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4-Dimethylamino Pyridine-Promoted One-Pot Three-Component Regioselective Synthesis of Highly Functionalized 4*H*-Thiopyrans via Heteroannulation of β-Oxodithioesters

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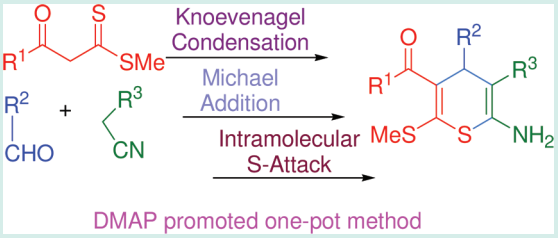
Supporting Information

ABSTRACT: A highly convergent and regioselective heteroannulation protocol for the synthesis of hitherto unreported highly substituted 2-amino-4-(aryl/alkyl)-5-(aroyl/heteroaroyl)-3-(cyano/carboalkoxy)-6-methylthio-4*H*-thiopyran derivatives has been developed. This one-pot three-component domino coupling of β-oxodithioesters, aldehydes, and malononitrile/ethyl or methyl cyanoacetate is promoted by 4-dimethylamino pyridine (DMAP) in solvent (dichloromethane (DCM)) as well as under solvent-free conditions. Systematic optimization of reaction parameters identified that the three-component coupling (3CC) protocol is tolerant to a wide array of functionality providing densely functionalized 4*H*-thiopyrans in excellent yields. The merit of this cascade Knoevenagel condensation/Michael addition/cyclization sequence is highlighted by its high atom-economy, excellent yields, and efficiency of producing three new bonds (two C−C and one C−S) and one stereocenter in a single operation.



KEYWORDS: *4H-Thiopyrans, β-oxodithioesters, malononitrile, ethyl/methyl cyanoacetate, 4-dimethylaminopyridine, regioselective heteroannulation*

INTRODUCTION

The strategies regarding the construction and cleavage of bonds represent the central theme in organic synthesis. A major challenge of modern synthesis is to design efficient cascades that provide maximum structural diversity and complexity with a minimum number of synthetic steps for the rapid generation of functionalized molecules with interesting properties.[1] One approach to address this challenge involves the development of eco-compatible, multicomponent procedures. Multicomponent reactions[2−4] (MCRs) have become important tools for the rapid construction of molecules with predefined complexity and diversity to find their applications in chemical biology and drug discovery.[5,6] MCRs have been investigated extensively in organic and diversity oriented synthesis; primarily because of their convergent nature, superior atom economy, and straightforward experimental procedures.[7] Solvent-free methods have several advantages over reactions in solvents. Thus, solvent-free methods can be used to modernize classical procedures by making them simpler, cleaner, safer (depending on scale and exothermicity), and easier.[8,9]

Thiopyrans are targets for both synthetic and medicinal chemists because of their various applications in medicinal,[10,11] biological,[12] and industrial fields.[10] They constitute the core of many natural products as well as serve as versatile building blocks in organic synthesis.[13] Thiopyrans are contained in potent drug precursors for the synthesis of various bioactive compounds such as tetrahydrodicranenone B,[14] serricornin,[15] thromoboxanes,[16] and cyclopentanoids.[17] Moreover, 4-oxothiopyran derivatives are used as DNA dependent protein kinase inhibitors.[18] Several synthetic methods are available for the synthesis of 4*H*-thiopyran derivatives. One such strategy involves hetero Diels−Alder reaction of α, β-unsaturated thioketones with activated dienophiles.[19] Substituted 4*H*-thiopyrans have been generated from a three-component reaction of α,β-unsaturated ketone, Lawesson's reagent, and alkynes under microwave irradiation.[20] In addition 4*H*-thiopyrans have also been synthesized utilizing various 2-cyanothioacetamide derivatives, malononitrile, and aldehydes[21]/dimethyl acetylenedicarboxylate derivatives.[22] Recently, an easy access to substituted 4*H*-thiopyran-4-ones from α-alkenoyl-α-carbamoyl ketene-*S*,*S*-acetals has been reported.[23]

Albeit the reported approaches are useful tools for the synthesis of 4*H*-thiopyran derivatives, most of them suffer from significant limitations such as harsh reaction conditions, expensive catalysts/reagents, prolonged reaction times, and multistep synthesis.[20,24] Therefore, the discovery of more general, efficient, rapid, and viable routes are highly desirable.

β-Oxodithioesters exhibit promising structural features as versatile intermediates in organic synthesis, and their utility has been well recognized.[25] As a part of our current interest toward the development of new MCRs[26] for the synthesis of

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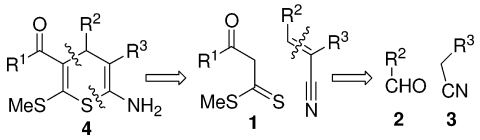
interesting heterocycles, recently, we reported the synthesis of important scaffolds such as thiochromene-5-ones,[27a] chromene-2-thiones,[27b] dihydropyrimidinones,[27c] and pyridopyrimidinones[27c] utilizing β-oxodithioesters as one of the components. Consequently, with the aim to devise a more general and simple synthetic route for thiopyrans, herein we report the first one-pot three-component regioselective synthesis of 4*H*-thiopyran frameworks via domino coupling of β-oxodithioesters, aldehydes, and malononitrile/ethyl or methyl cyanoacetate promoted by DMAP in solvent (dichloromethane (DCM)) as well as under solvent-free conditions in excellent yields.

RESULTS AND DISCUSSION

β-Oxodithioesters are not commercially sourced, and are prepared according to reported procedures.[25d,27b] To the best of our knowledge, there is no report on the synthesis of pentasubstituted-4*H*-thiopyran derivatives from β-oxodithioesters having aroyl/heteroaroyl groups at the 5-position and methylthio group at 6-position of the ring. In our effort to develop a new MCR for the synthesis of 4*H*-thiopyrans, we devised a cascade strategy as outlined retrosynthetically in Scheme 1.

Scheme 1. Retrosynthetic Pathways for the Synthesis of Target 4*H*-Thiopyran Derivatives



On the basis of retrosynthetic analysis, we envisioned that coupling of **1**, **2**, and **3** would lead to our desired thiopyran **4**. This strategy provided three new σ bonds and one stereogenic center in a single operation through Knoevenagel condensation/Michael addition/intramolecular cyclization sequence. On the basis of a proposed retrosynthetic scheme, a number of starting materials are readily available for the synthesis of a small combinatorial library of 4*H*-thiopyran derivatives (Figure 1).

Accordingly, 3-hydroxy-3-(*p*-methoxyphenyl)-prop-2-enedithioate **1**{1}, 2,4-dichlorobenzaldehyde **2**{1}, and malononitrile **3**{1} were selected as the substrates for reaction development. Thus, to achieve our goal, test reactions between **1**{1}, **2**{1}, and **3**{1} were performed by screening a variety of catalysts in different solvents as well as under solvent-free conditions (Table 1). Triethylamine (TEA) and K_2CO_3 could not trigger the reaction even after 15 h of reflux in EtOH and CH_3CN, respectively (Table 1, entries 1 and 2), while DMAP in refluxing dichloromethane provided the desired thiopyran **4**{1, 1, 1} as exclusive product in 90% yield (Table 1, entry 3). With DMAP base as good promoter in hand, next we intended to optimize its loading, and it was found that the use of 20 mol % of DMAP provided the best result (Table 1, entry 4). Reducing the mol % of DMAP in the reaction increased the reaction time and lowered the yield (Table 1, entry 5). However, a little β-oxodithioester remained unreacted, so we enhanced the molar ratio of aldehyde and malononitrile (1.1 equiv) to effect the complete consumption of β-oxodithioester. No better yield was obtained when the DMAP was increased to 1.0 equiv (Table 1, entry 3). Next, to find the most suitable solvent for DMAP, various solvents such as EtOH, THF, H_2O, and CH_3CN were

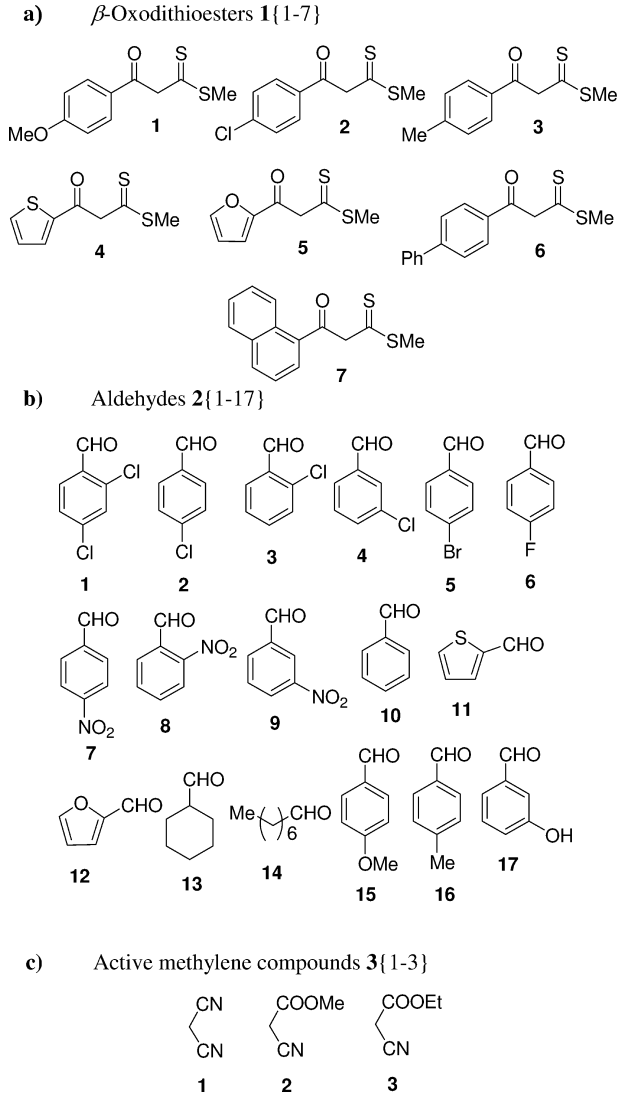


Figure 1. Diversity of Reagents.

screened (Table 1, entries 6–9). The results demonstrated that DCM appeared to be the best choice for this transformation in terms of reaction time and yield. Recently solvent-free reactions have gained much attention in organic synthesis, so we decided to carry out the reactions under solvent-free conditions. Thus, the above test reaction was performed in the presence of 20 mol % of DMAP at different temperatures under solvent-free conditions (Table 1, entries 10–12). It was found that 20 mol % of DMAP at 70 °C provided the desired 4*H*-thiopyran in 90% yield as major product under solvent-free conditions (Table 1, entry 11). Reducing the DMAP loading from 20 mol % to 10 mol % led to a significant decrease in the yield (Table 1, entry 13). Interestingly, the use of 20 mol % of pyridine in the model reaction did not give even a trace of the product (Table 1, entry 14). Some other basic and acidic catalysts such as piperidine, DBU, silica-H_2SO_4, and $SnCl_2{\cdot}2H_2O$ were also investigated under solvent-free conditions, but results were not satisfactory (Table 1, entries 15–18).

The above observations show the reaction proceeds well in DCM in presence of 20 mol % of DMAP. The mild reaction condition and clean TLC pattern are main advantages of the reaction in refluxing DCM. The reaction under solvent-free condition was faster and gives almost parallel yields, but some

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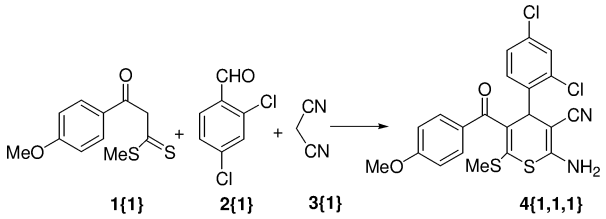
Table 1. Optimization of Reaction Conditions for the Synthesis of 4*H*-Thiopyran[a]



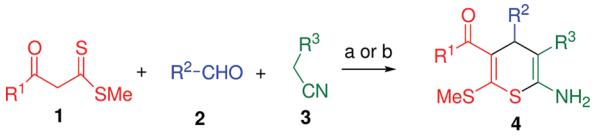
entry	catalyst	loading (mol %)	solvent	temp (°C)	time	yield[b] (%)
1	TEA	100	EtOH	reflux	15 h	*c*
2	K_2CO_3	100	CH_3CN	reflux	15 h	*c*
3	DMAP	100	CH_2Cl_2	reflux	2 h	90
4	DMAP	20	CH_2Cl_2	reflux	2 h	92
5	DMAP	10	CH_2Cl_2	reflux	8 h	82
6	DMAP	20	EtOH	reflux	4.5 h	75
7	DMAP	20	THF	reflux	3.5 h	72
8	DMAP	20	H_2O	reflux	4.5 h	70
9	DMAP	20	CH_3CN	reflux	40 min	80
10	DMAP	20	none	100	15 min	88
11	DMAP	20	none	70	20 min	90
12	DMAP	20	none	55	80 min	80
13	DMAP	10	none	70	70 min	78
14	pyridine	20	DCM	reflux	8 h	*c*
15	piperidine	20	none	70	4.5 h	40
16	DBU	20	none	70	6 h	20
17	$SnCl_2{\cdot}2H_2O$	20	none	70	10 h	15
18	SiO_2–H_2SO_4	20	none	70	12 h	*c*

[a]Reaction of methyl-3-oxo-3-(*p*-methoxyphenyl)dithiopropionate **1**{1}, 2,4-dichlorobenzaldehyde **2**{1}, and malononitrile **3**{1}. [b]Isolated pure yields. [c]No desired product or complex TLC pattern.

color impurities were visible on TLC, which interferes with purification of the product. Thus, most of the reactions have been carried out in DCM.

Having identified the optimized conditions (DMAP 20 mol %, DCM, 40 °C), we then explored the generality and synthetic scope of this three-component coupling protocol by synthesizing a chemset 4 (Scheme 2). A wide range of *β*-oxodithioesters

Scheme 2. Synthesis of Pentasubstituted-4*H*-Thiopyrans 4



Reaction conditions:
a, DMAP (20 mol %), DCM, reflux
b, DMAP (20 mol %), solvent-free, 70 °C

1{1–7}, aldehydes (aromatic, heteroaromatic, and aliphatic) **2**{1–17}, and malononitrile/cyanoacetic esters **3**{1–3} were well tolerated under the reaction conditions providing the corresponding 4*H*-thiopyrans in excellent yields (Table 2). Even extremely electron-rich aromatic *β*-oxodithioesters such as **1**{4} and **1**{5} proceeded smoothly (Table 2, entries 15–24). However, in comparison to aromatic aldehydes, heterocyclic and aliphatic aldehydes gave lower yields and required longer reaction times.

To add further diversity to the thiopyran framework, reaction of **1**{1} and **2**{1} with some other active cyano partners such as phenyl acetonitrile, cyanoacetamide, and benzoyl acetonitrile was also performed under optimized reaction conditions. To our surprise, in case of phenylacetonitrile no reaction was observed and the starting materials were completely unconsumed, while cyanoacetamide and benzoyl acetonitrile showed several very close spots on TLC plate that could not be isolated. Notably, reaction with 2-hydroxybenzaldehyde and ferrocene carboxaldehyde yielded only a Knoevenagel condensation product. Thus, these observations limit the scope of this reaction to some extent. To overcome the above problems, the test reaction was performed under a variety of conditions, but to no avail.

The structures of all the thiopyran derivatives **4** were deduced from their satisfactory elemental and spectral (IR, ^{1}H, ^{13}C NMR, and Mass) studies. The FT IR spectra of compounds show a peak at 2100–2200 cm^{-1} for CN stretching and a doublet for symmetric and antisymmetric stretching bands around 3200–3300 cm^{-1} for NH_2 groups. ^{1}H NMR spectra showed a sharp singlet in the range 4.59–5.74 ppm for the proton present on C-4 and the sharp singlet around 2.30 ppm for the methylthio group at the 6-position of the ring. The presence of D_2O exchangeable signal at 4.6–4.8 ppm can be assigned to NH_2 group at C-2 position. The shifting of this signal to higher δ (6.5–6.6 ppm) in case of ethyl and methyl cyanoacetate may be attributed to intramolecular hydrogen bonding with ester functionality present at the C-3 position, which further proved the formation of the expected skeleton. The mass spectra of these compounds displayed molecular ion peaks at the appropriate m/z values. Finally, the structure of one representative compound 2-amino-6-methylthio-5-(thiophene-2-carbonyl)-4-thiophen-2-yl-4*H*-thiopyran-3-carbonitrile **4**{4,11,1} was confirmed unambiguously by single crystal X-ray

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Table 2. Scope Exploration: Variation of R^1, R^2, and R^3 for the Synthesis of Chemset 4

entry	R^1	R^2	R^3	product	yield[a] (%)
1	4-OMeC$_6$H$_4$	2,4-Cl$_2$C$_6$H$_3$	CN	4{1,1,1}	92, 90[b]
2	4-OMeC$_6$H$_4$	4-NO$_2$C$_6$H$_4$	CN	4{1,7,1}	93
3	4-OMeC$_6$H$_4$	4-ClC$_6$H$_4$	CN	4{1,2,1}	91
4	4-OMeC$_6$H$_4$	4-MeC$_6$H$_4$	CN	4{1,16,1}	87
5	4-OMeC$_6$H$_4$	4-BrC$_6$H$_4$	CN	4{1,5,1}	88
6	4-OMeC$_6$H$_4$	4-OMeC$_6$H$_4$	CN	4{1,15,1}	84
7	4-OMeC$_6$H$_4$	4-NO$_2$C$_6$H$_4$	CO$_2$Me	4{1,7,2}	92
8	4-ClC$_6$H$_4$	4-NO$_2$C$_6$H$_4$	CN	4{2,7,1}	90
9	4-ClC$_6$H$_4$	4-OMeC$_6$H$_4$	CN	4{2,15,1}	82
10	4-ClC$_6$H$_4$	C$_6$H$_5$	CN	4{2,10,1}	88
11	4-ClC$_6$H$_4$	4-ClC$_6$H$_4$	CN	4{2,2,1}	86, 85[b]
12	4-MeC$_6$H$_4$	4-NO$_2$C$_6$H$_4$	CN	4{3,7,1}	88, 89[b]
13	4-MeC$_6$H$_4$	4-BrC$_6$H$_4$	CO$_2$Me	4{3,5,2}	85
14	4-MeC$_6$H$_4$	C$_6$H$_5$	CO$_2$Et	4{3,10,3}	86
15	2-thienyl	4-BrC$_6$H$_4$	CN	4{4,5,1}	80, 80[b]
16	2-thienyl	2-thienyl	CN	4{4,11,1}	78
17	2-thienyl	4-ClC$_6$H$_4$	CO$_2$Me	4{4,2,2}	84
18	2-thienyl	Cyclohexyl	CN	4{4,13,1}	70
19	2-furyl	2-furyl	CN	4{5,12,1}	76
20	2-furyl	3-NO$_2$C$_6$H$_4$	CN	4{5,9,1}	81
21	2-furyl	4-FC$_6$H$_4$	CN	4{5,6,1}	80
22	2-furyl	*n*-heptane	CN	4{5,14,1}	65
23	2-furyl	2-thienyl	CO$_2$Et	4(5,11,3}	81
24	2-furyl	3-NO$_2$C$_6$H$_4$	CO$_2$Me	4{5,9,2}	81, 79[b]
25	4-biphenyl	2-NO$_2$C$_6$H$_4$	CN	4{6,8,1}	84
26	4-biphenyl	2-ClC$_6$H$_4$	CN	4{6,3,1}	81
27	1-naphthyl	4-MeC$_6$H$_4$	CN	4{7,16,1}	84
28	1-naphthyl	3-OHC$_6$H$_4$	CN	4{7,17,1}	80
29	1-naphthyl	3-ClC$_6$H$_4$	CN	4{7,4,1}	85, 82[b]
30	1-naphthyl	2,4-Cl$_2$C$_6$H$_3$	CO$_2$Et	4{7,1,3}	87

[a]Isolated yields under optimized conditions in DCM. [b]Isolated yields under solvent-free conditions.

diffraction (XRD) analysis (see the Supporting Information) (Figure 2).[28]

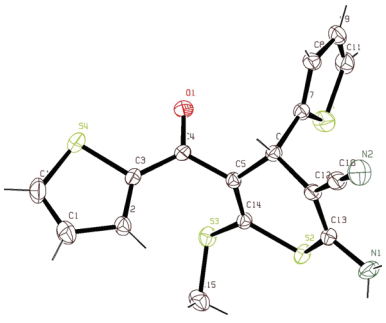
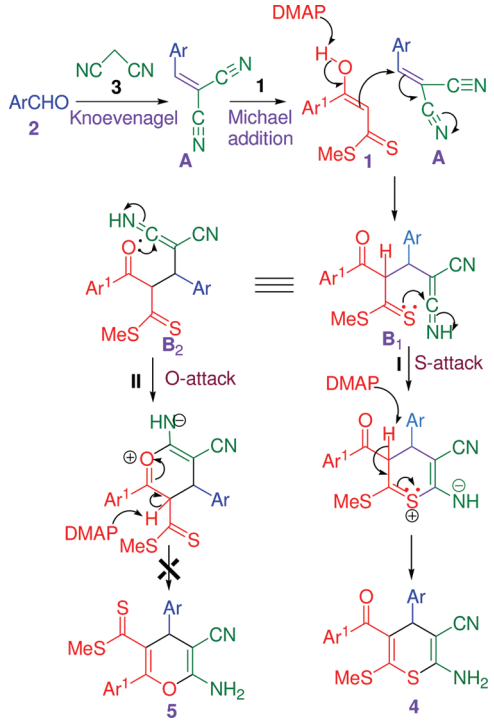


Figure 2. ORTEP diagram of compound 4{4,11,1}.

On the basis of the above experimental results together with the related reports, a plausible reaction scenario for this one-pot three-component heteroannulation is outlined in Scheme 3. It is conceivable that initially the aldehyde **2** undergoes DMAP promoted Knoevenagel condensation with malononitrile **3** to give adduct **A**, which acts as Michael acceptor. The enol form of *β*-oxodithioester **1** attacks the Knoevenagel adduct **A** in a Michael-type addition to produce an open chain azaketene type intermediate **B**. Intermediate **B** may undergo intramolecular cyclization via its two possible rotamers $\mathbf{B_1}$ and $\mathbf{B_2}$ through

Scheme 3. Plausible Mechanism for the Formation of Thiopyran 4



pathways **I** and **II** to furnish thiopyran **4** and pyran **5**, respectively. $\mathbf{B_1}$ undergoes regiospecific S-cyclization via route **I** to give the desired thiopyran **4**. The alternative O-cyclization of $\mathbf{B_2}$ could lead to pyran **5** via route **II**. During our investigation, we did not observe a trace of **5**, and only **4** was obtained exclusively. It should be emphasized that because of higher nucleophilicity of sulfur, S-cyclization is more favorable over O-cyclization making this protocol highly regioselective. The above-mentioned regioselectivity has also been supported by the presence of a peak corresponding to C═O and absence of C═S peak in ^{13}C NMR spectra of the thiopyrans.

CONCLUSION

In summary, a facile and efficient regioselective access to hitherto unreported 2-amino-4-(aryl/alkyl)-5-(aroyl/heteroaroyl)-3-(cyano/carboalkoxy)-6-methylthio-4*H*-thiopyran derivatives has been developed via direct annulation of *β*-oxodithioesters with aldehydes and malononitrile promoted by DMAP by 1−2 (C−S) and 3−4, 4−5 (C−C) bond formation through domino Knoevenagel/Michael/cyclization sequence. The versatility of the functionality such as amino, cyano, carbonyl, and alkylthio groups make these compounds promising candidates as precursors for further synthetic transformations to meet the need of combinatorial chemistry, chemical biology, and drug discovery. The simplicity of execution, mild conditions, excellent yields, easy purification, and high reactivity profile of DMAP make this protocol most attractive for academic research and practical applications.

EXPERIMENTAL PROCEDURES

General Information. All reagents were commercial and purchased from Merck, Aldrich, and Fluka and were used as received. ^{1}H and ^{13}C NMR spectra were recorded on JEOL AL 300 FT-NMR spectrometer. Chemical shifts are given as *δ*

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value with reference to tetramethylsilane (TMS) as the internal standard. The IR spectra were recorded on Varian 3100 FT-IR spectrophotometer. Mass spectra were recorded on Thermo LCQ Advantage Max Ion Trap Mass Spectrometer from Central Drug Research Institute, Lucknow. The C, H, and N analyses were performed from microanalytical laboratory with an Exeter Analytical Inc. "Model CE-400 CHN Analyzer". XRD was measured on Xcalibur Oxford CCD Diffractometer. All the reactions were monitored by TLC using precoated sheets of silica gel G/UV-254 of 0.25 mm thickness (Merck $60F_{254}$) using UV light for visualization. Melting points were determined with Büchi B-540 melting point apparatus and are uncorrected.

General Procedure for the Synthesis of β-Oxodithioester 1{1-7}..[27b] Appropriate aryl/heteroaryl ketone (10 mmol) was added to a suspension of NaH (60% suspension in mineral oil, 0.80 g, 20 mmol) in DMF/hexane solvent mixture (1:4, 20 mL). After 30 min, dimethyl trithiocarbonate (10 mmol) was slowly added to the reaction mixture and stirred well for 2 h. After completion of the reaction (monitored by TLC), the reaction mixture was washed with hexane to remove unreacted ketone and dimethyl trithiocarbonate. Reaction mixture was acidified with 1 N HCl (20 mL) to get the β-oxodithioester precipitated. The precipitated β-oxodithioester was extracted with dichloromethane (2 × 20 mL) followed by washing with brine (2 × 25 mL) and dried over anhydrous sodium sulfate. The solvent was evaporated under vacuum, and the residue obtained was purified by column chromatography over silica gel using hexane as eluent to give the corresponding β-oxodithioesters **1**{1−7} in high yields. Experimental data of **1**{1} is as follows: Yellow solid, yield 73%, mp. 74−75 °C. FT IR (KBr, cm^{-1}): 3430, 1603, 1582, 1545, 1503, 1430, 1232, 1180, 1052 ^{1}H NMR (300 MHz, $CDCl_3$): δ 15.16 (s, 1H, OH), 7.86 (d, J = 8.7 Hz, 2H, ArH), 6.94 (d + s, J = 8.7 Hz, 3H, ArH + H_{Olefin}), 3.87 (s, 3H, OCH_3), 2.65 (s, 3H, SCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 215.5, 169.4, 162.7, 128.6, 126.1, 114.1, 107.0, 55.4, 16.9. FAB MS (m/z): 241 (M^++1); Anal. Calcd for $C_{11}H_{12}O_2S_2$: C, 54.97%; H, 5.03%. Found: C, 54.88%; H, 4.91%.

General Procedure for the Synthesis of Highly Substituted 2-Amino-6-methylthio-4*H*-thiopyrans Derivatives 4. *Method A.* To a mixture of β-oxodithioester **1** (1.0 mmol), aldehyde **2** (1.1 mmol), and malononitrile (or cyanoacetates) **3** (1.1 mmol) in dichloromethane (10 mL), 4-dimethylaminopyridine (20 mol %, 0.2 mmol, 0.024 g) was added. The reaction mixture was heated at reflux with constant stirring until the completion of the reaction (monitored by TLC). The reaction mixture was cooled to room temperature, and the solvent was evaporated under vacuum. The contents were dissolved in chloroform (20 mL) and washed with water (1 × 20 mL) followed by brine (1 × 20 mL). The organic layer was dried over anhydrous Na_2SO_4, and the solvent was evaporated under vacuum. The residue thus obtained was purified by column chromatography over silica gel using ethyl acetate/*n*-hexane (1:3) as eluent to afford pure thiopyrans.

Method B. A mixture of β-oxodithioester **1** (1.0 mmol), aldehyde **2** (1.1 mmol), and malononitrile (or cyanoacetates) **3** (1.1 mmol) was heated in the presence of DMAP (20 mol %, 0.2 mmol, 0.024 g) at 70 °C. After completion of the reaction (monitored by TLC), the contents was dissolved in chloroform (20 mL) and washed with water (1 × 20 mL) followed by brine (1 × 20 mL). The organic layer was dried over anhydrous Na_2SO_4, and the solvent was evaporated under vacuum. The residue thus obtained was purified by column chromatography over silica gel using ethyl acetate/*n*-hexane (1:3) as eluent to afford pure thiopyrans. Experimental Data of **4**{1,1,1} is as follows: Yellow solid, mp 136−137 °C. FT IR (KBr, cm^{-1}): 3320, 3208, 2926, 2842, 2187, 1626, 1594, 1256, 1167, 843. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69 (d, J = 9.0 Hz, 2H, ArH), 7.45 (d, J = 8.4 Hz, 1H, ArH), 7.25−7.20 (m, 2H, ArH), 6.88 (d, J = 8.7 Hz, 2H, ArH), 5.18 (s, 1H, CH), 4.67 (s, 2H, NH_2), 3.86 (s, 3H, OCH_3), 2.28 (s, 3H, SCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.0, 164.1, 153.6, 137.6, 136.2, 134.2, 133.5, 131.5, 130.6, 129.6, 128.7, 127.8, 126.0, 117.4, 114.0, 75.3, 55.5, 43.4, 18.2. ESI MS (m/z): 463 (M^++1); Anal. Calcd for $C_{21}H_{16}Cl_2N_2O_2S_2$: C, 54.43; H, 3.48; N, 6.05%. Found: C, 54.34; H, 3.60; N, 5.44%.

■ ASSOCIATED CONTENT

Supporting Information

Representative experimental procedures, analytical and spectral data of chemset **4**, single crystal XRD data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(28) Crystal data for **4**{4,11,1}: $C_{16}H_{12}N_2OS_4$, Yellow, M = 376.56, monoclinic, space group $P21/c$, a = 8.6868(3), b = 12.0610(3), c = 16.5857(3) Å, V = 1737.5 Å^3, μ = 0.55 mm^{-1}, Z = 4, T = 293 K, F_{000} = 776, R = 0.0374, wR^2 = 0.1216. The CCDC deposition number: **CCDC 836399**.