melting points were measured with a Yanagimoto micromelting point apparatus and were not corrected. Microanalyses were carried out on a Perkin-Elmer 2400 elemental analyzer. The ^{1}H-NMR spectra were determined with a JEOL JNM-LA400 (^{1}H: 400 MHz) and Bruker DRX500 400 (^{1}H: 500 MHz) spectrometer in deuteriochloroform with tetramethylsilane used as the internal standard; the chemical shifts are expressed in δ values. The IR spectra were taken with JASCO FT/IR-5300 IR spectrophotometers.

Michael Additons of Pyrazolo[1,5-*a*]pyridine-2-thiolates with Ethyl Propiolate and Methyl 3-Phenylpropiolate. General Method: Potassium *tert*-butoxide (0.224 mg, 2 mmol) was added to a solution of 2-[(2-ethoxycarbonylethyl)thio]pyrazolo[1,5-*a*]pyridine (**1**, 1 mmol) in DMF (2 mL). The mixture was heated at 50-60 °C for 1h and concentrated thoroughly under reduced pressure to remove the generated ethyl acrylate completely. Ethyl propiolate (**3a**, 1.2 mmol) or methyl 3-phenylproiolate (**3b**, 1.2 mmol) was added to the residue and the mixture was stirred at 50-60 °C for

2h. Diluted hydrochloric acid were added, and the precipitates which separated were collected by filtration. The precipitates were dissolved in chloroform (30 ml) and water was removed through phase-separating filter paper. The filtrate was concentrated under reduced pressure and the residue was separated by silica gel column chromatography using chloroform as an eluent. The fractions containing the target acrylate were combined and concentrated under reduced pressure. Recrystallization of the crude product from ethanol provided the corresponding 2-[(pyrazolo[1,5-*a*]pyridin-2-yl)thio]acrylate derivatives (**4 and 5**) as colorless needles and colorless prisms.

The reactions using *S*-protected pyrazolo[1,5-*a*]pyridines (**1**) and propiolates **3a,b** at room temperature gave the expected acrylates **4** and **5** in very low yields (to 5%), and the corresponding pyrazolo[1,5-*a*]pyridine-2-thiols formed by the acidification of the potassium salts were obtained.

The ^{1}H-NMR spectral data for these compounds **5a–f** are shown in Table 1, and some other results and properties are as follows:

Ethyl 3-[[3-Cyanopyrazolo[1,5-*a*]pyridm-2-yl]thio]acrylate (*Z*-form **4a** : *E*-form **5a**=10:1): 46% (from pyrazolo[1,5-*a*]pyridine (**1a**) and ethyl propiolate (**3a**)), colorless needles. IR (KBr) cm^{-1}: 2212, 1687, 1572. *Anal.* Calcd for $C_{13}H_{11}N_3O_2S$: C, 57.13; H, 4.06; N, 15.37. Found: C, 57.10; H, 4.00; N, 15.46.

Ethyl 3-[[3-Cyano-7-methylpyrazolo[1,5-*a*]pyridin-2-yl]thio]acrylate (*Z*-form **4b** : *E*-form **5b**=9:1): 26% (from **1b** and **3a**), colorless needles. IR (KBr) cm^{-1}: 2206, 1687, 1578. *Anal.* Calcd for $C_{14}H_{13}N_3O_2S$: C, 58.52; H, 4.56; N, 14.62. Found: C, 58.42; H, 4.56; N, 14.72.

Ethyl 3-[[3-Cyano-5-methylpyrazolo[1,5-*a*]pyridin-2-yl]thio]acrylate (*Z*-form **4c** : *E*-form **5c**=9:1): 61% (from **1c** and **3a**), colorless needles. IR (KBr) cm^{-1}: 2219, 1700, 1578. *Anal.* Calcd for $C_{14}H_{13}N_3O_2S$: C, 58.52; H, 4.56; N, 14.62. Found: C, 58.33; H, 4.54; N, 14.83.

Ethyl 3-[[3-Cyano-4,6-dimethylpyrazolo[1,5-*a*]pyridin-2-yl]thio]acrylate (*Z*-form **4d** : *E*-form **5d**=40:1): 16% (from **1d** and **3a**), colorless needles. IR (KBr) cm^{-1}: 2214, 1692, 1576. *Anal.* Calcd for $C_{15}H_{15}N_3O_2S$: C, 59.78; H, 5.02; N, 13.94. Found: C, 59.60; H, 4.91; N, 14.23.

Ethyl 3-[[3-(Ethoxycarbonyl)pyrazolo[1,5-*a*]pyridin-2-yl]thio]acrylate (*Z*-form **4e** : *E*-form **5e**=9:1): 29% (from **1e** and **3a**), colorless prisms. IR (KBr) cm^{-1}: 1690, 1560. *Anal.* Calcd for $C_{15}H_{16}N_2O_4S$: C, 56.24; H, 5.03; N, 8.74. Found: C, 56.31; H, 5.06; N, 8.64.

Ethyl 3-[[3-Ethoxycarbonyl-7-methylpyrazolo[1,5-*a*]pyridin-2-yl]thio]acrylate (*Z*-form **4f** : *E*-form **5f**=7:3): 52% (from **1f** and **3a**), colorless needles. IR (KBr) cm^{-1}: 1688, 1583. *Anal.* Calcd for $C_{16}H_{18}N_2O_4S$: C, 57.47; H, 5.43; N, 8.38. Found: C, 57.41; H, 5.46; N, 8.27.

Ethyl 3-[[3-Ethoxycarbonyl-5-methylpyrazolo[1,5-*a*]pyridin-2-yl]thio]acrylate (*Z*-form **4g** : *E*-form **5g**=9:1): 52% (from **1g** and **3a**), colorless prisms. IR (KBr) cm^{-1}: 1690, 1583. *Anal.* Calcd for $C_{16}H_{18}N_2O_4S$: C, 57.47; H, 5.43; N, 8.38. Found: C, 57.55; H, 5.44; N, 8.29.

Ethyl 3-[[3-Ethoxycarbonyl-4,6-dimethylpyrazolo[1,5-*a*]pyridin-2-yl]thio]acrylate (*Z*-form **4h** : *E*-form **5h**=4:1): 47% (from **1h** and **3a**), colorless needles. IR (KBr) cm^{-1}: 1690, 1583. *Anal.* Calcd for $C_{17}H_{20}N_2O_4S$: C, 58.60; H, 5.79; N, 8.04. Found: C, 58.62; H, 5.81; N, 8.02.

Methyl *Z*-3-[[3-Cyanopyrazolo[1,5-*a*]pyridin-2-yl]thio]-3-phenylacrylate (**4i**): 75% (from **1a** and methyl phenylpropiolate (**3b**)), colorless prisms, mp 149–152 °C. IR (KBr) cm^{-1}: 2220, 1684, 1576. *Anal.* Calcd for $C_{18}H_{13}N_3O_2S$: C, 64.46; H, 3.91; N, 12.53. Found: C, 64.55; H, 3.67; N, 12.43.

Methyl *Z*-3-[[3-Cyano-7-methylpyrazolo[1,5-*a*]pyridin-2-yl]thio]-3-phenylacrylate (**4j**): 82% (from **1b** and **3b**), colorless needles, mp 165–167 °C. IR (KBr) cm^{-1}: 2220, 1708, 1580. *Anal.* Calcd for $C_{19}H_{15}N_3O_2S$: C, 65.31; H, 4.33; N, 12.03. Found: C, 65.12; H, 4.33; N, 12.08.

Methyl *Z*-3-[[3-Cyano-5-methylpyrazolo[1,5-*a*]pyridin-2-yl]thio]-3-phenylacrylate (**4k**): 68% (from **1c** and **3b**), colorless prisms, mp 154–156 °C. IR (KBr) cm^{-1}: 2219, 1690, 1565. *Anal.* Calcd for $C_{19}H_{15}N_3O_2S$: C, 65.31; H, 4.33; N, 12.03. Found: C, 65.42; H, 4.10; N, 11.89.

Methyl *Z*-3-[[3-Cyano-4,6-dimethylpyrazolo[1,5-*a*]pyridin-2-yl]thio]-3-phenylacrylate (**4l**): 80% (from **1d** and **3b**), colorless prisms, mp 171–174 °C. IR (KBr) cm^{-1}: 2213, 1694, 1580. *Anal.* Calcd for $C_{20}H_{17}N_3O_2S$: C, 66.10; H, 4.83; N, 11.56. Found: C, 66.04; H, 4.69; N, 11.56.

Methyl 3-[[3-(Ethoxycarbonyl)pyrazolo[1,5-*a*]pyridin-2-yl]thio]-3-phenylacrylate (*Z*-form **4m**: *E*-form **5m**=97:3): 17% (from **1e** and **3b**), colorless prisms. IR (KBr) cm^{-1}: 1700, 1693, 1580. *Anal.* Calcd for $C_{20}H_{18}N_2O_4S$: C, 62.81; H, 4.74; N, 7.33. Found: C, 62.58; H, 4.83; N, 7.24.

Methyl 3-[[3-Ethoxycarbonyl-7-methylpyrazolo[1,5-*a*]pyridin-2-yl]thio]-3-phenylacrylate (*Z*-form **4n** : *E*-form **5n**=10:1): 55% (from **1f** and **3b**), colorless prisms. IR (KBr) cm^{-1}: 1714, 1672, 1587. *Anal.* Calcd for $C_{21}H_{20}N_2O_4S$: C, 63.62; H, 5.08; N, 7.07. Found: C, 63.56; H, 5.12; N, 6.91.

Methyl *Z*-3-[[3-Ethoxycarbonyl-5-methylpyrazolo[1,5-*a*]pyridin-2-yl]thio]-3-phenylacrylate (**4o**): 56% (from **1g** and **3b**), colorless prisms, mp 123–125 °C. IR (KBr) cm^{-1}: 1707, 1689, 1581. *Anal.* Calcd for $C_{21}H_{20}N_2O_4S$: C, 63.62; H, 5.08; N, 7.07. Found: C, 63.57; H, 5.15; N, 6.92.

Methyl *Z*-3-[[3-ethoxycarbonyl-4,6-dimethylpyrazolo[1,5-*a*]pyridin-2-yl]thio]-3-phenyl-acrylate (**5p**): 54% (from **1h** and **3b**), colorless needles, mp 134–137 °C. IR (KBr) cm^{-1}: 1707, 1690, 1565. *Anal.* Calcd for $C_{22}H_{22}N_2O_4S$: C, 64.37; H, 5.40; N, 6.82. Found: C, 64.53; H, 5.46; N, 6.59.

Crystallography of Methyl *Z*-3-[[3-Cyano-7-methylpyrazolo[1,5-*a*]pyridin-2-yl]thio]-3-phenylacrylate (4j) A colorless prismatic single crystal (0.32x0.48x0.58 mm) grown from $CHCl_3$-hexane was used for the unit-cell determinations and data collection by a Rigaku AFC5S four-circle diffractometer with graphite-monochromated MoK_α radiation (λ=0.71069 Å). The crystal data of this compounds is as follows: 4j: $C_{19}H_{15}N_3O_2S$; M=349.41; monoclinic, space group $P2_1/c$ (#14), Z=4 with a=9.272 (3) Å, b=11.063 (4) Å, c=17.273 (2) Å, β=90.63 (1); V=1771.8 (8) Å^3 and $D_{calc.}$=1.310 g/cm^3. All calculations were performed using CrystalStructures (version 3.8).[10] The structure was solved by a direct method (SIR).[11] The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were attached at the idealized position and not refined. The final R- and R_w-factors after full-matrix least-squares refinements were 0.065 and 0.056 for 2271 (I>2.00σ(I)) observed reflections, respectively.

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