Novel directed synthesis of functionalized pyrazole derivatives *via* regioselective solvent-free thiylation of 3-alkenylpyrazoles with arenethiols

Galina G. Levkovskaya, Elena V. Rudyakova, Valentina A. Kobelevskaya, Aleksandr V. Popov,* and Igor B. Rozentsveig

A. E. Favorsky Irkutsk Institute of Chemistry Russian Academy of Sciences, Siberian Branch, Favorsky Str. 1, Irkutsk 664 033, Russia
E-mail: popov@irioch.irk.ru

DOI: http://dx.doi.org/10.3998/ark.5550190.p009.383

Abstract
Unprecedented easy (3 min., room temperature) regioselective addition of thiols to the endocyclic double bond of 3-vinyl-, prop-1-enyl- and isopropenyl, including those with bulky substituents in the position 1 of the pyrazole ring, has been found for the reaction of arenethioles with 3-alkenyl-5-chloropyrazoles. The reaction proceeds under solvent-free and catalyst-free conditions to afford 3-[(2-arylsulfanyl)alkyl]-5-chloropyrazoles in excellent yields. High rate of the process is likely due to protonation of the "pyridine" nitrogen atom of the pyrazole ring to give a pyrazolium ion which activates the vinyl group towards nucleophilic attack by the simultaneously formed arylthiolate anions.

Keywords: Solvent-free reactions, catalyst-free reactions, *C*-alkenylpyrazoles, arenethiols, thiylation

Introduction

Pyrazole and its derivatives attract the attention of the chemical community mainly on account of the wide spectrum of their pharmacological activities,[1-6] including antibacterial,[7] antidepressant,[8] antiinflammatory,[9] antitumor,[10] etc. They are widely used as agrochemicals.[11-14] Pyrazole derivatives exhibiting acaricidal action and applied in modern practical disinfection and decontamination are of special importance.[15-17]

In recent years, increasing interest has been focused on polypyrazole constructs which are promising ligands.[18] Some pyrazole ligands can be used in transition metal-catalyzed reactions.[19]

Pyrazoles are used in supramolecular[20] and polymer chemistry,[21] in the food industry, as cosmetic colorings[22] and UV stabilizers[23] and some possess liquid crystal properties.[24,25] They are also applied in the design of complexes with unusual magnetic properties.[26,27]

In the search for novel pyazoles as building blocks for the synthesis of biologically active and technologically useful substances,[1-6] the development of new methods for the preparation of functionalized pyrazoles and the synthesis of new pyrazole derivatives present an urgent challenge.

Alkenylpyrazoles are valuable and promising building blocks for the synthesis of diverse pyrazole derivatives including pyrazole-containing multi-nuclear and annelated heterocyclic systems.[1-6,28-39] The chemical transformations of alkenylpyrazoles are still poorly understood. It is known that *N*-alkenyl- and some 4-alkenylpyrazoles can participate in polymerization,[21,29] complex formation,[30, 31] thiylation,[32] and cycloaddition.[33-35] Imidoalkylation of 1-, 3-, 4-, and 5-vinylpyrazoles with *N*-(2,2,2-trichloroethylidene)ethoxycarbonylamines is also reported[34,36] Chemical transformations of the difficult-to-access 3-alkenylpyrazoles[36-38] and 3-alkenyl-5-chloropyrazoles[28] are even less studied and only very few reactions with oxygen and sulphur nucleophiles have been published. [39,40]

We have recently developed methodology for the preparation of hitherto unknown 3-alkenylpyrazoles,[28] possible building blocks for the directed synthesis of substances and materials for advanced technologies, from the corresponding 3-haloalkyl pyrazoles. The aim of the present work is to study of chemical behavior of 3-alkenylpyrazoles in the reactions with aromatic and aliphatic thiols.

The reactions of 1-vinyl- and 1-*iso*-propenylpyrazoles with thiols have been reported.[32,41] As is known,[32] 1-vinylpyrazoles react with thiols via both ionic (in the presence of S, SO_2, $BF_3 \cdot Et_2O$, *p*-toluenesulfonic acid) and free radical mechanisms to afford α- and β-adducts.

The reaction turns out to be non-chemoselective. Radical inhibitors (benzoquinone, hydroquinone, sulfur) did not exclude formation of β-adducts.[32] The yield of α-adducts in the reaction of 1-vinylpyrazole with thiols under ionic conditions did not exceed 53%. Upon heating from 20°C to 80°C and in the presence of radical initiators (photoirradiation or AIBN), the process was considerably accelerated (from 24 h to 10 min), but without improving the selectivity.

1-Isopropenylpyrazole reacts with EtSH in the presence of AIBN at 65 °C for 3.5 h with total conversion of the initial pyrazole. The yield of the target β-adduct was 75%.[41] The reaction with thiophenol under the same conditions proceeds with low conversion of the 1-alkenylpyrazole (42%) to give the adduct in 74% yield (based on the reacted alkenylpyrazole). At higher temperatures conversion of the isopropenylpyrazole increases, but the yield of the target product dramatically drops due to side reactions.[41] There are no essential differences in the reactions of 1-alkenylpyrazoles with aromatic or aliphatic thiols.[32,41]

Similar reactions of 1-vinylpyrroles, 1-vinylimidazoles, and 1-vinylindoles[42,43] with thiols also occur in the presence of AIBN. Aromatic thiols react without catalyst over a longer time

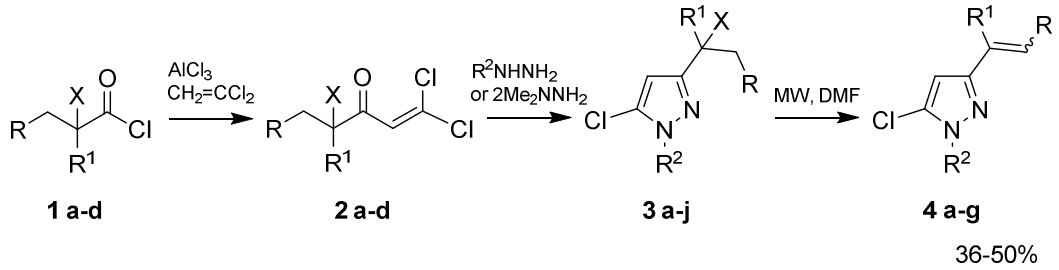
(18-25 h, 70-80 ºC) to deliver β-adducts.[42,43] *N*-Vinylpyrroles react with thiophenols giving rise to both β- (80%) and α-adducts (20%).[43]

Addition of arenethiols to electron deficient double bonds of α,β-unsaturated carbonyl compounds or nitriles are catalyzed by sodium borate[44] or lithium perchlorate.[45]

We have developed a synthesis of the so far scarcely accessible 3-alkenylpyrazoles[37,38] and hitherto unknown 3-alkenyl-5-chloropyrazoles.[28] This enables pioneering data on the chemical properties of these compounds to be obtained, and to allow comparison of their structural peculiarities and reactivity with those the 1-alkenylpyrazoles.

Results and Discussion

In the present work a series of 3-vinyl-, 3-propenyl- and 3-isopropenyl-5-chloropyrazoles (**4a-g**) from synthesized 2,2-dichlorovinyl-[1-chloro(bromo)alkyl]ketones and 1,1-dimethylhydrazines or alkylhydrazines using the methodology developed recently.[28] (Scheme 1)



1a, 2a: R = R^1 = H, X = Cl, **3a, 4a**: R^2 = Me, **3b, 4b**: R^2 = Bn, **3d, 4c**: R^2 = *i*-Pr, **3f, 4d**: R^2 = *i*-C_5H_{11}, **3h, 4e**: R^2 = *n*-C_7H_{15},
1b, **2b**: R = R^1 = H, X = Br, **3c**: R^2 = *i*-Pr, **3e**: R^2 = *i*-C_5H_{11}, **3g**: R^2 = *n*-C_7H_{15},
1c, 2c: R = H, R^1 = Me, X = Br, **3i, 4f**: R^2 = Me,
1d, **2d**: R = Me, R^1 = H, X = Br, **3j, 4g**: R^2 = Me.

Scheme 1. Reagents, intermediate products and resulting 3-(alkenyl)pyrazoles **4.**

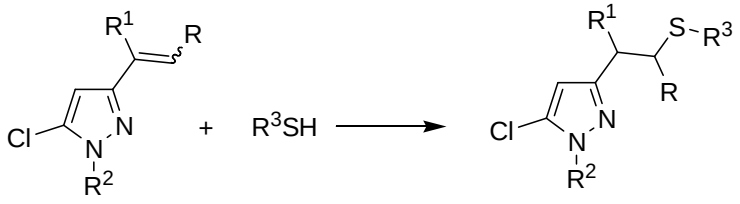
Yields of the target pyrazoles calculated from starting acyl chlorides **1**, and the synthesis of 3-vinylpyrazoles **4a,b** were described in our previous publication;[28] pyrazole **4g** was obtained as a mixture of *E*-and *Z*-isomers in a 4:1 ratio. The reactions of 2,2-dichlorovinylketone **2a** with dimethylhydrazine and benzylhydrazine, synthesis of intermediate 3-(1-chloroethyl)pyrazoles **3a,b** and final 3-vinylpyrazoles **4a,b** were also described in the previous paper.[28] The reactions of dichlorovinylketones **2a,b** with other hydrazines, the reactions of ketones **2c,d** with dimethylhydrazine, and the synthesis of pyrazole derivatives **3c-j** and **4c-g** are presented here for the first time.

According to the methodology,[28] α-chloroacyl chlorides **1** were involved into the reaction with vinylidene dichloride in the presence of $AlCl_3$. For α-bromopropionyl chloride **1b**, the

substitution of bromine by a chlorine atom in α-position under the action of $AlCl_3$ took place and mixtures of intermediate (α-haloalkyl)(dichlorovinyl)ketones **2a,b** were produced. In these cases ketones **2a,b** were introduced into further reactions with hydrazines without isolation in pure form to give mixtures of corresponding intermediate 3-(1-haloethyl)pyrazoles **3c,d**, **3e,f** and **3g,h**, which were transformed without separation into the final 3-vinylpyrazoles **4c-e**.

The systematic investigations of the reactions between 3-alkenylpyrazoles and aromatic or aliphatic thiols showed that arenethiols instantly reacted with 3-alkenylpyrazoles **4a-g** to afford 3-[(2-arylsulfanyl)alkyl]pyrazoles in quantitative yields (Table 1). The process was carried out under solvent-free and catalyst-free conditions. 3-Vinyl-, 3-propenyl and 3-isopropenyl-pyrazoles **4a-g**, all reacted in a couple of minutes under similar conditions to give β-adducts. Side-products including α-adducts or oligomers (polyvinylpyrazoles) were not detected.

Table 1. Reaction[a] of 3-alkenylpyrazoles **4** with thiols **5**; adducts **6**



4 **5** **6**

Entry	3-Alkenylpyrazoles **4**				Thiols **5**		Adducts **6**	
		R	R^1	R^2		R^3		yield, %
1	**4a**	H	H	Me	**5a**	Ph	**6aa**	86
2	**4a**	H	H	Me	**5b**	4-ClC_6H_4	**6ab**	94
3	**4a**	H	H	Me	**5c**	4-BrC_6H_4	**6ac**	92
4	**4a**	H	H	Me	**5d**	4-MeC_6H_4	**6ad**	90
5	**4b**	H	H	Bn	**5a**	Ph	**6ba**	89
6	**4b**	H	H	Bn	**5b**	4-ClC_6H_4	**6bb**	94
7	**4b**	H	H	Bn	**5c**	4-BrC_6H_4	**6bc**	93
8	**4c**	H	H	*i*-Pr	**5a**	Ph	**6ca**	95
9	**4c**	H	H	*i*-Pr	**5b**	4-ClC_6H_4	**6cb**	95
10	**4d**	H	H	*i*-Am	**5a**	Ph	**6da**	98
11	**4e**	H	H	*n*-Ht	**5a**	Ph	**6ea**	98
12	**4e**	H	H	*n*-Ht	**5b**	4-ClC_6H_4	**6eb**	95
13	**4f**	H	Me	Me	**5a**	Ph	**6fa**	97
14	**4f**	H	Me	Me	**5b**	4-ClC_6H_4	**6fb**	98
15	**4g**	Me	H	Me	**5b**	4-ClC_6H_4	**6gb**	96
16[a]	**4a**	H	H	Me	**5e**	*n*-Pr	**6ae**	0
17[a]	**4a**	H	H	Me	**5f**	Bn	**6af**	0

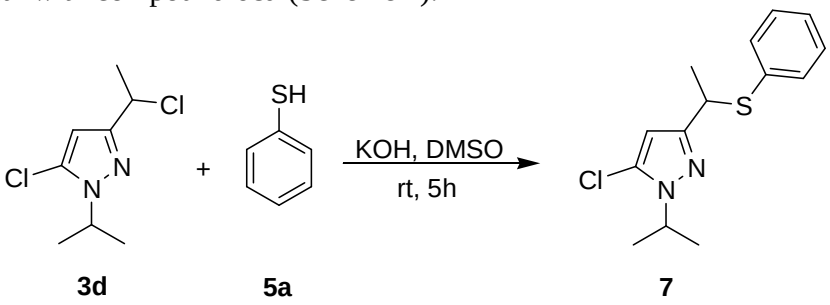
[a] Reaction conditions: **4** (1 mmol), thiol **5** (1 mmol), solvent-free, r.t., 3 min.

In contrast to aromatic thiols, alkanetiols did not react with 3-alkenyl-5-chloropyrazoles under the same conditions. For example, 1-methyl-3-vinyl-5-chloropyrazole (**4a**) did not give adducts with propylmercaptan or benzylmercaptan (Table 1, Entries 16, 17).

The structures of sulfur-containing pyrazoles **6** were proved by IR and NMR spectra, the composition was confirmed by the data of elemental analysis.

In the ^{1}H and ^{13}C NMR spectra of products **6** signals of the alkenyl groups (typical for the starting 3-alkenylpyrazoles **4** are absent, while signals of organylsulfanylethyl moieties with characteristic shifts are observed. A feature of the ^{1}H NMR spectra of compounds **6fa, 6fb** is the presence of diastereotropic protons of the CH_2SR and CH_2 groups which are non-equivalent and show as multiplets with different chemical shifts.

Furthermore, we directly synthesized 3-(1-phenylsulfanylethyl)pyrazole **7** which is isomeric and non-identical with compound **6ca** (Scheme 2).



3d **5a** **7**

Scheme 2. Reaction of 3-(α-chloroethyl)pyrazole **3d** with thiol **5a.**

It was shown previously[28] that 3-(α-chloroalkyl)pyrazoles do not give the corresponding 3-alkenylpyrazoles under the action of KOH in DMSO at r.t. This fact allows suggesting, that reaction in Scheme 2, proceeds by nucleophilic substitution of the α-chlorine atom by the thiol without dehydrochlorination-addition stages.

Comparison of NMR spectra for isomers **7** and **6ca** unambiguously proves the direction of reaction of alkenylpyrazoles **4** with arenethiols **6** and the formation only of β-adducts.

Conclusions

In conclusion, an efficient one-pot method for the synthesis of hitherto unknown pyrazoles via the atom economical reaction between 3-alkenylpyrazoles and arenethiols has been developed. The synthesized pyrazoles combine two biologically relevant fragments in their structures (the azole ring and the sulfanyl group) and represent promising building blocks for drug design, pesticides, and other useful products.

The reaction of arenethiols with 3-alkenylpyrazoles is chemo- and regio-selective. The high rate of the process is likely due to protonation of the "pyridine" nitrogen atom of the pyrazole ring to give a pyrazolium fragment which activates the vinyl group towards nucleophilic attack by the

simultaneously formed arylthiolate anions (more nucleophilic than neutral thiols) thus generated are easy added to the activated alkenyl group.
Interestingly, the studied reaction does not represent classical electrophilic addition of arenethiols to the double bond. Apparently it is an autocatalytic process which accompanied by electrophilic assistance to nucleophilic addition. This reaction allows synthesis of new derivatives of the pyrazole. Besides, it can ensure a promising route to other pyrazole derivatives through the activation of alkenyl groups of 3-alkenylpyrazoles by mild protonation with subsequent nucleophilic addition of the reagents to the double bond.

Experimental Section

General. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer (400.13 and 100.61 MHz, respectively) in $CDCl_3$. Chemical shifts (δ) in ppm are reported with use of the residual chloroform (7.25 for ^{1}H and 77.20 for ^{13}C) as internal standards. IR spectra were recorded on a Bruker Vertex 70 spectrometer in the region of 400-4000 cm^{-1}. MS analyses were recorded on a Shimadzu GCMS-QP5050A instrument (ionization potential 70 eV). Monitoring of the reaction progress and the analysis of the resulting liquid products were performed on a chromatograph LHM 80-MD-2 (column 3 × 2000 mm, liquid phase is DC-550, 5% on the recording medium Chromaton N-AW-HMDS, linear programming mode temperature 12 deg/min, carrier gas helium). The elemental analyses were carried out on Flash EA 1112 elemental analyzer. MW activation was carried out with an Anton Paar Monowave 300 oven at the temperature control. Commercially available α-haloacylchlorides **1a-d**, thiols **5** and alkyl hydrazines were used. Alkyl hydrazines were distilled before reaction.
Synthesis of 2,2-dichlorovinylketones **2a-d**, 3-(1-chloroethyl)pyrazoles **3a,b**, and 3-vinyl-pyrazoles **4a,b** was presented in a previous paper.[28] Pyrazole derivatives **3c-j** and **4c-g** are described here for the first time.

General procedure for the synthesis of pyrazole derivatives 3c-h and 4c-e
A mixture of triethylamine (50 mmol, 5.05 g) and the corresponding alkylhydrazine (50 mmol) was added dropwise to a of dichlorovinylketones **2a** or **2b** or to a mixture of dichlorovinylketones **2a** and **2b** (50 mmol)[28] in diethyl ether (150 mL) for 20 min. After completion of the exotherm, the reaction mixture was stirred for 5 h and poured into water (150 mL). The organic layer was separated and the water layer was extracted with diethyl ether (3 × 50 mL). The organic layer combined with the extract was dried over $CaCl_2$, filtered off. After evaporating of diethyl ether 3-(1-chloroethyl)pyrazoles **3d**, **3f**, **3h** or mixtures of 3-(1-haloethyl)pyrazoles **3c** and **3d**, **3e** and **3f**, **3g** and **3h** or mixtures of 3-(1-bromo-1-methylethyl)-5-chloro-1-methyl-1*H*-pyrazole (**3i**) and 5-chloro-1-methyl-3-(1-methylethenyl)-1*H*-pyrazole (**4f**) were used for further dehydrohalogenation without additional purification. The corresponding 3-(1-chloroethyl pyrazoles or mixtures of 3-(1-haloethyl)pyrazoles or mixture

pyrazoles (**3i**) and (**4f**) in DMF (20 mL) was exposed under MW irradiation (150°C) for 10-20 min. Then the reaction mass was diluted with water (200 mL) and extracted with diethyl ether (3 × 50 mL). The extract was dried over $MgSO_4$ and filtered off. Diethyl ether was evaporated off and the target 3-alkenylpyrazoles (**4c-f**) colourless liquid were distilled in vacuum.

Mixture of 3-(1-bromoethyl)-5-chloro-1-(1-methylethyl)-1*H*-pyrazole (3c) and 5-chloro-3-(1-chloroethyl)-1-(1-methylethyl)-1*H*-pyrazole (3d). Colourless liquid, bp 112-118 °C (25 mm Hg), (9.7 g, **3c** 8.2 g, 77%; **3d** 1.5 g, 14.5%), ratio **3c** (88%) : **3d** (12%), is determined from the intensity signals of the protons of the groups of CHCl and CHBr in the ^{1}H NMR spectrum; IR (ν_{max}, cm^{-1}): **3c** and **3d**: 3131 (=C-H_{Pyr}), 2950, 2919, 2855 (CH_{Alk}), 1601, 1515 (C=C, C=N).

3c. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 6.25 (s, 1H, H^4), 5.19 (q, *J* 6.9 Hz, 1H, CHBr), 4.60 (spt, *J* 6.6 Hz, 1H, NCH), 1.98 (d, *J* 6.9 Hz, 3H, CH_3), 1.42 (d, *J* 6.6 Hz, 6H, CH_3). MS (EI, 70 eV), m/z (%): 250 (M^+, 2), 235 (9), 208 (4), 193 (35), 178 (62), 136(100).

3d. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 6.23 (s, 1H, H^4), 5.18 (q, *J* 6.9 Hz, 1H, CHCl), 4.35 (spt, *J* 6.8 Hz, 1H, NCH), 1.82 (d, *J* 6.9 Hz, 3H, CH_3), 1.44 (d, *J* 6.8 Hz, 6H, CH_3). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ_C 152.8 (C^3), 125.8 (C^5), 101.7 (C^4), 58.3 (CHCl), 52.7 (NCH_2), 50.1 (CH_2), 24.6 (CH_3), 21.6 (CH_3). MS (EI, 70 eV), m/z (%): 206 (M^+, 15), 171 (50), 129 (100).

5-Chloro-3-(1-chloroethyl)-1-(1-methylethyl)-1*H*-pyrazole (3d). Synthesized from ketones **2a** and 1-methylethylhydrazine**.** Colourless liquid (7.9 g, 76 %), bp 112-113°C (24 mm Hg), IR (ν_{max}, cm^{-1}): 3131 (=C-H_{Pyr}), 2950, 2919, 2855 (CH_{Alk}), 1601, 1515 (C=C, C=N). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 6.25 (s, 1H, H^4), 5.10 (q, *J*=6.9 Hz, 1H, CHCl), 4.61 (spt, *J*=6.7 Hz, 1H, NCH), 1.82 (d, *J*=6.9 Hz, 3H, CH_3), 1.46 (d, *J*=6.7 Hz, 6H, $2CH_3$). MS (EI, 70 eV), m/z (%): 206 (M^+, 15), 171 (50), 129 (100). Elemental anal. Calcd for $C_8H_{12}Cl_2N_2$: C, 46.40; H 5.84; Cl, 34.24; N, 13.53. Found: C, 46.47; H, 5.77; Cl, 34.30; N, 13.39.

Mixture of 3-(1-bromoethyl)-5-chloro-1-(3-methylbutyl)-1*H*-pyrazole (3e) and 5-chloro-3-(1-chloroethyl)-1-(3-methylbutyl)-1*H*-pyrazole (3f). Colourless liquid (12.5 g: **3e** 10.3 g, 67%; **3f.** 2.2 g, 16.8%), bp 145-147 °C (25 mm Hg), ratio **3e** (63%) : **3f** (37%) is determined from the intensity signals of the protons of the groups of CHCl and CHBr in the 1H NMR spectrum; IR (ν_{max}, cm^{-1}): **3e** and **3f**: 3132 (=C-H_{Pyr}), 2952, 2920, 2858 (CH_{Alk}), 1603, 1517 (C=C, C=N).

3e. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 6.28 (s, 1H, H^4), 5.19 (q, *J* 6.9 Hz, 1H, CHBr), 4.09 (t, *J* 7.6 Hz, 2H, NCH_2), 1.86 (d, *J* 6.9 Hz, 3H, CH_3), 1.77 (m, 3H, CH, CH_2), 0.93 (d, *J* 6.7, 6H, $2CH_3$).

3f. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 6.28 (s, 1H, H^4), 5.12 (q, *J* 6.8 Hz, 1H, CHCl), 4.16 (q, *J* 7.2 Hz, 2H, NCH_2,), 1.92 (d, *J* 6.8 Hz, 3H, CH_3), 1.58 (m, 3H, CH, CH_2), 0.95 (d, *J* 6.7 Hz, 6H, $2CH_3$).). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ_C 153.6 (C^3), 127.4 (C^5), 102.5 (C^4), 52.3 (CHCl), 48.0 (NCH_2), 38,8 (CH), 26.01 (CH_2), 25.1 (CH_3), 22.6 (CH_3).

5-chloro-3-(1-chloroethyl)-1-(3-methylbutyl)-1*H*-pyrazole (3f). Synthesized from ketones **2a** and 3-methylbutylhylhydrazine. Colourless liquid (7.3 g, 62 %), bp 145-147°C (25 mm Hg). IR (ν_{max}, cm^{-1}): 3131 (=C-H_{Pyr}), 2950, 2919, 2855 (CH_{Alk}), 1601, 1515 (C=C, C=N). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 6.26 (s, 1H, H^4), 5.09 (q, *J*=6.9 Hz, 1H, CHCl), 4.10 (m, *J*=6.8, 1.3 Hz, 2H, NCH_2), 1.83 (d, *J*=6.9 Hz, 3H, CH_3), 1.72 (m, *J*=6.9, 6.8 Hz, 2H, CH_2), 1.62 (m, *J*=6.9,

6.8 Hz, 1H, CH), 0.95 (d, *J*=6.9, 6H, $2CH_3$). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ_C 153.6 (C^3), 127.4 (C^5), 102.5 (C^4), 52.3 (CHCl), 48.0 (NCH_2), 38.8 (CH), 26.01 (CH_2), 25.1 (CH_3), 22.6 (CH_3). MS (EI, 70 eV), m/z (%): 234 (M^+, 0,4), 219 (2.5), 199 (100), 177 (98), 163 (28), 141 (30), 129 (85). Anal. Calcd for $C1_{10}H_{16}Cl_2N_2$: C, 51.08; H 6.86; Cl, 30.15; N, 11.91. Found: C, 50.07; H, 6.76; Cl, 30.31; N, 11.90.

Mixture of 3-(1-bromoethyl)-5-chloro-1-(1-heptyl)-1*H*-pyrazole (3g) and 5-chloro-3-(1-chloroethyl)-1-(1-heptyl)-1*H*-pyrazole (3h). Colourless liquid (10.2 g, **3g** 7.7 g, 50%; **3h** 2.2 g, 18.5%), bp 142-150 °C (15 mm Hg), ratio **3g** (72%) : **3h** (28%) is determined from the intensity signals of the protons of the groups of CHCl and CHBr in the ^1H NMR spectrum; IR (ν_{max}, cm^{-1}): **3g** and **3h**. 3135, 3100 (=CH), 2964, 2979, 2875 (CH_{Alk}), 1510 (C=C, C N).

3g. ^1H NMR (400.13 MHz, $CDCl_3$): δ_H 6.24 (s, 1H, H^4), 5.16 (q, *J* 6.9 Hz, 1H, CHBr), 4.05 (t, *J* 7.0 Hz, 2H, NCH_2), 1.98 (d, *J* 6.9 Hz, 3H, CH_3), 1.80 (dd, *J* 7.0, 6.8 Hz, 2H, CH_2), 1.27 (m, 8H, $4CH_2$), 0.84 (t, *J* 6.9 Hz, 3H, CH_3).

3h. ^1H NMR (400.13 MHz, $CDCl_3$): δ_H 6.24 (s, 1H, H^4), 5.05 (q, *J* 6.9 Hz, 1H, CHCl), 4.05 (t, *J* 7.0 Hz, 2H, NCH_2), 1.98 (d, *J* 6.9 Hz, 3H, CH_3), 1.80 (dd, *J* 7.0, 6.8 Hz, 2H, CH_2), 1.27 (m, 8H, $4CH_2$), 0.85 (t, *J* 6.9 Hz, 3H, CH_3).

5-Chloro-3-(1-chloroethyl)-1-heptyl-1*H*-pyrazole (3h). Colourless liquid (10.2 g, 78%), bp 142-144°C (15 mm Hg), IR (ν_{max}, cm^{-1}): **3h**: 3135, 3100 (=CH), 2964, 2979, 2875 (CH_{Alk}), 1510 (C=C, C=N). ^1H NMR(400.13 MHz, $CDCl_3$): δ_H 6.24 (s, 1H, H^4), 5.05 (q, *J*=6.9 Hz, 1H, CHCl), 4.05 (t, *J*=7.0 Hz, 2H, NCH_2), 1.98 (d, *J*= 6.9 Hz, 3H, CH_3), 1.80 (dd, *J*=7.0, 6.8 Hz, 2H, CH_2), 1.27 (m, 8H, $4CH_2$), 0.85 (t, *J*=6.9 Hz, 3H, CH_3). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ_C 153.6 (C^3), 127.4 (C^5), 102.6 (C^4), 52.3 (CHCl), 48.0 (NCH_2), 38,75 (CH), 26.0 (CH_2), 25.1 (CH_3), 22.6 (CH_3).

Anal. Calcd for $C1_{12}H_{20}Cl_2N_2$: C, 54.76; H 7.66; Cl, 26.94; N, 10.64. Found: C, 54.46; H, 7.75; Cl, 26.81; N, 10.80.

General procedure for the synthesis of pyrazole derivatives 3i,j

Dimethylhydrazine (100 mmol, 6.1 g) was added dropwise to a solution of dichlorovinylketone **2c,d** (50 mmol, 12.3 g)[28] in diethyl ether (150 mL) for 20 min. Then the reaction mass was treated as described for **3c-h** and **4c-e**.

3-(1-Bromo-1-methylethyl)-5-chloro-1-methyl-1*H*-pyrazole (3i). Obtained in mixture with pyrazole **4f** (80% **3i** and 20% **4f**). The mixture was used for further synthesis without separation. Light yellow liquid (10.1 g 92%), (8.7 g, **3i**, 1.4 g, **4f**).

3i. ^1H NMR (400.13 MHz, $CDCl_3$): δ_H 6.41 (s, 1H, H^4), 3.82 (s, 3H, NCH_3), 1.95 (s, 6H, CH_3).
^{13}C NMR (100.61 MHz, $CDCl_3$): δ_C 156.6 (C^3), 135.4 (C^5), 128.1 (C=), 113.6 (CH_2), 101.7 (C^4), 32.6 (NCH_3), 19.8 (CH_3).MS (EI, 70 eV), m/z (%): 236 (M^+, 9), 157 (55), 143 (100).

4f. ^1H NMR (400.13 MHz, $CDCl_3$): δ_H 6.31 (s, 1H, H^4), 5.44 (s, 1H, =CH), 5.06 (s, 1H, =CH), 3.82 (s, 3H, NCH_3), 2.09 (s, 3H, CH_3). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ_C 152.1 (C^3), 136.4 (C^5), 127.7 (C^4), 112.2 (=CH), 101.4 (=CH), 36.1 (NCH_3), 19.7 (CH_3).

3-(1-Bromopropyl)-5-chloro-1-methyl-1*H*-pyrazole (3j). Light yellow liquid, (9.3 g, 78%). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 6.26 (s, 1H, H^4), 4.90 (t, *J*=7.4 Hz, 1H, CHBr), 3.81 (s, 3H, NCH_3), 2.20 (m, *J*=7.4, 7.2 Hz, 2H, CH_2), 1.04 (t, *J*=7.2 Hz, 3H, CH_3). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ_C 152.9 (C^3), 128.0 (C^5), 102.9 (C^4), 49.2 (CHBr), 36.2 (NCH_3), 32.0 (CH_2), 12.7 (CH_3). MS (EI, 70 eV), m/z (%): 236 (M^+, 0.4), 207 (1), 157 (100), 128 (38). Anal. Calcd for $C_7H_{10}BrClN_2$: C, 35.40; H 4.24; Br, 33.64; Cl, 14.93; N, 11.79. Found: C, 35.28; H, 4.38; Br, 33.44; Cl, 14.68; N, 11.64.

5-Chloro-3-ethenyl-1-(1-methylethyl)-1*H*-pyrazole (4c). Obtained from mixture of **3c** and **3d** or **3d**, the reaction time was 20 min. Colourless liquid (5.16 g, 61%), bp 56-58 °C (1 mm Hg). IR (ν_{max}, cm^{-1}): 3137, 3018, 3091 (=CH), 2944, 2852 (CH_{Alk}), 1638, 1505 (C=C, C=N). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 6.65 (dd, *J* 11.0, 17.1 Hz, 1H, CH=), 6.30 (s, 1H, H^4), 5.65 (dd, *J* 1.1, 17.1 Hz, 1H, $=CH_2$), 5.27 (dd, *J* 1.1, 11.0, 1H, $=CH_2$), 4.62 (spt, *J* 6.7 Hz, 1H, CH), 1.45 (d, *J* 6.7 Hz, 6H, $2CH_3$). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ_C 150.3 (C^3), 129.3 (CH=), 126.5 (C^5), 115.4 ($=CH_2$), 101.0 (C^4), 50.3 (NCH), 22.1 (CH_3). Anal. Calcd for $C_8H_{11}ClN_2$: C, 56.31; H 6.50; Cl, 20.78; N, 16.42. Found: C, 56.37; H, 6.58; Cl, 20.53; N, 16.39 %.

5-Chloro-3-ethenyl-1-(3-methylbutyl)-1*H*-pyrazole (4d). Obtained from mixture of **3e** and **3f** or **3f**, the reaction time was 20 min. Colourless liquid (8.4 g, 85%), bp 79-82 °C (15 mm Hg). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 6.61 (dd, *J* 11.1, 17.7 Hz, 1H, CH=), 6.29 (s, 1H, H^4), 5.62 (dd, *J* 1.2, 17.7 Hz, 1H, $=CH_2$), 5.26 (dd, *J* 1.2, 11.1 Hz, 1H, $=CH_2$), 4.08 (t, *J* 7.5 Hz, 2H, NCH_2), 1.71 (m, *J* 7.5, 6.8 Hz, 2H, CH_2), 1.62 (m, *J* 6.8, 6.5 Hz, 1H, CH), 0.94 (d, *J* 6.5 Hz, 6H, $2CH_3$). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ_C 150.5 (C^3), 129.2 (CH=), 127.4 (C^5), 115.6 ($=CH_2$), 101.3 (C^4), 47.8 (NCH_2), 38.8 (CH), 25.9 (CH_2), 22.5 (CH_3) ppm. Anal. Calcd for $C_{10}H_{15}ClN_2$: C, 60.45; H 7.61; Cl, 17.84; N, 14.10. Found: C, 60.37; H, 7.58; Cl, 17.53; N, 13.89 %.

5-Chloro-3-ethenyl)-1-heptyl-1*H*-pyrazole (4e). Obtained from mixture of **3g** and **3h**, the reaction time was 10 min. Colourless liquid (7.17 g, 63%), bp 165-169 °C (25 mm Hg). IR (ν_{max}, cm^{-1}): 3137, 3100 (=CH), 2964, 2957, 2857 (CH_{Alk}), 1504 (C=C, C=N). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 6.58 (dd, *J* 11.0, 17.7 Hz, 1H, CH=), 6.25 (s, 1H, H^4), 5.62 (dd, *J* 2.7, 17.7 Hz, 1H, $=CH_2$), 5.24 (dd, *J* 2.7, 11.0 Hz, 1H, $=CH_2$), 4.02 (t, *J* 7.4 Hz, 2H, NCH_2), 1.77 (m, 2H, CH_2), 1.25 (m, 8H, $4CH_2$), 0.82 (t, *J* 6.9 Hz, 3H, CH_3). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ_C 150.4 (C^3), 129.1 (CH=), 127.4 (C^5), 115.5 ($=CH_2$), 101.2 (C^4), 49.2 (NCH_2), 31.7 (CH_2), 30.0 (CH_2), 28.9 (CH_2), 26.5 (CH_2), 22.6 (CH_2), 14.1 (CH_3). Anal. Calcd for $C_{12}H_{19}ClN_2$: C, 63.56; H, 8.45; Cl, 15.64; N, 12.35. Found: C, 63.69; H, 8.57; Cl, 15.25; N, 12.57 %.

5-Chloro-1-methyl-3-(1-methylethenyl)-1*H*-pyrazole (4f). Obtained from mixture of **3i** and **4f** The reaction time was 20 min. Colourless liquid (5.33 g, 68%), bp 56 °C (1 mm Hg). IR (ν_{max}, cm^{-1}): 3137, 3100 (=CH), 2964, 2957, 2857 (CH_{Alk}), 1504 (C=C, C=N). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 6.31 (s, 1H, H^4), 5.44 (s, 1H, = CH), 5.06 (s, 1H, =CH), 3.82 (s, 3H, CH_3), 2.09 (s, 3H, CH_3). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ_C 152.1 (C^3), 136.4 (C^5), 127.7 (C^4), 112.2 (=CH), 101.4 (=CH), 36.1 (NCH_3), 19.7 (CH_3). Anal. Calcd for $C_7H_9ClN_2$: C, 53.68; H, 5.79; Cl, 22.64; N, 17.89. Found: C, 53.33; H, 5.62; Cl, 22.28; N, 18.04 %.

5-Chloro-1-methyl-3-[prop-1-en-1-yl]-1*H*-pyrazole (4g). The reaction time was 20 min. Colourless liquid (6.42 g, 82% from pyrazole **3j**), (mixture of *E* and *Z*-isomers). The ratio E/Z isomer 4:1; bp 86 °C (2 mm Hg). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 6.31-6.14 (m, 3H, CH=CH, H^4), 3.82, 3.78 (s, 3H, NCH_3), 1.96, 1.86 (d, *J*=6.4 Hz, 3H, CH_3). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ_C 150.3 (C^3), 127.9 (C^5), 122.8 (C^4), 109.6 (=CH), 104.8 (=CH), 100.9 (=CH), 37.3, 35.9 (NCH_3), 18.2 (CH_3). Anal. Calcd for $C_7H_9ClN_2$: C, 53.68; H, 5.79; Cl, 22.64; N, 17.89. Found: C, 53.63; H, 5.82; Cl, 22.48; N, 17.65.

5-Chloro-1-methyl-3-(1-methylethenyl)-1*H*-pyrazole (4f). Obtained from mixture of **3i** and **4f.** The reaction time was 20 min. Colourless liquid (5.33 g, 68%), bp 56 °C (1 mm Hg). IR (ν_{max}, cm^{-1}): 3137, 3100 (=CH), 2964, 2957, 2857 (CH_{Alk}), 1504 (C=C, C=N). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 6.31 (s, 1H, H^4), 5.44 (s, 1H, = CH_2), 5.06 (s, 1H, =CH_2), 3.82 (s, 3H, CH_3), 2.08 (s, 3H, CH_3). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ_C 152.1 (C^3), 136.4 (C^5), 127.7 (C^4), 112.2 (=CH), 101.4 (=CH), 36.1 (NCH_3), 19.7 (CH_3). Anal. Calcd for $C_7H_9ClN_2$: C, 53.68; H, 5.79; Cl, 22.64; N, 17.89. Found: C, 53.33; H, 5.62; Cl, 22.28; N, 18.04 %.

5-Chloro-1-methyl-3-[prop-1-en-1-yl]-1*H*-pyrazole (4g). The reaction time was 20 min. Colourless liquid (6.42 g, 82% yield, from pyrazole **3j**, mixture of *E* and *Z*-isomers, the ratio E/Z isomer 4:1), bp 86 °C (2 mm Hg). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 6.31-6.14 (m, 3H, CH=CH, H^4), 3.82, 3.78 (s, 3H, NCH_3), 1.96, 1.86 (d, *J*=6.4 Hz, 3H, CH_3). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ_C 148.5 (C^3), 127.5 (C^5), 126.8 (C^4), 107.7 (=CH), 103.94 (=CH), 36.9, 35.6 (NCH_3), 14.8, 14.38 (CH_3). Anal. Calcd for $C_7H_9ClN_2$: C, 53.68; H, 5.79; Cl, 22.64; N, 17.89. Found: C, 53.63; H, 5.82; Cl, 22.48; N, 17.65 %.

General procedure for the synthesis of 1-alkyl-3-[2-(arylsulfanyl)alkyl]-1*H*-pyrazoles 6.

3-Alkenyl-5-chloropyrazole **4** (1 mmol) and aromatic thiol **5** (1 mmol) were mixed and kept for 1-3 min. The resulting pyrazoles **6** were washed with hexane and dried under vacuum.

5-Chloro-1-methyl-3-[2-(phenylsulfanyl)ethyl]-1*H*-pyrazole (6aa). Obtained from vinylpyrazole **4a** (0.14 g) and benzenethiol **5a** (0.11 g). Colourless oil, bp 210-212 °C (15 mm Hg), 0.22 g, 86% yield. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 7.49-7.14 (m, 5H, C_6H_5), 6.03 (s, 1H, H^4_{Pyr}), 3.75 (s, 3H, NCH_3), 3.17 (t, *J* 7.4 Hz, 2H, SCH_2), 2.87 (t, *J* 7.4 Hz, 2H, $C\underline{H}_2CH_2S$). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ_C 150.5 (C^3_{Pyr}), 136.2 (C^i), 129.1 ($C^{2,6}$), 128.9 ($C^{3,5}$), 127.2 (C^5_{Pyr}), 126.1 (C^4), 103.6 (C^4_{Pyr}), 35.9 (NCH_3), 33.2 (SCH_2), 28.7 ($\underline{C}H_2CH_2S$). Anal. Calcd for $C_{12}H_{13}ClN_2S$: C, 57.02; H, 5.18; Cl, 14.03; N, 11.08; S 12.68. Found: C, 57.06; H, 5.19; Cl, 14.05; N, 11.04; S, 12.65 %.

5-Chloro-3-{2-[(4-chlorophenyl)sulfanyl]ethyl}-1-methyl-1*H*-pyrazole (6ab). Obtained from vinylpyrazole **4a** (0.14 g) and 4-chlorobenzenethiol **5b** (0.14 g). Colourless oil (0.26 g, 94%), bp 243-246 °C (15 mm Hg). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 7.26, 7.20 (AA′BB′, *J* 6.6 Hz, 4H, C_6H_4), 6.00 (s, 1H, H^4_{Pyr}), 3.74 (s, 3H, NCH_3), 3.12 (t, *J* 7.5 Hz, 2H, SCH_2), 2.83 (t, *J* 7.5 Hz, 2H, $C\underline{H}_2CH_2S$). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ_C 150.4 (C^3_{Pyr}), 134.8 (C^i), 132.2 (C^4), 131.0 ($C^{3,5}$), 129.1 ($C^{2,6}$), 127.5 (C^5_{Pyr}), 103.7 (C^4_{Pyr}), 36.1 (NCH_3), 33.6 (SCH_2), 28.8 ($\underline{C}H_2CH_2S$). Anal. Calcd for $C_{12}H_{12}Cl_2N_2S$: C, 50.18; H, 4.21; Cl, 24.69; N, 9.75; S, 11.16. Found: C, 50.22; H, 4.20; Cl, 24.65; N, 9.76; S, 11.18 %.

3-{2-[(4-Bromophenyl)sulfanyl]ethyl}-5-chloro-1-methyl-1*H*-pyrazole (6ac). Obtained from vinylpyrazole **4a** (0.14 g) and 4-bromobenzenethiol **5c** (0.19 g). Colourless oil (0.30 g, 92%), bp 259-264 °C (15 mm Hg). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 7.32, 7.14 (AA′BB′, *J* 8.7 Hz, 4H, C_6H_4), 5.96 (s, 1H, H^4_{Pyr}), 3.69 (s, 3H, NCH_3), 3.09 (t, *J* 7.3 Hz, 2H, SCH_2), 2.80 (t, *J* 7.3 Hz, 2H, $C\underline{H}_2CH_2S$). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ_C 150.2 (C^3_{Pyr}), 135.5 (C^i), 131.9 (C^2), 131.0 (C^3), 127.3 (C^5_{Pyr}), 119.9 (C^4), 103.6 (C^4_{Pyr}), 36.0 (NCH_3), 33.3 (SCH_2), 28.6 ($\underline{C}H_2CH_2S$). Anal. Calcd for $C_{12}H_{12}BrClN_2S$: C, 43.46; H, 3.65; N, 8.45; S, 9.67. Found: C, 43.49; H, 3.65; N, 8.46; S, 9.64 %.

5-Chloro-1-methyl-3-{2-[(4-methylphenyl)sulfanyl]ethyl}-1*H*-pyrazole (6ad). Obtained from vinylpyrazole **4a** (0.14 g) and 4-methylbenzenethiol **5d** (0.12 g). Colourless oil (0.23 g, 90%), bp 230-234 °C (15 mm Hg). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 7.24, 7.06, (AA′BB′, *J* 8.2 Hz, 4H, C_6H_4), 6.00 (s, 1H, H^4_{Pyr}), 3.72 (s, H, NCH_3), 3.09 (t, *J* 7.3 Hz, 2H, SCH_2), 2.82 (t, *J* 7.3 Hz, 2H, $C\underline{H}_2CH_2S$), 2.28 (s, 3H, CH_3). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ_C 150.7 (C^3_{Pyr}), 136.4 (C^4), 132.3 (C^i), 130.6 ($C^{2,6}$), 129.8 ($C^{3,5}$), 127.4 (C^5_{Pyr}), 103.7 (C^4_{Pyr}), 36.0 (NCH_3), 34.1 (SCH_2), 28.9 $\underline{C}H_2CH_2S$), 20.9 (CH_3). Anal. Calcd for $C_{13}H_{15}ClN_2S$: C, 58.53; H, 5.67; Cl, 13.29; N, 10.50; S, 12.02. Found: C, 58.58; H, 5.66; Cl, 13.33; N, 10.51; S 12.00 %.

1-Benzyl-5-chloro-3-[2-(phenylsulfanyl)ethyl]-1*H*-pyrazole (6ba). Obtained from vinylpyrazole **4b** (0.22 g) and benzenethiol **5a** (0.11 g). Colourless oil (0.29 g, 89%), bp 266-270 °C (15 mm Hg).^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 7.86-7.65 (m, 10H, C_6H_5S, C_6H_5), 6.59 (s, 1H, H^4_{Pyr}), 5.77 (s, 2H, NCH_2), 3.69 (t, *J* 7.3 Hz, 2H, SCH_2), 3.42 (t, *J* 7.3 Hz, 2H, $C\underline{H}_2CH_2S$). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ_C 151.1 (C^3_{Pyr}), 136.1 (C^i_S), 129.6 (C^2_S), 129.1 (C^i_{Bn}), 129.0 (C^3_S), 128.8 (C^3_{Bn}), 127.9 (C^4_{Bn}), 127.9 (C^5_{Pyr}), 127.3 (C^2_{Bn}), 126.2 (C^4_S), 104.2 (C^4_{Pyr}), 52.6 (NCH_2), 33.3 (SCH_2), 28.8 ($\underline{C}H_2CH_2S$). Anal. Calcd for $C_{18}H_{17}ClN_2S$: C, 65.74; H, 5.21; Cl, 10.78; N, 8.52; S, 9.75. Found: C, 65.79; H, 5.22; Cl, 10.75; N, 8.50; S, 9.77 %.

1-Benzyl-5-chloro-3-{2-[(4-chlorophenyl)sulfanyl]ethyl}-1*H*-pyrazole (6bb). Obtained from vinylpyrazole **4b** (0.22 g) and 4-chlorobenzenethiol **5b** (0.14 g). Colourless oil (0.34 g, 94%), bp 275-279 °C (5 mm Hg). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 7.79-7.67 (m, 9H, 4-ClC_6H_4S, C_6H_5), 6.56 (s, 1H, H^4_{Pyr}), 5.76 (s, 2H, NCH_2), 3.65 (t, *J* 7.4 Hz, 2H, SCH_2), 3.38 (t, *J* 7.4 Hz, 2H, $C\underline{H}_2CH_2S$). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ_C 150.8 (C^3_{Pyr}), 136.1 (C^i_S), 134.7 (C^i_{Bn}), 132.1 (C^4_S), 130.9 ($C^{3,5}_S$), 129.3 (C^5_{Pyr}), 129.0 ($C^{2,6}_S$), 128.70 ($C^{3,5}_{Bn}$), 127.9 (C^4_{Bn}), 127.3 ($C^{2,6}_{Bn}$), 104.1 (C^4_{Pyr}), 52.6 (NCH_2), 33.5 (SCH_2), 28.7 ($\underline{C}H_2CH_2S$). Anal. Calcd for $C_{18}H_{16}Cl_2N_2S$: C, 59.51; H, 4.44; Cl, 19.52; N, 7.71; S, 8.83. Found: C, 59.53; H, 4.45; Cl, 19.50; N, 7.69; S, 8.85 %.

1-Benzyl-3-{2-[(4-bromophenyl)sulfanyl]ethyl}-5-chloro-1*H*-pyrazole (6bc). Obtained from vinylpyrazole **4b** (0.22 g) and 4-bromobenzenethiol **5c** (0.19 g). Colourless oil (0.38 g, 93%), bp 288-292 °C (15 mm Hg),. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 7.86-7.66 (m, 9H, 4-BrC_6H_4S, C_6H_5), 6.56 (s, 1H, H^4_{Pyr}), 5.76 (s, 2H, NCH_2), 3.65 (t, *J* 7.7 Hz, 2H, SCH_2), 3.38 (t, *J* 7.7 Hz, 2H, $C\underline{H}_2CH_2S$). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ_C 150.8 (C^3_{Pyr}), 136.2 (C^i_S), 132.3 (C^i_{Bn}), 132.0 ($C^{2,6}_S$), 131.1 ($C^{3,5}_S$), 129.5 (C^5_{Pyr}), 128.8 ($C^{3,5}_{Bn}$), 127.9 (C^4_{Bn}), 127.3 ($C^{2,6}_{Bn}$), 120.0 (C^4_S),

104.2 (C^4_{Pyr}), 52.7 (NCH_2), 33.4 (SCH_2), 28.7 ($\underline{C}H_2CH_2S$). Anal. Calcd for $C_{18}H_{16}BrClN_2S$: C, 53.02; H, 3.96; N, 6.87; S, 7.86. Found: C, 53.06; H, 3.97; N, 6.87; S, 7.84 %.

5-Chloro-1-(1-methylethyl)-3-[2-(phenylsulfanyl)ethyl]-1*H*-pyrazole (6ca). Obtained from vinylpyrazole **4c** (0.17 g) and benzenethiol **5a** (0.11 g). Colourless oil (0.27 g, 95%). IR (ν_{max}, cm^{-1}): 3130 (=C-H_{Pyr}), 3085, 3076, 3058 (=C-H_{Ph}), 2980, 2933 (CH_{Alk}), 1584, 1514 (C=C, C=N). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 7.19-7.13 (m, 5H, C_6H_5), 6.02 (s, 1H, H^4_{Pyr}), 4.58 (spt, *J* 6.6 Hz, 2H, NCH), 3.17 (t, *J* 7.3 Hz, 2H, SCH_2), 2.90 (t, *J* 7.3 Hz, 2H, $C\underline{H}_2CH_2S$), 1.43 (d, *J* 6.6 Hz, 6H, $2CH_3$). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ_C 150.4, (C^3_{pyr}), 136.4 (C^i), 129.6 ($C^{2,6}$), 129.0 (C^4), 126.1 ($C^{3,5}$), 124.3 (C^3_{pyr}), 103.4 (C^4_{pyr}), 50.1 (NCH), 33.4 (SCH_2), 29.0 ($\underline{C}H_2CH_2S$), 22.1 ($\underline{C}H_3$). Anal. Calcd for $C_{14}H_{17}ClN_2S$: C, 59.88; H, 6.10; Cl, 12.62; N, 9.98; S, 11.42. Found: C, 59.53; H, 6.17; Cl, 12.69; N, 10.12; S, 11.33 %.

5-Chloro-3-{2-[(4-Chlorophenyl)sulfanyl]ethyl}-1-(1-methylethyl)-1*H*-pyrazole (6cb). Obtained from vinylpyrazole **4c** (0.17 g) and 4-chlorobenzenethiol **5b** (0.14 g). Colourless oil (0.29 g, 95%). IR (ν_{max}, cm^{-1}): 3131 (=C-H_{Pyr}), 3104, 3070 (=C-H_{Ph}), 2980, 2933, 2876 (CH_{Alk}), 1578, 1513 (C=C, C=N). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 7.39-7.18 (AA′BB′, *J* 8.7 Hz, 4H, C_6H_4), 6.00 (s, 1H, H^4_{Pyr}), 4.59 (spt, *J* 6.7 Hz, 2H, NCH_2), 3.14 (t, *J* 7.3 Hz, 2H, SCH_2), 2.87 (t, *J* 7.3 Hz, 2H, $C\underline{H}_2CH_2S$), 1.43 (d, *J* 6.7 Hz, 6H, $2CH_3$). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ_C 150.1 (C^3_{pyr}), 134.9 (C^i), 132.1 (C^4), 130.9 ($C^{3,5}$), 129.1 ($C^{2,6}$), 125.7 (C^5_{pyr}), 103.3 (C^4_{pyr}), 50.1 (NCH), 33.7 (SCH_2), 28.9 ($\underline{C}H_2CH_2S$), 22.1 (CH_3). Anal. Calcd for $C_{14}H_{16}Cl_2N_2S$: C, 53.34; H 5.12; Cl, 22.49; N, 8.89; S, 10.17. Found: C, 53.28; H 5.03; Cl, 22.35; N, 8.69; S, 10.03 %.

5-Chloro-1-(3-methylbutyl)-3-[2-(phenylsulfanyl)ethyl]-1*H*-pyrazole (6da). Obtained from vinylpyrazole **4d** (0.20 g) and benzenethiol **5a** (0.11 g). Colourless oil (0.30 g, 98%). IR (ν_{max}, cm^{-1}): 3131 (=C-H_{Pyr}), 3104, 3069 (=C-H_{Ph}), 2980, 2933, 2876 (CH_{Alk}), 1578, 1513 (C=C, C=N). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 7.37-7.16 (m, 5H, C_6H_5), 6.04 (s, 1H, H^4_{Pyr}), 4.07 (t, *J* 7.6 Hz, 2H, NCH_2), 3.18 (t, *J* 7.0 Hz, 2H, SCH_2), 2.88 (t, *J* 7.0 Hz, 2H, $C\underline{H}_2CH_2S$), 1.69 (m, 2H, CH_2), 1.61 (m, 1H, CH), 0.95 (d, *J* 6.4 Hz, 6H, $2CH_3$). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ_C 150.4, (C^3_{pyr}), 136.2 (C^i), 129.4 ($C^{2,6}$), 128.8 ($C^{3,5}$), 126.4(C^4), 125.9 (C^5_{pyr}), 103.4 (C^4_{pyr}), 47.3 (NCH_2), 38.5 (CH_2), 33.2 (CH_2S), 28.7 ($\underline{C}H_2CH_2S$), 25.6 (CH), 22.3 (CH_3). MS (EI, 70 eV), m/z (%): 308 (M^+, 0.1), 286 (46), 253 (15), 157 (52), 143 (80), 130 (100). Anal. Calcd for $C_{16}H_{21}ClN_2S$: C, 62.22; H 6.85; Cl, 11.48; N, 9.07; S, 10.38. Found: C, 62.17; H 6.73; Cl, 11.26; N, 9.01; S, 10.33 %.

5-Chloro-1-heptyl-3-[2-(phenylsulfanyl)ethyl]-1*H*-pyrazole (6ea). Obtained from vinyl-pyrazole **4e** (0.23 g) and benzenethiol **5a** (0.11 g). Colourless oil (0.33 g, 98%). IR (ν_{max}, cm^{-1}): 3132 (=C-H_{Pyr}), 3071, 3058 (=C-H_{Ph}), 2956, 2928, 2856 (CH_{Alk}), 1584, 1513 (C=C, C=N). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 7.33-7.11 (m, 5H, C_6H_5), 5.99 (s, 1H, H^4_{Pyr}), 4.01 (t, *J* 7.4 Hz, 2H, NCH_2), 3.14 (t, *J* 7.8 Hz, 2H, CH_2S), 2.86 (t, *J* 7.8 Hz, 2H, $C\underline{H}_2CH_2S$), 1.25 (m, 10H, $5CH_2$), 0.85 (t, *J* 6.9 Hz, 3H, CH_3). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ_C 150.6 (C^3_{pyr}), 136.3 (C^i), 129.7 ($C^{2,6}$), 129.0 ($C^{3,5}$), 126.8 (C^4), 126.2 (C^5_{pyr}), 103.5 (C^4_{pyr}), 49.1 (NCH_2), 33.5 (CH_2S), 31.8 ($\underline{C}H_2CH_2S$), 30.0 (CH_2), 28.9 (CH_2), 28.9 (CH_2), 26.6 (CH_2), 22.7 (CH_2), 14.2 (CH_3). MS (EI, 70 eV), m/z (%): 336 (M^+, 63), 301 (92), 251 (24), 227 (37), 214 (30), 191 (16), 179 (22), 129 (67),

123 (100). Anal. Calcd for $C_{18}H_{25}ClN_2S$: C, 64.17; H 7.48; Cl, 10.52; N, 8.31; S, 9.52. Found: C, 64.12; H 7.63; Cl, 10.26; N, 8.11; S, 9.33 %.

5-Chloro-3-2-[(4-chlorophenyl)sulfanyl]ethyl-1-heptyl-1*H*-pyrazole (6eb). Obtained from vinylpyrazole **4e** (0.23 g) and 4-chlorobenzenethiol **5b** (0.14 g). Colourless oil (0.35 g, 95%). IR (ν_{max}, cm^{-1}): 3133 (=C-H_{Pyr}), 3107, 3070, 3042 (=C-H_{Ph}), 2928, 2856 (CH_{Alk}), 1573, 1513 (C=C, C=N). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 7.28, 7.21 (AA′BB′, *J* 8.7 Hz, 4H, C_6H_4), 6.01 (s, 1H, H^4_{Pyr}), 4.04 (t, *J* 7.2 Hz, 2H, NCH_2), 3.15 (t, *J* 7.4 Hz, 2H, CH_2S), 2.87 (t, *J* 7.4 Hz, 2H, $C\underline{H}_2CH_2S$), 1.28 (m, 10H, $5CH_2$), 0.87 (t, *J* 7.4 Hz, 3H, CH_3). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ_C 150.2 (C^3_{pyr}), 134.8 (C^i), 132.1 (C^4), 130.9 ($C^{3,5}$), 129.0 ($C^{2,6}$), 126.7 (C^5_{pyr}), 103.4 (C^4_{pyr}), 48.9 (NCH_2), 33.6 (CH_2S), 31.7 ($\underline{C}H_2CH_2S$), 29.9 (CH_2), 28.8 (CH_2), 28.7 (CH_2), 26.4 (CH_2), 22.6 (CH_2), 14.1 (CH_3). MS (EI, 70 eV), m/z (%): 370 (M^+, 74), 335 (97), 285 (25), 227 (42), 214 (58), 157 (72), 129 (100).Anal. Calcd for $C_{18}H_{24}Cl_2N_2S$: C, 58.22; H, 6.51; Cl, 19.09; N, 7.54; S, 8.63. Found: C, 58.14; H, 6.69; Cl, 19.26; N, 7.31; S, 8.43 %.

5-Chloro-1-methyl-3-[1-methyl-2-(phenylsulfanyl)ethyl]-1*H*-pyrazole (6fa). Obtained from vinylpyrazole **4f** (0.16 g) and benzenethiol **5a** (0.11 g). Colourless oil, (0.26 g, 97%). IR (ν_{max}, cm^{-1}): 3135 (=C-H_{Pyr}), 3110, 3072, 3045 (=C-H_{Ph}), 2927, 2860 (CH_{Alk}), 1570, 1515 (C=C, C=N). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 7.37-7.16 (m, 5H, C_6H_5), 6.05 (s, 1H, H^4_{Pyr}), 3.78 (s, 3H, NCH_3), 3.30 (m, 1H, CH), 3.05 (m, 2H, CH_2S), 1.37 (d, *J* 6.6 Hz, 3H, CH_3). Anal. Calcd for $C_{13}H_{15}ClN_2S$: C, 58.53; H, 5.67; Cl, 13.29; N, 10.50; S, 12.02. Found: C, 58.17; H, 5.43; Cl, 13.20; N, 10.31; S, 12.13 %.

5-Chloro-3-{2-[(4-chlorophenyl)sulfanyl]-1-methylethyl}-1-methyl-1*H*-pyrazole (6fb). Obtained from vinylpyrazole **4f** (0.16 g) and 4-chlorobenzenethiol **5b** (0.14 g). Colourless oil (0.29 g, 98%). IR (ν_{max}, cm^{-1}): 3133 (=C-H_{Pyr}), 3108, 3070, 3043 (=C-H_{Ph}), 2981, 2934, 2860 (CH_{Alk}), 1573, 1513 (C=C, C=N). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 7.21-7.13 (AA′BB′, 4H, C_6H_4), 5.95 (s, 1H, H^4_{Pyr}), 3.69 (s, 3H, NCH_3), 3.18 (m, 1H, CH), 2.95 (m, 2H, CH_2S), 1.28 (d, *J* 6.5 Hz, 3H, CH_3). Anal. Calcd for $C_{13}H_{14}Cl_2N_2S$: C, 51.83; H, 4.68; Cl, 23.54; N, 9.30; S, 10.64. Found: C, 51.67; H, 4.53; Cl, 23.26; N, 9.11; S, 10.46 %.

5-Chloro-3-{2-[(4-chlorophenyl)sulfanyl]propyl}-1-methyl-1*H*-pyrazole (6gb). Obtained from vinylpyrazole **4g** (0.16 g) and 4-chlorobenzenethiol **5b** (0.14 g). Colourless oil (0.29 g, 96%). IR (ν_{max}, cm^{-1}): 3131 (=C-H_{Pyr}), 3110, 3072, 3040 (=C-H_{Ph}), 2983, 2931, 2856 (CH_{Alk}), 1575, 1515 (C=C, C=N). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 7.26-7.13 (AA′BB′, 4H, C_6H_4), 5.97 (s, 1H, H^4_{Pyr}), 3.69 (s, 3H, NCH_3), 3.39 (m, 1H, CH), 2.81, 2.63 (m, 2H, CH_2), 1.21 (d, *J* 6.6 Hz, 3H, CH_3). Anal. Calcd for $C_{13}H_{14}Cl_2N_2S$: C, 51.83; H, 4.68; Cl, 23.54; N, 9.30; S, 10.64. Found: C, 51.30.17; H 4.37; Cl, 23.18; N, 9.14; S, 10.38 %.

5-Chloro-1-(1-methylethyl)-3-[1-(phenylsulfanyl)ethyl]-1*H*-pyrazole (7). Potassium hydroxide (5 mmol, 0.30 g) and benzenethiol **5a** (1.5 mmol, 0.17 g) was stirred for 20 min in DMSO (1.5 mL). Then pyrazole **3d** (1.5 mmol, 0.31 g) was added and the reaction mixture was stirred for 5 h at rt. A mixture was poured into water and extracted with dichloromethane (3 × 10 mL). The extract was dried over $MgSO_4$, dichloromethane was evaporated to give the target pyrazole derivative **7** as yellow oil (0.35 g, 82%). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 7.32-717

(m, 5H, C_6H_5), 6.13 (s, 1H, H^4_{Pyr}), 4.56 (m, J 6.6, 6.7 Hz, 1H, NCH), 4.44 (q, J 7.0 Hz, 1H, CHS), 1.58 (d, J 7.0 Hz, 3H, CH_3), 1.40 (d, J 6.6 Hz, 3H, CH_3), 1.34 (d, J 6.7 Hz, 3H, CH_3). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ_C 153.8 (C^3_{pyr}), 135.2 (C^i), 132.3 ($C^{2,6}$), 128.7 ($C^{3,5}$), 127.1 (C^5_{pyr}), 125.8 (C^4), 102.1 (C^4_{pyr}), 50.2 (NCH), 41.6 (CHS), 22.1, 21.0, 21.2 (CH_3). MS, m/z (%) 280 (M+, 12), 171 (84), 129 (100), 109 (11). Anal. Calcd for $C_{15}H_{17}ClN_2S$: C, 59.88; H, 6.10; Cl, 12.62; N, 9.98. Found: C, 59.95; H, 6.07; Cl, 12.25; N, 9.77 %.

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