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Nickel-Catalyzed Thiolation/ and Selenylation of Cycloketone Oxime Esters with Thiosulfonate or Selenium sulfonate

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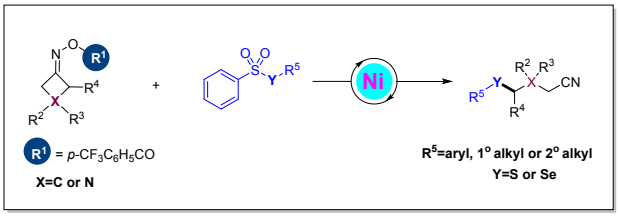


ABSTRACT: A nickel-catalyzed ring opening and subsequently reductive cross-coupling of cycloketone oxime esters with thiosulfonate or seleniumsulfonate is reported, which involves C-C bond cleavage and C(sp^3)-S or C(sp^3)-Se bond formation. Notably, *S*-aryl/alkyl sulfonothioates and *Se*-alkyl seleniumsulfonothioates could be employed in this reaction to afford a variety of 1°, 2° alkyl sulfides, aryl sulfides and 1°, 2° alkyl selenides in one step. This strategy features easily available substrates and mild reaction conditions.

KEYWORDS: Nickel catalysis, reductive coupling, ring opening, sulfides, selenides.

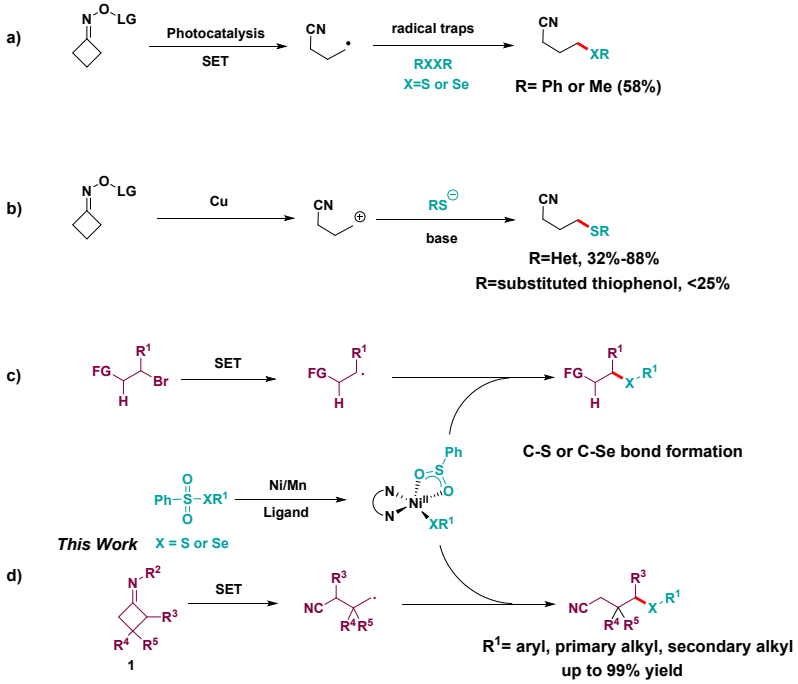
1. INTRODUCTION

The cleavage of C-C bonds attracts fundamental attention and plays an important role in various unique transformations.[1] In recent years, C–C bond cleavage of cycloketone oxime ester derivatives has attracted considerable interest to construct C–C, C-O, C-X and C-N bonds.[2-4] Among them, sp^3C–S and sp^3C–Se bonds *via* C–C bond cleavage of cycloketone oxime esters has been rarely studied. In 2005, Uemura and co-workers first reported an Ir-catalyzed reaction of cycloketone oxime esters with diphenyl dichalcogenides to construct phenyl alkyl sulfide and phenyl alkyl sulfides with limited substrates through the reaction of carbon radical with dichalcogenides.[5] Recently, Zhou group developed a visible light promoted reaction of cycloketone oxime esters with disulfide and diselenide at room temperature based on a similar radical trapping strategy. However, only diphenyl disulfide,

diphenyl diselenide and dimethyl disulfide were studied (Scheme 1, a).[6] More recently, Lin group reported a copper catalyzed reaction of cycloketone oxime esters with heteroaryl thiols through the reaction of carbocation with sulfur nucleophile in the presence of excess DBU.[7] However, the reaction of substituted thiophenols led to the desired products in <25% yields (Scheme 1, b).

Sulfur-containing and selenium-containing compounds play important roles in synthetic chemistry, medicinal chemistry and functional materials.[8] The traditional C-S and C-Se bonds.

Scheme 1. Methods for Activation of Cyclobutanone Oximes.

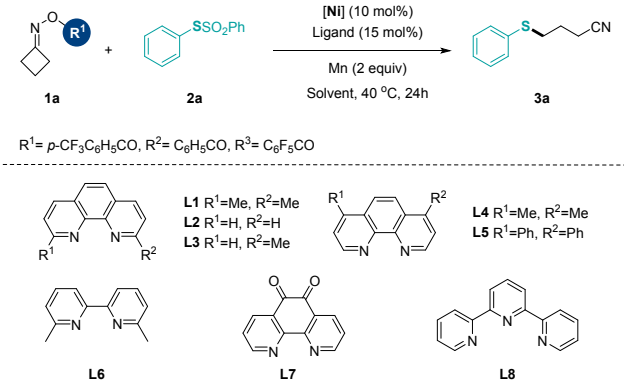


formation strategy need thiols or limited dichalcogenides. It is more desirable to apply odourless and easily prepared thiosulfonates and seleniumsulfonates to construct C-S and C-Se bonds.[9] Recently, we developed a Ni-catalyzed reductive cross-coupling of alkyl bromides with sulfonothioates or seleniumsulfonates to synthesize sulfides and selenides (Scheme 1, c).[10] The key process for the reaction is that an alkyl radical reacts with Ni^{II} intermediate, which is in situ generated by the oxidative addition of sulfonothioate with Ni^0 . We reasoned that the carbon radical could be generated from cycloketone oxime esters through C-C bond cleavage, which could react with Ni^{II} intermediate generated by the oxidative addition sulfonothioate with Ni^0. Herein, we report a Ni-catalyzed ring opening and subsequently reductive cross-coupling of cycloketone oxime esters with thiosulfonate or seleniumsulfonate to afford a variety of cyano-containing sulfides and selenides (Scheme 1, d).

2. RESULTS AND DISCUSSION

The initial study was focused on the reaction of cyclobutanone *O*-(4-(trifluoromethyl)benzoyl) oxime **1a** with *S*-phenyl benzenesulfonothioate **2a** in the presence of $NiBr_2$ (10 mol%), 2,9-dimethyl-1,10-phenanthroline **L1** (15 mol%), and Mn powder (2 equiv) in N,N-dimethylformamide (DMF) at 40 °C for 24 h. To our delight, the desired product 4-(phenylthio)butanenitrile **3a** was obtained in 67% yield (Table 1, entry 1). It was found that no desired product was obtained at all in the absence of $NiBr_2$, Mn or ligand (Table 1, entries 2-4). These results clearly indicate that the nickel catalyst, reductant and ligand are necessary for this reaction. Other Ni-salts such as NiF_2, $NiCl_2$, NiI_2, $Ni(PPh_3)_2Cl_2$, $Ni(acac)_2$ or $Ni(OAc)_2$ were ineffective for this reaction. (Table 1, entries 5-10) Notably, the ligand was critical for this transformation. Other phenanthroline-based ligands **L2-5**, bipyridine **L6**, phenanthrenequinone **L7** and terpyridine **L8** were also applied to the reaction (Table 1, entries 11-17). **L1** is the best choice to afford the designed product. Replacing Mn by Zn as reducing reagent resulted in a lower yield (Table 1, entry 18). When other solvents such as DMA and DMSO were used, the reaction afforded the cross-coupled product **3a** in lower yields (entries 19-20). *O*-Acyl oximes bearing different substituted aryl groups including C_6H_5 and C_6F_5 led to **3a** in 51% and 64% yields, respectively (entries 21-22). The yield of **3a** increased to 95% with a higher oxime ester loading (entry 23).

Table 1. Optimization of the Reaction Conditions. [a]



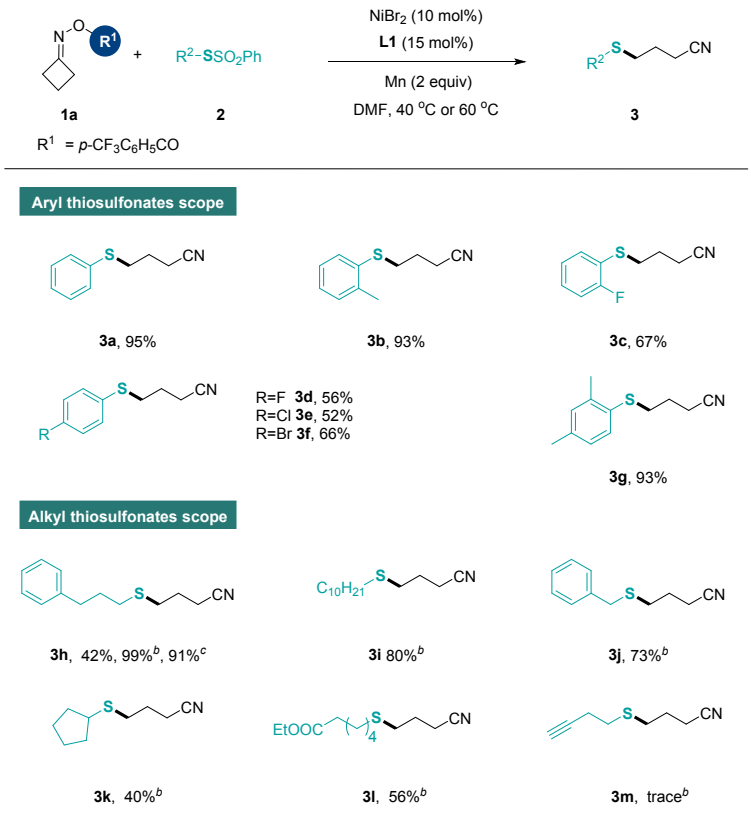
Entry	[Ni]	Ligand	Solvent	Reductant	R	yield (%)[c]
1	$NiBr_2$	**L1**	DMF	Mn	R^1	67
2	-	**L1**	DMF	Mn	R^1	0
3	$NiBr_2$	**L1**	DMF	-	R^1	0
4	$NiBr_2$	-	DMF	Mn	R^1	0
5	NiF_2	**L1**	DMF	Mn	R^1	0
6	$NiCl_2$	**L1**	DMF	Mn	R^1	0
7	NiI_2	**L1**	DMF	Mn	R^1	6
8	$Ni(PPh_3)_2Cl_2$	**L1**	DMF	Mn	R^1	39
9	$Ni(acac)_2$	**L1**	DMF	Mn	R^1	24
10	$Ni(OAc)_2$	**L1**	DMF	Mn	R^1	0
11	$NiBr_2$	**L2**	DMF	Mn	R^1	25
12	$NiBr_2$	**L3**	DMF	Mn	R^1	53

13	$NiBr_2$	**L4**	DMF	Mn	R^1	32
14	$NiBr_2$	**L5**	DMF	Mn	R^1	24
15	$NiBr_2$	**L6**	DMF	Mn	R^1	61
16	$NiBr_2$	**L7**	DMF	Mn	R^1	16
17	$NiBr_2$	**L8**	DMF	Mn	R^1	35
18	$NiBr_2$	**L1**	DMF	Zn	R^1	25
19	$NiBr_2$	**L1**	DMA	Mn	R^1	52
20	$NiBr_2$	**L1**	DMSO	Mn	R^1	58
21	$NiBr_2$	**L1**	DMF	Mn	R^2	51
22	$NiBr_2$	**L1**	DMF	Mn	R^3	64
23[b]	**$NiBr_2$**	**L1**	**DMF**	**Mn**	**R^1**	**95**

[a] Standard conditions: **1a** (0.1 mmol), **2a** (0.1 mmol), $NiBr_2$ (10 mol%), Mn (2 equiv), liand (15 mol%), solvent (0.5 mL) at 40 °C under N_2 for 24h. [b] 0.2 mmol **2a** was used. [c] Yields of isolated product.

With the optimal reaction conditions in hand, we first explored the scope of various sulfonothioates in this Nickel-catalyzed reductive cross-coupling reaction (Scheme 2).

Scheme 2. Scope of thiosulfonates. [a,d]

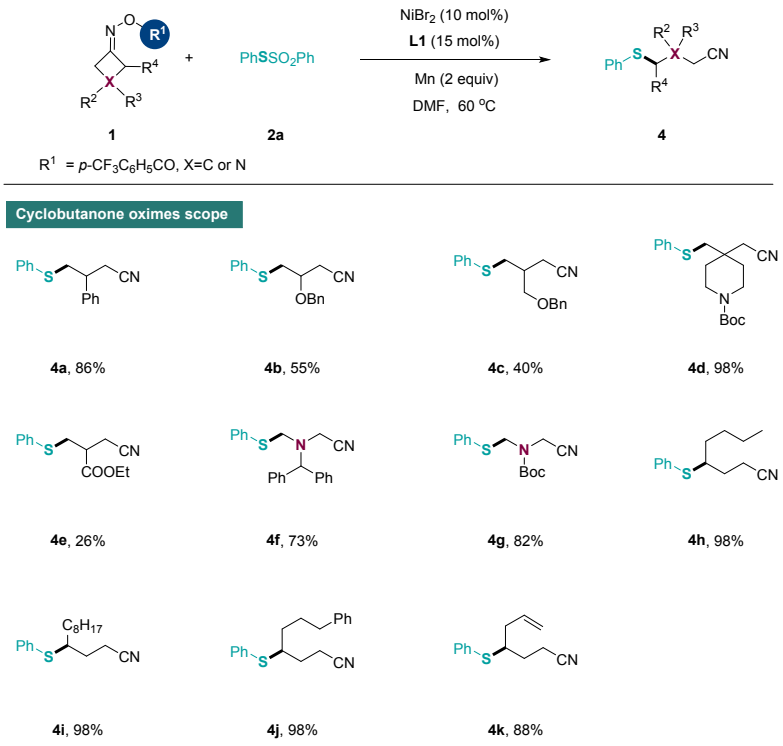


[a] Standard conditions: **1a** (0.4 mmol), **2** (0.2 mmol), $NiBr_2$ (10 mol%), **L1** (15 mol%) Mn (2 equiv), DMF (1.0 mL) at 40 °C under N_2. [b] At 60 °C [c] At 100 °C [d] Yields of isolated product.

ortho-substituted *S*-aryl benzenesulfonothioates with electron-neutral (Me) groups underwent the transformation smoothly (93% yields). Substrates containing transformable groups such as fluoro, chloro and bromo showed good reactivity, and the corresponding thioethers (**3c-3f**) were obtained in 52-

67% yields. More bulky *S*-(2,6-dimethylphenyl) benzenesulfonothioate **2g** was also suitable, and the desired product **3g** was isolated in up to 93% yield. Thus, a variety of *S*-alkyl benzenesulfonothioates were also investigated and results are summarized in Scheme 2. By contrast, these compounds showed slightly lower reactivity than *S*-aryl benzenesulfonothioates. It was found that higher temperature led to satisfactory results (**4h-4j**). Moreover, the cyanopropyl sulfide product is not limited to the the 1° alkyl sulfide, secondary *S*-alkyl thiosulfonates were also compatible with **1a**. and the 2° alkyl sulfide **3k** was successfully obtained in 40% yield under the modified reaction conditions. It is worth mentioning that substrates bearing functionalized group such as aster gave product in 56% yield (**3l**). However, alkynyl group could not tolerate this condition (**3m**).

Scheme 3. Scope of cyclobutanone oximes. [a] [b]

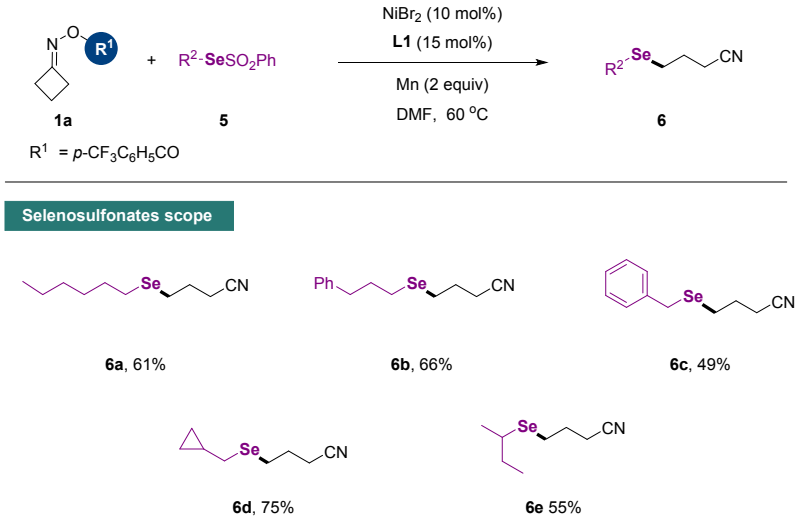


[a] Standard conditions: 1 (0.4 mmol), 2a (0.2 mmol), $NiBr_2$ (10 mol%), L1 (15 mol%) Mn (2 equiv), DMF (1.0 mL) at 40 °C under N_2. [b] Yields of isolated product.

Subsequently, a range of cycloketone oxime esters were tested to react with *S*-phenyl benzenesulfonothioate **2a** (Scheme 3). A variety of 3-aryl, oxybenzyl and alkyl substituted oxime esters were efficiently engaged in this nickel-catalyzed reductive cross-coupling reaction to provide the corresponding thioethers **4a**–**4c** in moderate to good isolated yields (40%-86%). The 3,3-disubstituted substrates **1d** also afforded the target products **4d** in up to 76% yield, respectively. Unfortunately, the reactions of 3-ester oxime esters **1e** with **2a** provided **4e** in 26% yield. In this case, 3-heteroatom was also explored and products **4f** and **4g** were obtained in 73-82% yields. The *α*-substituted cyclobutanone

oxime esters with diverse functional groups, such as *n*-butyl (**1h**), *n*-octyl (**1i**) phenylpropyl (**1j**) and allyl (**1k**), could all undergo the desired pathway to deliver the corresponding thioethers **4h-4k** in 88-98% yield under this conditions.

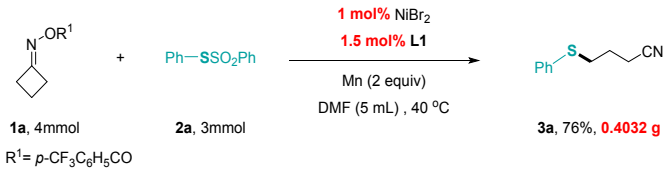
Scheme 4. Scope of selenosulfonates. [a,b]



[a] Standard conditions: **1a** (0.4 mmol), **2** (0.2 mmol), $NiBr_2$ (10 mol%), **L1** (15 mol%) Mn (2 equiv), DMF (1.0 mL) at 60 °C under N_2. [b] Yields of isolated product.

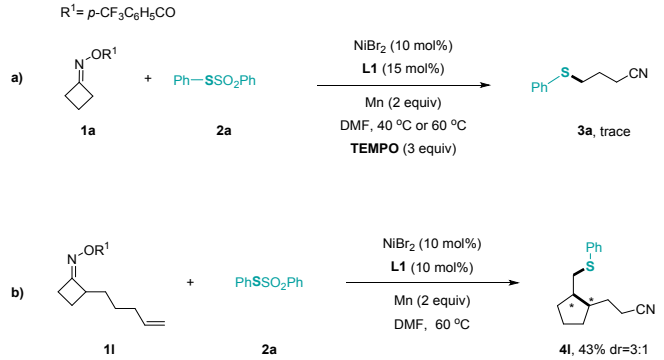
A variety of *Se*-primary alkyl benzenesulfonoselenoates were well tolerated under the standard conditions and produced the corresponding 1° alkyl selenides **6a-6d** in moderate to good yields (49-75%). Additionally, *Se*-secondary alkyl benzenesulfonoselenoates **5e** was also suitable for this transformation under this conditions and afforded corresponding 2° alkyl selenides **6e** in 55% yield (Scheme 3).

Scheme 5. The Ni-catalyst loading could be reduced to 1 mol% without loss of catalytic activity.



To illustrate the application of this reductive cross coupling reactions, the scale-up reaction of **1a** (4 mmol) with **2a** (3 mmol) in the presecne of only 1 mol% $NiBr_2$ was investigated. As shown in Scheme 5, the desired product **3a** was obtained in 76% isolated yield with decreased Ni- catalyst.

Scheme 6. Control experiments.

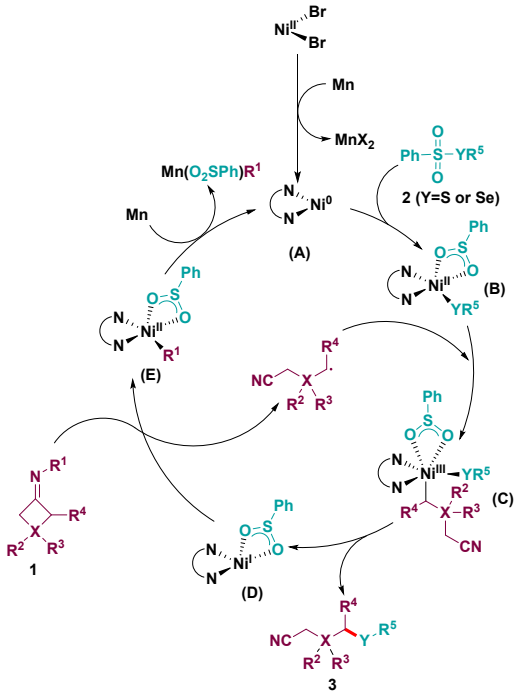


Several radical trapping experiments were conducted to preliminarily probe into the mechanism of the reaction. When TEMPO as radical scavenger was added in this reaction system, no desired product **3a** was observed (Scheme 6, a).

As expected, when cyclobutanone oxime ester **1l** incorporating a bishomoallyl group was used to react with *S*-phenyl benzenesulfonothioate **2a**, a cyclic product **4l** could be afforded with a good diastereomeric ratio (Scheme 6, b). These experiments suggested that a radical intermediate was generated in this transformation.

Based on above experimental results and also inspired by Wang's work[11] and literature reports,[12,13] we proposed the mechanism for this Ni-catalyzed reductive cross-coupling of cycloketone oxime ester with thiosulfonate. (Scheme 7). Initially, the in situ generated active $Ni^0(L)_2$ complex **A** reacts with thiosulfonate **2** to afford R^1S-$Ni^{II}(L)2$ species (**B**) by oxidative addition. **B** recombines rapidly with C-centered radical to form $Ni^{III}(L)_2$ **C**. The cyano-containing sulfides (**3**) is formed by reductive elimination of **C** and a Ni^I $(L)_2$ **D** intermediate is generated. Next, **D** reacts with cycloketone oxime ester **1** to generate the C-centered radical by instant C-C bond cleavage and provide Ni^{II} **E**, which subsequently undergoes an reductive elimination to regenerate the $Ni^0(L)_2$ species **A** for the next catalytic cycle.

Scheme 7. Proposed mechanism.



3. CONCLUSION

In summary, we have developed a Ni-catalyzed reductive cross-coupling of cycloketone oxime ester with thiosulfonate or seleniumsulfonate, which involves C-C bond cleavage and C(sp^3) -S or C(sp^3) -Se bond formation. Notably, all of the *S*-aryl/alkyl sulfonothioate and Se-alkyl seleniumsulfonothioate could be employed in this reaction to produce a variety of 1º, 2º alkyl sulfide, aryl sulfides and 1º, 2º alkyl Selenide through one step. This method showed a wide substrate scope, providing ready access to various cyanopropyl sulfides and cyanopropyl selenides. A mechanism involving iminyl radical-triggered C–C bond cleavage is described. Further studies including detailed mechanistic studies are currently underway.

4. EXPERIMENTAL SECTION

1. General Information All the solvents for routine isolation of products and chromatography were reagent grade. Flash chromatography was performed using silica gel (300−400 mesh) with the indicated solvents. Melting points were recorded on an electrothermal digital melting point apparatus and were uncorrected. IR spectra were recorded on a spectrophotometer using KBr optics. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR) spectrometer using $CDCl_3$ or DMSO-*d*6 as solvent and TMS as internal standard. The ^{1}H NMR data are reported as the chemical shift in parts per million, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant in hertz, and number of protons. High resolution mass spectra were obtained using a high resolution ESI-TOF mass spectrometer and high resolution CI-TOF mass spectrometer.

2.1. General procedures for the synthesis cyclobutanone oximes.
1a-1b, 1d, 1k[14], **1e, 1g**[15] and**1h**[16] were prepared following the reported procedures.
2.2. General procedures for the synthesis thiosulfonate or selenium sulfonate.
2a-2k, 5a[17]**, 5b**[18]**, 5c**[19]**,** and **5d-5e**[20] were prepared following the reported procedures.
2.3. General Procedure for the construction of 3a. In glovebox, an oven-dried screw-capped 8 mL vial equipped with a magnetic stir bar was charged with O-(*p*-CF_3-benzoyl)oxime **1a** (102.8 mg, 0.4 mmol) and *S*-phenyl benzenesulfonothioate **2a** (50.0 mg 0.2 mmol) $NiBr_2$ (4.4 mg, 0.02 mmol), 2,9-dimethyl-1,10-phenanthroline (**L1**, 6.2 mg, 0.03 mmol) and Mn powder (22.0 mg, 0.4 mmol). DMF (1.0 mL)

was added via syringe. The resulting solution was stirred for 24 h at 40 °C (heat source: oil bath). After this time, the crude reaction mixture was diluted with ethyl acetate (100 mL) and washed with water (20 mL × 3). The organic layer was dried over Na_2SO_4, filtered, and evaporation of the solvent under reduced pressure gave a crude product which was purified by silica gel (200–300 mesh) column chromatography by using hexane : EtOAc (20 : 1) as an eluent to afford the colorless oil product **3a** (34.6mg, 95%).

2.4. General Procedure for the construction of 3h. In glovebox, an oven-dried screw-capped 8 mL vial equipped with a magnetic stir bar was charged with O-(*p*-CF_3-benzoyl)oxime **1a** (102.8 mg, 0.4 mmol) and *S*-(3-phenylpropyl) benzenesulfonothioate **2h** (58.4 mg 0.2 mmol) $NiBr_2$ (4.4 mg, 0.02 mmol), 2,9-dimethyl-1,10-phenanthroline (**L1**, 6.2 mg, 0.03 mmol) and Mn powder (22.0 mg, 0.4 mmol). DMF (1.0 mL) was added via syringe. The resulting solution was stirred for 24 h at 60 °C (heat source: oil bath). After this time, the crude reaction mixture was diluted with ethyl acetate (100 mL) and washed with water (20 mL × 3). The organic layer was dried over Na_2SO_4, filtered, and evaporation of the solvent under reduced pressure gave a crude product which was purified by silica gel (200–300 mesh) column chromatography by using hexane : EtOAc (20 : 1) as an eluent to afford the colorless oil product **3h** (34.4mg, 99%).

2.5 General Procedure for the construction of 1c and 1f

The ketone (5.0 mmol, 1.0 eq.) and hydroxylamine hydrochloride (5.5 mmol, 1.5 eq.) were placed in a 100 mL flask equipped with stirrer. The pH of the solution was held at 7–8 by adding saturated aq. sodium carbonate (10 mL). The resulting solution was stirred at 40°C. After extraction with ether, the solution was dried over Na_2SO_4 and evaporated to provide cyclobutanone oxime which were used in the next step without further purification; To a mixture of cyclobutanone oxime (1.0 equiv.), triethylamine (2.0 equiv.) and DCM (0.5 M) in a 50 mL flask was added *p*-CF_3 benzoyl chloride (1.5 equiv.) at 0 °C. After 3 h, water was added to the above solution, and the mixture was diluted with diethyl ether. The organic layer was washed with water and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was subjected to column chromatography on SiO_2 with pentane/EtOAc as an eluent to give cyclobutanone oxime esters.

2.6 General Procedure for the construction of 1i, 1j and 1l

The cyclobutanone (5.0 mmol, 1.0 equiv.) and hydroxylamine hydrochloride (5.5 mmol, 1.5 equiv.) were placed in a 100 mL flask equipped with stirrer. The pH of the solution was held at 7–8 by adding saturated aq. sodium carbonate (10 mL). The resulting solution was stirred at 80°C. After extraction with ether, the organic layer was washed with water and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was subjected to column chromatography to give cyclobutanone oxime as a white solid; Cyclobutanone oxime (1.0 equiv.) in absolute dry THF (0.5 M) was added nBuLi (2.0 equiv.) slowly at 0 °C, then continuing to stir for another 15 min at this temperature for the formation of syn dianion. Then RX (1.0 equiv.) was added dropwise at 0 °C, then the mixture was warmed to RT for 2 h. Subsequently, the reaction was quenched by cold water, and the mixture was diluted with EtOAc. The organic layer was washed with water and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was subjected to column chromatography on SiO_2 with EtOAc– pentane as an eluent to give *α*-substituted cyclobutanone oximes; To a mixture of *α*-substituted cyclobutanone oxime (1.0 equiv.), triethylamine (2.0 equiv.) and DCM (0.5 M) in a 50 mL flask was added *p*-CF_3 benzoyl chloride (1.5 equiv.) at 0 °C. After 3 h, water was added to the above solution, and the mixture was diluted with diethyl ether. The organic layer was washed with water and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was subjected to column chromatography on SiO_2 with pentane/EtOAc as an eluent to give *α*-substituted cyclobutanone oxime esters.

3-((Benzyloxy)methyl)cyclobutan-1-one O-(4-(trifluoromethyl)benzoyl) oxime ***(1c)*** White solid (1.36 g, 75%), Following the reported procedures[14]; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (d, J = 8.1 Hz, 2H), 7.72 (d, J = 8.5 Hz, 2H), 7.51 – 7.19 (m, 5H), 4.56 (s, 2H), 3.57 (dq, J = 6.8, 3.3 Hz, 2H), 3.32 – 3.14 (m, 2H), 3.03 – 2.89 (m, 2H), 2.86 – 2.66 (m, 1H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 167.8, 162.8, 138.0, 134.7 (q, $J_{C\text{-}F}$ = 32.5 Hz), 132.4, 132.4, 130.1, 128.6, 127.9, 127.8, 125.6 (q, $J_{C\text{-}F}$ = 3.6 Hz), 123.6 (q, $J_{C\text{-}F}$ = 271.5 Hz), 73.3, 72.4, 34.8, 28.0; ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.2. HRMS (ESI) *m/z*: calcd for $C_{20}H_{18}F_3NO_3Na$: $(M+Na)^+$ 400.1131, found: 400.1141.

1-Benzhydrylazetidin-3-one O-(4-(trifluoromethyl)benzoyl oxime ***(1f)*** White solid (1.48 g, 70%), Following the reported procedures[14]; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, J = 8.1 Hz, 2H), 7.68 (d, J = 8.3 Hz, 2H), 7.52 – 7.43 (m, 4H), 7.32 (t, J = 7.4 Hz, 4H), 7.52 – 7.20 (m, 2H), 4.59 (s, 1H), 4.22 – 4.08 (m, 4H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 162.7, 162.6, 141.6, 135.1 (q, $J_{C\text{-}F}$ = 32.7 Hz),132.0, 130.2, 129.0, 128.0, 127.4, 125.7 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.6 (q, $J_{C\text{-}F}$ = 271.4 Hz), 61.0, 60.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.2. HRMS (ESI) *m/z*: calcd for $C_{24}H_{19}F_3N_2O_2Na$: $(M+Na)^+$ 447.1291, found: 447.1289.

2-Octylcyclobutan-1-one O-(4-(trifluoromethyl)benzoyl) oxime ***(1i)*** Yellow oil (1.40 g, 76%), Following the reported procedures[14]; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 (d, J = 8.1 Hz, 2H), 7.74 (d, J = 8.2 Hz, 2H), 3.64 – 3.38 (m, 1H), 3.18 – 2.87 (m, 2H), 2.34 – 2.11 (m, 1H), 2.06 – 1.88 (m, 1H), 1.87– 1.59 (m, 2H), 1.54 – 1.09 (m, 12H), 0.86 (t, J = 6.9 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 172.1, 162.7, 134.4 (q, $J_{C\text{-}F}$ = 32.5 Hz), 132.4, 129.8, 125.4 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.4 (q, $J_{C\text{-}F}$ = 271.0 Hz), 46.2, 31.7, 31.2, 29.3, 29.2, 29.1, 28.8, 26.5, 22.5, 19.7, 13.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.4. HRMS (ESI) *m/z*: calcd for $C_{20}H_{26}F_3NONa$: $(M+Na)^+$ 392.1808, found: 392.1807.

2-(3-Phenylpropyl)cyclobutan-1-one O-(4-(trifluoromethyl)benzoyl) oxime ***(1j)*** Yellow oil (1.44 g, 77%), Following the reported procedures[14]; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, J = 8.1 Hz, 2H), 7.66 (d, J = 8.3 Hz, 2H), 7.32 – 6.85 (m, 5H), 3.66 – 3.33 (m, 1H), 3.23 – 2.86 (m, 2H), 2.64 (t, J = 7.0 Hz, 2H), 2.29 – 2.12 (m, 1H), 2.09 – 1.88 (m, 1H), 1.88 – 1.60 (m, 4H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 172.1, 1631, 141.7, 134.7 (q, $J_{C\text{-}F}$ = 32.7 Hz), 132.5, 130.0, 128.5, 128.5, 126.1, 125.7 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.7 (q, $J_{C\text{-}F}$ = 271.3 Hz), 46.3, 35.6, 30.9, 29.1, 28.4, 19.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.2. HRMS (ESI) *m/z*: calcd for $C_{21}H_{20}F_3NO_2Na$: $(M+Na)^+$ 398.1338, found: 398.1330.

2-(Pent-4-en-1-yl)cyclobutan-1-one O-(4-(trifluoromethyl)benzoyl) oxime ***(1l)*** Yellow oil (0.89 g, 55%), Following the reported procedures[14]; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, J = 8.1 Hz, 2H), 7.62 (d, J = 8.2 Hz, 2H), 6.00 – 5.58 (m, 1H), 5.04 – 4.73 (m, 2H), 3.58 – 3.35 (m, 1H), 3.13 – 2.77 (m, 2H), 3.18 – 2.04 (m, 1H), 2.03 – 1.82 (m, 3H), 1.76 – 1.51 (m, 2H), 1.51 – 1.16 (m, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 171.99, 162.76, 137.94, 134.5 (q, $J_{C\text{-}F}$ = 32.6 Hz), 132.29, 129.83, 125.0 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.4 (q, $J_{C\text{-}F}$ = 271.1 Hz), 114.82, 45.99, 33.17, 30.53, 28.77, 25.61, 19.64; ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.3. HRMS (ESI) *m/z*: calcd for $C_{17}H_{18}F_3NO_2Na$: $(M+Na)^+$ 348.1182, found: 348.1192.

Ethyl 6-((phenylsulfonyl)thio)hexanoate ***(2l)*** Colourless oil (1.30 g, 82%), Following the reported procedures[10]; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, J = 8.0 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.57 (t, J = 7.7 Hz, 2H), 4.11 (q, J = 6.8 Hz, 2H), 3.00 (t, J = 7.3 Hz, 2H), 2.24 (t, J = 7.4 Hz, 2H), 1.59 (dp, J = 22.8, 7.4 Hz, 4H), 1.33 (p, J = 7.8 Hz, 2H), 1.28 – 1.17 (m, 3H); ^{13}C{^{1}H}NMR (101 MHz,

$CDCl_3$) δ 173.3, 144.8, 133.7, 129.3, 126.9, 60.3, 35.8, 33.9, 28.3, 27.9, 24.2, 14.2. HRMS (ESI) *m/z*: calcd for $C_{14}H_{20}NO_4S_2Na$: $(M+Na)^+$ 399.0695, found: 399.0695.

S-(but-3-yn-1-yl) benzenesulfonothioate ***(2m)*** Colourless oil (0.81 g, 72%), Following the reported procedures[10]; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 7.89 (m, 2H), 7.73 – 7.63 (m, 1H), 7.61 – 7.48 (m, 2H), 3.14 (td, J = 7.2, 1.3 Hz, 2H), 2.60 – 2.49 (m, 2H), 2.02 (t, J = 2.6 Hz, 1H); $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$) δ 144.6, 134.0, 129.5, 127.09, 80.8, 70.7, 34.6, 19.3. HRMS (ESI) *m/z*: calcd for $C_{10}H_{10}O_2S_2Na$: $(M+Na)^+$ 249.0014, found: 249.0019.

4-(Phenylthio)butanenitrile ***(3a)*** Yellow oil (34.6 mg, 95%), IR (neat, ν, cm^{-1}): 3059, 2929, 1733, 1583, 1480, 1439, 1242, 1025, 738 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.24 (m, 4H), 7.24 – 7.18 (m, 1H), 3.02 (t, J = 6.9 Hz, 2H), 2.49 (t, J = 7.1 Hz, 2H), 1.94 (m, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 134.8, 130.1, 129.2, 126.8, 119.1, 32.6, 24.9, 16.0 ppm. HRMS (ESI) *m/z*: calcd for $C_{10}H_{11}NSNa$: $(M+Na)^+$ 200.0504, found: 200.0503.

4-(O-tolylthio)butanenitrile ***(3b)*** Yellow oil (35.5 mg, 93%), IR (neat, ν, cm^{-1}): 2925, 2246, 1589, 1469, 1424, 1065, 1048, 743 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.26 (m, 1H), 7.22 – 7.09 (m, 3H), 3.00 (t, J = 6.9 Hz, 2H), 2.51 (t, J = 7.1 Hz, 2H), 2.39 (s, 3H), 1.96 (p, J = 7.0 Hz, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 138.4, 134.1, 130.5, 129.1, 126.7, 126.6, 119.1, 31.8, 24.9, 20.5, 16.2 ppm. HRMS (CI) *m/z*: calcd for $C_{11}H_{14}NS$: $(M+H)^+$ 192.0841, found: 192.0853.

4-((2-Fluorophenyl)thio)butanenitrile ***(3c)*** Yellow oil (26.1 mg, 67%), IR (neat, ν, cm^{-1}): 2928, 2247, 1570, 1446, 1219, 1072, 819, 750 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.23 (m, 1H), 7.22-7.16 (m, 1H), 7.09 – 6.92 (m, 2H), 2.93 (t, J = 6.9 Hz, 2H), 2.45 (t, J = 7.1 Hz, 2H), 1.85 (q, J = 7.0 Hz, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 162.0 (d, $J_{C\text{-}F}$= 244.2 Hz), 133.4 (d, $J_{C\text{-}F}$= 1.2 Hz), 129.5 (d, $J_{C\text{-}F}$= 7.9 Hz),124.8 (d, $J_{C\text{-}F}$=3.7 Hz), 121.3 (d, $J_{C\text{-}F}$= 17.6 Hz), 119.0, 116.0 (d, $J_{C\text{-}F}$= 225.0 Hz), 32.4, 25.0, 15.9 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.7. HRMS (CI) *m/z*: calcd for $C_{10}H_{11}FNS$: $(M+H)^+$ 196.0591, found: 196.0598.

4-((4-Fluorophenyl)thio)butanenitrile ***(3d)*** Yellow oil (21.8 mg, 56%), IR (neat, ν, cm^{-1}): 2927, 2247, 1589, 1489, 1220, 1157, 1090, 824 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.29 (m, 2H), 7.12 – 6.86 (m, 2H), 2.98 (t, J = 6.9 Hz, 2H), 2.51 (t, J = 7.1 Hz, 2H), 1.92 (p, J = 7.0 Hz, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 162.2 (d, $J_{C\text{-}F}$= 246.0 Hz), 133.3 (d, $J_{C\text{-}F}$= 8.0 Hz), 129.6 (d, $J_{C\text{-}F}$= 3.1 Hz), 119.0, 116.3 (d, $J_{C\text{-}F}$= 21.7 Hz), 33.9, 24.8, 15.9 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.3. HRMS (CI) *m/z*: calcd for $C_{10}H_{11}FNS$: $(M+H)^+$ 196.0591, found: 196.0596.

4-((4-Chlorophenyl)thio)butanenitrile ***(3e)*** Yellow (21.9 mg, 52%), IR (neat, ν, cm^{-1}): 2927, 2247, 1668, 1475, 1389, 1093, 1010, 811 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.28 (s, 4H), 3.01 (t, J = 6.9 Hz, 2H), 2.50 (t, J = 7.0 Hz, 2H), 1.94 (p, J = 7.0 Hz, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 133.4, 132.9, 131.5, 119.0, 32.9, 24.8, 16.0 ppm. HRMS (ESI) *m/z*: calcd for $C_{10}H_{11}ClNS$: $(M+H)^+$ 212.0295, found: 212.0285.

4-((4-Bromophenyl)thio)butanenitrile ***(3f)*** Yellow (33.7 mg, 66%), IR (neat, ν, cm^{-1}): 2925, 2246, 1472, 1090, 1005, 806 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.38 (m, 2H), 7.25 – 7.18 (m, 2H), 3.02 (t, J = 6.9 Hz, 2H), 2.51 (t, J = 7.0 Hz, 2H), 1.95 (p, J = 7.0 Hz, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 134.1, 132.3, 131.6, 120.8, 119.0, 32.7, 24.8, 16.1 ppm. HRMS (CI) *m/z*: calcd for $C_{10}H_{11}BrNS$: $(M+H)^+$ 255.9790, found: 255.9796.

4-((2,4-Dimethylphenyl)thio)butanenitrile ***(3g)*** Yellow oil (38.1 mg, 93%), IR (neat, ν, cm^{-1}): 2921, 2246, 2246, 1477, 1444, 1057, 807 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.22 (d, J = 7.9 Hz, 1H), 7.06 – 6.93 (m, 2H), 2.94 (t, J = 6.9 Hz, 2H), 2.50 (t, J = 7.1 Hz, 2H), 2.37 (s, 3H), 2.29 (s, 3H), 1.92 (p, J = 7.0 Hz, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 139.1, 137.0, 131.5, 130.7, 130.2, 127.4, 119.2, 32.5, 24.9, 21.0, 20.6, 16.1 ppm. HRMS (CI) *m/z*: calcd for $C_{12}H_{16}NS$: $(M+H)^+$ 206.0998, found: 206.1008.

4-((3-Phenylpropyl)thio)butanenitrile ***(3h)*** Yellow oil (43.4 mg, 99%), IR (neat, ν, cm^{-1}): 2925, 2246, 1496, 1453, 744, 699 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.28 (t, J = 7.3 Hz, 2H), 7.18 (t, J = 7.6 Hz, 3H), 2.71 (t, J = 7.5 Hz, 2H), 2.62 (t, J = 6.9 Hz, 2H), 2.52 - 2.45 (m, 4H), 1.89 (m, 4H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 141.3, 128.5, 128.5, 126.0, 119.2, 34.7, 31.3, 31.0, 30.5, 25.2, 16.0 ppm. HRMS (ESI) *m/z*: calcd for $C_{13}H_{17}NSNa$: $(M+Na)^+$ 242.0974, found: 242.0963.

4-(Decylthio)butanenitrile ***(3i)*** Yellow oil (38.6 mg, 80%), IR (neat, ν, cm^{-1}): 2922, 2853, 2247, 2656, 1457, 1365, 1260, 1099, 721 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 2.64 (t, J = 6.9 Hz, 2H), 2.53 - 2.49 (m, 4H), 1.94 (p, J = 7.0 Hz, 2H), 1.57 (q, J = 7.7 Hz, 2H), 1.27 (s, 14H), 0.88 (t, J = 6.7 Hz, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 119.3, 32.2, 32.0, 30.7, 29.7, 29.6, 29.6, 29.4, 29.3, 29.0, 25.4, 22.8, 16.1, 14.2 ppm. HRMS (ESI) *m/z*: calcd for $C_{14}H_{27}NSNa$: $(M+Na)^+$ 264.1756, found: 264.1740.

4-(Benzylthio)butanenitrile ***(3j)*** Yellow oil (27.9 mg, 73%), IR (neat, ν, cm^{-1}): 2921, 2246, 1494, 1453, 1421, 1241, 1071, 1027, 700 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.22 (m, 5H), 3.71 (s, 2H), 2.53 (t, J = 6.9 Hz, 2H), 2.42 (t, J = 7.1 Hz, 2H), 1.85 (p, J = 7.0 Hz, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 138.0, 129.0, 128.7, 127.3, 119.3, 36.3, 29.9, 25.0, 16.1 ppm. HRMS (CI) *m/z*: calcd for $C_{11}H_{14}NS$: $(M+H)^+$ 192.0841, found: 192.0850.

4-(Cyclopentylthio)butanenitrile ***(3k)*** Yellow oil (13.5 mg, 40%), IR (neat, ν, cm^{-1}): 2952, 2867, 2246, 1651, 1448, 1243, 935 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 3.08 (p, J = 7.0 Hz, 1H), 2.67 (t, J = 6.9 Hz, 2H), 2.52 (t, J = 7.1 Hz, 2H), 1.97 (dp, J = 21.0, 7.0, 6.3 Hz, 4H), 1.81 – 1.68 (m, 2H), 1.63 – 1.42 (m, 4H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 119.4, 43.9, 33.9, 30.5, 25.5, 24.8, 16.2 ppm. HRMS (CI) *m/z*: calcd for $C_9H_{16}NS$: $(M+H)^+$ 170.0998, found: 170.1008.

Ethyl 6-((3-cyanopropyl)thio)hexanoate ***(3l)*** Yellow oil (27 mg, 56%), IR (neat, ν, cm^{-1}): 2933, 2859, 2246, 1728, 1655, 1447, 1422, 1371, 1257, 1178, 1126, 1098, 858, 736 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 4.13 (q, J = 7.1 Hz, 2H), 2.64 (t, J = 6.9 Hz, 2H), 2.52 (t, J = 7.2 Hz, 4H), 2.30 (t, J = 7.5 Hz, 2H), 1.93 (p, J = 7.0 Hz, 2H), 1.71 – 1.54 (m, 4H), 1.48 – 1.37 (m, 2H), 1.26 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$) δ 173.6, 119.3, 60.3, 34.2, 31.9, 30.7, 29.3, 28.3, 25.3, 24.6, 16.1, 14.3. HRMS (ESI) *m/z*: calcd for $C_{12}H_{21}NO_2SNa$: $(M+Na)^+$ 266.1185 , found: 266.1196.

3-Phenyl-4-(phenylthio)butanenitrile ***(4a)*** Yellow oil (43.5 mg, 86%), IR (neat, ν, cm^{-1}): 3060, 3029, 2921, 2246, 1783, 1582, 1480, 1025, 738, 690 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.26 (m, 7H), 7.26 – 7.17 (m, 3H), 3.33 (dd, J = 13.4, 5.8 Hz, 1H), 3.24 - 3.19 (m, 1H), 3.16-3.09 (m, 1H), 2.94 – 2.70 (m, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 140.3, 134.9, 130.2, 129.3, 129.1, 128.1, 127.2, 127.0, 118.2, 41.5, 39.0, 23.3 ppm. HRMS (CI) *m/z*: calcd for $C_{16}H_{16}NS$: $(M+H)^+$ 254.0998, found: 254.1013.

3-(Benzyloxy)-4-(phenylthio)butanenitrile ***(4b)*** Yellow oil (31.1 mg, 55%), IR (neat, ν, cm^{-1}): 3061, 3031, 2927, 2869, 2250, 1583, 1439, 1415, 1088, 1066, 1025, 736 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.11 (m, 10H), 4.59 (s, 2H), 3.80 - 3.74 (m, 1H), 3.25 (dd, J = 14.1, 4.8 Hz, 1H), 3.01 (dd, J = 14.1, 7.7 Hz, 1H), 2.81 – 2.61 (m, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 137.1, 134.8, 130.0, 129.4,

128.7, 128.3, 128.1, 127.0, 117.3, 73.6, 72.3, 37.3, 22.5 ppm. HRMS (ESI) *m/z*: calcd for $C_{17}H_{17}NOSNa$: $(M+Na)^+$ 306.0923, found: 306.0922.

4-(Benzyloxy)-3-((phenylthio)methyl)butanenitrile ***(4c)*** Yellow oil. (23.8 mg, 40%), IR (neat, *v*, cm^{-1}): 2923, 2860, 2246, 1583, 1480, 1439, 1364, 1099, 1025, 736 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.16 (m, 10H), 4.48 (s, 2H), 3.57 (qd, J = 9.5, 5.4 Hz, 2H), 3.11 (dd, J = 13.8, 6.4 Hz, 1H), 2.94 (dd, J = 13.8, 7.6 Hz, 1H), 2.63 (d, J = 6.9 Hz, 2H), 2.23 - 2.17 (m, 1H); $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$) δ 137.8, 135.1, 130.0, 129.3, 128.6, 128.0, 127.8, 126.8, 118.3, 73.5, 70.2, 36.3, 34.9, 18.9 ppm. HRMS (ESI) *m/z*: calcd for $C_{18}H_{19}NOSNa$: $(M+Na)^+$ 320.1080, found: 320.1077.

Tert-butyl 4-(cyanomethyl)-4-((phenylthio)methyl)piperidine-1-carboxylate ***(4d)*** Yellow oil (67.8 mg, 98%), IR (neat, *v*, cm^{-1}): 2975, 2929, 2861, 1783, 1683, 1478, 1418, 1365, 1245, 1148, 972, 741, 690 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.37 (m, 2H), 7.36 – 7.07 (m, 3H), 3.42 (m, 2H), 3.34 (m, 2H), 3.15 (s, 2H), 2.59 (s, 2H), 1.64 (tt, J = 13.8, 9.2 Hz, 4H), 1.47 (s, 9H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 154.7, 135.8, 130.8, 129.3, 127.2, 117.2, 80.0, 56.5, 42.3, 36.6, 33.8, 28.5, 26.0 ppm. HRMS (ESI) *m/z*: calcd for $C_{19}H_{26}N_2O_2SNa$: $(M+Na)^+$ 369.1607, found: 369.1607.

Methyl 3-cyano-2-((phenylthio)methyl)propanoate ***(4e)*** Yellow oil (12.9 mg, 26%), IR (neat, *v*, cm^{-1}): 2954, 2250, 1734, 1438, 1198, 1025, 829, 741, 691 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.13 (m, 5H), 3.68 (s, 3H), 3.42 (dd, J = 14.1, 5.2 Hz, 1H), 3.14 (dd, J = 14.1, 7.8 Hz, 1H), 3.02 – 2.86 (m, 1H), 2.86 – 2.75 (m, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 171.3, 133.8, 131.0, 129.4, 127.6, 117.4, 52.8, 41.5, 35.2, 18.3 ppm. HRMS (CI) *m/z*: calcd for $C_{12}H_{14}NO_2S$: $(M+H)^+$ 236.0740, found: 236.0736.

2-(Benzhydryl((phenylthio)methyl)amino)acetonitrile ***(4f)*** Yellow oil (50.2 mg, 73%), IR (neat, *v*, cm^{-1}): 3061, 3028, 2935, 2836, 2251, 1809, 1584, 1492, 1454, 1273, 1132, 1075, 908, 730, 693 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.36 (m, 2H), 7.34 – 7.16 (m, 13H), 4.78 (s, 1H), 4.25 (s, 2H), 3.77 (s, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 140.5, 134.6, 133.0, 129.2, 129.1, 128.0, 127.8, 127.9, 115.8, 71.3, 59.5, 38.8 ppm. HRMS (CI) *m/z*: calcd for $C_{22}H_{21}N_2S$: $(M+H)^+$ 345.1420, found: 345.1438.

Tert-butyl (cyanomethyl)((phenylthio)methyl)carbamate ***(4g)*** White solid (45.6 mg, 82%), mp: 66.2-69.0 °C. IR (neat, *v*, cm^{-1}): 2977, 2913, 1686, 1472, 1441, 1392, 1242, 1184, 926, 873, 750, 678 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.39 (m, 2H), 7.29 (d, J = 13.3 Hz, 3H), 4.81 (d, J = 19.6 Hz, 2H), 4.24 (d, J = 69.5 Hz, 2H), 1.30 (d, J = 67.4 Hz, 9H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 153.3, 134.1, 132.5, 132.3, 129.3, 128.6, 127.9, 115.8, 82.6, 82.2, 53.5, 52.2, 34.04, 33.1, 28.0, 27.8 ppm. HRMS (ESI) *m/z*: calcd for $C_{14}H_{18}N_2O_2SNa$: $(M+Na)^+$ 301.0981, found: 301.0969.

4-(Phenylthio)octanenitrile ***(4h)*** Yellow oil (45.7 mg, 98%), IR (neat, *v*, cm^{-1}): 2956, 2929, 2859, 2246, 1583, 1477, 1438, 1091, 1068, 1024, 744, 692 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 6.99 (m, 5H), 3.04 (p, J = 7.3, 6.8 Hz, 1H), 2.60 – 2.39 (m, 2H), 1.92 - 1.83 (m, 1H), 1.80 – 1.64 (m, 1H), 1.59 – 1.31 (m, 4H), 1.23 (dp, J = 13.3, 6.8, 6.4 Hz, 2H), 0.82 (t, J = 7.3 Hz, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 133.8, 132.9, 129.2, 127.6, 119.6, 48.4, 34.3, 30.3, 29.1, 22.5, 14.8, 14.0. HRMS (ESI) *m/z*: calcd for $C_{14}H_{19}NSNa$: $(M+Na)^+$ 256.11130, found: 256.1129.

4-(Phenylthio)dodecanenitrile ***(4i)*** Yellow oil (56.6 mg, 98%), IR (neat, *v*, cm^{-1}): 2924, 2854, 2247, 1584, 1466, 1366, 1090, 1025, 745, 692 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.36 (m, 2H), 7.34 – 7.24 (m, 3H), 3.15 - 3.08 (m, 1H), 2.70 – 2.46 (m, 2H), 2.03 – 1.89 (m, 1H), 1.84 - 1.75 (m, 1H), 1.61 – 1.44 (m, 4H), 1.26 (s, 10H), 0.88 (t, J = 6.9 Hz, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 133.9, 132.9, 129.2, 127.6, 119.6, 48.4, 34.6, 31.9, 30.3, 29.5, 29.4, 29.3, 26.9, 22.8, 14.8, 14.2 ppm. HRMS (ESI) *m/z*: calcd for $C_{18}H_{27}NSNa$: $(M+Na)^+$ 312.1756, found: 312.1746.

7-Phenyl-4-(phenylthio)heptanenitrile ***(4j)*** Yellow oil (57.8 mg, 98%), IR (neat, *v*, cm^{-1}): 2931, 2857, 2245, 2583, 1495, 1452, 1483, 1088, 1025, 744, 693 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.01 (m, 10H), 3.20 – 2.98 (m, 1H), 2.77 – 2.33 (m, 4H), 1.98 – 1.66 (m, 4H), 1.65 – 1.46 (m, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 141.8, 133.5, 133.1, 129.2, 128.5, 127.7, 126.0, 119.5, 48.3, 35.5, 33.9, 30.3, 28.5, 14.8 ppm. HRMS (CI) *m/z*: calcd for $C_{19}H_{22}NS$: $(M+H)^+$ 296.1467, found: 296.1472.

4-(Phenylthio)hept-6-enenitrile ***(4k)*** Yellow oil (42.6 mg, 88%), IR (neat, *v*, cm^{-1}): 3075, 2926, 2247, 2640, 1583, 1475, 1438, 1421, 1024, 993, 918, 744, 691 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.44 - 7.41 (m, 2H), 7.37 – 7.20 (m, 3H), 5.89 - 5.79 (m, 1H), 5.22 – 4.98 (m, 2H), 3.28 – 3.08 (m, 1H), 2.75 – 2.50 (m, 2H), 2.46 - 2.39 (m, 1H), 2.33 - 2.26 (m, 1H), 2.09 – 1.88 (m, 1H), 1.88 – 1.67 (m, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 134.4, 133.4, 133.0, 129.2, 127.8, 119.4, 118.2, 47.5, 39.0, 29.4, 14.9 ppm. HRMS (CI) *m/z*: calcd for $C_{13}H_{16}NS$: $(M+H)^+$ 218.0998, found: 218.1008.

3-(2-((Phenylthio)methyl)cyclopentyl)propanenitrile (4l) Yellow oil (21.1 mg, 43%), IR (neat, *v*, cm^{-1}): 2945, 2868, 2245, 1583, 1479, 1438, 1089, 1025, 737 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.26 (m, 4H), 7.24 – 7.13 (m, 1H), 3.06 - 2.91 (m, 1H), 2.89 – 2,73 (m, 1H), 2.45 – 2.23 (m, 2H), 2.22 – 1.51 (m, 9H), 1.37 – 1.29 (m, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 136.7, 129.2, 128.9, 126.0, 119.7, 44.7, 44.5, 41.7, 41.5, 39.0, 34.7, 32.2, 31.8, 30.8, 30.5, 29.5, 25.5, 23.9, 22.3, 16.2 ppm. HRMS (CI) *m/z*: calcd for $C_{15}H_{20}$: $(M+H)^+$ 246.1311, found: 246.1311.

4-(Hexylselanyl)butanenitrile ***(6a)*** Yellow oil (28.4 mg, 61%), IR (neat, *v*, cm^{-1}): 2924, 2854, 2246, 1451, 1423, 1233, 1189, 724 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 2.67 (t, J = 7.1 Hz, 2H), 2.59 - 2.50 (m, 4H), 2.00 (p, J = 7.1 Hz, 2H), 1.66 (p, J = 7.3 Hz, 2H), 1.46 – 1.15 (m, 6H), 0.89 (t, J = 6.9 Hz, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 119.3, 31.4, 30.6, 29.7, 26.3, 24.6, 22.7, 22.0, 17.3, 14.2 ppm. HRMS (CI) *m/z*: calcd for $C_{10}H_{20}NSe$: $(M+H)^+$ 234.0755, found: 234.0768.

4-((3-Phenylpropyl)selanyl)butanenitrile ***(6b)*** Yellow oil (35.2 mg, 66%), IR (neat, *v*, cm^{-1}): 2926, 2854, 2245, 1495, 1452, 1421, 1234, 1029, 743, 699 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.28 (q, J = 6.7, 6.2 Hz, 2H), 7.19 (t, J = 8.4 Hz, 3H), 2.72 (t, J = 7.5 Hz, 2H), 2.66 (t, J = 7.1 Hz, 2H), 2.57 (t, J = 7.4 Hz, 2H), 2.49 (t, J = 7.1 Hz, 2H), 1.98 (h, J = 7.4 Hz, 4H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 141.3, 128.6, 128.6, 126.1, 119.3, 35.9, 32.1, 26.2, 23.7 22.1, 17.3 ppm. HRMS (ESI) *m/z*: calcd for $C_{13}H_{17}NSeNa$: $(M+Na)^+$ 290.0418, found: 290.0420.

4-(Benzylselanyl)butanenitrile ***(6c)*** Yellow oil (23.4 mg, 49%), IR (neat, *v*, cm^{-1}): 2926, 2245, 1603, 1495, 1452, 1421, 1234, 1029, 743, 699 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.10 (m, 5H), 3.79 (s, 2H), 2.58 (t, J = 7.1 Hz, 2H), 2.41 (t, J = 7.1 Hz, 2H), 1.88 (p, J = 7.1 Hz, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 138.9, 128.9, 128.8, 127.1, 119.2, 27.4, 26.0, 22.1, 17.2 ppm. HRMS (CI) *m/z*: calcd for $C_{11}H_{14}NSe$: $(M+H)^+$ 240.0286, found: 240.0299.

4-((Cyclopropylmethyl)selanyl)butanenitrile ***(6d)*** Yellow oil (30.5 mg, 75%), IR (neat, *v*, cm^{-1}): 3077, 3002, 2860, 2245, 1422, 1208, 1016, 958, 824, 772 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 2.74 (t, J = 7.1 Hz, 2H), 2.60 – 2.46 (m, 4H), 2.02 (p, J = 7.1 Hz, 2H), 1.04 (pt, J

= 7.5, 4.9 Hz, 1H), 0.72 – 0.55 (m, 2H), 0.24 - 0.20 (m, 2H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 119.3, 29.7, 26.4, 21.8, 17.3, 12.1, 6.8 ppm. HRMS (CI) *m/z*: calcd for $C_8H_{14}NSe$: $(M+H)^+$ 204.0286, found: 204.0300.

4-(Sec-butylselanyl)butanenitrile ***(6e)*** Yellow oil (22.6 mg, 55%), IR (neat, *v*, cm^{-1}): 2962, 2924, 2872, 2246, 1450, 1187, 956, 748 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 2.91 (q, J = 6.8 Hz, 1H), 2.68 (t, J = 7.1 Hz, 2H), 2.52 (t, J = 7.0 Hz, 2H), 2.00 (p, J = 7.1 Hz, 2H), 1.72 - 1.59 (m, 2H), 1.43 (t, J = 6.1 Hz, 3H), 0.99 (t, J = 7.4 Hz, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 119.2, 37.4, 30.8, 26.4, 22.0, 20.6, 17.3, 12.3 ppm. HRMS (CI) *m/z*: calcd for $C_8H_{16}NSe$: $(M+H)^+$ 206.0442, found: 206.0455.

ASSOCIATED CONTENT

Supporting Information Available.

The copies of ^1H and ^{13}C NMR spectra of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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