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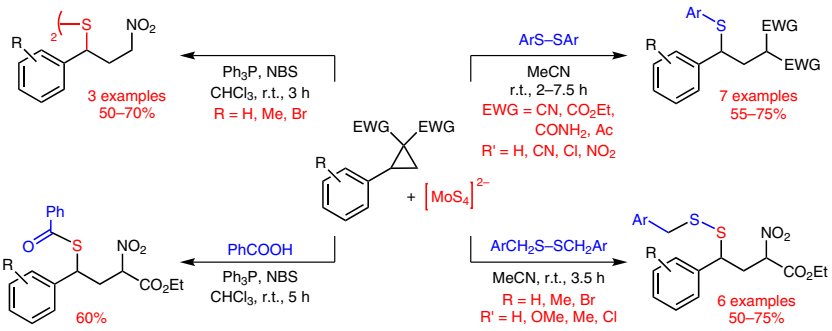
Catalyst-Free, Regioselective Ring Opening of Donor–Acceptor Cyclopropanes: Synthesis of Functionalized Mono- and Disulfides

Purushothaman Gopinath
Srinivasan Chandrasekaran*

Department of Organic Chemistry,
Indian Institute of Science, Bangalore
560012, India
scn@orgchem.iisc.ernet.in



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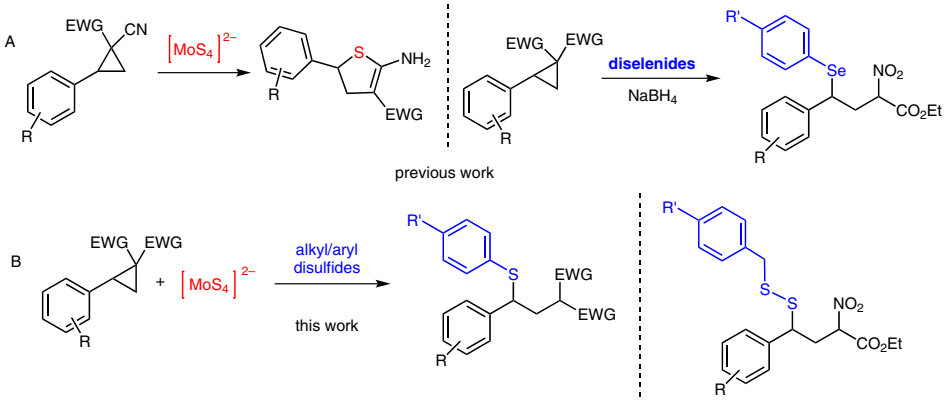
Abstract Interesting sulfur compounds such as monosulfides, symmetrical disulfides, unsymmetrical disulfides, and other 1,3-bifunctionalized compounds were synthesized using benzyltriethylammonium tetrathiomolybdate, $[BnNEt_3]_2MoS_4$, as the sulfur transfer reagent via regioselective ring opening of donor–acceptor cyclopropanes without the addition of any catalyst.

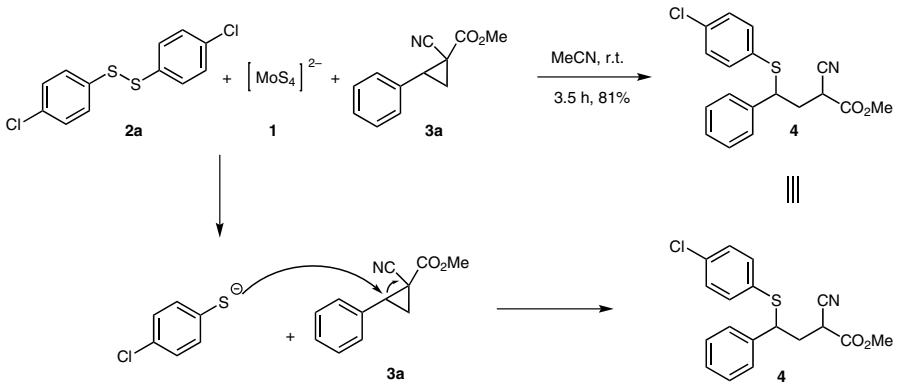
Key words cyclopropanes, ring opening, monosulfides, disulfides, thioesters

Functionalized monosulfides and disulfides are an important class of organic compounds present in many biologically relevant molecules such as methionine, biotin, gliotoxin, sporidesmin, acetyl aranotin, etc. They find wide applications in organic synthesis, medicinal chemistry,[1] and function as antioxidants.[2] Disulfides in particular play an important role in the folding and stability of a few proteins.[3] The most common method for the synthesis of monosulfides involves the alkylation of thiols with bases.[2a,4] Other methods involve metal-mediated cross-coupling reactions (between aryl/alkyl halide and thiols and hydrothiolation of alkynes),[5] Michael addition of thiols,[6] addition of thiols to alkenes,[7] etc. On the other hand, the most commonly employed method for the synthesis of disulfides involves the oxidation of the corresponding thiols, and for mixed disulfides,[8] the most common method is the activation of thiols via sulfenyl derivatives followed by nucleophilic substitution with another thiol partner. But the main disadvantage of this method is the use of free thiols, harsh reaction conditions, disulfide-thiol exchange reactions,[9] higher temperature, use of excess base, isolation of activated sulfenyl derivatives, etc. Thus, an alternative and mild protocol for their synthesis is desirable.

Nucleophilic ring opening of donor–acceptor cyclopropanes[10] is one of the most valuable synthetic tools for the synthesis of a wide variety of 1,3-bifunctionalized molecules and also a key step in the synthesis of many natural



Scheme 1 A: Previous work on cyclopropane ring opening; B: Present work

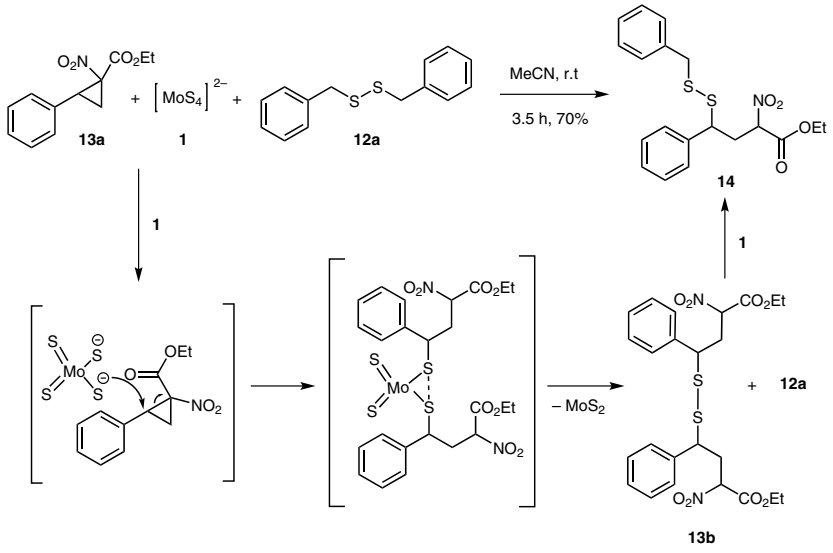


Scheme 2 Reaction of diphenyl disulfide **2a** with cyclopropane **3a**

products.[11] We recently reported an interesting method for the synthesis of dihydrothiophenes from cyano-substituted donor–acceptor cyclopropanes using tetrathiomolybdate[12] and also a one-pot protocol for the synthesis of functionalized organoselenium compounds via cyclopropane ring opening.[13] In continuation of these studies, we present herein our work focused on the synthesis of interesting sulfur compounds such as monosulfides, disulfides, mixed disulfides, and thioesters using benzyltriethylammonium tetrathiomolybdate $\{[BnNEt_3]_2MoS_4$, **1**$\}$[14] as the sulfur transfer reagent via cyclopropane ring opening (Scheme 1).

In order to avoid the use of thiols as starting materials, it was decided to use simple organic disulfides as substrates since tetrathiomolybdate **1** is known to reduce[14,15] the disulfide bonds to generate the corresponding thiolates in situ in an internal redox process. The thiolate ion can then open the doubly activated cyclopropane ring to furnish the corresponding functionalized monosulfides. After some initial screening of reaction conditions, the most optimal reaction conditions was found wherein disulfide **2a** and tetrathiomolybdate **1** were stirred together in MeCN for 1 hour to generate the thiolate ion and to this was added cyclopropane **3a**. The reaction mixture was then stirred for 2 hours at room temperature to form the corresponding functionalized monosulfide **4** (as a diastereomeric mixture) in 81% yield (Scheme 2).

This method is advantageous over the existing methods for the ring opening of cyclopropanes with thiols because of better yield, mild reaction conditions, shorter reaction time, and issues related to handling of free thiols. The reaction was then repeated with other organic disulfides and cyclopropane derivatives as well to show the synthetic utility of the protocol. The results of this study are summarized in Table 1. It was observed that cyano amide substituted cyclopropanes (Table 1, entries 2, 5, and 7) in general are less reactive as compared to cyano ester substituted cyclopro-



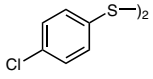
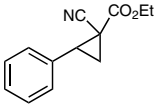
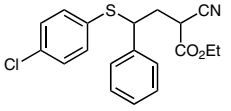
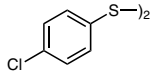
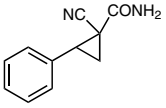
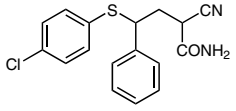
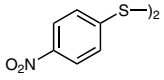
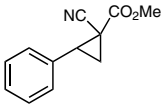
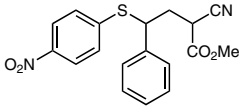
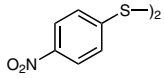
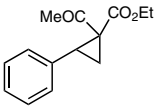
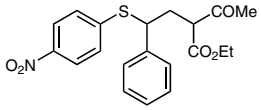
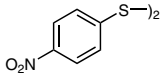
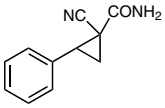
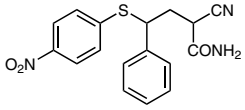
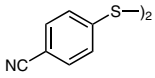
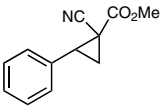
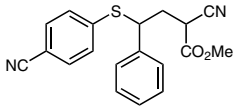
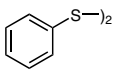
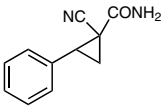
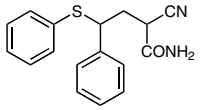
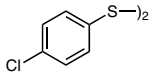
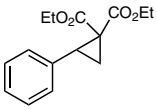
Scheme 3 Reaction of dibenzyl disulfide (**12a**) with cyclopropane **13a**

panes (entries 1 and 3) and also gave lower yields of the resulting monosulfides. Interestingly, the diester-substituted cyclopropane derivative **3e** (entry 8) did not react under the conditions to give the expected product (starting material recovered).

In the next stage, the synthesis of functionalized mixed disulfides was carried out starting with simple alkyl disulfides, which are known to produce mixed disulfides in the presence of tetrathiomolybdate **1**.[16] Accordingly, dibenzyl disulfide (**12a**) (alkyl disulfide) on treatment with reagent **1** and cyclopropane **13a** gave the mixed disulfide **14** (as a diastereomeric mixture) in 70% yield. Since dibenzyl disulfide is less reactive compared to diphenyl disulfide, reagent **1** first reacts with cyclopropane **13a** to form the corresponding disulfide **13b** (formed by cyclopropane ring opening), which in the presence of **12a** undergoes disulfide exchange reaction mediated by tetrathiomolybdate **1** to give the corresponding mixed disulfide **14** (Scheme 3). The reaction was then carried out on a number of other activated cyclopropanes and alkyl disulfides and all of them gave the corresponding mixed disulfides as the major products. The results of this study are summarized in Table 2.

We have already shown that alkyl halides on treatment with tetrathiomolybdate, **1** furnishes the corresponding disulfides.[17] Hence, we decided to carry out the reaction of an alkyl halide with **1** to form the corresponding disulfide in situ, which in turn may be used for the ring opening of cyclopropane to provide a mixed disulfide. Accordingly, ben-

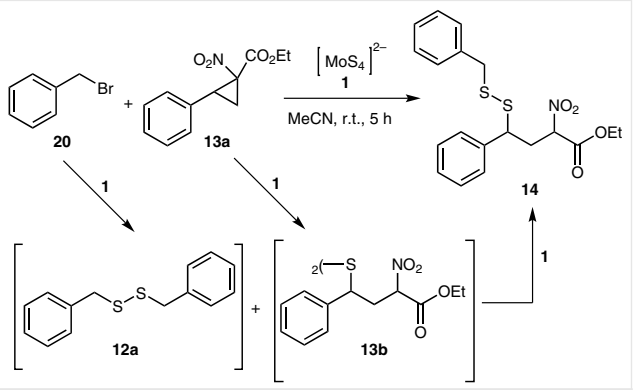
Table 1 Synthesis of Functionalized Monosulfides through Cyclopropane Ring Opening

Entry	Disulfide		Cyclopropane		Product		Time (h)	Yield (%)
1	**2a**		**3b**		**5**		3.5	72
2	**2a**		**3c**		**6**		7.5	62
3	**2b**		**3a**		**7**		2	62
4	**2b**		**3d**		**8**		6.5	60
5	**2b**		**3c**		**9**		3	60
6	**2c**		**3a**		**10**		2	75
7	**2d**		**3c**		**11**		3.5	55
8	**2a**		**3e**			no reaction	5	–

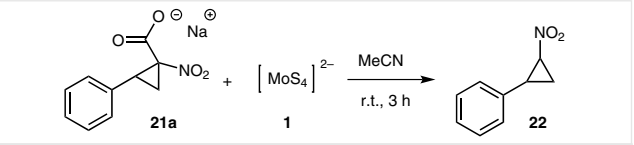
zyl bromide (**20**) on treatment with tetrathiomolybdate **1** forms disulfide **12a** while the cyclopropane derivative **13a** in the presence of tetrathiomolybdate **1** provides the symmetrical disulfide **13b** in situ. In the presence of excess tetrathiomolybdate **1**, the two disulfides **12a** and **13b** formed undergo an exchange reaction to produce the final product, the mixed disulfide **14** in 50% yield (Scheme 4).

Table 2 Synthesis of Mixed Disulfides from Nitro Ester Substituted Cyclopropanes

Entry	Disulfide	Cyclopropane	Product	Yield (%)
1	**12a**	**13a**	**14**	70
2	**12a**	**13b**	**15**	60
3	**12a**	**13c**	**16**	58
4	**12b**	**13a**	**17**	50
5	**12c**	**13a**	**18**	75
6	**12d**	**13a**	**19**	75



Scheme 4 Synthesis of mixed disulfide **14** from benzyl bromide (**20**)

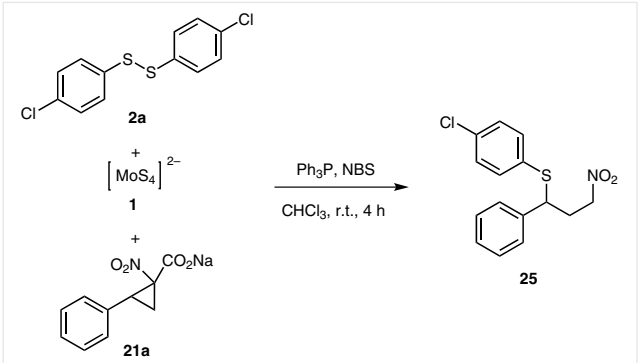


Scheme 5 Reaction of cyclopropane **21a** with tetrathiomolybdate **1**

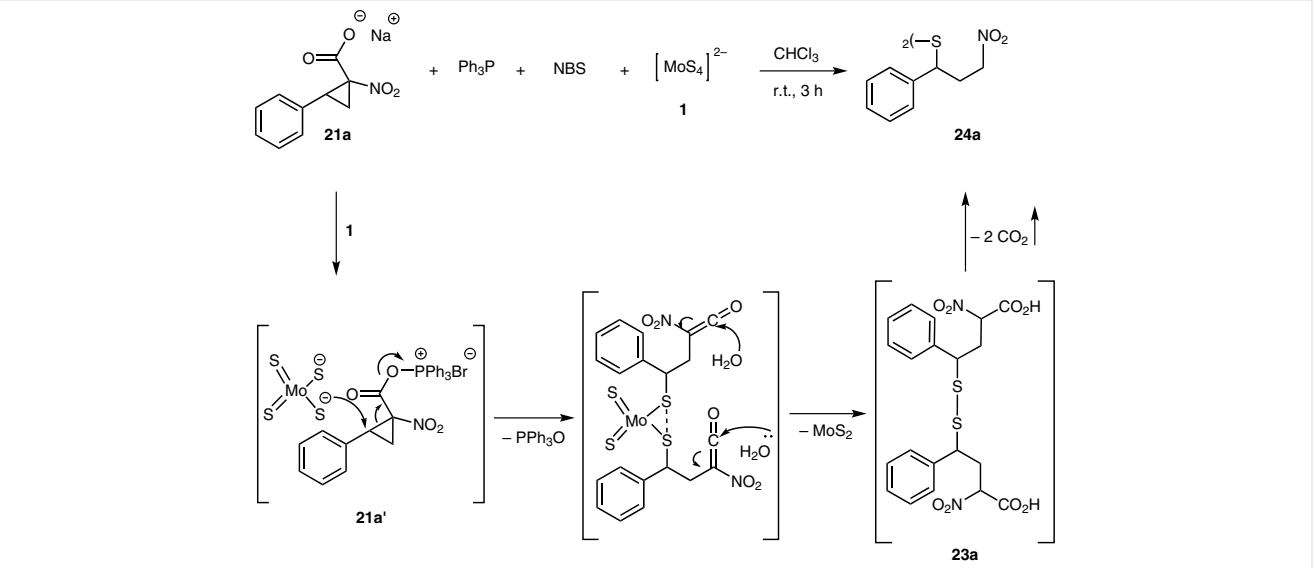
Since monoactivated cyclopropanes are inert to our reagent **1**, a synthetic strategy was designed for the formation of disulfides starting from a doubly activated cyclopropane followed by the removal of one of the activating groups during the course of the reaction. For this study, nitro and carboxylic acid-substituted cyclopropane derivative **21a** was synthesized. When the ring opening reaction on **21a** was attempted the carboxylic acid group decarboxylated well before its reaction with reagent **1** to give the corresponding nitro cyclopropane derivative **22** (Scheme 5).

In order to prevent decarboxylation at an early stage triphenylphosphine and NBS were added to form the acyloxyphosphonium salt **21a′**,[18] which then reacts with reagent **1** to give the disulfide intermediate **23a** followed by decarboxylation to give the corresponding disulfide **24a** (as a diastereomeric mixture) in 70% yield (Scheme 6). The reaction was then carried on with other activated cyclopropanes as well to show the synthetic utility of the methodology (Table 3).

The same methodology was then extended to a one-pot disulfide cleavage, ring opening and decarboxylation sequence to form the corresponding monosulfide. Accordingly, **2a** was stirred with reagent **1** to generate the corresponding thiolate ion, which then reacts with cyclopropane **21a** previously activated with PPh_3 and NBS to give the corresponding monosulfide **25** in 63% yield (Scheme 7).

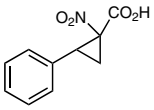
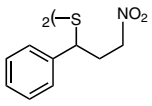
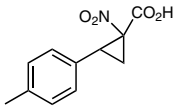
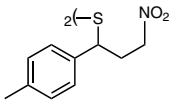
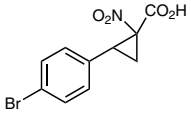
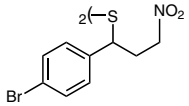


Scheme 7 Reaction of disulfide **2a** with cyclopropane **21a**



Scheme 6 Reaction of cyclopropane **21a** with tetrathiomolybdate **1** via acyloxyphosphonium intermediate

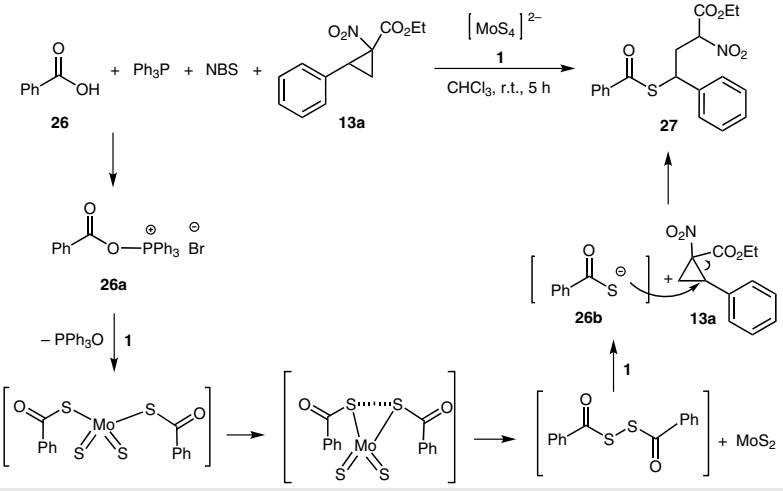
Table 3 Synthesis of Symmetrical Disulfides from Nitro-Substituted Cyclopropanes

Entry	Cyclopropane		Product		Yield (%)
1	**21a**		**24a**		70
2	**21b**		**24b**		60
3	**21c**		**24c**		50

From a synthetic perspective a thioester group could be readily transformed to a more versatile SH group as compared to thioethers and hence the ring opening of doubly activated cyclopropane **13a** was done with thioacid equivalents. Accordingly, benzoic acid, PPh_3, and NBS were stirred together to generate benzoyloxy phosphonium salt **26a**, which on further treatment with reagent **1**, gave the thiobenzoate ion[19] **26b**. The thiobenzoate ion was then used for the ring opening of doubly activated cyclopropane **13a** to give the corresponding ring opened product **27** (as a diastereomeric mixture) in 60% yield (Scheme 8).

In conclusion, we have demonstrated the synthetic utility of benzyltriethylammonium tetrathiomolybdate (**1**) in the synthesis of various interesting sulfur containing molecules such as monosulfides, symmetrical disulfides, unsymmetrical disulfides, and other 1,3-bifunctionalized systems under mild reaction conditions without need for any Lewis acid activation. Additionally, we have shown an alternative protocol for the ring opening of monoactivated cyclopropanes by starting from nitro carboxylate-substituted cyclopropanes.

All reactions were carried out in oven-dried apparatus using anhydrous solvents, unless otherwise noted. Reaction mixtures were stirred magnetically unless otherwise stated. Commercial grade solvents were distilled and dried. Analytical TLC was performed on commercial plates coated with silica gel GF254 (0.25 mm). Silica gel (230–400 mesh) was used for column chromatography. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise stated. NMR spectra were recorded on 300 or 400 MHz instruments and calibrated using residual undeuterated solvent as an internal reference. Standard abbreviations are used for the multiplicities. The superscript abbreviations d1 and d2 shown in the assignments of ^{1}H NMR refer to diastereomer 1 and diastereomer 2. IR spectra were recorded on a FT-IR spectrometer. ESI-HRMS were recorded on a Q-TOF mass spectrometer.



Scheme 8 Synthesis of thioester **27** from cyclopropane **13a** and benzoic acid (**26**)

Cyclopropanes **3a–d** were synthesized from bromosulfonium bromides (inseparable *E*/*Z* mixture was used for the ring-opening reaction).[12] Nitro ester-substituted cyclopropanes **13a–c** were synthesized using a protocol developed by Charette et al.[20] starting from the corresponding alkene and $PhI(OAc)_2$ (*E*-isomer was used for the ring-opening reactions, except for cyclopropane **13b** wherein the *E*/*Z* mixture were inseparable). Cyclopropanes **21a–c** were obtained by the hydrolysis of the corresponding nitro ester substituted cyclopropanes.[21] Disulfides **2a**, **2d**, and **12a** are commercially available and disulfides **2b**,[22] **2c**,[23] **12b**,[24] **12c**,[25] and **12d**[25] were synthesized starting from the corresponding thiols using I_2 as oxidant.[26]

Monosulfides 4–11; General Procedure

To a previously stirred solution (28 °C, 1.5 h) of tetrathiomolybdate **1** (0.609 g, 1.0 mmol) and disulfide **2** (0.8 mmol) in MeCN (10 mL) was added the corresponding cyclopropane **3** (1.0 mmol). The reaction mixture was then stirred for the time given in Table 1. The solvent was removed and the residue was extracted with CH_2Cl_2 (5 mL) and Et_2O (20 mL), and filtered through a Celite pad. The residue was again extracted with CH_2Cl_2 (5 mL) followed by extraction with Et_2O (20 mL) and filtered again through a Celite pad. The combined extracts were evaporated and the residue was purified by column chromatography on silica gel to give the corresponding monosulfide as an inseparable diastereomeric mixture.

Methyl 4-[(4-Chlorophenyl)thio]-2-cyano-4-phenylbutanoate (4)

Colorless liquid; yield: 0.280 g (81%) (60:40 dr).

IR (neat): 2250, 1749, 1475 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.32–7.17 (m, 9 H), 4.34–4.26 (m, 1 H), 3.89 (dd, J_1 = 6.3 Hz, J_2 = 8.1 Hz, 1 H^{d1}), 3.76 (s, 3 H^{d2}), 3.72 (s, 3 H^{d1}), 3.32 (dd, J_1 = 5.7 Hz, J_2 = 9.9 Hz, 1 H^{d2}), 2.65–2.40 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.9, 165.8, 139.4, 138.3, 134.7, 134.3, 131.6, 129.7, 129.1, 129.0, 128.8, 128.7, 128.3, 128.0, 127.9, 127.7, 115.8, 115.5, 53.6, 53.5, 51.3, 50.7, 35.7, 35.5, 35.3.

HRMS: *m*/*z* [M + Na^+] calcd for $C_{18}H_{16}ClNO_2SNa^+$: 368.0488; found: 368.0486.

Ethyl 4-[(4-Chlorophenyl)thio]-2-cyano-4-phenylbutanoate (5)

Colorless liquid; yield: 0.259 g (72%) (55:45 dr).

IR (neat): 2251, 1749, 1476, 1262 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.17 (m, 9 H), 4.34–4.09 (m, 3 H), 3.87 (dd, J_1 = 6.6 Hz, J_2 = 8.1 Hz, 1 H^{d1}), 3.30 (dd, J_1 = 6.0 Hz, J_2 = 9.9 Hz, 1 H^{d2}), 2.88–2.39 (m, 2 H), 1.31–1.22 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.4, 165.3, 139.5, 138.4, 134.8, 134.4, 131.7, 131.2, 129.7, 129.6, 129.2, 129.1, 128.9, 128.8, 128.4, 128.1, 128.0, 127.7, 115.9, 115.7, 63.1, 63.0, 51.4, 50.8, 35.9, 35.8, 35.4, 13.9.

HRMS: *m*/*z* [M + Na^+] calcd for $C_{19}H_{18}ClNO_2SNa^+$: 382.0644; found: 382.0637.

4-[(4-Chlorophenyl)thio]-2-cyano-4-phenylbutanamide (6)

White solid; yield: 0.205 g (62%) (50:50 dr); mp 130.5 °C.

IR (neat): 3442, 3340, 2248, 1689 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.13 (m, 9 H), 6.12 (br s, 1 H), 5.96 (br s, 1 H), 4.33–4.26 (m, 1 H), 3.75 (dd, J_1 = 6.3 Hz, J_2 = 8.4 Hz, 1 H^{d1}), 3.20 (dd, J_1 = 5.4 Hz, J_2 = 10.5 Hz, 1 H^{d2}), 2.70–2.58 (m, 1 H), 2.50–2.35 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.9, 165.7, 139.6, 138.4, 134.8, 134.5, 134.3, 131.6, 131.1, 129.2, 129.1, 128.8, 128.4, 128.1, 127.8, 127.5, 117.5, 117.2, 51.5, 50.9, 36.0, 33.5.

HRMS: *m*/*z* [M + Na^+] calcd for $C_{17}H_{15}ClN_2OSNa^+$: 353.0491; found: 353.0487.

Methyl 2-Cyano-4-[(4-nitrophenyl)thio]-4-phenylbutanoate (7)

Light yellow solid; yield: 0.221 g (62%) (50:50 dr); mp 93.2 °C.

IR (neat): 2237, 1715, 1524, 1145 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.29–8.21 (m, 2 H), 7.50–7.23 (m, 7 H), 4.64 (dd, J_1 = 5.4 Hz, J_2 = 10.5 Hz, 1 H^{d1}), 4.33 (t, *J* = 8.1 Hz, 1 H^{d2}), 3.91–3.83 (m, 1 H^{d1}), 3.83 (s, 3 H^{d1}), 3.81 (s, 3 H^{d2}), 3.66 (dd, J_1 = 5.4 Hz, J_2 = 10.5 Hz, 1 H^{d2}), 2.80–2.71 (m, 2 H^{d1} + 1 H^{d2}), 2.48–2.38 (m, 1 H^{d2}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 183.9, 169.6, 168.7, 147.9, 141.9, 141.3, 137.9, 129.4, 129.3, 128.3, 128.7, 128.3, 127.6, 127.2, 124.4, 119.0, 118.3, 45.5, 47.4, 47.1, 42.0, 41.0, 35.4, 34.9.

HRMS: *m*/*z* [M + Na^+] calcd for $C_{18}H_{16}N_2O_4SNa^+$: 379.0728; found: 379.0728.

Ethyl 2-Acetyl-4-[(4-nitrophenyl)thio]-4-phenylbutanoate (8)

Light yellow liquid; yield: 0.232 g (60%) (50:50 dr).

IR (neat): 1738, 1716, 1514 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.08–8.05 (m, 2 H), 7.39–7.30 (m, 7 H), 4.45–4.37 (m, 1 H), 4.28–4.09 (m, 2 H), 3.51–3.40 (m, 1 H), 2.69–2.52 (m, 2 H), 2.21 (s, 3 H^{d1}), 2.16 (s, 3 H^{d2}), 1.36–1.20 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.2, 201.6, 168.9, 168.7, 145.6, 145.4, 139.2, 139.1, 129.1, 128.7, 128.5, 128.3, 128.1, 127.7, 124.2, 123.9, 123.7, 61.8, 57.1, 56.9, 49.1, 34.2, 29.8, 29.1, 14.1, 14.0.

HRMS: *m*/*z* [M + Na^+] calcd for $C_{20}H_{21}NO_5SNa^+$: 410.1038; found: 410.1034.

2-Cyano-4-[(4-nitrophenyl)thio]-4-phenylbutanamide (9)

Light yellow liquid; yield: 0.205 g (60%) (50:50 dr).

IR (neat): 3448, 3551, 2249, 1693, 1508, 1338 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.09–8.05 (m, 2 H), 7.41–7.27 (m, 7 H), 6.15 (br s, 1 H), 5.92 (br s, 1 H), 4.65–4.57 (m, 1 H), 3.58 (t, *J* = 7.5 Hz, 1 H^{d1}), 3.22 (dd, J_1 = 5.4 Hz, J_2 = 10.2 Hz, 1 H^{d2}), 2.78–2.42 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.6, 165.4, 146.2, 143.8, 138.5, 137.7, 129.6, 129.5, 129.4, 129.2, 128.8, 128.6, 128.1, 127.7, 124.0, 117.3, 117.1, 49.5, 49.2, 36.1, 35.8, 35.4.

HRMS: *m*/*z* [M + Na^+] calcd for $C_{17}H_{15}N_3O_3SNa^+$: 364.0732; found: 364.0732.

Methyl 2-Cyano-4-[(4-cyanophenyl)thio]-4-phenylbutanoate (10)

Colorless liquid; yield: 0.252 g (75%) (50:50 dr).

IR (neat): 2228, 1749, 1592 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.52–7.48 (m, 2 H), 7.37–7.29 (m, 7 H), 4.56–4.49 (m, 1 H), 3.80–3.74 (m, 3 H^{d1} + 3 H^{d2} + 1 H^{d1}), 3.30 (dd, J_1 = 6.0 Hz, J_2 = 9.3 Hz, 1 H^{d2}), 2.67–2.45 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.7, 141.1 138.6, 137.7, 132.2, 130.6, 130.3, 129.3, 129.1, 128.8, 128.5, 127.7, 118.3, 115.5, 53.7, 49.7, 49.1, 35.9, 35.7, 35.5.

HRMS: *m*/*z* [M + Na^+] calcd for $C_{19}H_{16}N_2O_2SNa^+$: 359.0830; found: 359.0831.

2-Cyano-4-phenyl-4-(phenylthio)butanamide (11)

Light yellow liquid; yield: 0.163 g (55%) (50:50 dr).

IR (neat): 3441, 3342, 2248, 1692, 1684 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.34–7.19 (m, 10 H), 6.09 (br s, 1 H), 5.91 (br s, 1 H), 4.37–4.29 (m, 1 H), 3.76 (dd, J_1 = 6.3 Hz, J_2 = 8.7 Hz, 1 H^{d1}), 3.21 (dd, J_1 = 5.4 Hz, J_2 = 10.2 Hz, 1 H^{d2}), 2.70–2.58 (m, 1 H), 2.51–2.36 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.1, 165.9, 140.0, 138.8, 133.4, 133.0, 129.0, 128.9, 128.7, 128.2, 128.0, 127.9, 127.8, 117.3, 116.1, 51.2, 50.7, 36.2, 36.1, 35.74, 35.69.

HRMS: *m*/*z* [M + Na^+] calcd for $C_{17}H_{16}N_2OSNa^+$: 319.0881; found: 319.0869.

Mixed Disulfides 14–19; General Procedure

To a previously stirred solution (28 °C, 1.5 h) of tetrathiomolybdate **1** (0.731 g, 1.2 mmol) and disulfide **12** (0.8 mmol) in MeCN (10 mL) was added the corresponding cyclopropane **13** (1.0 mmol). The reaction mixture was then stirred for 2 h. The solvent was removed and the residue was extracted with CH_2Cl_2 (5 mL) and Et_2O (20 mL) and filtered through a Celite pad. The residue was again extracted with CH_2Cl_2 (5 mL) followed by extraction with Et_2O (20 mL) and filtered again through a Celite pad. The combined extracts were evaporated and the residue was purified by column chromatography on silica gel to give the corresponding mixed disulfide as an inseparable diastereomeric mixture.

Ethyl 4-(Benzyldisulfanyl)-2-nitro-4-phenylbutanoate (14)

Colorless liquid; yield: 0.274 g (70%) (40:60 dr).

IR (neat): 1750, 1562, 1454 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.11 (m, 10 H), 5.19 (dd, J_1 = 6.0 Hz, J_2 = 8.0 Hz, 1 H^{d1}), 4..77 (dd, J_1 = 4.0 Hz, J_2 = 10.4 Hz, 1 H^{d2}), 4.31–4.16 (m, 2 H), 3.68–3.59 (m, 2 H^{d2} + 1 H^{d1}), 3.45 (s, 2 H), 3.24 (dd, J_1 = 4.8 Hz, J_2 = 11.6 Hz, 1 H^{d2}), 3.10–3.03 (m, 1 H^{d2}), 2.89–2.86 (m, 1 H^{d1}), 2.82–2.77 (m, 1 H^{d1}), 2.61–2.54 (m, 1 H^{d2}), 1.31–1.22 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.98, 163.97, 138.8, 137.4, 136.9, 136.8, 129.5, 129.3, 129.1, 128.8, 128.6, 128.5, 128.4, 127.9, 127.6, 127.5, 85.9, 85.8, 63.2, 50.7, 50.1, 43.2, 43.1, 35.1, 34.8, 13.84, 13.79.

HRMS *m*/*z* [M + Na^+] calcd for $C_{19}H_{21}NO_4S_2Na^+$: 414.0810; found: 414.0800.

Ethyl 4-(Benzyldisulfanyl)-2-nitro-4-(*p*-tolyl)butanoate (15)

Colorless liquid; yield: 0.243 g (60%) (40:60 dr).

IR (neat): 1751, 1562, 1019 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.35–6.97 (m, 9 H), 5.14 (m, 1 H^{d1}), 4.46 (dd, J_1 = 3.6 Hz, J_2 = 10.8 Hz, 1 H^{d2}), 4.30–4.15 (m, 2 H), 3.69 (d, *J* = 12.6 Hz, 1 H^{d1}), 3.64 (d, *J* = 12.5 Hz, 1 H^{d1}), 3.56 (t, *J* = 8.0 Hz, 1 H^{d1}), 3.50 (s, 2 H^{d1}), 3.19 (dd, J_1 = 4.4 Hz, J_2 = 11.6 Hz, 1 H^{d2}), 3.10–3.02 (m, 1 H^{d2}), 2.89–2.87 (m, 1 H^{d1}), 2.79–2.73 (m, 1 H^{d1}), 2.57–2.50 (m, 1 H^{d2}), 2.35 (s, 3 H^{d1}), 2.33 (s, 3 H^{d2}), 1.31–1.23 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.1, 138.6, 138.3, 137.0, 136.9, 134.2, 129.7, 129.53, 129.47, 129.4, 128.62, 128.55, 128.0, 127.8, 127.6, 127.5, 85.9, 85.8, 63.18, 63.15, 50.5, 49.7, 43.2, 35.1, 35.0, 21.2, 13.9, 13.8.

HRMS: *m*/*z* [M + Na^+] calcd for $C_{20}H_{23}NO_4S_2Na^+$: 428.0966; found: 428.0966.

Ethyl 4-(Benzyldisulfanyl)-4-(4-bromophenyl)-2-nitrobutanoate (16)

Colorless liquid; yield: 0.272 g (58%) (40:60 dr).

IR (neat): 1749, 1559 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.49–6.93 (m, 9 H), 5.16 (dd, J_1 = 6.0 Hz, J_2 = 8.8 Hz, 1 H^{d1}), 4.71 (dd, J_1 = 3.6 Hz, J_2 = 11.2 Hz, 1 H^{d2}), 4.28–4.17 (m, 2 H), 3.72 (d, *J* = 12.5 Hz, 1 H^{d2}), 3.66 (d, *J* = 12.6 Hz, 1 H^{d2}), 3.55 (s, 2 H^{d1}), 3.49 (t, *J* = 7.6 Hz, 1 H^{d1}), 3.11 (dd, J_1 = 4.4 Hz, J_2 = 11.2 Hz, 1 H^{d2}), 3.05–2.98 (m, 1 H^{d2}), 2.82–2.72 (m, 2 H^{d1}), 2.53–2.45 (m, 1 H^{d2}), 1.31–1.23 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.9, 163.8, 137.9, 136.83, 136.76, 136.6, 132.2, 132.0, 129.7, 129.51, 129.47, 129.3, 128.69, 128.65, 127.73, 127.69, 122.6, 122.3, 85.8, 85.7, 63.3, 50.52, 49.5, 43.4, 43.3 35.1, 35.0, 13.9, 13.8.

HRMS: *m*/*z* [M + Na^+] calcd for $C_{19}H_{20}BrNO_4S_2Na^+$: 491.9915; found: 491.9902.

Ethyl 4-[(4-Methylbenzyl)disulfanyl]-2-nitro-4-phenylbutanoate (17)

Colorless liquid; yield: 0.203 g (55%) (40:60 dr).

IR (neat): 1754, 1564 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.01 (m, 9 H), 5.21 (dd, J_1 = 6.0 Hz, J_2 = 8.1 Hz, 1 H^{d1}), 4.77 (dd, J_1 = 3.9 Hz, J_2 = 10.8 Hz, 1 H^{d2}), 4.29–4.15 (m, 2 H), 3.65–3.55 (m, 1 H^{d1} + 2 H^{d2}), 3.41 (s, 2 H^{d1}), 3.22 (dd, J_1 = 4.2 Hz, J_2 = 11.4 Hz, 1 H^{d2}), 3.10–3.00 (m, 1 H^{d2}), 2.94–2.72 (m, 2 H^{d1}), 2.62–2.32 (m, 1 H^{d2}), 2.37 (s, 3 H^{d2}), 2.34 (s, 3 H^{d1}), 1.32–1.22 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.0, 137.5, 133.8, 129.34, 129.26, 129.0, 128.9, 128.6, 128.4, 128.2, 127.9, 86.0, 63.2, 50.9, 50.2, 44.0, 43.1, 35.2, 21.1, 13.8.

HRMS: *m*/*z* [M + Na] calcd for $C_{20}H_{23}NO_4S_2Na^+$: 428.0966; found: 428.0965.

Ethyl 4-[(4-Chlorobenzyl)disulfanyl]-2-nitro-4-phenylbutanoate (18)

Colorless liquid; yield: 0.320 g (75%) (40:60 dr).

IR (neat): 1749, 1564, 1250 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.02 (m, 9 H), 5.21 (dd, J_1 = 6.0 Hz, J_2 = 8.4 Hz, 1 H^{d1}), 4.82 (dd, J_1 = 4.2 Hz, J_2 = 10.5 Hz, 1 H^{d2}), 4.30–4.18 (m, 2 H), 3.67 (t, *J* = 7.8 Hz, 1 H^{d1}), 3.58 (d, *J* = 16.4 Hz, 1 H^{d2}), 3.52 (d, *J* = 16.8 Hz, 1 H^{d2}), 3.39–3.34 (m, 2 H^{d1} + 1 H^{d2}), 3.12–3.02 (m, 1 H^{d2}), 2.91–2.80 (m, 2 H^{d1}), 2.65–2.55 (m, 1 H^{d2}), 1.32–1.23 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.9, 138.8, 137.5, 135.3, 133.6, 130.7, 130.6, 129.2, 128.9, 128.8,128.7, 128.5, 128.1, 127.9, 85.9, 85.7, 63.3, 50.9, 50.4, 42.3, 42.2, 35.2, 34.9, 13.9, 13.8.

HRMS: *m*/*z* [M + Na] calcd for $C_{19}H_{20}ClNO_4S_2Na^+$: 448.0420; found: 448.0421.

Ethyl 4-[(4-Methoxybenzyl)disulfanyl]-2-nitro-4-phenylbutanoate (19)

Colorless liquid; yield: 0.316 g (75%) (40:60 dr).

IR (neat): 1748, 1564, 1250 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.39–7.05 (m, 7 H), 6.90–6.81 (m, 2 H), 5.22 (dd, J_1 = 6.0 Hz, J_2 = 8.4 Hz, 1 H^{d1}), 4.78 (dd, J_1 = 3.9 Hz, J_2 = 7.2 Hz, 1 H^{d2}), 4.31–4.16 (m, 2 H), 3.83 (s, 3 H^{d2}), 3.80 (s, 3 H^{d1}), 3.66 (m, 2 H^{d2} + 1 H^{d1}), 3.41 (s, 2 H^{d1}), 3.24 (dd, J_1 = 4.2 Hz, J_2 = 11.4 Hz, 1 H^{d2}), 3.11–3.01 (m, 1 H^{d2}), 2.94–2.73 (m, 2 H^{d1}), 2.62–2.52 (m, 1 H^{d2}), 1.32–1.23 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.02, 163.97, 159.2, 159.1, 138.9, 137.6, 130.6, 130.5, 129.0, 128.8, 128.7, 128.6, 128.3, 128.1, 127.9, 114.04, 113.96, 86.0, 85.8, 63.2, 55.29, 55.27, 50.7, 50.0, 42.7, 35.1, 34.9, 13.80, 13.78.

HRMS: *m*/*z* [M + Na] calcd for $C_{20}H_{23}NO_5S_2Na^+$: 444.0915; found: 444.0914.

Mixed Disulfide 14 from Benzyl Bromide (20)

To a well stirred solution of benzyl bromide (**20**; 0.274 g, 1.6 mmol) in MeCN was added tetrathiomolybdate **1** (1.705 g, 2.8 mmol) in MeCN (4 mL) and the mixture was stirred for 1.5 h. To this was added nitrocyclopropane **13a** (0.235 g, 1.0 mmol) and the reaction mixture was again stirred for 2 h at r.t. (28 °C). After the completion of reaction, the solvent was removed and Et_2O (20 mL) was added to it and filtered through a Celite pad. The residue was again extracted with CH_2Cl_2 (5 mL) followed by extraction with Et_2O (20 mL) and filtered again through a Celite pad. The combined extracts were evaporated and the residue was purified by column chromatography on silica gel to give compound **14** as a colorless liquid; yield: 0.196 g (50%).

Disulfides 24a–c; General Procedure

Cyclopropane derivative **21** (1.0 mmol) was stirred together with PPh_3 (0.288 g, 1.1 mmol) and NBS (0.196 g, 1.1 mmol) in $CHCl_3$ (10 mL) for 15 min. Tetrathiomolybdate **1** (0.609 g, 1.0 mmol) was then added to the reaction mixture and stirring continued for 3 h. Et_2O (30 mL) was then added to the reaction mixture followed by filtration through a Celite pad. The residue was again extracted with CH_2Cl_2 (5 mL) followed by extraction with Et_2O (20 mL) and filtered again through a Celite pad. The combined extracts were evaporated and the residue was purified by column chromatography on silica gel to give the corresponding disulfide as an inseparable diastereomeric mixture.

1,2-Bis(3-nitro-1-phenylpropyl)disulfane (24a)

Colorless liquid; yield: 0.153 g (70%) (50:50 dr).

IR (neat): 1552, 1380 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37–7.35 (m, 6 H), 7.19–7.12 (m, 4 H), 4.39–4.23 (m, 2 H), 4.21–4.12 (m, 2 H), 3.39–3.33 (m, 2 H). 2.78–2.66 (m, 2 H), 2.48–2.38 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.4, 129.1, 129.0, 128.6, 128.59, 128.55, 128.0, 127.9, 73.0, 72.9, 51.3, 50.9, 31.9, 31.6.

HRMS: *m*/*z* [M + Na] calcd for $C_{18}H_{20}N_2O_4S_2Na^+$: 415.0762; found: 415.0743.

1,2-Bis[3-nitro-1-(*p*-tolyl)propyl]disulfane (24b)

Colorless liquid; yield: 0.126 g (60%) (50:50 dr).

IR (neat): 1552 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23–7.16 (m, 4 H), 7.09–6.97 (m, 4 H), 4.31–4.23 (m, 2 H), 4.17–4.12 (m, 2 H), 3.40–3.35 (m, 2 H), 2.74–2.65 (m, 2 H), 2.41–2.37 (m, 8 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.6, 138.5, 135.3, 129.70, 129.68, 127.9, 127.8, 73.1, 73.0, 51.0, 50.7, 32.0, 31.7, 21.1.

HRMS: *m*/*z* [M + Na] calcd for $C_{20}H_{24}N_2O_4S_2Na^+$: 443.1075; found: 443.1071.

1,2-Bis[1-(4-bromophenyl)-3-nitropropyl]disulfane (24c)

Colorless liquid; yield: 0.138 g (50%) (50:50 dr).

IR (neat): 1552, 1513 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.49 (m, 4 H), 7.04–6.99 (m, 4 H), 4.36–4.30 (m, 2 H), 4.22–4.15 (m, 2 H), 3.42–3.38 (m, 2 H), 2.72–2.63 (m, 2 H), 2.41–2.35 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.8, 132.8, 132.7, 130.1, 130.0, 123.1, 73.24, 73.19, 51.4, 51.2, 32.44, 32.36.

HRMS: *m*/*z* [M + Na] calcd for $C_{18}H_{18}Br_2N_2O_4S_2Na^+$: 570.8972; found: 570.8973.

(4-Chlorophenyl)(3-nitro-1-phenylpropyl)sulfane (25)

To a well stirred solution of cyclopropane derivative **21a** (0.229 g, 1.0 mmol) in $CHCl_3$ (10 mL) were added PPh_3 (0.288 g, 1.1 mmol) and NBS (0.196 g, 1.1 mmol). After stirring the reaction mixture for 15 min, a mixture of *p*-chlorodiphenyl disulfide (**2a**; 0.230 g, 0.8 mmol) and tetrathiomolybdate **1** (0.609 g, 1.0 mmol), previously stirred for 1.5 h, was added. After the completion of reaction (2.5 h, 28 °C), solvent was removed and Et_2O (30mL) was added and filtered through a Celite pad. The residue was again extracted with CH_2Cl_2 (5 mL) followed by extraction with Et_2O (20 mL) and filtered again through a Celite pad. The combined extracts were evaporated and the residue was purified by column chromatography on silica gel to give compound **25** as a colorless liquid; yield: 0.194 g (63%).

IR (neat): 1550, 1089 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31–7.18 (m, 9 H), 4.51–4.14 (m, 2 H). 3.99 (dd, J_1 = 6.0 Hz, J_2 = 9.6 Hz, 1 H), 2.95–2.83 (m, 1 H), 2.66–2.49 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.8, 135.2, 133.3, 129.1, 128.9, 128.6, 128.0, 127.8.

HRMS: *m*/*z* [M + Na] calcd for $C_{15}H_{14}ClNO_2SNa^+$: 330.0331; found: 330.0328.

Ethyl 4-(Benzoylthio)-2-nitro-4-phenylbutanoate (27)

To a well-stirred solution of benzoic acid (**26**; 0.146 g, 1.2 mmol), PPh_3 (0.341 g, 1.3 mmol), and NBS (0.231 g, 1.3 mmol) in $CHCl_3$ (10 mL) (stirred for 15 min) was added benzyltriethylammonium tetrathiomolybdate **1** (0.731 g, 1.2 mmol). The cyclopropane derivative **13a** (0.235 g, 1.0 mmol) was then added after 20 min and stirred at r.t. for 5 h. Et_2O (30 mL) was then added to the reaction mixture followed by filtration through Celite pad. The residue was again extracted with CH_2Cl_2 (5 mL) followed by extraction with Et_2O (20 mL) and filtered again through a Celite pad. The combined extracts were evaporated and the residue was purified by column chromatography on silica gel to give compound **27** as a colorless liquid in a 1:1 diastereomeic ratio; yield: 0.224 g (70%) (based on the recovery of starting material).

IR (neat): 1748, 1666, 1564, 1206 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.94–7.90 (m, 2 H), 7.60–7.46 (m, 1 H), 7.44–7.31 (m, 1 H), 5.17 (dd, J_1 = 6.0 Hz, J_2 = 8.1 Hz, 1 H^{d1}), 5.01 (dd, J_1 = 5.4 Hz, J_2 = 9.0 Hz, 1 H^{d2}), 4.92–4.87 (m, 1 H^{d1}), 4.81 (dd, J_1 = 6.6 Hz, J_2 = 9.3 Hz, 1 H^{d2}), 4.37–4.21 (m, 2 H), 3.11–2.98 (m, 1 H), 2.93–2.81 (m, 1 H), 1.35–1.25 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.8, 164.2, 163.9, 139.4, 138.8, 136.4, 133.8, 129.2, 129.1, 128.7, 128.4, 128.3, 127.9, 127.7, 127.5, 127.4, 86.0, 85.6, 63.3, 63.2, 44.4, 37.0, 36.9, 13.9, 13.8.

HRMS: *m*/*z* [M + Na] calcd for $C_{19}H_{19}NO_5SNa^+$: 396.0882; found: 396.0874.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1561629.

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