Facile Ring-Expansion Substitution Reactions of 1,3-Dithiolanes and 1,3-Dithianes Initiated by Electrophilic Reagents to Produce Monohalo-, -cyano-, -azido- and -thiocyanato-1,4-dithiins and -1,4-dithiepins

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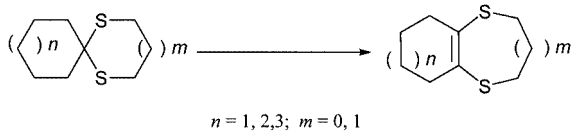
Keywords: Ring-expansion / Electrophilic substitution / 1,3-Dithiolane / 1,3-Dithiane / 1,4-Dithiin / 1,4-Dithiepin / *N*-Halosuccinimide / *N*-Thiocyanatosuccinimide / *N*-Cyanosuccinimide / *N*-Azidosuccinimide

Mild and convenient methods for the high yielding ring-expansion substitution reactions of 1,3-dithiolanes and 1,3-dithianes generated from different aryl methyl ketones using different electrophilic reagents are reported. In this study, facile preparations of monohalo-, -cyano-, -azido-, -thiocyanato-1,4-dithiins and -1,4-dithiepins are described. A general mechanism is also proposed for the reactions described in this article.

Introduction

The ring-expansion annelation reactions of 1,3-dithiolanes ($m = 0$) and 1,3-dithianes ($m = 1$), which are five- and six-membered ring thioacetals, are very useful for the construction of larger rings bearing sulfur atoms (Scheme 1).



Scheme 1

A review of the literature reveals that little attention has been paid to the ring enlargement reactions of 1,3-dithiolanes and 1,3-dithianes to their corresponding 1,4-dithiins ($m = 0$) and 1,4-dithiepins ($m = 1$) as shown in Scheme 1. For this purpose, PhSeCl has been employed for the ring-expansion reactions in some steroidal compounds.[1] Molecular chlorine in refluxing CH_2Cl_2/CCl_4 has been used for the conversion of 2,2-dimethyl-1,3-oxathiolane to 2-methyl-1,4-oxathiin in moderate yield (54%).[2] $TeCl_4$ has also been applied for the ring enlargements of 1,3-dithiolanes, 1,3-dithianes and 1,3-oxathiolanes.[3,4] Br_2 or Cl_2 in anhydrous $CHCl_3$ or CCl_4 has been used for the synthesis of 2,3-dihydro-1,4-dithiins from 1,3-dithilane derivatives of unsymmetrical ketones[5] and 2,4,6-trichloro-1,3,5-triazine in the presence of DMSO has been recently used for deprotection and ring enlargement of cyclic thioacetals and oxathioacetals. Ring expansion chlorination of only one cyclic thioacetal has also been reported using this method.[6] In recent years, we have been involved in exploring some new applications of molybdenum pentachloride ($MoCl_5$),[7] tungsten hexachloride (WCl_6)[8] and silica chloride (SiO_2Cl)[9] in organic reactions. We have found that molybdenum pentachloride ($MoCl_5$),[7] tungsten hexachloride (WCl_6)[8] and silica chloride (SiO_2Cl)[9] in the presence of DMSO in dry dichloromethane can be successfully applied for the one pot ring-expansion chlorination reactions of 1,3-dithiolanes and 1,3-dithianes derived from aryl methyl ketones which bear enolizable hydrogen atoms. Br_2 or NBS has also been used for ring expansion of cyclic thioacetals.[10] 1,4-Dithiins have also been transformed into derivatives of 5,6-dihydro-1,4-dithiin by the reaction of BuLi with various electrophiles.[11–13] 1,3-Dithiolanes bearing a phenyl or substituted aromatic group and a methyl (or methylene) group attached to the C-2 atom of the dithiolane rings undergo rapid rearrangement to 1,3-dithiolane-dihydro-1,4-dithiin in the presence of NBS or 1,3-dibromo-5,5-dimethylhydantoin (DBH).[14]

It has been reported that some derivatives of 1,4-dithiins and 1,4-dithiepins show activities as nonpeptide antagonists of the human Galanin hGAL-1 receptor.[10]

In this article, we report an extensive study of the ring enlarging monosubstitution reactions of 1,3-dithiolanes and 1,3-dithianes prepared from aryl methyl ketones. These reactions were conducted in the presence of *N*-chloro-, *N*-bromo-, *N*-iodo-, *N*-cyano-, *N*-azido- and *N*-thiocyanatosuccinimides in order to prepare monosubstituted (Cl, Br, I, CN, N_3 and SCN) 1,4-dithiins and 1,4-dithiepins in good

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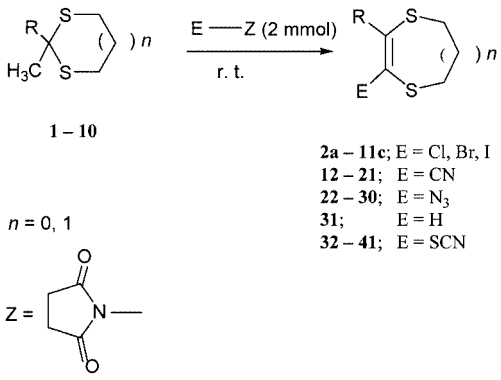
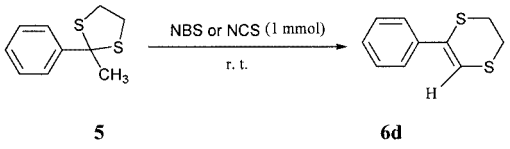
to excellent yields under neutral and mild reaction conditions (Scheme 2).



Scheme 2

Results and Discussion

In continuation of our interests in the chemistry of cyclic thioacetals, we have investigated the reactions of different *N*-substituted succinimides with 1,3-dithiolanes and 1,3-dithianes derived from aryl methyl ketones at room temperature. First, we studied the reaction of 2-methyl-2-phenyl-1,3-dithiolane (**5**), as a model compound, with *N*-chlorosuccinimide (NCS) and *N*-bromosuccinimide (NBS) in dry dichloromethane at room temperature. The reactions proceeded smoothly with an equivalent amount of NCS or NBS to produce the corresponding 1,4-dithiin **6d** in excellent yield as the only isolated product from the reaction mixture (Scheme 3).



Scheme 3

We then attempted a similar reaction with two equivalents of NCS and NBS under similar reaction conditions. We found that under such conditions, **6a** and **6b** were produced and could be isolated in yields of 87 and 89%, respectively, after 30 min. We also applied similar reaction conditions with *N*-iodosuccinimide (NIS) for the preparation of **6c** from **5** . This reaction also proceeded well and produced the desired product **6c** in 89% yield after 30 min.

We also studied the ring expansion bromination and iodination reactions of **5** and 2-methyl-2-phenyl-1,3-dithiane (**6**) as model compounds using *N*-bromosaccharin (NBSac) and *N*-iodosaccharin (NISac)[15] as electrophilic reagents. When two equivalents of NBSac in refluxing acetonitrile reacted with **5** or **6**, the corresponding monobromo-1,4-dithiin **6b** and monobromo-1,4-dithiepin **7b** were isolated in yields of 75% and 70% with the production of acetophenone as a by-product in yields of 25 and 30%, respectively, within 10 to 16 h. Similar substrates in the presence of three equivalents of NISac and one equivalent of DMSO in refluxing acetonitrile resulted in the formation of the corresponding monoiodo-1,4-dithiin **6c** and monoiodo-1,4-dithiepin **7c** in yields of 60% and 58%, respectively, accompanied by the formation of acetophenone in yields of 40 and 42% after 5 h. NBSac and NISac were, therefore, not suitable reagents for these reactions.

We observed that when 2-methyl-2-(4-nitrophenyl)-1,3-dithiolane (**9**) and 2-methyl-2-(4-nitrophenyl)-1,3-dithiane (**10**), the phenyl groups of which carry the strong electron-withdrawing nitro group, were treated with NCS, the desired ring-expanded monochlorinated products **10a** and **11a** could be isolated in yields of 89 and 90%, respectively. In comparison, ring expansion chlorination reactions of similar substrates by the previously reported methods using the WCl_6/DMSO,[8] $MoCl_5$/DMSO[7] or SiO_2Cl/DMSO[9] systems completely failed and the corresponding 1,4-dithiin and 1,4-dithiepin compounds were isolated as the sole products from the reaction mixtures. In order to show the general applicability of the methods, we studied the reactions of structurally diverse 1,3-dithiolanes and 1,3-dithianes with *N*-halosuccinimides in CH_2Cl_2 at room temperature. We observed that the reactions proceeded smoothly and the desired ring-expanded mono-halogeneted compounds **2a**−**11c** were produced in good to high yields. The results of this study are summarised in Table 1.

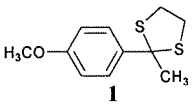
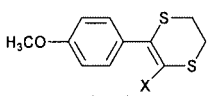
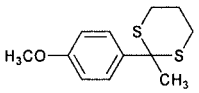
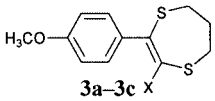
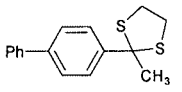
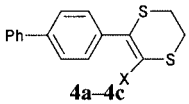
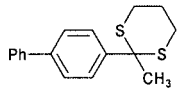
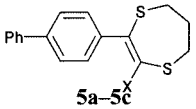
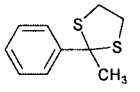
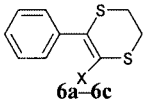
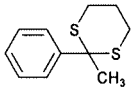
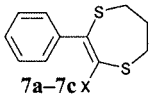
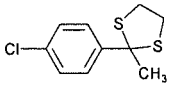
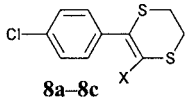
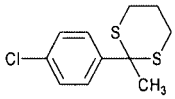
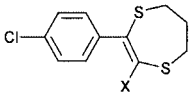
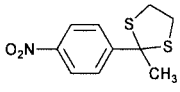
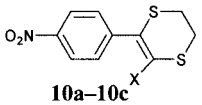
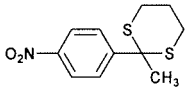
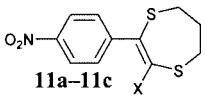
In order to show the merit of the methods described, we compared the experimental results for ring-expansion chlorination reactions of 1,3-dithiolanes **3**, **5**, **9** and 1,3-dithianes **2**, **6**, **8**, **10** using *N*-chlorosuccinimide (NCS) with the previously reported methods using molybdenum pentachloride ($MoCl_5$),[7] tungsten hexachloride (WCl_6)[8] and silica chloride (SiO_2Cl)[9] in the presence of DMSO in dry dichloromethane at room temperature (Table 2).

The successful halogenation reactions encouraged us to study the possibility of using some other *N*-substituted succinimides for the ring-enlargement substitution of 1,3-dithiolanes and 1,3-dithianes.

However, we first studied the ring-enlargement cyanation reactions of 1,3-dithiolanes and 1,3-dithianes **1**−**10**. To this end, one equivalent of **5**, as a model compound, was treated with a mixture of two equivalents of Bu_4NCN and NBS in dry CH_3CN at room temperature. The reaction proceeded smoothly to completion and **16** was isolated in 88% yield after 30 min. In order to show the role of NBS in this reaction, we studied a similar reaction in the absence of NBS with Bu_4NCN. We found that **5** was isolated intact after a prolonged reaction time (12 h).

The cyanation reaction was extended to the structurally diverse 1,3-dithiolanes and 1,3-dithianes **1**−**10** under similar reaction conditions. The corresponding 2-cyanato-1,4-dithiins **12**, **14**, **16**, **18** and **20** and the 2-cyanato-1,4-dithiepins **13**, **15**, **17**, **19** and **21** were isolated in high yields. However, the presence of an electronegative atom such as chlorine or a strong electron-withdrawing group such as NO_2 on the aromatic ring retarded the reactions effectively. The results of this study are shown in Table 3. All the compounds prepared by this protocol showed sharp and strong

Table 1. Ring-expansion halogenation of 1,3-dithiolanes and 1,3-dithianes by *N*-halosuccinimides in dry CH_2Cl_2 at room temperature

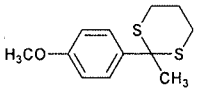
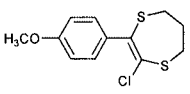
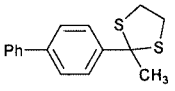
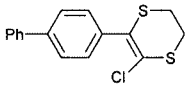
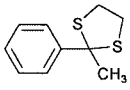
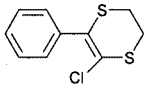
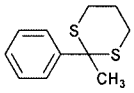
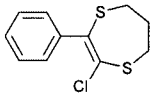
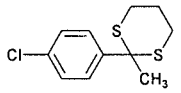
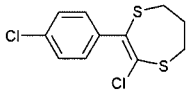
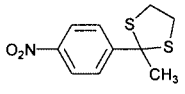
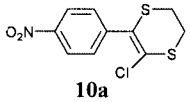
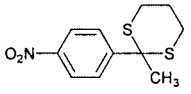
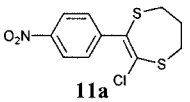
Substrate	Product		Yield(%)[a,b]
 **1**	 **2a–2c**	**2a**; X = Cl **2b**; X = Br **2c**; X = I	88 99 70
 **2**	 **3a–3c**	**3a**; X = Cl **3b**; X = Br **3c**; X = I	79[c] 98 80
 **3**	 **4a–4c**	**4a**; X = Cl **4b**; X = Br **4c**; X = I	85[c] 87 78
 **4**	 **5a–5c**	**5a**; X = Cl **5b**; X = Br **5c**; X = I	72 70 82
 **5**	 **6a–6c**	**6a**; X = Cl **6b**; X = Br **6c**; X = I	87[c] 89 89
 **6**	 **7a–7c**	**7a**; X = Cl **7b**; X = Br **7c**; X = I	87[c] 90 79
 **7**	 **8a–8c**	**8a**; X = Cl **8b**; X = Br **8c**; X = I	89 92 71
 **8**	 **9a–9c**	**9a**; X = Cl **9b**; X = Br **9c**; X = I	89[c] 90 78
 **9**	 **10a–10c**	**10a**; X = Cl **10b**; X = Br **10c**; X = I	89 92 86
 **10**	 **11a–11c**	**11a**; X = Cl **11b**; X = Br **11c**; X = I	90 97 87

[a] Reaction time is 30 min. [b] Yields refer to the isolated products. [c] All the compounds are known and gave satisfactory ^1H NMR and ^{13}C NMR spectroscopic data in comparison with authentic samples (see refs.[8,9]).

characteristic IR absorption bands at about 2320 cm^{-1} and a peak at about 112 ppm in their ^{13}C NMR spectra indicating the presence of a CN group in the molecules.

In this study, we also investigated the ring-expansion azidation of 1,3-dithiolanes and 1,3-dithianes **1**−**10**. For this purpose, we first studied the reaction of **5**, as a model compound, in the presence of a mixture of two equivalents of Bu_4NN_3 and NBS in dry CH_3CN at room temperature. The reaction proceeded well and the desired compound **26** was isolated in a good yield. The protocol was then applied to

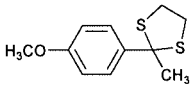
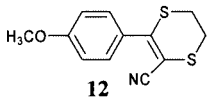
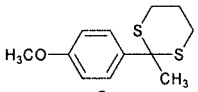
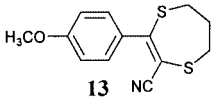
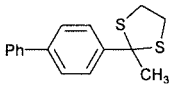
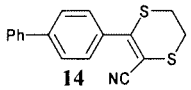
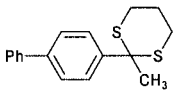
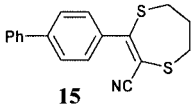
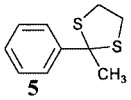
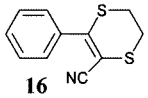
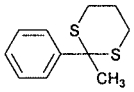
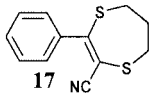
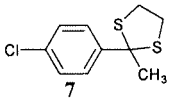
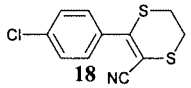
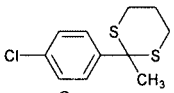
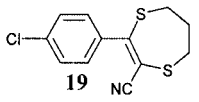
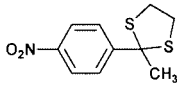
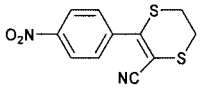
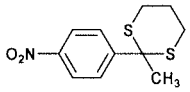
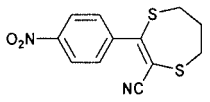
Table 2. Comparison of the experimental results obtained for the ring-expansion chlorination of 1,3-dithiolanes and 1,3-dithianes using *N*-chlorosuccinimide (NCS) with the previously reported methods using $MoCl_5$,[7] WCl_6 [8] and SiO_2Cl[9] in CH_2Cl_2 at room temperature

Substrate	Product	WCl_6/DMSO[8]		$MoCl_5$/DMS[7]		SiO_2Cl/DMS[9]		NCS	
		Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)
 **2**	 **3a**	30	30	–	–	48	27	30	79
 **3**	 **4a**	12	89	40	79	120	85	30	85
 **5**	 **6a**	30	90	40	85	90	80	30	87
 **6**	 **7a**	30	91	60	75	90	82	30	87
 **8**	 **9a**	20	88	70	80	90	84	30	89
 **9**	 **10a**	15	0	30	0	60	0	30	89
 **10**	 **11a**	15	0	30	0	60	0	30	90

the other 1,3-dithiolanes and 1,3-dithianes successfully and the corresponding azido-substituted 1,4-dithiins **22**, **24**, **26**, **28** and **30** and 1,4-dithiepins **23**, **25**, **27**, **29** and **31** were isolated in good to excellent yields. The results of this study are summarised in Table 4.

In general, we noticed that azidation reactions of 1,3-dithiolanes were much faster than those of their corresponding 1,3-dithianes. We also observed that the presence of an electronegative atom such as chlorine or an electron-withdrawing group such as $-NO_2$ retarded the rate of the reactions drastically. As an example, our efforts to prepare 2-azido-3-(4-nitrophenyl)dihydro[1,4]dithiepin from its corresponding 1,3-dithiane **10** in the presence of excess amounts of Bu_4NN_3 and NBS (3× molar ratio) under re-

Table 3. Ring-expansion cyanation of 1,3-dithiolanes and 1,3-dithianes by *N*-cyanosuccinimide in dry CH_3CN at room temperature

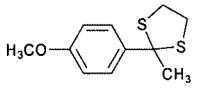
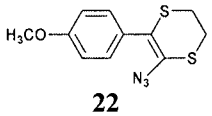
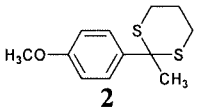
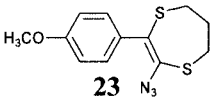
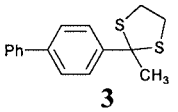
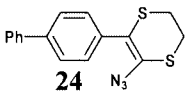
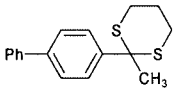
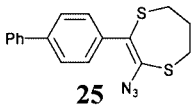
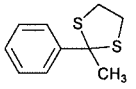
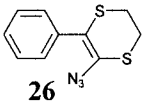
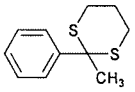
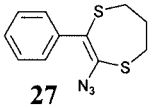
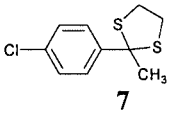
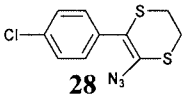
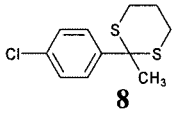
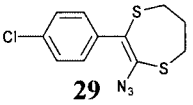
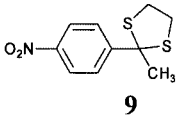
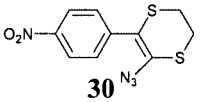
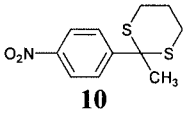
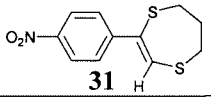
Substrate	Product	Time	Yield[a] (%)
 **1**	 **12**	5 (min)	98
 **2**	 **13**	30 (min)	73
 **3**	 **14**	30 (min)	82
 **4**	 **15**	30 (min)	85
 **5**	 **16**	30 (min)	88
 **6**	 **17**	30 (min)	88
 **7**	 **18**	30 (min)	98
 **8**	 **19**	8 (h)	74
 **9**	 **20**	5 (h)	97
 **10**	 **21**	20 (h)	70

[a] Yields refer to isolated products.

flux conditions failed after two days. The workup of the reaction mixture resulted in the formation of the unsubstituted ring-expansion product **31** in 51% yield (Table 4).

Ring-expansion thiocyanation reactions of 1,3-dithiolanes and 1,3-dithianes **1**−**10** were also studied. For this purpose, **5** was chosen as a model compound and treated with two equivalents of NH_4SCN and NBS in dry CH_3CN at room temperature. The reaction proceeded smoothly and was complete within 30 minutes. On the basis of ^1H NMR spectroscopic analysis, the product was found to be a mixture of **36** and its isothiocyanato isomer with a ratio of about 9:1. When a similar reaction was carried out at 0 °C, **36** was obtained as the only product of the reaction. The IR spectrum of the isolated product showed a distinctive absorption band at 2150 cm^{-1} (sharp) for the SCN group in the molecule. In the ^{13}C NMR spectrum of the product, the related peak for the SCN group could be observed at 113 ppm. In order to show the general application of the method, structurally different 1,3-dithiolanes and 1,3-dithianes derived from acetophenones **1**−**10** were treated with the two equivalent amounts of NH_4SCN and NBS in dry CH_3CN at 0 °C. The desired reactions proceeded well and

Table 4. Ring-expansion azidation of 1,3-dithiolanes and 1,3-dithianes by a Bu_4NN_3 and NBS mixture in dry CH_3CN at room temperature

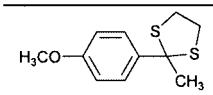
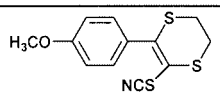
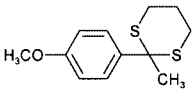
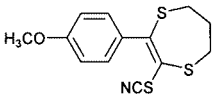
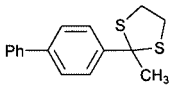
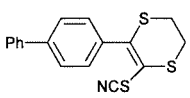
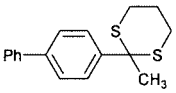
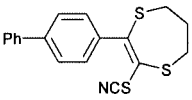
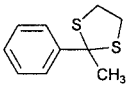
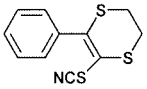
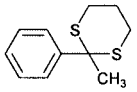
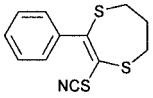
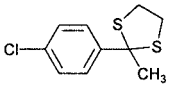
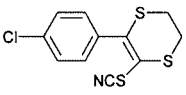
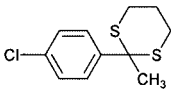
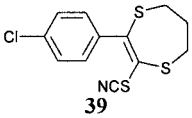
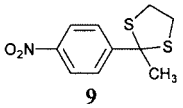
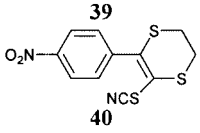
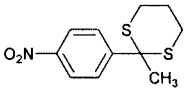
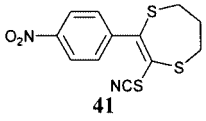
Substrate	Product	Time	Yield[a](%)
 **1**	 **22**	30 (min)	84
 **2**	 **23**	3 (h)	86
 **3**	 **24**	30 (min)	70
 **4**	 **25**	14 (h)	90
 **5**	 **26**	30 (min)	70
 **6**	 **27**	16 (h)	80
 **7**	 **28**	14 (h)	93
 **8**	 **29**	21 (h)	79
 **9**	 **30**	18 (h)	77
 **10**	 **31**	48 (h)	51

[a] Yields refer to the isolated products.

the products were isolated in high yields. The results of this study are shown in Table 5.

Similar to the ring expansion cyanation and azidation reactions of dithiolanes **1**, **3**, **5**, **7** and **9**, thiocyanation reactions of these compounds with a mixture of Bu_4NSCN and NBS were also faster than those of the corresponding dithianes **2**, **4**, **6**, **8** and **10**. The presence of electron-withdrawing groups on the aromatic rings in **7**, **8**, **9** and **10** effectively retarded the reactions. This rate retardation is probably due to the formation of intermediates with cationic character (Scheme 4, **II**) and also to the generation of the straight chain intermediates (Scheme 4, **III**) which should rearrange to cyclic compounds to produce 1,4-dithiins or 1,4-dithiepins during the progress of the reaction. As has been established, the formation of six-membered rings (1,4-dithiins) from the straight chain intermediates (Scheme 4, **III**) is easier than the formation of the seven-membered rings (1,4-dithiepins) from their corresponding straight chain intermediates. We have also studied several key-step reactions in order to propose a general mechanism for the reactions. First, we treated NBS with NH_4SCN or Bu_4NCN in CH_3CN at room temperature in order to isolate the corresponding substituted succinimides. From the reaction of NBS and NH_4SCN, immediate precipitation of NH_4Br was observed. The precipitate was isolated by filtration. Evaporation of the solvent resulted in *N*-thiocyanatosuccinimide

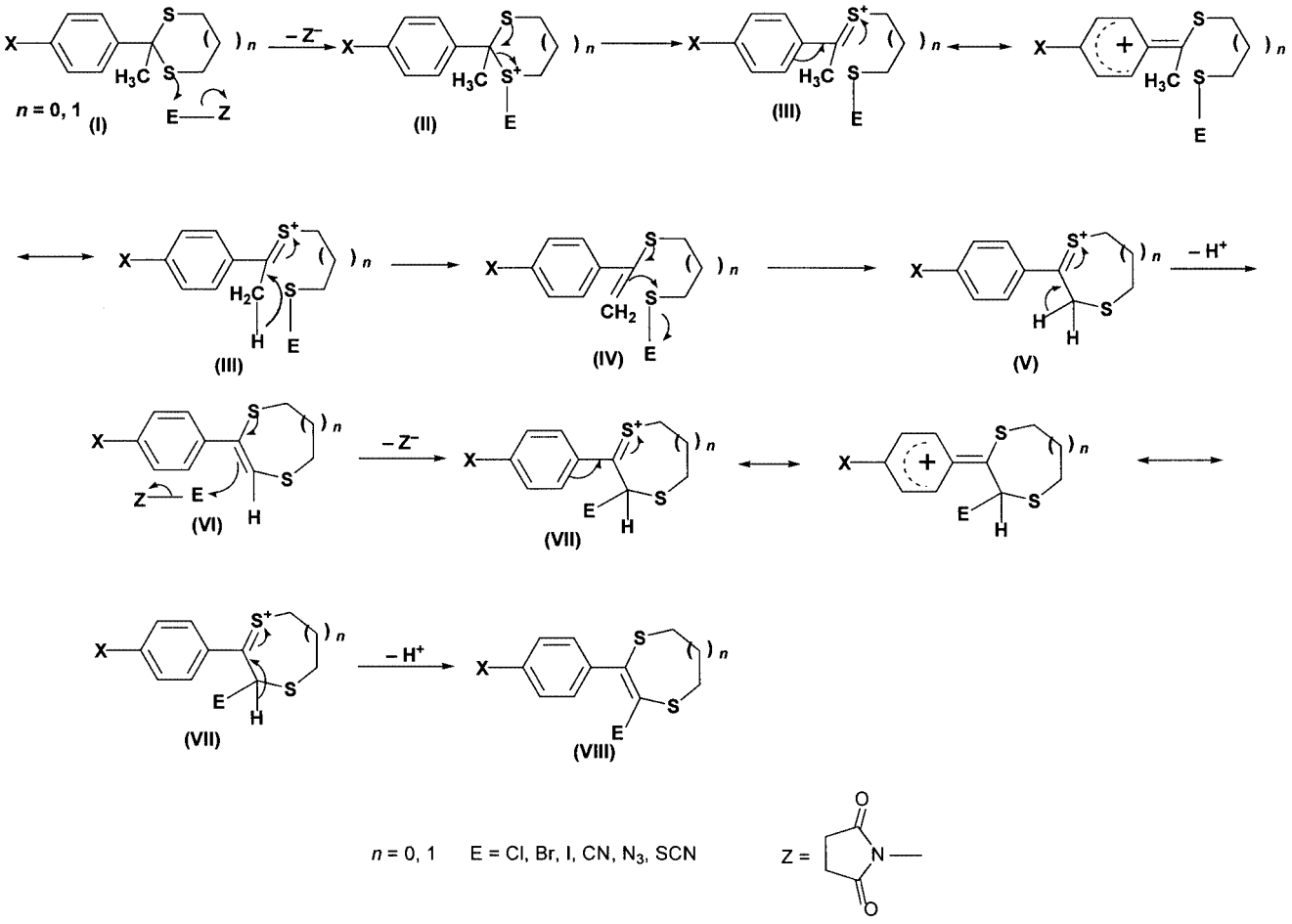
Table 5. Ring-expansion thiocyanation of 1,3-dithiolanes and 1,3-dithianes by a NH_4SCN and NBS mixture in dry CH_3CN at 0 °C

Substrate	Product	Time	Yield(%)[a]
 **1**	 **32**	30 (min)	91
 **2**	 **33**	2 (h)	88
 **3**	 **34**	30 (min)	92
 **4**	 **35**	8 (h)	87
 **5**	 **36**	30 (min)	95
 **6**	 **37**	12 (h)	93
 **7**	 **38**	8 (h)	90
 **8**	 **39**	18 (h)	93
 **9**	 **40**	15 (h)	98
 **10**	 **41**	40 (h)	92

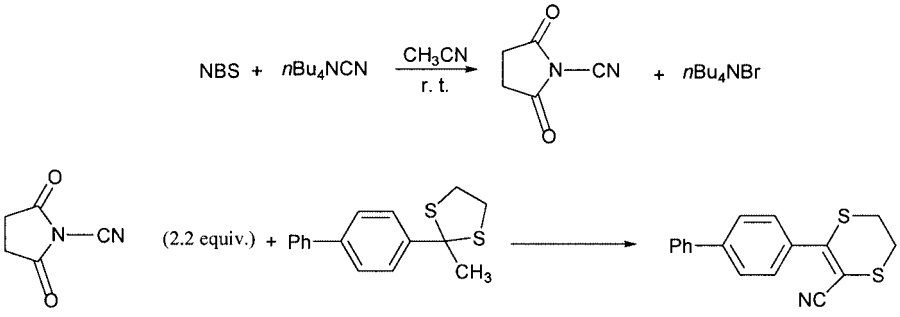
[a] Yields refer to the total yields of the isolated products.

as a white powder. Preparation of *N*-cyanosuccinimide was performed by the treatment of NBS with Bu_4NCN in $CHCl_3$ which, after washing with water, drying and evaporation of the solvent, was isolated as a white powder. As a model reaction, the dithiolane **3** was treated with 2.2 equivalents of the isolated *N*-cyano- or *N*-thiocyanato-succinimides, respectively. We observed that the dithiolane **3** underwent a ring-expansion substitution reaction and produced the desired substituted 1,4-dithiins **14** and **34** in high yields (Schemes 5 and 6).

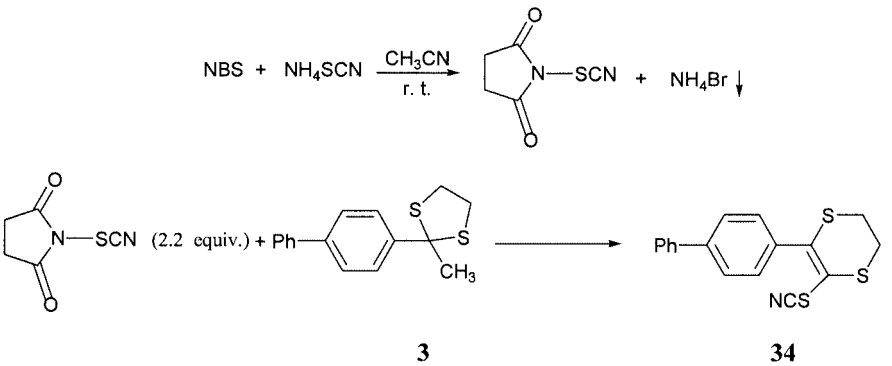
These results show that both *N*-cyanosuccinimide and *N*-thiocyanatosuccinimide carrying electrophilic SCN and CN moieties were able to bring about facile ring expansion substitution reactions. In order to eliminate the possibility of



Scheme 4

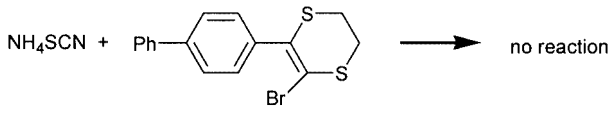


Scheme 5



Scheme 6

direct formation of these products through substitution reactions of bromine in the dithiin with SCN^-, CN^- and N_3^- nucleophiles, we studied the reaction of 3-bromo-1,4-dithiin **4b** as a model compound with NH_4SCN in CH_3CN in the absence of NBS at room temperature. Our findings have shown that the 3-bromo-1,4-dithiin **4b** could be isolated intact after 24 h (Scheme 7).



4b

Scheme 7

With these facts in mind, we have proposed a general mechanism which clarifies the probable steps involved in the reaction presented in this article (Scheme 4).

In this study we have presented a simple and high yield one pot preparation of substituted (Cl, Br, I, CN, N_3, SCN) 1,4-dithiins and 1,4-dithiepines from their corresponding 1,3-dithiolanes and 1,3-dithanes. We have also presented a mechanism which clarifies the probable steps involved in the reactions.

Experimental Section

General: All solvents and reagents were purchased from Fluka or Merck. The products were purified by column or thick layer chromatography techniques. FT-IR spectra were recorded on a Shimadzu DR-8001 spectrometer. NMR spectra were recorded on a Bruker Avance DPX 250 MHz instrument. Mass spectra were recorded on a Shimadzu GC-MS-QP 1000PX apparatus. Melting points are not corrected.

Typical Procedure for Conversion of 2 to 3a: To a solution of 2-(4-methoxy-phenyl)-2-methyl-1,3-dithiane (1 mmol, 0.24 g) in dry CH_2Cl_2 (20 mL) was added NCS (2 mmol, 0.267 g) in dry CH_2Cl_2 (20 mL) from a dropping funnel over a period of 5 min while the resultant solution was stirred at room temperature. After completion of the addition, the solution was stirred for 30−45 min and the reaction was then quenched with an aqueous solution of NaOH (10% 25 mL) and extracted with CH_2Cl_2 (3×25 mL). The organic extracts were washed successively with brine (15 mL) and water (2×10 mL). The organic layer was separated and dried with anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure to afford the crude product. Further purification was performed by chromatography over a short column of silica gel (petroleum ether 60−80 °C as eluent) which, after evaporation of the solvent, afforded the desired pure **3a** in 79% yield (0.215 g).

Typical Procedure for Conversion of 1 to 2b: To a solution of 2-(4-methoxy-phenyl)-2-methyl-1,3-dithiolane (1 mmol, 0.226 g) in dry CH_2Cl_2 (20 mL) was added NBS (2 mmol, 0.356 g) in dry CH_2Cl_2 (20 mL) from a dropping funnel over a period of 5 min while the resultant solution was stirred at room temperature. After completion of the addition, the solution was stirred for 30−45 min and the reaction was then quenched with an aqueous solution of NaOH (25 mL, 10%) and extracted with CH_2Cl_2 (3×25 mL). The organic extracts were washed successively with brine (15 mL) and water (2×10 mL). The organic layer was separated and dried with anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure to afford the crude products. Further purification was performed using chromatography over a short column of silica gel (petroleum ether 60−80 °C as eluent) which, after evaporation of the solvent, afforded the desired pure **2b** in 99% yield (0.300 g).

Typical Procedure for Conversion of 2 to 3c: To a solution of 2-(4-methoxy-phenyl)-2-methyl-1,3-dithiane (1 mmol, 0.24 g) in dry CH_2Cl_2 (20 mL) was added NIS (2 mmol, 0.45 g) in dry CH_2Cl_2 (20 mL) from a dropping funnel over a period of 5 min while the resultant solution was stirred at room temperature. After completion of the addition, the solution was stirred for 30−45 min and the reaction was then quenched with an aqueous solution of NaOH (25 mL, 10%) and extracted with CH_2Cl_2 (3×25 mL). The organic extracts were washed successively with brine (15 mL) and water (2×10 mL). The organic layer was separated and dried with anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure to afford the crude product. Further purification was performed using chromatography over a short column of silica gel (petroleum ether 60−80 °C as eluent) which, after evaporation of the solvent, afforded the desired pure **3c** with 80% yield (0.291 g).

Typical Procedure for Conversion of 1 to 12: A solution of NBS (2.2 mmol, 0.391 g) and tetrabutylammonium cyanide (2.2 mmol, 0.59 g) in dry acetonitrile (10 mL) was stirred at room temperature for 15 min. 2-(4-Methoxyphenyl)-2-methyl-1,3-dithiolane (1.0 mmol, 0.226 g) was then added to the solution and the resultant mixture was stirred at room temperature for 5 min. Silica gel was added to the reaction mixture and the solvent was evaporated on a rotary evaporator. The resultant powder was applied to a silica gel column and eluted with hexane/ethyl acetate, 9:1, to afford **12** in 98% yield (0.244 g).

Typical Procedure for Conversion of 7 to 28: A solution of NBS (2.2 mmol, 0.391 g) and tetrabutylammonium azide (2.2 mmol, 0.624 g) in dry acetonitrile (10 mL) was stirred at room temperature for 15 min. 2-(4-Chlorophenyl)-2-methyl-1,3-dithiolane (1.0 mmol, 0.23 g) was added to the solution and the resultant mixture was stirred at room temperature for 14 h. To the resultant mixture, was added silica gel and the solvent was evaporated on a rotary evaporator. The resultant powder was applied to a silica gel column and eluted with hexane/ethyl acetate, 9:1, to afford **28** in 93% yield (0.250 g).

Typical Procedure for Conversion of 5 to 36: A solution of NBS (2.2 mmol, 0.391 g) and ammonium thiocyanate (2.2 mmol, 0.167 g) in dry CH_3CN (10 mL) was stirred at 0 °C for 15 min. **5** (1.0 mmol, 0.196 g) was added to the solution and the resultant mixture was stirred at room temperature for 30 min. To the resultant mixture was added silica gel and the solvent was evaporated on a rotary evaporator. The resultant solid mass was applied to a silica gel column and eluted with hexane/EtOAc, 9:1, to afford **36** in 79% yield (0.198 g).

Preparation of Tetrabutylammonium Azide: To a solution of tetrabutylammonium bromide (2.2 mmol, 0.709 g) in distilled water (10 mL) was added sodium azide (2.2 mmol, 0.143 g). The mixture was stirred for 30 min. The resultant mixture was extracted with CH_2Cl_2 (4×10 mL). The organic layer was separated and dried with anhydrous $CaCl_2$. The solvent was evaporated under reduced pressure to afford tetrabutylammonium azide as a white powder in 90% yield (0.256 g).

2a: Yellow viscous liquid; 88% yield (0.227 g). ^1H NMR (250 MHz, $CDCl_3$): δ = 3.19−3.33 (m, 4 H, CH_2CH_2), 3.68(s, 3 H, OCH_3),

6.77 (d, J = 8.8 Hz, 2 H, Ar), 7.23 (d, J = 8.8 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 30.8, 32.6, 55.7, 113.2, 114.2, 126.5, 130.4, 133.1, 163.9 ppm. $[M]^+$ calcd for $C_{11}H_{11}ClOS_2$: 258, found 258. $C_{11}H_{11}ClOS_2$ (258.8): calcd. C 51.1, H 4.2; found C 51.2, H 4.2.

2b: Yellow viscous liquid; 99% yield (0.303 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.28−3.35 (m, 4 H, CH_2CH_2), 3.74(s, 3 H, OCH_3), 6.79 (d, J = 8.7 Hz, 2 H, Ar), 7.28 (d, J = 8.7 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 31.0, 33.2, 55.6, 113.9, 114.2, 126.5, 131.2, 133.9, 161.6 ppm. $[M]^+$ calcd for $C_{11}H_{11}BrOS_2$: 302, found 302. $C_{11}H_{11}BrOS_2$ (303.2): calcd. C 43.6, H 3.6; found C 43.8, H 3.7.

2c: Yellow viscous liquid; 70% yield (0.245 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.10−3.25 (m, 4 H, CH_2CH_2), 3.69(s, 3 H, OCH_3), 6.70 (d, J = 8.1 Hz, 2 H, Ar), 7.20 (d, J = 8.1 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 27.1, 29.1, 55.7, 69.5, 113.0, 114.1, 126.5, 130.7, 163.9 ppm. $[M]^+$ calcd for $C_{11}H_{11}IOS_2$: 350, found 350. $C_{11}H_{11}IOS_2$ (350.2): calcd. C 37.7, H 3.1; found C 37.7, H 3.2.

3b: Yellow viscous liquid; 98% yield (0.311 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.45−2.46 (m, 2 H, $CH_2CH_2CH_2$), 3.78−3.79 (m, 4 H, $CH_2CH_2CH_2$), 3.73 (s, 3 H, OCH_3), 6.70 (d, J = 8.7 Hz, 2 H, Ar), 7.79 (d, J = 8.7 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 24.4, 27.9, 29.4, 53.9, 111.5, 112.3, 126.5, 129.2, 131.6, 162.2 ppm. $[M]^+$ calcd for $C_{12}H_{13}BrOS_2$: 316, found 316. $C_{12}H_{13}BrOS_2$ (317.3): calcd. C 45.4, H 4.1; found C 45.5, H 4.2.

3c: White viscous liquid; 80% yield (0.291 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.16−2.23 (m, 2 H, $CH_2CH_2CH_2$), 3.52−3.61 (m, 4 H, $CH_2CH_2CH_2$), 3.80 (s, 3 H, OCH_3), 6.82 (d, J = 8.5 Hz, 2 H, Ar), 7.41 [(d, J = 8.5 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 25.9, 28.6, 32.0, 55.1, 69.5, 113.1, 123.3, 129.9, 130.2, 163.1 ppm. $[M]^+$ calcd for $C_{12}H_{13}IOS_2$: 364, found 364. $C_{12}H_{13}IOS_2$ (364.3): calcd. C 39.6, H 3.6; found C 39.6, H 3.7.

4b: Yellow solid; 87% yield (0.304 g); m.p. 94 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.24 (m, 4 H, CH_2CH_2), 7.23−7.54 (m, 9 H, biphenyl) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 30.2, 32.6, 112.9, 127.7, 128.4, 129.1, 129.5, 130.0, 130.6, 131.3, 131.9, 146.6 ppm. $[M]^+$ calcd for $C_{16}H_{13}BrS_2$: 348, found 348. $C_{16}H_{13}BrS_2$ (349.3): calcd. C 55.0, H 3.7; found C 55.0, H 3.7.

4c: Yellow solid; 78% yield (0.309 g); m.p. 105 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.26−3.32 (m, 4 H, CH_2CH_2), 7.36−8.08 (m, 9 H, biphenyl) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 27.3, 28.3, 69.6, 126.6, 127.4, 127.6, 127.8, 128.6, 128.8, 129.4, 129.8, 143.6 ppm. $[M]^+$ calcd for $C_{16}H_{13}IS_2$: 396, found 396. $C_{16}H_{13}IS_2$ (396.3): calcd. C 48.5, H 3.3; found C 48.5, H 3.2.

5a: Yellow viscous liquid; 72% yield (0.229 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.44 (m, 2 H, $CH_2CH_2CH_2$), 3.28 (m, 4 H, $CH_2CH_2CH_2$), 7.17−7.87 (m, 9 H, biphenyl) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 27.2, 28.8, 29.7, 113.0, 127.3, 127.6, 127.9, 128.3, 128.7, 129.3, 129.5, 130.6, 143.2 ppm. $[M]^+$ calcd for $C_{17}H_{15}ClS_2$: 318, found 318. $C_{17}H_{15}ClS_2$ (318.9): calcd. C 64.0, H 4.7; found C 64.0, H 4.9.

5b: Yellow viscous liquid; 70% yield (0.253 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.04−2.13 (m, 2 H, $CH_2CH_2CH_2$), 2.79−2.81 (m, 4 H, $CH_2CH_2CH_2$), 7.41−8.08 (m, 9 H, biphenyl) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 26.7, 28.3, 30.8, 113.05, 127.2, 127.5, 128.4, 128.9, 129.0, 129.4, 129.6, 131.4, 146.6 ppm. $[M]^+$ calcd for $C_{17}H_{15}BrS_2$: 362, found 362. $C_{17}H_{15}BrS_2$ (363.3): calcd. C 56.2, H 4.1; found C 56.3, H 4.2.

5c: Yellow viscous liquid; 82% yield (0.336 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.21−2.25 (m, 2 H, $CH_2CH_2CH_2$), 3.57−3.66 (m, 4 H, $CH_2CH_2CH_2$), 7.25−7.60 (m, 9 H, biphenyl) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 30.5, 31.0, 32.6, 69.6, 125.0, 126.9, 127.0, 127.4, 127.5, 127.7, 128.2, 128.8, 143.9 ppm. $[M]^+$ calcd. for $C_{17}H_{15}IS_2$: 410, found 410. $C_{17}H_{15}IS_2$ (410.3): calcd. C 49.8, H 3.7; found C 49.8, H 3.9.

6b: Yellow viscous liquid; 89% yield (0.243 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.21 (m, 4 H, CH_2CH_2), 7.40 (m, 5 H, Ph) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 30.2, 32.6, 111.9, 125.0, 128.4, 130.2, 147.7, 148.7 ppm. $[M]^+$ calcd. for $C_{10}H_9BrS_2$: 272, found 272. $C_{10}H_9BrS_2$ (273.2): calcd. C 44.0, H 3.3; found C 44.2, H 3.3.

6c: Yellow viscous liquid; 89% yield (0.284 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.04−3.18 (m, 4 H, CH_2CH_2), 7.19−7.23 (m, 5 H, Ph) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 27.2, 28.3, 69.5, 126.3, 128.4, 128.7, 129.4, 140.7 ppm. $[M]^+$ calcd. for $C_{10}H_9IS_2$: 320, found 320. $C_{10}H_9IS_2$ (320.2): calcd. C 37.5, H 2.8; found C 37.5, H 2.9.

7b: Yellow viscous liquid; 90% yield (0.258 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.29 (m, 2 H, $CH_2CH_2CH_2$), 3.5 (m, 4 H, $CH_2CH_2CH_2$), 7.5−8.2 (m, 5 H, Ph) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 29.2, 31.5, 33.3, 110.0, 124.3, 130.6, 131.1, 147.6, 148.5 ppm. $[M]^+$ calcd. for $C_{11}H_{11}BrS_2$: 286, found 286. $C_{11}H_{11}BrS_2$ (287.2): calcd. C 46.0, H 3.8; found C 46.2, H 3.7.

7c: Yellow viscous liquid; 79% yield (0.264 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.99−2.04 (m, 2 H, $CH_2CH_2CH_2$), 3.00−3.06 (m, 4 H, $CH_2CH_2CH_2$), 7.34−7.88 (m, 5 H, Ph) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 28.9, 31.5, 33.9, 69.5, 127.7, 130.0, 131.2, 133.5, 137.5 ppm. $[M]^+$ calcd. for $C_{11}H_{11}IS_2$: 334, found 334. $C_{11}H_{11}IS_2$ (334.2): calcd. C 39.5, H 3.3; found C 39.5, H 3.4.

8a: Yellow viscous liquid; 89% yield (0.234 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.24−3.27 (m, 4 H, CH_2CH_2), 7.18 (d, J = 8.5 Hz, 2 H, Ar), 7.39 (d, J = 8.5 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 30.4, 32.6, 113.6, 125.4, 128.7, 131.4, 134.7, 136.7 ppm. $[M]^+$ calcd. for $C_{10}H_8Cl_2S_2$: 262, found 262. $C_{10}H_8Cl_2S_2$ (263.2): calcd. C 45.7, H 3.0; found C 45.7, H 3.3.

8b: Yellow viscous liquid; 92% yield (0.282 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.25−3.36 (m, 4 H, CH_2CH_2), 7.18 (d, J = 8.4 Hz, 2 H, Ar), 7.30 (d, J = 8.4 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 30.9, 33.3, 113.7, 126.4, 128.9, 131.4, 134.7, 138.6 ppm. $[M]^+$ calcd. for $C_{10}H_8BrClS_2$: 306, found 306. $C_{10}H_8BrClS_2$ (307.7): calcd. C 39.1, H 2.6; found C 39.3, H 2.7.

8c: Yellow viscous liquid; 71% yield (0.251 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.13−3.20 (m, 4 H, CH_2CH_2), 7.12 [(d, J = 8.6 Hz, 2 H, Ar),7.28 (d, J = 8.6 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 27.2, 28.1, 69.1, 127.1, 127.5, 128.9, 133.8, 139.1 ppm. $[M]^+$ calcd. for $C_{10}H_8ClIS_2$: 354, found 354. $C_{10}H_8ClIS_2$ (354.7): calcd. C 33.9, H 2.3; found C 33.7, H 2.4.

9b: Yellow viscous liquid; 90% yield (0.289 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.09−2.39 (m, 2 H, $CH_2CH_2CH_2$), 3.28−3.48 (m, 4 H, $CH_2CH_2CH_2$), 7.29 (d, J = 8.5 Hz, 2 H, Ar), 7.38 (d, J = 8.5 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 29.8, 33.4, 33.6, 113.8, 126.2, 129.5, 132.1, 134.8, 138.8 ppm. $[M]^+$ calcd. for $C_{11}H_{10}BrClS_2$: 320, found 320. $C_{11}H_{10}BrClS_2$ (321.7): calcd. C 41.1, H 3.1; found C 41.2, H 3.2.

9c: White viscous liquid; 78% yield (0.287 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.16−2.26 (m, 2 H, $CH_2CH_2CH_2$), 3.55−3.64 (m, 4 H, $CH_2CH_2CH_2$), 7.24 (d, J = 7.9 Hz, 2 H, Ar), 7.55 (d, J =

7.9 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 30.3, 30.9, 32.6, 69.1, 129.2, 129.9, 130.6, 135.8, 139.9 ppm. $[M]^+$ calcd. for $C_{11}H_{10}ClIS_2$: 368, found 368. $C_{11}H_{10}ClIS_2$ (368.7): calcd. C 35.9, H 2.7; found C 35.8, H 2.6.

10a: Yellow solid; 89% yield (0.243 g); m.p. 92 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.24 (m, 4 H, CH_2CH_2), 7.49 (d, J = 8.7 Hz, 2 H, Ar), 7.89 [(d, J = 8.7 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 30.3, 33.1, 115.2, 125.5, 127.5, 130.1, 141.6, 148.5 ppm. $[M]^+$ calcd. for $C_{10}H_8ClNO_2S_2$: 273, found 273. $C_{10}H_8ClNO_2S_2$ (273.8): calcd. C 43.9, H 2.9; found C 44.0, H 3.0.

10b: Yellow solid; 92% yield (0.293 g); m.p. 98 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.23 (m, 4 H, CH_2CH_2), 7.48 (d, J = 8.8 Hz, 2 H, Ar), 7.77 (d, J = 8.8 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 30.6, 33.1, 115.9, 125.3, 127.2, 130.9, 141.6, 148.5 ppm. $[M]^+$ calcd. for $C_{10}H_8BrNO_2S_2$: 317, found 317. $C_{10}H_8BrNO_2S_2$ (318.2): calcd. C 37.7, H 2.5; found C 37.9, H 2.8.

10c: Orange solid; 86% yield (0.314 g); m.p. 110 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.21 (m, 4 H, CH_2CH_2), 7.46 (d, J = 7.6 Hz, 2 H, Ar), 8.0 (d, J = 7.6 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 25.1, 25.3, 115.8, 69.5, 123.7, 127.4, 139.5, 144.2 ppm. $[M]^+$ calcd. for $C_{10}H_8INO_2S_2$: 365, found 365. $C_{10}H_8INO_2S_2$ (365.2): calcd. C 32.9, H 2.2; found C 33.0, H 2.3.

11a: Yellow solid; 90% yield (0.258 g); m.p. 93 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.05−2.40 (m, 2 H, $CH_2CH_2CH_2$), 3.41−3.50 (m,4 H, $CH_2CH_2CH_2$), 7.22 (d, J = 8.5 Hz, 2 H, Ar), 7.45 (d, J = 8.5 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 29.9, 31.7, 33.8, 120.1, 125.4, 128.2, 130.9, 141.5, 148.5 ppm. $[M]^+$ calcd. for $C_{11}H_{10}ClNO_2S_2$: 287, found 287. $C_{11}H_{10}ClNO_2S_2$ (287.8): calcd. C 45.9, H 3.5; found C 46.0, H 3.7.

11b: Yellow solid; 97% yield (0.322 g); m.p. 88 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.99−2.23 (m, 2 H, $CH_2CH_2CH_2$), 3.41−3.50 (m,4 H, $CH_2CH_2CH_2$), 7.43 (d, J = 8.2 Hz, 2 H, Ar), 7.74 (d, J = 8.2 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 29.8, 31.4, 33.6, 115.8, 125.3, 126.9, 130.8, 141.4, 148.5 ppm. $[M]^+$ calcd. for $C_{11}H_{10}BrNO_2S_2$: 331, found 331. $C_{11}H_{10}BrNO_2S_2$ (332.2): calcd. C 39.8, H 3.0; found C 40.2, H 3.1.

11c: Orange solid; 87% yield (0.330 g); m.p. 108 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.00 (m, 2 H, $CH_2CH_2CH_2$), 2.67 (m, 4 H, $CH_2CH_2CH_2$), 8.08 (d, J = 7.3 Hz, 2 H, Ar), 8.30 (d, J = 7.3 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 24.4, 25.7, 28.9, 69.5, 125.8, 127.5, 128.0, 139.5, 148.5 ppm. $[M]^+$ calcd. for $C_{11}H_{10}INO_2S_2$: 379, found 379. $C_{11}H_{10}INO_2S_2$ (379.2): calcd. C 34.8, H 2.6; found C 34.9, H 2.7.

12: Yellow viscous liquid; 98% yield (0.244 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.25−3.38 (m, 4 H, CH_2CH_2), 3.73(s, 3 H, OCH_3), 6.79 (d, J = 8.7 Hz, 2 H, Ar), 7.22 (d, J = 8.7 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 31.1, 33.2, 55.7, 100.0, 113.2, 114.0, 127.5, 131.2, 159.9, 163.9 ppm. $[M]^+$ calcd. for $C_{12}H_{11}NOS_2$: 249, found 249. $C_{12}H_{11}NOS_2$ (249.3): calcd. C 57.8, H 4.5; found C 58.0, H 4.7.

13: Dark green viscous liquid; 73% yield (0.192 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.97−2.06 (m, 2 H, $CH_2CH_2CH_2$), 2.60−3.26 (m, 4 H, $CH_2CH_2CH_2$), 3.80 (s, 3 H, OCH_3), 6.85 (d, J = 8.4 Hz, 2 H, Ar),7.89 (d, J = 8.4 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 25.2, 26.8, 28.5, 55.5, 113.6, 113.8, 113.8, 130.5, 131.3, 159.9, 162.8 ppm. $[M]^+$ calcd. for $C_{13}H_{13}NOS_2$: 263, found 263. $C_{13}H_{13}NOS_2$ (263.4): calcd. C 59.3, H 4.9; found C 59.1, H 4.8.

14: Yellow viscous liquid; 82% yield (0.242 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.32−3.37 (m, 4 H, CH_2CH_2), 7.18−7.53 (m, 9 H, biphenyl) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 30.8, 33.3, 111.2, 112.9, 127.3, 127.5, 127.9, 128.3, 128.9, 129.2, 130.4, 130.6, 151.1 ppm. $[M]^+$ calcd. for $C_{17}H_{13}NS_2$: 295, found 295. $C_{17}H_{13}NS_2$ (295.4): calcd. C 69.2, H 4.4; found C 68.9, H 4.5.

15: Yellow viscous liquid; 85% yield (0.263 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.45−2.49 (m, 2 H, $CH_2CH_2CH_2$), 3.42−3.47 (m, 4 H, $CH_2CH_2CH_2$), 7.29−8.00 (m, 9 H, biphenyl) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 27.2, 28.8, 31.2, 111.2, 113.0, 127.1, 127.7, 127.9, 128.2, 128.9, 129.3, 129.4, 129.7, 150.9 ppm. $[M]^+$ calcd. for $C_{18}H_{15}NS_2$: 309, found 309. $C_{18}H_{15}NS_2$ (309.4): calcd. C 69.9, H 4.9; found C 69.7, H 5.1.

16: Yellow viscous liquid; 88% yield (0.193 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.19−3.29 (m, 4 H, CH_2CH_2), 7.27 (m, 5 H, Ph) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 30.1, 33.2, 100.4, 112.3, 126.3, 128.2, 128.8, 129.9, 150.2 ppm. $[M]^+$ calcd. for $C_{11}H_9NS_2$: 219, found 219. $C_{11}H_9NS_2$ (219.3): calcd. C 60.3, H 4.1; found C 60.1, H 4.2.

17: Yellow viscous liquid; 88% yield (0.205 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.08−2.17 (m, 2 H, $CH_2CH_2CH_2$), 3.44−3.49 (m, 4 H, $CH_2CH_2CH_2$), 7.27 (m, 5 H, Ph) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 30.1, 32.6, 34.9, 111.2, 112.2, 128.6, 129.1, 129.3, 129.9, 150.9 ppm. $[M]^+$ calcd. for $C_{12}H_{11}NS_2$: 233, found 233. $C_{12}H_{11}NS_2$ (233.3): calcd. C 61.8, H 4.7; found C 61.6, H 4.6.

18: White viscous liquid; 98% yield (0.248 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.27−3.35 (m, 4 H, CH_2CH_2), 7.20 [(d, J = 8.4 Hz, 2 H, Ar (AA′XX′ system)], 7.28 (d, J = 8.4 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 29.0, 31.6, 99.6, 112.3, 125.9, 127.3, 129.7, 133.1, 151.1 ppm. $[M]^+$ calcd. for $C_{11}H_8ClNS_2$: 253, found 253. $C_{11}H_8ClNS_2$ (253.8): calcd. C 52.1, H 3.2; found C 52.1, H 3.4.

19: Yellow viscous liquid; 74% yield (0.198 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.97−2.04 (m, 2 H, $CH_2CH_2CH_2$), 3.24−3.34 (m, 4 H, $CH_2CH_2CH_2$), 7.35 (d, J = 7.3 Hz, 2 H, Ar), 7.69 (d, J = 7.3 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 24.0, 25.6, 28.7, 111.2, 112.2, 127.6, 128.2, 129.1, 135.2, 150.9 ppm. $[M]^+$ calcd. for $C_{12}H_{10}ClNS_2$: 267, found 267. $C_{12}H_{10}ClNS_2$ (267.8): calcd. C 53.9, H 3.7; found C 53.7, H 3.9.

20: Yellow solid; 97% yield (0.256 g); m.p. 80 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.23−3.39 (m, 4 H, CH_2CH_2), 7.45 (d, J = 7.5 Hz, 2 H, Ar), 8.16 (d, J = 7.5 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 27.6, 30.1, 111.1, 117.9, 123.9, 124.3, 126.5, 144.8, 151.1 ppm. $[M]^+$ calcd. for $C_{11}H_8N_2O_2S_2$: 264, found 264. $C_{11}H_8N_2O_2S_2$ (264.3): calcd. C 50.0, H 3.0; found C 49.8, H 2.9.

21: Yellow solid; 70% yield (0.195 g); m.p. 82 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.15−2.20 (m, 2 H, $CH_2CH_2CH_2$), 3.58−3.62 (m, 4 H, $CH_2CH_2CH_2$), 7.42 (d, J = 7.3 Hz, 2 H, Ar), 8.08 (d, J = 7.3 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 26.6, 31.1, 33.3, 111.2, 112.2, 123.9, 127.5, 128.1, 145.1, 150.9 ppm. $[M]^+$ calcd. for $C_{12}H_{10}N_2O_2S_2$: 278, found 278. $C_{12}H_{10}N_2O_2S_2$ (278.3): calcd. C 51.8, H 3.6; found C 51.8, H 3.4.

22: White viscous liquid; 84% yield (0.223 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.25−3.38 (m, 4 H, CH_2CH_2), 3.73(s, 3 H, OCH_3), 6.76 (d, J = 8.7 Hz, 2 H, Ar), 7.13 (d, J = 8.7 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 31.1, 33.2, 55.7, 114.0, 114.2, 127.5, 131.2, 141.2, 159.9 ppm. $[M]^+$ calcd. for $C_{11}H_{11}N_3OS_2$: 265, found 265. $C_{11}H_{11}N_3OS_2$ (265.3): calcd. C 49.8, H 4.1; found C 49.8, H 4.2.

23: Dark green viscous liquid; 86% yield (0.240 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.02−2.04 (m, 2 H, $CH_2CH_2CH_2$), 3.23−3.33 (m, 4 H, $CH_2CH_2CH_2$), 3.78(s, 3 H, OCH_3), 6.82 (d, J = 8.0 Hz, 2 H, Ar), 7.86 (d, J = 8.0 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 25.6, 27.2, 31.0, 55.8, 114.4, 128.2, 130.9, 131.3, 141.3, 164.1 ppm. $[M]^+$ calcd. for $C_{12}H_{13}N_3OS_2$: 279, found 279. $C_{12}H_{13}N_3OS_2$ (279.4): calcd. C 51.6, H 4.7; found C 51.5, H 4.8.

24: Yellow solid; 70% yield (0.218 g); m.p. 62 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.18−3.42 (m, 4 H, CH_2CH_2), 7.37−7.55 (m, 9 H, biphenyl) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 30.8, 33.3, 113.0, 126.6, 127.3, 127.5, 127.8, 127.9, 128.5, 129.1, 130.8, 141.2 ppm. $[M]^+$ calcd. for $C_{16}H_{13}N_3S_2$: 311, found 311. $C_{16}H_{13}N_3S_2$ (311.4): calcd. C 61.7, H 4.2; found C 61.6, H 4.4.

25: Yellow solid; 90% yield (0.292 g); m.p. 60 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.02−2.07 (m, 2 H, $CH_2CH_2CH_2$), 3.25−3.36 (m, 4 H, $CH_2CH_2CH_2$), 7.27−7.97 (m, 9 H, biphenyl) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 25.6, 27.1, 31.3, 118.2, 127.6, 127.7, 127.9, 128.6, 128.9, 129.3, 129.7, 130.0, 140.2 ppm. $[M]^+$ calcd. for $C_{17}H_{15}N_3S_2$: 325, found 325. $C_{17}H_{15}N_3S_2$ (325.4): calcd. C 62.8, H 4.7; found C 62.7, H 4.5.

26: Yellow viscous liquid; 70% yield (0.164 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.13−3.23 (m, 4 H, CH_2CH_2), 7.15−7.27 (m, 5 H, Ph) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 30.8, 33.2, 112.9, 126.3, 128.9, 129.3, 129.9, 140.7 ppm. $[M]^+$ calcd. for $C_{10}H_9N_3S_2$: 235, found 235. $C_{10}H_9N_3S_2$ (235.3): calcd. C 51.1, H 3.8; found C 51.1, H 4.0.

27: Yellow viscous liquid; 80% yield (0.199 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.10 (m, 2 H, $CH_2CH_2CH_2$), 3.28−3.46 (m, 4 H, $CH_2CH_2CH_2$), 7.19−7.43 (m, 5 H, Ph) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 25.5, 27.0, 30.8, 120.6, 127.5, 129.7, 130.1, 131.6, 141.0 ppm. $[M]^+$ calcd. for $C_{11}H_{11}N_3S_2$: 249, found 249. $C_{11}H_{11}N_3S_2$ (249.3): calcd. C 53.0, H 4.4; found C 53.1, H 4.6.

28: Yellow viscous liquid; 93% yield (0.250 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.12−3.21 (m, 4 H, CH_2CH_2), 7.17 (d, J = 8.6 Hz, 2 H, Ar), 7.29 (d, J = 8.6 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 30.7, 33.2, 113.7, 127.5, 128.9, 129.0, 131.4, 139.2 ppm. $[M]^+$ calcd. for $C_{10}H_8ClN_3S_2$: 269, found 269. $C_{10}H_8ClN_3S_2$ (269.8): calcd. C 44.6, H 3.0; found C 44.5, H 3.3.

29: Yellow viscous liquid; 79% yield (0.224 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.07 (m, 2 H, $CH_2CH_2CH_2$), 3.23−3.33 (m, 4 H, $CH_2CH_2CH_2$), 7.35 (d, J = 7.5 Hz, 2 H, Ar), 7.85 (d, J = 7.5 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 25.4, 26.9, 30.1, 118.2, 129.3, 129.6, 130.1, 130.5, 141.0 ppm. $[M]^+$ calcd. for $C_{11}H_{10}ClN_3S_2$: 283, found 283. $C_{11}H_{10}ClN_3S_2$ (283.8): calcd. C 46.6, H 3.5; found C 46.4, H 3.7.

30: Orange solid; 77% yield (0.216 g); m.p. 78 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.23 (m, 4 H, CH_2CH_2), 7.45 [(d, J = 8.6 Hz, 2 H, Ar (AA′XX′ system), 7.87 (d, J = 8.6 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 26.1, 28.7, 116.5, 122.8, 125.1, 126.9, 141.2, 144.8 ppm. $[M]^+$ calcd. for $C_{10}H_8N_4O_2S_2$: 280, found 280. $C_{10}H_8N_4O_2S_2$ (280.3): calcd. C 42.9, H 2.9; found C 43.0, H 3.1.

31: Yellow solid; 51% yield (0.129 g); m.p. 70 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.15−2.22 (m, 2 H, $CH_2CH_2CH_2$), 3.50−3.62 (m, 4 H, $CH_2CH_2CH_2$), 6.20 (s, 1 H, CH), 7.53 (d, J = 8.6 Hz, 2 H, Ar), 8.08 (d, J = 8.6 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 29.2, 31.1, 33.3, 123.3, 124.5, 128.1, 131.1, 132.8, 147.9 ppm. $[M]^+$ calcd. for $C_{11}H_{11}NO_2S_2$: 253, found 253. $C_{11}H_{11}NO_2S_2$ (253.3): calcd. C 52.1, H 4.4; found C 52.1, H 4.4.

32: Yellow viscous liquid; 91% yield (0.256 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.11−3.24 (m, 4 H, CH_2CH_2), 3.72 (s, 3 H, OCH_3), 6.74 (d, J = 8.7 Hz, 2 H, Ar), 7.36 (d, J = 8.7 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 26.0, 27.5, 54.6, 110.2, 112.5, 113.1, 126.5, 127.4, 127.5, 158.7 ppm. $[M]^+$ calcd. for $C_{12}H_{11}NOS_3$: 281, found 281. $C_{12}H_{11}NOS_3$ (281.4): calcd. C 51.2, H 3.9; found C 51.2, H 4.1.

33: Yellow viscous liquid; 88% yield (0.259 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.09−2.14 (m, 2 H, $CH_2CH_2CH_2$), 2.48 (m, 4 H, $CH_2CH_2CH_2$), 3.79(s, 3 H, OCH_3), 6.80 (d, J = 8.8 Hz, 2 H, Ar), 7.87 (d, J = 8.8 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 28.9, 32.7, 34.3, 54.4, 112.6, 112.9, 129.3, 129.6, 130.1, 136.9, 162.4 ppm. $[M]^+$ calcd. for $C_{13}H_{13}NOS_3$: 295, found 295. $C_{13}H_{13}NOS_3$ (295.4): calcd. C 52.9, H 4.4; found C 52.8, H 4.6.

34: Yellow solid; 92% yield (0.301 g); m.p. 75 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.39−3.44 (m, 4 H, CH_2CH_2), 7.19−7.55 (m, 9 H, biphenyl) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 27.7, 28.8, 112.7, 125.7, 127.0, 127.4, 128.2, 128.5, 128.9, 129.2, 130.1, 130.8, 132.4 ppm. $[M]^+$ calcd. for $C_{17}H_{13}NS_3$: 327, found 327. $C_{17}H_{13}NS_3$ (327.5): calcd. C 62.4, H 4.0; found C 62.3, H 4.2.

35: Yellow viscous liquid; 87% yield (0.297 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.09−2.19 (m, 2 H, $CH_2CH_2CH_2$), 3.48−3.57 (m, 4 H, $CH_2CH_2CH_2$), 7.29−7.59 (m, 9 H, biphenyl) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 30.9, 31.4, 32.9, 110.7, 118.6, 126.1, 127.3, 127.8, 128.0, 128.2, 128.6, 129.1, 129.5, 131.5 ppm. $[M]^+$ calcd. for $C_{18}H_{15}NS_3$: 341, found 341. $C_{18}H_{15}NS_3$ (341.5): calcd. C 63.3, H 4.4; found C 63.2, H 4.3.

36: Yellow viscous liquid; 95% yield (0.238 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.12−3.35 (m, 4 H, CH_2CH_2), 7.20−7.37 (m, 5 H, Ph) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 27.2, 28.3, 113.0, 125.8, 126.3, 128.2, 128.9, 129.9, 140.7 ppm. $[M]^+$ calcd. for $C_{11}H_9NS_3$: 251, found 251. $C_{11}H_9NS_3$ (251.4): calcd. C 52.6, H 3.6; found C 52.7, H 3.8.

37: White viscous liquid; 93% yield (0.246 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.07−2.19 (m, 2 H, $CH_2CH_2CH_2$), 3.43−3.57 (m, 4 H, $CH_2CH_2CH_2$), 7.19−7.39 (m, 5 H, Ph) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 29.4, 33.1, 34.9, 104.8, 125.8, 127.7, 128.7, 129.4, 129.8, 130.1 ppm. $[M]^+$ calcd. for $C_{12}H_{11}NS_3$: 265, found 265. $C_{12}H_{11}NS_3$ (265.4): calcd. C 54.3, H 4.2; found C 54.2, H 4.6.

38: Yellow viscous liquid; 90% yield (0.256 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.14−3.23 (m, 4 H, CH_2CH_2), 7.12 (d, J = 8.7 Hz, 2 H, Ar), 7.27 (d, J = 8.7 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 27.2, 28.1, 113.6, 127.2, 128.4, 128.9, 129.4, 133.8, 139.2 ppm. $[M]^+$ calcd. for $C_{11}H_8ClNS_3$: 285, found 285. $C_{11}H_8ClNS_3$ (285.8): calcd. C 46.3, H 2.8; found C 46.2, H 3.2.

39: Yellow viscous liquid; 93% yield (0.278 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.08−2.16 (m, 2 H, $CH_2CH_2CH_2$), 3.48−3.57 (m, 4 H, $CH_2CH_2CH_2$), 7.16 (d, J = 8.7 Hz, 2 H, Ar), 7.35 (d, J = 8.7 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 29.3, 29.9, 31.6, 104.0, 117.7, 125.6, 127.3, 127.5, 128.2, 132.7 ppm. $[M]^+$ calcd. for $C_{12}H_{10}ClNS_3$: 299, found 299. $C_{12}H_{10}ClNS_3$ (299.9): calcd. C 48.1, H 3.3; found C 48.1, H 3.5.

40: Yellow solid; 98% yield (0.290 g); m.p. 90−91 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.21−3.40 (m, 4 H, CH_2CH_2), 7.43 (d, J = 7.2 Hz, 2 H, Ar), 8.13 (d, J = 7.2 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 31.1, 33.3, 112.7, 123.3, 125.4, 128.1, 132.1,

147.2, 147.9 ppm. $[M]^+$ calcd. for $C_{11}H_8N_2O_2S_3$: 296, found 296. $C_{11}H_8N_2O_2S_3$ (296.4): calcd. C 44.6, H 2.7; found C 44.5, H 2.9.

41: Orange solid; 92% yield (0.285 g); m.p. 86−88 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.11−2.23 (m, 2 H, $CH_2CH_2CH_2$), 3.53−3.60 (m, 4 H, $CH_2CH_2CH_2$), 7.55 (d, J = 8.8 Hz, 2 H, Ar), 8.06 (d, J = 8.8 Hz, 2 H, Ar) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 26.1, 28.7, 32.2, 116.6, 122.2, 124.6, 126.9, 129.7, 145.1, 145.7 ppm. $[M]^+$ calcd. for $C_{12}H_{10}N_2O_2S_3$: 310, found 310. $C_{12}H_{10}N_2O_2S_3$ (310.4): calcd. C 46.4, H 3.2; found C 46.4, H 3.4.

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