Synthesis and Herbicidal Activities of a Series of Di(aminopyrazoly) Ketone Derivatives

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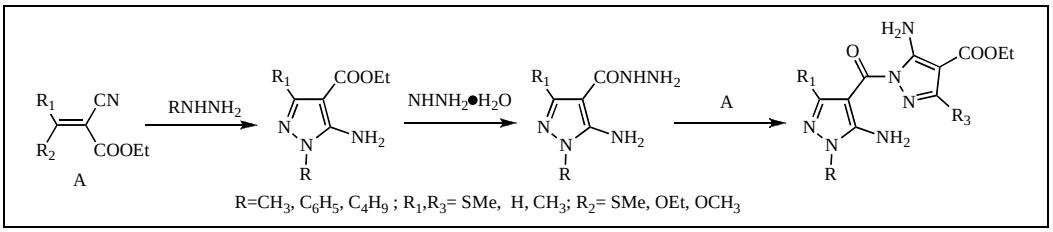

In order to obtain new lead compounds with high herbicidal activity, a series of 5-amino pyrazole derivatives were designed and synthesized using a series of relational synthons. Their structures were determined by IR, ^{1}H NMR, and elemental analyses. These compounds were screened for herbicidal activities against rape and barnyard grass. Their structure-activity relationships are discussed.

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INTRODUCTION

4-Hydoxyphenylpyruvate dioxygenase (4-HPPD) catalyzes the conversion of the 4-hydroxyphenylpyruvate to homogentisate in the biosynthesis pathway of plastoquinone and tocopherol. Inhibition of the production of homogentisate by 4-HPPD inhibitors down-regulates the production of plastoquinone, which is thought to be an acceptor of hydrogen from phytoene. Therefore, the absence of plastoquinone leads to an accumulation of the phytoene, which results in the impairment of carotenoid biosynthesis that is essential for the growth and survival of herbs. Generally, potent herbicides of this kind must possess the following structural features: (1) a di- or tricarbonyl methane structure, with one of the carbonyl groups being a substituted benzoyl group; (2) the compound must be able to enolize so that the enolate is capable of inhibiting the HPPD enzyme by competitive combination with Fe^{2+}, the reaction center of the HPPD enzyme [1-5]. As reported, many 4-carbonyl pyrazole derivatives classified as the inhibitors of 4-HPPD displayed excellent herbicidal activities, such as pyrazolynate **1**, pyrazoxyfen **2** and benzofenap **3** [6-9] (Figure 1). By comparisons with other HPPD inhibitors, it was concluded that their main pharmacophore was 5-hydroxyl-4-benzoyl pyrazole. It was also noticed that amino group possessed a similar capability of forming complex compounds with hydroxyl group, and according to the bioisosterism theory, both pyrazole ring and benzene ring were ring equivalents. However, the pyrazole derivatives containing two pyrazole rings used as herbicide have been rarely reported. In order to find valuable lead compounds with high herbicidal activity, a series of the title compounds **4** (Figure 1) were designed and synthesized.

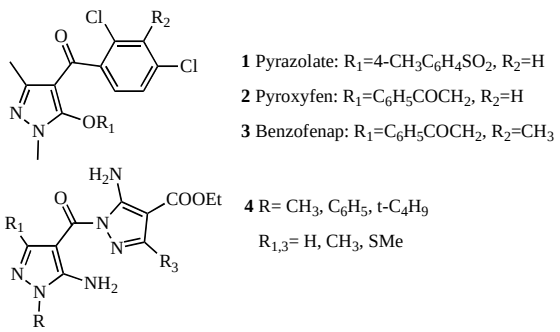
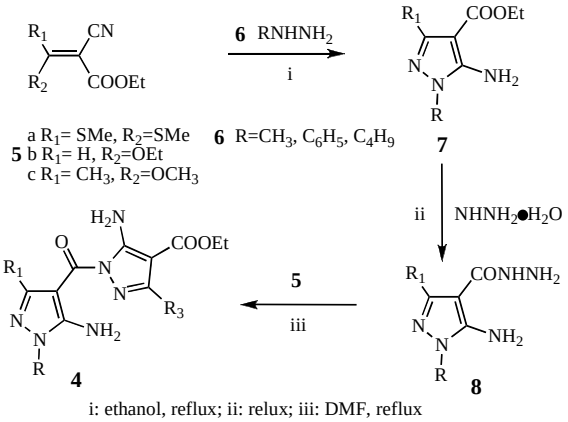


Figure 1. Chemical structure 1-4

Schemes 1



i: ethanol, reflux; ii: relux; iii: DMF, reflux

RESULTS AND DISCUSSION

1. Synthesis. The title compounds were synthesized according to Scheme 1 by in a parallel synthesis fashion, by which a number of compounds with various substitution patterns could be efficiently prepare in a short time. First, three ethyl 2-cyano-acrylates (**5**) were reacted with three substituted hydrazine (**6**) to obtained nine ethyl 1,3-disubstituted-5-amino-pyrazoly-4-carboxyacate (**7**) according to a reported procedure [10], then (**7**) was transformed to its hydrazine derivatives (**8**). Finally, the title compounds (**4**) were prepared by reaction of (**8**) with synthons (**5**). This pathway had the advantages of mild reaction conditions and high yields (listed in Tables 1 and 2).

During the reaction of the pyrazole carbohydrazide **8g** and intermediate **5c** in ethanol at room temperature a solid (mp 159-160 °C) was obtained. Its infrared spectrum showed that the cyano group still existed (2204 cm^{-1}) and the ^1H NMR spectrum showed there were two singlets at 8.97 and 10.90 ppm which corresponded to the NH and CONH, so its structure was confirmed to be **10** and the reaction from **8g** to **4u** was thought to proceed according to Scheme 2 [11].

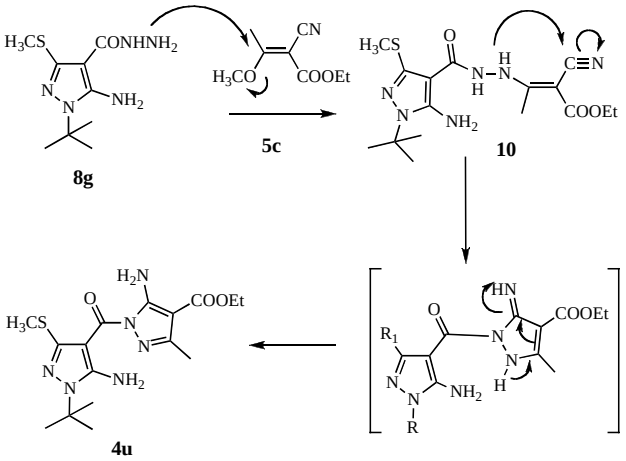
2. Herbicidal activity. These compounds were screened for herbicidal activities against rape and barnyard grass (Table 2). The results showed that, when R was *t*-butyl group, 1) compounds **4** always possessed better herbicidal activities against barnyard grass than methyl or phenyl group at 100ug/mL; 2) among them, the compound **4z** and **4aa** exhibited bleaching activities and only the compounds **4w** and **4x** exhibited some extent inhibition against rape; 3) the compounds with R1 = SMe delivere no inhibited activity on Rape root. When the substitute R was phenyl group, the compounds displayed some inhibition against rape root but have no influence on barnyard grass. In general, the results indicated that all the compounds possessed a certain extent inhibiting activities against the rape root growth and exhibited activities against barnyard grass, but their activities are not as good as the diketone herbicides.

Table 1

Physical and Analytical Data of Compounds **2**

Compd	R	R_1	Mp(°C)	Yield(%)
7a	CH_3	CH_3S	181-183 (litt. [12] 182-183)	93
7b	CH_3	H	98-99 (litt. [13] 99-101)	85
7c	CH_3	CH_3	107-109 (litt. [14] 111)	88
7d	C_6H_5	CH_3S	99-100(litt. [15])	91
7e	C_6H_5	H	98-100(litt. [16])	82
7f	C_6H_5	CH_3	96-98(litt. [17])	87
7g	t-C_4H_9	CH_3S	37-38	78
7h	t-C_4H_9	H	liquid(litt. [18])	83
7i	t-C_4H_9	CH_3	61-63	85
8a	CH_3	CH_3S	243-245 (litt. [19] 245-247)	75
8b	CH_3	H	245-247 (litt. [20] 245-247)	70
8c	CH_3	CH_3	205-207	65
8d	C_6H_5	CH_3S	153-154	78
8e	C_6H_5	H	183-184(litt. [21])	75
8f	C_6H_5	CH_3	115-116	70
8g	t-C_4H_9	CH_3S	73-75	75
8h	t-C_4H_9	H	165-167	74
8i	t-C_4H_9	CH_3	156-158	79

Scheme 2



3. Crystal structure [22]. The compound **4r** was recrystallized from ethanol and obtained a light crystal. The data of crystal structure was collected by BRUKER SMART 1000 CCD diffractometer and the structure (Figure 2) was solved by using differential techniques using SHELX-97 [23]. It was surprising to find that the two hydrogen atoms in N4 combine with the oxygen O1

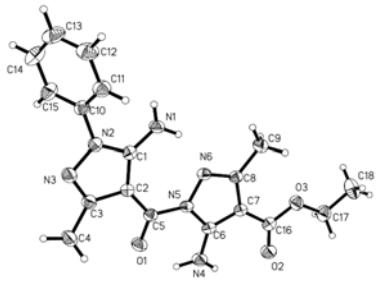


Figure 2

and O2 and constitute two intramolecular hydrogen bonds, the hydrogen atom in N1 associate with O1 in another molecule and form a hydrogen intermolecular bond. he data showed that the hydrogen bond between O1 and N4 was stronger than the bond between N4 and O2, the bonds, by which the molecules constitute a sandwich. The one between N1 and O2 in another molecule is the

weakest. The rings O1/C5/N5/C6/N4, N4/C6/C7/C16/O2 and the pyrazole ring (N5/N6/C8/C7/C6) formed a coplanar structure by the action of the association, the ratio of deviation is 0.0187. The data was found to be accorded with our assumption and exhibits the conjunction of the compounds and the HPPD enzyme indirectly.

CONCLUSION

In conclusion, a number of diaminopyrazolyl ketone compounds were synthesized and tested for herbicidal activity. However, only a few compounds exhibited moderate activity against rape or barnyard grass. Further biological evaluation and structure modifications are in progress in our laboratory.

EXPERIMENTAL

General Methods. Melting points were measured on a Thomas-Hoover apparatus and are not corrected. Infrared spectra were recorded on a Bruker Equinox55 spectrophotometer as potassium bromide tablets. ^{1}H-NMR spectra were measured on a Varian 400 spectrometer (400 MHz). Elemental analyses were performed on Yanaco-CHN CORDER MT-3 elementary analyzer. Compounds **5** were prepared according to literature [24-25].

1. Preparation of ethyl 5-amino-1*H*-pyrazole-4-carboxylates (7) [9-10]. To a solution of **5** (0.10 mol) in 40 mL ethanol, hydrazine **6** (0.11 mol) was added. The mixture was refluxed for 4 h and cooled to room temperature, and then poured into 100 mL water, the precipitate was collected by filtration and the solid was purified by recrystallization with ethanol to afford desired product **7**.

Ethyl 5-amino-1-*t*-butyl-3-(thiomethyl)-1*H*-pyrazole-4-carboxylate (7g). This compound is obtained as colorless solid (alcohol), yield 78%, mp 37~38°. ^{1}H nmr (400 MHz, δ ppm, $CDCl_3$): 1.36 (t, J = 7.2, 3H, CH_3), 1.60 (s, 9H, t-C_4H_9), 2.46 (s, 3H, SCH_3), 4.30 (q, J = 7.20, 2H, CH_2), 5.28 (s, 2H, NH_2); ir (potassium bromide): 3423, 3332 (NH), 1670 (C=O), 1524 (C=N), 1231 (O=C-O)cm^{-1}. *Anal.* Calcd. for $C_{11}H_{19}N_3O_2S$: C, 51.34; H, 7.44; N, 16.33. Found C, 51.12; H, 7.51; N, 16.38.

Ethyl 5-amino-1-*t*-butyl-3-methyl-1*H*-pyrazole-4-carboxylate (7i). This compound is obtained as colorless solid (alcohol), yield 85%; mp 61~63°. ^{1}H nmr (400 MHz, δ ppm, $CDCl_3$): 1.34 (t, J = 7.2, 3H, CH_3), 1.60 (s, 9H, t-C_4H_9), 2.36 (s, 3H, 3-CH_3), 4.30 (q, J = 7.20, 2H, CH_2), 5.28 (s, 2H, NH_2); ir (potassium bromide): 3425, 3333 (NH), 1669 (C=O), 1520 (C=N), 1210 (O=C-O)cm^{-1}. *Anal.* Calcd. for $C_{11}H_{19}N_3O_2$: C, 58.64; H, 8.50; N, 18.65. Found C, 58.52; H, 8.51; N, 18.38.

2. General Procedure for the Reaction of 5-amino-1*H*-pyrazole-4-carbohydrazide (8) [20,25,26]. A suspension of pyrazole derivatives **7** (0.05mol) in 14.7mL 85% hydrazine hydrate is heated at 105° for 6 h. Then the solution is evaporated under vacuum and cooled to room temperature. The residue is filtrated; washed with 25 mL diethyl ether three times. A white crystalline solid **8** is obtained.

5-amino-3-methyl-1-methyl-1*H*-pyrazole-4-carbohydrazide (8c). This compound is obtained as colorless

Table 2
Structure and herbicidal activity of targeted compounds.

Compound	R	R_1	R_3	Mp(℃)	Yield(%)	Rape root test		Barnyardgrass cup test	
						10ug/mL	100ug/mL	10ug/mL	100ug/mL
4a	- CH_3	- SMe	-SMe	156-158	85	3.70	13.50	5.10	30.10
4b	- CH_3	- SMe	-H	198-200	78	15.05	51.80	0.00	5.00
4c	- CH_3	- SMe	- CH_3	200-202	87	20.96	40.10	0.00	0.00
4d	- CH_3	- H	-SMe	191-192	92	0.00	0.00	8.71	17.66
4e	- CH_3	- H	-H	198-200	82	0.00	0.00	0.00	11.19
4f	- CH_3	- H	- CH_3	193-198	83	0.00	0.00	18.08	23.01
4g	- CH_3	- CH_3	-SMe	103-104	77	0.00	25.21	21.25	48.88
4h	- CH_3	- CH_3	-H	166-168	88	0.00	0.00	23.88	26.37
4i	- CH_3	- CH_3	- CH_3	196-198	79	0.00	32.84	0.00	36.18
4j	- Ph	- SMe	-SMe	192-194	80	15.23	22.99	0.00	0.00
4k	- Ph	- SMe	-H	159-160	75	9.43	27.61	0.00	5.00
4l	- Ph	- SMe	- CH_3	169-170	85	14.85	33.51	0.00	5.00
4m	- Ph	- H	-SMe	146-148	90	13.23	34.28	0.00	0.00
4n	- Ph	- H	-H	185-186	83	5.27	31.50	0.00	0.00
4o	- Ph	- H	- CH_3	145-147	80	21.86	28.06	0.00	0.00
4p	- Ph	- CH_3	-SMe	184-185	79	39.48	66.08	0.00	10.00
4q	- Ph	- CH_3	-H	213-215	81	8.97	18.87	0.00	5.00
4r	- Ph	- CH_3	- CH_3	169-171	75	24.33	32.99	0.00	15.00
4s	t-C_4H_9	- SMe	-SMe	203-205	85	0.00	0.00	8.96	18.66
4t	t-C_4H_9	- SMe	-H	101-102	85	0.00	0.00	43.28	47.89
4u	t-C_4H_9	- SMe	- CH_3	135-137	76	0.00	0.00	8.08	17.66
4v	t-C_4H_9	- H	-SMe	173-175	90	0.00	0.00	0.00	18.69
4w	t-C_4H_9	- H	-H	165-166	81	52.69	60.13	0.00	9.95
4x	t-C_4H_9	- H	- CH_3	108-110	85	26.74	54.62	0.00	20.40
4y	t-C_4H_9	- CH_3	-SMe	134-135	76	0.00	0.00	0.00	6.47
4z	t-C_4H_9	- CH_3	-H	116-118	87	0.00	11.29	30.85	48.01
4aa	t-C_4H_9	- CH_3	- CH_3	101-103	79	0.00	7.72	26.62	45.15

solid, yield 65%; mp 205~207°. ^{1}H nmr (400 MHz, δ ppm, $CDCl_3$): 2.33 (s, 3H, 3-CH_3), 3.55 (s, 3H, 3-CH_3), 3.97 (s, 2H, NH_2), 5.19 (s, 2H, 5-NH_2), 6.68 (s, 1H, CONH) ; ir (potassium bromide): 3410, 3280 (NH), 1615 (C=O), 1548 (C=N), 1401 (O=C-N)cm^{-1}. *Anal.* Calcd. for $C_6H_{11}N_5O$: C, 42.60; H, 6.55; N, 41.39. Found C, 42.55; H, 6.53; N, 41.59.

5-Amino-3-(methylthio)-1-phenyl-1*H*-pyrazole-4-carbohydrazide (8d). This compound is obtained as colorless solid, yield 78%; mp 153~154°; ^{1}H nmr (400 MHz, δ ppm, DMSO-d_6): 2.47 (s, 3H, SCH_3), 4.34 (s, 2H, NH_2), 6.34 (s, 2H, 5-NH_2), 6.92 (s, 1H, CONH) 7.34-7.52 (m, 5H, Ph); ir (potassium bromide): 3456, 3344 (NH), 1615 (C=O), 1595, 1501(-Ph), 1389 (O=C-N) cm^{-1}. *Anal.* Calcd. for $C_{11}H_{13}N_5OS$: C, 50.17; H, 4.98; N, 26.60. Found C, 50.11; H, 4.82; N, 26.84.

5-Amino-3-methyl-1-phenyl-1*H*-pyrazole-4-carbohydrazide (8f). This compound is obtained as colorless solid, yield 70%; mp 115~116°. ^{1}H nmr (400 MHz, δ ppm, $CDCl_3$): 2.42 (s, 3H, CH_3), 4.01 (s, 2H, NH_2), 5.55 (s, 2H, 5-NH_2), 6.80 (s, 1H, CONH), 7.3-7.512 (m, 5H, Ph); ir (potassium bromide): 3432, 3320 (NH), 1608 (C=O), 1550, 1501 (-Ph), 1396 (O=C-N) cm^{-1}. *Anal.* Calcd. for $C_{11}H_{13}N_5O$: C, 57.13; H, 5.65; N, 30.28. Found C, 56.87; H, 5.53; N, 30.59.

5-Amino-1-*t*-butyl-3-(methylthio)-1*H*-pyrazole-4-carbohydrazide (8g). This compound is obtained as colorless solid, yield 75%; mp 73~75°; ^{1}H nmr (400 MHz, δ ppm, DMSO-d_6): 1.61(s, 9H, t-C_4H_9), 2.46 (s, 3H, SCH_3), 3.90 (s, 2H, NH_2), 5.34 (s, 2H, 5-NH_2), 8.15 (s, 1H, NH, CONH) ; ir (potassium bromide): 3436, 3318 (NH), 1610 (C=O), 1508 (C=N), 1398 (O=C-N)cm^{-1}. *Anal.* Calcd. for $C_9H_{17}N_5OS$: C, 44.42; H, 7.04; N, 28.78. Found C, 44.23; H, 6.82; N, 28.84.

5-Amino-1-*t*-butyl-1*H*-pyrazole-4-carbohydrazide (8h). This compound is obtained as colorless solid, yield 74%; mp 165~167°. ^{1}H nmr (400 MHz, δ ppm, $CDCl_3$): 1.62(s, 9H, t-C_4H_9), 3.96 (s, 2H, NH_2), 5. 30 (s, 2H, 5-NH_2), 6.84 (s, 1H, CONH), 7.58(s, 1H, 3-H); ir (potassium bromide): 3430, 3315 (NH), 1614 (C=O), 1556 (C=N), 1400 (O=C-N)cm^{-1}. *Anal.* Calcd. for $C_8H_{15}N_5O$: C, 48.72; H, 7.67; N, 35.51. Found C, 48.77; H, 7.76; N, 35.49.

5-Amino-1-*t*-butyl-3-methyl-1*H*-pyrazole-4-carbohydrazide (8i). This compound is obtained as colorless solid, yield 79%; mp 156~158°. ^{1}H nmr (400 MHz, δ ppm, $CDCl_3$): 1.62(s, 9H, t-C_4H_9), 2.42 (s, 3H, CH_3), 3.98 (s, 2H, NH_2), 5.40 (s, 2H, 5-NH_2), 6.80 (s, 1H, CONH); ir (potassium bromide): 3437, 3312 (NH), 1600 (C=O), 1533 (C=N), 1401 (O=C-N)cm^{-1}. *Anal.* Calcd. for $C_9H_{17}N_5O$: C, 51.17; H, 8.11; N, 33.15. Found C, 51.10; H, 8.23; N, 33.29.

3. General procedure for the synthesis of title compounds 4 [10-11]. To a solution of intermediate **5** (5.0 mmol) in 15mL DMF is added compound **8** (5.5 mmol). The mixture is refluxed for 8 h and cooled to room temperature, then poured into 30 mL water. The precipitate is collected by filtration and a white solid is obtained. The solid is purified by recrystallization from ethanol/water. Desired product **4** is obtained.

Ethyl 5-amino-1-(5'-amino-3'-(methylthio)-1'-methyl-1*H*-pyrazole-4'-carbonyl)-3-methyl-1*H*-pyrazole-4-carboxylate (4c). This compound is obtained as colorless white crystals (alcohol), yield 87%, mp 200~202 °; ^{1}H nmr (400 MHz, δ ppm, $CDCl_3$): 1.4 (t, J = 7.2, 3H, CH_3), 2.3 (s, 3H, 3-CH_3), 2.5 (s, 3H, SCH_3), 3.6 (s, 3H, 1'-CH_3), 4.3 (q, J = 7.2, 2H, CH_2), 5.6 (s, 2H, 5'-NH_2), 7.1 (s, 2H, 5-NH_2); ir (potassium bromide): 3445, 3349 (NH), 1675, 1624 (C=O), 1508 (C=N), 1400 (O=C-N), 1223 (O=C-O)cm^{-1}. *Anal.* Calcd. for $C_{13}H_{18}N_6O_3S$: C, 46.14; H, 5.36; N, 24.84. Found C, 46.18; H, 5.12; N, 25.10.

Ethyl 5-amino-1-(5'-amino-1'-methyl-1*H*-pyrazole-4'-carbonyl)-3-(methylthio)-1*H*-pyrazole-4-carboxylate (4d). This compound is obtained as colorless solid (alcohol), yield 92%, mp 191~192°. ^{1}H nmr (400 MHz, δ ppm, $CDCl_3$): 1.38 (t, J = 7.2, 3H, CH_3), 2.55 (s, 3H, SCH_3), 3.64 (s, 3H, 1'-CH_3), 4.32 (q, J = 7.2, 2H, CH_2), 5.58 (s, 2H, 5'-NH_2), 7.20 (s, 2H, 5-NH_2), 8.43 (s, 1H, 3'-H); ir (potassium bromide): 3455, 3329 (NH), 1686, 1622 (C=O), 1515 (C=N), 1398 (O=C-N), 1198 (O=C-O) cm^{-1}. *Anal.* Calcd. for $C_{12}H_{16}N_6O_3S$: C, 44.43; H, 4.97; N, 25.91. Found C, 44.71; H, 4.63; N, 25.88.

Ethyl 5-amino-1-(5'-amino-1'-methyl-1*H*-pyrazole-4'-carbonyl)-1*H*-pyrazole-4-carboxylate (4e). This compound is obtained as colorless solid (alcohol), yield 82%, mp 198~200°. ^{1}H nmr (400 MHz, δ ppm, $CDCl_3$): 1.35 (t, J = 7.2, 3H, CH_3), 3.64 (s, 3H, 1'-CH_3), 4.28 (q, J = 7.2, 2H, CH_2), 5.59 (s, 2H, 5'-NH_2), 7.15 (s, 2H, 5-NH_2), 7.73 (s, 1H, 3-H), 8.44 (s, 1H, 3'-H); ir (potassium bromide): 3469, 3336 (NH), 1698, 1632 (C=O), 1521 (C=N), 1396 (O=C-N), 1167 (O=C-O)cm^{-1}. *Anal.* Calcd. for $C_{11}H_{13}N_6O_3$: C, 47.48; H, 5.07; N, 30.20. Found C, 47.31; H, 4.79; N, 29.98.

Ethyl 5-amino-1-(5'-amino-1'-methyl-1*H*-pyrazole-4'-carbonyl)-3-methyl-1*H*-pyrazole-4-carboxylate (4f). This compound is obtained as colorless solid (alcohol), yield 83%, mp 193~195°. ^{1}H nmr (400 MHz, δ ppm, $CDCl_3$): 1.36 (t, J = 7.2, 3H, CH_3), 2.38 (s, 3H, 3-CH_3), 3.64 (s, 3H, 1'-CH_3), 4.28 (q, J = 7.2, 2H, CH_2), 5.57 (s, 2H, 5'-NH_2), 7.20 (s, 2H, 5-NH_2), 8.49 (s, 1H, 3'-H); ir (potassium bromide): 3448, 3334 (NH), 1686, 1627 (C=O), 1506 (C=N), 1400 (O=C-N), 1200 (O=C-O)cm^{-1}. *Anal.* Calcd. for $C_{12}H_{16}N_6O_3$: C, 49.31; H, 5.52; N, 28.75. Found C, 49.03; H, 5.57; N, 28.78.

Ethyl 5-amino-1-(5'-amino-3'-methyl-1'-methyl-1*H*-pyrazole-4'-carbonyl)-3-(methylthio)-1*H*-pyrazole-4-carboxylate (4g). This compound is obtained as colorless solid (alcohol), yield 77%, mp 103~104°. ^{1}H nmr (400 MHz, δ ppm, $CDCl_3$): 1.38 (t, J = 7.2, 3H, CH_3), 2.36 (s, 3H, 3'-CH_3), 2.47 (s, 3H, 3-SCH_3), 3.58 (s, 3H, 1'-CH_3), 4.32 (q, J = 7.2, 2H, CH_2), 5.56 (s, 2H, 5'-NH_2), 7.28 (s, 2H, 5-NH_2); ir (potassium bromide): 3447, 3341 (NH), 1688, 1608 (C=O), 1518 (C=N), 1405 (O=C-N), 1201 (O=C-O)cm^{-1}. *Anal.* Calcd. for $C_{13}H_{18}N_6O_3S$: C, 46.14; H, 5.36; N, 24.84. Found C, 46.17; H, 5.32; N, 24.75.

Ethyl 5-amino-1-(5'-amino-3'-methyl-1'-methyl-1*H*-pyrazole-4'-carbonyl)-1*H*-pyrazole-4-carboxylate (4h). This compound is obtained as colorless solid (alcohol), yield 88%, mp 166~168°. ^{1}H nmr (400 MHz, δ ppm, $CDCl_3$): 1.35 (t, J = 7.2, 3H, CH_3), 2.38 (s, 3H, 3'-CH_3), 3.58 (s, 3H, 1'-CH_3), 4.30 (q, J = 7.2, 2H, CH_2), 5.69 (s, 2H, 5'-NH_2), 7.18 (s, 2H, 5-NH_2), 7.74 (s, 1H, 3-H); ir (potassium bromide): 3470, 3362 (NH), 1688, 1624 (C=O), 1546 (C=N), 1401 (O=C-N), 1151 (O=C-O)cm^{-1}. *Anal.* Calcd. for r $C_{12}H_{16}N_6O_3$: C, 49.31; H, 5.52; N, 28.75. Found C, 49.45; H, 5.55; N, 28.53.

Ethyl 5-amino-1-(5'-amino-3'-methyl-1'-methyl-1*H*-pyrazole-4'-carbonyl)-3-methyl-1*H*-pyrazole-4-carboxylate (4i). This compound is obtained as colorless solid (alcohol), yield 79%, mp 196~198°. ^{1}H nmr (400 MHz, δ ppm, $CDCl_3$): 1.36 (t, J = 7.2, 3H, CH_3), 2.38 (s, 6H, 3, 3'- CH_3), 3.59 (s, 3H, 1'-CH_3), 4.31 (q, J = 7.2, 2H, CH_2), 5.74 (s, 2H, 5'-NH_2), 7.30 (s, 2H, 5-NH_2); ir (potassium bromide): 3462, 3391 (NH), 1679, 1606 (C=O), 1544 (C=N), 1403 (O=C-N), 1200 (O=C-O)cm^{-1}. *Anal.* Calcd. for $C_{13}H_{18}N_6O_3$: C, 50.90; H, 5.92; N, 27.44. Found C, 50.64; H, 5.79; N, 27.73.

Ethyl 5-amino-1-(5'-amino-3'-(methylthio)-1'-phenyl-1*H*-pyraz ole-4'-carbonyl)-3-(methylthio)-1*H*-pyrazole-4-carboxylate (4j). This compound is obtained as colorless solid (alcohol), yield 80%, mp 192~194ºC. ^{1}H nmr (400 MHz, δ ppm, $CDCl_3$): 1.38 (t, J = 7.2, 3H, CH_3), 2.46 (s, 3H, 3-SCH_3), 2.52 (s, 3H, 3'-SCH_3), 4.33 (q, J = 7.20, 2H, CH_2), 6.40(s, 2H, 5'-NH_2), 7.36 (s, 2H, 5-NH_2), 7.43-7.55 (m, 5H, Ph); ir (potassium bromide): 3423, 3343 (NH), 1685, 1621(C=O), 1520, 1437 (-Ph), 1410 (O=C-N), 1196(O=C-O)cm^{-1}. *Anal.* Calcd. for $C_{18}H_{20}N_6O_3S_2$: C, 49.98; H, 4.66; N, 19.43. Found C, 49.62; H, 4.31; N, 19.56.

Ethyl 5-amino-1-(5'-amino-3'-(methylthio)-1'-phenyl-1*H*-pyrazole-4'-carbonyl)-1*H*-pyrazole-4-carboxylate (4k). This compound is obtained as colorless solid (alcohol), yield 75%, mp 159~160 °; ^{1}H nmr (400 MHz, δ ppm, $CDCl_3$): 1.35 (t, J = 7.2, 3H, CH_3), 2.52 (s, 3H, SCH_3), 4.30 (q, J = 7.2, 2H, CH_2), 6.53 (s, 2H, 5'-NH_2), 7.21 (s, 2H, 5-NH_2), 7.43-7.55 (m, 5H, -Ph), 7.74 (s, 1H, 3-H); ir (potassium bromide): 3481, 3360 (NH), 1685, 1610 (C=O), 1500, 1455 (-Ph), 1404 (O=C-N), 1298 (HC=C), 1179(O=C-O)cm^{-1}. *Anal.* Calcd. for $C_{17}H_{18}N_6O_3S$: C, 52.84; H, 4.70; N, 21.75. Found C, 52.57; H, 4.70; N, 21.75.

Ethyl 5-amino-1-(5'-amino-3'-(methylthio)-1'-phenyl-1*H*-pyrazole-4'-carbonyl)-3-methyl-1*H*-pyrazole-4-carboxylate (4l). This compound is obtained as colorless solid (alcohol), yield 85%, mp 169~170°; ^{1}H nmr (400 MHz, δ ppm, $CDCl_3$): 1.36 (t, J = 7.2, 3H, CH_3), 2.36 (s, 3H, 3-CH_3), 2.51 (s, 3H, SCH_3), 4.30 (q, J = 7.2, 2H, CH_2), 6.61 (s, 2H, 5'-NH_2), 7.15 (s, 2H, 5-NH_2), 7.41-7.55 (m, 5H, -Ph); ir (potassium bromide): 3423, 3343 (NH), 1685, 1621 (C=O), 1520, 1437 (-Ph), 1410 (O=C-N), 1196(O=C-O)cm^{-1}. *Anal.* Calcd. for $C_{18}H_{20}N_6O_3S$: C, 53.99; H, 5.03; N, 20.99. Found C, 53.78; H, 4.92; N, 21.10.

Ethyl 5-amino-1-(5'-amino-1'-phenyl-1*H*-pyrazole-4'-carbonyl)-3-(methylthio)-1*H*-pyrazole-4-carboxylate (4m). This compound is obtained as colorless solid (alcohol), yield 90%, mp 146~148 °. ^{1}H nmr (400 MHz, δ ppm, $CDCl_3$): 1.39 (t, J = 7.2, 3H, CH_3), 2.58 (s, 3H, SCH_3), 4.31 (q, J = 7.20, 2H, CH_2), 5.93 (s, 2H, 5'-NH_2), 7.19 (s, 2H, 5-NH_2), 7.43-7.56 (m, 5H, Ph), 8.65 (s, 1H, 3'-H); ir (potassium bromide): 3401, 3343 (NH), 1671, 1601 (C=O), 1519, 1467 (-Ph), 1403 (O=C-N), 1201(O=C-O)cm^{-1}. *Anal.* Calcd. For. $C_{17}H_{18}N_6O_3S$: C, 52.84; H, 4.70; N, 21.75. Found C, 52.74; H, 4.63; N, 21.88.

Ethyl 5-amino-1-(5'-amino-1'-phenyl-1*H*-pyrazole-4'-carbonyl)-1*H*-pyrazole-4-carboxylate (4n). This compound is obtained as colorless solid (alcohol), yield 83%, mp 185~186°. ^{1}H nmr (400 MHz, δ ppm, $CDCl_3$): 1.36 (t, J = 7.2, 3H, CH_3), 4.30 (q, J = 7.2, 2H, CH_2), 5.94 (s, 2H, 5'-NH_2), 7.18 (s, 2H, 5-NH_2),7.24-7.55 (m, 5H, -Ph), 7.77 (s, 1H, 3-H), 8.7 (s, 1H, 3'-H); ir (potassium bromide): 3425, 3326 (NH), 1677, 1600 (C=O), 1531, 1456 (-Ph), 1398 (O=C-N), 1201(O=C-O)cm^{-1}. *Anal.* Calcd. For. $C_{16}H_{16}N_6O_3$: C, 56.47; H, 4.74; N, 24.65. Found C, 52.48; H, 4.74; N, 24.64.

Ethyl 5-amino-1-(5'-amino-1'-phenyl-1*H*-pyrazole-4'-carbonyl)-3-methyl-1H-pyrazole-4-carboxylate (4o). This compound is obtained as colorless solid (alcohol), yield 80%, mp 145~147°. ^{1}H nmr (400 MHz, δ ppm, $CDCl_3$): 1.37 (t, J = 7.2, 3H, CH_3), 2.40 (s, 3H, 3-CH_3), 4.30 (q, J = 7.2, 2H, CH_2), 5.92 (s, 2H, 5'-NH_2), 7.19 (s, 2H, 5-NH_2), 7.42-7.55 (m, 5H, Ph), 8.70 (s, 1H, 3'-H); ir (potassium bromide): 3458, 3360 (NH), 1679, 1604 (C=O), 1501, 1459 (-Ph), 1397 (O=C-N), 1208(O=C-O)cm^{-1}. *Anal.* Calcd. for $C_{17}H_{18}N_6O_3$: C, 57.62; H, 5.12; N, 23.72. Found C, 57.90; H, 5.07; N, 23.78.

Ethyl 5-amino-1-(5'-amino-3'-methyl-1'-phenyl-1*H*-pyrazole-4'-carbonyl)-3-(methylthio)-1*H*-pyrazole-4-carboxylate (4p). This compound is obtained as colorless solid (alcohol), yield 79%, mp 184~185°. ^{1}H nmr (400 MHz, δ ppm, $CDCl_3$): 1.36 (t, J = 7.2, 3H, CH_3), 2.45 (s, 3H, 3'-CH_3), 2.50(s, 3H, SCH_3), 4.32 (q, J = 7.2, 2H, CH_2), 6.0 (s, 2H, 5'-NH_2), 7.18 (s, 2H, 5-NH_2), 7.42-7.55 (m, 5H, -Ph); ir (potassium bromide): 3435, 3366 (NH), 1685, 1610 (C=O), 1535, 1455 (-Ph), 1391(O=C-N), 1197(O=C-O)cm^{-1}. *Anal.* Calcd. for $C_{18}H_{20}N_6O_3S$: C, 53.99; H, 5.03; N, 20.99. Found C, 53.72; H, 5.32; N, 21.15.

Ethyl 5-amino-1-(5'-amino-3'-methyl-1'-phenyl-1*H*-pyrazole-4'-carbonyl)-1*H*-pyrazole-4-carboxylate (4q). This compound is obtained as colorless solid (alcohol), yield 81%, mp 213~215°. ^{1}H nmr (400 MHz, δ ppm, $CDCl_3$): 1.35 (t, J = 7.2, 3H, CH_3), 2.45 (s, 3H, 3'-CH_3), 4.30 (q, J = 7.2, 2H, CH_2), 5.97 (s, 2H, 5'-NH_2), 7.19 (s, 2H, 5-NH_2), 7.42-7.52 (m, 5H, Ph), 7.75 (s, 1H, 3-H); ir (potassium bromide): 3458, 3372 (NH), 1684, 1599 (C=O), 1518, 1478 (-Ph), 1398(O=C-N), 1197(O=C-O)cm^{-1}. *Anal.* Calcd. for $C_{17}H_{18}N_6O_3$: C, 57.62; H, 5.12; N, 23.72. Found C, 57.45; H, 5.25; N, 23.53.

Ethyl 5-amino-1-(5'-amino-3'-methyl-1'-phenyl-1*H*-pyrazole-4'-carbonyl)-3-methyl-1*H*-pyrazole-4-carboxylate (4r). This compound is obtained as colorless white crystals (alcohol), yield 75%, mp 169~171°. ^{1}H nmr (400 MHz, δ ppm, $CDCl_3$): 1.36 (t, J = 7.2, 3H, CH_3), 2.36 (s, 3H, 3-CH_3), 2.45 (s, 3H, 3'-CH_3), 4.32 (q, J = 7.2, 2H, CH_2), 6.03 (s, 2H, 5'-NH_2), 7.29 (s, 2H, 5-NH_2), 7.4-7.5 (m, 5H, -Ph); ir (potassium bromide): 3458, 3400 (NH), 1679, 1604 (C=O), 1517, 1466 (-Ph), 1402(O=C-N), 1198(O=C-O)cm^{-1}. *Anal.* Calcd. for $C_{18}H_{20}N_6O_3$: C, 58.69; H, 5.47; N, 22.81. Found C, 58.64; H, 5.29; N, 22.74.

Ethyl 5-amino-1-(5'-amino-1'-*t*-butyl-3'-(methylthio)-1*H*-pyrazole-4'-carbonyl)-3-(methylthio)-1*H*-pyrazole-4-carboxylate (4s). This compound is obtained as colorless solid (alcohol), yield 85%, mp 203~205°. ^{1}H nmr (400 MHz, δ ppm, $CDCl_3$): 1.38 (t, J = 7.2, 3H, CH_3), 1.63 (s, 9H, t-C_4H_9), 2.43 (s, 3H, 3'-SCH_3), 2.52 (s, 3H, 3-SCH_3), 4.30 (q, J = 7.2, 2H, CH_2), 6.00 (s, 2H, 5'-NH_2), 7.20 (s, 2H, 5-NH_2); ir (potassium bromide): 3458, 3337 (NH), 1687, 1611 (C=O), 1493 (C=N), 1400 (O=C-N), 1224 (O=C-O)cm^{-1}. *Anal.* Calcd. for $C_{16}H_{24}N_6O_3S_2$: C, 46.85; H, 5.86; N, 20.37. Found C, 46.62; H, 5.73; N, 20.56.

Ethyl 5-amino-1-(5'-amino-1'-*t*-butyl -3'-(methylthio)-1*H*-pyrazole-4'-carbonyl)-1*H*-pyrazole-4-carboxylate (4t). This compound is obtained as colorless solid (alcohol), yield 85%, mp 101~102 °; ^{1}H nmr (400 MHz, δ ppm, $CDCl_3$): 1.35 (t, J = 7.2, 3H, CH_3), 1.63(s, 9H, t-C_4H_9), 2.45 (s, 3H, 3'-SCH_3), 4.30 (q, J = 7.2, 2H, CH_2), 6.27 (s, 2H, 5'-NH_2), 7.17 (s, 2H, 5-NH_2), 7.72 (s, 1H, 3-H); ir (potassium bromide): 3466, 3345 (NH), 1690, 1614 (C=O), 1535 (C=N), 1401 (O=C-N), 1194 (O=C-O)cm^{-1}. *Anal.* Calcd. for $C_{15}H_{22}N_6O_3S$: C, 49.17; H, 6.05; N, 22.93. Found C, 49.26; H, 6.10; N, 22.75.

Ethyl 5-amino-1-(5'-amino-1'-*t*-butyl-3'-(methylthio)-1*H*-pyrazole-4'-carbonyl)-3-methyl-1*H*-pyrazole-4-carboxylate (4u). This compound is obtained as colorless solid (alcohol), yield 76%, mp 135~137 °; ^{1}H nmr (400 MHz, δ ppm, $CDCl_3$): 1.35 (t, J = 7.2, 3H, CH_3), 1.64 (s, 9H, t-C_4H_9), 2.38 (s, 3H, 3-CH_3), 2.44 (s, 3H, 3'-SCH_3), 4.30 (q, J = 7.2, 2H, CH_2), 5.60 (s, 2H, 5'-NH_2), 7.21 (s, 2H, 5-NH_2); ir (potassium bromide): 3454, 3348 (NH), 1688, 1610(C=O), 1529(C=N), 1400(O=C-N), 1225(O=C-O)cm^{-1}; *Anal.* Calcd. for $C_{16}H_{24}N_6O_3S$: C, 50.51; H, 6.36; N, 22.09. Found C, 50.78; H, 6.32; N, 21.99.

Ethyl 5-amino-1-(5'-amino-1'-*t*-butyl-1*H*-pyrazole-4'-car–bonyl)-3-(methylthio)-1*H*-pyrazole-4-carboxylate (4v). This compound is obtained as colorless solid (alcohol), yield 90%, mp 173~175 °. ^{1}H nmr (400 MHz, δ ppm, $CDCl_3$): 1.38 (t, J = 7.2, 3H, CH_3), 1.66 (s, 9H, t-C_4H_9), 2.54 (s, 3H, 3-SCH_3), 4.31 (q, J = 7.2, 2H, CH_2), 5.91 (s, 2H, 5'-NH_2), 7.2 (s, 2H, 5-NH_2), 8.46 (s, 1H, 3'-H); ir (potassium bromide): 3441, 3352 (NH), 1686, 1607 (C=O), 1500 (C=N), 1392 (O=C-N), 1226 (O=C-O)cm^{-1}. *Anal*. Calcd. for $C_{15}H_{22}N_6O_3S$: C, 49.17; H, 6.05; N, 22.93. Found C, 49.14; H, 6.03; N, 22.88.

Ethyl 5-amino-1-(5'-amino-1'-*t*-butyl-1*H*-pyrazole-4'-carbonyl)-1*H*-pyrazole-4-carboxylate (4w). This compound is obtained as colorless solid (alcohol), yield 81%, mp 165~166°. ^{1}H nmr (400 MHz, δ ppm, $CDCl_3$): 1.4 (t, J = 7.2, 3H, CH_3), 1.6 (s, 9H, t-C_4H_9), 4.28 (q, J = 7.2, 2H, CH_2), 5.90 (s, 2H, 5'-NH_2), 7.18 (s, 2H, 5-NH_2), 7.72 (s, 1H, 3-H), 8.43 (s, 1H, 3'-H); ir (potassium bromide): 3457, 3327 (NH), 1692, 1611 (C=O), 1508 (C=N), 1401 (O=C-N), 1233 (O=C-O)cm^{-1}. *Anal*. Calcd. for $C_{14}H_{20}N_6O_3$: C, 52.49; H, 6.29; N, 26.23. Found C, 52.48; H, 6.54; N, 26.34.

Ethyl 5-amino-1-(5'-amino-1'-*t*-butyl-1*H*-pyrazole-4'-carbonyl)-3-methyl-1*H*-pyrazole-4-carboxylate (4x). This compound is obtained as colorless solid (alcohol), yield 85%, mp 108~110°. ^{1}H nmr (400 MHz, δ ppm, $CDCl_3$): 1.35 (t, J = 7.2, 3H, CH_3), 1.65 (s, 9H, t-C_4H_9), 2.35 (s, 3H, 3-CH_3), 4.29 (q, J = 7.2, 2H, CH_2), 5.87 (s, 2H, 5'-NH_2), 7.25 (s, 2H, 5-NH_2), 8.50 (s, 1H, 3'-H); ir (potassium bromide): 3463, 3346 (NH), 1686, 1619 (C=O), 1508 (C=N), 1400 (O=C-N), 1238 (O=C-O)cm^{-1}. *Anal*. Calcd. for $C_{15}H_{22}N_6O_3$: C, 53.88; H, 6.63; N, 25.13. Found C, 53.90; H, 6.47; N, 25.18.

Ethyl 5-amino-1-(5'-amino-1'-*t*-butyl-3'-methyl-1*H*-pyrazole-4'-carbonyl)-3-(methylthio)-1*H*-pyrazole-4-carboxylate (4y). This compound is obtained as colorless solid (alcohol), yield 76%, mp 134~135°. ^{1}H nmr (400 MHz, δ ppm, $CDCl_3$): 1.38 (t, J = 7.2, 3H, CH_3), 1.63 (s, 9H, t-C_4H_9), 2.31 (s, 3H, 3'-CH_3), 2.47 (s, 3H, 3-SCH_3), 4.32 (q, J = 7.2, 2H, CH_2), 5.55 (s, 2H, 5'-NH_2), 7.16 (s, 2H, 5-NH_2); ir (potassium bromide): 3459, 3342 (NH), 1688, 1604 (C=O), 1521 (C=N), 1400 (O=C-N), 1232 (O=C-O)cm^{-1}.*Anal*. Calcd. for $C_{16}H_{24}N_6O_3S$: C, 50.51; H, 6.36; N, 20.09. Found C, 50.72; H, 6.32; N, 20.15.

Ethyl 5-amino-1-(5'-amino-1'-*t*-butyl-3'-methyl-1*H*-pyrazole-4'-carbonyl)-1*H*-pyrazole-4-carboxylate (4z). This compound is obtained as colorless solid (alcohol), yield 87%, mp 116~118°. ^{1}H nmr (400 MHz, δ ppm, $CDCl_3$): 1.35 (t, J = 7.2, 3H, CH_3), 1.63 (s, 9H, t-C_4H_9), 2.29 (s, 3H, 3'-CH_3), 4.30 (q, J = 7.2, 2H, CH_2), 5.68 (s, 2H, 5'-NH_2), 7.05 (s, 2H, 5-NH_2), 7.72 (s, 1H, 3-H); ir (potassium bromide): 3475, 3353 (NH), 1688, 1615 (C=O), 1539 (C=N), 1401 (O=C-N), 1194 (O=C-O)cm^{-1}. *Anal*. Calcd. for $C_{15}H_{22}N_6O_3$: C, 53.88; H, 6.63; N, 25.13. Found C, 53.75; H, 6.65; N, 25.23.

Ethyl 5-amino-1-(5'-amino-1'-*t*-butyl-3'-methyl-1*H*-pyrazole-4'-carbonyl)-3-methyl-1*H*-pyrazole-4-carboxylate (4aa). This compound is obtained as colorless solid (alcohol), yield 79%, mp 101~103°. ^{1}H nmr (400 MHz, δ ppm, $CDCl_3$): 1.36 (t, J = 7.2, 3H, CH_3), 1.63 (s, 9H, t-C_4H_9), 2.30 (s, 3H, 3'-CH_3), 2.36 (s, 6H, 3-CH_3), 4.30 (q, J = 7.2, 2H, CH_2), 5.73 (s, 2H, 5'-NH_2), 7.14 (s, 2H, 5-NH_2); ir (potassium bromide): 3455, 3340 (NH), 1688, 1610 (C=O), 1529 (C=N), 1397 (O=C-N), 1236 (O=C-O)cm^{-1}. *Anal*. Calcd. for $C_{16}H_{24}N_6O_3$: C, 55.16; H, 6.94; N, 24.12. Found C, 55.24; H, 6.99; N, 24.14.

4. Procedure for synthesis of compound ethyl 3-(*N*'-(5'-amino-1'-*t*-butyl-3'-(methylthio)-1*H*-pyrazole-4-carbonyl)-hydrazineyl)-2-cyanobut-2-enoate (10). To a solution of intermediate **5c** (1.0 mmol) in 40 mL ethanol, the pyrazole carbohydrazide **8g** (1.1 mmol) is added. The mixture is stirred for 2 h at room temperature and poured into 100 mL water. The solid precipitate is collected by filtration and purified by recrystallization from ethanol to give a white solid 0.35 g, yield 92%, mp 159-160°. ^{1}H nmr (400 MHz, δ ppm, $CDCl_3$): 1.32 (t, J = 7.2, 3H, CH_3), 1.62 (s, 9H, t-C_4H_9), 2.31 (s, 3H, SCH_3), 2.52 (s, 3H, CH_3), 4.26 (q, J = 7.2, 2H, CH_2), 5.62 (s, 2H, 5'-NH_2), 8.97 (s, 1H, NH), 10.90 (s, 1H, CONH); ir (potassium bromide): 3451, 3334 (NH), 2204 (CN), 1688, 1602 (C=O), 1402 (O=C-N), 1233 (O=C-O)cm^{-1}. *Anal*. Calcd. for $C_{16}H_{24}N_6O_3S$: C, 50.51; H, 6.36; N, 22.09. Found C, 50.28; H, 6.36; N, 22.13.

Herbicidal Activity Tests [27-28]

1. Inhibition of the root-growth of rape (*Brassicacampestris L*). The compounds to be tested are made into emulsions to aid dissolution. Rape seeds are soaked in distilled water for 4 h before being placed on a filter paper in a 6-cm Petri plate, to which 2 ml of inhibitor solution had been added in advance. Usually, 15 seeds are used on each plate. The plate is placed in a dark room and allowed to germinate for 65 h at 28° (±1). The lengths of 10 rape roots selected from each plate are measured and the means are calculated. The percentage inhibition is calculated relative to controls using distilled water instead of the inhibitor solution.

2. Inhibition of the seedling growth of barnyard grass (Echinochloacrus-galli (L) Beauv). The compounds to be evaluated are made into emulsions to aid dissolution. Ten barnyard grass seeds are placed into a 50-ml cup covered with a layer of glass beads and a piece of filter paper at the bottom, to which 5 ml of inhibitor solution had been added in advance. The cup is placed in a bright room and the seeds allowed to germinate for 65 h at 28° (±1). The height of the above-ground parts of the seedlings in each cup is measured and the means calculated. The percentage inhibition is calculated relative to controls using distilled water instead of the inhibitor solution. The results of herbicidal activity listed in Table 2.

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