# Reaction under Ball-Milling: Solvent-, Ligand-, and Metal-Free Synthesis of Unsymmetrical Diaryl Chalcogenides

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Ⓢ Supporting Information

ABSTRACT: A convenient, efficient, and general procedure for the synthesis of diaryl chalcogenides including sulfides, selenides and tellurides has been developed by the reaction of diazonium tetrafluoroborates and diaryl dichalcogenides on the surface of alumina under ball-milling without any solvent or metal. A wide range of functionalized diaryl chalcogenides are obtained in high purity by this procedure.
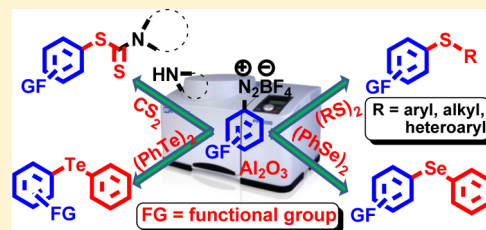
In recent times ball-milling (intense mechanical grinding) is of considerable interest as a greener tool for effecting a chemical transformation.[1] A variety of reactions involving carbon–carbon coupling,[2] carbon–heteroatom bond formation,[3] oxidation,[4] and hydrogenation[5] among others[6] have been efficiently performed by ball-milling. Currently we are also actively engaged in exploring useful chemical transformations under ball-milling.[7] As a part of our continuing program we report here another application of ball-milling for the synthesis of unsymmetrical diaryl chalcogenides.

The aryl chalcogenides are of much importance and continued interest because of their presence as structural motifs in a variety of molecules of biological, pharmaceutical, and material interest.[8] Moreover, they are employed as useful intermediates in organic synthesis.[9] Thus, a number of methods have been developed for their synthesis.[10] One of the most common and efficient practices is the transition-metal-mediated aryl-chalcogen bond formation. Several metals including palladium,[11] nickel,[12] copper,[13] and iron[14] have been employed to catalyze the reaction of aryl halides/boronic acids with aryl thiols/selenols/diselenides/ditellurides to achieve the synthesis of the diaryl chalcogenides. Usually, diaryl dichalcogenides being stable and readily available are preferred over foul smelling thiol and less stable and more toxic selenols as chalcogenating agents. However, reaction of diaryl dichalcogenides and aryl halides/boronic acids requires a reductant for the generation of chalcogenide anion and a transition metal for subsequent carbon-chalcogen bond formation. Usually a metal such as Zn or In is used as reducing agent, or a strong base is used for the cleavage of dichalcogenides. In recent times a metal-free reaction is of much interest as it avoids loss of expensive metals and prevents environment pollution due to toxicity of metal salts. A few metal-free procedures involving the reactions of diazonium salts and lithium, sodium, or potassium salts of arene thiolate/selnolate/tellurolate have also been reported.[15a−c] However, these reactions use hazardous solvents such as acetonitrile and DMSO, and the arene selenolate and tellurolates are also toxic.[16] Very recently Kumar et al.

reported[15d] a transition-metal-free reaction of substituted benzene and diaryl dichalcogenides under oxidative condition using potassium persulfate in trifluoroacetic acid at room temperature (80 °C in few reactions) for 8−16 h to produce aryl chalcogenides. This procedure too involved highly corrosive and toxic trifluoroacetic acid and long reaction time.

Recently, we reported[17] a microwave-assisted reaction of aryl diazonium tetrafluoroborates and diaryl dichalcogenides in dimethyl carbonate in the presence of zinc dust. In conventional heating at 80 °C, the reaction required 8−10 h. For further improvement we report here a solvent- and metal-free reaction of aryl diazonium tetrafluoroborate and diaryl dichalcogenides under ball-milling at ambient temperature for the synthesis of unsymmetrical aryl chalcogenides (Scheme 1).

Scheme 1. Synthesis of Unsymmetrical Functionalized Aryl/Alkyl/Heteroaryl Chalcogenides

FG = functional group
R = aryl, alkyl, heteroaryl
X = S, Se, Te
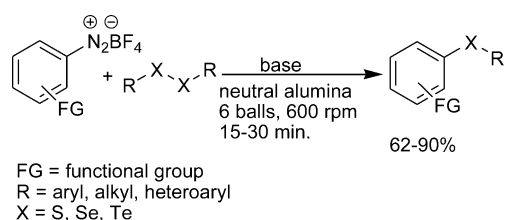
To optimize the reaction conditions for thiolation, a series of experiments were performed for a representative reaction of 4-methoxydiazonium tetrafluoroborate and di-4-chlorodiphenyl disulfide with variation of grinding auxiliary, base, and time. All three types of alumina and silica gel were tested as grinding auxiliary, and it was found that neutral and basic alumina in presence of 0.75 equiv of KOH worked most efficiently (Table 1, enries 8 and 12). Use of other milder bases such as K$_2$CO$_3$

Table 1. Optimization of Reaction Parameters for the Reaction of Diazonium Tetrafluoroborate and Diaryl Disulfide
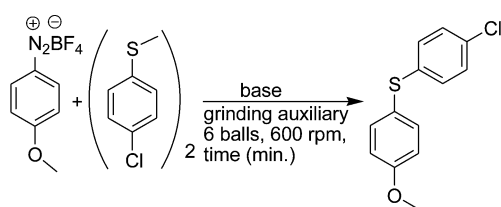
entry	grinding auxiliary	base (equiv)	time (min)	yield (%)
1	neutral Al_2O_3	Cs_2CO_3 (3)	15	0
2	neutral Al_2O_3	K_2CO_3 (3)	15	0
3	neutral Al_2O_3	NaOH (3)	15	68
4	neutral Al_2O_3	NaOH (1)	15	78
5	neutral Al_2O_3	NaOH (0.75)	15	83
6	neutral Al_2O_3	KOH (3)	15	78
7	neutral Al_2O_3	KOH (1)	15	85
8	**neutral Al_2O_3**	**KOH (0.75)**	**15**	**90**[a]
9	neutral Al_2O_3	KOH (0.5)	15	83
10	neutral Al_2O_3	KOH (0.75)	10	68
11	neutral Al_2O_3	KOH (0)	15	0
12	basic Al_2O_3	KOH (0.75)	15	90
13	basic Al_2O_3	KOH (0)	15	0
14	acidic Al_2O_3	KOH (0.75)	15	24
15	silica	KOH (0.75)	15	21

[a]Best condition.

and Cs_2CO_3 did not yield satisfactory results; however, the stronger base NaOH provided comparable yields as with KOH (Table 1, entry 5). It was observed that in place of ball-milling, stirring the reaction mixture by a magnetic stirrer did not provide any product. Thus in a typical general procedure a mixture of diazonium tetrafluoroborate (1 mmol), diaryl disulfide (0.5 mmol), and KOH (0.75 mmol) on neutral alumina (3 g) was ball-milled at 600 rpm using 6 balls for 15–30 min (TLC). Extraction of product by elution with ethanol or ethyl acetate followed by short column chromatography provided the pure product. This procedure is also effective for reactions with diaryl diselenides and ditellurides. Several diversely substituted diazonium tetrafluoroborates underwent reactions with diphenyl disulfides by this procedure to produce the corresponding sulphides. The results are summarized in Table 2. The substitution of electron-withdrawing and electron-donating groups on the phenyl ring of diazonium fluoroborate and disulfides did not have any appreciable influence on the outcome of the reaction. Several functional groups such as OCH_3, $COCH_3$, CF_3, NO_2, Cl, and Br are compatible with these reaction conditions. The heterocyclic disulfide pyridinyl disulfide also underwent reaction without any difficulty (Table 2, entry 2) to provide the corresponding aryl heteroaryl sulfide. The aryl-alkyl sulphides were also obtained successfully by the reaction of aryl diazonium fluoroborate and dialkyl disulfides (Table 2, entries 5–8). The sterically hindered disulfide di-(2,6-dimethylphenyl) disulfide also underwent reaction with 2-bromophenyl diazonium fluoroborate successfully (Table 2, entry 9).

The same procedure was followed for the reactions with diphenyl diselenide and diphenyl ditelluride. Several unsymmetrical functionalized diaryl selenides and tellurides were obtained. The results are reported in Table 3 for selenides and

Table 2. Synthesis of Unsymmetrical Diaryl or Aryl-Alkyl Sulfides by Ball-Milling
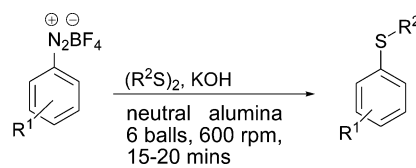
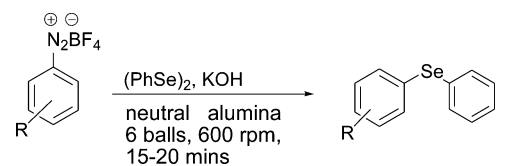| entry	product	time (min.)	yield (%)	ref[a]
1		15	90	18a
2		18	82	18b
3		15	78	18c
4		20	73	18d
5		15	78	18e
6		15	80	18e
7		18	72	-
8		18	73	-
9		20	70	-

[a]Denotes the earlier reference of the corresponding product. Reaction conditions: A mixture of diazonium salt (1 mmol), disulfane (0.5 mmol), KOH (0.75 mmol), and neutal alumina (3 g) was ball-milled at 600 rpm.
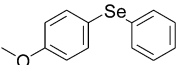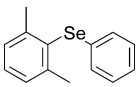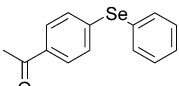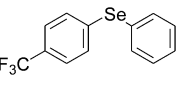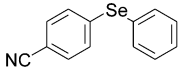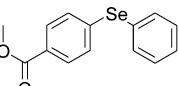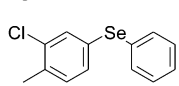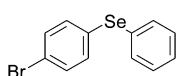
in Table 4 for tellurides. The synthesis of a sterically hindered selenide was also achieved by this procedure (Table 3, entry 2).

This procedure is also effective for the solvent-free synthesis of S-aryl dithiocarbamates by the reaction of aryl diazonium fluoroborate, carbon disulfide, and an amine. A variety of functionalized dithiocarbamates were obtained. The results are reported in Table 5. Cyclic amines such as thiomorpholine, morpholine, pyrrolidine, and piperidine and the acyclic amine dimethyl amine are compatible under this condition. This procedure provides more advantages such as use of no solvent and faster reaction (15–20 min) compared to our earlier method running the reaction in water for 3–4 h.[18j]

In general, the reactions are clean and high yielding. The only byproduct formed is the corresponding phenol (2–5%), which

Table 3. Synthesis of Unsymmetrical Diaryl Selenides by Ball-Milling
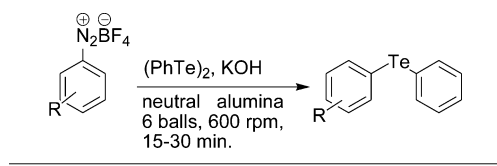

entry	R	product	time (min.)	yield (%)	ref.[a]
1	4-OCH$_3$-		15	78	15d
2	2,6-diMe-		20	73	18f
3	4-COCH$_3$-		15	76	18g
4	4-CF$_3$-		20	78	18h
5	4-CN-		30	74	17
6	4-CO$_2$CH$_3$-		20	75	17
7	3-Cl, 4-Me-		20	77	17
8	4-Br-		20	75	17
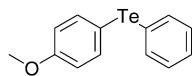
[a]Denotes the earlier reference of the corresponding product. Reaction condtions: A mixture of diazonium salt (1 mmol), diselenide (0.5 mmol), KOH (0.75 mmol), and neutral alumina (3g) was ball-milled at 600 rpm.

Table 4. Synthesis of Unsymmetrical Diaryl Tellurides by Ball-Milling

entry	R	product	time (min.)	yield (%)	ref[a]
1	4-OCH$_3$-		15	76	18g
2	4-COCH$_3$-		15	78	18g
3	4-CF$_3$-		20	68	18i
4	4 - CN-		30	62	18g
5	3-Cl, 4-Me-		20	76	-

[a]Denotes the earlier reference of the corresponding product. Reaction conditions: A mixture of diazonium salt (1 mmol), ditelluride (0.5 mmol), KOH (0.75 mmol), and neutral alumina (3g) was ball-milled at 600 rpm.

is easily separated out during column chromatography. Ball-milling made the reactions remarkably faster. The nature and position of substituents did not have any effect on the reaction rates and yields. The chalcogen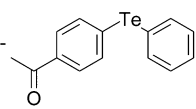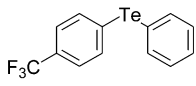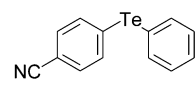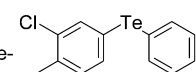ides are obtained pure and are characterized properly by spectroscopic data. Several of these products are new. Ball-milling makes this protocol proceed in the absence of any metal, ligand, or solvent at ambient temperature. It is predicted that the reaction proceeds through an interaction of the chalcogenide anion, formed by the cleavage of dichalcogenides in presence of KOH, with the diazonium fluoroborate to provide the product via release of nitrogen by a usual mechanism.[17]

In conclusion, we have developed a general procedure for the synthesis of unsymmetrical diaryl chalcogenides (sulphides, selenides, and tellurides) by a reaction of aryl diazonium tetrafluoroborates and diaryl dichalcogenides under ball-milling on the surface of alumina without requirement of any metal, ligand, or solvent. To best of our knowledge this is the first report of such synthesis involving diaryl dichalcogenides in the absence of any metal and solvent under ball-milling. In addition, the simplicity in operation, general applicability to all three chalcogenides and S-aryl dithiocarbamates, scope of functionalization, remarkably short reaction time at ambient

temperature, and use of stable and readily available diaryl dichalcogenide in place of foul smelling and toxic thiols/selenols/thiolate/selenoate makes this procedure a greener, cost-effective, and better alternative to existing ones. Moreover, this demonstrates the potential of ball-milling for clean organic synthesis.

■ EXPERIMENTAL SECTION

General. A PM 100, Retsch GmbH Germany, ball-milling apparatus was used for all reactions. HRMS analysis was performed in a QTOF mass analyzer using the ESI ionization method.

General Procedure for the Synthesis of Diaryl/Aryl-Heteroaryl Sulfides. Representative Experimental Procedure for the Synthesis of (4-Chlorophenyl)-(4-methoxyphenyl) Sulfane (Table 2, Entry 1). A mixture of 4-methoxy diazonium tetrafluoroborate (272 mg, 1 mmol), 1,2-bis(4-chlorophenyl) disulfane (143.6 mg, 0.5 mmol), and KOH (42 mg, 0.75 mmol) adsorbed on neutral alumina (3 g) was ball-milled in a 25 mL stainless steel beaker with six balls (d = 10 mm) of the same material at 600 rpm for 15 min (Caution: The diazonium salts are, in general, susceptible to explosion on heating/grinding, although we did not encounter any such incidence during our investigation. However the reactions should be performed in a closed fume cupboard.). The ball-milling operation was performed using inverted rotation directions, with an interval of 10 min and taking an interval break of 30 s. Extraction of the reaction residue by simple elution with ethanol or ethyl acetate followed by evaporation of the solvent gave the crude product, which was purified by a short column chromatography over silica gel (60−120 mesh) using a 9:1 hexane/diethyl ether mixed solvent as eluant to give (4-chlorophenyl)-(4-methoxyphenyl) sulfane as a white solid (225 mg, 90%); mp 60−62 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.83 (s, 3H), 5.90 (d, J = 9 Hz, 2H), 7.08 (d, J = 6 Hz, 2H), 7.19 (d, J = 9 Hz, 2H), 7.40 (d, J = 9 Hz, 2H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 55.5, 115.2 (2C), 123.8, 129.1 (2C), 129.4 (2C), 131.7,

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Table 5. Synthesis of S-Aryl Dithiocarbamates by Ball-Milling

entry	product	time (min.)	yield (%)	ref[a]
1		15	86	-
2		15	88	18j
3		15	82	18j
4		20	77	-
5		15	80	-

[a]Denotes the earlier reference of the corresponding product. Reaction conditions: CS$_2$ (2.5 mmol) and amine (1.2 mmol) were added dropwise to neutral alumina (3 g) at 0–5 °C and subjected to ball-milling at 600 rpm for 2 min. Diazonium salt (1 mmol) was added and further ball-milled at 600 rpm.

135.5 (2C), 137.5, 160.2. These data are in good agreement with those of an authentic sample reported earlier.[18a]

This procedure was followed for all of the reactions listed in Table 2. Almost all of these products are known compounds (see the references in Table 2) and were easily identified by comparison of their spectroscopic data with those previously reported. The unknown compounds were characterized by their IR and ^{1}H and ^{13}C NMR spectroscopic data and HRMS or elemental analysis. These data are given below in the order of their entries in Table 2.

(4-Methoxyphenyl)-(octadecyl) Sulfane (Table 2, Entry 7). Dirty white solid (282 mg, 72%); mp 64–66 °C; IR (KBr) 2955, 2918, 2849, 1726, 1498, 1464, 1288, 1247, 1220, 1180, 1120, 1029 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.86–0.93 (m, 3H), 1.25–1.29 (m, 28H), 1.34–1.39 (m, 2H), 1.56–1.60 (m, 2H), 2.80 (t, J = 7.5 Hz, 2H), 3.79 (s, 3H), 6.83 (d, J = 8.5 Hz, 2H), 7.33 (d, J = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 14.2, 22.8, 28.9, 29.0, 29.3, 29.5, 29.6, 29.7 (8C), 29.8, 32.0, 36.0, 55.5, 114.6 (2C), 127.2, 133.0 (2C), 158.9. Anal. Calcd for C$_{25}$H$_{44}$OS: C, 76.47; H, 11.29. Found: C, 76.42; H, 11.25.

(4-(4-Nitrophenoxy)butyl)-(phenyl) Sulfane (Table 2, Entry 8). White solid (221 mg, 73%); mp 92–94 °C; IR (KBr) 2920, 2850, 1593, 1510, 1340, 1298, 1261, 1172, 1111 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.79–1.89 (m, 2H), 1.94–2.04 (m, 2H), 3.0 (t, J = 11.5 Hz, 2H), 4.06 (t, J = 10 Hz, 2H), 6.89–6.94 (m, 2H), 7.16–7.21 (m, 1H),

7.26–7.36 (m, 4H), 8.16–8.21 (m, 2H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 25.7, 28.1, 33.5, 68.3, 114.5 (2C), 126.0 (2C), 126.2, 129.1 (2C), 129.5 (2C), 136.4, 141.6, 164.1. Anal. Calcd for C$_{16}$H$_{17}$NO$_3$S: C, 63.34; H, 5.65; N, 4.62. Found: C, 63.39; H, 5.69; N, 4.66.

(2-Bromophenyl)-(2,6-dimethylphenyl) Sulfane (Table 2, Entry 9). White solid (205 mg, 70%); mp 70–73 °C; IR (KBr) 3747, 3055, 3010, 2970, 2951, 2920, 2731, 1940, 1574, 1556, 1543, 1522, 1458, 1441, 1375, 1246, 1163, 1103, 1015 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.41 (s, 6H), 6.34 (d, J = 8.5 Hz, 1H), 6.92–6.94 (m, 1H), 7.01 (t, J = 4 Hz, 1H), 7.21 (d, J = 10 Hz, 2H), 7.26–7.27 (m, 1H), 7.51 (d, J = 7 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 21.8 (2C), 122.7, 125.4, 125.7, 127.8 (2C), 128.2, 128.8 (2C), 129.9, 133.4, 139.2, 144.3. Anal. Calcd for C$_{14}$H$_{13}$BrS: C, 57.35; H, 4.47. Found: C, 57.38; H, 4.45.

General Procedure for the Synthesis of Diaryl Selenides. Representative Experimental Procedure for the Synthesis of (4-Methoxyphenyl)-(phenyl) Selane (Table 3, Entry 1). A mixture of 4-methoxy diazonium tetrafluoroborate (272 mg, 1 mmol), diphenyl diselenide (156 mg, 0.5 mmol), and KOH (42 mg, 0.75 mmol) adsorbed on neutral alumina (3g) was ball-milled as in earlier procedure. Extraction and purification as mentioned earlier provided the product as a colorless oil (205 mg, 78%); ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.72 (s, 1H), 6.77 (d, J = 8.5 Hz, 2H), 7.09–7.16 (m, 3H), 7.25 (d, J = 5 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 55.4, 115.3 (2C), 120.1, 126.6, 129.3 (2C), 131.0 (2C), 133.3, 136.6 (2C), 159.9. This compound is identified as (4-methoxyphenyl)-(phenyl) selane by comparison of its spectroscopic data with those reported earlier.[18f]

This procedure was followed for all of the reactions in Table 3. All of these products are known compounds (see the references in Tables 3) and were easily identified by comparison of their spectroscopic data with those previously reported.

General Procedure for the Synthesis of Diaryl Tellurides. Representative Experimental Procedure for the Synthesis of (4-Methoxyphenyl)-(phenyl) Tellane (Table 4, Entry 1). A mixture of 4-methoxy diazonium tetrafluoroborate (272 mg, 1 mmol), diphenyl ditelluride (200 mg, 0.5 mmol), and KOH (42 mg, 0.75 mmol) adsorbed on neutral alumina (3 g) was ball-milled under the same conditions as earlier. Extraction and purification of the reaction residue provided the product, (4-methoxyphenyl)-(phenyl) tellane, as a white solid (236 mg, 76%); mp 60–62 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.80 (s, 3H), 6.78–6.81 (m, 2H), 7.16–7.20 (m, 3H), 7.55–7.58 (m, 2H), 7.71–7.74 (m, 2H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 55.3, 103.4, 115.7 (2C), 127.4, 129.5 (2C), 136.6 (2C), 136.7, 141.3 (2C), 160.2. These data are in agreement with those reported earlier.[18h]

This procedure was followed for all of the reactions in Table 4. Almost all of these products are known compounds (see the references in Table 4) and are easily identified by comparison of their spectroscopic data with those previously reported. The unknown compound (Table 4, entry 5) was characterized by its IR and ^{1}H and ^{13}C NMR spectroscopic data and elemental analysis. These data are given below.

(3-Chloro-4-methylphenyl)-(phenyl) Tellane (Table 4, Entry 5). Brown viscous oil (251 mg, 76%); IR (neat) 3049, 2951, 2922, 2850, 1574, 1545, 1471, 1435, 1363, 1051 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.36 (s, 3H), 7.05–7.08 (m, 1H), 7.20–7.30 (m, 3H), 7.45–7.49 (m, 1H), 7.68–7.70 (m, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 20.0, 112.0, 114.6, 128.2, 129.7, 132.0, 132.1, 135.4, 136.4, 136.5 (2C), 138.1 (2C). Anal. Calcd for C$_{13}$H$_{11}$ClTe: C, 47.27; H, 3.36. Found: C, 47.21; H 3.39.

General Procedure for the Synthesis of S-Aryl Dithiocarbamate. Representative Experimental Procedure for the Synthesis of 4-Methoxyphenyl Thiomorpholine-4-carbodithioate (Table 5, Entry 1). A mixture of carbon disulfide (190 mg, 2.5 mmol) and thiomorpholine (124 mg, 1.2 mmol) was added dropwise to neutral alumina (3 g) in the ball-milling stainless steel beaker (25 mL) kept at 0–5 °C (at this stage the beaker remained outside the ball-mill machine), and the beaker containing the reaction mixture was then subjected to ball-milling with six balls (d = 10 mm) at 600 rpm for 2 min. 4-Methoxy diazonium tetrafluoroborate (272 mg, 1 mmol) was

added, and the reaction mixture was further subjected to ball-milling for 15 min as earlier. Extraction and purification of the reaction mixture in the same way as mentioned earlier provided the product, 4-methoxyphenyl thiomorpholine-4-carbodithioate, as a pale yellow solid (245 mg, 86%); mp 122−125 °C ; IR (KBr) 2955, 2924, 2852, 1736, 1591, 1493, 1464, 1439, 1410, 1290, 1250, 1172, 1030 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.80 (t, J = 6 Hz, 4H), 3.85 (s, 3H), 4.42−4.57 (broad, 4H), 6.95−6.97 (m, 2H), 7.36−7.38 (m, 2H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 54.3 (2C), 55.4, 60.5 (2C), 114.9 (2C), 121.8, 138.7 (2C), 161.3, 198.7. Anal. Calcd for C$_{12}$H$_{15}$NOS$_3$: C, 50.49; H, 5.30; N, 4.91. Found: C, 50.43; H, 5.35; N, 4.94.

This procedure was followed for all of the reactions in Table 5. A few of these products are known compounds (see the references in Table 5) and were easily identified by comparison of their spectroscopic data with those previously reported. The unknown compounds were characterized by their IR, ^{1}H and ^{13}C NMR, and HRMS spectroscopic data. These data are given below in order of their entries in Table 5.

4-Nitrophenyl Pyrrolidine-1-carbodithioate (Table 5, Entry 4). Pale yellow gummy oil (207 mg, 77%) ; IR (neat) 3096, 2970, 2949, 2922, 2868, 2847, 1597, 1574, 1518, 1472, 1433, 1392, 1337, 1281, 1250, 1221, 1178, 1153, 1105, 1078 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.02−2.06 (m, 2H), 2.14−2.19 (m, 2H), 3.80−3.86 (m, 2H), 3.91−3.99 (m, 2H), 7.68 (d, J = 7 Hz, 2H), 8.26 (d, J = 7 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 24.4, 26.5, 51.0, 55.6, 123.9 (2C), 137.6 (2C), 139.1, 148.8, 190.1. HRMS calcd for C$_{11}$H$_{12}$N$_2$O$_2$S$_2$ [M + H]$^+$ 269.0413, found 269.0391.

Naphthalene-5-yl 4-Methyl piperidine-1carbodithioate (Table 5, Entry 5). Yellow viscous oil (241 mg, 80%); IR (neat) 3053, 2988, 2949, 2924, 2868, 2849, 1558, 1502, 1473, 1429, 1379, 1364, 1304, 1263, 1225, 1192, 1138, 1082, 1020 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.03 (d, J = 6 Hz, 3H), 1.40 (s, 2H), 1.76−1.80 (m, 3H), 3.12 (s, 1H), 3.39 (s, 1H), 4.87 (s, 1H), 5.44 (s, 1H), 7.49−7.56 (m, 3H), 7.75−7.80 (m, 1H), 7.84−7.89 (m, 1H), 7.98 (d, J = 8.5 Hz, 1H), 8.24 (d, J = 8 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 21.4, 31.0, 33.6, 34.2, 51.4, 52.2, 125.8, 126.0, 126.4, 127.3, 128.7, 129.1, 131.5, 134.3, 135.4, 137.2, 195.3. HRMS calcd for C$_{17}$H$_{19}$NS$_2$ [M + H]$^+$ 302.1032, found 302.1016.

Although these reactions were performed on 1 mmol scale, the 10 mmol scale reactions also provided uniform results.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H NMR and ^{13}C NMR spectra of all products listed in Tables 2−5. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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