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Preparation and Reactivity of Polyfunctional Zinc and Copper Organometallics Bearing Sulfur Functionalities

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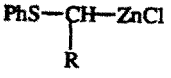
Abstract: *Iodomethylthiobenzoate* ***5*** *and α-chloroalkyl phenyl sulfides* ***6*** *were found to insert zinc dust in THF under very mild conditions (10-25 °C, 0.5-2 h) leading to zinc α-thioorganometallics. After a transmetallation with CuCN•2 LiCl, the corresponding copper reagents* ***8*** *and* ***7*** *reacted with various electrophiles (1-haloalkynes, aldehydes, enones, acyl chlorides, allylic halides, trialkyltin halides) affording polyfunctional thioesters and sulfides of type* ***9*** *or* ***10*** *in excellent yields. Of special interest is that, contrary to lithium α-thiocarbanions, these zinc-copper reagents can bear various functional groups like esters or nitriles. The same approach allowed the preparation of various γ-thio-substituted zinc and copper reagents bearing phenylthio, phenylsulfinyl, or α-(phenylsulfonyl)vinyl functionalities (20-22) which also display a good ability to form new carbon-carbon bonds.*

The development of many new synthetic methods using main group organometallics was stimulated by the applications of sulfur stabilized lithium organometallics in organic chemistry.[1] In this paper we wish to report the preparation of the first polyfunctional zinc and copper organometallic compounds bearing sulfur functionalities in the alpha or gamma position to the carbon-metal bond as well as their reactivity toward typical organic electrophiles. In a preliminary report[2] we showed that a phenylthio group (PhS) and a phenylsulfinyl group (PhS(O)) were tolerated in the zinc insertion forming organometallics such as **1** and **2**.



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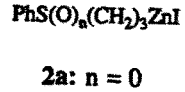
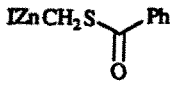


2a: n = 0
2b: n = 1
2c: n = 2



3

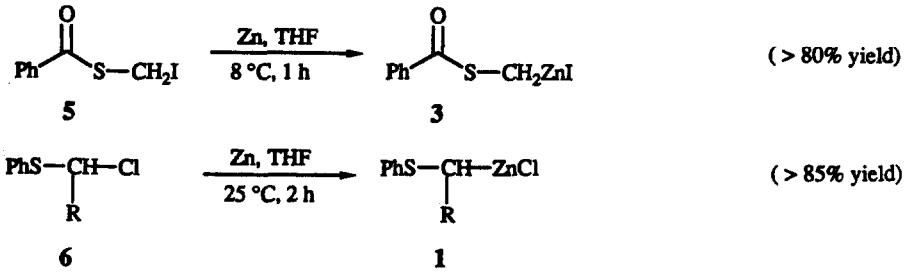
4

Herein, we extended our previous study and found that a thioester function (SCOPh) or an unsaturated sulfone functionality (H_2C=C(SO_2t-Bu)-) can also be present during the formation and subsequent reactions of a zinc organometallic such as **3** or **4**. Compared to the more classical lithium α-thiocarbanions, the organozinc derivatives **1-4** tolerate the presence of functional groups like an ester or nitrile. After their transmetallation to the corresponding copper compounds, they were found to react in high yields with various classes of electrophiles such as enones, allylic bromides, aldehydes, acid chlorides and alkynyl bromides.

RESULTS AND DISCUSSION

Whereas a primary alkyl iodide requires a temperature of 40-45 °C to be converted to the corresponding alkylzinc iodide, the presence of a heteroatom in close proximity to the carbon-iodine bond greatly facilitates the organozinc formation. Thus, iodomethyl pivalate ($ICH_2OCOtert\text{-}Bu$) can be transformed into pivaloyloxymethylzinc iodide ($IZnCH_2OCOtert\text{-}Bu$) within 1 h at 12-13 °C in THF.[3] An even stronger acceleration was observed in the case of iodomethylthiobenzoate[4] **5** which forms the zinc derivative **3** at 8 °C in less than an hour (Scheme I). Usually unactivated zinc dust does not insert into carbon-chlorine bonds in THF solution and rarely into carbon-bromine bonds.[5] However, the phenylthio group of α-chloroalkyl phenyl sulfides[6] of type **6** facilitates the zinc insertion to such an extent that these substrates can be converted to α–phenylthioalkylzinc chlorides **1** in THF at 25 °C in 2 h in over 85% yield (Scheme I).

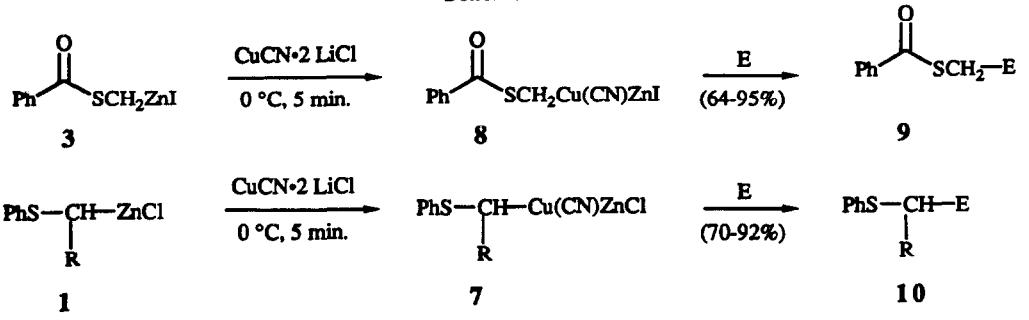
Scheme I



5 **3** **6** **1**

In strong contrast, it was found that α-chloroalkyl alkyl sulfides such as chloromethyl methyl sulfide do not insert zinc under these reaction conditions. Interestingly, the thioester function present in **5** is tolerated in the organozinc formation.[7] Furthermore, the chlorides **6** can contain a cyano or an ester functional group, allowing the *first* preparation of highly functionalized α-thiocarbanions. The organometallics **1** and **3** are unreactive toward most classes of organic electrophiles. However, transmetallation to the corresponding copper derivatives **7** and **8** respectively, using the THF soluble copper salt CuCN•2 LiCl[8], affords reagents that react with various electrophiles[9] like allylic halides, acyl chlorides, trialkyltin halides, enones, 1-alkynyl halides and aldehydes in good to excellent yields, giving polyfunctional thioesters of type **9** and polyfunctional phenylthioethers of type **10** (Scheme II and Table I).

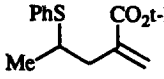
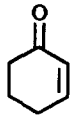
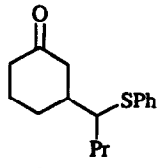
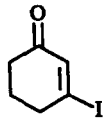
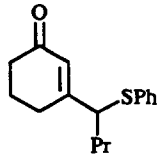
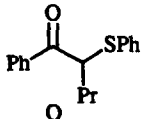
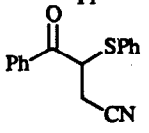
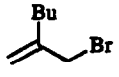
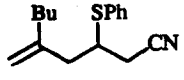
Scheme II

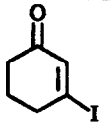
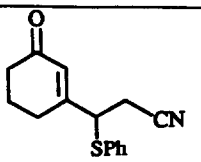
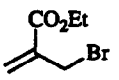
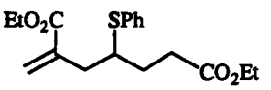
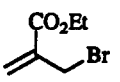
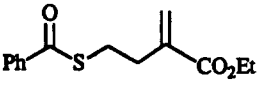
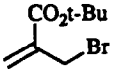
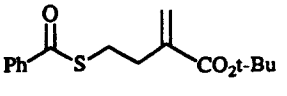
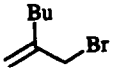
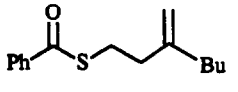
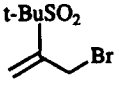
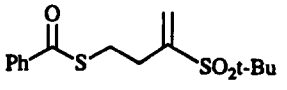
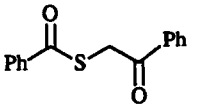
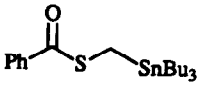


3 **8** **9** **1** **7** **10**

The zinc-copper α-thiocarbanions **7** were found to be less reactive than copper reagents derived from primary or secondary alkylzinc halides and did not react under various reaction conditions with diethyl benzylidenemalonate or nitrostyrene. Similarly, the more stabilized reagent **8** reacted only with allylic bromides, acid chlorides and tributyltin chloride. No reaction was observed with benzaldehyde, 6-acetoxy-1-nitrocyclohexene,[10] dimethyl acetylenedicarboxylate and 1,3-dichloro- 2-phenylthio-1-propene.[11] It should be mentioned that similar lithioalkylthio derivatives display a far higher reactivity. Unfortunately, they cannot bear functional groups due to the high reactivity of the carbon-lithium bond.[7] The coupling of the zinc-copper reagent **7a** with 1-bromo-1-octyne (0.75 eq. , THF -60 °C, 12 h) produces the propargylic thioether **10a** in 70% yield (entry 1 of Table I).

Table I. Thioesters of Type **9** and Phenylthio Ethers of Type **10** Obtained by the Reaction of the Zinc-Copper α-Thiocarbanions **7a-7e** and **8** with Electrophiles.

Entry	Zinc-Copper Reagent	Electrophile	Products of Type **9** or **10**		Yield (%)[a]
1	$PhSCH_2Cu(CN)ZnCl$	1-bromooctyne	$PhSCH_2$—≡—Hex	**10a**	70
2	**7a**	PhCHO[b]	$PhSCH_2CH(OH)Ph$	**10b**	71
3	$PhSCH(CH_3)Cu(CN)ZnCl$ **7b**			**10c**	87
4	PhSCH(Pr)Cu(CN)ZnCl **7c**			**10d**	78[c,d]
5	**7c**			**10e**	88
6	**7c**	PhCOCl		**10f**	93
7	$PhSCH(CH_2CN)Cu(CN)ZnCl$ **7d**	PhCOCl		**10g**	79
8	**7d**			**10h**	75

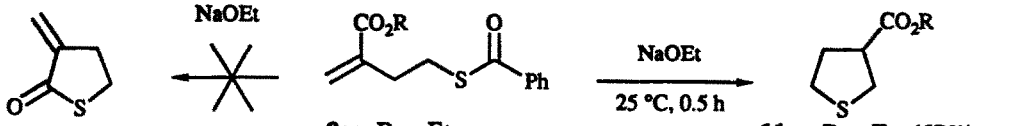
Entry	Zinc-Copper Reagent	Electrophile	Products of Type **9** or **10**		Yield (%)[a]
9	**7d**			**10i**	86
10	$PhSCH((CH_2)_2CO_2Et)Cu(CN)ZnCl$ **7e**			**10j**	92
11	$PhC(O)SCH_2Cu(CN)ZnI$ **8**			**9a**	95
12	**8**			**9b**	89
13	**8**			**9c**	75
14	**8**			**9d**	70
15	**8**	PhCOCl		**9e**	85
16	**8**	Bu_3SnCl		**9f**	64

[a] All yields refer to isolated yields of analytically pure products (see Experimental Section); [b] The reaction is performed in the presence of $BF_3{\cdot}OEt_2$ (2 equiv.); [c] The thioether **10d** is obtained as a 1:1 mixture of diastereoisomers; [d] The reaction is performed in the presence of Me_3SiCl (*ca.* 1.5 equiv.)

In the presence of $BF_3{\cdot}OEt_2$ (2 equiv.), the organometallic **7a** adds to benzaldehyde (0.5 eq.) under mild conditions[12] (-78 °C to -20 °C, 2 h, entry 2) leading to the β-hydroxy thioether **10b**. The coupling of allylic bromides with the reagents **7b, 7d, 7e** and **8** proceed in excellent

yields (70-95%) affording the homoallylic phenylthioethers **10c, h, j** (entries 3, 8 and 10) and the homoallylic thioesters **9a-d** (entries 11-14). Interestingly, the thioesters **9a** and **9b** undergo a ring closure when treated with base (NaH (4.5 equiv.), EtOH, 25 °C, 0.5 h) affording, in both cases, exclusively the disfavored 5-Endo-Trig[13] tetrahydrothiophenes **11a** and **11b** in 67% and 82% yields, respectively (Scheme III). No methylene thiobutyrolactone **12** could be detected in the crude reaction mixture. The Michael addition of **7c** to cyclohexenone (0.63 eq.) in the presence of

Scheme III



12

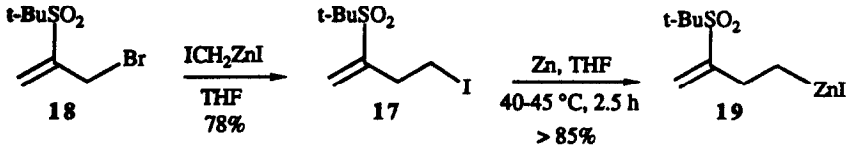
9a: R = Et
9b: R = tert-Bu

11a: R = Et (67%)
11b: R = tert-Bu (82%)

Me_3SiCl[14] (2 equiv.) produces, with a satisfactory yield, the 1,4-adduct **10d** as a 1:1 mixture of diastereoisomers (THF, -78 °C to 25 °C, overnight; 78% yield; entry 4). 3-Iodo-2-cyclohexen-1-one[15] reacts readily with the zinc-copper α-thiocarbanions **7c** and **7d** giving after an addition-elimination reaction (THF, -78 °C to 20 °C, 12 h at 20 °C), the 3-substituted enones **10e** and **10i** in 88% and 86% yields, respectively (entries 5 and 9). The reaction of **7c, 7d** or **8** with benzoyl chloride (0.5-0.62 equiv.) gives the α-thioketones **10f, 10g** and **9e** in 93%, 72%, 85% yields, respectively (entries 6, 7, and 15). Finally, the stannylation of **8** by tributyltin chloride furnishes the tin derivative **9f** (-20 °C, 12 h) in 64% yield (entry 16).

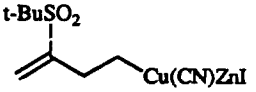
Attempts to prepare β-sulfur substituted zinc organometallics did not succeed. Thus, 2-iodoethyl isopropyl sulfoxide could not be converted to the corresponding zinc reagent; this may be due to the high propensity of such β-functionalized organometallics to undergo elimination reactions. The introduction of sulfur functionalities in the γ-position to the carbon-metal bond was more successful. The readily available 3-iodopropyl phenyl sulfide[4,20] **13**, 3-iodopropyl phenyl sulfoxide **14** and 3-iodopropyl phenyl sulfone **15** were converted under mild conditions to the corresponding zinc organometallics **16a-c**. Interestingly, whereas the sulfide **13** requires a reaction temperature of 40 °C to insert zinc (40 °C, 3 h), the sulfoxide **14** reacts within 0.5 h at 25 °C, showing that the sulfoxide in close proximity to the carbon-iodine bond functions like other polar groups (CN,[4d,16] $P(O)(OEt)_2$[5d]) is greatly facilitating the formation of the organozinc reagent. This effect may be explained by assuming that the polar group (cyanide, sulfoxide or phosphonate) complexes efficiently to the zinc surface, and that this complexation facilitates the initial electron transfer from zinc to the carbon-iodine bond, and thus enhances the rate of organozinc formation. It was also found that 4-iodo-2-(*tert*-butylsulfonyl)-1-butene **17**, which is readily available from 3-bromo-2-(tert-butylsulfonyl)-1-propene[17] **18** using a direct iodomethyl homologation[3a] developed previously in our laboratories (ICH_2ZnI (3.5 equiv.), THF, 0-5 °C, 15 h; 78% yield), can be readily converted into the corresponding zinc organometallic **19** (THF, 40-45 °C, 2.5 h; > 85% yield; Scheme IV). The zinc reagents **16a-c** were transmetallated to the respective zinc- copper reagents **20, 21,22**

Scheme IV



and **23** (CuCN•2 LiCl (1.0 equiv.), -10 °C, 5 min.) which were found to react with allylic bromides, enones, benzoyl chloride and trimethyltin chloride in excellent yields (Table II). The allylation with all four reagents **20-23** with tert-butyl or ethyl (α-bromomethyl)acrylate[18] affords

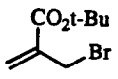
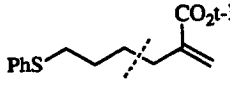
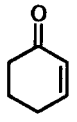
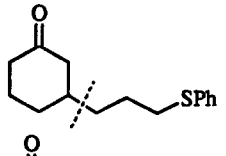
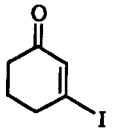
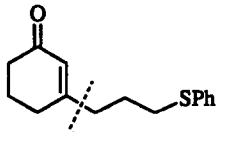
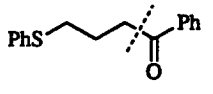
$PhS(O)_n(CH_2)_3ZnI$	$PhS(O)_n(CH_2)_3Cu(CN)ZnI$	
16a: n = 0	**20:** n = 0	
16b: n = 1	**21:** n = 1	
16c: n = 2	**22:** n = 2	

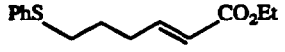
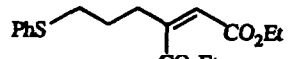
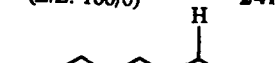
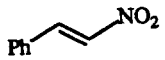
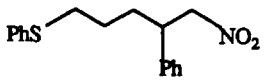
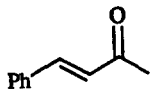
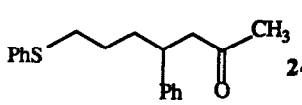
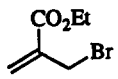
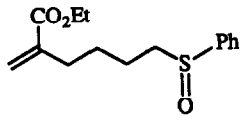
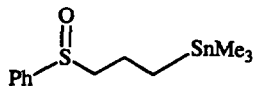
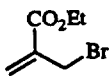
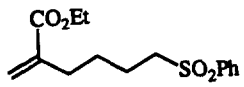
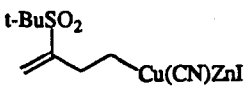
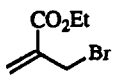
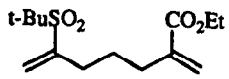
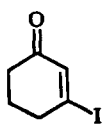
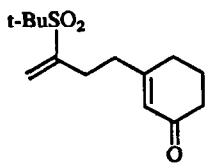


23

the desired allylated products **24a, 25a, 26, 27a** in 85-90% yield (entries 1,10, 12, 13 of Table II). The Michael addition to an enone such as 2-cyclohexen-1-one (0.75 equiv.) in the presence of chlorotrimethylsilane (2 equiv.) gives the 1,4-adduct **24b** (THF, -78 °C to 25 °C, overnight; 84% yield, entry 2). An addition-elimination of **20** or **23** to 3-iodo-2-cyclohexen-1-one (0.75 equiv.; -78 °C to 25 °C, 15 h) affords the 3-substituted cyclohexenones **24c** and **27b** in 85% and 93% yields respectively (entries 13 and 14 of Table II).

Table II. Products of Type **24-27** Obtained by the Reaction of the γ-Zinc-Copper Reagents **20-23** with Electrophiles.

Entry	Copper Reagent	Electrophile	Products of Type **23**		Yield (%)[a]
1	$PhS(CH_2)_3Cu(CN)ZnI$			**24a**	87
2	**20**			**24b**	84
3	**20**			**24c**	85
4	**20**	PhCOCl		**24d**	80

Entry	Copper Reagent	Electrophile	Products of Type 23	Yield (%)[a]
5	**20**	$H-C\equiv C-CO_2Et$	 (*E*/*Z*: 100/0) **24e**	95
6	**20**	$EtO_2C-C\equiv C-CO_2Et$	 (*E*/*Z*: 100/0) **24f**	87
7	**20**	$Bu-C\equiv C-SMe$	 (*E*/*Z*:95/5) **24g**	82
8	**20**		 **24h**	83
9	**20**		 **24i**	81
10	$PhS(O)(CH_2)_3Cu(CN)ZnI$ **21**		 **25a**	76
11	**21**	Me_3SnCl	 **25b**	90
12	$PhSO_2(CH_2)_3Cu(CN)ZnI$ **22**		 **26**	88
13	 **23**		 **27a**	90
14	**23**		 **27b**	93

[a] All yields refer to isolated yields of analytically pure products (see Experimental Section).

The acylation of **20** with benzoyl chloride (0.75 equiv., -10 °C, 10 h; 80% yield, entry 4) furnishes the desired ketone **24d**. The carbometallation of activated alkynes such as ethyl propiolate, diethyl acetylenedicarboxylate, 1-methylthio-1-hexyne with **20** proceeds in excellent yields (82%-95%) and affording the *syn* adducts **24e-24g** with high stereoselectivity (entries 5-7 of Table II). The Michael additions of **20** to nitrostyrene and benzylideneacetone gives the expected adducts **24h** and **24i** in 83% and 81% yields respectively (entries 8 and 9 of Table II). The reaction of trimethyltin chloride with reagent **21** proceeds readily (THF, -20 °C to 25 °C, 0.5 h; 90% yield; entry 11) leading to the trimethyltin substituted sulfoxide **25b**.

CONCLUSION

The preparation of zinc α-thiocarbanions has several synthetic advantages over the more conventional α-thiocarbanions. Besides their considerably higher thermal stability (no decomposition at 25 °C for 10 h), these reagents show a very high functional group tolerance, allowing the synthesis of highly functionalized α-thiocarbanions. As a consequence of this excellent compatibility with functional groups, the carbon-zinc bond was found to be very unreactive. However, the transmetallation with CuCN•2 LiCl affords zinc-copper reagents which display an excellent reactivity toward many types of electrophiles as shown in Table I. Although β-thiosubstituted zinc organometallics could not be prepared, several γ-thiosubstituted zinc compounds bearing sulfoxide, sulfone and sulfide functionalities could be obtained. All of these organometallics readily form new carbon-carbon bonds after a transmetallation to the corresponding copper compound. This study also showed that an α-thio functionality considerably facilitates the initial insertion of zinc into the carbon-halide bond. In fact, α-chloroalkyl phenyl sulfides were found to be the first class of organic halides for which a direct insertion of zinc into a *carbon-chlorine* bond is possible under mild conditions.

EXPERIMENTAL SECTION

General. Unless otherwise indicated, all reactions were carried out under argon. Solvents such as THF and diethyl ether were dried and freshly distilled from sodium/benzophenone. The zinc dust was obtained from Aldrich Chemical Company, Inc. (-325 mesh). Reactions were monitored by gas chromatography (GC) or thin layer chromatography (TLC) analysis of hydrolyzed reaction aliquots. Fourier transform infrared spectra (FT-IR) were recorded under a nitrogen atmosphere on sodium chloride plates on a Nicolet 5DXB FT-IR spectrometer. Infrared frequencies are reported in wave number units (cm^{-1}). Proton nuclear magnetic resonance spectra (^1H NMR) were recorded on a Brucker WM-300 (300 MHz) nuclear magnetic resonance spectrometer. Chemical shifts are reported as d in units of parts per million (ppm) relative to an internal reference of tetramethylsilane (δ 0.00). Coupling constants are reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were recorded on a Bruker WM-300 (75.5 MHz) nuclear magnetic resonance spectrometer. Chemical shifts are reported as δ in units of parts per million (ppm) relative to chloroform-d (δ 77.0) as an internal reference. Mass spectra (MS) and exact mass spectra were recorded on a VG-70-250 S mass spectrometer. The ionization methods used were desorption chemical ionization (CI) and electron impact ionization (EI). Spectra are reported in units of mass to charge and relative intensity.

Preparation of α-chloroalkyl phenyl sulfides and related starting materials. All reported α-chloroalkyl phenyl sulfides were prepared according to literature procedures.[6]
Typical procedure. *N*-Chlorosuccinimide (2.67 g, 22 mmol) freshly recrystallized from benzene was added between 5-10 °C in three portions within 15 min to a solution of an alkyl phenyl sulfide (20 mmol) in 20 mL of CCl_4. The reaction mixture was stirred two hours at 25 °C and poured into water (100 mL). The two layers were separated and the aqueous phase was extracted with CCl_4

(2x50 mL). The combined organic phase was washed with brine (50 mL), dried over anhydrous $MgSO_4$ and filtered. After evaporation of the solvents, the crude product was used directly for the formation of the zinc organometallics. Attempts to further purify the crude chloroalkyl phenyl sulfide by distillation led to the decomposition of the product. The purity was determined by ^1H NMR spectroscopy and was usually > 90%.

(1-Chloro-2-cyano)ethyl phenyl sulfide[19]. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.65-7.57 (m, 2H), 7.46-7.38 (m, 3H), 5.35 (t, 1H, J = 6.0 Hz), 3.05 (d, 2H, J = 6.0 HZ).
3-Chloropropyl phenyl sulfide[20] (bp 120-130 °C (0.02 Torr)) as well as 3-(phenylthio)-propionitrile[21] were prepared according to the literature, whereas ethyl 4-(phenylthio) butanoate was prepared by the reaction of PhSLi with ethyl 4-iodobutyrate in THF (25 °C, 8 h, 85% yield; bp 124-127 °C/0.6 mmHg; compare with ref. 22)

Preparation of the alkyl iodides **13-15** and **17**.
3-Iodopropyl phenyl sulfide **13** was prepared according to the literature[20] by refluxing a mixture of 3-chloropropyl phenyl sulfide (18.6 g, 100 mmol) and sodium iodide (30 g, 200 mmol) in 50 mL of acetone for 12 h. After the usual work-up, the residue was distilled under reduced pressure (113-115 °C; 0.2 mmHg) to obtain 3-iodopropyl phenyl sulfide in 85% yield (23.6 g). IR (neat): 3072 (s), 3056 (s), 2956 (br s), 1584 (s), 1480 (s), 1438 (s), 1210 (s), 738 (s), 690 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.4-7.15 (m, 5H), 3.28 (t, 2H, J = 6.0 Hz), 2.98 (t, 2H, J = 6.0 Hz), 2.1-2.0 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 135.5, 129.5, 128.8, 126.1, 34.2, 32.3, 4.7.

3-Iodopropyl phenyl sulfoxide **14**. A solution of m-chloroperbenzoic acid (6.0 g, 19 mmol, 50%) in 50 mL of dichloromethane was added to a solution of 3-iodopropyl phenyl sulfide (5.3 g, 19 mmol) in 20 mL of dichloromethane at 0 °C for 10 min. A white precipitate was formed after addition is over and stirred for another 30 min. at 5-10 °C. After the usual work-up, the crude product was purified by flash chromatography (hexane:ethyl acetate, 7:3) giving the pure sulfoxide **14** (4.58 g, 82% yield). IR (neat): 3053 (s), 2958 (br s), 1477 (s), 1443 (s), 1288 (m), 1207 (m), 1041 (m), 749 (s), 691 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.7-7.5 (m, 5H), 3.34-3.2 (m, 2H), 3.04-2.94 (m, 1H), 2.9-2.8 (m, 1H), 2.4-2.25 (m, 1H), 2.22-2.05 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 142.9, 130.7, 128.9, 123.5, 56.7, 25.4, 3.8; MS (EI): 41(95), 49(51), 78 (32), 84 (41), 97 (11), 125 (34), 169 (100), 294 (5). Exact mass calcd. for $C_9H_{11}IOS$: 293.9575. Observed 293.9567.

3-Iodopropyl phenyl sulfone **15**: 3-chloropropyl phenyl sulfone (2.18 g, 10 mmol) and sodium iodide (3.0 g, 20 mmol) in 20 mL of acetone was refluxed for 12 h to obtain 3-iodopropyl phenyl sulfone (2.82 g, 91% yield). After the usual work-up, the crude material was used for carrying out the reactions.
IR (neat): 3063 (br s), 2962 (br s), 1584 (s), 1403 (m), 1283 (m), 1094 (m), 1024 (s), 998 (s), 977 (s), 946 (s), 779 (m), 691 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.96-7.9 (m, 2H), 7.7-7.56 (m, 3H), 3.3-3.2 (m, 4H), 2.32-2.2 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 138.7, 133.6, 129.1, 127.6, 56.4, 26.3, 2.7; MS (EI): 41 (48), 51 (18), 77 (54), 125 (17), 141 (28), 183 (100), 311 $[M+H]^+$ (7). Exact mass calcd. for $C_9H_{11}IO_2SH$: 310.9602. Observed: 310.9598.

4-Iodo-2-(tert-butylsulfonyl)-1-butene **17**: A THF solution of iodomethylzinc iodide (36 mmol in 20 mL of THF) prepared from diiodomethane (10.7 g, 40 mmol) and zinc foil (2.6 g, 40 mmol) in 20 mL of THF at 25-26 °C (3 h) was added at -10 °C to a THF solution of 3-bromo-2-(tert-butylsulfonyl)-1-propene **18** (1.96 g, 8 mmol), CuI (1.52 g, 8 mmol), LiI (2.14 g, 16 mmol) in 10 mL of THF which had been stirred at 0 °C for 0.5 h. After stirring the reaction mixture at 0°C overnight, the reaction mixture was worked up as described above. Flash chromatography of the residue (hexane:dichloromethane 3:2) gives 1.73 g (5.7 mmol; 71% yield) of the pure sulfone **17**. IR (neat): 3022 (s), 2987 (s), 2975 (s), 2935 (s), 1478 (m), 1294 (m), 1252 (s), 1216 (m), 1197 (s), 1109 (s), 1102 (s), 960 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 6.28 (s, 1H), 6.08 (s, 1H), 3.35 (t, 2H, J = 7.5 Hz), 2.95 (t, 2H, J = 7.5 Hz), 1.35 (s, 9H); ^{13}C, NMR ($CDCl_3$, 75.5 MHz): δ 145.9, 130.3, 60.5, 36.4, 23.6, 1.2; MS (CI with methane): 89 (7), 105 (17), 119 (54), 136 (12), 233 (12), 247 (100), 264 (15), 275 (17), 287 (8), 303 $[M+H]^+$ (7), 320 $[M+NH_4]^+$ (40). Exact mass calcd. for $C_8H_{15}O_2ISH$: 302.9915. Observed: 302.9907 $[M+H]^+$.

Iodomethylthiobenzoate **5**: A solution of chloromethyl thiobenzoate (12 g, 60 mmol) in 60 mL of actone was sitrred for 5 h at 25 °C with NaI (30 g , 200 mol). After addition of hexane (300 mL), filtration of the sodium salts, evaporation of solvents, a crude oil was obtained (14.2 g, 89% yield, purity *ca.* 85%) which was used directly for the formation of the zinc reagent **3**. IR (neat): 3059 (m), 3031 (m), 1673 (s), 1595 (s), 1581 (s), 1448 (s), 1356 (m), 1314 (m), 1306 (m), 1207 (s), 1176 (s), 1145 (s), 1000 (m), 906 (s), 772 (s), 730 (s), 685 (s), 645 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.95-7.86 (m, 2H), 7.62-7.54 (m, 1H), 7.47-7.38 (m, 2H), 4.58 (s, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 188.78, 136.04, 134.08, 128.81, 127.54, -8.85; MS (EI): 51 (12.4), 77 (29.1), 105 (100.0), 151 (11.7). Exact mass calcd. for C_8H_7IOSH: 278.9341. Observed: 278.9346.

General procedure for the preparation of α-phenylthioalkylzinc chlorides of type **1**. A dry, 100 mL, three-necked flask equipped with a magnetic stirring bar, a 25 mL pressure equalizing addition funnel bearing a rubber septum, a three-way stopcock and a thermometer, was charged with zinc dust (1.95 g, 30 mmol, Aldrich, -325 mesh) and was flushed three times with argon. 1,2-Dibromoethane (200 mg, *ca.* 1 mmol) in 2 mL of THF was added and the zinc suspension was gently heated with a heat gun until ebullition of the solvent. After stirring the reaction mixture for a minute, the same activation process was repeated twice and chlorotrimethylsilane (0.15 mL, 1.2 mmol) was added. After 10 min of sitrring, the α-chloroalkyl phenyl sulfide (10 mmol) dissolved in 7 mL of THF was added dropwise over 10 min. The internal reaction temperature raises from 25 °C to 45 °C. The reaction mixture was then stirred for 1.5-2 h at 25 °C in the case of the alkyl substituted chlorides **1**, for 3 h in the case of 3-chloro-3-phenylthiopropionitrile and for 10 h in the case of ethyl 4-chloro-4-(phenylthio)butanoate. The completion of the reaction was monitored by GLC analysis of hydrolyzed reaction aliquots and yield of *ca.* 85% of the desired organozinc compound **1** were usually obtained. The excess zinc was allowed to settle and the resulting clear solution is ready to use for further transformations.

Preparation of benzoylthioxymethylzinc iodide **3**. The same activation procedure was used and the iodomethylthiobenzoate **5** was added to zinc dust as a 1.5 M THF solution at 8 °C. The insertion was completed after 1 h at this temperature affording the desired organozinc reagent **3** in > 90% yield.

Preparation of γ-thiosubstituted organozinc iodides: 3-Iodopropyl phenyl sulfide, sulfoxide and sulfone **13**, **14** and **15** were converted to the corresponding zinc reagents **16a-c** under the above described conditions. After the addition of the thiosubstituted iodides as a 2.0-2.5 M THF solution, the reaction mixture was stirred for 4 h at 40 °C with the sulfide, 0.5 h at 25 °C with the sulfoxide and 1 h at r.t. with the sulfone. The yields of organozinc iodides were *ca.* 90%. In the case of 3-tert-butylsulfonyl-3-butenyl iodide **17**, the corresponding zinc reagent **19** was formed in over 85% yield after a reaction time of 2.5 h at 40-45 °C.

Conversion of thio-substituted organozinc halides to the corresponding copper reagents **7a-e**, **8**, **20-23**. A dry, 100 mL, three-necked flask equipped with a magnetic stirring bar, a 25 mL pressure equalizing addition funnel bearing a rubber septum, a three-way stopcock and a thermometer was charged with a mixture of LiCl (0.84 g, 20 mmol; dried under vacuum at 130 °C for 2 h) and CuCN (0.89 g, 10 mmol) and was flushed three times with argon. The mixture was dissolved in 10 mL of dry THF. The resulting yellow-greenish solution was cooled to -60 °C and a THF solution of the thiosubstituted organozinc compound was added via a syringe. The reaction mixture was warmed to 0 °C and cooled back to -70 °C after 5 min. Various electrophiles (usually 7 mmol) were then added and allowed to react for various times and temperatures (see specific description of the products **9**, **10** and **23**). After the completion of the reaction determined by GLC analysis, the reaction mixture was poured into a saturated aqueous ammonium chloride solution (50 mL) and ammonium hydroxyde (50 mL) and was diluted with ether (100 mL). After separation of the two layers, the aqueous phase was extracted with ether (2x100 mL) and the combined organic layer was washed with water (100 mL), brine solution (100 mL) and dried over $MgSO_4$. After filtration and evaporation of the solvent, the resulting crude product was purified by flash chromatography affording the desired products with the yields indicated in Table I and II. GLC analysis of all of these products indicateds a purity greater than 98%.

Analytical data for products 9a-f (Table I).

Ethyl 2-(2-benzoylthioxyethyl)acrylate **9a**. Prepared by the reaction of ethyl α-(bromomethyl)acrylate (0.5 equiv.) with **8**: -78 °C to 0 °C, 30 min.; 95% yield; purified by flash chromatography (hexane:ether, 10:1). IR (neat): 3061 (br s), 2981 (m), 2936 (m), 2906 (br s), 1715 (s), 1664 (s), 1631 (m), 1606 (m), 1581 (m), 1448 (m), 1407 (m), 1369 (m), 1335 (m), 1314 (m), 1304 (m), 1276 (m), 1206 (s), 1186 (s), 1170 (s), 1126 (m), 1027 (m), 948 (m), 911 (s), 773 (m), 688 (s), 647 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.96-7.92 (m, 2H), 7.57-7.52 (m, 1H), 7.45-7.39 (m, 2H), 6.23 (d, 1H, J = 1.2 Hz), 5.64 (q, 1H, J = 1.2 Hz), 4.22 (q, 2H, J = 7.2 Hz), 3.23 (t, 2H, J = 7.5 Hz), 2.66 (td, 2H, J = 7.5 Hz, J = 0.8 Hz), 1.30 (t, 3H, J = 7.2 Hz); MS (EI): 51 (14), 77 (55), 105 (100), 106 (10), 165 (17), 264 (0.04, M^+). Exact mass calcd. for $C_{14}H_{16}O_3SH$: 265.0898. Observed: 265.0902.

tert-Butyl 2-(benzoylthioxyethyl)-2-propenoate **9b**. Prepared by the reaction of tert-butyl α-(bromomethyl)acrylate (0.65 equiv.) with **8**: -70 °C to 0 °C, 30 min., 89% yield; purified by flash chromatography (hexane:ether, 10:1). IR (neat): 3003 (m), 2977 (m), 2932 (m), 1710 (s), 1666 (s), 1632 (m), 1596 (m), 1582 (m), 1477 (m), 1448 (s), 1404 (m), 1392 (m), 1368 (s), 1343 (m), 1312 (m), 1280 (m), 1256 (m), 1233 (m), 1207 (s), 1175 (s), 1157 (s), 1128 (s), 947 (m), 912 (s), 851 (m), 818 (m), 773 (m), 689 (s), 647 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.97-7.92 (m, 2H), 7.58-7.52 (m, 1H), 7.47-7.40 (m, 2H), 6.16 (dd, 1H, J = 14.5 Hz, J = 1.56 Hz), 5.56 (m, 1H), 3.21 (t, 2H, J = 8.0 Hz), 2.62 (td, 2H, J = 7.5 Hz, J = 0.9 Hz), 1.47 (s, 9H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 191.27, 165.60, 139.82, 137.00, 133.10, 128.40, 127.03, 125.51, 80.64, 32.18, 27.95, 27.78; MS (EI): 35 (21), 39 (16), 41 (42), 45 (10), 47 (31), 49 (69), 51 (30), 57 (54), 77 (29), 84 (60), 86 (40), 105 (100), 114 (21). Exact mass calcd. for $C_{16}H_{20}O_3SH^+$: 293.1211. Observed: 293.1210.

3-Butyl-3-butenyl thiobenzoate **9c**. Prepared by the reaction of 2-(bromomethyl)hexene (0.5 equiv.) with **8**: -70 °C to 0 °C, 30 min.; 75% yield; purified by flash chromatography (hexane:ether, 15:1). IR (neat): 3081 (br s), 3008 (br s), 2956 (s), 2929 (s), 2871 (m), 2859 (m), 1664 (s), 1587 (br s), 1582 (br s), 1465 (br s), 1448 (m), 1207 (s), 1175 (m), 912 (s), 772 (m), 689 (s), 647 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.97-7.93 (m, 2H), 7.55-7.50 (m, 1H), 7.43-7.38 (m, 2H), 4.81 (s, 2H), 3.17 (t, 2H, J = 7.5 Hz), 2.36 (t, 2H, J = 7.5 Hz), 2.06 (t, 2H, J = 7.5 Hz), 1.48-1.25 (m, 4H), 0.90 (t, 3H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 191.88, 147.84, 137.38, 133.22, 128.58, 127.24, 110.50, 35.83, 35.69, 29.96, 27.54, 22.41, 13.91; MS (EI): 41 (11), 51 (10), 77 (35), 105 (100), 110 (20), 248 (0.49, M^+). Exact mass calcd. for $C_{15}H_{20}OS$: 248.1234. Observed: 248.1234.

3-tert-Butyl-3-butenyl thiobenzoate **9d**. Prepared by the reaction of 3-bromo-2-tert-butylsulfonyl-1-propene (0.5 equiv.) with **8**: -70 °C to 0 °C, 1h; 70% yield; purified by flash chromatography (hexane:ether, 10:1). IR (CCl_4): 3088 (m), 3071 (m), 2955 (m), 2930 (m), 2855 (br s), 1666 (s), 1582 (m), 1478 (m), 1457 (br s), 1449 (m), 1301 (s), 1207 (s), 1177 (m), 1129 (m), 1107 (s), 959 (br s), 912 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.90-7.87 (m, 2H), 7.52 (t, 1H, J = 7.5 Hz), 7.39 (t, 2H, J = 7.5 Hz), 6.23 (s, 1H), 6.09 (s, 1H), 3.25 (t, 2H, J = 7.5 Hz), 2.76 (t, 2H, J = 7.5 Hz), 1.32 (s, 9H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 191.00, 146.5, 136.5, 133.53, 130.09, 128.64, 127.18, 60.32, 32.48, 27.88, 23.65; MS (EI): 41 (13), 57 (34), 77 (25), 105 (100), 312 (M^+, 0.08). Exact mass calcd. for $C_{15}H_{20}O_3S_2H^+$: 313.0932. Observed: 313.0930.

Benzoylmethyl thiobenzoate **9e**. Prepared by the reaction of benzoyl chloride (0.5 equiv.) with **8**: -70 °C to 25 °C, 8 h at 25 °C; 85% yield; purified by flash chromatography (hexane:ether, 10:1). IR (neat): 3067 (br s), 1669 (s), 1598 (m), 1582 (m), 1449 (m), 1285 (m), 1275 (m), 1262 (br s), 1206 (s), 1176 (s), 1000 (br s), 911 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 8.1-8.0 (m, 4H), 7.65-7.55 (m, 2H), 7.54-7.45 (m, 4H), 4.60 (s, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 193.29, 190.24, 136.42, 135.82, 133.66, 133.60, 128.74, 128.66, 128.52, 127.44, 36.55; MS (EI): 77 (34), 105 (100), 256 (2.68, M^+). Exact mass calcd. for $C_{15}H_{12}O_2S$: 256.0558. Observed: 256.0558.

Tributylstannylmethyl thiobenzoate **9f**. Prepared by the reaction of **8** with tributyltin chloride (0.5 equiv.): -70 °C to -20 C, 8 h; 64% yield; purified by flash chromatography (hexane:ether, 20:1). IR (neat): 2955 (s), 2933 (s), 2870 (s), 2852 (s), 1662 (s), 1646 (s), 1580 (m), 1477 (m), 1452 (m), 1443 (m), 1208 (s), 1175 (m), 921 (s), 910 (s), 771 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz):

δ 7.96-7.92 (m, 2H), 7.55-7.50 (m, 1H), 7.44-7.23 (m, 2H), 2.20 (s, 2H), 1.56-1.45 (m, 6H), 1.35-1.23 (m, 6H), 1.07-0.93 (m, 6H), 0.87 (t, 9H, J = 3.9 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 193.7, 137.53, 132.84, 128. 49, 127.00, 28.99, 27.24, 13.60, 10.27, 4.71; MS (EI): 77 (27), 105 (100). Exact mass calcd. for $C_{20}H_{34}OS^{120}SnH^+$: 443.1431. Observed: 443.1431.

Analytical data for products **10a-j** (Table I).

2-Nonynyl phenyl sulfide **10a**. Prepared by the reaction of **7a** with 1-bromooctyne (0.7 equiv.): -70 °C to - 60 °C, 15 h; 70% yield; purified by flash chromatography (hexane:ether 24:1). IR (neat): 3059 (s), 2953 (br s), 2869 (s), 2200 (s), 1713 (s), 1670 (s), 1583 (s), 1479 (m), 1053 (m), 740 (s), 689 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.48-7.4 (m, 2H), 7.35-7.2 (m, 3H), 3.6 (s, 2H), 2.2-2.1 (m, 2H), 1.5-1.3 (m, 8H), 0.9 (t, 3H, J = 6.2 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): *d* 136.0, 129.7, 128.5, 126.2, 84.0, 75.5, 31.1, 28.5, 28.3, 23.0, 22.3, 18.6, 13.8; MS (EI): 39 (57), 41 (100), 53 (45), 67 (34), 81 (42), 91 (13), 109 (25), 129 (20), 147 (48), 161 (26), 232 (75). Exact mass calcd. for $C_{15}H_{20}S$: 232.1285. Observed: 232.1276.

1-Phenyl-2-phenylthio-1-ethanol **10b**. Prepared by the reaction of **7a** with benzaldehyde (0.5 equiv.) in the presence of BF_3•OEt_2 (1 equiv.): -70 °C to 0 °C; 36 h; 71% yield; purified by flash chromatography (hexane:ethyl acetate, 9:1). IR (neat): 3389 (br), 3059 (s), 3030 (s), 2920 (s), 1583 (s), 1452 (m), 1055 (m), 738 (s), 688 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.45-7.2 (m, 10H), 4.7 (dd, 1H, J = 6.5 Hz, J = 3.7 Hz), 3.3 (dd, 1H, J = 12.5 Hz, J = 3.7 Hz), 3.15-3.0 (m, 1H), 2.9 (br s, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 142.2, 135.2, 130.0, 128.9, 128.3, 127.7, 126.5, 125.7, 71.9, 43.8; MS (EI): 39 (17), 45 (40), 51 (31), 77 (40), 79 (48), 107 (35), 124 (100), 230 (6). Exact mass calcd. for $C_{14}H_{14}SO$: 230.0765. Observed: 230.0768.

tert-Butyl 2-((2-phenylthio)propyl)-2-propenoate **10c**. Prepared by the reaction of **7b** with tert-butyl α-(bromomethyl)acrylate (0.7 equiv.): -70 °C to 0 °C, 0.5 h; 87% yield, purified by flash chromatography (hexane:ether, 19:1). IR (neat): 3025 (s), 2976 (s), 2927 (br s), 1708 (s), 1629 (s), 1584 (s), 1438 (m), 1339 (m), 1147 (m), 946 (s), 850 (s), 747 (s), 692 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.46-7.38 (m, 2H), 7.3-7.15 (m, 3H), 6.15 (s, 1H), 5.5 (s, 1H), 3.5-3.4 (m, 1H), 2.68 (dd, 1H, J = 12.0 Hz, J = 6.0 Hz), 2.42 (dd, 1H, J = 12.0 Hz, J = 6.0 Hz), 1.5 (s, 9H), 1.27 (d, 3H, J = 6.0 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 165.8, 139.2, 135.3, 131.8, 128.5, 126.5, 126.1, 80.4, 41.7, 39.7, 27.9, 20.5; MS (EI): 39 (33), 41 (68), 49 (20), 57 (61), 67 (25), 110 (34), 111 (49), 137 (100), 175 (8), 205 (15), 222 (8), 278 (10). Exact mass calcd. for $C_{16}H_{22}SO_2$: 278.1340. Observed: 278.1339.

3-((1-Phenylthio)butyl)-cyclohexanone **10d**. Prepared by the reaction of **7c** with cyclohexenone (0.6 equiv.) in the presence of Me_3SiCl (1.2 equiv.); -70 ° C to 25 °C, 12 h; 78% yield; purified by flash chromatography (hexane:ethylacetate, 5:1); obtained as a 1:1 mixture of diastereomers. IR (neat): 3057 (s), 2920 (br s), 1712 (s), 1582 (s), 1422 (m), 1269 (m), 1067 (m), 1025 (s), 743 (s), 701 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.4-7.32 (m, 2H), 7.3-7.15 (m, 3H), 3.1-2.98 (m, 1H), 2.56-2.18 (m, 4H), 2.14-2.0 (m, 2H), 1.98-1.87 (m, 1H), 1.7-1.4 (m, 6H), 0.96-0.86 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 210.8, 210.7, 136.2, 131.18, 131.15, 128.6, 126.3, 55.1, 54.7, 45.6, 44.1, 43.0, 42.7, 41.07, 35.0, 34.3, 28.3, 26.9, 24.8, 20.5, 20.4, 13.6; MS (EI): 41 (88), 55 (100), 69 (36), 97 (19), 110 (46), 123 (34), 165 (23), 262 (21). Exact mass calcd. for $C_{16}H_{22}SO$: 262.1391. Observed: 262.1380.

3-(1-Phenylthiobutyl)-2-cyclohexen-1-one **10e**. Prepared by the reaction of **7c** with 3-iodo-2-cyclohexen-1-one (0.6 equiv.); -70 °C to r.t., 12 h; 88% yield; purified by flash chromatography (hexane:ethyl acetate, 4:1). IR (neat): 3057 (s), 2956 (br s), 1767 (s), 1618 (s), 1582 (s), 1438 (m), 1346 (m), 1254 (s), 1169 (s), 1133 (s), 1090 (s), 964 (s), 887 (s), 751 (s), 702 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.38-7.3 (m, 2H), 7.29-7.2 (m, 3H), 5.55 (s, 1H), 3.68 (t, 1H, J = 6.2 Hz), 2.62-2.52 (m, 1H), 2.35-2.25 (m, 3H), 2.03-1.82 (m, 2H), 1.8-1.6 (m, 2H), 1.52-1.35 (m, 2H), 0.95 (t, 3H, J = 6.0 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 198.5, 162.7, 133.3, 132.8, 128.4, 127.4, 126.5, 55.6, 37.2, 33.7, 24.9, 22.3, 20.4, 13.3; MS (EI): 41 (30), 49 (37), 55 (20), 67 (27), 81 (50), 110 (33), 133 (29), 151 (100), 189 (12), 203 (11), 217 (11), 260 (74). Exact mass calcd. for $C_{16}H_{20}SO$: 260.1234. Observed: 260.1228.

Phenyl (1-Phenylthio)butyl ketone **10f**. Prepared by the reaction of **7c** with benzoyl chloride (0.6 equiv.); -70 °C to -10 °C, 12 h, 93% yield; purified by flash chromatography (hexane:ethyl acetate, 4:1). IR (neat): 3059 (s), 2958 (s), 2932 (s), 2872 (s), 1678 (s), 1596 (s), 1581 (s), 1469 (m),

1247 (m), 1025 (s), 965 (s), 748 (s), 689 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 9.95-7.9 (m, 2H), 7.6-7.2 (m, 8H), 4.48 (t, 1H, *J* = 6.5 Hz), 2.06-1.95 (m, 1H), 1.9-1.78 (m, 1H), 1.6-1.4 (m, 2H), 0.94 (t, 3H, *J* = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 75.5 Hz): δ 195.8, 136.2, 134.1, 132.7, 128.7, 128.69, 128.65, 128.5, 128.2, 51.3, 33.1, 20.4, 13.7; MS (EI): 45 (12), 55 (24), 77 (48), 105 (55), 123 (100), 165 (94), 270 (30). Exact mass calcd. for $C_{17}H_{18}SO$: 270.1078. Observed: 270.1078.

4-Oxo-4-phenyl-(3-phenylthio)butane nitrile **10g**. Prepared by the reaction of **7d** with benzoyl chloride (0.5 equiv.); -70 °C to -10 °C, 15 h, 79% yield; purified by flash chromatography (hexane:ethyl acetate, 4:1). IR (neat): 3074 (s), 2932 (s), 2250 (s), 1748 (s), 1644 (s), 1574 (s), 1439 (m), 1315 (m), 1025 (s), 900 (s), 750 (s), 693 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.98 (d, 2H, *J* = 7.3 Hz), 7.68-7.26 (m, 8H), 4.72 (t, 1H, *J* = 6.2 Hz), 2.85 (dd, 2H, *J* = 6.7 Hz, *J* = 9 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 192.0, 135.7, 134.2, 133.6, 129.8, 129.2, 128.67, 128.61, 128.2, 117.6, 46.6, 19.4; MS (EI): 41 (31), 42 (35), 43 (100), 51 (25), 57 (11), 77 (45), 105 (97), 109 (9), 267 (5). Exact mass calcd. for $C_{16}H_{13}SNO$: 267.0717. Observed: 267.0709.

5-Butyl-3-phenylthio-hexane nitrile **10h**. Prepared by the reaction of **7d** with (2-bromomethyl) hexane (0.6 equiv.): -78 °C to 0 °C, 30 min., 75% yield; purified by flash chromatography (hexane:ether, 6:4). IR (neat): 3074 (s), 2929 (br s), 2859 (s), 2248 (s), 1640 (s), 1417 (m), 1284 (m), 900 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.56-7.48 (m, 2H), 7.4-7.3 (m, 3H), 4.94 (d, 2H, *J* = 9.0 Hz), 3.46-3.36 (m, 1H), 2.63-2.35 (m, 4H), 2.06 (t, 2H, *J* = 6.5 Hz), 1.48-1.28 (m, 4H), 0.93 (t, 3H, *J* = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 144.7, 133.0, 132.4, 128.7, 128.0, 116.7, 112.9, 42.6, 40.2, 34.8, 29.5, 22.8, 22.0, 13.6; MS (EI): 41 (100), 51 (24), 55 (49), 65 (27), 77 (22), 109 (55), 120 (30), 135 (19), 162 (79), 259 (20). Exact mass calcd. for $C_{16}H_{21}SN$: 259.1394. Observed: 259.1391.

3-(3-Oxo-1-cyclohexenyl)-(3-phenylthio)propane nitrile **10i**. Prepared by the reaction of **7d** with 3-iodo-2-cyclohexen-1-one (0.6 equiv.); -78 °C to r.t., 12 h, 86% yield; purified by flash chromatography (hexane:ethyl acetate, 1:1). IR (neat): 3046 (s), 2932 (br s), 2249 (s), 1735 (s), 1673 (s), 1426 (m), 1265 (m), 1030 (s), 910 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.4-7.23 (m, 5H), 5.5 (s, 1H), 3.78 (t, 1H, *J* = 6.5 Hz), 2.74-2.66 (m, 2H), 2.48 (d, 2H, *J* = 6.5 Hz), 2.38-2.2 (m, 2H), 2.05-1.95 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 197.9, 158.5, 134.1, 130.6, 130.3, 129.5, 128.9, 128.8, 126.5, 116.3, 50.2, 36.9, 26.4, 22.1, 21.1; MS (EI): 39 (57), 51 (34), 65 (66), 79 (48), 93 (49), 110 (100), 120 (19), 147 (26), 161 (18), 189 (14), 203 (31), 217 (60), 257 (81). Exact mass calcd. for $C_{15}H_{15}SNO$: 257.0874. Observed: 257.0867.

Ethyl 6-carboethoxy-4-phenylthio-6-heptenoate **10j**. Prepared by the reaction of **7e** with ethyl α-(bromomethyl)acrylate (0.6 equiv.): -70 °C to 0 °C, 0.5 h, 92% yield; purified by flash chromatography (hexane:ether, 4:1). IR (neat): 3040 (s), 2935 (br s), 1721 (s), 1629 (s), 1583 (s), 1439 (m), 1302 (m), 1194 (m), 1026 (s), 950 (s), 818 (s), 744 (s), 692 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.45-7.4 (m, 2H), 7.3-7.15 (m, 3H), 6.28 (s, 1H), 5.65 (s, 1H), 4.18 (q, 2H, *J* = 6.5 Hz), 4.1 (q, 2H, *J* = 6.5 Hz), 3.44-3.36 (m, 1H), 2.71-2.5 (m, 4H), 2.09-2.0 (m, 1H), 1.8-1.7 (m, 1H), 1.28 (t, 3H, *J* = 6.5 Hz), 1.24 (t, 3H, *J* = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 172.7, 166.4, 137.5, 134.6, 131.8, 128.6, 127.4, 126.6, 60.4, 60.0, 46.8, 38.3, 31.3, 29.0, 14.0, 13.9; MS (EI): 41 (31), 49 (45), 79 (41), 84 (30), 109 (34), 135 (62), 149 (100), 177 (40), 181 (31), 223 (26), 291 (10), 336 (7). Exact mass calcd. for $C_{18}H_{24}SO_4$: 336.1395. Observed: 336.1396.

Preparation of 3-carboethoxy and 3-carbo tert-butoxy-tetrahydrothiophene **11a** and **11b**. A solution of the thioester **9a** (530 mg, 2 mmol) in 10 mL of dry ethanol was added under argon at 25 °C to an ethanol solution of sodium ethoxide (2.67 mmol) (prepared by the reaction of NaH (80 mg, 2.67 mmol, 80% in oil) with ethanol). GLC analysis of the reaction mixture show the completion of the reaction after 0.5 h of stirring. The solvent was evaporated and the crude residue was dissolved in ether washed with a saturated aqueous ammonium chloride solution (50 mL), a brine solution (30 mL), dried over magnesium sulfate, and filtered. After evaporation of the solvent, the crude residue was purified by flash chromatography to afford **11a** as the sole product (solvent: ethyl acetate:hexane, 1:99); 225 mg, 67% yield. The same procedure was used to prepare **11b** starting from **9b**.

3-Carboethoxy tetrahydrothiophene **11a**. IR (neat): 2979 (s), 2961 (s), 2937 (s), 2907 (m), 2867 (m), 1732 (s), 1462 (m), 1443 (m), 1391 (m), 1370 (m), 1347 (m), 1312 (m), 1276 (m), 1258 (s), 1225 (s), 1185 (s), 1156 (s), 1160 (m), 1071 (s), 1032 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 4.14 (q, 2H, J = 7.2 Hz), 3.05-3.02 (m, 3H), 2.91-2.85 (m, 2H), 2.28-2.13 (m, 2H), 1.25 (t, 3H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 173.18, 60.94, 33.99, 33.51, 30.74, 14.20; MS (EI): 39 (14), 41 (18), 45 (52), 46 (10), 47 (16), 53 (16), 55 (11), 59 (15), 60 (13), 73 (32), 85 (48), 86 (100), 87 (59), 88 (12), 101 (14), 115 (17), 160 (50), 161 (71). Exact mass calcd. for $C_7H_{12}O_2S$: 160.0558. Observed: 160.0553.

3-Carbo tert-butoxy tetrahydrothiophene **11b**. IR (neat): 3003 (m), 2977 (s), 2935 (s), 2866 (m), 1728 (s), 1478 (m), 1457 (m), 1392 (m), 1368 (s), 1279 (m), 1257 (m), 1230 (m), 1212 (m), 1151 (s), 847 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 3.07-2.80 (m, 5H), 2.24-2.11 (m, 2H), 1.44 (s, 9H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 172.25, 80.85, 49.35, 34.00, 33.50, 30.68, 28.04; MS (EI): 39 (30), 41 (73), 43 (16), 45 (41), 47 (11), 53 (13), 57 (100), 59 (12), 60 (13), 73 (11), 85 (25), 86 (41), 87 (48), 115 (19), 131 (10), 132 (39), 188 (M^+, 9.24). Exact mass calcd. for $C_9H_{16}O_2S$: 188.0871. Observed: 188.0859.

Analytical data for products **24a-24i** (Table II).

tert-Butyl (4-phenylthiobutyl) acrylate **24a**. Prepared by the reaction of **20** with tert-butyl α-(bromomethyl)acrylate (0.7 equiv.): -70 °C to 0 °C, 0.5 h, 87% yield; purified by flash chromatography (hexane:ether, 9:1). IR (neat): 3040 (s), 2930 (br s), 1711 (s), 1620 (s), 1480 (s), 1367 (s), 1152 (s), 738 (s), 691 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.32-7.12 (m, 5H), 6.04 (s, 1H), 5.45 (s, 1H), 2.94 (t, 2H, J = 6.0 Hz), 2.25 (t, 2H, J = 6.0 Hz), 1.72-1.58 (m, 4H), 1.48 (s, 9H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 165.9, 141.6, 136.6, 128.6, 128.4, 125.3, 123.3, 79.9, 33.0, 31.1, 28.4, 27.7, 27.3; MS (EI): 41 (41), 57 (100), 81 (26), 110 (64), 123 (45), 190 (12), 219 (18), 236 (75), 292 (24). Exact mass calcd. for $C_{17}H_{24}SO_2$: 292.1497. Observed: 292.1494.

3-(3-phenylthiopropyl)cyclohexanone **24b**. Prepared by the reaction of **20** with cyclohex-2-en-1-one (0.6 equiv.) in the presence of Me_3SiCl (1.2 equiv.), -70 °C to 25 °C, 8 h, 84% yield; purified by flash chromatography (hexane:ether, 4:1). IR (neat): 3057 (s), 2924 (br s), 2861 (s), 1716 (s), 1583 (s), 1447 (m), 1312 (m), 1226 (s), 1092 (s), 1025 (s), 740 (s), 691 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.35-7.24 (m, 4H), 7.2-7.12 (m, 1H), 2.9 (t, 2H, J = 6.5 Hz), 2.43-2.2 (m, 3H), 2.08-1.25 (m, 10H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 210.5, 136.3, 128.8, 128.7, 128.5, 125.5, 47.6, 41.0, 38.2, 35.1, 33.4, 30.8, 25.9, 24.8; MS (EI): 41 (47), 55 (26), 69 (20), 97 (82), 110 (90), 123 (51), 139 (20), 152 (29), 248 (100). Exact mass calcd. for $C_{15}H_{20}SO$: 248.1234. Observed: 248.1223.

3-(3-Phenylthiopropyl)-2-cyclohexen-1-one **24c**. Prepared by the reaction of **20** with 3-iodo-2-cyclohexen-1-one (0.6 equiv.); -70 °C to -25 °C, 12 h, 85% yield; purified by flash chromatography (hexane:ether, 4:1). IR (neat): 3042 (s), 2939 (br s), 1668 (s), 1624 (s), 1480 (s), 1438 (s), 1325 (m), 1254 (s), 740 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.35-7.24 (m, 4H), 7.2-7.12 (m, 1H), 5.86 (s, 1H), 2.9 (t, 2H, J = 6.0 Hz), 2.38-2.26 (m, 4H), 2.22 (t, 2H, J = 6.0 Hz), 2.0-1.9 (m, 2H), 1.85-1.75 (m, 2H); ^{13}C NMR ($CDCl_3$, 300 MHz): δ 198.4, 164.2, 135.5, 128.7, 128.3, 125.7, 125.4, 36.7, 36.0, 32.5, 25.7, 22.0, 19.7; MS (EI): 41 (12), 49 (17), 53 (9), 65 (10), 79 (14), 84 (14), 110 (100), 123 (38), 136 (14), 168 (4), 246 (21). Exact mass calcd. for $C_{15}H_{18}SO$: 246.1078. Observed: 246.1066.

Phenyl (3-phenylthiopropyl) ketone **24d**. Prepared by the reaction of **20** with benzoyl chloride (0.6 equiv.); -70 °C to -20 °C, 12 h, 80% yield; purified by flash chromatography (hexane:ether:dichloromethane, 9:2:1). IR (neat): 3050 (s), 2930 (br s), 1684 (s), 1612 (s), 1584 (s), 1348 (m), 1274 (m), 740 (s), 690 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.98-7.92 (m, 2H), 7.6-7.15 (m, 8H), 3.18 (t, 2H, J = 6.5 Hz), 3.08 (t, 2H, J = 6.5 Hz), 2.15-2.05 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 198.8, 136.5, 136.0, 132.7, 128.8, 128.6, 128.3, 127.7, 125.6, 36.7, 32.8, 23.2; MS (EI): 45 (16), 51 (18), 77 (63), 105 (54), 136 (100), 147 (50), 256 (17). Exact mass calcd. for $C_{16}H_{16}OS$: 256.0921. Observed: 256.0915.

(E)-Ethyl 6-Phenylthio-2-hexenoate **24e**. Prepared by the reaction of **20** with ethyl propiolate (0.7 equiv.); -60 °C to -50 °C, 2 h, 95% yield; purified by flash chromatography (hexane:ether, 9:1). IR (neat): 3057 (s), 2935 (br s), 1718 (s), 1654 (s), 1439 (m), 1287 (m), 1200 (m), 1026

(m), 739 (s), 691 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.35-7.15 (m, 5H), 6.95 (td, 1H, *J* = 7.0 Hz, *J* = 1.7 Hz), 5.74 (td, 1H, *J* = 15.6 Hz, *J* = 1.6 Hz), 4.2 (q, 2H, *J* = 7.1 Hz), 2.95 (t, 2H, *J* = 7.0 Hz), 2.35 (qd, 2H, *J* = 7.7 Hz, *J* = 1.5 Hz), 1.86-1.75 (m, 2H), 1.3 (t, 3H, *J* = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 166.2, 147.4, 136.0, 129.3, 128.7, 125.9, 122.0, 60.0, 33.0, 30.8, 27.3, 14.1; MS (EI): 41 (18), 45 (21), 49 (100), 84 (86), 99 (32), 110 (43), 123 (58), 141 (11), 176 (5), 205 (7), 250 (12). Exact mass calcd. for $C_{14}H_{18}O_2S$: 250.1027. Observed: 250.1023.

(Z)-Ethyl 3-carboethoxy-6-phenylthio-2-hexenoate **24f**. Prepared by the reaction of **20** with diethyl acetylenedicarboxylate (0.7 equiv.); -70 °C to -50 °C, 1 h, 87% yield; purified by flash chromatography (hexane:ethyl acetate, 9:1). IR (neat): 3058 (s), 2938 (br s), 1723 (s), 1649 (s), 1594 (s), 1466 (m), 1346 (m), 1219 (m), 1069 (m), 740 (s), 692 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.4-7.15 (m, 5H), 5.8 (s, 1H), 4.26 (q, 2H, *J* = 7.1 Hz), 4.19 (q, 2H, *J* = 7.1 Hz), 2.96 (t, 2H, *J* = 7.1 Hz), 2.5 (t, 2H, *J* = 7.3 Hz), 1.9-1.79 (m, 2H), 1.36-1.2 (m, 6H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 168.1, 164.4, 148.6, 135.6, 129.3, 128.6, 125.9, 120.2, 61.0, 60.4, 32.8, 32.5, 26.2, 13.8, 13.7; MS (EI): 41 (20), 45 (38), 65 (22), 112 (86), 123 (96), 140 (100), 149 (32), 167 (31), 186 (32), 248 (11), 277 (10), 322 (11). Exact mass calcd. for $C_{17}H_{22}O_4S$: 322.1238. Observed: 322.1227.

1-Methylthio-2-((3-phenylthio)propyl)-1-hexene **24g**. Prepared in the following way: The organozinc reagent **16a** (12 mmol) was treated at -60 °C with $Me_2Cu(CN)Li_2$ (12 mmol) and warmed to 0 °C, then cooled to -60 °C and 1-methylthio-1-hexyne (6 mmol, 768 mg) was added. The reaction mixture was brought 0 °C and stirred for 3 h. After the usual workup, residue was purified by flash chromatography (hexane:ether, 49:1). IR (neat): 3074 (s), 3058 (s), 2923 (br s), 1585 (s), 1438 (m), 1298 (m), 1092 (s), 1025 (s), 737 (s), 690 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.36-7.14 (m, 5H), 5.6 (s, 1H), 2.92 (t, 2H, *J* = 7.1 Hz), 2.25-2.15 (m, 5H), 2.1 (t, 2H, *J* = 7.3 Hz), 1.8-1.7 (m, 2H), 1.4-1.24 (m, 4H), 0.9 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 139.1, 136.6, 129.1, 128.7, 125.7, 121.2, 35.3, 33.1, 31.6, 29.6, 27.2, 22.6, 17.2, 13.9; MS (EI): 41 (32), 49 (100), 67 (48), 84 (83), 123 (51), 136 (19), 155 (12), 233 (70), 280 (4). Exact mass calcd. for $C_{16}H_{24}S_2$: 280.1319. Observed: 280.1322.

2-Phenyl-5-phenylthio-1-nitropentane **24h**. Prepared by the reaction of **20** with nitrostyrene (0.7 equiv.); -70 °C to 0 ° C, 1h , 83% yield; purified by flash chromatography (hexane:ether, 48:2). IR (neat): 3029 (s), 2936 (br s), 1583 (s), 1550 (s), 1438 (m), 1379 (s), 1089 (s), 1025 (s), 763 (s), 692 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.35-7.1 (m, 10 H), 4.54 (d, 2H, *J* = 6.5 Hz), 3.49-3.37 (m, 1H), 2.92-2.75 (m, 2H), 1.89-1.8 (m, 2H), 1.6-1.45 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 138.7, 136.0, 129.0, 128.77, 128.70, 127.4, 127.3, 125.7, 80.5, 43.7, 33.1, 31.5, 26.1; MS (EI): 45 (23), 65 (11), 77 (14), 91 (44), 109 (20), 117 (20), 123 (30), 136 (18), 145 (100), 255 (10), 301 (5). Exact mass calcd. for $C_{17}H_{19}NO_2S$: 301.1136. Observed: 301.1131.

4-Phenyl-7-phenylthio-2-heptanone **24i**. Prepared by the reaction of **20** with benzylideneacetone (0.7 equiv.) in the presence of Me_3SiCl (1.5 equiv.); -70 °C to -10 °C, 15 h, 81% yield; purified by flash chromatography (hexane:ether, 9:1). IR (neat): 3059 (s), 3027 (s), 2928 (br s), 1716 (s), 1583 (s), 1452 (m), 1356 (s), 1248 (m), 1161 (s), 1092 (m), 1025 (s), 740 (s), 692 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.32-7.1 (m, 10 H), 3.19-3.06 (m, 1H), 2.9-2.75 (m, 2H), 2.74-2.62 (m, 2H), 2.0 (s, 3H), 1.86-1.62 (m, 2H), 1.6-1.4 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 207.0, 143.7, 136.5, 128.9, 128.6, 128.3, 127.2, 126.3, 125.5, 50.6, 40.9, 35.0, 33.4, 30.5, 26.6; MS (EI): 43 (100), 65 (5), 77 (7), 84 (10), 91 (16), 110 (20), 123 (25), 131 (30), 147 (34), 240 (2), 298 (13). Exact mass calcd. for $C_{19}H_{22}OS$: 298.1391. Observed: 298.1393.

3-(3-phenylthiopropyl)cyclohexanone **24b**. Prepared by the reaction of **20** with cyclohex-2-en-1-one (0.6 equiv.) in the presence of Me_3SiCl (1.2 equiv.), -70 °C to 25 °C, 8 h, 84% yield; purified by flash chromatography (hexane:ether, 4:1). IR (neat): 3057 (s), 2924 (br s), 2861 (s), 1716 (s), 1583 (s), 1447 (m), 1312 (m), 1226 (s), 1092 (s), 1025 (s), 740 (s), 691 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.35-7.24 (m, 4H), 7.2-7.12 (m, 1H), 2.9 (t, 2H, *J* = 6.5 Hz), 2.43-2.2 (m, 3H), 2.08-1.25 (m, 10H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 210.5, 136.3, 128.8, 128.7, 128.5, 125.5, 47.6, 41.0, 38.2, 35.1, 33.4, 30.8, 25.9, 24.8; MS (EI): 41

(47), 55 (26), 69 (20), 97 (82), 110 (90), 123 (51), 139 (20), 152 (29), 248 (100). Exact mass calcd. for $C_{15}H_{20}SO$: 248.1234. Observed: 248.1223.

3-(3-Phenylthiopropyl)-2-cyclohexen-1-one **24c**. Prepared by the reaction of **20** with 3-iodo-2-cyclohexen-1-one (0.6 equiv.); -70 °C to -25 °C, 12 h, 85% yield; purified by flash chromatography (hexane:ether, 4:1). IR (neat): 3042 (s), 2939 (br s), 1668 (s), 1624 (s), 1480 (s), 1438 (s), 1325 (m), 1254 (s), 740 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.35-7.24 (m, 4H), 7.2-7.12 (m, 1H), 5.86 (s, 1H), 2.9 (t, 2H, J = 6.0 Hz), 2.38-2.26 (m, 4H), 2.22 (t, 2H, J = 6.0 Hz), 2.0-1.9 (m, 2H), 1.85-1.75 (m, 2H); ^{13}C NMR ($CDCl_3$, 300 MHz): δ 198.4, 164.2, 135.5, 128.7, 128.3, 125.7, 125.4, 36.7, 36.0, 32.5, 25.7, 22.0, 19.7; MS (EI): 41 (12), 49 (17), 53 (9), 65 (10), 79 (14), 84 (14), 110 (100), 123 (38), 136 (14), 168 (4), 246 (21). Exact mass calcd. for $C_{15}H_{18}SO$: 246.1078. Observed: 246.1066.

Phenyl (3-phenylthiopropyl) ketone **24d**. Prepared by the reaction of **20** with benzoyl chloride (0.6 equiv.); -70 °C to -20 °C, 12 h, 80% yield; purified by flash chromatography (hexane:ether:dichloromethane, 9:2:1). IR (neat): 3050 (s), 2930 (br s), 1684 (s), 1612 (s), 1584 (s), 1348 (m), 1274 (m), 740 (s), 690 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.98-7.92 (m, 2H), 7.6-7.15 (m, 8H), 3.18 (t, 2H, J = 6.5 Hz), 3.08 (t, 2H, J = 6.5 Hz), 2.15-2.05 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 198.8, 136.5, 136.0, 132.7, 128.8, 128.6, 128.3, 127.7, 125.6, 36.7, 32.8, 23.2; MS (EI): 45 (16), 51 (18), 77 (63), 105 (54), 136 (100), 147 (50), 256 (17). Exact mass calcd. for $C_{16}H_{16}OS$: 256.0921. Observed: 256.0915.

(E)-Ethyl 6-Phenylthio-2-hexenoate **24e**. Prepared by the reaction of **20** with ethyl propiolate (0.7 equiv.); -60 °C to -50 °C, 2 h, 95% yield; purified by flash chromatography (hexane:ether, 9:1). IR (neat): 3057 (s), 2935 (br s), 1718 (s), 1654 (s), 1439 (m), 1287 (m), 1200 (m), 1026 (m), 739 (s), 691 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.35-7.15 (m, 5H), 6.95 (td, 1H, J = 7.0 Hz, J = 1.7 Hz), 5.74 (td, 1H, J = 15.6 Hz, J = 1.6 Hz), 4.2 (q, 2H, J = 7.1 Hz), 2.95 (t, 2H, J = 7.0 Hz), 2.35 (qd, 2H, J = 7.7 Hz, J = 1.5 Hz), 1.86-1.75 (m, 2H), 1.3 (t, 3H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 166.2, 147.4, 136.0, 129.3, 128.7, 125.9, 122.0, 60.0, 33.0, 30.8, 27.3, 14.1; MS (EI): 41 (18), 45 (21), 49 (100), 84 (86), 99 (32), 110 (43), 123 (58), 141 (11), 176 (5), 205 (7), 250 (12). Exact mass calcd. for $C_{14}H_{18}O_2S$: 250.1027. Observed: 250.1023.

(Z)-Ethyl 3-carboethoxy-6-phenylthio-2-hexenoate **24f**. Prepared by the reaction of **20** with diethyl acetylenedicarboxylate (0.7 equiv.); -70 °C to -50 °C, 1 h, 87% yield; purified by flash chromatography (hexane:ethyl acetate, 9:1). IR (neat): 3058 (s), 2938 (br s), 1723 (s), 1649 (s), 1594 (s), 1466 (m), 1346 (m), 1219 (m), 1069 (m), 740 (s), 692 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.4-7.15 (m, 5H), 5.8 (s, 1H), 4.26 (q, 2H, J = 7.1 Hz), 4.19 (q, 2H, J = 7.1 Hz), 2.96 (t, 2H, J = 7.1 Hz), 2.5 (t, 2H, J = 7.3 Hz), 1.9-1.79 (m, 2H), 1.36-1.2 (m, 6H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 168.1, 164.4, 148.6, 135.6, 129.3, 128.6, 125.9, 120.2, 61.0, 60.4, 32.8, 32.5, 26.2, 13.8, 13.7; MS (EI): 41 (20), 45 (38), 65 (22), 112 (86), 123 (96), 140 (100), 149 (32), 167 (31), 186 (32), 248 (11), 277 (10), 322 (11). Exact mass calcd. for $C_{17}H_{22}O_4S$: 322.1238. Observed: 322.1227.

1-Methylthio-2-((3-phenylthio)propyl)-1-hexene **24g**. Prepared in the following way: The organozinc reagent **16a** (12 mmol) was treated at -60 °C with $Me_2Cu(CN)Li_2$ (12 mmol) and warmed to 0 °C, then cooled to -60 °C and 1-methylthio-1-hexyne (6 mmol, 768 mg) was added. The reaction mixture was brought to 0 °C and stirred for 3 h. After the usual workup, residue was purified by flash chromatography (hexane:ether, 49:1). IR (neat): 3074 (s), 3058 (s), 2923 (br s), 1585 (s), 1438 (m), 1298 (m), 1092 (s), 1025 (s), 737 (s), 690 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.36-7.14 (m, 5H), 5.6 (s, 1H), 2.92 (t, 2H, J = 7.1 Hz), 2.25-2.15 (m, 5H), 2.1 (t, 2H, J = 7.3 Hz), 1.8-1.7 (m, 2H), 1.4-1.24 (m, 4H), 0.9 (t, 3H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 139.1, 136.6, 129.1, 128.7, 125.7, 121.2, 35.3, 33.1, 31.6, 29.6, 27.2, 22.6, 17.2, 13.9; MS (EI): 41 (32), 49 (100), 67 (48), 84 (83), 123 (51), 136 (19), 155 (12), 233 (70), 280 (4). Exact mass calcd. for $C_{16}H_{24}S_2$: 280.1319. Observed: 280.1322.

2-Phenyl-5-phenylthio-1-nitropentane **24h**. Prepared by the reaction of **20** with nitrostyrene (0.7 equiv.); -70 °C to 0 ° C, 1h , 83% yield; purified by flash chromatography (hexane:ether, 48:2). IR (neat): 3029 (s), 2936 (br s), 1583 (s), 1550 (s), 1438 (m), 1379 (s), 1089 (s), 1025 (s), 763 (s), 692 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.35-7.1 (m, 10 H), 4.54 (d, 2H, J = 6.5 Hz),

3.49-3.37 (m, 1H), 2.92-2.75 (m, 2H), 1.89-1.8 (m, 2H), 1.6-1.45 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 138.7, 136.0, 129.0, 128.77, 128.70, 127.4, 127.3, 125.7, 80.5, 43.7, 33.1, 31.5, 26.1; MS (EI): 45 (23), 65 (11), 77 (14), 91 (44), 109 (20), 117 (20), 123 (30), 136 (18), 145 (100), 255 (10), 301 (5). Exact mass calcd. for $C_{17}H_{19}NO_2S$: 301.1136. Observed: 301.1131.

4-Phenyl-7-phenylthio-2-heptanone **24i**. Prepared by the reaction of **20** with benzylideneacetone (0.7 equiv.) in the presence of Me_3SiCl (1.5 equiv.); -70 °C to -10 °C, 15 h, 81% yield; purified by flash chromatography (hexane:ether, 9:1). IR (neat): 3059 (s), 3027 (s), 2928 (br s), 1716 (s), 1583 (s), 1452 (m), 1356 (s), 1248 (m), 1161 (s), 1092 (m), 1025 (s), 740 (s), 692 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.32-7.1 (m, 10 H), 3.19-3.06 (m, 1H), 2.9-2.75 (m, 2H), 2.74-2.62 (m, 2H), 2.0 (s, 3H), 1.86-1.62 (m, 2H), 1.6-1.4 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 207.0, 143.7, 136.5, 128.9, 128.6, 128.3, 127.2, 126.3, 125.5, 50.6, 40.9, 35.0, 33.4, 30.5, 26.6; MS (EI): 43 (100), 65 (5), 77 (7), 84 (10), 91 (16), 110 (20), 123 (25), 131 (30), 147 (34), 240 (2), 298 (13). Exact mass calcd. for $C_{19}H_{22}OS$: 298.1391. Observed: 298.1393.

5-Carboethoxy-5-hexenyl phenyl sulfoxide **25a**. Prepared by the reaction of **21** with ethyl α-(bromomethyl)acrylate (0.7 equiv.) -70 °C to 0 °C, 0.5 h, 76% yield; purified by flash chromatography (hexane:ethyl acetate, 7:1). IR (neat): 3055 (s), 2936 (br s), 1712 (s), 1630 (s), 1407 (m), 1258 (m), 1161 (m), 946 (s), 750 (s), 693 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.68-7.5 (m, 5H), 6.16 (s, 1H), 5.52 (s, 1H), 4.2 (q, 2H, J = 7.1 Hz), 2.86 (t, 2H, J = 7.0 Hz), 2.3 (t, 2H, J = 7.0), 1.9-1.55 (m, 4H), 1.3 (t, 3H, J = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 166.4, 143.6, 139.6, 130.4, 128.7, 124.4, 123.5, 60.1, 56.5, 31.0, 27.1, 21.2, 13.8; MS (EI): 41 (30), 81 (100), 109 (89), 126 (43), 155 (68), 168 (6), 235 (27), 263 (32), 280 (18). Exact mass calcd. for $C_{15}H_{20}O_3S$: 280.1133. Observed: 280.1144.

Phenyl (3-trimethylstannyl)propyl sulfoxide **25b**. Prepared by the reaction of **21** with chlorotrimethylstannane (0.7 equiv.); -70 °C to 0 °C, 1 h, 90% yield; purified by flash chromatography (hexane:ether:dichloromethane, 6:2:2). IR (neat): 3040 (s), 2930 (br s), 1458 (s), 1100 (s), 1044 (s), 747 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.68-7.6 (m, 2H), 7.56-7.45 (m, 3H), 2.86-2.7 (m, 2H), 2.0-1.74 (m, 2H), 0.96-0.74 (m, 2H), 0.09 (s, 9H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 144.1, 130.6, 128.9, 123.7, 61.2, 19.7, 9.6, -10.4; MS (CI with methane): 91 (5), 111 (9), 119 (14), 136 (8), 161 (26), 163 (44), 165 (58), 185 (15), 301 (14), 313 (58), 315 (88), 317 (100), 329 (24), 331 (39), 333 $[M+H]^+$ (45). Exact mass calcd. for $C_{12}H_{20}{}^{120}SnSOH$: 333.0335. Observed: 333.0346 $[M+H]^+$.

5-Carboethoxy-5-hexenyl phenyl sulfone **26**. Prepared by the reaction of **22** with ethyl α-(bromomethyl)acrylate (0.7 equiv.); -70 °C to 0 °C, 0.5 h, 88%; purified by flash chromatography (hexane:ethyl acetate, 4:1). IR (neat): 3050 (s), 2941 (br s), 1715 (s), 1630 (s), 1406 (m), 1260 (m), 1148 (m), 916 (s), 732 (s), 690 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.98-7.9 (m, 2H), 7.7-7.54 (m, 3H), 6.15 (s, 1H), 5.5 (s, 1H), 4.18 (q, 2H, J = 7.0 Hz), 3.16 (t, 2H, J = 8.0 Hz), 2.3 (t, 2H, J = 7.5 Hz), 1.8-1.7 (m, 2H), 1.62-1.5 (m, 2H), 1.3 (t, 3H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 166.3, 139.4, 138.8, 133.2, 128.8, 127.5, 124.6, 60.2, 55.5, 30.8, 26.7, 21.8, 13.8; MS (CI with ammonia): 108 (5), 136 (41), 148 (5), 202 (24), 234 (14), 243 (15), 297 $[M+H]^+$ (13), 314 $[M+NH_4]^+$ (100). Exact mass calcd. for $C_{15}H_{20}O_4SH$: 297.1160. Observed: 297.1161.

Ethyl 4-tert-butylsulfonyl-4-pentenyl acrylate **27a**. Prepared by the reaction of **23** with ethyl α-(bromomethyl)acrylate (0.7 equiv.); -70 °C to 0 °C, 0.5 h, 90% yield; purified by flash chromatography (hexane:ethyl acetate, 8:2). IR (neat): 3048 (s), 2984 (br s), 1717 (s), 1640 (s), 1428 (m), 1289 (s), 1103 (m), 1040 (s), 980 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.22 (s, 1H), 6.16 (s, 1H), 6.0 (s, 1H), 5.56 (s, 1H), 4.2 (q, 2H, J = 7.5 Hz), 2.46 (t, 2H, J = 7.5 Hz), 2.35 (t, 2H, J = 7.5 Hz), 1.85-1.74 (m, 2H), 1.4 (s, 9H), 1.3 (t, 3H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 167.7, 147.3, 139.8, 128.2, 125.0, 60.6, 60.0, 31.4, 31.2, 27.5, 23.7, 14.1; MS (CI with methane): 95 (5), 119 (6), 136 (5), 151 (3), 169 (20), 187 (41), 197 (14), 215 (100), 233 (38), 243 (16), 261 (10), 273 (8), 289 $[M+H]^+$ (52), 306 $[M+NH_4]^+$ (33). Exact mass calcd. for $C_{14}H_{24}O_4SH$: 289.1473. Observed: 289.1472 $[M+H]^+$.

3-((3-tert-Butylsulfonyl)-3-butenyl)-2-cyclohexen-1-one **27b**. Prepared by the reaction of **23** with 3-iodo-2-cyclohexen-1-one (0.7 equiv.); -78 °C to -30 °C, 23 h, 93% yield; purified by flash chromatography (hexane:ether:dichloromethane, 6:3:1). IR (neat): 3095 (s), 2991 (s), 2972 (s), 2925 (br s), 1663 (s), 1623 (s), 1477 (m), 1265 (m), 1132 (m), 980 (s), 750 (s), 625 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 6.28 (s, 1H), 6.0 (s, 1H), 5.9 (s, 1H), 2.7-2.52 (m, 4H), 2.4-2.3 (m, 4H), 2.06-1.98 (m, 2H), 1.4 (s, 9H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 198.9, 163.2, 146.0, 129.0, 125.9, 59.9, 36.9, 36.7, 29.3, 29.2, 23.3, 22.2; MS (CI with methane and ammonia): 75 (4), 85 (6), 91 (6), 101 (5), 111 (17), 119 (35), 136 (51), 151 (19), 167 (4), 179 (5), 197 (6), 215 (17), 243 (4), 271 $[M+H^+]$ (100), 288 $[M+NH_4]^+$ (18). Exact mass calcd. for $C_{14}H_{22}O_3SH$: 271.1367. Observed: 271.1361 $[M+H]^+$.

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