Supporting Information

Synthesis, structures and reactions of acylsulfenyl iodides with the theoretical investigations

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Contents

Experimental

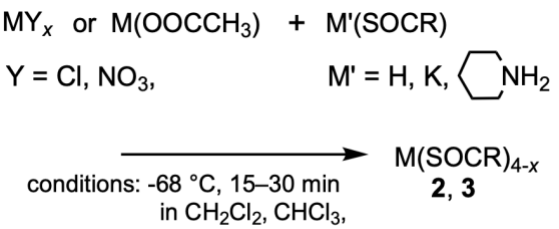
The melting points were measured by a Yanako micro-melting point apparatus and uncorrected. The IR spectra were measured on a PERKIN ELMER FT-IR 1640 and a JASCO grating IR spectrophotometer IR-G. The ^{1}H-NMR spectra were recorded on JEOL R-22 (90 MHz) and JEOL JNM-GX-270 (270 MHz) instruments. ^{13}C-NMR spectra were recorded on a JEOL JNM-GX-270 (67.5 MHz) and JEOL JNM-α400 (100 MHz) instruments. ^{77}Se and ^{25}Te NMR spectra were recorded on a JEOL JNM-α400 at 76.2 and 126 MHz, respectively. For the NMR measurements, $CDCl_3$ was used as the solvent. As the internal standard, Me_4Si was used for ^{1}H and ^{13}C NMR, while the external standards Me_2Se and Me_2Te were used for ^{77}Se NMR and ^{125}Te NMR, respectively. The following abbreviations were used: singlet = s, doublet = d, doublet of doublets = dd, doublet of doublet of doublets = ddd, triplet = t, quartet = q, sextet = sex, septet = sep, doublet of triplets = td, doublet of quartets = qd, multiplet = m, germinal = g. Electron spectra were measured on a JASCO U-Best 55. The mass spectra (H.R.M.S.) were recorded on Shimadzu GCMS QP1000 (A) (EI/CI, model) and GCMS 9020DF high resolution mass spectrometers and on a Hitachi RMU-6 (20 eV) high resolution mass spectrometer. Elemental analyses were performed by the Elemental Analysis Center of Kyoto University and Gifu College of Pharmacy.

Materials

Amines (diethylamine, *n*-propyl and iso-propylamines, *n*-butyl, *iso*-butyl and tertbutylamines, phenyl and diphenylamines, cyclohexene, 3,3-dimethylbutene, 1-hexene, 2-methyl-2-butene, 2-norbornene and benzoyl chloride were obtained from Nakalai Tesque. 2-Methyl-propene (99%), *cis*- and *trans*-2-butene (99%), 1,3-butadiene and cyclopentene (96%) were obtained from Aldrich. Potassium *tert*-butoxide, iodine and phenol were Tokyo Kasei and used without further purification. Ethane- and propane- butane- and benzene-thiol were purchased from Tokyo Kasei. Ether, tetrahydrofuran (THF), hexane and ethanol were dried over sodium/benzophenone and distilled before use. Dichloromethane and chloroform were dried on phosphorus pentoxide and distilled before use. Silica gel on the preparative thine layer chromatography was Wako gel B-5F of Wako Pure Chemical Industry, Ltd.

Carbothioic acids and their potassium[30] and piperidinium salts[31] were prepared according to previous reports.

Silver carbothioates,[32] zinc and cadmium di(carbothioates) (**2**) were prepared by the reaction of the corresponding metal chlorides, acetates or nitrates with carbothioic acids and their potassium or piperidinium salts, respectively (Scheme S1).[33] Their yields and spectral data are shown in Tables S34–S36.



2, **3**	M	*x*	**2**, **3**	M	*x*
2a	Ag	2	**3c**	Ph_3Sn	3
2b	Zn	2	**3d**	Ph_2Sn	2
2c	Cd	3	**3e**	Ph_3Pb	3
3a	Ph_3Ge	3	**3f**	Ph_2Pb	2
3b	Ph_2Ge	2			

Scheme S1. Synthesis of **2** and **3**.

S-Triphenylgermenium carbothioates **3a**,[34,35] *S*-diphenyl-germenium di(carbothioates) **3b**,[34,35] *S*-triphenyltin carbothioates **3c**,[34,35] *S*-diphenyltin di(carbothioates) **3d**,[34,35] *S*-triphenyllead carbo-thioates **3e**,[35] and *S*-diphenyllead di(carbothioates) **3f**[35] were prepared according to the literatures (Scheme S1 of the ESI). Their yields and physical properties and spectral data were shown in Tables S37–S42 and procedures in Exp. S2 (pp. S40–S44).

The yields, physical properties and spectral data of acylsulfenyl iodides **1a**–**1o** are shown in Tables S1–S7 of the ESI. Recrystallized solvents for compounds **1a**–**1h** are dichloromethane and hexane, while those for compounds **1i**–**1o** are hot hexane.

X-ray Measurements

The measurement was carried out on a Rigaku AFC7R four-circle diffract meter with graphite-monochromated Mo-Kα radiation (λ= 0.71069 Å). All of the structures were solved and refined using the teXsan crystallo-graphic software package on an IRIS Indigo computer.[35] X-ray quality crystals of **3a** were obtained by recrystallization from ether/petroleum ether. These crystals were cut and coated with an epoxy resin and mounted on a glass fiber. The cell dimensions were determined from a least-squares refinement of the setting diffract-meter angles for 25 automatically centered reflections. Lorentz and polarization corrections were applied to the data, and empirical absorption corrections (ψ-scans[36]) were also applied. The structures were solved by direct method using SHELXL-97[37] and expanded using DIRDIF92.[38] Scattering factors for neutral atoms were from Cromer and Waber[39] and anomalous dispersion[40] was used. The function minimized was $\Sigma w(|F_o|-|F_c|)^2$, and the weighting scheme employed was $w = [\sigma^2(F_o) + p^2(F_o)^2/4]^{-1}$. A full-matrix least-squares refinement was executed with non-hydrogen atoms being anisotropic. The final least-square cycle included fixed hydrogen atoms at calculated positions of which each isotropic thermal parameter was set to 1.2 times of that of the connecting atom.

[Exp. S1]

***Preparation of acylsulfenyl iodides* (1)**

Spectral data of the iodides **1** are collected in Table S7.

Benzoylsulfenyl iodide **1a** *from silver benzenecarbothioate* **2aa** *and* I_2

Method A: A solution of iodine (0.735 g, 3.0 mmol) in dichloromethane (20 mL) was added to a suspension of silver benzenecarbothioate **2aa** (0.732 g, 3.0 mmol) in dichloromethane/methanol (7:3, 20 mL) and stirred at –68 ºC for 30 min. After removal of solid (AgI), the solvents were evaporated under reduced pressure below 10 ºC. Recrystalli-zation of the resulting residue from hexane gave benzoylsulfenyl iodide **1a** as orange crystals; yield: 0.350 g (44%); m.p. 45–48 ºC (decomp); anal found, C, 31.74; H, 1.95; S, 12.15%; calc. for C_7H_5IOS (264.08) requires C, 31.84; H, 1.91; S, 12.14; i.r. ν_{max} (KBr)/cm^{-1}: 1667 ($\nu_{C=O}$); δ_H (90 MHz, $CDCl_3$, Me_4Si) 7.02–7.78 (m, 5H, arom); δ_C (100 Hz; $CDCl_3$; Me_4Si): 184.4 (*C*=O); 109.1–133.5 (m, 5H, arom); *m/z* (EI, 20 eV); found: M^+ 263.91021; calc. for C_7H_5IOS requires 263.91058.

Benzoylsulfenyl iodide **1a** *from zinc di(benzenecarbothioate)* **2ba** *and NIS*

Method B: A solution of excess *N*-iodosuccinimide (here after cited as NIS) 1.374 g, 6.0 mmol) in chloroform (10 mL) was added to a suspension of zinc di(benzenecarbothioate) **2ba** (0.583 g, 2.0 mmol) in methanol (20 mL) and stirred at –68 ºC for 15 min. The solvents were evaporated under reduced pressure below 20 ºC. After removal of solids (ZnI_2), the solvents were evaporated below 10 ºC under reduced pressure (8 Pa). Recrystallization of the resulting precipitates from hexane gave benzoylsulfenyl iodide **1a** as orange crystals; yield 0.327 g (62%).

2-Methylbenzoylsulfenyl iodide **1b** *from silver 2-methylbenzenecarbothioate* **2ab** *and NIS*
Similarly to *Method B* for compound **1a**, the reaction of silver 2-methylbenzenecarbothioate **2ab** (0.777 g, 3.0 mmol) and NIS (1.374 g, 6.0 mmol) in dichloromethane/methanol (7:3, 40 mL), followed by recrystallization of resulting residue from hexane, gave 2-methylbenzoylsulfenyl iodide **1b** as orange yellow crystals; yield 0.349 g (42%); m.p. 44–46 ºC (decomp); anal found, C, 34.43; H, 2.56%; calc. for C_8H_7IOS (278.11) requires C, 34.55; H, 2.54); i.r. ν_{max} (KBr)/cm^{-1} 1674 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 2.29 (s, 3H, C*H*$_3$Ar); 6.89–7.75 (m, 4H, arom); *m/z* (EI, 20 eV) found M^+ 277.92781; calc. for C_8H_7IOS requires 277.92623.

3-Methylbenzoylsulfenyl iodide **1c** *from silver 3-methylbenzenecarbothioate* **2ac** *and NIS*
Similarly to *Method B* for compound **1a**, the reaction of silver 3-methylbenzenecarbothioate **2ac** (0.777 g, 3.0 mmol) and NIS (1.374 g, 6.0 mmol) in dichloromethane/methanol (7:3, 40 mL), followed by recrystallization of resulting residue from hexane, gave 2-methylbenzoylsulfenyl iodide **1c** as orange yellow crystals; yield 0.183 g (67%); m.p. 49–52 ºC (decomp); anal found, C, 34.52; H, 2.57%; calc. for C_8H_7IOS (278.11) requires C, 34.55; H, 2.54); i.r. ν_{max} (KBr)/cm^{-1} 1680 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 2.31 (s, 3H, C*H*$_3$Ar); 7.00–7.88 (m, 4H, arom); *m/z* (EI, 20 eV) found M^+ 277.92548; calc. for C_8H_7IOS requires 277.92623.

4-Methylbenzoylsulfenyl iodide **1d** from silver 4-methylbenzenecarbothioate **2ad** *and NIS*
Similarly to *Method A* for compound **1a**, the reaction of silver 4-methylbenzenecarbothioate **2ad** (0.777 g, 3.0 mmol) and NIS (1.374 g, 6.0 mmol) in dichloromethane/methanol (7:3, 40 mL), followed by recrystallization of resulting residue from hexane, gave 4-methylbenzoylsulfenyl iodide **1d** as orange crystals; yield 0.523 g (63%); m.p. 40–43 ºC (decomp); anal found C, 34.51; H, 2.55; calc. for C_8H_7IOS (278.11) requires C, 34.55; H, 2.54%; i.r. ν_{max} (KBr)/cm^{-1} 1649, 1655 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 2.34 (s, 3H, C*H*$_3$); 7.06–7.90 (m, 4H, arom); δ_C (270 MHz; $CDCl_3$, Me_4Si) 183.8 (*C*=O); 21.6 (*C*H$_3$); 128.3–144.9 (arom); *m/z* (EI, 20 eV) found M^+ 277.92552; calc. for C_8H_7IOS requires 277.92623.

2-Methoxybenzoylsulfenyl iodide **1e** from *silver 2-methoxybenzenecarbothioate* **2ae** *and NIS*
Similarly to *Method A* for compound **1a**, the reaction of silver 2-methoxybenzenecarbothioate **2ae** (0.550 g, 2.0 mmol) and NIS (1.374 g, 6.0 mmol) in dichloromethane/methanol (7:3, 40 mL), followed by recrystallization of resulting residue from hexane, gave 2-methoxybenzoylsulfenyl iodide **1e** as orange crystals; yield 0.326 g (37%); m.p. 48–50 ºC (decomp); anal found, C, 32.61; H, 2.41%; calc. for $C_8H_7IO_2S$ (294.11) requires C, 32.67; H, 2.40%; i.r. ν_{max} (KBr)/cm^{-1} 1668, 1676 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 4.02 (s, 3H, C*H*$_3$O); 7.06–7.90 (m, 4H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 183.3 (*C*=O); 55.6 (*C*H$_3$O); 112.0–149.3 (arom); *m/z* (EI, 20 eV) found M^+ 293.921145; calc. for $C_8H_7IO_2S$ requires 293.92115.

4-Methoxybenzoylsulfenyl iodide **1f** *from silver 4-methoxybenzenecarbothioate* **2af** *and NIS*
Similarly to *Method A* for compound **1a**, the reaction of silver 4-methoxybenzenecarbothioate **2af** (0.826 g, 3.0 mmol) and NIS (1.374 g, 6.0 mmol) in dichloromethane/methanol (7:3, 40 mL), followed by recrystallization of resulting residue from hexane, gave 4-methoxybenzoylsulfenyl iodide **1f** as orange crystals; yield 0.688 g (76%); m.p. 38–40 ºC (decomp); anal found, C, 32.59; H, 2.41; calc. for $C_8H_7IO_2S$ (294.11) requires C, 32.67; H, 2.40%; i.r. ν_{max} (KBr)/cm^{-1} 1645, 1658, 1672 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 3.89 (s, 3H, C*H*$_3$OAr); 6.91 (d, J = 7.8 Hz, 2H, arom); 7.98 (d, J = 7.8 Hz, 2H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 183.3 (*C*=O); 55.6 (*C*H$_3$O); 115.0–166.2 (arom); *m/z* (EI, 20 eV) found M^+ 293.92101; calc. for $C_8H_7IO_2S$ requires 293.92115.

3-Chlorobenzoylsulfenyl iodide **1h** *from silver 3-chlorobenzenecarbothioate* **2ah** *and NIS*

Similarly to *Method A* for compound **1a**, the reaction of silver 3-chlorobenzenecarbothioate **2ah** (0.840 g, 3.0 mmol) and NIS (1.374 g, 6.0 mmol), in dichloromethane/methanol (7:3, 40 mL), followed by recrystallization of resulting residue from hexane, gave 3-chlorobenzoylsulfenyl iodide **1h** as orange crystals; yield 0.436 g (47%); m.p. 56–58 ºC (decomp); anal found, C, 28.14; H, 1.38%; calc. for C_7H_4ClIOS (298.53) requires C, 28.16; H, 1.35; i.r. ν_{max} (KBr)/cm^{-1} 1675 ($\nu_{C=O}$); δ_H (90 MHz, $CDCl_3$, Me_4Si) 6.76–7.92 (m, 4H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 183.3 (*C*=O), 121.2–155.3 (arom); *m/z* (EI, 20 eV) found M^+ 297.87001; calc. for C_7H_4ClIOS requires 297.87161.

4-Chlorobenzoylsulfenyl iodide **1i** *from silver 4-chlorobenzenecarbothioate* **2ai** *and NIS*
Similarly to *Method A* for compound **1a**, the reaction of silver 4-chlorobenzenecarbothioate **2ai** (0.840 g, 3.0 mmol) and NIS (1.374 g, 6.0 mmol) in dichloromethane/methanol (7:3, 40 mL), followed by recrystallization of resulting residue from hexane, gave 4-chlorobenzoylsulfenyl iodide **1i** as orange crystals; yield 0.599 g (67%); m.p. 46–48 ºC (decomp); anal found, C, 28.12; H, 1.36%; calc. for C_7H_4ClIOS (298.53) requires C, 28.16; H, 1.35; i.r. ν_{max} (KBr)/cm^{-1} 1680 ($\nu_{C=O}$); δ_H (90 MHz, $CDCl_3$, Me_4Si) 6.78–7.93 (m, 4H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 183.5 (*C*=O), 128.2–158.3 (arom);; *m/z* (EI, 20 eV) found M^+ 297.87001; calc. for C_7H_4ClIOS (298.53) requires 297.87161.

2-Nitrobenzoylsulfenyl iodide **1j** *from silver 2-nitrobenzenecarbothioate* **2aj** *and NIS*
Similarly to *Method A* for compound **1a**, the reaction of silver 2-nitrobenzenecarbothioate **2aj** (0.870 g, 3.0 mmol) and NIS (1.374 g, 6.0 mmol) in dichloromethane/methanol (7:3, 40 mL), followed by recrystallization of resulting residue from hexane, gave 2-nitro-benzoylsulfenyl iodide **1j** as orange crystals; yield 0.538 g (58%); m.p. 82–85 ºC (decomp); anal found C, 27.19; H, 1.32%; calc. for $C_7H_4INO_3S$ (309.08) requires C, 27.20; H, 1.30; i.r. ν_{max} (KBr)/cm^{-1} 1686 ($\nu_{C=O}$); δ_H (90 MHz, $CDCl_3$, Me_4Si) 6.80–7.94 (m, 4H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 1831.4 (*C*=O), 127.2–158.3 (arom); *m/z* (EI, 20 eV) found M^+ 308.86362; calc. for $C_7H_4INO_3S$ (309.08) requires 308.89566.

3-Nitrobenzoylsulfenyl iodide **1k** *from silver 3-nitrobenzenecarbothioate* **2ak** *and NIS*
Similarly to *Method A* for compound **1a**, the reaction of silver 3-nitrobenzenecarbothioate **2ak** (0.870 g, 3.0 mmol) and NIS (1.374 g, 6.0 mmol) in dichloromethane/methanol (7:3, 40 mL), followed by recrystallization of the resulting residue from hexane, gave 3-nitrobenzoylsulfenyl iodide **1k** as orange crystals; yield 0.584 g (63%); m.p. 52–54 ºC (decomp); anal found C, 27.17; H, 1.31%; calc. for $C_7H_4INO_3S$ (309.08) requires C, 27.20; H, 1.30; i.r. ν_{max} (KBr)/cm^{-1} 1662, 1672 ($\nu_{C=O}$); δ_H (90 MHz, $CDCl_3$, Me_4Si) 6.80–7.98 (m, 4H, arom); *m/z* (EI, 20 eV) found M^+ 308.89532; calc. for $C_7H_4INO_3S$ (309.08) requires 308.89566.

4-Nitrobenzoylsulfenyl iodide **1l** *from silver 4-nitrobenzenecarbothioate* **2al** *and NIS*
Similarly to *Method A* for compound **1a**, the reaction of silver 4-nitrobenzenecarbothioate **2al** (0.870 g, 3.0 mmol) and NIS (1.374 g, 6.0 mmol) in dichloromethane/methanol (7:3, 40 mL), followed by recrystallization of resulting residue from hexane, gave 4-nitrobenzoylsulfenyl iodide **1l** as orange crystals; yield 0.343 g (37%); m.p. 64–66 ºC (decomp); anal found C, 27.16; H, 1.30%. calc. for $C_7H_4INO_3S$ (309.08) requires C, 27.20; H, 1.30; i.r. ν_{max} (KBr)/cm^{-1} 1672 ($\nu_{C=O}$); δ_H (90 MHz, $CDCl_3$, Me_4Si) 6.75–7.99 (m, 4H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 181.1 (*C*=O), 128.8–162.1 (arom); *m/z* (EI, 20 eV) found: M^+ 308.89577; calc. for $C_7H_4INO_3S$ (309.08) requires 308.89566.

Benzoylsulfenyl iodide **1a** *from zinc di(benzenecarbothioate)* **2ba** *and NIS*
Method B: A solution of excess iodosuccinimide (here after cited as NIS) (2.700 g, 12.0 mmol) in chloroform (10 mL) was added to a suspension of zinc di(benzenecarbothioate) **2ba** (0.582 g, 2.0 mmol) in methanol (20 mL) and stirred at –68 ºC for 15 min. The solvents were evaporated under reduced

pressure below 20 ºC. After removal of solids (ZnI_2 + dibenzoyl disulfide), the solvents were evaporated below 10 ºC under reduced pressure. Recrystallization of the resulting solid and recrystallization from hexane gave benzoylsulfenyl iodide **1a** as orange crystals; yield 0.327 g (62%).

The i.r. and ^{1}H NMR spectra of the iodide **1a** were exactly consistent with those of the authentic sample which was obtained by the reaction of silver benzencarbothioate **2aa** with NIS.

Benzoylsulfenyl iodide **1a** *from zinc di(benzenecarbothioate)* **2ba** *and* I_2

Method C: A solution of 0.1N iodine/dichloromethane (60 mL) in chloroform (20 mL) was added to a suspension of zinc di(benzenecarbothioate) **2ba** (292 g, 1.0 mmol) in methanol (20 mL) at –15 ºC and stirred at 0 ºC for 30 min. The solven was evaporated below 0 ºC under reduced pressure and hexane (40 mL) was added. After filteration of precipitates (ZnI_2 + dibenzoyl disulfide), the filterate was allowed to stand at 0 ºC for 10 min. Filteration of the resulting precipitates and recrystallization from hexane gave benzoylsulfenyl iodide **1a** as orange crystals; yield; 0.026 g (5%).

The i.r. and ^{1}H NMR spectra of the iodide **1a** were consistent with those of the authentic sample which was obtained by the reaction of silver benzencarbothioate **2aa** with NIS.

2-Chlorobenzoylsulfenyl iodide **1g** *from zinc di(2-chlorobenzenecarbothioate)* **2bg** *and* I_2

Similarly to *Method A* for compound **1a**, the reaction of zinc di(2-chlorobenzenecarbothioate) **2bg** (0.560 g, 2.0 mmol) and a solution of iodine (1.016 g, 4.0 mmol) in dichloromethane (20 mL), followed by recrystallization of resulting residue from hexane, gave 2-chlorobenzoylsulfenyl iodide **1g** as orange crystals; yield 0.072 g (6%); m.p. 47–49 ºC (decomp); anal found, C, 28.14; H, 1.38%; calc. for C_7H_4ClIOS (298.53) requires C, 28.16; H, 1.35H; i.r. ν_{max} (KBr)/cm^{-1} 1684 ($\nu_{C=O}$); δ_H (90 MHz, $CDCl_3$, Me_4Si) 6.66–7.90 (m, 4H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 182.9 (*C*=O), 113.0–157.2 (arom); *m/z* (EI, 20 eV) found M^+ 297.87231; calc. for C_7H_4ClIOS requires 297.87161.

Ethanylsulfenyl iodide **1m** *from zinc di(ethanothioate)* **2am** *and NIS*

A solution of NIS (1.350 g, 6.0 mmol)/dichloromethane (60 mL) was dropwised to zinc bis(methanecarbothioate) (0.215 g, 1.0 mmol) in the same solvent (20 mL) and stirred at 20 ºC for 10 min (*caution to the change of the color of the reaction solution due to avoid an excess addition of the iodine solution*). The reaction mixture was concentrated to ca. 5 mL under reduced pressure and hexane (10 mL) was added and chilled at –68 ºC for 30 min. The resulting precipitates (ZnI_2 + a small amount of di(ethanoyl) disulfide) were filtered out. Hexane (5 mL) was added to the filtrate and cooled to –68 ºC. Removal of the solvents below 0 ºC in vacuo gave ethanoylsulfenyl iodide **1m** as slight yellow oil; yield 0.007 g (3%); i.r. ν_{max} (KBr)/cm^{-1} 1726 ($\nu_{C=O}$); δ_H (90 MHz, CDCl, Me_4Si) 2.67 (s, 3H, CH_3); *m/z* (EI, 20 eV) found M^+ 201.89466; calc. for C_2H_3IOS requires 201.89493.

tert-Butanoylsulfenyl iodide **1n** *from zinc di(tert-butanothioate)* **2an** *and NIS*

A solution of NIS (1.350 g, 6.0 mmol)/dichloromethane (60 mL) was dropwised to zinc di(*tert*-butanothioate) (0.360 g, 1.2 mmol) in the same solvent (20 mL) at –68 ºC and stirred at 0 ºC for 30 min. The reaction mixture was concentrated to ca. 5 mL under reduced pressure and hexane (10 mL) was added and chilled at –68 ºC for 30 min. The resulting precipitates (ZnI_2 + a small amount of di(*tert*-butanoyl) disulfide) were filtered out. Hexane (5 mL) was added to the filtrate and cooled to –68 ºC. Removal of the solvents below –15 ºC in vacuo gave *tert*-butanoylsulfenyl iodide **1n** as slight yellow oil; yield 0.021 g (4 %); i.r. ν_{max} (KBr)/cm^{-1} 1642 ($\nu_{C=O}$); δ_H (90 MHz, CDCl, Me_4Si) 1.01 (s, 9H, CH_3); *m/z* (EI, 20 eV) found M^+ 243.9433; calc. for C_5H_9IOS requires 243.9418.

n-Octadecanoylsulfenyl iodide **1o** *from zinc di(n-octadecano-thioate)* **2ao** *and NIS*

A solution (60 mL) of NIS (0.900 g, 4.0 mmol)/dichloromethane was dropwised to zinc di(*n*-octadecanothioate) **2bo** (0.344 g, 0.5 mmol) in the same solvent (20 mL) at 68 ºC and stirred at 0 ºC for 30 min. The reaction mixture was concentrated to ca. 5 mL under reduced pressure and hexane (10 mL) was added. The resulting precipitates (ZnI_2 + a small amount of di(dodecyl-decanoyl) disulfide) were filtered out. Hexane (5 mL) was added to the filtrate and cooled to ca. –15 ºC. Removal of the solvents below –15 ºC in vacuo gave *n*-dodecyldecanoylsulfenyl iodide **1o** as slight yellow solid (crystals); yield 0.035 g (8 %); i.r. ν_{max} (KBr)/cm^{-1} 1736 ($\nu_{C=O}$); δ_H (90 MHz, CDCl, Me_4Si) 1.21 (t, J = 7.5 Hz, 3H, CH_3); 2.02 (m, 30H, CH_2); 2.74 (t, J = 7.4 Hz, 2H, $CH_2C(O)$); *m/z* (EI, 20 eV) found M^+ 438.14765; calc. for $C_{19}H_{35}IOS$ requires 438.14533.

4-Methylbenzoylsulfenyl iodide **1d** *from cadmium di(4-methylbenzenecarbothioate) and NIS*
Method D: A solution of excess NIS (1.350 g, 6 mmol) in chloroform (10 mL) was added to a suspension of cadmium di(4-methylbenzenecarbothioate) **2cd** (0.367 g, 1.0 mmol) in methanol (20 mL) and stirred at –15 ºC for 15 min. The solvents were evaporated under reduced pressure below 40 ºC. After removal of solids (CdI_2 + di(4-methylbenzoyl) disulfide + succinimide), the solvents were evaporated below 10 ºC under reduced pressure. Recrystallization of the resulting solid and recrystallization from hexane gave 4-methylbenzoylsulfenyl iodide **1d** as orange crystals; yield 0.338 g (64%).
The i.r. and ^{1}H NMR spectra of the iodide **1d** were exactly consistent with those of the authentic sample which was obtained by the reaction of silver 4-methylbenzencarbothioate **2ad** with NIS.

Benzoylsulfenyl iodide **1a** from *S-triphenylgermanium benzenecarbothioate and* I_2
A solution of 0.1N iodine/dichloromethane (60 mL) was dropwised to triphenylgermanium benzenecarbothioate **3aa** (0.441 g, 1.0 mmol) in the same solvent (20 mL) at –17 ºC and stirred at –15 ºC for 15 min (*caution to the change of the color of the reaction solution due to avoid an excess addition of the iodine solution*) . The reaction mixture was concentrated to ca. 5 mL under reduced pressure and hexane (10 mL) was added and chilled at –15 ºC for 30 min. The resulting precipitates (Ph_3GeI + a small amount of dibenzoyl disulfide) were filtered out. Hexane (5 mL) was added to the filtrate and cilled to –68 ºC. Removal of the solvents below 0 ºC in vacuo gave benzoylsulfenyl iodide **1a** as slight yellow crystals; yield 0.116 g (44%); i.r. ν_{max} (KBr)/cm^{-1} 1667 ($\nu_{C=O}$).
The i.r. and ^{1}H NMR spectra of the iodide **1a** were exactly consistent with those of the authentic sample which was obtained by the reaction of silver benzencarbothioate **2aa** with NIS.

Benzoylsulfenyl iodide **1a** *from S-diphenylgermanium di(benzenecarbothioate) and* I_2
A solution (60 mL) of 0.1N iodine/dichloromethane was dropwised to *S*-diphenylgermanium di(benzenecarbothioate) **3ba** (0.501 g, 1.0 mmol) in the same solvent (20 mL) and stirred at –15 ºC for 30 min (*caution to the change of the color of the reaction solution due to avoid an excess addition of the iodine solution*) . The reaction mixture was concentrated to ca. 5 mL under reduced pressure and hexane (10 mL) was added and chilled at –15 ºC for 30 min. The resulting precipitates (Ph_2GeI_2 + a small amount of dibenzoyl disulfide) were filtered out. Hexane (5 mL) was added to the filtrate and cooled to –68 ºC. Removal of the solvents below 0 ºC in vacuo gave benzoylsulfenyl iodide **1a** as slight yellow crystals; yield 0.195 g (37%); i.r. ν_{max} (KBr)/cm^{-1} 1667 ($\nu_{C=O}$).
The i.r. and ^{1}H NMR spectra of the iodide **1a** were exactly consistent with those of the authentic sample which was obtained by the reaction of silver benzencarbothioate **2aa** with NIS.

*Benzoylsulfenyl iodide (***1a***) from S-diphenylgermanium di(benzenecarbothioate) and NIS*
A solution of excess NIS (1.350 g, 6 mmol) in chloroform (20 mL) in chloroform (10 mL) was dropwised in to *S*-diphenylgermanium di(benzenecarbothioate) **3ba** (0.501 g, 1.0 mmol) in the same solvent (20 mL) and stirred at –15 ºC for 30 min (*caution to the change of the color of the reaction*

solution due to avoid an excess addition of the iodine solution). The reaction mixture was concentrated to ca. 5 mL under reduced pressure and hexane (10 mL) was added and chilled at –15 ºC for 30 min. The resulting precipitates (Ph_2GeI_2 + a small amount of dibenzoyl disulfide) were filtered out. Hexane (5 mL) was added to the filtrate and cooled to –68 ºC. Removal of the solvents below 0 ºC in vacuo gave benzoylsulfenyl iodide **1a** as slight yellow crystals; yield 0.412 g (78%); i.r. ν_{max} (KBr)/cm^{-1} 1667 ($\nu_{C=O}$).
The i.r. and ^1H NMR spectra of the iodide **1a** were exactly consistent with those of the authentic sample which was obtained by the reaction of silver benzencarbothioate **2aa** with NIS.

Benzoylsulfenyl iodide **1a** from *triphenyltin benzenecarbothioate* **3ca** *and* I_2
A solution (60 mL) of 0.1N iodine/dichloromethane was dropwised to *S*-triphenyltin benzenecarbothioate **3ca** (0487 g, 1.0 mmol) in the same solvent (20 mL) and stirred at –15 ºC for 30 min (*caution to the change of the color of the reaction solution due to avoid an excess addition of the iodine solution*). The reaction mixture was concentrated to ca. 5 mL under reduced pressure and hexane (10 mL) was added and chilled at –15 ºC for 30 min. The resulting precipitates (Ph_3SnI + a small amount of dibenzoyl disulfide) were filtered out. Hexane (5 mL) was added to the filtrate and cooled to –68 ºC. Removal of the solvents below 0 ºC in vacuo gave benzoylsulfenyl iodide **3a** as slight yellow crystals; yield 0.095 g (36%); i.r. ν_{max} (KBr)/cm^{-1}: 1667 ($\nu_{C=O}$).
The i.r. and ^1H NMR spectra of the iodide **3a** were exactly consistent with those of the authentic sample which was obtained by the reaction of silver benzencarbothioate **2aa** with NIS.

Benzoylsulfenyl iodide **1a** from *triphenyltin benzenecarbothioate* **3ca** *and NIS*
A solution of excess NIS (1.350 g, 6 mmol in dichloromethane (10 mL) was dropwised to triphenyltin benzenecarbothioate **3ca** (0.509 g, 0.8 mmol) in the same solvent (20 mL) and stirred at –15 ºC for 30 min. The reaction mixture was concentrated to ca. 5 mL under reduced pressure and hexane (10 mL) was added and chilled at –68 ºC for 30 min. The resulting precipitates (Ph_3SnI + a small amount of dibenzoyl disulfide) were filtered out. Hexane (5 mL) was added to the filtrate and cooled to –15 ºC. Removal of the solvents below 0 ºC in vacuo gave benzoylsulfenyl iodide **1a** as slight yellow crystals; yield 0.172 g (65%); i.r. ν_{max} (KBr)/cm^{-1}: 1667 ($\nu_{C=O}$).
The i.r. and ^1H NMR spectra of the iodide **1a** were exactly consistent with those of the authentic sample which was obtained by the reaction of silver benzencarbothioate **2aa** with NIS.

*Benzoylsulfenyl iodid**e*** **1a** from *diphenyltin di(benzenecarbothioate)* **3da** *and NIS*
A solution of excess NIS (1.350 g, 6 mmol in dichloromethane (10 mL) was dropwised to diphenyltin di(benzenecarbothioate) **3da** (0.274 g, 0.5 mmol) in the same solvent (20 mL) and stirred at –15 ºC for 30 min (*caution to the change of the color of the reaction solution due to avoid an excess addition of the iodine solution*). The reaction mixture was concentrated to ca. 5 mL under reduced pressure and hexane (10 mL) was added and chilled at –68 ºC for 30 min. The resulting precipitates (Ph_2SnI_2 + a small amount of dibenzoyl disulfide) were filtered out. Hexane (5 mL) was added to the filtrate and cilled to –15 ºC. Removal of the solvents below 5 ºC in vacuo gave benzoylsulfenyl iodide **1a** as slight yellow crystals; yield 0.354 g (67%); i.r. ν_{max} (KBr)/cm^{-1}: 1667 ($\nu_{C=O}$).
The i.r. and ^1H NMR spectra of the iodide **1a** were exactly consistent with those of the authentic sample which was obtained by the reaction of silver benzencarbothioate **2aa** with NIS.

Benzoylsulfenyl iodide **1a** from *triphenyllead benzenecarbothioate* **3ea** *and* I_2
A solution of 0.1N iodine/dichloromethane (60 mL) was dropwised to triphenyllead benzenecarbothioate **3ea** (0.690 g, 1.2 mmol) in the same solvent (20 mL) and stirred at –15 ºC for 10 min (*caution to the change of the color of the reaction solution due to avoid an excess addition of the*

iodine solution). The reaction mixture was concentrated to ca. 5 mL under reduced pressure and hexane (10 mL) was added and chilled at –68 ºC for 30 min. The resulting precipitates (SnI_2 + a small amount of dibenzoyl disulfide) were filtered out. Hexane (5 mL) was added to the filtrate and cooled to –68 ºC. Removal of the solvents below 0 ºC in vacuo gave benzoylsulfenyl iodide **1a** as slight yellow crystals; yield 0.051 g (16%); i.r. ν_{max} (KBr)/cm^{-1}: 1667 ($\nu_{C=O}$).
The i.r. and ^{1}H NMR spectra of the iodide **1a** were exactly consistent with those of the authentic sample which was obtained by the reaction of silver benzencarbothioate **2aa** with NIS.

Benzoylsulfenyl iodide **1a** from *diphenyllead di(benzenecarbothioate)* **3fa** *and* I_2
A solution of 0.1N iodine/dichloromethane (60 mL) was dropwised to diphenyllead di(benzenecarbothioate) **3fa** (0.509 g, 0.8 mmol) in the same solvent (20 mL) at –15 ºC and stirred at 0 ºC for 30 min. The reaction mixture was concentrated to ca. 5 mL under reduced pressure and hexane (10 mL) was added and chilled at –68 ºC for 30 min. The resulting precipitates (Ph_2PbI_2 + a small amount of dibenzoyl disulfide) were filtered out. Hexane (5 mL) was added to the filtrate and cooled to –15 ºC. Removal of the solvents below 0 ºC in vacuo gave benzoylsulfenyl iodide **1a** as slight yellow crystals; yield 0.072 g (17%); i.r. ν_{max} (KBr)/cm^{-1}: 1667 ($\nu_{C=O}$).
The i.r. and ^{1}H NMR spectra of the iodide **1a** were exactly consistent with those of the authentic sample which was obtained by the reaction of silver benzencarbothioate **2aa** with NIS.

Benzoylsulfenyl iodide **1a** from *triphenyllead benzenecarbothioate* **3ea** *and NIS*
A solution of excess NIS (0.900 g, 4.0 mmol) in dichloromethane (50 mL) was dropwised to triphenyllead benzenecarbothioate **3ea** (0.690 g, 1.2 mmol) in the same solvent (20 mL) at –15 ºC and stirred at 0ºC for 30 min. The reaction mixture was concentrated to ca. 5 mL under reduced pressure and hexane (10 mL) was added and chilled at –68 ºC for 30 min. The resulting precipitates (SnI_2 + a small amount of dibenzoyl disulfide) were filtered out. Hexane (5 mL) was added to the filtrate and cooled to –68 ºC. Removal of the solvents below 0 ºC in vacuo gave benzoylsulfenyl iodide **1a** as slight yellow crystals; yield 0.155 g (49%); ν_{max} (KBr)/cm^{-1}: 1667 ($\nu_{C=O}$).
The i.r. and ^{1}H NMR spectra of the iodide **1a** were exactly consistent with those of the authentic sample which was obtained by the reaction of silver benzencarbothioate **2aa** with NIS.

Benzoylsulfenyl iodide **1a** from *diphenyllead di(benzenecarbothioate)* **3fa** *and NIS*
A solution of excess NIS (0.81 g, 3.0 mmol) in dichloromethane (50 mL) was dropwised to diphenyllead di(benzenecarbothioate) **3fa** (0.636 g, 1.0 mmol) in the same solvent (20 mL) at –16 ºC and stirred at 0 ºC for 30 min. The reaction mixture was concentrated to ca. 5 mL under reduced pressure and hexane (10 mL) was added and chilled at –68 ºC for 30 min. The resulting precipitates (Ph_2PbI_2 + a small amount of dibenzoyl disulfide) were filtered out. Hexane (5 mL) was added to the filtrate and cooled to –68 ºC. Removal of the solvents below 0 ºC in vacuo gave benzoylsulfenyl iodide **1a** as slight yellow crystals; yield 0.332 g (63%); i.r. ν_{max} (KBr)/cm^{-1}: 1667 ($\nu_{C=O}$).
The i.r. and ^{1}H NMR spectra of the iodide **1a** were exactly consistent with those of the authentic sample which was obtained by the reaction of silver benzencarbothioate **2aa** with NIS.

Addition of acylsulfenyl iodides 2 to alkenes
Typical procedures are described for the reactions of acylsulfenyl iodides with alkenes, enamine and α-trimethylsioxyalkenes. All procedures were carried out under nitrogen atomospher.

Reaction of benzoylsulfenyl iodide **1a** *with 1-hexene* **4a** *in dichloromethane* (entry 1 in Table 1)
Similar to Pocedure *A*, benzoylsulfenyl iodide **1a** (0.264 g, 1.0 mmol) and 1-hexene **4a** (0.20 mL, 2.4 mmol) were stirred in dichloromethane (5 mL) at 0 ºC for 60 min. Filteration of the precipitates and the

solvent was removed under reduced pressure (ca. 12 Pa). Chromatographic separation of the resulting concentrate on silica gel ptlc [eluant: dichloromethane/hexane (1:2), Rf = 0.56] afforded a mixture (64:36) of 2-iodohexyl benzoyl sulfide **6aa** and 1-iodohexyl benzoyl sulfide **7aa** as a slight yellow oil; yield 0.075 g (22%); anal found C, 44.72; H, 4.94%; calc. for $C_{13}H_{17}IOS$ (348.24) requies C, 44.84; H, 4.92%; i.r. ν_{max} (KBr)/cm^{-1}: 1660 ($\nu_{C=O}$); δ_H (270 MHz, CDCl, Me_4Si) for **6aa**:0.92–1.88 (m, 9H, CH_2, CH_3), 3.62 (dd, *J*= 2.2 Hz, 13.9 Hz, 1H, CH_2), 3.77 (dd, *J*= 2.2 Hz, 7.0 Hz, 1H, CH_2), 4.22 (dd, *J*= 7.0, 13.9 Hz, 1H, CH_2), 7.43–7.62 (m, 3H, arom), 7.95–7.99 (m, 2H, arom); for **7aa**: 0.92–1.88 (m, 9H, CH_2, CH_3), 3.39 (dd, *J*= 2.1, 9.9 Hz, 1H, CH_2), 3.72 (dd, *J*= 2.1, 8.1 Hz, 1H, CH_2), 4.05 (dd, *J*= 8.1, 9.9 Hz, 1H, CH_2), 7.43–7.62 (m, 3H, arom), 7.95–7.99 (m, 2H, arom); *m/z* (EI, 20 eV) found M$^+$ 348.00491; calc. for $C_{13}H_{17}IOS$ requires 348.00448.
The integratiopn ratio of the two peaks at δ 3.41and δ 4.22 was 64:36, indicating that the product consisted of compounds **6aa** (64%) and **7aa** (36%).

Reaction of benzoylsulfenyl iodide **1a** *with cyclopentene* **4b** *in dichloromethane* (entry 2 in Table 1)
Similar to Procedure *B*, benzoylsulfenyl iodide **1a** (0.264 g, 1.0 mmol) and cyclopentene **4b** (0.10 mL, 0. 1 mmol) were stirred in dichloromethane (5 mL) at 0 ºC for 60 min. After usual workup of the reaction mixture, chromatographic separation of the resulting concentrate on silica gel ptlc [eluant: dichloromethane/hexane (1:2), Rf = 0.75] of crude product afforded *trans*-2-iodocyclopentyl benzoyl sulfide **6ab** as a slight yellow oil; yield 0.186 g (56%); anal found C, 43.22; H, 3.98%; calc. for $C_{12}H_{13}IOS$ (332.20) requies C, 43.39; H, 3.94%; i.r. ν_{max} (KBr)/cm^{-1}: 1656 ($\nu_{C=O}$); δ_H (270 MHz, CDCl, Me_4Si) 1.71–2.61 (m, 6H, CH_2); 4.14 (dt, J_{ab}= 3.5 Hz, *J* = 7.5 Hz, 1H, CH^a); 4.37 (dt, J_{ab}= 3.5 Hz, *J* = 7.5 Hz, 1H, CH^b); 7.41–7.95 (m, 5H, arom); *m/z* (EI, 20 eV) found M$^+$ 331.97366; calc. for $C_{12}H_{13}IOS$ requires 331.97318.

Reaction of benzoylsulfenyl iodide **1a** *with cyclohexene* **4c** (Procedure *B*) (entry 3 in Table 1)
To a solution of benzoylsulfenyl iodide **1a** (0.264 g, 1.0 mmol) in dichloromethane (5 mL) was added cyclohexene **4c** (0.10 mL, 0.1 mmol) at 0 ºC and stirred at this temperature for 60 min. Dichloromethane (20 mL) was added and washed with 5% sodium hydrogen sulfite and then water (20 mL x 3), followed by drying over anhydrous sodium sulfate. After filtration of the sulfate , the filtrate was concentrated to ca. 2 mL. The concentrate was chromatographed on silica gel ptlc [eluant: dichloromethane/hexane (1:2), Rf = 0.57] to afford *trans*-2-iodocyclohexyl benzoyl sulfide **6ac** as a slight yellow oil; yield 0.194 g (56%); anal found C, 45.02; H, 4.41%; calc. for $C_{13}H_{15}IOS$ (346.23) requies C, 45.10; H, 4.37; i.r. ν_{max} (KBr)/cm^{-1}: 1663 ($\nu_{C=O}$); δ_H (270 MHz, CDCl, Me_4Si) 1.25–2.51 (m, 8H, CH_2); 4.14 (dt, J_{ab}= 6.4 Hz, *J* = 7.6 Hz, 1H, SCH^a); 4.37 (dt, J_{ab}= 6.4 Hz, *J* = 7.6 Hz, 1H, ICH^b); 7.40–8.00 (m, 5H, arom); *m/z* (EI, 20 eV) found M$^+$ 345.98851; calc. for $C_{13}H_{15}IOS$ requires 345.98883.); *m/z* (EI, 20 eV) found M$^+$ 345.98864; calc. for $C_{13}H_{15}IOS$ requires 345.98883.

Reaction of 4-methylbenzoylsulfenyl iodide ***1d*** *with cyclohexene* ***4c*** *(*Procedure *B)* (entry 4 in Table 1)
To a solution of 4-methylbenzoylsulfenyl iodide **1d** (0.264 g, 1.0 mmol) in dichloromethane (5 mL) was added cyclohexene **4c** (0.10 mL, 0.1 mmol) at 0 ºC and stirred at this temperature for 60 min. Dichloromethane (20 mL) was added and washed with 5% sodium hydrogen sulfite and then water (20 mL x 3), followed by drying over anhydrous sodium sulfate. After filtration of the sulfate , the filtrate was concentrated to ca. 2 mL. The concentrate was chromatographed on silica gel ptlc [eluant: dichloromethane/hexane (1:2), Rf = 0.57] to afford *trans*-2-iodocyclohexyl 4-methylbenzoyl sulfide **6dc** as a slight yellow oil; yield 0.267 g (74%); anal found C, 46.65; H, 4.79%; calc. for $C_{13}H_{15}IOS$ (360.25) requies C, 46.68; H, 4.76%; i.r. ν_{max} (KBr)/cm^{-1}: 1662 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 1.25–1.75 (m, 5H, CH_2); 2.02–2.25 (m, 2H, CH_2); 2.39 (s, 3 H, CH_3Ar); 4.30 (dt, *J* = 6.2, 7.5 Hz, 1H,

C*H*); 4.63 (dt, *J* = 6.2, 7.5 Hz, 1H, C*H*; *m/z* (EI, 20 eV) found M^+ 360.00513; calc. for $C_{14}H_{17}IOS$ requires 360.00448.

Reaction benzoylsulfenyl iodide **1a** *with 2-methylpropene* **4d** *in dichloromethane at 0 ºC (*Procedure *B)* (entry 5 in Table 1)
Similarly to Procedure *B*, benzoylsulfenyl iodide **1a** (0.264 g, 1.0 mmol) and 2-methylpropene **4d** [2.8 mL (0.168 g), 3.0 mmol –68 ºC were stirred in dichloromethane (8.2 mL) at 0 ºC for 60 mi. After the usual workup of the reaction mixture, chromatographic separation of the resulting concentrate on silica gel ptlc [eluant: dichloromethane/hexane (1:2), Rf = 0.50] afforded 2-iodo-2-methylpropyl benzoyl sulfide **6ad** as a slight yellow oil; yield 0.035g (10%) (anal found C, 41.22; H, 4.10%; calc. for $C_{11}H_{13}IOS$ (320.19) requires C, 41.26; H, 4.09%); i.r. ν_{max} (KBr)/cm^{-1}: 1664 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 2.00 (s, 6H, CH_3); 3.78 (s, 2H, CH_2); 7.44–7.62 (m, 3H, arom); 7.99–8.02 (m, 2H, arom); *m/z* (EI, 20 eV) found M^+ 319.97274l; calc. for $C_{11}H_{13}IOS$ requires 319.97318.

Reaction benzoylsulfenyl iodide **1a** *with 2-methyl-2-butene* **4e** *in dichloromethane at 0 ºC (*Procedure *A)* (entry 6 in Table 1)
Similarly to Procedure *A*, benzoylsulfenyl iodide **1a** (0.264 g, 1.0 mmol) and 2-methyl-2-butene **4e** (0.52 mL, 5.0 mmol) were stirred in dichloromethane (5 mL) at 0 ºC for 60 min. After the usual workup of the reaction mixture, chromatographic separation of the resulting concentrate on silica gel ptlc (eluant: dichloromethane/hexane (1:2), Rf = 0.60) afforded 1,2-dimethyl-2-iodopropyl benzoyl sulfide **6ae** (Markovnikov adduct) as a slight yellow oil; yield 0.215g (64%) (anal. found C, 43.09; H, 4.54 %; calc. for $C_{12}H_{15}IOS$ (334.22) requires C, 43.12; H, 4.52%); i.r. ν_{max} (KBr)/cm^{-1}: 1660 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 1.62 (d, *J* = 6.6 Hz, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 3.56 (q, J_{ab}= 6.6 Hz, 1H, C*H*); 7.23–7.87 (m, 5H, arom); *m/z* (EI, 20 eV) found M^+ 333.98671; calc. for $C_{12}H_{15}IOS$ requires 333.98883.

Reaction 4-methylbenzoylsulfenyl iodide **1d** *with 2-methyl-2-butene* **4e** *in dichloromethane at 0 ºC (*Procedure *A)* (entry 7 in Table 1)
Similarly to Procedure *A*, 4-methylbenzoylsulfenyl iodide **1d** (0.278 g, 1.0 mmol) and 2-methyl-2-butene **4e** (0.52 mL, 5 mmol) were stirred in dichloromethane (6.5 mL) at 0 ºC for 60 min. After the usual workup of the reaction mixture, chromatographic separation of the resulting concentrate on silica gel ptlc (eluant: dichloromethane/hexane (1:2), Rf = 0.60) afforded 1,2-dimethyl-2-iodopropyl 4-methylbenzoyl sulfide **6de** (Markovnikov adduct)) as a slight yellow oil; yield 0.192 g (55%) (anal. found C, 44.83; H, 4.95%; calc. for $C_{13}H_{17}IOS$ (348.24) requires C, 44.84; H, 4.92%); i.r. ν_{max} (KBr)/cm^{-1}: 1660 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$; Me_4Si) 1.62 (d, *J* = 6.6 Hz, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.39 (s, 3H, CH_3Ar), 3.56 (q, *J* = 6.6 Hz, 1H C*H*); 7.23 (d, *J* = 8.2 Hz, 2H, arom); 7.87 (d, *J* = 8.2 Hz, 2H, arom); *m/z* (EI, 20 eV) found M^+ 348.00393; calc. for $C_{13}H_{17}IOS$ requires 348.00448.

Reaction 4-chlorobenzoylsulfenyl iodide **1i** *with 2-methyl-2-butene* **4e** *in dichloromethane at 0 ºC for 3 h (*Procedure *A)* (entry 8 in Table 1)
Similarly to Procedure *A*, 4-chlorobenzoylsulfenyl iodide **1i** (0.298 g, 1.0 mmol) and 2-methyl-2-butene **4e** [0.52 mL, 5.0 mmol] were stirred in dichloromethane (5 mL) at 0 ºC for 60 min. After the usual workup of the reaction mixture, chromatographic separation of the resultig concentrate on silica gel ptlc [eluant: dichloromethane/hexane (1:2), Rf = 0.62] afforded 1,2-dimethyl-2-iodopropyl 4-chlorobenzoyl sulfide **6ie** (Markovnikov adduct) as a slight yellow oil; yield 0.184g (50%) (anal. found C, 39.07; H, 3.85%; calc. for $C_{12}H_{14}ClIOS$ (368.66) requires C, 39.10; H, 3.83%); i.r. ν_{max} (KBr)/cm^{-1}: 1665 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 1.58 (d, J_{ab}= 6.8 Hz, 3H, CH_3[a]); 2.00 (s, 3H, CH_3); 2.01 (s, 3H, CH_3);

3.50 (q, J_{ab}= 6.8 Hz, 1H, CH^{b}); 7.34–7.40 (m, 2H, arom); 7.82–7.89 (m, 2H, arom); *m/z* (EI, 20 eV) found M^+ 367.94707; calc. for $C_{12}H_{14}ClIOS$ requires 367.94986.

Reaction benzoylsulfenyl iodide **1a** *with 3,3-dimethyl-1-butene* **4f** *in dichloromethane at 0 ºC (*Procedure *A)* (entry 9 in Table 1)

Similarly to Procedure *A*, benzoylsulfenyl iodide **1a** (0.264 g, 1.0 mmol) and 3,3-dimethyl-1-butene **4f** (1.3 mL, 10.0 mmol) were stirred in dichloromethane (5 mL) at 0 ºC for 60 min. After the usual workup of the reaction mixture, chromatographic separation of the resulting concentrate on silica gel ptlc [eluant: dichloromethane/hexane (1:2), Rf = 0.53] afforded a mixture (70:30) of 1-iodomethyl-2,2-dimethylpropyl benzoyl sulfide **6af** and 2-iodo-3,3-dimethylbutyl benzoyl sulfide **7af** as a slight yellow oil; yield 0.224 g (64%).

Compound **6af**: i.r. ν_{max} (KBr)/cm^{-1}: 1666 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 1.22 (s, 3.9H, CH_3); 3.30 (dd, *J* = 2.4 Hz, 14.4 Hz, 1H, CH^{a}); 4.02 (dd, *J* = 2.4 Hz, 11.4 Hz, 1H, CH^{a}); 4.16 (dd, *J* = 11.4 Hz, 14.4 Hz, 1H, CH^{b}); 7.43–7.61 (m, 3H, arom); 7.97–8.05 (m, 2H, arom); *m/z* (EI, 20 eV) found 348.00346; calc. for $C_{13}H_{17}IOS$ requires 348.00448.

Compound **7af**: i.r. ν_{max} (KBr)/cm^{-1}: 1666 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 1.10 (s, 9H, CH_3); 3.27 (dd, *J* = 3.2, 14.5 Hz, 1H, CH^{a}); 3.84 (dd, *J* = 3.2, 10.6 Hz, 1H, CH^{a}); 4.00 (dd, *J* = 10.6, 14.5 Hz, 1H, CH^{b}); 7.38–7.59 (m, 3H, arom); 7.98–8.11 (m, 2H, arom); *m/z* (EI, 20 eV) found 348.00355; calc. for $C_{13}H_{17}IOS$ requires 348.00448.

The integratiopn ratio of the two peaks at δ 4.02 and δ 3.84 was 30:70, indicating that the product consisted of compounds **6af** (30%) and **7af** (70%).

Reaction benzoylsulfenyl iodide **1a** *with cis-2-butene* **4gz** *in hexane at 0 ºC (*Procedure *B)* (entry 10 in Table 1)

Similarly to the reaction with cyclohexene (Procedure *B*), to a suspension of benzoylsulfenyl iodide **1a** (0.132 g, 0.5 mmol) in hexane (10 mL) was added a solution (2.8 mL) of hexane containing *cis*-2-butene **4gz** (1.5 mL) that liquefied at –68 ºC by syringe at 0 ºC and the mixture was sirred at for 60 min at this temperature. Dichloromethane (20 mL) was added and washed with 5% aqueous sodium thiosulfate (10 mL) and then washed with water (20 mL x 3), followed by drying over anhydrous sodium sulfate. After iodine quenched by 5% aqueous sodium thiosulfate (10 mL), washed with water (30 mL x 3) and then dried over anhydrous sodium sulfate. The sodium sulfate was filtered out and concentrated to ca 2 mL by rotary evaporator (13 Pa). Chromatographic separation of the resulting concentrate on silica gel ptlc [eluant: dichloromethane/hexane (1:2), Rf = 0.46] afforded a mixture (50:50) of *threo*-**6ag$_{th}$** and *erythro*-1-methyl-2-iodopropyl benzoyl sulfide **6ag$_{er}$** as a slight yellow oil; yield 0.015 g (10%); i.r. ν_{max} (KBr)/cm^{-1}: 1658 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 1.51 (t, *J* = 6.5 Hz, 3H, CH_3); 1.92 (d, *J* = 7.0 Hz, 1.5H, CH_3); 2.00 (d, *J* = 7.0 Hz, 1.5 H, CH_3); 3.55 (dq, *J* = 4.3, 7.0 Hz, 1H, C*H*); 3.91 (dq, *J* = 2.8, 7.0 Hz, 0.5H, C*H*); 4.47–4.60 (m, 0.5H, C*H*); 7.42–7.60 (m 3H, arom), 7.89–8.01 (m, 2H, arom); *m/z* (EI, 20 eV) found: M^+ 319.97264; calc. for $C_{11}H_{13}IOS$ requires 319.97318.

The integratiopn ratio of the two peaks at δ 3.55 and δ 3.91 was 50:50, indicating that the product consisted of compounds **6ag$_{th}$** (50%) and **6ag$_{er}$** (50%).

Reaction benzoylsulfenyl iodide **1a** *with cis-2-butene* **4gz** *in dichloromethane at 0 ºC (*Procedure *B)* (entry 11 in Table 1)

Similarly to the reaction with cyclohexene **4c** (Procedure *B*), to a solution of benzoylsulfenyl iodide **1a** (0.229 g, 0.87 mmol) in dichloromethane (3 mL) was added a dichloromethane (5.8 mL) soution containing *cis*-2-butene **4gz** (1.5 mL) at –68 ºC and sirred at 0 ºC for 60 min. Dichloromethane (20 mL) was added and washed with 5% aqueous sodium hydrogen sulfate (10 mL) and then washed with water (20 mL x 3), followed by drying over anhydrous sodium sulfate. After removal of the sodium sulfate,

the filtrate was concentrated to ca 2 mL by rotary evaporator (13 Pa). Chromatographic separation of the resulting concentrate on silica gel ptlc [eluant: dichloromethane/hexane (1:2), Rf = 0.56] afforded a mixture (68 : 32) of *threo*-**6ag$_{th}$** and *erythro*-1-methyl-2-iodopropyl benzoyl sulfide **7ag$_{er}$** as a slight yellow oil; yield 0.215 g (77%); anal. found C, 41.20; H, 4.12%; calc. for $C_{11}H_{13}IOS$ (320.19) requies C, 41.26; H, 4.09%); i.r. ν_{max} (KBr)/cm^{-1}: 1658 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 1.51 (t, J = 7.0 Hz, 3H, CH_3); 1.92 (d, J = 7.0 Hz, 3H, CH_3); 2.00 (d, J = 7.0 Hz, 1 H, CH_3); 3.55 (dq, J = 4.3, 7.0 Hz, 1H, C*H*); 3.91 (dq, J = 2.8, 7.0 Hz, 0.5H, C*H*); 4.47–4.60 (m, 0.5 H, C*H*); 7.42–7.60 (m, 3H, arom); 7.94–7.98 (m, 2H, arom); *m/z* (EI, 20 eV) found: M$^+$ 319.97264; calc. for $C_{11}H_{13}IOS$ requires 319.97318.
The integratiopn ratio of the two peaks at δ 3.55 and δ 3.91 was 68 : 32, indicating that the product consisted of compounds **6ag$_{th}$** (68%) and **7ag$_{er}$** (32%).

Reaction benzoylsulfenyl iodide **1a** *with cis-2-butene* **4gz** *in acetonitrile at 0* ºC (entry 12 in Table 1)
Similar to the reaction of compond **1a** with *cis*-2-butene **4gz** in hexane (Procedure *B*), benzoylsulfenyl iodide **1a** (0.132 g, 0.5 mmol) and an acetnitrile solution (6 mL) containing *cis*-2-butene (0.8 mL, –68 ºC) were stirred at 0 ºC for 60 min. After the usual workup of the reaction mixture, chromatographic separation of the resulting concentrate on silica gel ptlc [eluant: dichloromethane/hexane (1:2), Rf = 0.45] afforded amixture of *threo*-1-methyl-2-iodopropyl benzoyl sulfide **6ag$_{th}$** and *erythro*-1-methyl-2-iodopropyl benzoyl sulfide **6ag$_{er}$** as a slight yellow oil; yield 0.086 g (54%); *m/z* (EI, 20 eV) found M$^+$ 319.97288; calc. for $C_{11}H_{13}IOS$ requires 319.97318.
The integratiopn ratio of the two peaks at δ 3.55 and δ 3.91 was 79:21, indicating that the product consisted of compounds **6ag$_{th}$** (100%) and **6ag$_{er}$** (0%).

Reaction 4-methylbenzoylsulfenyl iodide **1d** *with cis-2-butene* **4gz** *in dichloromethane at 0 ºC* (entry 13 in Table 1)
Similarly to Procedure *B*, to a solution of 4-methylbenzoylsulfenyl iodide **1d** (0.229 g, 0.87 mmol) in dichloromethane (3 mL) was added *cis*-2-butene **4gz** (1.5 mL, at –68 ºC) and stirred at 0 ºC for 60 min. Dichloromethane (20 mL) was added and washed with water (20 mL x 3), followed by drying over anhydrous sodium sulfate. After usual workup, chromatographic separation of the resulting concentrate on silica gel ptlc [eluant: dichloromethane/hexane (1:2), Rf = 0.53] afforded a mixture (87:13) of *threo*-**6dg$_{th}$** and *erythro*-1-methyl-2-iodopropyl 4-methylbenzoyl sulfide **6dg$_{er}$** as a slight yellow oil; yield 0.227 g (68%).
Compound **6dg$_{th}$**: i.r. ν_{max} (KBr)/cm^{-1}: 1658 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 1.50 (d, J = 7.0 Hz, 3H, CH_3), 1.90 (d, J = 6.5 Hz, 3H, CH_3), 2.39 (s, 3H, CH_3Ar), 3.91 (dq, J = 2.9, 7.0 Hz, 1H, C*H*), 4.55 (dq, J = 2.9, 6.5 Hz, 1H, C*H*), 7.21–7.24 (m, 2H, arom), 7.83–7.87 (m, 2H, arom); *m/z* (EI, 20 eV) found M$^+$ 334.21539; calc. for $C_{12}H_{15}IOS$ requires 334.21637.
Compound **6dg$_{er}$**: i.r. ν_{max} (KBr)/cm^{-1}: 1658 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si): 1.48 (d, J = 7.0 Hz, 3H, CH_3), 1.99 (d, J = 6.5 Hz, 3H, CH_3), 2.39 (s, 3H, CH_3Ar), 3.53 (dq, J = 4.4, 7.0 Hz, 1H, C*H*), 4.49 (dq, J = 4.4, 6.7 Hz, 1H, C*H*), 7.21–7.87 (m, 2H, arom), 7.82–7.87 (m, 2H, arom).
The integratiopn ratio of the two peaks at δ 3.53 and δ 3.91 was 87:13, indicating that the product consisted of compounds **6dg$_{th}$** (87%) and **6dg$_{er}$** (13%).

Reaction of 4-chlorobenzoylsulfenyl iodide **1i** *with cis-2-butene* **4gz** *in dichloromethane at 0* ºC *in the presence of methyltriethyl-ammonium iodide* (entry 14 in Table 1)
Similar to Procedure *B*, 4-chlorobenzoylsulfenyl iodide **1i** (0.242 g, 0.8 mmol), *cis*-2-butene **4gz** (1.5 mL, –68 ºC) and methyl-triethylammonium iodide (0.122 g, 0.50 mmol) were stirred in dichloromethane (6.5 mL) at 0 ºC for 60 min. Dichloromethane (20 mL) was added. After usual workup of the reaction mixture [removal of formed iodine with 5% aquous sodium thiosulfate (10 mL), washing with water (30 mL x 3) and then drying over anhydrous sodium sulfate, followed by the resulting

concentrate to ca. 2 mL], chromatographic separation of the concentrate on silica gel ptlc [eluant: dichloromethane/hexane (1:2), Rf = 0.50] afforded *threo*-1-methyl-2-iodopropyl 4-chlorobenzoyl sulfide **6ig$_{th}$** and a trace amount of *erythro*-1-methyl-2-iodopropyl 4-chlorobenzoyl sulfide **6ig$_{er}$**; yield 0.168 g (59%); δ_H (270 MHz, $CDCl_3$, Me_4Si) 1.48–2.01 (m, 6H, C*H*$_3$); 3.55 (dq, *J*= 4.2, 7.0 Hz, 1H, C*H*); 3.91 (dq, *J*= 2.9, 7.0 Hz, 0.5H, C*H*); 4.46–4.59 (m, 0.5H, C*H*); 7.40–7.43 (m, 2H, arom); 7.87–7.91 (m, 2H, arom); *m/z* (EI, 20 eV) found M^+ 353.93452; calc. for $C_{11}H_{12}ClIOS$ requires 353.93421.
The integration ratio of two peaks at δ 3.55 and 3.90 was a mixture of *threo*-**6ig$_{th}$** and *erythro*-isomer **6iger** (95: a trace)

Reaction of benzoylsulfenyl iodide **1a** *with trans-2-butene* **4g$_E$** *in dichloromethane* at 0 ºC *(*Procedure *B)* (entry 15 in Table 1)
Similar to Procedure *B*, benzoylsulfenyl iodide **1a** (0.264 g, 1.0 mmol) are *trans*-2-butene **4g$_E$** (1.5 mL) were stirred in dichloromethane (4.5 mL) at 0 ºC for 60 min. After the usual workup of the reaction mixture, chromatographic separation the resulting concentrate on silica gel ptlc [eluant: eluant: dichloromethane/hexane (1:2), Rf = 0.57] afforded a mixture (50:50) of *threo*-**6ag$_{th}$** and *erythro*-1-methyl-2-iodopropyl benzoyl sulfide **6ag$_{er}$** as a slight yellow oil; yield 0.236 g (9%); *m/z* (EI, 20 eV) found: M^+ 319.97194; calc. for $C_{11}H_{13}IOS$ requires 319.97318.

Reaction of benzoylsulfenyl iodide **1a** *with trans-2-butene* **4g$_E$** *in dichloromethane* at 0 ºC *(*Procedure *B)* (entry 16 in Table 1)
Similar to Procedure *B,* benzoylsulfenyl iodide **1a** (0.264 g, 1.0 mmol) are *trans*-2-butene **4g$_E$** (1.5 mL) were stirred in dichloromethane (4.5 mL) at 0 ºC for 3 h. After the usual workup of the reaction mixture, chromatographic separation the resulting concentrate on silica gel ptlc [eluant: eluant: dichloromethane/hexane (1:2), Rf = 0.57] afforded a mixture (48:52) of *threo*-**6ag$_{th}$** and *erythro*-1-methyl-2-iodopropyl benzoyl sulfide **6ag$_{er}$** as a slight yellow oil; yield 0.236 g (74%); *m/z* (EI, 20 eV) found: M^+ 319.97194; calc. for $C_{11}H_{13}IOS$ requires 319.97318.

Reaction benzoylsulfenyl iodide **1a** *with trans-2-butene* **4g$_E$** *in acetonitrile at 0* ºC (entry 17 in Table 1)
Similar to the reaction of compound **1a** with *cis*-2-butene in acetonitrile (*Pocedure B*), benzoylsulfenyl iodide **1a** (0.132 g, 0.5 mmol) and an acetnitrile solution (6 mL) containing *cis*-2-butene **4g$_E$** (0.8 mL, –68 ºC) were stirred at 0 ºC for 60 min. After the usual workup of the reaction mixture, chromatographic separation of the resulting concentrate on silica gel ptlc [eluant: dichloromethane/hexane (1:2), Rf = 0.45] afforded a mixture (7 : 93) of *threo*-**6ag$_{th}$** and *erythro*-1-methyl-2-iodopropyl benzoyl sulfide **6ag$_{er}$** as a slight yellow oil; yield 0.111 g (69%); *m/z* (EI, 20 eV) found M^+ 319.97288; calc. for $C_{11}H_{13}IOS$ requires 319.97318.
The integratiopn ratio of the two peaks at δ 3.55 and δ 3.91 was 79:21, indicating that the product consisted of compounds **6ag$_{th}$** (46%) and **6ag$_{er}$** (54%).

Reaction benzoylsulfenyl iodide **1a** *with 1,3-butadiene* **4h** *in dichloromethane at 0 ºC for 6 h (*Procedure *B)* (entry 18 in Table 1)
Similarly to the Procedures *B*, benzoylsulfenyl iodide**1a** (0.202 g, 0.77 mmol) and 1-3-butadiene **4h** (2 mL, at –68 ºC) were stirred in dichloromethane (4 mL) at 0 ºC for 60 min. After the usual workup of the reaction mixture, chromatographic separation of the resulting concentrate on silica gel ptlc [eluant: dichloromethane/hexane (1:2), Rf = 0.63] afforded 4-iodo-2-butnyl benzoyl sulfide **6ah** as a slight yellow oil; yield 0.082 g (33%); anal. found C, 41.49; H, 3.49%; calc. for $C_{11}H_{11}IOS$ (318.17) requires C, 41.52; H, 3.48%); i.r. ν_{max} (KBr)/cm^{-1}: 1658 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 3.70 (d, J_{ab}= 7.1 Hz, 2H, C*H*$_2$); 3.86 (d, J_{ab}= 8.0 Hz, 2H, C*H*$_2$); 5.77 (dt, J_{ab}= 7.1, 14.8 Hz, 1H, =C*H*); 6.01 (dt, J_{ab}=8.0,

14.8 Hz, 1H, =C*H*); 7.42–7.60 (m, 3H, arom), 7.79–7.93 (m, 2H, arom); *m/z* (EI, 20 eV) found M^+ 317.95733; calc. for $C_{11}H_{11}IOS$ requires 317.95753.

Reaction of benzoylsulfenyl iodide **1a** *with cis-2-butene* **4gz** *in dichloromethane at 0* ºC *in the presence of iodine*

Similar to Procedure *B*, to a solution of benzoylsulfenyl iodide **1a** (0.132 g, 0.5 mmol) in dicloromethane (3 mL), a dichloromethane solution (2.8 mL) containing *cis*-2-butene **4gz** (0.8 mL) that liquefied at –68 ºC by syringe and a dichloromethane solution (2 mL) containing iodide (0.025 g, 0.10 mmol) by pipet. The mixture was stirred in dichloromethane (5.8 mL) at 0 ºC for 60 min. Dichloromethane (20 mL) was added. After usual workup of the reaction mixture [removal of iodine with 5% aquous sodium thiosulfate (10 mL)], washing with water (30 mL x 3) and then drying over anhydrous sodium sulfate, followed by concentration to ca. 2 mL], chromatographic separation of the resulting concentrate on silica gel ptlc [eluant: dichloromethane/hexane (1:2), Rf = 0.55] afforded a mixture of *threo*-1-methyl-2-iodopropyl benzoyl sulfide **6ag$_{th}$** and *erythro*-1-methyl-2-iodopropyl benzoyl sulfide **6ag$_{er}$** as a slight yellow oil; yield 0.104 g (65%); *m/z* (EI, 20 eV) found M^+ 319.97272; calc. for $C_{11}H_{13}IOS$ requires 319.97318.

Reaction of 4-chlorobenzoylsulfenyl iodide **1i** *with trans-2-butene* **4g$_E$** *in dichloromethane at 0* ºC *in the presence of methyltriethyl-ammonium iodide* (additional Exp. S1)

Similar to Procedure *B*, 4-chlorobenzoylsulfenyl iodide **1i** (0.299 g, 1.0 mmol), *trans*-2-butene **4g$_E$** (1.5 mL, –68 ºC) and methyltriethylammonium iodide (0.122g, 0.5 mmol) were stirred in dichloromethane (7 mL) at 0 ºC for 60 min. Dichloromethane (20 mL) was added. After usual workup of the reaction mixture [removal of byproduct iodine with 5% aquous sodium thiosulfate (10 mL), washing with water (30 mL x 3) and then drying over anhydrous sodium sulfate, followed by the resulting concentrate to ca. 2 mL], chromatographic separation of the concentrate on silica gel ptlc [eluant: dichloromethane/hexane (1:2), Rf = 0.61] afforded a mixture (22:78) of *threo*-1-methyl-2-iodopropyl 4-chlorobenzoyl sulfide **6ig$_{th}$** and *erythro*-1-methyl-2-iodopropyl 4-chlorobenzoyl sulfide **6ig$_{er}$** as a slight yellow oil; yield 0.139g (39%); i.r. ν_{max} (KBr)/cm^{-1}: 1665 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 1.48–2.01 (m, 6H, C*H*$_3$); 3.55 (dq, *J*= 4.2, 7.0 Hz, 1H, C*H*); 3.91 (dq, *J*= 2.8, 7.0 Hz, 0.5H, C*H*); 4.46–4.59 (m, 1.5H, C*H*); 7.40–7.43 (m, 2H, arom); 7.87–7.91 (m, 2H, arom); *m/z* (EI, 20 eV) found M^+ 353.93452; calc. for $C_{11}H_{12}ClIOS$ requires 353.93421.

The integration ratio of two peaks at δ 3.55 and 3.91 was a mixture (22:78) of *threo*-**6ig$_{th}$** and *erythro*-isomer **6ig$_{er}$**.

Reaction benzoylsulfenyl iodide **1a** *with cis-2-butene* **4gz** *in dichloromethane at –68 ºC for 96 h (*Procedure *B)* (additional Exp. S2)

Similarly to Procedure *B*, benzoylsulfenyl iodide **1a** (0.132 g, 0.50 mmol) and *cis*-2-butene **4gz** (0.8 mL, added at –68 ºC) were stirred in dichloromethane (6 mL) at ⁻68 ºC for 96 h. After the usual workup of the reaction mixture, chromatographic separation of the resulting concentrate on silica gel ptlc [eluant: dichloromethane/hexane (1:2), Rf = 0.50] afforded a mixture (82:12) of *threo*-**6ag$_{th}$** and *erythro*-1-methyl-2-iodopropyl benzoyl sulfide **6ag$_{er}$** as a slight yellow oil; yield 0.006 g (4%); *m/z* (EI, 20 eV) found M^+ 319.97304; calc. for $C_{11}H_{13}IOS$ requires 319.97318.

The integration ratio of the two peaks at δ 3.55 and δ 3.91 was 82:12, indicating that the presence of compounds **6ag$_{th}$** and **6ag$_{er}$**.

Reaction benzoylsulfenyl iodide **1a** *with trans-2-butene* **4g$_E$** *in dichloromethane at –68* ºC *96 h (*Procedure *B)* (additional Exp. S3)

Similarly to Procedure *B*, benzoylsulfenyl iodide **1a** (0.132 g, 0.5 mmol) and *trans*-2-butene **4g**$_{E}$ (0.8 mL) were stirred in dichloromethane (23 mL) at –68 ºC for 96 h. After the usual workup of the reaction mixture, chromatographic separation of the resulting concentrate on silica gel ptlc [eluant: dichloromethane/hexane (1:2), Rf = 0.51] afforded a mixture (48:52) of *threo*-**6ag**$_{th}$ and *erythro*-1-methyl-2-iodopropyl benzoyl sulfide **6ag**$_{er}$ as a slight yellow oil; yield 0.007 g (5%); *m/z* (EI, 20 eV) found M^+ 319.97254; calc. for $C_{11}H_{13}IOS$ requires 319.97318.

Reaction of benzoylsulfenyl iodide **1a** *with cis-2-butene* **4gz** *in dichloromethane at 0* ºC *in the presence of iodine* (additional Exp. S4)
Similar to Procedure *B*, to a solution of benzoylsulfenyl iodide **1a** (0.132 g, 0.5 mmol) in diclorometane (3 mL), a dichloromethane solution (2.8 mL) containing *cis*-2-butene **4gz** (0.8 mL) that liquefied at –68 ºC by syringe and a dichloromethane solution (2 mL) containing iodide (0.025 g, 0.10 mmol) by pipet. The mixture was stirred in dichloromethane (5.8 mL) at 0 ºC for 60 min. Dichloromethane (20 mL) was added. After usual workup of the reaction mixture [removal of iodine with 5% aquous sodium thiosulfate (10 mL)], washing with water (30 mL x 3) and then drying over anhydrous sodium sulfate, followed by concentration to ca. 2 mL], chromatographic separation of the resulting concentrate on silica gel ptlc [eluant: dichloromethane/hexane (1:2), Rf = 0.55] afforded a mixture of *threo*-1-methyl-2-iodopropyl benzoyl sulfide **6ag**$_{th}$ and *erythro*-1-methyl-2-iodopropyl benzoyl sulfide **6ag**$_{er}$ as a slight yellow oil; yield 0.104 g (65%); *m/z* (EI, 20 eV) found M^+ 319.97272; calc. for $C_{11}H_{13}IOS$ requires 319.97318.

Reaction of benzoylsulfenyl iodide **1a** *with trans-2-butene* **4g**$_{E}$ *in dichloromethane at 0* ºC *in the presence of iodine* (additional Exp. S5)
Similar to Procedure *B*, benzoylsulfenyl iodide **1a** (0.132 g, 0.5 mmol) and *transs*-2-butene **4g**$_{E}$ (0.8 mL, at –68 ºC) were stirred in dichloromethane (5.8 mL) at 0 ºC for 60 min and dichloromethane (20 mL) was added. After usual workup of the reaction mixture [removal of formed iodine with 5% aquous sodium thiosulfate (10 mL)], washing with water (30 mL x 3) and then drying over anhydrous sodium sulfate, followed by concentration to ca. 2 mL], chromatographic separation of the resulting concentrate on silica gel ptlc [eluant: dichloromethane/hexane (1:2), Rf = 0.43] afforded a mixture of *threo*-**6ag**$_{th}$ and *erythro*-1-methyl-2-iodopropyl benzoyl sulfide **6ag**$_{er}$ as a slight yellow oil; yield 0.084 g (52%); *m/z* (EI, 20 eV) found M^+ 319.97302; calc. for $C_{11}H_{13}IOS$ requires 319.97318.

Reaction of 4-chlorobenzoylsulfenyl iodide **1i** *with trans-2-butene* **4g**$_{E}$ *in dichloromethane at 0* ºC *in the presence of methyltriethylammonium iodide* (additional Exp. S6)
Similar to Procedure *B*, 4-chlorobenzoylsulfenyl iodide **1i** (0.299 g, 1.0 mmol), *trans*-2-butene **4g**$_{E}$ (1.5 mL, –68 ºC) and methyltriethylammonium iodide (0.122g, 0.5 mmol) were stirred in dichloromethane (7 mL) at 0 ºC for 60 min. Dichloromethane (20 mL) was added. After usual workup of the reaction mixture [removal of byproduct iodine with 5% aquous sodium thiosulfate (10 mL), washing with water (30 mL x 3) and then drying over anhydrous sodium sulfate, followed by the resulting concentrate to ca. 2 mL], chromatographic separation of the concentrate on silica gel ptlc [eluant: dichloromethane/hexane (1:2), Rf = 0.61] afforded a mixture (22:78) of *threo*-1-methyl-2-iodopropyl 4-chlorobenzoyl sulfide **6ig**$_{th}$ and *erythro*-1-methyl-2-iodopropyl 4-chlorobenzoyl sulfide **6ig**$_{er}$ as a slight yellow oil; yield 0.139g (39%); i.r. ν_{max} (KBr)/cm^{-1}: 1665 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 1.48–2.01 (m, 6H, C*H*$_3$); 3.55 (dq, *J* = 4.2, 7.0 Hz, 1H, C*H*); 3.91 (dq, *J* = 2.8, 7.0 Hz, 0.5H, C*H*); 4.46–4.59 (m, 1.5H, C*H*); 7.40–7.43 (m, 2H, arom); 7.87–7.91 (m, 2H, arom); *m/z* (EI, 20 eV) found M^+ 353.93452; calc. for $C_{11}H_{12}ClIOS$ requires 353.93421.
The integration ratio of two peaks at δ 3.55 and 3.91 was a mixture of *threo*-**6ig**$_{th}$ and *erythro*-isomer **6ig**$_{er}$.

Reaction benzoylsulfenyl iodide **1a** *with trans-2-butene* **4g**$_{E}$ *in dichloromethane at 0* ºC *(*Procedure *B)* (additional Exp. S7)

Similarly to Procedure *B*, benzoylsulfenyl iodide **1a** (0.264 g, 1.0 mmol) and *trans*-2-butene **4g**$_{E}$ (1.5 mL) were stirred in dichloromethane (4.5 mL) at 0 ºC for 60 min. After the usual workup of the reaction mixture, chromatographic separation of the resulting concentrate on silica gel ptlc [eluant: dichloromethane/hexane (1:2), Rf = 0.57] afforded a mixture of *threo*-**6ag**$_{th}$ and *erythro*-1-methyl-2-iodopropyl benzoyl sulfide **6ag**$_{er}$ as a slight yellow oil; yield 0.236 g (74%); *m/z* (EI, 20 eV) found M^+ 319.97266l; calc. for $C_{11}H_{13}IOS$ requires 319.97318.

Reaction benzoylsulfenyl iodide **1a** *with trans-2-butene* **4g**$_{E}$ *in dichloromethane at 30* ºC *(*Procedure *B)* (additional Exp. S8)

Similarly to Procedure *B*, benzoylsulfenyl iodide **1a** (0.132 g, 0.5 mmol) and *trans*-2-butene **4g**$_{E}$ (0.8 mL) were stirred in dichloromethane (6 mL) at 30 ºC for 60 min. After the usual workup of the reaction mixture, chromatographic separation of the resulting concentrate on silica gel ptlc [eluant: dichloromethane/hexane (1:2), Rf = 0.52] afforded a mixture (46:54) of *threo*-**6ag**$_{th}$ and *erythro*-1-methyl-2-iodopropyl benzoyl sulfide **6ag**$_{er}$ as a slight yellow oil; yield 0.110g (69%); *m/z* (EI, 20 eV) found M^+ 319.97282l; calc. for $C_{11}H_{13}IOS$ requires 319.97318.

Reaction benzoylsulfenyl iodide **1a** *with trans-2-butene* **4g**$_{E}$ *in dichloromethane at –68 ºC in the presence of* C_6H_5OH (additional Exp. S9)

To a solution of benzoylsulfenyl iodide **1a** (0.264 g, 1.0 mmol) and phenol (0.020 g, 0.2 mmol) in dichloromethane (5 mL) was added *trans* 2-butene **4g**$_{E}$ (1.5 mL) that liquefied at –68 ºC) in the same solvent (3 mL) and stirred at 0 ºC for 30 min. Dichloro-methane (20 mL) was added and washed with 5% aqueous sodium thiosulfate (10 mL) and then with water (20 mL x 3), followed by drying over anhydrous sodium sulfate. After removal of the sodium sulfate, the filtrate was concentrated to ca. 2 mL by rotary evaporator (13 Pa). Chromatographic separation of the resulting concentrate on silica gel ptlc [eluant: dichloromethane/hexane (1:2), Rf = 0.60] afforded a mixture (49:51) of *threo*-**6ag**$_{th}$ and *erythro*-1-methyl-2-iodopropyl benzoyl sulfide **6ag**$_{er}$ as a slight yellow oil; yield 0.215 g (77%); *m/z* (EI, 20 eV) found M^+ 319.97294; calc. for $C_{11}H_{13}IOS$ requires 319.97318.

The integratiopn ratio of the two peaks at δ 3.55 and δ 3.91 was 49:51, indicating the presence of compounds **6ag**$_{th}$ (49%) and **6ag**$_{er}$ (51%).

Reaction of benzoylsulfenyl iodide **1a** *with trans-2-butene* **4g**$_{E}$ *in dichloromethane at 0* ºC *in the presence of iodine*

Similar to Procedure *B*, benzoylsulfenyl iodide **1a** (0.132 g, 0.5 mmol) and *transs*-2-butene **4g**$_{E}$ (0.8 mL, at –68 ºC) were stirred in dichloromethane (5.8 mL) at 0 ºC for 60 min and dichloromethane (20 mL) was added. After usual workup of the reaction mixture [removal of formed iodine with 5% aquous sodium thiosulfate (10 mL)], washing with water (30 mL x 3) and then drying over anhydrous sodium sulfate, followed by concentration to ca. 2 mL], chromatographic separation of the resulting concentrate on silica gel ptlc [eluant: dichloromethane/hexane (1:2), Rf = 0.43] afforded a mixture of *threo*-**6ag**$_{th}$ and *erythro*-1-methyl-2-iodopropyl benzoyl sulfide **6ag**$_{er}$ as a slight yellow oil; yield 0.084 g (52%); *m/z* (EI, 20 eV) found M^+ 319.97302; calc. for $C_{11}H_{13}IOS$ requires 319.97318.

Reaction of 4-methylbenzoylsulfenyl iodide **1d** *with trans-2-butene* **4g**$_{E}$ *in dichloromethane at 0* ºC

Similar to Procedure *B*, 4-methylbenzoylsulfenyl iodide **1d** (0.278 g, 1.0 mmol) and a dichloromethane solution (1.5 mL) containing *trans*-2-butene **4g**$_{E}$ (1.5 mL, –68 ºC) were stirred in dichloromethane (6.5 mL) at 0 ºC for 60 min. After the usual workup of the reaction mixture, the resulting concentrate was

separated by silica gel ptlc [eluant: dichloromethane/hexane (1:2), Rf = 0.53] afforded a mixture (87:13) of *threo*-**6dg$_{th}$** and *erythro*-methyl-2-iodopropyl 4-methylbenzoyl sulfide **6dg$_{er}$** as a slight yellow oil; yield 0.220 g (67%); i.r. ν_{max} (KBr)/cm^{-1}: 1658 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 1.47–2.00 (m, 3H, C*H*$_3$); 2.39 (s, 3H, C*H*$_3$Ar); 3.53 (dq, *J* = 4.4, 7.0 Hz, 0.5H, C*H*); 3.91 (dq, *J* = 2.9, 7.0 Hz, 0.5H, C*H*); 4.49–4.59 (m, 1.1H, C*H*); 7.40–7.43 (m, 2H, arom); 7.83–7.87 (m, 2H, arom); *m/z* (EI, 20 eV) found M$^+$ 334.21615; calc. for $C_{12}H_{15}IOS$ requires 334.21637.
The integration ratio of two peaks at δ 3.53 and 3.91 was a mixture of *threo*- and *erythro*-isomer.

Treatment of 1,2-dimethyl-2-iodopropyl benzoyl sulfide **6ad** *with potassium tert-butoxide*
To a solution of 1,2-dimethyl-2-iodopropyl benzoyl sulfide **6ad** (0.154 g, 0.46 mmol) in tetrahydrofuran (15 mL) was added potassium *tert*-butoxide (0.062 g, 0.56 mmol) and the mixture was stirred at 0 ºC for 6 h. Dichloromethane (40 mL) was added and washed with water (40 mL x 3), followed by drying over anhydrous sodium sulfate. Filtration of the sodium sulfate, the concentration of the filtrate to ca. 2 mL and chromatographic separation of the resulting concentrate on silica gel ptlc [eluant: dichloromethane/hexane (1:2), Rf = 0.48] afforded 1,2-dimethyl-2-propyl benzoyl sulfide **5ch** as a colorless oil; yield 0.048 g (51%); i.r. ν_{max} (KBr)/cm^{-1}: 1663 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 1.84 (s, 6H, C*H*$_3$); 2.03 (s, 3H, C*H*$_3$); 7.33–7.50 (m, 3H, arom); 7.88–7.91 (m, 2H, arom); *m/z* (EI, 20 eV) found M$^+$ 206.07558; calc. for $C_{12}H_{14}OS$ requires 206.07654.

Reaction of benzoylsulfenyl iodide **1a** *with 1-morpholino-1-cyclohexene* **4j**
A solution of benzoylsulfenyl iodide **1a** (0.264 g, 1.0 mmol) in ether (30 mL) was added at 15 ºC to 1-morpholino-1-cyclohexene **4j** (0.167 g, 1.0 mmol) in the same solvent (10 mL) and stirred at 20 ºC for 30 min. Hydrochloric acid (0.1N, 20 mL) was added and stirred for 30 min. The reaction mixture was extracted with ether (20 mL x 2). The extracts were washed with 5% aqueous sodium thiosulfate (30 mL) and water (50 mL x 2), followed by drying over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure. Chromatographic separation of the resulting concentrate on silica gel ptlc [eluant: dichloromethane/hexane (2:1)] gave 2-(benzoylsulfenyl)cyclohexanone **6aj** (Rf = 0.45) as colorless oil; yield 0.520 g (22%) and 2,6-di(benzoylsulfenyl)cyclohexanone **7aj** (Rf = 0.58) as colorless crystals; m.p. 163–166 ºC; yield 0.004 g (2%).
Compound **6aj**: i.r. ν_{max} (KBr)/cm^{-1}: 1659, 1715 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 1.42–2.92 (m, 8H, C*H*$_2$); 4.31–4.83 (m, 1H, C*H*; 7.21–8.24 (m, 5H, arom); *m/z* (EI, 20 eV) found M$^+$ 234.07074; calc. for $C_{13}H_{14}O_2S$ requires 234.07145.
Compound **7aj**: i.r. ν_{max} (KBr)/cm^{-1}: 1666, 1731 (C=O); δ_H (270 MHz, $CDCl_3$, Me_4Si) 1.62–2.81 (m, 6H, C*H*$_2$); 4.46–5.21 (m, 2H, C*H*); 7.42–8.02 (m, 10H, arom); *m/z* (EI, 20 eV) found M$^+$ 371.07623; calc. for $C_{20}H_{19}O_3S_2$ requires 371.07756.

Reaction of benzoylsulfenyl iodide **1a** *with 2-methyl-3-morpholinopropene* **4k**
Similarly to the reaction with 1-morpholino-1-cyclohexene **4j**, benzoylsulfenyl iodide **1a** (0.264 g, 1.0 mmol) and 2-methyl-3-morpholinopropene **4k** (0.158 g, 1.0 mmol) were stirred in ether (40 mL) at 20 ºC for 30 min. After usual workup, chromatographic separation of the resulting concentrate on silica gel ptlc [eluant: dichloromethane/hexane (3:2), Rf = 0.3] gave 2-benzoylsulfenylated aldehyde **6ak** and a very small amount of dibenzoyl disulfide **7'ak** as colorless crystals; yield 0.04 g (3%).
No spot near Rf = 0.50 indicating the formation of the expected 2-(benzoylsulfenyl)diisoproyl ketone **6ak** was observed.
The i.r. spectrum of compound **7'ak** was exactly extend with that of the authentic sample.

Compound **7'ak**: m.p. 129–131 ºC; i.r. ν_{max} (KBr)/cm^{-1}: 1683 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 7.44–7.61 (m, 3H, arom), 7.80–7.95 (m, 2H, arom); *m/z* (EI) *m/z* (EI, 20 eV) found M^+ 274.01156; calc. for $C_{14}H_{10}O_2S_2$ requires 274.01222.

Reaction of benzoylsulfenyl iodide **1a** *with 3,3-dimethyl-2-morpholinobutene* **4l**
The reaction of benzoylsulfenyl iodide **1a** (0.264 g, 1.0 mmol) with 3,3-dimethyl-2-morpholinobutene **4l** (0.169 g, 1.0 mmol) in ether (40 mL) at ºC for 30 min, followed by chromatographic separation of the resulting concentrate on ptlc [silica gel, eluant: dichloromethane/hexane (1:1), Rf= 0.58] gave 1-benzoylsulfenyl-3,3-dimethyl-2-butanone **6al** as colorless oil; yield 0.005 g (< 2%).
i.r. ν_{max} (KBr)/cm^{-1}: 1643 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 1.55 (s, 9H, CH_3); 2.96 (s, 2H, CH_2); 7.42–7.62 (m, 3H, arom); 7.95–8.01 (m, 2H, arom); *m/z* (EI) *m/z* (EI, 20 eV) found M^+ 208.05596; calc. for $C_{11}H_{12}O_2S$ requires 208.05580.

Reaction of benzoylsulfenyl iodide **1a** *with 2-methylsiloxybutene* **4m**
The reaction of benzoylsulfenyl iodide **1a** (0.264 g, 1.0 mmol) with 2-methylsiloxybutene **4m** (0.144 g, 1.0 mmol) in ether (40 mL) at ºC for 30 min, followed by chromatographic separation of the resulting concentrate on ptlc [silica gel, eluant: dichloromethane/hexane (1:1), Rf= 0.58] gave 4-benzoylsulfenyl-2-pentanone **6am** as colorless oil; yield 0.007 g (< 3%); i.r. ν_{max} (KBr)/cm^{-1}: 1648 (C=O); δ_H (270 MHz, $CDCl_3$, Me_4Si) 1.21 (d, *J* = 7.5 Hz, 3H, CH_3); 1.48 (t, *J* = 7.6 Hz, 3H, CH_3); 3.38 (q, *J* = 7.6 Hz, 2H, CH_2); 4.76 (q, *J* = 7.5 Hz, 1H, C*H*); 7.43–7.67 (m, 3H, arom); 7.94–8.02 (m, 2H, arom); *m/z* (EI) *m/z* (EI, 20 eV) found M^+ 208.05596; calc. for $C_{11}H_{12}O_2S$ requires 208.05580.

Preparation of *O*-alkyl acylsulfenates 8
O-Methyl benzoylsulfenate **8aa** (in Table S19)
Method A: A solution of benzoylsulfenyl iodide **1a** (0.264 g, 1.0 mmol) in methanol (10 mL) was added to a solution of sodium methoxide (0.054 g, 1 mmol) in methanol (20 mL) and stirred at –68 ºC for 30 min. After evaporation of the solvent under reduced pressure, ether (30 mL) was added. The resulting precipitates was filtered out and the filtrate was concentrated to ca. 1 mL under reduced pressure. The residue was chromatographed on preparative thine layer chromatograpy (after here: ptlc) [thick plate: 20 cm x 20 cm x 0.75 mm, eluant: dichloromethane/hexane (1:1), Rf = 0.37] to give *O*-methyl benzoylsulfenate **8aa** as colorless liquid ; yield 0.099 g (43%); i.r. ν_{max} (KBr)/cm^{-1}: 1679 ($\nu_{C=O}$); δ_H (270 MHz; $CDCl_3$; Me_4Si) 3.91 (s, 3H, OCH_3), 7.21–8.20 (m, 5H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 184.2 (*C*=O), 52.4 (O*C*H$_3$), 128.2–130.3 (arom); *m/z* (EI, 20 eV) found M^+ 168.02436; calc. for $C_8H_8O_2S$ requires 168.02450.

Method A: A solution of benzoylsulfenyl iodide **1a** (0.264 g, 1.0 mmol) in methanol (10 mL) was added to a solution of triethylammonium methoxide (0.133 g, 1 mmol) in methanol (20 mL) and stirred at –68 ºC for 30 min. Ether (30 mL) was added and washed with water (30 mL). After drying of the ether part over anhydrous sodium sulfate, the solvent was removed under reduced pressure (ca. 12 Pa). The residue was chromatographed on ptlc [thick plate: 20 cm x 20 cm x 0.75 mm, eluant: dichloromethane/hexane (1:1), Rf = 0.37] to give *O*-methyl benzoylsulfenate **8aa** as colorless liquid; yield 0.082 g (36%); i.r. ν_{max} (KBr)/cm^{-1}: 1679 ($\nu_{C=O}$).

O-Benzyl benzoylsulfenate **8ab** (in Table S19)
A solution of sodium benzyloxide (0.103 g, 0.8 mmol) in benzyl alcohol (2 mL) was added to benzoylsulfenyl iodide **1a** (0.264 g, 1.0 mmol) in ether (8 mL) and stirred at –15 ºC for 10 min and then –10 ºC for 15 min. After evaporation of the solvent under reduced pressure (ca. 15 Pa), the resulting residue was dissolved in hexane (40 mL) and the hexane-soluble part was concentrated to ca. 2 mL.

Chromatographic separation of the resulting concentrate on silica gel ptlc [eluant: chloroform/petroleum ether (b.p. < 45 ºC), (2:1), Rf = 0.6–0.9] gave *O*-benzyl benzoylsulfenate **8ab** as colorless microfine crystals; m.p. 54–56 ºC; yield 0.117 g (61%); anal. found C, 68.81; H, 4.99; calc. for $C_{14}H_{12}O_2S$ (244.31) requires C, 68.83; H, 4.95; i.r. ν_{max} (KBr)/cm^{-1}: 1671 ($\nu_{C=O}$); δ_H (90 MHz; $CDCl_3$; Me_4Si) 4.12 (s, 2H, OC*H*$_2$), 7.18–8.11 (m, 5H, arom); *m/z* (EI, 20 eV) found M$^+$ 244.05499; calc. for $C_{14}H_{12}O_2S$ requires 244.05580.

O-Ethyl benzoylsulfenate **8ac** (in Table S19)
Similarly to the entry 1, the reaction of benzoylsulfenyl iodide **1a** (0.264 g, 1 mmol) with sodium ethoxide (0.054 g, 1 mmol) in ethanol, followed by silica gel ptlc [eluant: dichloromethane/hexane (1:1), Rf = 0.37] gave *O*-ethyl benzoylsulfenate **8ac** as colorless oil; yield 0.114 g (63%); found C, 59.30; H, 5.56; calc. for $C_9H_{10}O_2S$ (182.24) requires C, 59.32; H, 5.53; i.r. ν_{max} (KBr)/cm^{-1}: 1679 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 1.36 (t, *J* = 7.8 Hz, 3H, C*H*$_3$); 4.02 (q, *J* = 7.8 Hz, 2H, OC*H*$_2$); 7.21–8.11 (m, 5H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 184.3 (*C*=O); 84.5 (O*C*H$_2$), 20.2 (*C*H$_3$), 128.2–130.3 (arom); δ_C(270 MHz; $CDCl_3$; Me_4Si) 84.5 (O*CH*$_2$), 20.2 (*C*H$_3$), 128.2–130.3 (arom);*m/z* (EI, 20 eV) found M$^+$ 182.04111; calc. for $C_9H_{10}O_2S$ requires 182.04015.

Ethylene-O,O'-di(benzoylsulfenate) **8ad** (in Table S19)
Similarly to the entry 1, the reaction of benzoylsulfenyl iodide **1a** (0.528 g, 2 mmol) with disodium ethyleneglycole (0.106 g, 1 mmol) in ethanol, fleshuly prepared from ethyleneglycole and sodium hydrooxide, followed by silica gel ptlc [eluant: dichloromethane/hexane (1:1), Rf = 0.47] gave ethylene-*O*,*O*'-di(benzoylsulfenate) **8ad** as colorless oil; yield 0.217 g (65%); found C, 57.44; H, 4.23; calc. for $C_{16}H_{14}O_4S_2$ (334.41) requires C, 57.47; H, 4.22; i.r. ν_{max} (KBr)/cm^{-1}: 1678 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 3.92 (s, 4H, C*H*$_2$); 7.21–8.11 (m, 10H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 184.8 (*C*=O); 85.3 (*C*H$_2$), 127.3–131.1 (arom); *m/z* (EI, 20 eV) found M$^+$ 334.03487; calc. for $C_{16}H_{14}O_4S_2$ requires 334.03335.

O-n-Propyl benzoylsulfenate **8ae** (in Table S19)
Similarly to the sulfenate **8aa**, the reaction of benzoylsulfenyl iodide **1a** (0.264 g, 1 mmol) with sodium *n*-propoxide (1 mmol) in *n*-propanol, by silica gel ptlc [eluant: dichloromethane/hexane (1:1), Rf = 0.38] gave *O-n*-propyl benzoylsulfenate **8ae** as colorless oil; yield 0.141 g (72%); found C, 61.19; H, 6.20; calc. for $C_{10}H_{12}O_2S$ (196.27) requires C, 61.20; H, 6.16; i.r. ν_{max} (KBr)/cm^{-1}: 1678 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 0.99 (t, *J* = 7.6 Hz, 3H, C*H*$_3$); 1.79 (sept, *J* = 7.8 Hz, 2H, C*H*$_2$); 4.29 (t, *J* = 7.8 Hz, 2H, OC*H*$_2$); 7.21–8.12 (m, 5H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 185.1 (*C*=O); 84.5 (O*C*H$_2$), 64.2 (*C*H$_2$), 20.2 (*C*H$_3$), 128.8–130.8 (arom); *m/z* (EI, 20 eV) found M$^+$ 196.05548; calc. for $C_{10}H_{12}O_2S$ requires 196.05580.

O-Isopropyl benzoylsulfenate **8af** (in Table S19)
Similarly to the entry 1, the reaction of benzoylsulfenyl iodide 1a (0.264 g, 1 mmol) with sodium *iso*-propoxide (1 mmol) in *iso*-propanol, followed by silica gel ptlc [eluant: dichloromethane/hexane (1:1), Rf = 0.32] gave *O-isopropyl* benzoylsulfenate 8af as colorless oil; yield 0.149 g (76%); i.r. ν_{max} (KBr)/cm^{-1}: 1681 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 1.38 (d, *J* = 7.7 Hz, 6H, C*H*$_3$), 4.01(sep, *J* = 7.7 Hz, 1H, OC*H*), 7.20–7.92 (m, 5H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 185.2 (*C*=O); 84.2 (O*C*H), 20.2 (*C*H$_3$), 128.4–130.6 (arom); *m/z* (EI, 20 eV) found M$^+$ 196.05622; calc. for $C_{10}H_{12}O_2S$ requires 196.05580.

O-Methyl 4-methylbenzoylsulfenate **8da** (in Table S20)

Similarly to theentry 1, the reaction of 4-methylbenzoyl-sulfenyl iodide **1d** (0.417 g, 1.5 mmol) with sodium methoxide (1.5 mmol) in methanol, followed by silica gel ptlc [eluant: dichloromethane/hexane (1:1), Rf = 0.35] gave *O*-methyl 4-methylbenzoyl-sulfenate **8da** as colorless oil; yield 0.145 g (53%); anal. found C, 59.30; H, 5.35%; calc. for $C_9H_{10}O_2S$ (182.24) requires C, 59.32; H, 5.53%; i.r. ν_{max} (KBr)/cm^{-1}: 1665 1670 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 2.35 (s, 3H, C*H*$_3$), 4.36 (s, 3H, OC*H*$_3$), 7.01–8.01 (m, 4H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 184.2 (*C*=O); 52.4 (O*C*H$_3$); 21.4 (*C*H$_3$Ar); 128.2–130.3 (arom); *m/z* (EI, 20 eV) found M$^+$ 182.04332; calc. for $C_9H_{10}O_2S$, requires 182.04015.

O-Ethyl 4-methylbenzoylsulfenate **8db** (in Table S20)
Similarly to entry 1, the reaction of 4-methylbenzoyl-sulfenyl iodide **1d** (0.396 g, 1.5 mmol) with sodium ethoxide (1.5 mmol) in ethanol, followed by silica gel ptlc [eluant: dichloromethane/hexane (1:1), Rf = 0.32] gave *O*-ethyl 4-methyl-benzoylsulfenate **8db** as colorless oil; yield 0.227 g (77%); anal. found C, 61.19; H, 6.18%; calc. for $C_9H_{10}O_2S$ (196.27) requires C, 61.20; H, 6.16%; i.r. ν_{max} (KBr)/cm^{-1}: 1673 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 1.36 (t, 7.9 Hz, 3H, C*H*$_3$), 2.35 (s, 3H, C*H*$_3$), 4.02 (q, 7.9 Hz, 2H, C*H*$_2$), 7.20–8.09 (m, 4H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 184.5 (*C*=O); 84.2 (*C*H$_2$); 21.6 (*C*H$_3$Ar); 20.2 (*C*H$_3$); 128.5–130.6 (arom); *m/z* (EI, 20 eV) found M$^+$ 196.05544; calc. for $C_9H_{10}O_2S$, requires 196.05580.

O-Methyl 4-methoxybenzoylsulfenate **8fa** (in Table S20)
Similarly to the entry 1, the reaction of 4-methoxybenzoyl-sulfenyl iodide **1f** (0.441 g, 1.5 mmol) with sodium methoxide (1.5 mmol) in methanol, followed by silica gel ptlc [eluant: dichloromethane/hexane (1:1), Rf = 0.39] gave *O*-methyl 4-methoxylbenzoyl-sulfenate **8fa** as colorless oil; yield 0.196 g (66%); i.r. ν_{max} (KBr)/cm^{-1}: 1645 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 3.85 (s, 3H, C*H*$_3$), 3.89 (s, 3H, C*H*$_3$), 7.20–7.89 (m, 4H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 184.9 (*C*=O); 56.4 (*C*H$_3$OAr), 54.3 (*C*H$_3$O); 128.3–132.3 (arom); *m/z* (EI, 20 eV) found M$^+$ 198.03549; calc. for $C_9H_{10}O_3S$, requires 198.03507.

O-Methyl 4-chlorobenzoylsulfenate **8ia** (in Table S20)
Similarly to the entry 1, the reaction of 4-chlorobenzoylsulfenyl iodide **1i** (0.448 g, 1.5 mmol) with sodium methoxide (1.5 mmol) in methanol, followed by silica gel ptlc [eluant: dichloro-methane/hexane (1:1), Rf = 0.35] gave *O*-methyl 4-chlorobenzoyl-sulfenate **8ia** as colorless oil; yield 0.185 g (57%); i.r. ν_{max} (KBr)/cm^{-1}: 1668, 1676 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 3.84 (s, 3H, C*H*$_3$), 7.2–7.8 (m, 4H, arom); δ_C (270 MH, $CDCl_3$, Me_4Si) 185.7 (*C*=O); 84.2 (*C*H$_2$O); 20.8 (s, C*H*$_3$); 128.3–132.3 (arom); *m/z* (EI, 20 eV) found M$^+$ 201.98432; calc. for $C_8H_7ClO_2S$ requires 201.98553.

O-Ethyl 4-chlorobenzoylsulfenate **8ib** (in Table S20)
Similarly to the entry 1, the reaction of 4-chlorobenzoylsulfenyl iodide **1i** (0.497 g, 1.5 mmol) with sodium ethoxide (1.5 mmol) in ethanol, followed by silica gel ptlc [eluant: dichloromethane/hexane (1:1), Rf = 0.35] gave *O*-ethyl 4-chlorobenzoyl-sulfenate **8ib** as colorless oil; yield 0.204 g (63%); i.r. ν_{max} (KBr)/cm^{-1}: 1668, 1676 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 1.36 (t, 7.9 Hz, 3H, C*H*$_3$), 4.02 (q, 7.9 Hz, 2H, C*H*$_2$), 7.2–8.1 (m, 4H, arom); δ_C (270 MH, $CDCl_3$, Me_4Si) 185.7 (*C*=O); 84.2 (*C*H$_2$O); 20.8 (s, C*H*$_3$); 128.3–132.3 (arom); *m/z* (EI, 20 eV) found M$^+$ 201.98432; calc. for $C_8H_7ClO_2S$ requires 201.98553.

O-Ethyl 4-chlorobenzoylsulfenate **8ib** (in Table S20)
Similarly to the entry 2, the reaction of 4-chlorobenzoylsulfenyl iodide **1i** (0.491 g, 1.5 mmol) with Et_3HN^+ $^-$OEt (1.5 mmol) in ethanol, followed by silica gel ptlc [eluant: dichloromethane/hexane (1:1), Rf = 0.32–0.76] gave *O*-ethyl 4-chlorobenzoyl-sulfenate **8ib** as colorless oil; yield 0.182 g (56%) for the use of Et_3HN^+ $^-$OEt]; anal. found C, 49.86; H, 4.20%; calc. for $C_9H_9ClO_2S$ (216.68) requires C,

49.89; H, 4.19%; i.r. ν_{max} (KBr)/cm^{-1}: 1668, 1676 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 1.36 (t, 7.9 Hz, 3H, CH_3), 4.02 (q, 7.9 Hz, 2H, CH_2), 7.2–8.1 (m, 4H, arom); δ_C (270 MH, $CDCl_3$, Me_4Si) 185.7 (*C*=O); 84.2 (*C*H_2O); 20.8 (s, CH_3); 128.3–132.3 (arom); *m/z* (EI, 20 eV) found M^+ 201.98432; calc. for $C_8H_7ClO_2S$ requires 201.98553.

Preparation of acyl alkyl/aryl disulfides 9

Benzoyl ethyl disulfide **9aa** (in Table S22)

To a solution of benzoylsulfenyl iodide **1a** (0.396 g, 1.5 mmol) in dichloromethane (5 mL) at –4 ºC, a solution of sodium ethanethiolate [0.068 g (98%)], 1.1 mmol) in ethanol (10 mL) was added and stirred for 15 min at and then 16 ºC for 15 min. Dichloromethane (40 mL) was added. The mixture was washed with 10% sodium thiosulfate (10 mL) and then water (3 x 10 mL). After drying sodium sulfate, evaporation of the solvents under reduced pressure (10–20 Pa) and silica gel ptlc [eluant: petroleum ether (b.p. < 40 ºC)/dichloromethane (1:2), Rf = 0.40–0.86] of the resulting residue gave benzoyl ethyl disulfide **9aa** as colorless oil; yield 0.187 g (63%); i.r. ν_{max} (KBr)/cm^{-1}: 1680 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 1.30 (t, *J* = 7.6 Hz, 3H, CH_3), 2.82 (q, *J* = 7.6 Hz, 2H, CH_2), 7.20–8.12 (m, 5H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 185.2 (*C*=O); 36.2 (*C*H_2); 16.2 (*C*H_3); 127.7–132.3 (arom); *m/z* (EI, 20 eV) found M^+ 198.01720; calc. for $C_9H_{10}OS_2$ requires 198.01731.

Benzoyl 2-hydoxyethyl disulfide **9ab** (in Table S22)

To a solution of benzoylsulfenyl iodide **1a** (0.396 g, 1.5 mmol) in dichloromethane (5 mL) at –4 ºC, a solution of 2-mercaptoethanol (98%) [0.132 g, 1.6 mmol] in the same solvent (10 mL) was added and stirred for 15 min at and then 16 ºC for 15 min. Dichloromethane (40 mL) was added. The mixture was washed with 10% sodium thiosulfate (10 mL) and then water (3 x 10 mL). After drying anhydrous sodium sulfate, evaporation of the solvent under reduced pressure (10–20 Pa) and silica gel ptlc [eluant: petroleum ether (b.p. < 40 ºC)/dichloromethane (1:2), Rf = 0.35–0.54] of the resulting residue gave benzoyl 2-hydroxyethyl disulfide **9ab** as colorless oil; yield 0.180 g (56%); i.r. ν_{max} (KBr)/cm^{-1}: 1688 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 3.37 (t, *J* = 7.7 Hz, 2H, OCH_2), 3.67 (t, *J* = 7.7 Hz, 2H, SCH_2), 4.8–5.1 (br. s, 1H, OH), 7.23–8.12 (m, 5H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 185.1 (*C*=O); 54.3 (S*C*H_2); 40.0 (O*C*H_2); 128.3–131.4 (arom); *m/z* (EI, 20 eV) found: M^+ 214.01128; calc. for $C_9H_{10}OS_2$ requires 214.01222. No obsevation of OH-signal (overlap with orther signals).

Benzoyl isopropyl disulfide **9ad** (in Table S22)

Similarly to the disulfide 9aa, the reaction of benzoylsulfenyl iodide **1a** (0.396 g, 1.5 mmol) with sodium isopropropylthiolate (1.5 mmol) in chloroform/ethanol (1:1), followed by silica gel ptlc [thick plate: 20 cm x 20 cm x 0.75 mm, eluant: petroleum ether (b.p. < 40 ºC)/dichloromethane (1:2), Rf = 0.83–0.87] gave benzoyl isopropyl disulfide 9ad as colorless oil; yield 0.162 g (51%); i.r. ν_{max} (KBr)/cm^{-1}: 1680 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$; Me_4Si) 1.29 (d, *J* = 7.7 Hz, 6H, CH_3), 3.11 (sept, *J* = 7.7 Hz, 1H, C*H*), 7.20–8,11 (m, 5H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 185.1 (*C*=O); 84.2 (*C*H); , 54.2 (*C*H_3); 20.2 (*C*H_3); 127.8–132.3 (arom); *m/z* (EI, 20 eV) found: M^+ 212.03221; calc. for $C_{10}H_{12}OS_2$ requires 212.03296.

Benzoyl n-butyl disulfide **9ae** (in Table S22)

Similarly to the disulfide 9aa, the reaction of benzoylsulfenyl iodide **1a** (0.396 g, 1.5 mmol) with sodium *n*-butanethiolate (1.5 mmol) in chloroform/ethanol (1:1), followed by silica gel ptlc [eluant: petroleum ether (b.p. < 40 ºC)/dichloromethane (1:2), Rf = 0.31–0.84] gave benzoyl *n*-butyl disulfide 9ad as colorless oil; yield 0.187 g (54%); anal. found C, 58.35; H, 6.25%; calc. for $C_{11}H_{14}OS_2$ (226.36) requires C, 58.37; H, 6.23%; i.r. ν_{max} (KBr)/cm^{-1}: 1686 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 0.71–2.00 (m, 7H, C$_3H_7$), 2.80 (t, *J* = 7.8 Hz, 2H, SCH_2), 7.31–8.22 (m, 5H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 185.1

(*C*=O); 40.3 (S*C*H$_2$); 32.2 (*C*H$_2$); 30.1 (*C*H$_2$); 16.3 (*C*H$_3$); 128.8–131.9 (arom); *m/z* (EI, 20 eV) found M$^+$ 226.04855; calc. for $C_{11}H_{14}OS_2$ requires 226.04861.

Benzoyl phenyl disulfide **9af** (in Table S22)
Similarly to the disulfide **9ad**, benzoylsulfenyl iodide **1a** (0.396 g, 1.5 mmol) was added to benzenecthiol (1.5 mmol) in chloroform/ethanol (1:1) at –15 ºC and stirred at 20 ºC for 20 min. After removal of the solvents, recrystallization of the resulting residue from petroleum ether (b.p. < 45 ºC)/dichloromethane gave benzoyl phenyl disulfide **9af**[52] as colorless crystals; m.p. 51–53 ºC; yield 0.181 g (49%); anal. found C, 63.37; H, 4.10%; calc. for $C_{13}H_{10}OS_2$ s(246.35) requires C, 63.38; H, 4.09%; i.r. ν_{max} (KBr)/cm^{-1}: 1688 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 6.32–7.88 (m, 10H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 184.1 (*C*=O); 127.8–131.1 (arom); *m/z* (EI, 20 eV) found M$^+$ 246.01745; calc, for $C_{13}H_{10}OS_2$ requires 246.01731.

(in Table S22)
Similarly to the disulfide **9af**, the reaction of benzoylsulfenyl iodide **1a** (0.396 g, 1.5 mmol) with sodium benezenethiolate (0.158 g, 1.5 mmol) in chloroform/ethanol (1:1), followed by recrystallization of the resulting residue from petroleum ether (b.p. < 45 ºC)/dichloromethane gave benzoyl phenyl disulfide **9af** as colorless crystals; yield 0.266 g (72%).

4-Methylbenzoyl phenyl disulfide **9df** (in Table S22)
Similarly to the disulfide **9af**, the reaction of 4-methylbenzoyl-sulfenyl iodide **1d** (0.417 g, 1.5 mmol) with piperidinium benezenethiolate (1.5 mmol) in chloroform/ethanol, following by recrystallization of the resulting residue from petroleum ether (b.p. < 45 ºC)/dichloromethane gave 4-methylbenzoyl phenyl disulfide **9df** as colorless crystals; m.p. 63–65 ºC; yield 0.25 g (55%); anal. found C, 65.57; H, 4.66%; calc. for $C_{14}H_{12}OS_2$ (260.37) requires C, 65.58; H, 4.65%; i.r. ν_{max} (KBr)/cm^{-1}: 1688 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 3.68 (s, 3H, C*H*$_3$); 7.32–7.88 (m, 9H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 184.7 (*C*=O); 21.7 (Ar*C*H$_3$); 127.8–131.1 (arom); *m/z* (EI, 20 eV) found M$^+$ 260.03243; calc. for $C_{14}H_{12}OS_2$ requires 260.03296.

4-Methoxybenzoyl ethyl disulfide **9fa** (in Table S22)
Similarly to the disulfide **9af**, the reaction of 4-methoxybenzoyl-sulfenyl iodide **1f** (0.441 g, 1.5 mmol) with sodium ethanethiolate (1.5 mmol) in ethanol, followed by silica gel ptlc [eluant: petroleum ether (b.p. < 45 ºC)/dichloromethane (1:2), Rf = 0.41–0.65] gave 4-methoxybenzoyl ethyl disulfide **9ff** as colorless oil; yield 0.223 g (70%); i.r. ν_{max} (KBr)/cm^{-1}: 1670 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 1.30 (t, *J* = 7.8 Hz, 3H, C*H*$_3$), 2.82 (q, *J* = 7.8 Hz, 2H, C*H*$_2$), 3.87 (s, 3H, OC*H*$_3$), 6.82–8.12 (m, 4H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 189.2 (*C*=O); 55.6 (*C*H$_3$O); 35.6 (*C*H$_2$); 16.4(*C*H$_3$); 128.5–132.4 (arom); *m/z* (EI, 20 eV) found M$^+$ 212.03743; calc. for $C_{10}H_{12}O_2S_2$, requires 212.0329.

4-Methoxybenzoyl n-butyl disulfide **9fe** (in Table S22)
Similarly to the disulfide **9aa**, the reaction of 4-methoxylbenzoyl-sulfenyl iodide **1f** (0.42 g, 1.4 mmol) with sodium ethanethiolate (1.5 mmol) in ethanol, followed by silica gel ptlc [eluant: petroleum ether (b.p. < 45 ºC)/dichloromethane (1:2), Rf = 0.48–0.75] gave 4-methoxybenzoyl *n*-butyl disulfide **9fa** as colorless oil; yield 0.261 g (52%); i.r. ν_{max} (KBr)/cm^{-1}: 1674 (C=O); δ_H (270 MHz, $CDCl_3$, Me_4Si) 0.70–1.82 (m, 7H, C$_3$*H*$_7$), 2.76(t, *J* = 7.8 Hz, 2H, SC*H*$_2$), 3.88 (s, 3H, ArOC*H*$_3$), 6.82–8.12 (m, 4H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 188.2 (C=O); 55.6 (C*H*$_3$OAr); 40.6 (C*H*$_2$); 32.6 (C*H*$_2$); 16.4 (C*H*$_3$); 127.9–131.6 (arom); *m/z* (EI, 20 eV) found M$^+$ 256.05883; calc, for $C_{12}H_{16}O_2S_2$, requires 256.05917.

4-Methoxybenzoyl phenyl disulfide **9ff** (in Table S22)

Similarly to the disulfide **9ad**, the reaction of 4-methoxylbenzoyl-sulfenyl iodide **1f** (0.412 g, 1.4 mmol) with sodium benzene-thiolate (0.189 g, 1.4 mmol) in ethanol, following by recrystallization of the resulting residue from petroleum ether (b.p. < 45 ºC)/dichloromethane gave 4-methoxybenzoyl phenyl disulfide **9fe** as colorless crystals; m.p. 54–56 ºC; yield 0.255 g (66%); anal. found C, 60.81; H, 4.39%; calc. for $C_{14}H_{12}O_2S_2$ (276.37) requires C, 60.84; H, 4.38%; i.r. ν_{max} (KBr)/cm^{-1}: 1685 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 3.86 (s, 3H, ArOC*H*$_3$); 6.82–8.12 (m, 9H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 188.3 (*C*=O); 55.5 (ArO*C*H$_3$); 127.8–131.1 (arom); *m/z* (EI, 20 eV) found M$^+$ 276.02694; calc. for $C_{14}H_{12}O_2S_2$, requires 276.02787.

4-Methoxybenzoyl phenyl disulfide **9ff** (in Table S22)
Similarly to the disulfide **9af**, the reaction of 4-methoxylbenzoyl-sulfenyl iodide **1f** (0.412 g, 1.4 mmol) with benzenethiol (0.154 g, 1.4 mmol) in ethanol, following by recrystallization of the resulting residue from petroleum ether (b.p. < 45 ºC)/dichloromethane gave 4-methoxybenzoyl phenyl disulfide **9ff** as colorless crystals; m.p. 54–56 ºC; yield 0.244 g (63%).

4-Methoxybenzoyl 4-methylphenyl disulfide **9fg** (in Table S22)
Similar to the disulfide **9af**, the reaction of 4-methoxylbenzoy-lsulfenyl iodide **1f** (0.294 g, 1.0 mmol) with 4-methylbenzenethiol (0.124 g, 1.0 mmol) in dichloromethane (25 mL), following by recrystallization of the resulting residue from petroleum ether (b.p. < 45 ºC)/dichloromethane gave 4-methoxybenzoyl 4-methylphenyl disulfide **9fg** as colorless crystals; m.p. 58–61 ºC; yield 0.209 g (73%); anal. found C, 62.01; H, 4.88%; calc. for $C_{15}H_{14}O_2S_2$ (290.40) requires C, 62.04; H, 4.86%; i.r. ν_{max} (KBr)/cm^{-1}: 1689 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 3.67 (t, *J* = 7.9 Hz, 3H, ArC*H*$_3$); 3.87 (s, 3H, ArOC*H*$_3$); 6.80–8.12 (m, 8H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 188.4 (*C*=O); 56.6 (*C*H$_3$OAr); 21.7 (*C*H$_3$Ar); 128.1–131.6 (arom); *m/z* (EI, 20 eV) found M$^+$ 290.04263; calc. for$C_{15}H_{14}O_2S_2$ requires 290.04352.

4-Methoxybenzoyl 4-chlorophenyl disulfide **9fh** (in Table S22)
Similar to the disulfide **9af**, the reaction of 4-methoxylbenzoyl-sulfenyl iodide **1f** (0.353 g, 1.2 mmol) with 4-chlorobenzenethiol (0.124 g, 1.0 mmol) in dichloromethane (25 mL), following by recrystallization of the resulting residue from petroleum ether (b.p. < 45 ºC)/dichloromethane gave 4-methoxybenzoyl 4-chlorolphenyl disulfide **9fh** as colorless crystals; m.p. 67–70 ºC; yield 0.265 g (71%); anal. found C, 54.08; H, 3.59%; calc. for $C_{14}H_{11}ClO_2S_2$ (310.82) requires 54.10; H, 3.57%; i.r. ν_{max} (KBr)/cm^{-1}: 1688 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 3.87 (s, 3H, ArOC*H*$_3$); 6.83–8.12 (m, 8H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 188.4 (*C*=O); 56.6 (*C*H$_3$OAr); 128.3–130.6 (arom); *m/z* (EI, 20 eV) found M$^+$ 309.98856; calc. for $C_{14}H_{11}ClO_2S_2$ requires 309.98890.

4-Chlorobenzoyl ethyl disulfide **9ia** (in Table S22)
Similar to the disulfide **9aa**, the reaction of 4-chlorobenzoyl-sulfenyl iodide **1i** (0.388 g, 1.3 mmol) with ethanethiol (1.3 mmol)/triethylamine (1.3 mmol) in dichloromethane (5 mL), following by silica gel ptlc [eluant: hexane/dichloromethane (1:2), Rf = 0.08–0.26] gave 4-chlorobenzoyl ethyl disulfide **9ia** as colorless oil; yield 0.224 g (74%); i.r. ν_{max} (KBr)/cm^{-1}: 1690 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 1.30 (t, *J* = 7.8 Hz, 3H, C*H*$_3$); 2.82 (q, *J* = 7.8 Hz, 2H, SC*H*$_2$); 6.83–8.11 (m, 4H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 190.4 (*C*=O); 37.2 (S*C*H$_2$); 16.9 (*C*H$_3$); 128.1–140.3 (arom); *m/z* (EI, 20 eV) found: M$^+$ 231.97864; calc. for $C_9H_9ClOS_2$ (232.75) requires 231.97833.

4-Chlorobenzoyl phenyl disulfide **9if** (in Table S22)
Similar to the disulfide **9af**, the reaction of 4-chlorobenzoyl-sulfenyl iodide **1i** (0.328 g, 1.1 mmol) with benzenethiol (0.110 g, 1.0 mmol) in dichloromethane (25 mL), following by recrystallization of the

resulting residue from petroleum ether (b.p. < 45 ºC)/dichloromethane gave 4-chlorobenzoyl phenyl disulfide **9if** as colorless crystals. m.p. 89–91 ºC; yield 0.142 g (46%); anal. found C, 55.58; H, 3.26%; calc. for $C_{13}H_9ClOS_2$ (280.79) requires C, 55.61; H, 3.23%; i.r. ν_{max} (KBr)/cm^{-1}: 1690 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 6.83–8.12 (m, 9H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 190.4 (*C*=O), 128.4–140.2 (arom); *m/z* (EI, 20 eV) found M^+ 279.97788; calc. for $C_{13}H_9ClOS_2$ requires 279.97833.

Preparation of *unsymmetrical diacyl disulfides* 10

Benzoyl 4-methylbenzoyl disulfide **10aa** (entry 1 in Table S23)

A solution of benzoylsulfenyl iodide **1a** (0.317 g, 1.2 mmol) in a mixed solvent ($CHCl_3$/MeOH (1:1)), 10 mL) is added to potassium 4-methylbenzenecarbothioate (0.210 g, 1.2 mmol) in ethanol 5 mL) at –16 ºC and stirred at 0 ºC for 30 min. After removal of the solvent under reduced pressure (ca. 2 Pa), dichloromethane (40 mL) was added. The mixture was washed with 10% sodium hydrogen sulfate (10 mL) and then water (3 x 10 mL). After removal of sodium sulfate and KI by glass filter, the solvent was evaporated under reduced pressure (ca.10 Pa). Recrystallization of the resulting residue from dichloromethane/hexane gave benzoyl 4-methylbenzoyl disulfide **10aa** as colorless crystals; m.p. 89–91 ºC; yield 0.228 g (66%); anal. found C, 62.46; H, 4.21%; calc. for $C_{15}H_{12}O_2S_2$ (288.38) requires C, 62.47; H, 4.19%; i.r. ν_{max} (KBr)/cm^{-1}: 1705, 1687 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 2.38 (s, 3H, C*H*$_3$); 7.21–7.88 (m, 5H, arom); 7.49–7.98 (m, 4H, arom); δ_C (270 MHz; $CDCl_3$; Me_4Si) 190.2 (*C*=O); 186.5 (*C*=O); 22.4 (*C*H$_3$Ar); 127.2–130.8 (arom); *m/z* (EI, 20 eV) found M^+ 288.02781; calc. for $C_{15}H_{12}O_2S_2$ requires 288.02787.

(entry 2 in Table S23)

Similarly to the entry 1, the reaction of benzoylsulfenyl iodide **1a**, wih piperidinium 4-methylbenzenecarbothioate in a mixed solvent ($CHCl_3$/MeOH (1:1)), 10 mL) gave benzoyl 4-methylbenzoyl disulfide **10aa** in 52% yield. The i.r. and ^{1}H NMR spectra were exactly coincided with those of the authentic sample prepared in entry 1.

(entry 3 in Table S23)

Similarly to the entry 3, the reaction of benzoylsulfenyl iodide **1a** with 4-methylbenzenecarbothoic acid in $CHCl_3$ (10 mL) for 30 min gave diacyl disulfide **10aa** in 58% yield.

The i.r. and ^{1}H NMR spectra exactly coincided with those of the authentic sample prepared in entry 1.

Benzoyl 4-methoxybenzoyl disulfide **10ab** (entry 5 in Table S23)

Similarly to the entr 3, the reaction of benzoylsulfenyl iodide **1a** (0.317 g, 1.2 mmol) with piperidinium 4-methoxybenzene-carbothioate (0.284 g, 1.2 mmol) in a mixed solvent ($CHCl_3$/MeOH (1:1)), 10 mL), following by recrystallization from dichloromethane/petroleum ether (b.p. < 45 ºC), gave benzoyl 4-methoxybenzoyl disulfide **10ab** as colorless crystals; m.p. 95–98 ºC; yield 0.170 g (49%); anal. found C, 59.17; H, 3.99%; calc. for $C_{15}H_{12}O_3S_2$ (304.38) requires C, 59.19; H, 3.97%; i.r. ν_{max} (KBr)/cm^{-1}: 1702, 1689 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 3.88 (s, 3H, C*H*$_3$O); 6.82–8.46 (m, 5H, arom); 7.10–8.55 (m, 4H, arom); δ_C (270 MHz; $CDCl_3$; Me_4Si) 199.2 (*C*=O); 185.7 (*C*=O); 54.6 (*C*H$_3$OAr); 127.2–131.8 (arom); *m/z* (EI, 20 eV) found: M^+ 304.02233; calc. for $C_{15}H_{12}O_3S_2$ requires 304.02279.

(entry 6 in Table S23)

Similarly to the entry 3, the reaction of benzoylsulfenyl iodide **1a** with 4-methoxybenzenecarbothoic acid in $CHCl_3$ (10 mL) at –15–0 ºC for 30 min, following by recrystallization from dichloromethane/petroleum ether (b.p. < 45 ºC), gave benzoyl 4-methoxybenzoyl disulfide **10ab** in 53% yield.

The i.r. and ^{1}H NMR spectra exactly coincided with those of the authentic sample prepared in entry 4.

Benzoyl 4-chlorobenzoyl disulfide ***10ac*** (entry 7 in Table S23)
Similarly to the entry 1, the reaction of benzoylsulfenyl iodide **1a** (0.317 g , 1.2 mmol) with potassium 4-chlorobenzenecarbothioate (0.252 g, 1.2 mmol in a mixed solvent ($CHCl_3$/MeOH (1:1)), 10 mL) at 0 – –15 ºC for 30 min, following by recrystallization with dichloromethane/petroleum ether (b.p. < 45 ºC), gave benzoyl 4-chlorobenzoyl disulfide **10ac** as colorless crystals; m.p. 89–92 ºC (89–92 ºC); yield 0.165 g (44%); anal. found C, 53.878; H, 2.94%; calc. for $C_{14}H_9ClO_2S_2$ (308.80) requires C, 53.85; H, 2.91%; i.r. ν_{max} (KBr)/cm^{-1}: 1690, 1681 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 6.82–8.46 (m, 5H, arom); 7.30–8.35 (m, 4H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 199.7 (*C*=O); 187.7 (*C*=O); 128.1–131.8 (arom); *m/z* (EI, 20 eV) found M^+ 310.95312; calc. for $C_{14}H_9ClO_2S_2$ requires 310.95227.

(entry 8 in Table S23)
Similarly to the entry 6, the reaction of benzoylsulfenyl iodide **1a** (1 mmol) with piperidinium 4-chlorobenzenecarbothioate (1 mmol) gave the disulfide **10ac** in 57% yield.
The i.r. and ^1H NMR spectra were exactly coincided with those of the authentic sample prepared in entry 6.

(entry 9 in Table S23)
Similarly to entry 5, the reaction of benzoylsulfenyl iodide **1a** with 4-chlorobenzenecarbothioic acid in $CHCl_3$. gave the disulfide **10ac** in 39% yield.
The i.r. and ^1H NMR spectra exactly coincided with those of the authentic sample prepared in entry 6.

4-Methylbenzoyl benzoyl disulfide **10da** (entry 10 in Table S23)
Similarly to the entry 1, the reaction of 4-methylbenzoylsulfenyl iodide **1d** (0.334 g, 1.2 mmol) with potassium benzenecarbothioate (0.211 g, 1.2 mmol) in $CHCl_3$/MeOH (1:1), following by recrystallization from dichloromethane/petroleum ether (b.p. < 45 ºC) gave 4-methylbenzoyl benzoyl disulfide **10da** (=**10da**) as colorless crystals; m.p. 90–92 ºC; yield 0.111 g (32%); anal. found C, 60.33; H, 4.44%; calc. for $C_{16}H_{14}O_3S_2$ (318.41) requires C, 60.35; H, 4.43%; i.r. ν_{max} (KBr)/cm^{-1}: 1702, 1671 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 2.38 (s, 3H, C*H*$_3$); 3.87 (s, 3H, C*H*$_3$O); 7.21–8.65 (m, 4H, arom); 7.12–8.42 (m, 4H, arom); δ_C (270 MHz; $CDCl_3$; Me_4Si) 199.5 (*C*=O); 187.3 (*C*=O); 58.4 (*C*H$_3$OAr); 22.6 (*C*H$_3$Ar); 127.5–133.6 (arom); *m/z* (EI, 20 eV) found M^+ 318.038059; calc. for $C_{16}H_{16}O_3S_2$ requires 318.03844.

4-Methylbenzoyl benzoyl disulfide **10da** (entry 11 in Table S23)
Similarly to the entry 3, the reaction of 4-methylbenzoylsulfenyl iodide **1d** (1.2 mmol) with benzenecarbothioic acid in a mixed solvent of $CHCl_3$, 10 mL), following by recrystallization from dichloromethane/petroleum ether (b.p. < 45 ºC), gave 4-methyl-benzoyl benzoyl disulfide **10da**; m.p. 89–91 ºC; yield 0.145 g (42%).
The i.r. and ^1H NMR spectra exactly coincided with those of the authentic sample prepared in entry 9.

4-Methylbenzoyl 4-methoxybenzoyl disulfide **10db** (entry 12 in Table S23)
Similarly to the entry 1, the reaction of 4-methylbenzoylsulfenyl iodide **1d** (0.334 g, 1.2 mmol) with potassium 4-methoxy-benzenecarbothioate **1f** in $CHCl_3$/MeOH (20 mL), following by recrystallization from dichloromethane/petroleum ether (b.p. < 45 ºC), gave 4-methoxybenzoyl 4-methylbenzoyl disulfide **10fa** (= **10db**). m.p. 100–102 ºC; yield 0.225 g (59%). *m/z* (EI, 20 eV) found M^+ 291.96443; calc for $C_{16}H_{14}O_2S_2$ requires 291.96527.

4-Methoxybenzoyl 4-methylbenzoyl disulfide **10fa** (= **10db**) (entry 13 in Table S23)

Similarly to the entry 3, the reaction of 4-methoxybenzoylsulfenyl iodide **1f** (0.353 g, 1.2 mmol) with 4-methylbenzenecarbothioic acid (1.2 mmol) in $CHCl_3$/MeOH (20 mL), following by recrystallization from chloroform 30 mL), gave 4-methoxybenzoyl 4-methylbenzoyl disulfide **10fa** (= **10db**). m.p. 99–101 ºC; yield 0.233 g (51%), *m/z* (EI, 20 eV) found M^+ 291.96443; calc for $C_{16}H_{14}O_2S_2$ requires 291.96527.
The i.r. and ^{1}H NMR spectra exactly coincided with those of the authentic sample prepared in entry 11.

4-Methoxybenzoyl 4-chlorobenzoyl disulfide ***10fb*** (entry 14 in Table S23)
Similarly to the entry 1, the reaction of 4-methoxybenzoylsulfenyl iodide **1f** (0.382 g, 1.3 mmol) with potassium 4-chlorobenzene-carbothioate (0.274 g, 1.3 mmol) in $CHCl_3$/MeOH (1:1), following by recrystallization of the residue from dichloromethane/petroleum ether (b.p. < 45 ºC), gave chemically pure 4-methoxybenzoyl 4-chlorobenzoyl disulfide **10fb** as colorless crystals; m.p. 90–92 ºC (89–90 ºC)[52]; yield 0.286 g (65%); anal. found C, 53.16; H, 3.29%; calc. for $C_{15}H_{11}ClO_3S_2$ (338.83) requires C, 53.17; H, 3.27%; i.r. ν_{max} (KBr)/cm^{-1}: 1692, 1673 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 3.87 (s, 3H, C*H*$_3$O); 7.12–8.46 (m, 4H, arom); 7.23–8.47 (m, 4H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 199.4 (*C*=O), 185.6 (*C*=O), 59.7 (*C*H$_3$OAr); 127.5–133.6 (arom); *m/z* (EI, 20 eV) found M^+ 337.98307; calc. for $C_{15}H_{11}ClO_3S_2$ requires 337.98381.

(entry 15 in Table S23),
Similarly to the entry 1, the reaction of 4-methoxybenzoylsulfenyl iodide **1f** (0.353 g, 1.2 mmol) with 4-chlorobenzenecarbothioic acid (0.173 g, 1.2 mmol) in chloroform (20 mL), following by recrystallization of the residue from dichloromethane/petroleum ether (b.p. < 45 ºC), gave 4-methoxybenzoyl 4-chlorobenzoyl disulfide **10fb** as colorless crystals; m.p. 89–91 ºC (89–90 ºC),[52] yield 0.224 g (55%).
The i.r. spectrrum coincided with that of the authentic sample which was prepared in entry 13.

_Se_-Organyl acylsulfenoselenoates 11
Se-Phenyl benzoylsulfenoselenoate **11aa** (entry 1 in Table S25)
A solution of benzoylsulfenyl iodide **1a** (0.396 g, 1.5 mmol) in $CHCl_3$ (40 mL) was added to sodium benzeneselenolate (0.268 g, 1.5 mmol) in MeOH/$CHCl_3$ (1/1) (20 mL) at –17 ºC and stirred for 16 min and then at 0 ºC for 30 min. After evaporation of the solvent, ether (40 mL) was added. The resulting precipitates was filtered out and the ether was removed under reduced pressure (ca. 12 Pa). Recrystallization of the resulting residue from dichloromethane/hexane (1:2) gave *Se*-phenyl benzoylsulfeno-selenoate **11aa** as pale yellow crystals; m.p. 35–37 ºC (35–37 ºC)[54]; yield 0.277 g (58%).); anal. found C, 53.21; H, 3.45%; calc. for $C_{13}H_{10}OSSe$ (293.24) requires C, 53.25; H, 3.44%; i.r. ν_{max} (KBr)/cm^{-1}: 1665 ($\nu_{C=O}$); δ_H (90 MHz, $CDCl_3$, Me_4Si) 6.71–8.24 (m, 10H, arom); δ_C (270 MHz; $CDCl_3$; Me_4Si) 186.9 (*C*=O); 127.8–131.2 (arom); δ_{Se} (270 MHz, $CDCl_3$, Me_4Si); 632.21 (*Se*); *m/z* (EI, 20 eV) found: M^+ 293.96097; calc. for $C_{13}H_{10}OSSe$ requires 293.96176.

(entry 2 in Table S25):
A solution of benzoylsulfenyl iodide **1a** (0.396 g, 1.5 mmol) in $CHCl_3$ (20 mL) was added to diphenyl diselenide (0.468 g, 1.5 mmol) in $CHCl_3$ (1/1) (20 mL) at –17 ºC and stirred for 16 min and then at 0 ºC for 30 min. Evaporation of the solvent and ether (40 mL) was added. The resulting precipitates was filtered out and the solvent was removed under reduced pressure (ca. 12 Pa). Recrystallization of the resulting residue from dichloromethane/hexane (1:2) gave *Se*-phenyl benzoylsulfenoselenoate **11aa**; yield 0.202 g (36%).
The i.r. spectrum exactly consistent with that of authentic sample prepared in entry 2.

Se-4-Methylphenyl benzoylsulfenoselenoate **11ab** (entry 3 in Table S25)
Similarly to the entry 1, the reaction of benzoylsulfenyl iodide **1a** (0.343 g, 1.3 mmol) with sodium 4-methylbenzeneselenolate (0.251 g, 1.3 mmol), following by recrystallization from dichloromethane/hexane (1:2) gave *Se*-4-methylphenyl benzoylsulfenoselenoate **11ab** as colorless crystals; m.p. 47–49 ºC (46–48 ºC) [33c]; yield 0.212 g (53%); i.r. ν_{max} (KBr)/cm^{-1}: 1680 ($\nu_{C=O}$); δ_H (90 MHz, $CDCl_3$, Me_4Si) 2.23(s, 3H, CH_3Ar); 6.74–8.24 (m, 9H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 2.23(s, 3H, CH_3Ar); 127.4–131.0 (arom); δ_{Se} (270 MHz, $CDCl_3$, Me_2Se) 601.43 (*Se*).
The i.r. and ^{1}H, ^{13}C and ^{77}Se NMR spectra were exactly consistent with those of authentic sample prepared by the reaction of benzoylsulfenyl bromide with di(4-methylphenyl) diselenide.[33c]

(entry 4 in Table S25)
Similarly to the entry 2 using diphenyl diselenide, the reaction of benzoylsulfenyl iodide **1a** (0.334 g, 1.2 mmol) with di(4-methyl-phenyl) diselenide (0.408 g, 1.2 mmol) gave *Se*-4-methylphenyl benzoylsulfenoselenoate **11ab**; yield 0.085 g (23%).

Se-Phenyl 4-methylbenzoylsulfenoselenoate **11da** (entry 5 in Table S25)
Similarly to the entry 1, the reaction of 4-methylbenzoylsulfenyl iodide **1d** (0.361 g, 1.3 mmol) with sodium benzeneselenolate (0.233 g, 1.3 mmol), following by recrystallization from dichloromethane/hexane (1:2) gave *Se*-phenyl 4-methylbenzoyl-sulfenoselenoate **11da** as colorless crystals; m.p. 92–94 ºC (93–94 ºC);[33c] yield 248 g (62%); i.r. ν_{max} (KBr)/cm^{-1}: 1690 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 2.24 (s, 3H, CH_3Ar); 6.73–8.25 (m, 9H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 186.6 (*C*=O); 20.45 (CH_3Ar); 127.4–131.0 (arom); δ_{Se} (270 MHz, $CDCl_3$, Me_2Se) 616.62 (*Se*); *m/z* (EI, 20 eV): found M^+ 307.97722, calc. for $C_{14}H_{12}OSSe$ requires 307.97741.
The i.r. and ^{1}H, ^{13}C and ^{77}Se NMR spectra were exactly consistent with those of authentic sample prepared by the reaction of 4-methylbenzoylsulfenyl bromide with diphenyl diselenide.[33c]

(entry 6 in Table S25)
Similarly to the entry 2, the reaction of 4-methylbenzoylsulfenyl iodide **1d** (0.334 g, 1.2 mmol) with di(phenyl) diselenide (0.374 g, 1.2 mmol) in chloroform (30 mL) gave *Se*-phenyl 4-methyl-benzoylsulfenoselenoate **11da**; yield 0.265 g (72%) yield.

(entry 7 in Table S25)
Se-Phenyl 4-methoxybenzoylsulfenoselenoate **11fa**
Similarly to the entry 1, the reaction of 4-methoxybenzoylsulfenyl iodide **1f** (0.382 g, 1.3 mmol) with sodium benzeneselenolate (0.233 g, 1.3 mmol), following by recrystallization of the resulting residue from dichloromethane/hexane (1:2) gave *Se*-phenyl 4-methoxybenzoylsulfenoselenoate **11fa** as pale yellow crystals; m.p. 61–63 ºC (62–63 ºC) [33c, 53]; yield 0.231 g (55%); i.r. ν_{max} (KBr)/cm^{-1}: 1680 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 3.47 (s, 3H, CH_3OAr); 6.54–8.32 (m, 9H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 187.4 (*C*=O); 55.41 (CH_3OAr); 127.2–130.3 (arom); δ_{Se} (270 MHz, $CDCl_3$, Me_2Se) 617.43 (*Se*); *m/z* (EI, 20 eV): found: M^+ 323.97529, calc. for $C_{14}H_{12}O_2SSe$ requires 323.97232.
The i.r. and ^{1}H, ^{13}C and ^{77}Se NMR spectra were exactly consistent with those of authentic sample prepared by the reaction of 4-methoxybenzoylsulfenyl bromide with diphenyl diselenide.[33c]

(entry 8 in Table S25)
Similarly to the entry 2, the reaction of 4-methoxybenzoylsulfenyl iodide **1f** (0.294 g, 1.0 mmol) with di(phenyl) diselenide (0.312 g, 1.0 mmol) gave *Se*-phenyl 4-methoxybenzoylsulfenoselenoate **11fa**; yield 0.245 g (76%).

The i.r. and ^{1}H, ^{13}C and ^{77}Se NMR spectra were exactly consistent with those of authentic sample prepared by the reaction of 4-methoxybenzoylsulfenyl bromide with diphenyl diselenide.[33c]

Se-4-Methylphenyl 4-methoxybenzoylsulfenoselenoate **11fb** (entry 9 in Table S25)
Similarly to the entry 1, the reaction of 4-methoxybenzoylsulfenyl iodide **1f** (0.353 g, 1.2 mmol) with sodium 4-methylbenzene-selenolate (0.232 g, 1.2 mmol), following by recrystallization from dichloromethane/hexane (1:2), gave *Se*-4-methylphenyl 4-methoxybenzoylsulfenoselenoate **11fb** as pale yellow crystals; m.p. 63–65 ºC (65–67 ºC)[33c]; yield 0.304 g (75%); anal. found C, 53.40; H, 4.20%; calc. for $C_{15}H_{14}O_2SSe$ (337.30) requires C, 53.41; H, 4.18%; i.r. ν_{max} (KBr)/cm^{-1}: 1680 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 2.25 (s, 3H, CH_3Ar); 3.48 (s, 3H, CH_3OAr); 6.36–8.66 (m, 8H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 187.2 (C=O); 56.21 (CH_3OAr); 21.65 (CH_3Ar); δ_{Se} (270 MHz, $CDCl_3$, Me_2Se) 607.28 (*Se*).

(entry 10 in Table S25)
Similarly to the entry 8, the reaction of 4-methoxybenzoylsulfenyl iodide **1f** (0.294 g, 1.0 mmol) with di(4-methylphenyl) diselenide (0.340 g, 1.0 mmol) gave *Se*-4-methyl-phenyl 4-methoxybenzoyl-sulfenoselenoate **11fb**: yield 0.212 g (66%).

Se-Phenyl 4-chlorobenzoylsulfenoselenoate **11ia** (entry 11 in Table S25)
A similarly to the entry 1, the reaction of 4-chlorobenzoylsulfenyl iodide **1i** (0.328 g, 1.1 mmol) with sodium benzeneselenolate (0.197 g, 1.1 mmol), following by recrystallization from dichloromethane/hexane (1:2), gave *Se*-phenyl 4-chlorobenzoyl-sulfenoselenoate **11ia** as pale yellow crystals; m.p. 90–92 ºC (83.5–84.5 ºC)[33c]; yield 0.252 g (67%); anal. found C, 47.64; H, 2.77%; calc. for $C_{13}H_9ClOSSe$ (327.69) requires C, 47.65; H, 2.77%; i.r. ν_{max} (KBr)/cm^{-1}: 1664 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 6.75–8.26 (m, 9H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 188.4 (*C*=O); 128.4–131.9 (arom); δ_{Se} (270 MHz, $CDCl_3$, Me_2Se) 654.83 (*Se*).
The i.r. and ^{1}H, ^{13}C and ^{77}Se NMR spectra were exactly consistent with those of authentic sample prepared by the reaction of 4-chlorobenzoylsulfenyl bromide with diphenyl diselenide.[33c]

(entry 12 in Table S25)
A similarly to the entry 2, the reaction of 4-chlorobenzoylsulfenyl iodide **1i** (0.268 g, 0.9 mmol) with di(phenyl) diselenide (0.280 g, 0.9 mmol) gave *Se*-phenyl 4-chlorobenzoylsulfenoselenoate **11ia**; yield 0.112 g (38%).

Se-4-Methylphenyl 4-chlorobenzoylsulfenoselenoate **11ib** (entry 13 in Table S25)
A similarly to the entry 1, the reaction of 4-chlorobenzoylsulfenyl iodide **1i** (0.418 g, 1.4 mmol) with sodium 4-methylbenzene-selenolate (0.270 g, 1.4 mmol), following by recrystallization from dichloromethane/hexane (1:2) gave *Se*-4-methylphenyl 4-chloro-benzoylsulfenoselenoate **11ib** as pale yellow crystals; m.p. 85–87 ºC (84–86 ºC)[33c]; yield 0.248 g (52%); i.r. ν_{max} (KBr)/cm^{-1}: 1657 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 2.24 (s, 3H, CH_3Ar); 6.45–8.66 (m, 8H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 188.2 (*C*=O); 22.07 (*C*H$_3$Ar); 128.4–131.9 (arom); δ_{Se} (270 MHz, $CDCl_3$, Me_2Se) 611.98 (*Se*).
The i.r. and ^{1}H, ^{13}C and ^{77}Se NMR spectra were exactly consistent with those of authentic compound prepared by the reaction of 4-chlorobenzoylsulfenyl bromide with di(4-methyl-phenyl) diselenide.[33c]

(entry 14 in Table S25)
A similarly to the entry 2, the reaction of 4-chlorobenzoylsulfenyl iodide **1i** (0.238 g, 0.8 mmol) with di(4-methylphenyl) diselenide (0.272 g, 0.8 mmol) gave *Se*-4-methylphenyl 4-chlorobenzoyl-sulfenoselenoate **11ib**; (0.253 g (53%).

***Te*-aryl areneoxomethanesulfenotelluroates 12**

Te-Phenyl benzoylsulfenotelluroate **12aa** (entry 1 in Table S27)

A solution of benzoylsulfenyl iodide **1a** (0.317 g, 1.2 mmol) in $CHCl_3$/MeOH (20 mL) was added to sodium benzenetellurolate (0.273 g, 1.2 mmol) in ethanol (20 mL) at –17 ºC and stirred for 16 min and then 0 ºC for 30 min. Evaporation of the solvent and ether (40 mL) was added. After the resulting precipitates was filtered out and the ether was removed under reduced pressure (ca. 12 Pa). Recrystallization of the resulting solid from dichloromethane/hexane (1:2) gave *Te*-phenyl benzoylsulfeno-telluroate **12aa** as pale yellow crystals as pale yellow crystals; m.p. 66–68 ºC (decomp) (66 ºC)[33d]; yield 0.279 g (68%); i.r. ν_{max} (KBr)/cm^{-1}: 1675 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 7.25–8.23 (m, 10H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 188.46 (*C*=O); 127.8–131.2 (arom); δ_{Te} (270 MHz, $CDCl_3$, Me_2Te) 918.35 (*Te*). The i.r. and ^1H, ^{13}C and ^{125}Te NMR spectra were exactly consistent with those of authentic compound prepared by the reaction of 4-chlorobenzoylsulfenyl bromide with sodium benzenetellurolate.[33c]

(entry 2 in Table S27)

Similarly to the entry 2 in Table S23, the reaction of benzoylsulfenyl iodide **1a** (0.317 g, 1.2 mmol) with diphenyl ditelluride in chloroform (30 mL) gave *Te*-phenyl benzoyl-sulfenotelluroate **12aa** ; yield 0.115 g (28%).

The i.r. spectrum exactly coincided with that of the authentic example prepared in entry 1 in Table S27.

Te-4-Methylphenyl benzoylsulfenotelluroate **12ab** (entry 3 in Table S27)

Similarly to the entry 1, the reaction of benzoylsulfenyl iodide **1a** (0.317 g, 1.2 mmol) with sodium 4-methylbenzenetellurolate (0.290 g, 1.2 mmol) in $CHCl_3$/MeOH (1:1, 20 mL), following by recrystallization from dichloro-methane/hexane (1:2) gave *Te*-4-methylphenyl benzoyl-sulfenotelluroate **12ab** as pale yellow crystals; m.p. 98–100 ºC (decomp); yield 0.269 g (63%); i.r. ν_{max} (KBr)/cm^{-1}: 1672 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 2.31 (s, 3H, CH_3Ar), 6.98–8.16 (m, 9H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 188.27 (*C*=O); 21.38 (*C*H_3Ar); 127.8–131.2 (arom); δ_{Te} (270 MHz, $CDCl_3$, Me_2Te) 910.63 (*Te*).

The i.r. and ^1H, ^{13}C and ^{125}Te NMR spectra exactly coincided with those of the authentic sample prepared by entry 4 in Table S27.

(entry 4 in Table S27)

Similarly to the entry 2, the reaction of benzoylsulfenyl iodide **1a** (0.317 g, 1.2 mmol) with di(4-methylphenyl) ditelluride in chloroform (30 mL), following by recrystallization from dichloromethane/hexane (1:2), gave *Te*-4-Methylphenyl benzoylsulfenotelluroate **12ab**; 0.094 g (22%).

Te-Phenyl 4-methylbenzoylsulfenotelluroate **12da** (entry 5 in Table S27)

Similarly to the entry 1 in Table S27, the reaction of 4-methylbenzoylsulfenyl iodide **1d** (0.306 g, 1.1 mmol) with sodium benzenetellurolate (0.250 g, 1.1 mmol), following by recrystallization from dichloromethane/hexane (1:2) gave *Te*-phenyl 4-methylbenzoylsulfenotelluroate **12da** as pale yellow crystals; m.p. 110–112 ºC (decomp) (109–111 ºC);[33c] yield 0.175 g (62%); i.r. ν_{max} (KBr)/cm^{-1}: 1675, 1658 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 2.38 (s, 3H, CH_3Ar); 7.11–8.91 (m, 9H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 187.87 (*C*=O); 21.68 (*C*H_3Ar); 127.6–130.6 (arom); δ_{Te} (270 MHz, $CDCl_3$, Me_2Te) 910.63 (*Te*). The i.r. and ^1H, ^{13}C and ^{125}Te NMR spectra were exactly consistent with those of authentic compound prepared by the reaction of 4-methylbenzoylsulfenyl bromide with sodium phenyltellurolate.[33c]

(entry 6 in Table S27)
Similarly to the entry 2, the reaction of 4-methyl-benzoylsulfenyl iodide **1d** (0.306 g, 1.1 mmol) with with diphenyl ditelluride in chloroform (30 mL) gave Te-phenyl 4-methylbenzoylsulfeno-telluroate **12da**; yield 0.142 g (35%).
The i.r. and ^{1}H, ^{13}C and ^{125}Te NMR spectra were exactly consistent with those of authentic compound prepared in entry 5.

Te-Phenyl 4-methoxybenzoylsulfenotelluroate **12fa** (entry 7 in Table S27)
A similarly to the entry 1, the reaction of 4-methoxybenzoylsulfenyl iodide **1f** (0.361 g, 1.3 mmol) with sodium benzene-tellurolate (0.299 g, 1.3 mmol) in $CHCl_3$/MeOH (1:1, 20 mL), following by recrystallization from dichloromethane/hexane (1:2), gave *Te*-phenyl 4-methoxybenzoylsulfenotelluroate **12fa** as pale yellow crystals; m.p. 91–93 ºC (decomp); yield 0.300 g (62%); anal. found C, 45.20; H, 3.26%; calc for $C_{14}H_{12}O_2STe$ (371.91) requires C, 45.21; H, 3.25%; i.r. ν_{max} (KBr)/cm^{-1}: 1655 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 3.82 (s, 3H, C*H*$_3$OAr); 6.87–8.10 (m, 9H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 01.44 (*C*=O); 56.21 (*C*H$_3$OAr); 127.6–130.6 (arom); δ_{Te} (270 MHz, $CDCl_3$, Me_2Te) 972.23 (*Te*).

(entry 8 in Table S27)
Similarly to the entry 4, the reaction of 4-methoxylbenzoylsulfenyl iodide **1f** (0.306 g, 1.1 mmol) with with diphenyl ditelluride in chloroform (30 mL) gave *Te*-phenyl 4-methoxylbenzoylsulfeno-telluroate **12fa**; 0.176 g (43%).
The i.r. and ^{1}H, ^{13}C and ^{125}Te NMR spectra were exactly consistent with those of authentic compound prepared in entry 7.

Te-4-Methylphenyl 4-methoxybenzoylsulfenotelluroate **12fb** (entry 9 in Table S27)
Similarly to the entry 1, the reaction of 4-methoxybenzoylsulfenyl iodide **1f** (0.353 g, 1.2 mmol) with sodium 4-methylbenzene-tellurolate (0.232 g, 1.2 mmol), following by recrystallization from dichloromethane/hexane (1:2), gave *Te*-4-methylphenyl 4-methoxybenzoylsulfenotelluroate **12fb** as pale yellow crystals; m.p. 85–87 ºC (decomp); yield 0.208 g (67%); anal. found C, 69.78; H, 5.53%; requires C, 59.74; H, 5.46%; for $C_{15}H_{14}O_2STe$ (258.34) requires C, 69.74; H, 5.46%; i.r. ν_{max} (KBr)/cm^{-1}: 1666 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 2.37 (s, 3H, C*H*$_3$Ar); 3.78 (s, 3H, C*H*$_3$OAr); 6.46–8.76 (m, 8H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 200.93 (*C*=O); 55.68 (*C*H$_3$OAr); 21.12 (*C*H$_3$Ar); δ_{Te} (270 MHz, $CDCl_3$, Me_2Te) 968.98 (*Te*).

(entry 10 in Table S27)
Similarly to the entry 4, the reaction of 4-methoxybenzoylsulfenyl iodide **1f** (0.306 g, 1.1 mmol) with with di(4-methylphenyl) ditelluride in chloroform (30 mL), following by recrystallization from dichloromethane/hexane (1:2), gave *Te*-4-methylphenyl 4-methoxylbenzoylsulfenotelluroate **12fb**; 0.176 g (55%) yield.
The i.r. and ^{1}H, ^{13}C and ^{125}Te NMR spectra were exactly consistent with those of authentic compound prepared in entry 9.

Te -Phenyl 4-chlorobenzoylsulfenotelluroate **12ia** (entry 11 in Table S27)
A similarly to the entry 1, the reaction of 4-chlorobenzoylsulfenyl iodide **1i** (0.328 g, 1.0 mmol) with sodium benzenetellurolate (0157 g, 1.0 mmol), following by recrystallization from dichloromethane/hexane (1:2), gave *Te*-phenyl 4-chloro-benzoylsulfenotelluroate **12ia** as pale yellow crystals; m.p. 115–117 ºC (decomp), (113–115 ºC)[33c]; yield 0.245 g (65%); i.r. ν_{max} (KBr)/cm^{-1}: 1665

($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 7.19–8.03 (m, 9H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 187.54 (*C*=O); 128.7–132.3 (arom); δ_{Te} (270 MHz, $CDCl_3$, Me_2Te) 945.55 (*Te*).
The i.r. and ^1H, ^{13}C and ^{125}Te NMR spectra were exactly consistent with those of the authentic compound prepared by the reaction of 4-chlorobenzoylsulfenyl bromide with sodium phenyltellurolate.[33c]

(entry 12 in Table S27)
Similarly to the entry 4, the reaction of 4-chlorobenzoylsulfenyl iodide **1i** (0.447 g, 1.5 mmol) with with diphenyl ditelluride in chloroform (30 mL) gave *Te*-phenyl 4-chlorobenzoylsulfenotelluroate **12ia**; 0.269 g (46%).
The i.r. and ^1H, ^{13}C and ^{125}Te NMR spectra were exactly consistent with those of the authentic compound prepared in entry 11.

Te-4-Methylphenyl 4-chlorobenzoylsulfenotelluroate **12ib** (entry 13 in Table S27)
Similarly to the entry 1, the reaction of 4-chlorobenzoylsulfenyl iodide **1i** (0.447 g, 1.5 mmol) with sodium 4-methylbenzene-tellurolate (0.363 g, 1.5 mmol), following by recrystallization from dichloromethane/hexane (1:2), gave *Te*-4-methylphenyl 4-chlorobenzoylsulfenotelluroate **12ib** as pale yellow crystals; m.p. 135–136 ºC (decomp); yield 0.217 g (55%); anal. found C, 43.05; H, 2,85%; calc for $C_{14}H_{11}ClOSTe$ (390.36) requires C, 43.08; H, 2.84%; i.r. ν_{max} (KBr)/cm^{-1}: 1667 ($\nu_{C=O}$); δ_H 270 MHz, $CDCl_3$, Me_4Si) 2.36 (s, 3H, C*H*$_3$Ar); 6.95–8.11 (m, 8H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 189.64 (*C*=O); 21.03 (*C*H$_3$Ar); 128.4–131.9 (arom); δ_{Te} (270 MHz, $CDCl_3$, Me_2Te) 932.26 (*Te*).

(entry 14 in Table S27)
Similarly to the entry 2 in Table S27, the reaction of 4-chloro-benzoylsulfenyl iodide **1i** (0.328 g, 1.1 mmol) with with di(4-methylphenyl) ditelluride in chloroform (30 mL), following by recrystallization from dichloromethane/hexane (1:2), gave *Te*-4-methylphenyl 4-chlorobenzoylsulfenotelluroate **12ib**; 0.146 g (34%) yield.
The i.r. and ^1H, ^{13}C and ^{125}Te NMR spectra were exactly consistent with those of the authentic compound prepared in entry 13.

Preparation of *S*-acyl sulfenamides 13
N-Benzyl benzoylsulfenamide **13aa** (entry 1 in Table S29)
Benzoylsulfenyl iodide **1a** (0.264 g, 1.0 mmol) in ether (30 mL) was added to benzylamine (0.217 g), 2.0 mmol in the same solvent (10 mL) at –68 ºC and stirred at room temperature. (ca. 20 ºC) for 20 min. After the solvent was evaporated under reduce pressure (ca. 4 Pa), ether (30 mL), ether (30 mL) was added. The precipitates (benzylammonium iodide) were filtered out. The filtrate was concentrated to ca. 3 mL under reduced pressure (ca. 10 Pa). The concentrate was chromatographed on silica gel ptlc [eluant: dichloromethane/hexane (1:1), Rf = 0.32–0.77] to give *N*-benzyl benzoylsulfenamide **13aa** as colorless crystals; m.p. 48–50 ºC; yield 0.134 g (55%); anal. found C, 69.10; H, 5.26%; calc. for $C_{14}H_{13}NOS$ (243.32) requires C, 69.11; H, 5.39%; i.r. ν_{max} (KBr)/cm^{-1}: 1659 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 3.21–3.52 (br. s, 1H, N*H*); 4.13 (s, 2H, C*H*$_2$); 7.10–8.06 (m, 10H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 184.6 (*C*=O); 46.1 (N*C*H$_2$); 127.4–140.3 (arom); *m/z* (EI, 20 eV) found M^+ 243.07269; calc. for $C_{14}H_{13}NO_sS$ requires 243.07179.

N,N-Diethyl benzoylsulfenamide **13ab** (entry 2 in Table S29)
Similarly to the entry 1, the reaction of benzoylsulfenyl iodide **1a** (0.290 g, 1.1 mmol) with 98 % diethylamine (0.114 mL, 1.1 mmol) in ether (40 mL), following by silica gel ptlc of the resulting residue [eluant: dichloromethane/hexane (1:1), Rf = 0.52–1.37] gave *N,N*-diethyl benzoyl-sulfenamide **13ab** as

colorless oil; yield 0.098 g (43%); anal. found C, 63.09; H, 7.15%; calc. for $C_{11}H_{15}NOS$ (209.31) requires C, 63.12; H, 7.22%; i.r. ν_{max} (KBr)/cm^{-1}: 1662 ($\nu_{C=O}$); δ_H (90 MHz, $CDCl_3$, Me_4Si) 1.21 (t, J = 8.0 Hz, 6H, CH_3); 3.15 (q, J = 8.0 Hz, 4H, CH_2); 7.10–8.03 (m, 5H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 184.6 (*C*=O); 46.1 (N*C*H$_2$); 127.4–140.3 (arom); *m/z* (EI, 20 eV) found M^+ 209.08687; calc. for $C_{11}H_{15}NOS$ requires 209.08744.

N-(Benzoylthio)ethyl benzoyl disulfide **13ac** (entry 3 in Table S29)
Similarly to the sulfenamide **13aa**, the reaction of benzoylsulfenyl iodide **1a** (0.528 g, 2.0 mmol) with 2-mercaptethylamine (0.08 mL, 1.0 mmol) in ether (40 mL), following by silica gel ptlc of the resulting residue [eluant: dichloromethane/hexane (1:1), Rf = 0.72–1.53] gave *N-(Benzoylthio)ethyl benzoyl disulfide* **13ac** as colorless crystals; m.p. 39 ºC; yield 0.143 g (41%); found C, 54.87; H, 4.36; calc. for $C_{16}H_{15}NO_2S_3$ (349.49) requires 54.99; H, 4.33; i.r. ν_{max} (KBr)/cm^{-1}: 1675, 1669 (C=O); δ_H (270 MHz, $CDCl_3$, Me_4Si) 3.56 (d, J = 7.7 Hz, 2H, NCH_2), 3.78 (d, J = 7.7 Hz, 2H, SCH_2), 3.88 (br. s, 1H, N*H*), 7.22–8.10 (m, 10H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 184.3 (*C*=O); 45.6 (N*C*H$_2$); 16.0 *C*H$_2$S); 127.4–133.0 (arom); *m/z* (EI, 20 eV) found M^+ 317.0559; calc. for $C_{16}H_{15}NO_2S_3$, requires 349.02649.

N-n-Propyl benzoylsulfenamide **13ad** (entry 4 in Table S29)
Similarly to the entry 1, the reaction of benzoylsulfenyl iodide **1a** (0.317 g, 1.2 mmol) with *n*-propylamine (0.12 mL, 1.2 mmol) in ether (40 mL), following by silica gel ptlc of the resulting residue [eluant: dichloromethane/hexane (1:1), Rf = 0.38–0.77], gave *N-n*-propyl benzoylsulfenamide **13ad** as colorless oil; yield 0.119 g (51%); i.r. ν_{max} (KBr)/cm^{-1}: 1660 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 0.96 (t, J = 7.8 Hz, 3H, CH_3); 2.7–3.3 (m, 4H, N*H*CH_2CH_2); 7.22–8.01 (m, 5H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 184.5 (*C*=O); 42.1 (N*C*H$_2$); 25.8 (*C*H$_2$); 11.1 *C*H$_3$); 127.4–132.6 (arom); *m/z* (EI, 20 eV) found M^+ 195.07198; calc. for $C_{10}H_{13}NOS$; requires 195.07179.

N,N-Di(isopropyl) benzoylsulfenamide **13ae** (entry 5 in Table S29)
Similarly to the entry 4, the reaction of benzoylsulfenyl iodide **1a** (0.343 g, 1.3 mmol) with di(isopropyl)amine (0.13 mL, 1.3 mmol) in ether (40 mL), following by silica gel ptlc of the resulting residue [eluant: dichloromethane/hexane (1:1), Rf = 0.55–0.91], gave *N,N*-di(isopropyl) benzoylsulfenamide **13ae** as colorless oil; yield 0.188 g (61%); anal. found C, 68.76; H, 8.09%; calc. for $C_{13}H_{19}NOS$ (237.36) requires C, 65.78; H, 8.07%; i.r. ν_{max} (KBr)/cm^{-1}: 1668 ($\nu_{C=O}$); δ_H (90 MHz, $CDCl_3$, Me_4Si) 1.17 (d, J = 7.8 Hz, 6H, CH_3); 2.9–3.3 (m, 1H, NC*H*); 7.21–8.10 (m, 5H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 184.6 (*C*=O); 44.3 (N*C*H); 25.7 (*C*H$_3$); 127.4–130.5 (arom); *m/z* (EI, 20 eV) found M^+ 237.11829; calc. for $C_{13}H_{19}NOS$ requires 237.11874.

N-n-Butyl benzoylsulfenamide **13af** (entry 6 in Table S29)
Similarly to the entry 4, the reaction of benzoylsulfenyl iodide **1a** (0.343 g, 1.3 mmol) with *n*-butylamine (0.14 mL, 1.3 mmol) in ether (40 mL), following by silica gel ptlc of the resulting residue [eluant: dichloromethane/hexane (1:1), Rf = 0.32–0.78], gave *N-n*-butyl benzoylsulfenamide **13af** as colorless oil; yield, 0.193 g (71%); anal. found C, 61.47; H, 6.74%; calc. for $C_{11}H_{15}NOS$ (209.31) requires C, 61.50; H, 6.71%; i.r. ν_{max} (KBr)/cm^{-1}: 1660 ($\nu_{C=O}$); δ_H (270 MHz, $CDCl_3$, Me_4Si) 0.7–1.9 (m, 7H, C_3H_7); 2.8–3.5 (m, 3H, N*H*, CH_2); 7.12–8.10 (m, 5H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 184.5 (*C*=O); 42.1 (N*C*H$_2$); 36.1 (*C*H$_2$), 25.8 (*C*H$_2$); 11.1 *C*H$_3$); 127.4–132.6 (arom); *m/z* (EI, 20 eV) found M^+ 209.08766; calc. for $C_{11}H_{15}NOS$ requires 209.08744.

N-tert-Butyl benzoylsulfenamide **13ag** (entry 7 in Table S29)
Similarly to the sulfenamide **13ad**, the reaction of benzoylsulfenyl iodide **1a** (0.264 g, 1.0 mmol) with *t*-butylamine (0.11 mL, 1.0 mmol) in ether (40 mL), following by silica gel ptlc of the resulting residue

[eluant: dichloromethane/hexane (1:1), Rf = 0.44–0.88] gave *N-tert*-butyl benzoylsulfenamide **13ag** as colorless oil; yield 0.25 g (12%); i.r. ν_{max} (KBr)/cm^{-1}: 1660 (C=O); δ_H (90 MHz, $CDCl_3$, Me_4Si) 1.20 (s, 9H, C*H*$_3$); 3.0–3.2 (br. s, 1H, N*H*); 7.20–8.03 (m, 5H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 184.5 (*C*=O); 48.3 (N*C*); 32.5 *C*H$_3$); 127.8–131.1 (arom); *m/z* (EI, 20 eV) found M$^+$ 209.08743; calc. for $C_{11}H_{15}NOS$ requires 209.08744.

Pyrrolidinyl benzoylsulfenamide **13ah** (entry 8 in Table S29)
Similarly to the entry 6, the reaction of benzoylsulfenyl iodide **1a** (0.396 g, 1.5 mmol) with pyrrolidine (0.124 mL, 1.5 mmol) in ether (40 mL), following by silica gel ptlc of the resulting residue [eluant: dichloromethane/hexane (1:1), Rf = 0.44–0.68], gave pyrrolidinyl benzoylsulfenamide **13ah** as a colorless oil; yield 0.174 g (56%); anal. found C, 63.71; H, 6.35%; calc. for $C_{11}H_{13}NOS$ (207.29) requires C, 63.74; H, 6.32%; i.r. ν_{max} (KBr)/cm^{-1}: 1662 ($\nu_{C=O}$); δ_H (90 MHz, $CDCl_3$, Me_4Si) 1.51–2.20 (m, 4H, C*H*$_2$); 2.80–3.81 (m, 4H, NC*H*$_2$); 7.01–7.98 (m, 5H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 183.6 (*C*=O); 48.3 (N*C*H$_2$); 25.5 (*C*H$_2$); 127.6–131.2 (arom); *m/z* (EI, 20 eV) found M$^+$ 207.07175; calc. for $C_{11}H_{13}NOS$ requires 207.07179.

Piperidinyl benzoylsulfenamide **13ai** (entry 9 in Table S29)
Similarly to the entry 8, the reaction of benzoylsulfenyl iodide **1a** (0.422 g, 1.6 mmol) with piperidine (0.15 mL, 1.6 mmol) in ether (40 mL), following by silica gel ptlc of the resulting residue [eluant: dichloromethane/hexane (1:1), Rf = 0.33–0.71], gave piperidinyl benzoylsulfenamide **13ai** as colorless crystals; m.p. 69–71 ºC; yield 0.258 g (73%); anal. found C, 65.10; H, 6.85%; calc. for $C_{12}H_{15}NOS$ (221.32) requires C, 65.12; H, 6.83%; i.r. ν_{max} (KBr)/cm^{-1}: 1658 ($\nu_{C=O}$); δ_H (90 MHz, $CDCl_3$, Me_4Si) 1.06–1.92 (m, 6H, C*H*$_2$); 2.80–3.79 (m, 4H, NC*H*$_2$); 7.02–8.10 (m, 5H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 184.1 (*C*=O); 55.5 (N*C*H$_2$); 46.0 (C*H*$_2$); 25.2 (*C*H$_2$); 127.5–131.0 (arom); *m/z* (EI, 20 eV) found M$^+$ 221.08762; calc. for $C_{12}H_{15}NOS$ requires 221.08744.

Morphorinyl benzoylsulfenamide **13aj** (entry 10 in Table S29)
Similarly to the entry 9, the reaction of benzoylsulfenyl iodide **1a** (0.475 g, 1.8 mmol) with morpholine (0.155 mL, 1.8 mmol) in ether (45 mL), following by silica gel ptlc of the resulting residue [eluant dichloromethane/hexane (1:1, Rf = 0.11–0.32), gave morphorinyl benzoylsulfenamide **13aj** as colorless crystals; m.p. 86–88 ºC; yield 0.217 g (54%); anal. found C, 59.15; H, 5.89%; calc. for $C_{11}H_{13}NO_2S$ (223.29) requires C, 59.17; H, 5.87%; i.r. ν_{max} (KBr)/cm^{-1}: 1668 ($\nu_{C=O}$); δ_H (90 MHz, $CDCl_3$, Me_4Si) 3.31–3.92 (m, 8H, C*H*$_2$); 7.14–7.82 (m, 5H, arom); δ_C (270 Hz; $CDCl_3$; Me_4Si) 184.2 (*C*=O); 66.5 (O*C*H$_2$); 54.1 (N*C*H$_2$); 127.6–131.2 (arom); *m/z* (EI, 20 eV) found M$^+$ 223.06623; calc. for $C_{11}H_{13}NO_2S$ requires 223.06670.

N-Phenyl benzoylsulfenamide **13ak** (entry 11 in Table S29)
A solution of benzoylsulfenyl iodide **1a** (0.528 g, 2.0 mmol) in ether (30 mL) was added to a solution of phenylamine (0.190 g, 2.0 mmol) in the same solvent (10 mL) at –68 ºC and stirred at 0 ºC for 30 min. After concentration of the reaction mixture under reduced pressure (ca. 8 Pa) to ca. 15 mL, the resulting white precipitates (phenylammonium iodide) was filtered out. The filtrate was evaporated off under reduced pressure (ca. 8Pa). The resulting residue was chromatographed on silica gel ptlc [eluant: dichloromethane/hexane (1:1), Rf = 0.33] to give *N*-phenyl benzoylsulfenamides **13ak** as colorless crystals; m.p. 95–101 ºC; yield 0.239 g (52%); anal. found C, 67.07; H, 4.86%; calc. for $C_{13}H_{11}NOS$ (229.30) requires C, 68.09; H, 4.84%; i.r. ν_{max} (KBr)/cm^{-1}: 1660 ($\nu_{C=O}$); δ_H (90 MHz, $CDCl_3$, Me_4Si) 4.80–5.31 (br. s, 1H, N*H*); 6.62–8.07 (m, 10H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 184.4 (*C*=O); 127.4–130.1 (arom); *m/z* (EI, 20 eV) found M$^+$ 229.05608; calc. for $C_{13}H_{11}NOS$, requires 229.05614.

N-Methyl-N-phenyl benzoylsulfenamide **13al** (entry 12 in Table S29)
Similarly to the sulfenamide **13ak**, the reaction of benzoylsulfenyl iodide **1a** (0.264 g, 1.0 mmol) with 2-methylphenylamine (0.107 mL, 1.0 mmol) in dichloromethane (20 mL), following by silica gel ptlc of the resulting residue [eluant: dichloromethane/hexane (1:1), Rf = 0.35–0.88] gave *N*-methyl-*N*-phenyl benzoylsulfenamide **13al** as colorless crystals; m.p. 75–77 ºC; yield 0.112 g (46%); found C, 69.10; H, 5.40; calc. for $C_{14}H_{13}NOS$ (243.32) requires C, 69.11; H, 5.39; i.r. ν_{max} (KBr)/cm^{-1}: 1666 (C=O); δ_H (90 MHz, $CDCl_3$, Me_4Si) 2.32 (s, 3H, C*H*$_3$); 4.81–5.12 (br. s, 1H, N*H*); 6.63–8.07 (m, 10H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 184.1 (*C*=O); 17.4 (*C*H$_3$Ar), 117.4–138.8 (arom); *m/z* (EI, 20 eV) found M$^+$ 243.07156; calc. for $C_{14}H_{13}NOS$ requires 243.07179.

N-4-Methylphenyl benzoylsulfenamide **13am** (entry 13 in Table S29)
Similarly to the entry 12, the reaction of benzoylsulfenyl iodide **1a** (0.317 g, 1.2 mmol) with 4-methylphenylamine (0.128 mL, 1.2 mmol) in dichloromethane (20 mL), following by silica gel ptlc of the resulting residue [eluant: dichloromethane/hexane (1:1), Rf = 0.55–0.93] gave *N*-4-methylphenyl benzoylsulfenamide **13am** as colorless crystals; m.p. 81–84 ºC; yield 0.192 g (66%); anal. found C, 68.88; H, 5.43%; calc. for $C_{14}H_{13}NOS$ (243.32) requires C, 68.91; H, 5.39%; i.r. ν_{max} (KBr)/cm^{-1}: 1666 ($\nu_{C=O}$); δ_H (90 MHz, $CDCl_3$, Me_4Si) 2.22 (s, 3H, C*H*$_3$); 4.82–5.14 (br. s, 1H, N*H*); 6.72–8.08 (m, 9H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 184.4 (*C*=O); 22.3 (*C*H$_3$Ar); 117.4–138.8 (arom); *m/z* (EI, 20 eV) found M$^+$ 243.07156; calc. for $C_{14}H_{13}NOS$ requires 243.07179.

N-4-Methoxyphenyl benzoylsulfenamide **13an** (entry 14 in Table S29)
Similarly to the entry 9, the reaction of benzoylsulfenyl iodide **1a** (0.317 g, 1.2 mmol) with 4-methoxyphenylamine (0.148 mL, 1.2 mmol) in dichloromethane (20 mL), following by silica gel ptlc of the resulting residue [eluant: dichloromethane/hexane (1:1), Rf = 0.35–0.86] gave *N*-4-methoxyphenyl benzoylsulfenamide **13an** as colorless crystals; m.p. 62–64 ºC; yield 0.208 g (67%); anal. found C, 64.80; H, 4.95%; calc. for $C_{14}H_{13}NO_2S$ (259.32) requires C, 64.84; H, 5.05%; i.r. ν_{max} (KBr)/cm^{-1}: 1668 ($\nu_{C=O}$); δ_H (90 MHz, $CDCl_3$, Me_4Si) 3.65 (s, 3H, OC*H*$_3$); 4.80–5.12 (br. s, 1H, N*H*); 6.52–7.92 (m, 9H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 184.2 (*C*=O); 34.2 (OC*H*$_3$); 127.6–131.2 (arom); *m/z* (EI, 20 eV) found M$^+$ 259.06578; calc. for $C_{14}H_{13}NO_2S$ requires 259.06670.

N-Benzyl 4-methylbenzoylsulfenamide **13da** (entry 15 in Table S30 (continued 1))
4-Methylbenzoylsulfenyl iodide **1a** (0.278g, 1.0 mmol) in ether (30 mL) was added to benzylamine (0.217 g), 2.0 mmol in the same solvent (10 mL) at –68 ºC and stirred at –15 ºC for 15 min. After the solvent was evaporated under reduce pressure (ca. 4 Pa), ether (30 mL) was added. The precipitates (benzylammonium iodide) were filtered out. The filtrate was concentrated to ca. 3 mL under reduced pressure (ca. 10 Pa). The concentrate was chromatographed on silica gel ptlc [eluant: dichloromethane/hexane (1:1), Rf = 0.32–0.77] gave *N*-benzyl 4-methylbenzoylsulfenamide **13da** as colorless crystals; m.p. 36–38 ºC; yield 0.170 g (66%); found C, 69.98; H, 5.88%; calc. for $C_{15}H_{15}NOS$ (257.35) requires C, 70.01; H, 5.87; i.r. ν_{max} (KBr)/cm^{-1}: 1656 (C=O); δ_H (270 MHz, $CDCl_3$, Me_4Si) 2.28 (s, 3H, C*H*$_3$); 3.18–3.50 (br. s, 1H, N*H*); 4.03 (s, 2H, C*H*$_2$); 7.20–8.20 (m, 9H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 184.6 (*C*=O); 46.4 (N*C*H$_2$); 21.4 (*C*H$_3$Ar); 128.3–130.7 (arom); *m/z* (EI, 20 eV) found M$^+$ 257.08553; calc. for $C_{15}H_{15}NOS$ requires 257.08744.

N-n-Propyl 4-methylbenzoylsulfenamide **13db** (entry 16 in Table S30 (continued 1))
Similarly to the sulfenamide **13ak**, the reaction of 4-methylbenzoylsulfenyl iodide **1d** (0.306 g, 1.1 mmol) with *n*-propylamine (0.1 mL, ca.1.3 mmol) in dichloromethane (20 mL), following by silica gel ptlc of the resulting residue [eluant: dichloromethane/hexane (1:1), Rf = 0.32–0.88] gave *N*-*n*-propyl 4-methylbenzoylsulfenamide **13db** as colorless oil; yield 0.159 g (69%); found C, 63.11; H, 7.25; calc.

for $C_{11}H_{15}NOS$ (209.31) requires C, 63.12; H, 7.22; i.r. ν_{max} (KBr)/cm^{-1}: 1659 (C=O); δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.93 (t, *J* = 7.8 Hz, 3H, C*H*$_3$), 1.57 (sex, *J* = 7.8 Hz, 2H, C*H*$_2$), 2.38 (s, 3H, C*H*$_3$), 3.12 (t, *J* = 7.8 Hz, 2H, C*H*$_2$), 5.27 (br. s, 1H, N*H*), 7.11–7.96 (m, 4H, arom); δ_C (270 Hz; $CDCl_3$; Me_4Si) 184.6 (*C*=O); 40.1 (N*C*H$_2$); 36.1 (*C*H$_2$); 21.1 (*C*H$_3$Ar); 13.5 (*C*H$_3$); 128.1–130.0 (arom); *m/z* (EI, 20 eV) found M$^+$ 209.08662; calc. for $C_{11}H_{15}NOS$ requires 209.08744.

N,N-(n-propyl) 4-methylbenzoylsulfenamide **13dc** (entry 17 in Table S30 (continued 1))
Similarly to the sulfenamide **13ak**, the reaction of 4-methylbenzoylsulfenyl iodide **1d** (0.334 g, 1.2 mmol) with di(*n*-propyl)amine (0.1 mL, ca.1.3 mmol) in dichloromethane (20 mL), following by silica gel ptlc of the resulting residue [eluant: dichloromethane/hexane (1:1), Rf = 0.32–0.88] gave *N,N*-(*n*-propyl) 4-methylbenzoylsulfenamide **13dc** as colorless oil; yield 0.183 g (56%); found C, 66.91; H, 8.45; calc. for $C_{11}H_{15}NOS$ (251.39) requires C, 66.89; H, 8.42; i.r. ν_{max} (KBr)/cm^{-1}: 1668 (C=O); δ_H (90 MHz, $CDCl_3$, Me_4Si) 0.89 (t, *J* = 7.8 Hz, 6H, C*H*$_3$), 1.56 (sept, *J* = 7.8 Hz, 4H, C*H*$_2$), 2.34 (s, 3H, C*H*$_3$), 3.10 (t, *J* = 7.8 Hz, 4H, C*H*$_2$), 7.0–8.0 (m, 4H, arom); δ_C (270 Hz; $CDCl_3$; Me_4Si) 184.6 (*C*=O); 57.3 (N*C*H$_2$); 24.2 (*C*H$_2$); 22.3 (*C*H$_3$Ar); 11.7 (*C*H$_3$); 127.4–130.7 (arom); *m/z* (EI, 20 eV) found M$^+$ 251.13332; calc. for $C_{14}H_{21}NOS$ requires 251.13439.

Pyrrolidinyl 4-Methylbenzoylsulfenamide **13dd** (entry 18 in Table S30 (continued 1))
Similarly to the sulfenamide **13ak**, the reaction of 4-methylbenzoylsulfenyl iodide **1d** (0.278 g, 1.0 mmol) with pyrrolidine (0.071 mL, 1.0 mmol) in ether (40 mL), following by silica gel ptlc of the resulting residue [eluant: dichloromethane/hexane (1:1), Rf = 0.35–0.70] gave pyrrolidinyl 4-methylbenzoylsulfenamide **13dd** as colorless oil; yield 0.086 g (39%); found C, 65.10; H, 6.86); calc. for $C_{12}H_{15}NOS$ (221.32) requires C, 65.12; H, 6.83; i.r. ν_{max} (KBr)/cm^{-1}: 1660 (C=O); δ_H (90 MHz, $CDCl_3$, Me_4Si) 1.40–2.20 (m, 4H, C*H*$_2$); 2.37 (s, 3H, C*H*$_3$Ar); 2.80–3.81 (m, 4H, NC*H*$_2$); 7.02–7.86 (m, 4H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 184.4 (*C*=O); 48.3 (N*C*H$_2$); 25.5 (*C*H$_2$); 22.3 (C*H*$_3$Ar), 127.6–131.2 (arom); *m/z* (EI, 20 eV) found M$^+$ 221.08762; calc. for $C_{12}H_{15}NOS$ requires 221.08744.

Piperidinyl 4-methylbenzoylsulfenamide **13de** (entry 19 in Table S30 (continued 1))
Similarly to the sulfenamide **13ak**, the reaction of 4-methylbenzoylsulfenyl iodide **1d** (0.389 g, 1.4 mmol) with piperidine (0.166 mL, 1.4 mmol) in ether (40 mL), following by silica gel ptlc of the resulting residue [eluant: dichloromethane/hexane (1:1), Rf = 0.32–0.72] gave piperidinyl 4-methylbenzoylsulfenamide **13de** as colorless crystals; m.p. 84–86 ºC; yield 0.260 g (79%); found C, 66.29; H, 7.31; calc. for $C_{13}H_{17}NOS$ (235.35) requires C, 66.34; H, 7.28; i.r. ν_{max} (KBr)/cm^{-1}: 1657 (C=O); δ_H (90 MHz, $CDCl_3$, Me_4Si) 1.21–1.93 (m, 6H, C*H*$_2$); 2.35 (s, 3H, C*H*$_3$); 3.21–3.72 (m, 4H, NC*H*$_2$); 7.06–8.05 (m, 4H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 184.2 (*C*=O); 55.5 (N*C*H$_2$); 46.0 (C*H*$_2$); 25.1 (*C*H$_2$); 22.2 (CH$_3$Ar); 127.6–131.2 (arom); *m/z* (EI, 20 eV) found M$^+$ 235.10321; calc. for $C_{13}H_{17}NOS$ requires 235.10309.

Morphorinyl 4-methylbenzoylsulfenamide **13df** (entry 20 in Table S30 (continued 1))
Similarly to the sulfenamide **13ak**, the reaction of 4-methylbenzoylsulfenyl iodide **1d** (0.362 g, 1.3 mmol) with morphorine (0.11 mL, 1.3 mmol) in ether (40 mL), following by silica gel ptlc of the resulting residue [eluant: dichloromethane/hexane (1:1), Rf = 0.11–0.32] gave morphorinyl 4-methylbenzoylsulfenamide **13df** as colorless crystals; m.p. 76–78 ºC; yield 0.225 g (73%); found C, 60.59; H, 6.38; calc. for $C_{12}H_{15}NO_2S$ (237.32) requires C, 60.73; H, 6.37; i.r. ν_{max} (KBr)/cm^{-1}: 1668 (C=O); δ_H 90 MHz, $CDCl_3$, Me_4Si) 2.39 (s, 3H, C*H*$_3$), 3.31–3.92 (m, 8H, NC*H*$_2$); 7.12–7.87 (m, 4H, arom); δ_C (270 Hz; $CDCl_3$; Me_4Si) 184.2 (*C*=O); 66.5 (O*C*H$_2$); 54.1 (N*C*H$_2$); 22.2 (*C*H$_3$Ar); 127.6–131.2 (arom); *m/z* (EI, 20 eV) found M$^+$ 237.08301; calc. for $C_{12}H_{15}NO_2S$ requires 237.08235.

N-Methyl, N-phenyl 4-methylbenzoylsulfenamide **13dg** (entry 21 in Table S30 (continued 1))
Similarly to the sulfenamide **13ak**, the reaction of 4-methylbenzoylsulfenyl iodide **1d** (0.278 g, 1.0 mmol) with methylphenylamine (0.107 mL, 1.0 mmol) in dichloromethane (20 mL), following by silica gel ptlc of the resulting residue [eluant: dichloromethane/hexane (1:1), Rf = 0.25–0.68] gave *N*-methyl, *N*-phenyl 4-methylbenzoylsulfenamide **13dg** as colorless crystals; m.p. 73–75 ºC; yield 0.167 g (73%); found C, 69.99; H, 5.89; calc. for $C_{15}H_{15}NOS$ (257.35) requires C, 70.01; H, 5.87; i.r. ν_{max} (KBr)/cm^{-1}: 1663 (C=O); δ_H (90 MHz, $CDCl_3$, Me_4Si) 2.38 (s, 3H, C*H*$_3$); 2.41 (s, 3H, C*H*$_3$); 4.81–5.14 (br. s, 1H, N*H*); 6.81–7.87 (m, 8H, arom); δ_C (270 Hz; $CDCl_3$; Me_4Si) 185.1 (*C*=O); 21.7 (*C*H$_3$C$_6$H$_4$CO), 20.9 (*C*H$_3$Ar), 127.9–160.1 (arom); *m/z* (EI, 20 eV) found M^+ 257.08733; calc. for $C_{15}H_{15}NOS$ requires 257.08744.

N-4-Methylphenyl 4-methylbenzoylsulfenamide **13di** (entry 23 in Table S30 (continued 1))
Similarly to the sulfenamide **13ak**, the reaction of 4-methylbenzoylsulfenyl iodide **1d** (0.334 g, 1.2 mmol) with 4-methylphenylamine (0.128 mL, 1.2 mmol) in dichloromethane (20 mL), following by silica gel ptlc of the resulting residue [eluant: dichloromethane/hexane (1:1), Rf = 0.46–1.11] gave *N*-4-methylphenyl 4-methylbenzoylsulfenamide **13di** as pale yellow crystals; m.p. 95–97 ºC; yield 0.138 g (45%); found C, 69.98; H, 5.90; calc. for $C_{15}H_{15}NOS$ (257.35) requires C, 70.01; H, 5.87; i.r. ν_{max} (KBr)/cm^{-1}: 1688 (C=O); δ_H (90 MHz, $CDCl_3$, Me_4Si) 2.38 (s, 3H, C*H*$_3$); 2.41 (s, 3H, C*H*$_3$); 4.81–5.14 (br. s, 1H, N*H*); 6.81–7.93 (m, 8H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 185.1 (*C*=O); 21.7 (*C*H$_3$C$_6$H$_4$CO); 20.9 (*C*H$_3$Ar); 127.9–160.1 (arom); *m/z* (EI, 20 eV) found M^+ 257.08733; calc. for requires 257.08744.

N-4-Chlorophenyl 4-methylbenzoylsulfenamide **13dj** (entry 24 in Table S30 (continued 1))
Similarly to the sulfenamide **13ak**, the reaction of 4-methylbenzoylsulfenyl iodide **1d** (0.278 g, 1.0 mmol) with 4-chlorophenylamine (0.128 g, 1.0 mmol) in dichloromethane (20 mL), following by silica gel ptlc of the resulting residue [eluant: dichloromethane/hexane (1:1), Rf = 0.36–0.65] gave *N*-4-chlorophenyl 4-methylbenzoylsulfenamide **13dj** as pale yellow crystals; m.p. 96–98 ºC; yield 169 g (61%); found C, 60.51; H, 4.36; calc. for $C_{14}H_{12}ClNOS$ (277.77) requires C, 60.54; H, 4.35; i.r. ν_{max} (KBr)/cm^{-1}: 1673 (C=O); δ_H (90 MHz, $CDCl_3$, Me_4Si) 2.40 (s, 3H, C*H*$_3$); 5.01–5.44 (br. s, 1H, N*H*); 7.10–8.20 (m, 8H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 186.3 (*C*=O), 22.0 (*C*H$_3$Ar), 128.1–132.7 (arom); *m/z* (EI, 20 eV) found: M^+ 277.03185; calc. for $C_{14}H_{12}ClNOS$ requires 277.03281.

N,N-Diethyl 4-methylbenzoylsulfenamide **13dk**
Similarly to the sulfenamide **13ak**, the reaction of 4-methylbenzoylsulfenyl iodide **1d** (0.278 g, 1.0 mmol) with diethylamine (0.169 g, 1.0 mmol) in dichloromethane (20 mL), following by silica gel ptlc of the resulting residue [eluant: dichloromethane/hexane (2:1), Rf = 0.45–0.88] gave *N,N-diethyl* 4-methylbenzoylsulfenamide **13dk** as colorless oil; yield 0.087 g (39%); i.r. ν_{max} (KBr)/cm^{-1}: 1664 (C=O); δ_H (90 MHz, $CDCl_3$, Me_4Si) 1.21 (t, *J* = 7.6 Hz, 6H, C*H*$_3$); 3.15 (q, *J* = 7.6 Hz, 4H, C*H*$_2$); 2.41 (s, 3H, C*H*$_3$Ar); 6.84–8.11 (m, 4H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 185.1 (*C*=O); 21.5 (*C*H$_3$Ar); 128.1–130.6 (arom); *m/z* (EI, 20 eV) found M^+ 223.10355; calc. for $C_{12}H_{17}NOS$ requires 223.10309. 1.21 (t, *J* = 8.0 Hz, 6H, C*H*$_3$); 3.15 (q, *J* = 8.0 Hz, 4H, C*H*$_2$);

N,N-Diphenyl 4-methylbenzoylsulfenamide **13dl**
Similarly to the sulfenamide **13ak**, the reaction of 4-methylbenzoylsulfenyl iodide **1d** (0.278 g, 1.0 mmol) with diphenylamine (0.169 g, 1.0 mmol) in dichloromethane (20 mL), following by silica gel ptlc of the resulting residue [eluant: dichloromethane/hexane (2:1), Rf = 0.45–0.88] gave *N,N*-diphenyl benzoylsulfenamide **13dl** as colorless micro crystals; m.p. 161–163 ºC; yield 0.112 g (35%); found C, 75.19; H, 5.37; calc. for $C_{20}H_{17}NOS$ (319.42) requires C, 75.20; H, 5.36; i.r. ν_{max} (KBr)/cm^{-1}: 1647,

1664 (C=O); δ_H (90 MHz, $CDCl_3$, Me_4Si) 2.41 (s, 3H, C*H*$_3$Ar); 6.84–8.11 (m, 14H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 185.1 (*C*=O); 21.5 (*C*H$_3$Ar); 128.1–130.6 (arom); *m/z* (EI, 20 eV) found M^+ 319.10323; calc. for $C_{20}H_{17}NOS$ requires 319.10309.

N-4-Methoxyphenyl 4-methylbenzoylsulfenamide **13dm**
Similarly to the sulfenamide **13ak**, the reaction of 4-methylbenzoylsulfenyl iodide **1d** (0.278 g, 1.0 mmol) with 4-methoxyphenylamine (0.123 g, 1.0 mmol) in dichloromethane (20 mL), following by silica gel ptlc of the resulting residue [eluant: dichloromethane/hexane (1:1), Rf = 0.36–0.72] gave *N*-4-methoxyphenyl 4-methylbenzoylsulfenamide **13dm** as pale yellow crystals; m.p. 61–64 ºC; yield 148 g (54%); found C, 65.87 H, 5.55; calc. for $C_{15}H_{15}NO_2S$ (273.35) requires C, 65.91; H, 5.53; i.r. ν_{max} (KBr)/cm^{-1}: 1663 (C=O); δ_H (90 MHz, $CDCl_3$, Me_4Si) 2.36 (s, 3H, C*H*$_3$Ar); 3.66 (s, 3H, C*H*$_3$OAr); 4.80–5.11 (br, 1H, N*H*); 6.63–7.90 (m, 8H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 186.3 (C=O); 34.2 (*C*H$_3$OAr); 21.4 (C*H*$_3$Ar); 128.1–132.1 (arom); *m/z* (EI, 20 eV) found M^+ 273.08193; calc. for $C_{15}H_{15}NO_2S$ requires 273.08235.

N-Phenyl 2-methoxybenzoylsulfenamide **13ea** (entry 25 in Table S30 (continued 1))
Similarly to the sulfenamide **13ak**, the reaction of 2-methoxybenzoylsulfenyl iodide **1e** (0.324 g, 1.1 mmol) with phenylamine (0.102 mL, 1.1 mmol) in dichloromethane (20 mL), following by silica gel ptlc of the resulting residue [eluant: dichloromethane/hexane (1:1), Rf = 0.7] gave *N*-phenyl 2-methoxybenzoylsulfenamide **13ea** as colorless crystals; m.p. 100–102 ºC; yield 0.168 g (59%); found C, 64.81; H, 5.07; calc. for $C_{14}H_{13}NO_2S$ (259.32) requires C, 64.84; H, 5.05; i.r. ν_{max} (KBr)/cm^{-1}: 1663 (C=O); δ_H (90 MHz, $CDCl_3$, Me_4Si) 4.00 (s, 3H, OC*H*$_3$); 5.12–5.43 (br. s, 1H, N*H*); 6.83–8.01 (m, 9H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 186.4 (*C*=O); 55.6 (*C*H$_3$OAr); 128.2–155.2 (arom); *m/z* (EI, 20 eV) found M^+ 259.06632; calc. for $C_{14}H_{13}NO_2S$ requires 259.06670.

N-Phenyl 4-methoxybenzoylsulfenamide **13fa** (entry 26 in Table S30 (continued 1))
Similarly to the sulfenamide **13ak**, the reaction of 4-methoxybenzoylsulfenyl iodide **1f** (0.382 g, 1.3 mmol) with phenylamine (0.102 mL, 1.1 mmol) in dichloromethane (20 mL), following by silica gel ptlc of the resulting residue [eluant: dichloromethane/hexane (1:1), Rf = 0.53–0.77] gave *N*-phenyl 4-methoxybenzoylsulfenamide **13fa** as colorless crystals; m.p. 118–120 ºC; yield 158 g (47%); found C, 64.80; H, 5.08; calc. for $C_{14}H_{13}NO_2S$ (259.32) requires C, 64.84; H, 5.05; i.r. ν_{max} (KBr)/cm^{-1}: 1660 (C=O); δ_H (90 MHz, $CDCl_3$, Me_4Si) 3.82 (s, 3H, C*H*$_3$O); 5.11–5.32 (br. s, 1H, N*H*); 6.82–8.06 (m, 9H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 184.1 (*C*=O), 35.3 (*C*H$_3$OAr); 127.9–160.1 (arom); *m/z* (EI, 20 eV) found M^+ 259.06699; calc. for $C_{14}H_{13}NO_2S$ requires 259.06670.

N-Phenyl 4-chlorobenzoylsulfenamide **13ia**
Similarly to the sulfenamide **13ak** the reaction of 4-chlorobenzoylsulfenyl iodide **1i** (0.328 g, 1.1 mmol) with phenylamine (0.102 mL, 1.1 mmol) in dichloromethane (20 mL), following by silica gel ptlc of the resulting residue [eluant: dichloromethane/hexane (1:1), Rf = 0.34–0.89] gave *N*-phenyl 4-chlorobenzoylsulfenamide **13ia** as pale yellow crystals; m.p. 110–112 ºC; yield 0.194 g (67%); i.r. ν_{max} (KBr)/cm^{-1}: 1660 (C=O); δ_H (90 MHz, $CDCl_3$, Me_4Si) 4.92–5.13 (br. s, 1H, N*H*); 6.72–7.92 (m, 9H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 185.3 (*C*=O); 128.9–135.6 (arom); *m/z* (EI, 20 eV) found M^+ 263.01701; calc. for $C_{13}H_{10}ClNOS$ requires 263.01716.

N-4-Methylphenyl 4-chlorobenzoylsulfenamide **13ib**
Similarly to the sulfenamide **13ak**, the reaction of 4-chlorobenzoylsulfenyl iodide **1i** (0.388 g, 1.3 mmol) with 4-methylphenylamine (0.139 mL, 1.3 mmol) in dichloromethane (20 mL), following by silica gel ptlc of the resulting residue [eluant: dichloromethane/hexane (1:1), Rf = 0.34–0.89] gave *N*-

methylphenyl 4-chlorobenzoylsulfenamide **13ib** as colorless crystals; m.p. 85–87 ºC; yield 0.264 g (73%); found C, 60.48; H, 4.36; calc. for $C_{14}H_{12}ClNOS$ (277.77) requires C, 60.54; H, 4.35; i.r. ν_{max} (KBr)/cm^{-1}: 1679 (C=O); δ_H (90 MHz, $CDCl_3$, Me_4Si) 2.39 (s, 3H, C*H*$_3$); 5.03–5.32 (br. s, 1H, N*H*); 6.80–8.01 (m, 8H, arom); δ_C (270 MHz, $CDCl_3$, Me_4Si) 186.4 (*C*=O); 21.4 (*C*H_3Ar); 128.1–132.1 (arom); *m/z* (EI, 20 eV) found: M^+ 277.03275; calc. for $C_{14}H_{12}ClNOS$ requires 277.03281.

[Exp. S2]

Silver benzencarbothioate **1aa** (Preparation)
Method A: To a solution of silver nitrate (1.700 g, 10 mmol) in water (80 mL), potassium benzenecarbothioate (1.851 g, 10.5 mmol) in water (80 mL) was added and stirred at 0 ºC for 30 min. The resulting precipitates were filtered and washed with methanol (3 x 10 mL). Drying of these micro crystals under reduced pressure (ca. 2 torr) for one day gave 2.215 g (92%) of chemically pure *S*-silver benzencarbothioate **1aa** as pale-yellow micro crystals, m.p.: 136 ºC (decomp); (Found C, 34.30; H, 2.11; Calcd for C_7H_5OSAg (245.05): C, 34.31; H, 2.06%).

Method B: To a solution of silver nitrate (1.700 g, 10 mmol) in water (80 mL), benzenecarbothioic acid (1.451 g, 10.5 mmol) in ether (80 mL) was added and stirred at 0 ºC for 30 min. The resulting precipitates were filtered and washed with methanol (3 x 10 mL). Drying of these micro crystals under reduced pressure (ca. 2 torr) for one day gave 2.150 g (92%) of chemically pure silver benzencarbothioate **1aa** as pale-yellow micro crystals, m.p.: 136 ºC (decomp)

Method C: To a solution of silver nitrate (1.700 g, 10 mmol) in water (80 mL), piperidinium benzenecarbothioic acid (2.340 g, 10.5 mmol) in methanol (80 mL) was added and stirred at 0 ºC for 30 min. The resulting precipitates were filtered and washed with methanol (3 x 10 mL). Drying of these micro crystals under reduced pressure (ca. 2 torr) for one day gave 2.150 g (88%) of silver benzencarbothioate **1aa** as pale micro yellow crystals, m.p.: 136 ºC (decomp).

Zinc di(benzencarbothioate) **1ba**
Method A: To a solution of anhydrous zinc dichloride (1.363 g, 10 mmol) in water (80 mL), potassium benzenecarbothioate (3.526 g, 20.0 mmol) in water (80 mL) was added and stirred at 20 ºC for 30 min. The resulting precipitates were filtered and washed with methanol (10 mL). Drying of these micro crystals under reduced pressure (ca. 2 torr) for one day gave 3.055 g (90%) of chemically pure zinc di(benzencarbothioate) **1ba** as colorless micro crystals, m.p.: 97–99 ºC (decomp); (Found C, 49.46; H, 2.99; Calcd for $C_{14}H_{10}O_2S_2Zn$ (339.75): C, 49.49; H, 2.97%).

Cadmium di(benzencarbothioate) **1ca**
Method A: To a solution of cadmium dichloride (1.832 g, 10 mmol) in water (80 mL), potassium benzenecarbothioate (3.526 g, 20.0 mmol) in water (80 mL) was added and stirred at 20 ºC for 30 min. The resulting precipitates were filtered and washed with methanol (10 mL). Drying of these micro crystals under reduced pressure (ca. 2 torr) for 20 h gave 3.055 g (90%) of chemically pure cadmium di(benzencarbothioate) **1ca** as colorless micro crystals, m.p.: 97–99 ºC (decomp); (Found C, 43.46; H, 2.64; Calcd for $C_{14}H_{10}O_2S_2Cd$ (386.77): C, 43.48; H, 2.61%).

S-Triphenylgermanium benzenecarboothioate **2aa**
To a solution of triphenylgermanium chloride (0.340 g, 1.00 mmol) in ether (15 mL), potassium benzenecarbothioate (0.180 g, 1.02 mmol) was added in 30 mL two necked flask and stirred at 20 ºC for 1 h. The reaction mixture was dissolved into dichloromethane (100 mL) and washed with water (3 x 90 mL). After drying on anhydrous $MgSO_4$ (ca. 2 g) for 1 h, the solvent solvents were removed by rotary evaporator (ca. 20 torr). Recrystallization of the resulting solid from a mixed solvent of dichloromethane (2 mL)/hexane (4 mL) in refrigerator (–17 ºC) for 24 h gave 0.355 g (80%) of chemically pure *S*-triphenylgermanium benzenecarbothioate **2aa** as colorless crystals; m.p. 134–136 ºC: (Found C, 68.59; H, 4.87; Calcd for $C_{25}H_{20}OSGe$ (455.11): C, 68.52; H, 4.87%).

S-Triphenylgermanium ethanothioate **2am**

To a solution of triphenylgermanium chloride (0.340 g, 1.0 mmol) in ether (15 mL), potassium methanecarbothioate (0.100 g, 1.02 mmol) was added in 30 mL two necked flask and stirred at 20 ºC for 1 h. The reaction mixture was dissolved into dichloromethane (100 mL) and washed with water (3 x 90 mL). After drying on anhydrous $MgSO_4$ (ca. 2 g) for 10 min, the solvent solvents were removed by rotary evaporator (ca. 20 torr). Recrystallization of the resulting solid from hot hexane (3 mL) in refrigerator (–17 ºC) for 24 h gave 0.277 g (73%) of chemically pure *S*-triphenylgermanium ethanothioate **2ai** as colorless micro crystals; m.p. 96–98 ºC: ν_{max}/(KBr, neat)/cm^{-1}: 3049, 2925, 1672(C=O), 1560, 1483, 1430, 1350, 1308, 1132, 1106, 1092, 1025, 998, 949, 738, 696, 627; (Found C, 63.58; H, 4.77; Calcd for $C_{20}H_{18}OSGe$ (379.02): C, 63.38; H, 4.79%).

S-Triphenylgermanium 1,1-dimethylethanothioate **2aj**

To a solution of triphenylgermanium chloride (0.333 g, 0.98 mmol) in ether (15 mL), potassium 1,1-dimethylethanothioate (0.140 g, 1.0 mmol) was added in 30 mL two necked flask and stirred at 20 ºC for 1 h. The reaction mixture was dissolved into dichloromethane (100 mL) and washed with water (3 x 90 mL). After drying on anhydrous $MgSO_4$ (ca. 2 g) for 1 h, the solvent solvents were removed by rotary evaporator (ca. 20 torr). Recrystallization of the resulting solid from hexane (3 mL) in refrigerator (–17 ºC) for 24 h gave 0.355 g (80%) of chemically pure *S*-triphenylgermanium 1,1-dimethylethanothioate **2aj** as colorless crystals; m.p. 87–89 ºC: (Found C, 65.78; H, 5.89; Calcd for $C_{23}H_{24}OSGe$ (421.10): C, 65.60; H, 5.74%).

S-Diphenylgermanium di(benzenecarbothioate) **2ba**

To a solution of diphenylgermanium dichloride (0.298 g, 1.00 mmol) in ether (15 mL), potassium benzenecarbothioate (0.355 g, 2.01 mmol) was added in 30 mL two necked flask and stirred at 20 ºC for 1 h. The reaction mixture was dissolved into dichloromethane (100 mL) and washed with water (3 x 90 mL). After drying on anhydrous $MgSO_4$ (ca. 2 g) for 1 h, the solvent solvents were removed by rotary evaporator (ca. 20 torr). Recrystallization of the resulting solid from a mixed solvent of dichloromethane (2 mL)/hexane (4 mL) in refrigerator (–17 ºC) for 24 h gave 0.430 g (86%) of chemically pure *S*-diphenylgermanium di(benzenecarbothioate) **2ba** as colorless crystals; m.p. 139–141 ºC; (Found C, 62.45; H, 4.18; Calcd for $C_{26}H_{20}O_2S_2Ge$ (501.16): C, 62.31; H, 4.02%).

S-Diphenylgermanium di(ethanothioate) **2bm**

To a solution of diphenylgermanium dichloride (0.299 g, 1.0 mmol) in ether (15 mL), sodium ethanothioate (0.155 g, 2.04 mmol) was added in 30 mL two necked flask and stirred at 20 ºC for 1 h. The reaction mixture was dissolved into dichloromethane (100 mL) and washed with water (3 x 90 mL). After drying on anhydrous $MgSO_4$ (ca. 2 g) for 10 min, the solvent solvents were removed by rotary evaporator (ca. 20 torr). Recrystallization of the resulting solid from hot hexane (5 mL) in refrigerator (–17 ºC) for 24 h gave 0.387 g (88%) of chemically pure *S*-diphenylgermanium di(ethanothioate) **2bm** as yellow oil; ν_{max}/(KBr, neat)/cm^{-1}: 3055, 2957, 1688 (C=O), 1585, 1484. 1434, 1353, 1307, 1185, 1119, 1092, 1026, 999, 950, 852, 737, 694, 623.

The i.r. and ^1H and ^{13}C NMR spectra were exactly consistent with those of authentic sample which was prepared by the reaction of potassium methanecarbothioate with diphenylgermanium dichloride.

S-Diphenylgermanium di(1,1-dimethylethanothioate) **2bn**

To a solution of diphenylgermanium dichloride (0.283 g, 0.95 mmol) in ether (15 mL), potassium 1,1-dimethylethanothioate (0.274 g, 1.95 mmol) was added in 30 mL two necked flask and stirred at 20 ºC for 1 h. The reaction mixture was dissolved into dichloromethane (100 mL) and washed with water (3 x 90 mL). After drying on anhydrous $MgSO_4$ (ca. 2 g) for 1 h, the solvent solvents were removed by

rotary evaporator (ca. 20 torr). Recrystallization of the resulting solid from a mixed solvent of dichloromethane (1 mL)/hexane (2 mL) in refrigerator (–17 ºC) for 24 h gave 0.450 g (85%) of chemically pure *S*-diphenylgermanium di(1,1-dimethylethanothioate) **2bn** as colorless crystals; m.p. 158–160 ºC; (Found C, 63.55; H, 4.59; Calcd for $C_{28}H_{24}O_2S_2Ge$ (529.21): C, 63.55; H, 4.57%).

S-Triphenyltin benzenecarbothioate **2ca**

To a solution of triphenyltin chloride (0.386 g, 1.00 mmol) in ether (15 mL), potassium benzenecarbothioate (0.178 g, 1.01 mmol) was added in 30 mL two necked flask and stirred at 20 ºC for 1 h. The reaction mixture was dissolved into dichloromethane (100 mL) and washed with water (3 x 90 mL). After drying on anhydrous $MgSO_4$ (ca. 2 g) for 1 h, the solvent solvents were removed by rotary evaporator (ca. 20 torr). Recrystallization of the resulting solid from a mixed solvent of dichloromethane (2 mL)/hexane (4 mL) in refrigerator (–17 ºC) for 24 h gave 0.416 g (83%) of chemically pure *S*-triphenyltin benzenecarbothioate **2ca** as colorless crystals; m.p. 106–108 ºC; (Found C, 61.53; H, 4.01; Calcd for $C_{25}H_{20}OSSn$ (487.19): C, 61.64; H, 4.14%).

S-Triphenyltin ethanothioate **2cm**

To a solution of triphenyltin chloride (0.385 g, 1.0 mmol) in ether (10 mL), potassium ethanothioate (0.103 g, 1.05 mmol) was added in 30 mL two necked flask and stirred at 20 ºC for 1 h. The reaction mixture was dissolved into dichloromethane (100 mL) and washed with water (3 x 90 mL). After drying on anhydrous $MgSO_4$ (ca. 2 g) for 10 min, the solvent solvents were removed by rotary evaporator (ca. 20 torr). Recrystallization of the resulting solid from hot hexane (5 mL) in refrigerator (–17 ºC) for 24 h gave 0.360 g (77%) of chemically pure *S*-triphenyltin ethanothioate **2cm** as colorless micro crystals; m.p. 78–80 ºC: ν_{max}/(KBr, neat)/cm^{-1}: 3049, 1732, 1651 (C=O), 1480, 1429, 1352, 1333, 1303, 1262, 1193, 1143, 1111, 1074, 1021, 996, 952, 734, 696, 660, 637, 531, 498; (Found C, 56.43; H, 4.18; Calcd for $C_{20}H_{18}OSSn$ (425.12): C, 56.51; H, 4.27%).

S-Triphenyltin 1,1-dimethylethaneothioate **2cn**

To a solution of triphenyltin chloride (0.385 g, 1.0 mmol) in ether (20 mL), potassium 1,1-dimethylethanothioate (0.149 g, 1.06 mmol) was added in 30 mL two necked flask and stirred at 20 ºC for 1 h. The reaction mixture was dissolved into dichloromethane (200 mL) and washed with water (3 x 90 mL). After drying on anhydrous $MgSO_4$ (ca. 2 g) for 10 min, the solvent solvents were removed by rotary evaporator (ca. 20 torr). Recrystallization of the resulting solid from hexane (3 mL) in refrigerator (–17 ºC) for 24 h gave 0.360 g (77%) of chemically pure *S*-triphenyltin 1,1-dimethylethanothioate **2cn** as colorless crystals; m.p. 78–79 ºC: (Found C, 59.05; H, 5.27; Calcd for $C_{23}H_{24}OSSn$ (467.20): C, 59.13; H, 5.18%).

S-Diphenyltin di(benzenecarbothioate) **2da**

To a solution of diphenyltin dichloride (0.344 g, 1.00 mmol) in ether (15 mL), potassium benzenecarbothioate (0.355 g, 2.01 mmol) was added in 30 mL two necked flask and stirred at 20 ºC for 1 h. The reaction mixture was dissolved into dichloromethane (100 mL) and washed with water (3 x 90 mL). After drying on anhydrous $MgSO_4$ (ca. 2 g) for 1 h, the solvent solvents were removed by rotary evaporator (ca. 20 torr). Recrystallization of the resulting solid from a mixed solvent of dichloromethane (2 mL)/hexane (4 mL) in refrigerator (–17 ºC) gave 0.519 g (95%) of chemically pure *S*-diphenyltin di(benzenecarbothioate) **2da** as colourless crystals; m.p. 154–156 ºC; (Found C, 56.88; H, 3.75; Calcd for $C_{26}H_{20}O_2S_2Sn$ (547.26): C, 57.05; H, 3.69%).

S-Diphenyltin di(ethanothioate) **2dm**

To a solution of diphenyltin dichloride (0.344 g, 1.0 mmol) in ether (20 mL), potassium ethanothioate (2.00 g, 2.04 mmol) was added in 30 mL two necked flask and stirred at 20 ºC for 1 h. The reaction mixture was dissolved into dichloromethane (150 mL) and washed with water (3 x 90 mL). After drying on anhydrous $MgSO_4$ (ca. 2 g) for 10 min, the solvent solvents were removed by rotary evaporator (ca. 20 torr). Recrystallization of the resulting solid from hot hexane (5 mL) in refrigerator (–17 ºC) for 24 h gave 0.368 g (87%) of chemically pure *S*-diphenyltin di(ethanothioate) **2dm** as colorless crystals; m.p. 48–50 ºC: ν_{max}/(KBr, neat)/cm^{-1}: 3060, 1646 (C=O), 1618, 1480. 1431, 1355, 1333, 1129, 1116, 1074, 1021, 998, 955, 728, 694, 639: (Found C, 45.38; H, 3.91; Calcd for $C_{16}H_{16}O_2S_2Sn$ (423.11): C, 45.12; H, 3.81%).

S-Diphenyltin di(1,1-dimethylethanothioate) **2dn**

To a solution of diphenyltin dichloride (0.350 g, 1.02 mmol) in ether (20 mL), potassium 1,1-dimethylethanothioate (2.90 g, 2.07 mmol) was added in 30 mL two necked flask and stirred at 20 ºC for 1 h. The reaction mixture was dissolved into dichloromethane (150 mL) and washed with water (3 x 90 mL). After drying on anhydrous $MgSO_4$ (ca. 2 g) for 10 min, the solvent solvents were removed by rotary evaporator (ca. 20 torr). Recrystallization of the resulting solid from hexane (3 mL) in refrigerator (–17 ºC) for 24 h gave 0.423 g (82%) of chemically pure *S*-diphenyltin di(1,1-dimethylethanothioate) **2dn** as colorless crystals; m.p. 48–50 ºC: (Found C, 52.15; H, 5.47; Calcd for $C_{22}H_{28}O_2S_2Sn$ (507.28): C, 52.09; H, 5.56%).

S-Triphenyllead benzencarbothioate **2ea**

To a solution of triphenyllead chloride (0.480 g, 1.02 mmol) in ether (15 mL), potassium benzenecarbothioate (0.183 g, 1.04 mmol) was added in 30 mL two necked flask and stirred at 20 ºC for 1 h. The reaction mixture was dissolved into dichloromethane (100 mL) and washed with water (3 x 90 mL). After drying on anhydrous $MgSO_4$ (ca. 2 g) for 1 h, the solvent solvents were removed by rotary evaporator (ca. 20 torr). Recrystallization of the resulting solid from a mixed solvent of dichloromethane (1.5 mL), ethyl acetate (0.5 mL) and hexane (4 mL) in refrigerator (–17 ºC) for 24 h gave 0.554 g (95%) of chemically pure *S*-triphenyllead benzenecarbothioate **2ea** as colorless crystals; m.p. 94–96 ºC; Found C, 52.22; H, 3.51; Calcd for $C_{25}H_{20}OSPb$ (575.68): C, 52.16; H, 3.50%.

S-Triphenyllead ethanothioate **2em**

To a solution of triphenyllead chloride (0.475 g, 1.0 mmol) in dichloromethane (15 mL), sodium ethanothioate (0.100 g, 1.02 mmol) was added in 30 mL two necked flask and stirred at 20 ºC for 1 h. The reaction mixture was dissolved into dichloromethane (50 mL) and washed with water (3 x 90 mL). After drying on anhydrous $MgSO_4$ (ca. 2 g) for 10 min, the solvent solvents were removed by rotary evaporator (ca. 20 torr). Recrystallization of the resulting solid from hot hexane (5 mL) in refrigerator (–17 ºC) for 24 h gave 0.360 g (77%) of chemically pure *S*-triphenyllead ethanothioate **2em** as colorless micro crystals; m.p. 91–93 ºC: ν_{max}/(KBr, neat)/cm^{-1}: 3053, 2996, 1762, 1622 (C=O), 1609, 1565, 1474, 1429, 1351, 1328, 1305, 1262, 1158, 1117, 1014, 993, 956, 911, 876, 802, 731, 688, 645, 532, 499; (Found C, 46.95; H, 3.57; Calcd for $C_{20}H_{18}OSPb$ (513.61): C, 46.77; H, 3.53%).

S-Triphenyllead 1,1-dimethylethanothioate **2en**

To a solution of triphenyllead chloride (0.483 g, 1.02 mmol) in dichloromethane (15 mL), sodium 1,1-dimethylethanothioate (0.150 g, 1.07 mmol) was added in 30 mL two necked flask and stirred at 20 ºC for 1 h. The reaction mixture was dissolved into dichloromethane (200 mL) and washed with water (3 x 90 mL). After drying on anhydrous $MgSO_4$ (ca. 2 g) for 1 h, the solvent solvents were removed by rotary evaporator (ca. 20 torr). Recrystallization of the resulting solid from hexane (3 mL) in refrigerator (–17 ºC) for 24 h gave 0.360 g (77%) of chemically pure *S*-triphenyllead 1,1-dimethylethanothioate **2e**

as colorless crystals; m.p. 75–77 ºC: (Found C, 46.95; H, 3.67; Calcd for $C_{20}H_{18}OSPb$ (513.61): C, 46.77; H, 3.53%).

S-Diphenyllead di(benzencarbothioate) **2fa**

To a solution of diphenyllead dichloride (0.264 g, 0.62 mmol) in methanol (15 mL), potassium benzenecarbothioate (0.230 g, 1.30 mmol) was added in 30 mL two necked flask and stirred at 20 ºC for 1 h. The reaction mixture was dissolved into dichloromethane (100 mL) and washed with water (3 x 90 mL). After drying on anhydrous $MgSO_4$ (ca. 2 g) for 1 h, the solvent solvents were removed by rotary evaporator (ca. 20 torr). Recrystallization of the resulting solid from a mixed solvents of dichloromethane (1 mL), ethyl acetate (0.5 mL) and hexane (45 mL) in refrigerator (–17 ºC) gave 0.519 g (95%) of chemically pure *S*-diphenyllead di(benzencarbothioate) **2fa** as colorless crystals; m.p. 173–175 ; (Found C, 49.35; H, 3.18; Calcd for $C_{26}H_{20}O_2S_2Pb$ (626.76): C, 49.12; H, 3.17%).

S-Diphenyllead di(ethanothioate) **2fm**

To a solution of diphenyllead dichloride (0.414 g, 0.98 mmol) in methanol 15 mL), sodium ethanothioate (0.155 g, 2.04 mmol) was added in 30 mL two necked flask and stirred at 20 ºC for 1 h. The reaction mixture was dissolved into dichloromethane (60 mL) and washed with water (3 x 90 mL). After drying on anhydrous $MgSO_4$ (ca. 2 g) for 10 min, the solvent solvents were removed by rotary evaporator (ca. 20 torr). Recrystallization of the resulting solid from hot hexane (3 mL) in refrigerator (–17 ºC) for 24 h gave 0.368 g (87%) of chemically pure *S*-diphenyllead di(ethanothioate) **2fm** as colorless crystals; m.p. 93–95 ºC: ν_{max}/(KBr, neat)/cm^{-1}: 3053, 2954, 1629 (C=O), 1567, 1474, 1434, 1352, 1327, 1187, 1151, 1117, 1014, 994, 955, 727, 688, 642, 499. The i.r. and 1H and 13C NMR spectra were exactly consistent with those of authentic sample which was prepared from the reaction of potassium ethanothioate with diphenyllead dichloride.

S-Diphenyllead di(1,1-dimethylethanothioate) **2fn**

To a solution of diphenyllead dichloride (0.432 g, 1.02 mmol) in methanol (15 mL), sodium 1,1-dimethylethanothioate (0.300 g, 2.14 mmol) was added in 30 mL two necked flask and stirred at 20 ºC for 1 h. The reaction mixture was dissolved into dichloromethane (100 mL) and washed with water (3 x 90 mL). After drying on anhydrous $MgSO_4$ (ca. 2 g) for 1 h, the solvent solvents were removed by rotary evaporator (ca. 20 torr). Recrystallization of the resulting solid from dichloromethane (1 mL)/hexane (3 mL) in refrigerator (–17 ºC) for 24 h gave 0.347 g (58%) of chemically pure *S*-diphenyllead di(1,1-dimethylethanothioate) **2fj** as colorless crystals; ν_{max}/(KBr, neat)/cm^{-1}: 3055, 1969, 1932, 1869, 1701, 1611 (C=O), 1568, 1475, 1460, 1434, 1393, 1365, 1038, 1015, 993, 948, 812, 798, 727, 688, 625, 510 cm^{-1}. The i.r. spectra were consistent with those of the authentic sample which was prepared from the reaction of piperidinium 1,1-dimethylethanothioate with diphenyllead dichloride.

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Table S1 Synthesis of acylsulfenyl iodides **1** from silver carbothioates **2a**

Ag(SC(O)R) **2a** R	compd no.	I_2 or NIS	method	RC(O)SI **1** R	yield[a] / %	m.p.[b] / °C
C_6H_5	**2aa**	I_2	A[c]	C_6H_5 (**1a**)	46	45-48
C_6H_5	**2aa**	NIS	B[d]		75	
2-MeC_6H_4	**2ab**	NIS	B	2-MeC_6H_4 (**1b**)	42	44-46
3-MeC_6H_4	**2ac**	NIS	B	3-MeC_6H_4 (**1c**)	67	49-52
4-MeC_6H_4	**2ad**	I_2	A	4-MeC_6H_4 (**1d**)	63	40-43
4-MeC_6H_4	**2ad**	NIS	B		78	
2-$MeOC_6H_4$	**2ae**	NIS	B	2-$MeOC_6H_4$ (**1e**)	37	48-50
4-$MeOC_6H_4$	**2af**	I_2	A	4-$MeOC_6H_4$ (**1f**)	8	38-40
4-$MeOC_6H_4$	**2af**	NIS	B		76	
2-ClC_6H_4	**2ag**	I_2	A	2-ClC_6H_4 (**1g**)	57	47-49
3-ClC_6H_4	**2ah**	NIS	B	3-ClC_6H_4 (**1h**)	47	56-58
4-ClC_6H_4	**2ai**	NIS	B	4-ClC_6H_4 (**1i**)	67	46-48
2-$NO_2C_6H_4$	**2aj**	NIS	B	2-$NO_2C_6H_4$ (**1j**)	58	82-85
3-$NO_2C_6H_4$	**2ak**	NIS	B	3-$NO_2C_6H_4$ (**1k**)	63	52-54
4-$NO_2C_6H_4$	**2al**	NIS	B	4-$NO_2C_6H_4$ (**1l**)	37	64-66
Me	**2am**	NIS	B	Me (**1m**)	3	oil
tert-Bu	**2an**	NIS	B	*tert*-Bu (**1n**)	4	oil
n-$CH_3(CH_2)_{16}$	**2ao**	I_2	A	*n*-$CH_3(CH_2)_{16}$ (**1o**)	8	oil
n-$CH_3(CH_2)_{16}$	**2ao**	NIS	B		-	-

[a]Isolated yield. [b]Decomposition. [c]$CH_2Cl_2/CHCl_3$ (1:4), -15 °C, 15-30 min.
[d]$CHCl_3$, -15 °C, 15-30 min.

Table S2 Synthesis of acylsulfenyl iodides **1** from zinc di(carbothioates) **2b**

M(SC(O)R)*x* **2b**			compd	I_2	method	RC(O)Sl **1**	yields[a]
M	R	*x*	no.	or NIS		R	/ %
Zn	C_6H_5	2	**2ba**	I_2	A[b]	C_6H_5 (**1a**)	5
Zn	C_6H_5	2	**2ba**	NIS	B[c]	C_6H_5 (**1a**)	62
Zn	2-MeC_6H_4	2	**2bb**	NIS	B	2-MeC_6H_4 (**1b**)	74
Zn	3-MeC_6H_4	2	**2bc**	I_2	A	3-MeC_6H_4 (**1c**)	4
Zn	4-MeC_6H_4	2	**2bd**	I_2	A	4-MeC_6H_4 (**1d**)	7
Zn	4-MeC_6H_4	2	**2bd**	NIS	B	4-MeC_6H_4 (**1d**)	68
Zn	2-$MeOC_6H_4$	2	**2be**	NIS	B	2-$MeOC_6H_4$ (**1e**)	77
Zn	4-$MeOC_6H_4$	2	**2bf**	I_2	A	4-$MeOC_6H_4$ (**1f**)	7
Zn	4-$Me_3OC_6H_4$	2	**2bf**	NIS	B	4-$MeOC_6H_4$ (**1f**)	70
Zn	2-ClC_6H_4	2	**2bg**	I_2	A	2-ClC_6H_4 (**1g**)	6
Zn	3-ClC_6H_4	2	**2bh**	NIS	B	3-ClC_6H_4 (**1h**)	73
Zn	4-ClC_6H_4	2	**2bi**	I_2	A	4-ClC_6H_4 (**1i**)	26
Zn	2-$NO_2C_6H_4$	2	**2bj**	NIS	B	2-$NO_2C_6H_4$ (**1j**)	71
Zn	3-$NO_2C_6H_4$	2	**2bk**	NIS	B	3-$NO_2C_6H_4$ (**1k**)	57
Zn	4-$NO_2C_6H_4$	2	**2bl**	I_2	A	4-$NO_2C_6H_4$ (**1l**)	15
Zn	4-$NO_2C_6H_4$	2	**2bl**	NIS	B	4-$NO_2C_6H_4$ (**1l**)	63
Zn	Me	2	**2bm**	NIS	A	Me (**1m**)	3
Zn	1-$CH_3(CH_2)_{16}$	2	**2bo**	I_2	A	1-$CH_3(CH_2)_{16}$ (**1o**)	4
Zn	1-$CH_3(CH_2)_{16}$	2	**2bo**	NIS	B	1-$CH_3(CH_2)_{16}$ (**1o**)	8

[a]Isolated yields. [b]$CHCl_3/CH_3OH$ (7:3), -15 °C, 15-30 min. [c]$CHCl_3$, -15 °C, 15-30 min.

Table S3 Synthesis of acylsulfenyl iodides **1** from cadmium di(carbothioates) **2c**

M(SC(O)R)*x* **2c**			compd	I_2	method	RC(O)SI **1**	yields[a]
M	R	*x*	no.	or NIS			/ %
Cd	C_6H_5	2	**2ca**	I_2	A[b]	C_6H_5 (**1a**)	11
Cd	C_6H_5	2	**2ca**	NIS	B[c]	3-MeC_6H_4 (**1c**)	44
Cd	3-MeC_6H_4	2	**2cc**	NIS	B	4-MeC_6H_4 (**1d**)	51
Cd	4-MeC_6H_4	2	**2cd**	NIS	B	4-$McOC_6H_4$ (**1f**)	64
Cd	4-$McOC_6H_4$	2	**2cf**	NIS	B	3-ClC_6H_4 (**1h**)	49
Cd	3-ClC_6H_4	2	**2ch**	NIS	B	4-ClC_6H_4 (**1i**)	53
Cd	4-ClC_6H_4	2	**2ci**	I_2	A	2-$NO_2C_6H_4$ (**1j**)	6
Cd	2-$NO_2C_6H_4$	2	**2cj**	NIS	B	3-$NO_2C_6H_4$ (**1k**)	58
Cd	3-$NO_2C_6H_4$	2	**2ck**	NIS	B	4-$NO_2C_6H_4$ (**1l**)	52
Cd	4-$NO_2C_6H_4$	2	**2cl**	NIS	B	*tert*-Bu (**1n**)	60
Cd	*tert*-Bu	2	**2cn**	NIS	B		-

[a]Isolated yields. [b]$CHCl_3$, -15 °C, 15-30 °C min. [c]$CHCl_3/CH_3OH$ (1 : 1), -15 °C, 15-30 min.

Table S4 Synthesis of acylsulfenyl iodides **1** from organogermanium carbothioates **3a** and **3b**

$M(SC(O)R)_x$ **3a**, **3b**			compd	I_2	method	RC(O)SI **1**	yields[a]
M	R	*x*	no.	or NIS			/ %
Ph_3Ge	C_6H_5	1	**3aa**	I_2	A[b]	C_6H_5 (**1a**)	44
Ph_3Ge	C_6H_5	1	**3aa**	NIS	B[c]	C_6H_5 (**1a**)	62
Ph_3Ge	3-MeC_6H_4	1	**3ab**	NIS	B	3-MeC_6H_4 (**1c**)	65
Ph_3Ge	4-MeC_6H_4	1	**3ac**	NIS	B	4-MeC_6H_4 (**1d**)	71
Ph_3Ge	2-$MeOC_6H_4$	1	**3ad**	NIS	B	2-$MeOC_6H_4$(**1e**)	58
Ph_3Ge	4-$MeOC_6H_4$	1	**3ae**	NIS	B	4-$MeOC_6H_4$ (**1f**)	67
Ph_3Ge	3-ClC_6H_4	1	**3af**	NIS	B	3-ClC_6H_4 (**1h**)	49
Ph_3Ge	4-ClC_6H_4	1	**3ag**	I_2	A	4-ClC_6H_4 (**1i**)	13
Ph_3Ge	4-$NO_2C_6H_4$	1	**3ah**	NIS	B	4-$NO_2C_6H_4$ (**1l**)	52
Ph_3Ge	Me	1	**3ai**	NIS	B	Me (**1m**)	21
Ph_3Ge	*tert*-Bu	1	**3aj**	I_2	A	*tert*-Bu (**1n**)	6
Ph_3Ge	*n*-$CH_3(CH_2)_{16}$	1	**3ak**	NIS	B	*n*-$CH_3(CH_2)_{16}$ (**1o**)	-
Ph_2Ge	C_6H_5	2	**3ba**	I_2	A	C_6H_5 (**1a**)	37
Ph_2Ge	C_6H_5	2	**3ba**	NIS	B	C_6H_5 (**1a**)	78
Ph_2Ge	3-MeC_6H_4	2	**3bb**	NIS	B	3-MeC_6H_4 (**1c**)	62
Ph_2Ge	4-MeC_6H_4	2	**3bc**	NIS	B	4-MeC_6H_4 (**1d**)	77
Ph_2Ge	2-$MeOC_6H_4$	2	**3bd**	NIS	B	2-$MeOC_6H_4$(**1e**)	58
Ph_2Ge	4-$MeOC_6H_4$	2	**3be**	NIS	B	4-$MeOC_6H_4$ (**1f**)	56
Ph_2Ge	3-ClC_6H_4	2	**3bf**	NIS	B	3-ClC_6H_4 (**1h**)	-
Ph_2Ge	4-ClC_6H_4	2	**3bg**	I_2	A	4-ClC_6H_4 (**1i**)	29
Ph_2Ge	4-$NO_2C_6H_4$	2	**3bh**	NIS	B	4-$NO_2C_6H_4$ (**1l**)	60
Ph_2Ge	Me	2	**3ai**	NIS	B	Me (**1m**)	7
Ph_2Ge	*tert*-Bu	2	**3aj**	I_2	A	*tert*-Bu (**1n**)	8
Ph_2Ge	*n*-$CH_3(CH_2)_{16}$	2	**3ak**	NIS	B	*n*-$CH_3(CH_2)_{16}$ (**1o**)	-

[a]Isolated yields. [b]CH_2Cl_2, -15 °C for 30 min. [c]$CHCl_3$, -15 °C for 30 min.

Table S5 Synthesis of acylsulfenyl iodides **1** from organotin carbothioates **3c** and **3d**

$M(SOCR)_x$ **3c**, **3d**			compd	I_2	method	RC(O)SI **1**	yields[a]
M	R	*x*	no.	or NIS			/ %
Ph_3Sn	C_6H_5	1	**3ca**	I_2	A[b]	C_6H_5 (**1a**)	36
Ph_3Sn	C_6H_5	1	**3ca**	NIS	B[c]	C_6H_5 (**1a**)	65
Ph_3Sn	3-MeC_6H_4	1	**3cb**	NIS	B	3-MeC_6H_4 (**1c**)	71
Ph_3Sn	4-MeC_6H_4	1	**3cc**	NIS	B	4-MeC_6H_4 (**1d**)	62
Ph_3Sn	2-$MeOC_6H_4$	1	**3cd**	NIS	B	2-$MeOC_6H_4$ (**1e**)	68
Ph_3Sn	4-$MeOC_6H_4$	1	**3ce**	I_2	B	4-$MeOC_6H_4$ (**1f**)	28
Ph_3Sn	3-ClC_6H_4	1	**3cf**	NIS	B	3-ClC_6H_4 (**1h**)	64
Ph_3Sn	4-ClC_6H_4	1	**3cg**	NIS	A	4-ClC_6H_4 (**1i**)	66
Ph_3Sn	4-$NO_2C_6H_4$	1	**3ch**	I_2	B	4-$NO_2C_6H_4$ (**1l**)	19
Ph_3Sn	Me	1	**3ci**	NIS	B	Me (**1m**)	-
Ph_3Sn	*tert*-Bu	1	**3cj**	I_2	A	*tert*-Bu (**1n**)	-
Ph_3Sn	*n*-$CH_3(CH_2)_{16}$	1	**3ck**	NIS	B	*n*-$CH_3(CH_2)_{16}$ (**1o**)	-
Ph_2Sn	C_6H_5	2	**3da**	I_2	A	C_6H_5 (**1a**)	31
Ph_2Sn	C_6H_5	2	**3da**	NIS	B	C_6H_5 (**1a**)	67
Ph_2Sn	3-MeC_6H_4	2	**3db**	NIS	B	3-MeC_6H_4 (**1c**)	58
Ph_2Sn	4-MeC_6H_4	2	**3dc**	NIS	B	4-MeC_6H_4 (**1d**)	33
Ph_2Sn	2-$MeOC_6H_4$	2	**3dd**	I_2	B	2-$MeOC_6H_4$ (**1e**)	66
Ph_2Sn	4-$MeOC_6H_4$	2	**3de**	NIS	B	4-$MeOC_6H_4$ (**1f**)	26
Ph_2Sn	3-ClC_6H_4	2	**3df**	I_2	B	3-ClC_6H_4 (**1h**)	67
Ph_2Sn	4-ClC_6H_4	2	**3dg**	NIS	A	4-ClC_6H_4 (**1i**)	6
Ph_2Sn	4-$NO_2C_6H_4$	2	**3dh**	NIS	B	4-$NO_2C_6H_4$ (**1l**)	73 <
Ph_2Sn	Mc	2	**3di**	NIS	B	Me (**1m**)	3 <
Ph_2Sn	*tert*-Bu	2	**3dj**	NIS	A	*tert*-Bu (**1n**)	6 <
Ph_2Sn	*n*-$CH_3(CH_2)_{16}$	2	**23k**	NIS	B	*n*-$CH_3(CH_2)_{16}$ (**1o**)	4

[a]Isolated yields. [b]CH_2Cl_2, -15 °C for 30 min. [c]$CHCl_3$, -15 °C for 30 min.

Table S6 Synthesis of acylsulfenyl iodides **1** from organolead carbothioates **3e** and **3f**

$M(SC(O)R)_x$ **3e**, **3f**			compd	I_2	method	RC(O)SI **1**	yields[a]
M	R	*x*	no.	or NIS			/ %
Ph_3Pb	C_6H_5	1	**3ca**	I_2	A[b]	C_6H_5 (**1a**)	16
Ph_3Pb	C_6H_5	1	**3ca**	NIS	B[c]	C_6H_5 (**1a**)	49
Ph_3Pb	3-MeC_6H_4	1	**3cb**	NIS	B	3-MeC_6H_4 (**1c**)	52
Ph_3Pb	4-MeC_6H_4	1	**3ec**	NIS	B	4-MeC_6H_4 (**1d**)	61
Ph_3Pb	2-$MeOC_6H_4$	1	**3ed**	NIS	B	2-$MeOC_6H_4$ (**1e**)	58
Ph_3Pb	4-$MeOC_6H_4$	1	**3ee**	NIS	B	4-$MeOC_6H_4$ (**1fa**)	68
Ph_3Pb	3-ClC_6H_4	1	**3ef**	NIS	B	3-ClC_6H_4 (**1h**)	43
Ph_3Pb	4-ClC_6H_4	1	**3eg**	I_2	A	4-ClC_6H_4 (**1i**)	27
Ph_3Pb	4-$NO_2C_6H_4$	1	**3eh**	NIS	B	4-$NO_2C_6H_4$ (**1l**)	70
Ph_3Pb	Me	1	**3ci**	NIS	B	Me (**1m**)	7
Ph_3Pb	*tert*-Bu	1	**3cj**	I_2	A	*tert*-Bu (**1n**)	-
Ph_3Pb	*n*-$CH_3(CH2)_{16}$	1	**3ek**	NIS	B	*n*-$CH_3(CH_2)_{16}$ (**1o**)	-
Ph_2Pb	C_6H_5	2	**3fa**	I_2	A	C_6H_5 (**1a**)	17
Ph_2Pb	C_6H_5	2	**3fa**	NIS	B	C_6H_5 (**1a**)	63
Ph_2Pb	3-MeC_6H_4	2	**3fb**	NIS	B	3-MeC_6H_4 (**1c**)	47
Ph_2Pb	4-MeC_6H_4	2	**3fc**	NIS	B	4-McC_6H_4 (**1d**)	64
Ph_2Pb	2-$MeOC_6H_4$	2	**3fd**	NIS	B	2-$MeOC_6H_4$ (**1e**)	48
Ph_2Pb	4-$MeOC_6H_4$	2	**3dc**	NIS	B	4-$McOC_6H_4$ (**1fa**)	56
Ph_2Pb	3-ClC_6H_4	2	**3ff**	NIS	B	3-ClC_6H_4 (**1h**)	-
Ph_2Pb	4-ClC_6H_4	2	**3fg**	I_2	A	4-ClC_6H_4 (**1i**)	59
Ph_2Pb	4-$NO_2C_6H_4$	2	**3fh**	NIS	B	4-$NO_2C_6H_4$ (**1l**)	47
Ph_2Pb	Me	2	**3fi**	NIS	B	Me (**1m**)	-
Ph_2Pb	*tert*-Bu	2	**3fj**	I_2	A	*tert*-Bu (**1n**)	-
Ph_2Pb	*n*-$CH_3(CH2)_{16}$	2	**3fk**	NIS	B	*n*-$CH_3(CH_2)_{16}$ (**1o**)	-

[a]Isolated yields. [b]CH_2Cl_2, -15 °C for 30 min. [c]$CHCl_3$, -15 °C for 30 min.

Table S7 Spectral data of acylsulfenyl iodides **1**

RC(O)SI **1** R	i.r. /cm^{-1} [a] νC=O	^{1}H NMR[b] / δ	^{13}C NMR[c] / δ
C_6H_5 (**1a**)	1667	7.02-7.78 (m, 5H, arom)	109.0-133.5(arom) 184.4 (*C*O)
2-MeC_6H_4 (**1b**)	1674	2.29 (s, 3H, ArCH_3) 6.89-7.75 (m, arom)	-
3-MeC_6H_4 (**1c**)	1680	2.31 (s, 3H, ArCH_3) 7.00-7.88 (m, arom)	-
4-MeC_6H_4 (**1d**)	1649,1655	2.34 (s, 3H, ArCH_3) 7.06-7.90 (d, 7.8 Hz, arom)	21.6 (*C*H_3), 128.3-144.9 (arom), 183.3 (*C*O)
2-MeOC_6H_4 (**1e**)	1668,1676	4.02 (s, 3H, OCH_3) 7.06-7.90 (m, arom)	55.6 (O*C*H_3), 112.0-149.3 (arom), 183.3 (*C*O)
4-MeOC_6H_4 (**1f**)	1645,1658	3.89 (s, 3H, OCH_3) 6.91 (d, 7.8 Hz, 2H arom) 7.98 (d, 7.8 Hz, 2H arom)	55.6 (O*C*H_3), 115.0-166.2 (arom), 183.3 (*C*O)
2-ClC_6H_4 (**1g**)	1672	6.66-7.90 (m, 4H, arom)	113.0-157.2 (arom), 182.9 (*C*O)
3-ClC_6H_4 (**1h**)	1684	6.76-7.92 (m, 4H, arom)	121.2-155.3 (arom) 183.5 (*C*O)
4-ClC_6H_4 (**1i**)	1675	6.78-7.93 (m, 4H, arom)	128.2-158.3 (arom) 183.4 (*C*O)
2-$NO_2C_6H_4$ (**1j**)	1680	6.80-7.94 (m, 4H, arom)	127.2-158.3 (arom) 181.1 (*C*O)
3-$NO_2C_6H_4$ (**1k**)	1686	6.80-7.98 (m, 4H, arom)	128.8-162.1 (arom) 183.4 (*C*O)
4-$NO_2C_6H_4$ (**1l**)	1662, 1672	6.75-7.99 (m, 4H, arom)	128.8-161.1 (arom) 182.4 (*C*O)
Me (**1m**)	1726	2.68 (s, 3H, CH_3)	-
tert-Bu (**1n**)	1642	1.01 (s, 9H, CH_3)	-
n-$CH_3(CH_2)_{16}$ (**1o**)	1736	1.21 (t, 7.5 Hz, 3H, CH_3), 2.02 (m, 30H, CH_2), 2.74 (t, 7.4 Hz, 2H, CH_2C(O))	-

[a]KBr. [b]90 MHz, $CDCl_3$, internal standard: Me_4Si. [c]270 MHz, $CDCl_3$, internal standard: Me_4Si.

Table S8 Crystal data of benzoyksulfenyl iodide **1a**

	compound **1a**
empirical formula	C_7H_5IOS
formula weight	264.07
color	yellow orange
crystal system	orthombic
unit-cell dimentions	a= 10.519(2)
(a, b, c = Å)	b= 14.285(2)
	c= 5.349(2)
volume of unit cell (Å^3)	803.8(4)
space group	$P2_12_12_1$ (#19)
Z value	4
D_{calc} (g/cm^3)	2.182
crystal size (mm)	0.40 x 0.29 x 0.14
μ (Mo-K_α) (cm^{-1})	41.69
temp (°C)	-80.0
$\lambda_{MoK\alpha}$(Å)	0.71069
$2\theta_{max}$ (deg)	55.0
no. of measured reflections	1092
no. of observations ($I > 2\sigma(I)$)	1024
no. of variables	91
residuals: R_1, wR_2	0.0254; 0.0690
R indices (all data): R_1, wR_2	0.0283; 0.0702
goodness-of-fit on F^2	1.174
Largest diff. peak / hole (e.Å^{-3})	0.633 / -0.958

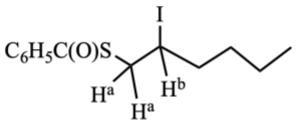
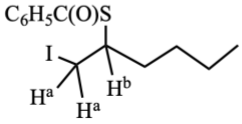
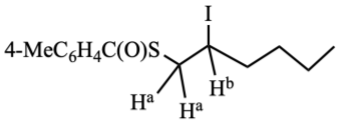
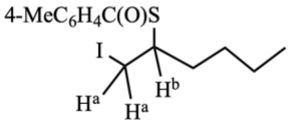
Table S9 Selected bond distances (Å), angles (°) and torsion angles (°) of benzoylsulfenyl iodide **1a**

C_6H_5COSI **1a**

bond lengths		angles	
I1–S1	2.3653(17)	O1–C1-S1	122.0(5)
S1–C1	1.799(7)	I1–S1-C1	100.5(2)
O1–C1	1.206(7)	O2–C1–C2	124.9(6)
O1···I1	3.153(5)	S1-I1···I1'	94.62(5)
		S1-I1···I1"	160.37(5)

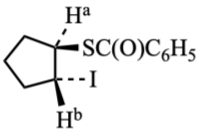
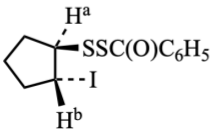
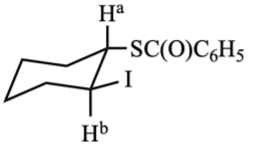
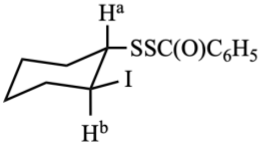
torsion angles	
I1–S1–C1-O1	4.8(6)
O1–C1–C2–C7	-165.9(7)
S1–C1-C2-C7	16.3(8)

Table S10 Spectral data of adducts of RC(O)SI **1** to alkenes and alkynes

alkene **4**	adducts	compd no.	m.p. / °C	i.r.[a] / cm^{-1} νC=O	^{1}H NMR[b] δ /ppm	
1-hexene (**4a**)		**6aa**	oil	1660	0.92-1.88 (m, 9H, CH_2, CH_3), 3.62 (dd, 1H, CH^a), 3.77 (dd, 1H, CH^a), 4.22 (dd, 1H, CH^b),	7.43-7.62 (m, 3H, arom), 7.95-7.99 (m, 2H, arom), J_{ab} = 7.0 Hz, 13.9 Hz J_{aa} = 2.2 Hz
1-hexene (**4a**)		**7aa**	oil	1660	0.92-1.88 (m, 9H, CH_2 , CH_3), 3.39 (dd, 1H, CH^a), 3.72 (dd, 1H, CH^a), 4.05 (dd, 1H, CH^b),	7.43-7.62 (m, 3H, arom), 7.95-7.99 (m, 2H, arom), J_{ab} = 8.1 Hz, 9.9 Hz J_{aa} = 2.1 Hz
1-hexene (**4a**)		**6da**	oil	1658	0.8-2.2 (m, 9H, C_4H_9), 2.41 (s, 3H, CH_3), 3.40 (dd, 1H, CH^a), 3.49 (dd, 1H, CH^a), 4.18 (dd, 1H, CH^b),	7.41-7.63 (m, 2H, arom), 7.96-8.18 (m, 2H, arom), J_{ab} = 8.1 Hz, 10.9 Hz J_{aa} = 1.9 Hz
1-hexene (**4a**)		**7da**[c]	oil	1658	0.8-2.2 (m, 9H, C_4H_9), 2.41 (s, 3H, CH_3), 3.67 (dd, 1H, CH^a), 3.85 (dd, 1H, CH^a), 4.08 (dd, 1H, CH^b),	7.38-7.56 (m, 2H, arom), 7.95-8.16 (m, 2H, arom), J_{ab} = 7.3 Hz, 11.0 Hz J_g = 1.9 Hz

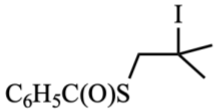
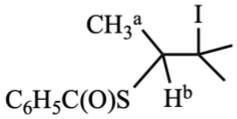
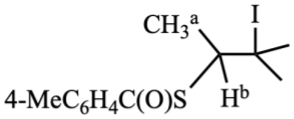
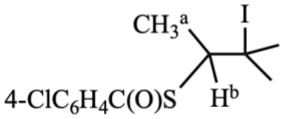
[a]KBr. [b]270 MHz, $CDCl_3$, internal standard: Me_4Si. [c]The mixture from the reaction of adducts **6da** and **7da**.

Table S11 Spectral data of adducts of RC(O)SI **1** to alkenes and alkynes

alkene **4**	adducts	compd. no.	m.p. / °C	i.r.[a] / cm^{-1} νC=O	^{1}H NMR[b] δ /ppm
cyclopentene (**4b**)		**6ab**[c]	oil	1668	1.71-2.61 (m, 6H, CH_2), 4.14 (dt, J = 3.5, 7.5 Hz, 1H, CH^a), 4.37 (dt, J = 3.5, 7.5 Hz, 1H, CH^b), 7.41-7.95 (m, 5H, arom)
		no detect			
cyclohexene (**4c**)		**6ac**[c]	80-82	1668	1.25-2.51 (m, 8H, CH_2), 4.14 (dt, J = 6.4, 7.6 Hz, 1H, CH^a), 4.37 (dt, J = 6.4, 7.6 Hz, 1H, CH^b), 7.40-8.00 (m, 5H, arom)
		no detect			

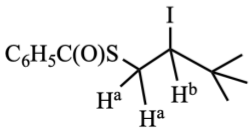
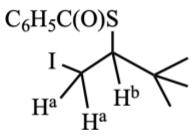
[a]KBr. [b]270 MHz, $CDCl_3$, internal standard: Me_4Si. [c]Markovnikov adduct.

Table S12 Spectral data of adducts of RC(O)SI **1** to alkenes and alkynes

alkene **4**	adducts	compd no.	m.p. / °C	i.r. / cm^{-1} [a] νC=O	^{1}H NMR[b] δ / ppm
2-methyl-1-propene (**4d**)		**6ad**[c]	oil	1664	2.00 (s, 6H, CH_3), 3.78 (s, 2H, CH_2), 7.44-8.02 (m, 5H, arom)
2-methyl-2-butene (**4e**)		**6ae**	oil	1660	1.62 (d, J = 6.6 Hz, 3H, CH_3^a), 2.04 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 3.56 (q, J = 6.6 Hz, 1H, CH^b), 7.23-7.87 (m, 5H, arom)
2-methyl-2-butene (**4e**)		**6de**[c]	oil	1660	1.62 (d, J = 6.6 Hz, 3H, CH_3^a) 2.04 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.39 (s, 3H, CH_3Ar) 3.56 (q, J = 6.6 Hz, 1H, CH^b), 7.23 (d, J = 8.2 Hz, 2H, arom), 7.87 (d, J = 8.2 Hz, 2H, arom)
2-methyl-2-butene (**4e**)		**6ie**	oil	1665	1.58 (d, J = 6.8 Hz, 3H, CH_3^a), 2.00 (s, 6H, CH_3), 2.01 (s, 6H, CH_3), 3.50 (q, J = 6.8 Hz, 1H, CH^b), 7.34-7.40 (m, 2H, arom), 7.82-7.89 (m, 2H, arom)

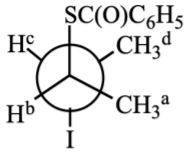
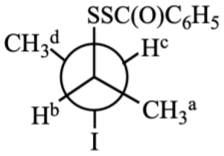
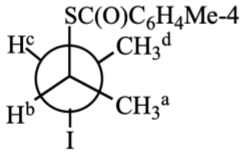
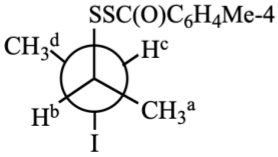
[a]KBr. [b]270 MHz, $CDCl_3$, internal standard: Me_4Si. [c]Markovnikov adduct.

Table S13 Spectral data of adducts of RC(O)SI **1** to alkenes and alkynes

alkene **4**	adducts	compd no.	m.p. / °C	i.r./ cm^{-1} [a] νC=O	^{1}H NMR[b] δ /ppm	
3,3-Dimethyl-2-butene (**4f**)		**6af**[c]	oil	1666	1.22 (s, 9H, CH_3), 3.30 (dd, J = 2.4, 14.4 Hz, 1H, CH^a), 4.02 (dd, J = 2.4, 11.4 Hz, 1H, CH^a), 4.16 (dd, J = 11.4, 14.4 Hz, 1H, CH^b),	7.43-7.61 (m, 3H, arom) 7.97-8.05 (m, 2H, arom) J_{ab} = 11.4 Hz, 14.4 Hz J_g = 2.4 Hz
3,3-Dimethyl-2-butene (**4f**)		**7af**[c]	oil	1666	1.10 (s, 9H, CH_3), 3.27 (dd, J = 3.2, 14.5 Hz, 1H, CH^a), 3.84 (dd, J = 3.2, 10.6 Hz, 1H, CH^a), 4.00 (dd, J = 10.6, 14.5 Hz, 1H, CH^b),	7.38-7.59 (m, 3H, arom) 7.98-8.11 (m, 2H, arom) J_{ab} = 10.6 Hz, 14.5 Hz J_g = 3.2 Hz

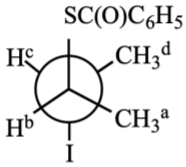
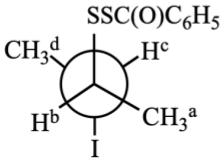
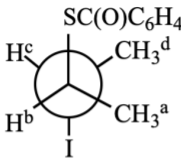
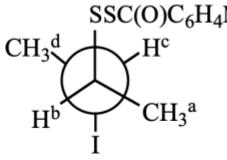
[a]KBr. [b]270 MHz, $CDCl_3$, internal standard: Me_4Si. [c]The data for a mixture of adducts **6af** (30%) and **7af** (70%).

Table S14 Spectral data of adducts of RC(O)SI **1** to alkenes and alkynes

alkene **4**	adducts	compd no.	m.p. / °C	i.r. / cm^{-1} [a] νC=O	^{1}H NMR[b] δ / ppm	
cis-2-butene (**4gz**)		**6ag$_{th}$**	oil	1651	1.51 (d, 3H, CH_3^a), 1.55 (d, 3H, CH_3^d), 4.16 (qd, 1H, CH^b), 4.34 (qd, 1H, CH^c),	7.42-7.60 (m, 3H, arom) 7.89-8.01 (m, 2H, arom) J_{ab} = 7.0 Hz, J_{bc} = 2.9 Hz J_{cd} = 6.5 Hz
		**7ag$_{er}$**		1648	1.43 (d, 3H, CH_3^a), 1.64 (d, 3H, CH_3^d), 3.28 (qd, 1H, CH^b), 4.31 (qd, 1H, CH^c),	7.42-7.60 (m, 3H, arom) 7.89-8.01 (m, 2H, arom) J_{ab} = 7.0 Hz, J_{bc} = 3.7 Hz J_{cd} = 6.6 Hz
cis-2-butene (**4gz**)		**6dg$_{th}$**	oil	1664sh	1.51 (d, 3H, CH_3^a), 1.55 (d, 3H, CH_3^d), 2.40 (s, 3H, CH_3) 4.15 (qd, 1H, CH^b), 4.33 (qd, 1H, CH^c),	7.22-7.24 (d, 2H, arom) 7.83-7.87 (d, 2H, arom) J_{ab} = 7.2 Hz, J_{bc} = 2.6 Hz J_{cd} = 6.7 Hz
		**7dg$_{er}$**	39-40	1687	1.43 (d, 3H, CH_3^a), 1.64 (d, 3H, CH_3^d), 2.42 (s, 1H, CH_3), 3.27 (qd, 1H, CH^b), 4.31 (qd, 1H, CH^c)	7.22-7.24 (d, 2H, arom) 7.83-7.87 (d, 2H, arom) J_{ab} = 7.1 Hz, J_{bc} = 3.3 Hz J_{cd} = 6.7 Hz

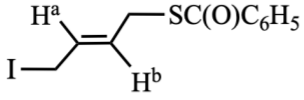
[a]KBr. [b]270 MHz, $CDCl_3$, internal standard: Me_4Si

Table S15 Spectral data of adducts of RC(O)SI **1** to alkenes and alkynes

alkene **4** / alkyne **5**	adducts	compd. no.	m.p. / °C	i.r. / cm^{-1} [a] νC=O	^{1}H NMR[b] δ /ppm
trans-2-butene (**4g**$_E$)		**6ag$_{th}$**	oil	1651	1.50 (d, 3H, CH_3^a), 7.42-7.60 (m, 3H, arom) 1.63 (d, 3H, CH_3^d), 7.94-7.98 (m, 2H, arom) 4.04 (qd, 1H, CH^b), J_{ab} = 7.1 Hz, J_{bc} = 4.0 Hz, 4.34 (qd, 1H, CH^c), J_{cd} = 6.7 Hz
		**7ag$_{er}$**	oil	1648	1.47 (d, 3H, CH_3^a), 7.42-7.60 (m, 3H, arom) 1.66 (d, 3H, CH_3^d), 7.94-7.98 (m, 2H, arom) 3.10 (qd, 1H, CH^b), J_{ab} = 6.6 Hz, J_{bc} = 5.4 Hz, 4.28 (qd, 1H, CH^c), J_{cd} = 6.6 Hz
trans-2-butene (**4g**$_E$)		**6dg$_{th}$**	oil	1664sh	1.51 (d, 3H, CH_3^a), 7.40-7.43 (m, 3H, arom) 1.55 (d, 3H, CH_3^d), 7.83-7.87 (m, 2H, arom) 2.40 (s, 3H, CH_3) J_{ab} = 7.2 Hz, J_{bc} = 2.6 Hz, 4.15 (qd, 1H, CH^b), J_{cd} = 6.7 Hz 4.33 (qd, 1H, CH^c),
		**7dg$_{er}$**	39-40	1687	1.46 (d, 3H, CH_3^a), 7.42-7.60 (m, 3H, arom) 1.66 (d, 3H, CH_3^d), 7.94-7.98 (m, 2H, arom) 2.43 (s, 1H, CH_3), J_{ab} = 7.0 Hz, J_{bc} = 5.1 Hz, 3.07 (qd, 1H, CH^b), J_{cd} = 6.7 Hz 4.27 (qd, 1H, CH^c)

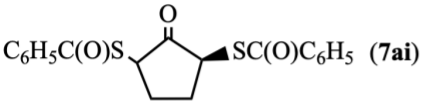
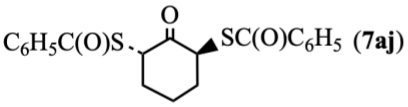
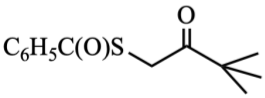
[a]KBr. [b]270 MHz, $CDCl_3$, internal standard: Me_4Si.

Table S16 Spectral data of adducts of RC(O)SI **1** to alkenes and alkynes

alkene **4** / alkyne **5**	adducts	compd no.	m.p. / °C	i.r. / cm^{-1} [a] νC=O	^{1}H NMR[b] δ / ppm
1,3-butadiene (**4h**)		**6ah**[c]	oil	1658	3.70 (d, 7.2 Hz, 2H, CH_2), 3.86 (d, 7.3 Hz, 2H, CH_2), 5.77 (dt, 7.3 Hz, 15 Hz, 1H, CH^a), 6.01 (dt, 7.2 Hz, 15 Hz, 1H, CH^b), 7.42-7.60 (m, 3H, arom), 7.79-7.93 (m, 2H, arom), J_{ab} = 15 Hz

[a]KBr. [b]270 MHz, $CDCl_3$, internal standard: Me_4Si. [c]Markovnikov adduct.

Table S17 Specral data of addition products **6a** and **7a** of benzoylsulfenyl iodides **1** to enamines

addition products **6a**, **7a**	m.p. / °C	i.r.[a] / cm^{-1} νC=O	^{1}H NMR[b] δ / ppm
 (**6ai**)	oil	1658 1744	1.72-2.80 (m, 6H, C*H*$_2$), 3.72-4.11 (m, 1H, C*H*), 7.21-8.12 (m, 5H, arom)
 (**7ai**)	oil	1654 1753	1.90-2.93 (m, 4H, C*H*$_2$), 4.03-4.52 (m, 2H, C*H*), 7.10-8.02 (m, 10H, arom)
 (**6aj**)	oil	1659 1715	1.43-2.92 (m, 8H, C*H*$_2$), 4.33-4.82 (m, 1H, C*H*), 7.20-8.22 (m, 5H, arom)
 (**7aj**)	164-166	1666 1731	1.61-2.83 (m, 6H, C*H*$_2$), 4.64-5.12 (m, 2H, C*H*), 7.31-8.30 (m, 10H, arom)
 (**6al**)	oil	1661 1711	1.27 (s, 9H, C*H*$_3$), 4.14 (s, 2H, C*H*$_2$), 7.20-8.07 (m, 5H, arom)
 (**6ak**)	oil	1659 1729	1.55 (s, 6H, C*H*$_3$), 7.30-8.27 (m, 5H, arom), 9.70 (s, 1H, C*H*O)

[a]KBr. [b]90 MHz, $CDCl_3$, internal standard: Me_4Si. [c]270 MHz, $CDCl_3$, internal standard: Me_4Si.

Table S18 Preparation of *O*-alkyl acylsulfenates **8** by the use of acylsulfenyl iodides **1**

entry	RC(O)SI **1** R	alcohole and its sodium or ammonium salt[a]	solvent	reaction conditions		*O*-alkyl/aryl acylsulfenates **8**	yields[b] / %
				temp./ °C	time/ min		
1	C_6H_5 (**1a**)	NaOMe	CH_3OH	-68	30	$C_6H_5C(O)SOMe$ (**8aa**)	43
2	C_6H_5	Et_3HN^+ ^-OMe	CH_3OH	-68	30	$C_6H_5C(O)SOMe$ (**8aa**)	36
3	C_6H_5	$NaOCH_2Ph$	$PhCH_2OH/Et_2O$	-15– -10	25	$C_6H_5C(O)SOCH_2Ph$ (**8ab**)	61
4	C_6H_5	Et_3HN^+ $^-OCH_2Ph$	$CHCl_3$	15	30	$C_6H_5C(O)SOCH_2Ph$ (**8ab**)	53
5	C_6H_5	NaOEt	EtOH	20	15	$C_6H_5C(O)SOEt$(**8ac**)	63
6	C_6H_5	$HOCH_2CH_2OH$	EtOH	24	15	$[C_6H_5C(O)SOCH_2]_2$ (**8ad**)	65
7	C_6H_5	NaOPr-*n*	*n*-PrOH	20	15	$C_6H_5C(O)SOPr$-*n* (**8ae**)	72
8	C_6H_5	NaOPr-*i*	*i*-PrOH	18	15	$C_6H_5C(O)SOPr$ -*i* (**8af**)	76
9	4-MeC_6H_4 (**1d**)	NaOMe	CH_3OH	18	15	4-$MeC_6H_4C(O)SOMe$ (**8da**)	53
10	4-MeC_6H_4	NaOMe	$CHCl_3/CH_3OH$ (2:1)	24	60	4-$MeC_6H_4C(O)SOMe$ (**8da**)	42
11	4-MeC_6H_4	NaOEt	EtOH	23	15	4-$MeC_6H_4C(O)SOEt$ (**8db**)	77
12	4-$MeOC_6H_4$ (**1f**)	NaOMe	CH_3OH	20	15	4-$MeOC_6H_4C(O)SOMe$ (**8fa**)	66
13	4-ClC_6H_4 (**1i**)	NaOMe	CH_3OH	20	15	4-$ClC_6H_4C(O)SOMe$ (**8ia**)	57
14	4-ClC_6H_4	Et_3HN^+ ^-OMe	CH_3OH	20	30	4-$ClC_6H_4C(O)SOMe$ (**8ia**)	48
15	4-ClC_6H_4	NaOEt	EtOH	20	15	4-$ClC_6H_4C(O)SOEt$ (**8ib**)	63
16	4-ClC_6H_4	Et_3HN^+ ^-OEt	EtOH	20	30	4-$ClC_6H_4C(O)SOEt$ (**8ib**)	56

[a]RCOSI/alcohole or its sodium or ammonium salt (1:1). [b]Isolated yields.

Table S19 Spectral data of *O*-alkyl acylsulfenates **8**

RC(O)SOR' **8**	m.p./ ˚C	i.r.[a]/ cm^{-1} νC=O	^{1}H NMR[b] δ/ ppm	^{13}C NMR[c] δ/ ppm
$C_6H_5C(O)SOMe$ (**8aa**)	oil	1679	3.91 (s, 3H, O*C*H_3), 7.21-8.20 (m, 5H, arom)	184.2 (*C*=O), 52.4 (O*C*H_3), 128.2 -130.3 (arom)
$C_6H_5C(O)SOCH_2Ph$ (**8ab**)	oil	1668	4.12 (s, 2H, CH_2), 7.18-8.11 (m, 10H, arom)	185.2 (*C*=O), 84.9 (*C*H_2), 128.2-131.2 (arom)
$C_6H_5C(O)SOEt$ (**8ac**)	oil	1677	1.36 (t, 7.8 Hz, 3H, CH_3), 4.02 (q, 7.8 Hz, 2H, CH_2), 7.2-8.1 (m, 5H, arom)	184.5 (*C*=O), 84.2 (*C*H_2), 20.2 (CH_3), 128.5-130.6 (arom)
$[C_6H_5C(O)SOCH_2]_2$ (**8ad**)	oil	1678	3.92 (s, 4H, CH_2), 7.2-8.1 (m, 10H, arom)	184.3 (*C*=O), 84.5 (*C*H_2), 128.8-130.8 (arom)
$C_6H_5C(O)SOPr$-*n* (**8ae**)	oil	1681	0.99 (t, *J* = 7.6 Hz, 3H, CH_3); 1.79 (sept, *J* = 7.8 Hz, 2H, CH_2); 4.29 (t, *J* = 7.8 Hz, 2H, O*C*H_2); 7.21–8.12 (m, 5H, arom)	185.1 (*C*=O), 84.5 (*C*H_2), 64.2 (*C*H_2), 20.2 (CH_3), 128.8-130.8(arom)
$C_6H_5C(O)SOPr$ -*iso* (**8af**)	oil	1677	1.38 (d, *J* = 7.7 Hz, 6H, CH_3), 4.01(sep, *J* = 7.7 Hz, 1H, O*C*H), 7.20–7.92 (m, 5H, arom)	185.2 (*C*=O), 84.2 (*C*H), 20.2 (*C*H_3), 128.4-130.6 (arom)
$C_6H_5C(O)SOBu$-*n* (**8ag**)	oil	1678	0.7-2.0 (m, 7H, C_3H_7), 3.98 (t, 7.6 Hz, 2H, O*C*H_2), 7.2-7.8 (m, 5H, arom)	184.8 (*C*=O), 85.2 (*C*H_2), 20.5 (*C*H_2), 20.2 (*C*H_2), 16.8 (*C*H_3), 128.4-130.8 (arom)
$C_6H_5C(O)SOBu$-*iso* (**8ah**)	oil	1675	1.32 (t, 7.7 Hz, 3H, CH_3), 1.78 (m, 4H, CH_2), 4.01 (m, 2H, CH_2), 7.2-7.9 (m, 5H, arom)	185.3 (*C*=O), 86.2 (*C*H), 34.1 (*C*H_2), 20.2 (*C*H_3), 16.4 (*C*H_3), 128.8-130.8
$C_6H_5C(O)SOBu$-*tert* (**8ai**)	oil	1658	4.33 (s, 9H, CH_3), 7.2-7.9 (m, 5H, arom)	184.9 (*C*=O), 93.3 (*C*), 29.6 (*C*H_3), 128.4-130.8 (arom)

[a]Neat (KBr). [b]90 MHz, $CDCl_3$; internal standard: Me_4Si. [c]270 MHz, $CDCl_3$; internal standard: Me_4Si.

Table S20 Spectral data of *O*-alkyl acylsulfenates **8** (continued 1)

RC(O)SOR' **8**	m.p. / °C	ir[a] /cm^{-1} ν C=O	^{1}H NMR[b] δ/ ppm	^{13}C NMR[c] δ/ ppm
4-MeC_6H_4C(O)SOMe (**8da**)	oil	1665, 1670	2.35 (s, 3H, CH_3), 4.36 (s, 3H, OCH_3), 7.01-8.01 (m, 4H, arom)	184.2 (*C*=O), 52.4 (OCH_3), 21.4 (*C*H_3Ar), 128.2-130.3 (arom)
4-MeC_6H_4C(O)SOEt (**8db**)	oil	1673	1.36 (t, 7.9 Hz, 3H, CH_3), 2.35 (s, 3H, CH_3), 4.02 (q, 7.9 Hz, 2H, CH_2), 7.20-8.09 (m, 4H, arom)	184.5 (*C*=O), 84.2 (OCH_2), 21.6 (*C*H_3Ar), 20.2 (*C*H_3), 128.5-130.6 (arom)
4-MeC_6H_4C(O)SOPr-*n* (**8dc**)	oil	1673	1.00 (t, 7.9 Hz, 3H, CH_3), 1.74 (sex, 7.8 Hz, 2H, CH_2), 2.39 (s, 3H, CH_3Ar), 3.92 (t, 7.9 Hz, 2H, OCH_2), 7.21-7.97 (m, 4H, arom)	185.1 (*C*=O), 84.5 (OCH_2), 64.1 (*C*H_2), 21.8 (*C*H_3Ar), 20.2 (*C*H_3), 128.8-130.8 (arom)
4-MeC_6H_4C(O)SOPr-*iso* (**8dd**)	oil	1677	1.37 (d, 7.8 Hz, 6H, CH_3), 2.39 (s, 3H, CH_3), 4.02 (sept, 7.8 Hz, 1H, C*H*), 7.03-7.84 (m, 4H, arom)	185.2 (*C*=O), 84.2 (*C*H), 21.6 (*C*H_3Ar), 20.2 (*C*H_3), 128.4-130.6 (arom)
4-MeC_6H_4C(O)SOBu-*n* (**8de**)	oil	1676	0.81-2.02 (m, 7H, C_3H_7), 2.39 (s, 3H, CH_3), 3.82 (sex, 7.8 Hz, 2H, OCH_2), 7.0-7.8 (m, 4H, arom)	184.8 (*C*=O), 85.2 (OCH_2), 21.3 (*C*H_3Ar), 20.5 (*C*H_2), 16.8 (*C*H_3), 128.5-130.7 (arom)
4-MeC_6H_4C(O)SOBu-*iso* (**8df**)	oil	1571	0.81-2.11 (m, 8H, C_3H_7), 2.39 (s, 3H, CH_3), 3.98 (d, 7.7 Hz, 2H, OCH_2), 7.2-7.8 (m, 4H, arom)	185.3 (*C*=O), 86.2 (*C*H), 34.1(*C*H_2), 21.4 (*C*H_3Ar), 20.2(*C*H_3), 16.4 (*C*H_3), 128.8-130.8 (arom)
2-$CH_3OC_6H_4$C(O)SOMe (**8ea**)	oil	1672	3.81 (s, 3H, CH_3), 3.82 (s, 3H, CH_3OAr), 7.22-8.09 (m, 4H, arom)	184.9 (*C*=O), 56.4 (*C*H_3OAr), 52.6 (*C*H_3O), 128.4-132.4 (arom)
4-$CH_3OC_6H_4$C(O)SOMe (**8fa**)	oil	1645	3.85 (s, 3H, CH_3), 3.89 (s, 3H, CH_3), 7.20-7.89 (m, 4H, arom)	184.4 (*C*=O), 56.4 (*C*H_3OAr), 54.3 (*C*H_3O), 128.3-132.3 (arom)
4-ClC_6H_4C(O)SOMe (**8ia**)	oil	1668, 1676	3.84 (s, 3H, CH_3), 7.2-7.8 (m, 4H, arom)	185.6 (*C*=O), 54.2 (*C*H_3O), 128.3-132.3 (arom)
4-ClC_6H_4C(O)SOEt (**8ib**)	oil	1674	1.36 (t, 7.9 Hz, 3H, CH_3), 4.02 (q, 7.9 Hz, 2H, CH_2), 7.2-8.1 (m, 4H, arom)	184.5 (*C*=O), 84.2 (OCH_2), 20.2 (*C*H_3), 128.5-130.6 (arom)

[a]Neat (KBr). [b]90 MHz, $CDCl_3$; internal standard: Me_4Si. [c]270 MHz, $CDCl_3$; internal standard: Me_4Si.

Table S21 Reaction conditions and acylsulfenyl iodides **1** with thiols or its sodium or piperidinium salts and yields of acyl aralkyl disulfides **9**

entry	RC(O)SI **1** R	R'SH, NaSR' or $\overset{+}{N}H_2$ $^{-}$SR'[a]	solvent	reaction conditions[b] temp./ °C, time/ min		RC(O)SSR' **9**	yields[c] / %
1	C_6H_5 (**1a**)	NaSEt	CH_2Cl_2/EtOH	0/20	r.t./15	C_6H_5C(O)SSEt (**9aa**)	63
2	C_6H_5	$HSCH_2CH_2O$	$CHCl_3$	0/20	r.t./15	C_6H_5C(O)SSCH_2CH_2OH (**9ab**)	56
						C_6H_5C(O)SSCH_2CH_2OSC(O)C_6H_5 (**9ac**)	21
3	C_6H_5	NaSPr-*iso*	$CHCl_3$/EtOH	0/20	r.t./15	C_6H_5C(O)SSPr-*iso* (**9ad**)	51
4	C_6H_5	NaSBu-*n*	$CHCl_3$/EtOH	0/20	r.t./15	C_6H_5C(O)SSBu-*n* (**9ae**)	54
5	C_6H_5	PhSH	$CHCl_3$/EtOH	0/20	r.t./15	C_6H_5C(O)SSPh (**9af**)	49
6	C_6H_5	NaSPh	$CHCl_3$	0/20	r.t./15	C_6H_5C(O)SSPh (**9af**)	72
7	4-MeC_6H_4 (**1d**)	$\overset{+}{N}H$ $^{-}$SPh	$CHCl_3$/EtOH	0/20	r.t./15	4-MeC_6H_4C(O)SSPh (**9df**)	55
8	4-MeOC_6H_4 (**1f**)	PhSH	$CHCl_3$	0/20	r.t./15	4-MeOC_6H_4C(O)SSPh (**9ff**)	70
9	4-MeOC_6H_4	NaSEt	$CHCl_3$ /EtOH	0/20	r.t./15	4-MeOC_6H_4C(O)SSEt (**9fa**)	52
10	4-MeOC_6H_4	NaSBu-*n*	CH_2Cl_2/EtOH	0/20	r.t./15	4-MeOC_6H_4C(O)SSBu-*n* (**9fe**)	66
11	4-MeOC_6H_4	PhSH	CH_2Cl_2/EtOH	0/20	r.t./15	4-MeOC_6H_4C(O)SSPh (**9ff**)	63
12	4-MeOC_6H_4	4-MeC_6H_4SH	$CHCl_3$	0/20	r.t./15	4-MeOC_6H_4C(O)SSC_6H_4Me-4 (**9fg**)	73
13	4-MeOC_6H_4	4-ClC_6H_4SH	$CHCl_3$	0/20	r.t./15	4-MeOC_6H_4C(O)SSC_6H_4Cl-4 (**9fh**)	71
14	4-ClC_6H_4 (**1i**)	NaSEt	CH_2Cl_2/EtOH	0/20	r.t./15	4-ClC_6H_4C(O)SSSEt (**9ia**)	74
15	4-ClC_6H_4	PhSH	$CHCl_3$	0/20	r.t./15	4-ClC_6H_4C(O)SSPh (**9if**)	46

[a]RCOSI/thiol or sodium or ammonium sallt (1:1). [b]At 0 °C for 20 min and then at 15–24 °C) for 15 min. [c]Isolated yield.

Table S22 Physical properties and spectral data of acyl alkyl/aryl disulfides **9**

RC(O)SSR' **9**	m.p./ °C	i.r./cm^{-1} [a] ν C=O	^{1}H NMR[b] δ/ ppm	^{13}C NMR[c] δ/ ppm
$C_6H_5C(O)SSEt$ (**9aa**)	oil	1680	1.30 (t, 7.6 Hz, 3H, CH_3), 2.82 (q, 7.6 Hz, 2H, CH_2), 7.20-8.12 (m, 5H, arom)	185.2 (*C*=O), 36.2 (*C*H$_2$), 16.3 (*C*H$_3$), 127.7-132.3 (arom)
$C_6H_5C(O)SSCH_2CH_2OH$ (**9ab**)	oil	1688	3.37 (t, 7.7 Hz, 2H, OCH_2), 3.67 (t, 7.7 Hz, 2H, SCH_2), 4.8-5.1 (br. s, 1H, OH), 7.23-8.12 (m, 5H, arom)	185.1 (*C*=O), 54.3 (S*C*H$_2$) 40.0 (O*C*H$_2$), 128.3-131.4 (arom)
$C_6H_5C(O)SSPr$-*iso* (**9ad**)	oil	1687	1.29 (d, 7.7 Hz, 6H, CH_3), 3.11 (sept, 7.7 Hz, 1H, C*H*), 7.20-8,11 (m, 5H, arom)	184.9 (*C*=O), 22.3 (*C*H$_3$), 54.2 (*C*H), 127.8-132.3 (arom)
$C_6H_5C(O)SSBu$-*n* (**9ae**)	oil	1686	0.71-2.00 (m, 7H, C_3H_7), 2.80 (t, 7.8 Hz, 2H, SCH_2), 7.31-8.22 (m, 5H, arom)	185.1 (*C*=O), 40.3 (S*C*H$_2$), 32.2 (*C*H$_2$), 30.1 (*C*H$_2$), 16.3 (*C*H$_3$), 128.8-131.9 (arom)
$C_6H_5C(O)SSPh$ (**9af**)	51-53 (53)[c]	1688	6.32-7.88 (m, 10H, arom)	184.1 (*C*=O), 127.8-131.1 (arom)
4-$MeC_6H_4C(O)SSPh$ (**9df**)	63	1689	3.68 (s, 3H, CH_3), 7.32-7.88 (m, 9H, arom)	184.7 (*C*=O), 21.7 (*C*H$_3$), 128.2-131.4 (arom)
4-$MeOC_6H_4C(O)SSEt$ (**9fa**)	oil	1670	1.30 (t, 7.8 Hz, 3H, CH_3), 2.82 (q, 7.8 Hz, 2H, CH_2), 3.87 (s, 3H, OCH_3), 6.82-8.12 (m, 4H, arom)	189.2 (*C*=O), 55.6 (*C*H$_3$OAr), 35.6 (*C*H$_2$), 16.4 (*C*H$_3$), 128.5-132.4 (arom)
4-$MeOC_6H_4C(O)SSBu$-*n* (**9fe**)	oil	1686	0.70-1.82 (m, 7H, C_3H_7), 2.76(t, 7.8 Hz, 2H, SCH_2), 3.88 (s, 3H, ArOCH_3), 6.82-8.12 (m, 4H, arom)	188.2 (*C*=O), 55.6 (*C*H$_3$OAr), 40.6 (*C*H$_2$), 32.6 (*C*H$_2$), 16.4 (*C*H$_3$), 127.9-131.6 (arom)
4-$MeOC_6H_4C(O)SSPh$ (**9ff**)	54-56	1674	3.86 (s, 3H, ArOCH_3), 6.82-8.12 (m, 9H, arom)	188.3 (*C*=O), 55.5 (*C*H$_3$OAr), 127.9-131.6 (arom)
4-$MeOC_6H_4C(O)SSC_6H_4Me$-4 (**9fg**)	58-61	1685	3.67 (t, 7.9 Hz, 3H, ArCH_3), 3.87 (s, 3H, ArOCH_3), 6.80-8.12 (m, 8H, arom)	188.4 (*C*=O), 56.6 (*C*H$_3$OAr), 21.7 (*C*H$_3$Ar), 128.1-131.6 (arom)
4-$MeOC_6H_4C(O)SSC_6H_4Cl$-4 (**9fh**)	67-70	1690, 1689	3.87 (s, 3H, ArOCH_3), 6.83-8.12 (m, 8H, arom)	188.4 (*C*=O), 56.6 (*C*H$_3$OAr), 128.3-130.5 (arom)
4-$ClC_6H_4C(O)SSEt$ (**9ia**)	oil	1688, 1690	1.30 (t, 7.8 Hz, 3H, CH_3), 2.82 (q, 7.8 Hz, 2H, CH_2), 6.83-8.11 (m, 4H, arom)	190.4 (*C*=O), 37.2 (*C*H$_2$), 16.9 (*C*H$_3$), 128.1-140.3 (arom)
4-$ClC_6H_4C(O)SSPh$ (**9if**)	78-81	1688	6.83-8.12 (m, 9H, arom)	190.4 (*C*=O), 128.1-140.3 (arom)

[a]Neat (KBr). [b]90 MHz, $CDCl_3$; internal standard: Me_4Si. [c]270 MHz, $CDCl_3$; internal standard: Me_4Si.

Table S23 Yields of unsymmetrical diacyl disulfides **10**

entry	RC(O)SI **1** R	R'COSH, KSC(O)R' or $\overset{+}{N}H_2^-SC(O)R'$	solvent	reaction conditions[a] temp./ °C	time/ min	RC(O)SSC(O)R' **10**	yields[b] / %
1	C_6H_5 (**1a**)	$KSC(O)C_6H_4Me$-4	$CHCl_3$/MeOH	-15–0	30	$C_6H_5C(O)SSC(O)C_6H_4Me$-4 (**10aa**)	66
2	C_6H_5	$\overset{+}{N}H\ ^-SC(O)C_6H_4Me$-4	$CHCl_3$/MeOH	-15–0	30	$C_6H_5C(O)SSC(O)C_6H_4Me$-4 (**10aa**)	52
3	C_6H_5	4-MeC_6H_4COSH	$CHCl_3$	-15–0	30	$C_6H_5C(O)SSC(O)C_6H_4Me$-4 (**10aa**)	58
4	C_6H_5	$KSC(O)C_6H_4Me$-4	$CHCl_3$/MeOH	-15–0	30	$C_6H_5C(O)SSC(O)C_6H_4Me$-4 (**10aa**)	64
5	C_6H_5	$\overset{+}{N}H\ ^-SC(O)C_6H_4OMe$-4	$CHCl_3$/MeOH	-15–0	30	$C_6H_5C(O)SSC(O)C_6H_4OMe$-4 (**10ab**)	49
6	C_6H_5	4-$MeOC_6H_4COSH$	$CHCl_3$	-15–0	30	$C_6H_5C(O)SSC(O)C_6H_4OMe$-4 (**10ab**)	53
7	C_6H_5	$KSC(O)C_6H_4Cl$-4	$CHCl_3$/MeOH	-15–0	30	$C_6H_5C(O)SSC(O)C_6H_4Cl$-4 (**10ac**)	44
8	C_6H_5	$\overset{+}{N}H\ ^-SC(O)C_6H_4Cl$-4	$CHCl_3$/MeOH	-15–0	30	$C_6H_5C(O)SSC(O)C_6H_4Cl$-4 (**10ac**)	57
9	C_6H_5	4-ClC_6H_4COSH	$CHCl_3$	-15–0	30	$C_6H_5C(O)SSC(O)C_6H_4Cl$-4 (**10ac**)	39
10	4-MeC_6H_4 (**1d**)	$KSC(O)C_6H_5$	$CHCl_3$/MeOH	-15–0	30	4-$MeC_6H_4C(O)SSC(O)C_6H_5$ (**10da**)	32
11	4-MeC_6H_4	C_6H_5COSH	$CHCl_3$	-15–0	30	4-$MeC_6H_4C(O)SSC(O)C_6H_5$ (**10da**)	42
12	4-MeC_6H_4	$KSC(O)C_6H_4OMe$-4	$CHCl_3$/MeOH	-15–0	30	4-$MeC_6H_4C(O)SSC(O)C_6H_4OMe$-4 (**10db**)	59
13	4-$MeOC_6H_4$ (**1f**)	4-MeC_6H_4 COSH	$CHCl_3$	-15–0	30	4-$MeOC_6H_4C(O)SSC(O)C_6H_4Me$-4 (**10fa**)	51
14	4-$MeOC_6H_4$	$KSC(O)C_6H_4Cl$-4	$CHCl_3$/MeOH	-15–0	30	4-$MeOC_6H_4C(O)SSC(O)C_6H_4Cl$-4 (**10fb**)	65
15	4-$MeOC_6H_4$	4-ClC_6H_4COSH	$CHCl_3$	-15–0	30	4-$MeOC_6H_4C(O)SSC(O)C_6H_4Cl$-4 (**10fb**)	55

[a]RCOSI/R'COSH or its potassium or piperidinium salts (1:1). [b]Isolated yields.

Table S24 Spectral data of unsymmetrical diacyl disulfides **10**

RC(O)SSC(O)R' **10**	m.p. / °C	i.r./ cm^{-1} [a] ν C=O	^{1}H NMR[b] δ/ ppm	^{13}C NMR[c] δ/ ppm
$C_6H_5C(O)SSC(O)C_6H_4Me$-4 (**10aa**)	90-92 (89-90.5)	1687,1705	2.38 (s, 3H, CH_3), 7.21-7.88 (m, 5H, arom) 7.49-7.98 (m, 4H, arom)	190.2 (*C*=O), 186.5 (*C*=O), 22.4 (CH_3Ar), 127.2-130.8 (arom)
$C_6H_5C(O)SSC(O)C_6H_4OMe$-4 (**10ab**)	95-98	1689,1702	3.88 (s, 3H, CH_3O), 6.82-8.46 (m, 5H, arom) 7.10-8.55 (m, 4H, arom)	199.2 (*C*=O), 185.7 (*C*=O), 54.6 (CH_3OAr), 127.2-131.8 (arom)
$C_6H_5C(O)SSC(O)C_6H_4Cl$-4 (**10ac**)	88-90 (89-91)	1682,1690	6.82-8.46 (m, 5H, arom) 7.30-8.35 (m, 4H, arom)	199.7 (*C*=O), 187.7 (*C*=O) 128.1-131.8 (arom)
4-$MeC_6H_4C(O)SSC(O)C_6H_4OMe$-4 (**10db**)	100-102	1671,1702	2.38 (s, 3H, CH_3), 3.87 (s, 3H, CH_3O), 7.21-8.65 (m, 4H, arom), 7.12-8.42 (m, 4H, arom)	199.5 (*C*=O), 187.3 (*C*=O), 58.4 (CH_3OAr), 22.6 (CH_3Ar), 127.5-133.6 (arom)
4-$MeOC_6H_4C(O)SSC(O)C_6H_4Cl$-4 (**10fb**)	90-92 (88-90)	1673,1692	3.87 (s, 3H, CH_3O), 7.12-8.46 (m, 4H, arom) 7.23-8.47 (m, 4H, arom)	199.4 (*C*=O), 185.6 (*C*=O), 59.7 (CH_3OAr) 128.5-132.7 (arom)

[a]KBr. [b]90 MHz, $CDCl_3$; internal standard: Me_4Si. [c]270 MHz, $CDCl_3$; internal standard: Me_4Si.

Table S25 Reaction conditions and acylsulfenyl iodides **1** with selenols, sodium selenolates and diaryl diselenides and yields of *Se*-aryl aryloxomethanesulfenoselenoates **11**

entry	RC(O)SI **1** R	NaSeR' or $(R'Se)_2$	solvent	reaction conditions temp./ °C[a]	time/ min[b]	RC(O)SSeR' **11**	yields[c] / %
1	C_6H_5 (**1a**)	NaSePh	$MeOH/CHCl_3$	-15–0	r.t./15	$C_6H_5C(O)SSePh$ (**11aa**)	58
2	C_6H_5	$(PhSe)_2$	$CHCl_3$	-15–0	r.t./15	$C_6H_5C(O)SSePh$ (**11aa**)	36
3	C_6H_5	$NaSeC_6H_4Me$-4	$MeOH/CHCl_3$	-15–0	r.t./15	$C_6H_5C(O)SSeC_6H_4Me$-4 (**11ab**)	53
4	C_6H_5	$(4\text{-}MeC_6H_4Se)_2$	$CHCl_3$	-15–0	r.t./15	$C_6H_5C(O)SSeC_6H_4Me$-4 (**11ab**)	23
5	4-MeC_6H_4 (**1d**)	NaSePh	$MeOH/CHCl_3$	-15–0	r.t./15	4-$MeC_6H_4C(O)SSePh$ (**11da**)	62
6	4-MeC_6H_4	$(PhSe)_2$	$CHCl_3$	-15–0	r.t./15	4-$MeC_6H_4C(O)SSePh$ (**11da**)	72
7	4-$MeOC_6H_4$ (**1f**)	NaSePh	$MeOH/CHCl_3$	-15–0	r.t./15	4-$MeOC_6H_4C(O)SSePh$ (**11fa**)	55
8	4-$MeOC_6H_4$	$(PhSe)_2$	$CHCl_3$	-15–0	r.t./15	4-$MeOC_6H_4C(O)SSePh$ (**11fa**)	76
9	4-$MeOC_6H_4$	$NaSeC_6H_4Me$-4	$MeOH/CHCl_3$	-15–0	r.t./15	4-$MeOC_6H_4C(O)SSeC_6H_4Me$-4 (**11fb**)	75
10	4-$MeOC_6H_4$	$(4\text{-}MeC_6H_4Se)_2$	$CHCl_3$	-15–0	r.t./15	4-$MeOC_6H_4C(O)SSeC_6H_4Me$-4 (**11fb**)	66
11	4-ClC_6H_4 (**1i**)	NaSePh	$MeOH/CHCl_3$	-15–0	r.t./15	4-$ClC_6H_4C(O)SSePh$ (**11ia**)	67
12	4-ClC_6H_4	$(PhSe)_2$	$CHCl_3$	-15–0	r.t./15	4-$ClC_6H_4C(O)SSSePh$ (**11ia**)	38
13	4-ClC_6H_4	$NaSeC_6H_4Me$-4	$MeOH/CHCl_3$	-15–0	r.t./15	4-$ClC_6H_4C(O)SSeC_6H_4Me$-4 (**11ib**)	52
14	4-ClC_6H_4	$(4\text{-}MeC_6H_4Se)_2$	$CHCl_3$	-15–0	r.t./15	4-$ClC_6H_4C(O)SSeC_6H_4Me$-4 (**11ib**)	53

[a]At 0 °C for 15 min. [b]At 15–24 °C for 15 min. [c]Isolated yield.

Table S26 Spectral data of *Se*-aryl acyloxomethanesulfenoselenoates **11**

RC(O)SSeR' **11**	m.p. / °C	i.r./ cm^{-1} [a] νC=O	^{1}H NMR[b] δ/ ppm	^{13}C NMR[c] δ/ ppm	^{77}Se NMR[d] δ/ ppm
$C_6H_5C(O)SSePh$ (**11aa**)	35-37 (35-37)[27b]	1665	6.71-8.24 (m, 10H, arom)	186.9 (*C*=O), 127.8-131.2 (arom)	615.19
$C_6H_5C(O)SSeC_6H_4Me$-4 (**11ab**)	47-49 (46-48)[27c]	1680	2.23 (s, 3H, CH_3) 6.74-8.24 (m, 9H, arom)	186.7 (*C*=O), 21.4 (CH_3), 127.4-131.0 (arom)	606.22
4-$MeC_6H_4C(O)SSePh$ (**11da**)	92-94 (93-94)[10]	1690	2.24 (s, 3H, CH_3) 6.73-8.25 (m, 9H, arom)	186.6 (*C*=O), 20.45 (CH_3), 127-131.1 (arom)	616.62
4-$MeOC_6H_4C(O)SSePh$ (**11fa**)	61-63 (62-63)[27b,27c]	1682	3.47 (s, 3H, CH_3O) 6.54-8.32 (m, 9H, arom)	187.4 (*C*=O), 55.41 (CH_3O), 127.2-130.3 (arom)	617.43
4-$MeOC_6H_4C(O)SSeC_6H_4Me$-4 (**11fb**)	63-65 (60)[27a] (58-59)[27d]	1680	2.25 (s, 3H, CH_3) 3.48 (s, 3H, CH_3O) 6.36-8.66 (m, 8H, arom)	187.2 (*C*=O), 56.21 (CH_3O), 21.65 (CH_3), 128.1-132.2 (arom)	607.28
4-$ClC_6H_4C(O)SSePh$ (**11ia**)	91-92 (83.5-84.5)[27b] (90-91)[27c]	1664	6.72-8.87 (m, 9H. arom)	188.4 (*C*=O), 128.4-131.9 (arom)	654.83
4-$ClC_6H_4C(O)SSeC_6H_4Me$-4 (**11ib**)	85-87 (84-86)[27c]	1657	2.24 (s, 3H, CH_3) 6.45-8.66 (m, 8H, arom)	188.2 (*C*=O), 22.07(CH_3), 128.4-131.9 (arom)	611.98

[a]KBr. [b]90 MHz, $CDCl_3$; internal standard: Me_4Si. [c]270 MHz, $CDCl_3$; internal standard: Me_4Si. [d]External standard: Me_2Se.

Table S27 Preparation conditions of *Te*-aryl acyloxomethanesulfenotelluroates **12**

entry	RC(O)SI **1** R	NaTeR' or $(R'Te)_2$	solvent	reaction conditions temp./ °C[a]	time/ min[b]	RC(O)STeR' **12**	yields[c] / %
1	C_6H_5 (**1a**)	NaTePh	$CHCl_3$	0/20	r.t./15	$C_6H_5C(O)STePh$ (**12aa**)	68
2	C_6H_5	$(PhTe)_2$	$MeOHCHCl_3$	0/20	r.t./15	$C_6H_5C(O)STePh$ (**12aa**)	28
3	C_6H_5	$NaTeC_6H_4Me$-4	$CHCl_3$	0/20	r.t./15	$C_6H_5C(O)STeC_6H_4Me$-4 (**12ab**)	63
4	C_6H_5	$(4\text{-}MeC_6H_4Te)_2$	$MeOHCHCl_3$	0/20	r.t./15	$C_6H_5C(O)STeC_6H_4Me$-4 (**12ab**)	22
5	4-MeC_6H_4 (**1d**)	NaTePh	$CHCl_3$	0/20	r.t./15	4-$MeC_6H_4C(O)STePh$ (**12da**)	62
6	4-MeC_6H_4	$(PhTe)_2$	$MeOHCHCl_3$	0/20	r.t./15	4-$MeC_6H_4C(O)STePh$ (**12da**)	35
7	4-$MeOC_6H_4$ (**1f**)	NaTePh	$CHCl_3$	0/20	r.t./15	4-$MeOC_6H_4C(O)STePh$ (**12fa**)	62
8	4-$MeOC_6H_4$	$(PhTe)_2$	$MeOHCHCl_3$	0/20	r.t./15	4-$MeOC_6H_4C(O)STePh$ (**12fa**)	43
9	4-$MeOC_6H_4$	$NaTeC_6H_4Me$-4	$CHCl_3$	0/20	r.t./15	4-$MeOC_6H_4C(O)STeC_6H_4Me$-4 (**12fb**)	67
10	4-$MeOC_6H_4$	$(4\text{-}MeC_6H_4Te)_2$	$MeOHCHCl_3$	0/20	r.t./15	4-$MeOC_6H_4C(O)STeC_6H_4Me$-4 (**12fb**)	55
11	4-ClC_6H_4 (**1i**)	NaTePh	$CHCl_3$	0/20	r.t./15	4-$ClC_6H_4C(O)STePh$ (**12ia**)	65
12	4-ClC_6H_4	$(PhTe)_2$	$MeOHCHCl_3$	0/20	r.t./15	4-$ClC_6H_4C(O)STePh$ (**12ia**)	46
13	4-ClC_6H_4	$NaTeC_6H_4Me$-4	$CHCl_3$	0/20	r.t./15	4-$ClC_6H_4C(O)STeC_6H_4Me$-4 (**12ib**)	55
14	4-ClC_6H_4	$(4\text{-}MeC_6H_4Te)_2$	$MeOHCHCl_3$	0/20	r.t./15	4-$ClC_6H_4C(O)STeC_6H_4Me$-4 (**12ib**)	34

[a]At 0 °C for 20 min. [b]At 15-24 °C for 15 min. [c]Isolated yield.

Table S28 Spectral data of *Te*-aryl acyloxomethanesulfenotelluroates **12**

RC(O)STeR' **12**	m.p. / ˚C	i.r./ cm^{-1} [a] νC=O	^{1}H NMR[b] δ / ppm	^{13}C NMR[c] δ / ppm	^{125}Te NMR[d] δ / ppm
$C_6H_5C(O)STePh$ (**12aa**)	66-68 (66)[27c]	1675	7.25-8.23 (m, 10H, arom)	188.46 (*C*=O) 127.7-131.2 (arom)	918.35
$C_6H_5C(O)STeC_6H_4Me$-4 (**12ab**)	99-100	1672	2.31 (s, 3H, CH_3) 6.98-8.16 (m, 9H, arom)	188.763 (*C*=O) 21.38 (CH_3) 127.8-131.2 (arom)	910.63
4-$MeC_6H_4C(O)STePh$ (**12da**)	110-112 (109-111)[27c]	1658	2.38 (s, 3H, CH_3) 7.11-8.91 (m, 9H, arom)	187.87 (*C*=O) 21.68 (CH_3) 127.6-130.6 (arom)	922.78
4-$MeOC_6H_4C(O)STePh$ (**12fa**)	91-93	1675	3.82 (s, 3H, CH_3O) 6.87-8.10 (m, 9H, arom)	201.44 (*C*=O) 56.21 (CH_3O) 127.0-130.9 (arom)	972.23
4-$MeOC_6H_4C(O)STeC_6H_4Me$-4 (**12fb**)	85-87	1655	2.37 (s, 3H, CH_3) 3.78 (s, 3H, CH_3O) 6.46-8.76 (m, 8H, arom)	200.93 (*C*=O) 55.68 (CH_3O) 21.12 (CH_3) 127.3-131.3 (arom)	968.98
4-$ClC_6H_4C(O)STePh$ (**12ia**)	115-117 (113-115)[27c]	1666	7.19-8.06 (m, 9H, arom)	187.54 (*C*=O) 128.7-132.3 (arom)	945.55
4-$ClC_6H_4C(O)STeC_6H_4Me$-4 (**12ib**)	135-136	1667	2.36 (s, 3H, CH_3) 6.95-8.11 (m, 8H, arom)	189.64 (*C*=O) 21.02 (CH_3) 128.4-131.9 (arom)	932.26

[a]KBr. [b]90 MHz, $CDCl_3$; internal standard: Me_4Si. [c]270 MHz, $CDCl_3$; internal standard: Me_4Si. [d]External standard: Me_2Te.

Table S29 Reaction conditions of acylsulfenyl iodides **1** with amines and yields of *S*-acylsulfenamides **13**

entry	RC(O)SI **1** R	amines	mole ratio **1** / amine	solvent	reaction conditions temp./ ˚C[a]	time/ min[b]	*S*-acylsulfenamides **13**	yields[c] / %
1	C_6H_5 (**1a**)	$PhCH_2NH_2$	1:1	Et_2O	0/15	r.t./20	$C_6H_5C(O)SNHCH_2Ph$ (**13aa**)	55
2	C_6H_5	Et_2NH	1:1	Et_2O	0/15	r.t./20	$C_6H_5C(O)SNEt_2$ (**13ab**)	43
3	C_6H_5	$H_2NCH_2CH_2SH$	1:1	Et_2O	0/15	r.t./20	$C_6H_5C(O)SNHCH_2CH_2SSC(O)C_6H_5$ (**13ac**)	41
4	C_6H_5	*n*-$PrNH_2$	1:1	Et_2O	0/15	r.t./20	$C_6H_5C(O)SNHPr$-*n* (**13ad**)	51
5	C_6H_5	(*i*-Pr)$_2$NH	1:1	Et_2O	0/15	r.t./20	$C_6H_5C(O)SN(Pr$-*i*$)_2$ (**13ae**)	61
6	C_6H_5	*n*-$BuNH_2$	1:1	Et_2O	0/15	r.t./20	$C_6H_5C(O)SNHBu$-*n* (**13af**)	71
7	C_6H_5	*t*-$BuNH_2$	1:1	Et_2O	0/15	r.t./20	$C_6H_5C(O)SNBu$-*t* (**13ag**)	12
8	C_6H_5		1:1	Et_2O	0/15	r.t./20	$C_6H_5C(O)OSN$  (**13ah**)	56
9	C_6H_5		1:1	Et_2O	0/15	r.t./20	$C_6H_5C(O)SN$  (**13ai**)	73
10	C_6H_5		1:1	Et_2O	0/15	r.t./20	$C_6H_5C(O)SN$  (**13aj**)	54
11	C_6H_5	$PhNH_2$	1:1	CH_2Cl_2	0/15	r.t./20	$C_6H_5C(O)SNHPh$ (**13ak**)	52
12	C_6H_5	Ph(Me)NH	1:1	CH_2Cl_2	0/15	r.t./20	$C_6H_5C(O)SN(Me)Ph$ (**13al**)	46
13	C_6H_5	4-$MeC_6H_4NH_2$	1:1	CH_2Cl_2	0/15	r.t./20	$C_6H_5C(O)SNC_6H_4Me$-4 (**13am**)	66
14	C_6H_5	4-$MeOC_6H_4NH_2$	1:1	CH_2Cl_2	0/15	r.t./20	$C_6H_5C(O)SNC_6H_4OMe$-4 (**13an**)	67

[a]At 0 ˚C for 15 min. [b]At 15–24 ˚C for 20 min. [c]Isolated yield.

Table S30 Reaction conditions of acylsulfenyl iodides **1** with amines and yields of *S*-acylsulfenamides **13** (continued 1)

entry	RC(O)SI **1** R	amines	mole ratio **1** / amine	solvent	reaction conditions temp./ ˚C[a]	time/ min[b]	*S*-acylsulfenamides **13**	yields[c] / %
15	4-MeC_6H_4 (**1d**)	$PhCH_2NH_2$	1:1	Et_2O	0/15	r.t./20	4-$CH_3C_6H_4C(O)SNHCH_2Ph$ (**13da**)	66
16	4-MeC_6H_4	*n*-$PrNH_2$	1:1	Et_2O	0/15	r.t./20	4-$CH_3C_6H_4C(O)SNHPr$-*n* (**13db**)	69
17	4-MeC_6H_4	(*n*-Pr)$_2$NH	1:1	Et_2O	0/15	r.t./20	4-$CH_3C_6H_4C(O)SN(Pr$-*n*$)_2$ (**13dc**)	56
18	4-MeC_6H_4		1:1	Et_2O	0/15	r.t./20	4-$MeC_6H_4C(O)SN$  (**13dd**)	39
19	4-MeC_6H_4		1:1	Et_2O	0/15	r.t./20	4-$MeC_6H_4C(O)SN$  (**13de**)	79
20	4-MeC_6H_4		1:1	Et_2O	0/15	r.t./20	4-$MeC_6H_4C(O)SN$  (**13df**)	73
21	4-MeC_6H_4	Ph(Me)NH	1:1	Et_2O	0/15	r.t./20	4-$MeC_6H_4C(O)SN(Me)Ph$ (**13dg**)	73
22	4-MeC_6H_4	(*i*-Pr)$_2$NH	1:1	CH_2Cl_2	0/15	r.t./20	4-$MeC_6H_4C(O)SN(Pr$-*i*$)_2$ (**13dh**)	39
23	4-MeC_6H_4	4-MeC_6H_4	1:1	CH_2Cl_2	0/15	r.t./20	4-$MeC_6H_4C(O)SNHC_6H_4$Me-4 (**13di**)	45
24	4-MeC_6H_4	4-ClC_6H_4	1:1	CH_2Cl_2	0/15	r.t./20	4-$MeC_6H_4C(O)SNHC_6H_4$Cl-4 (**13dj**)	61
25	2-$MeOC_6H_4$	$PhNH_2$	1:1	CH_2Cl_2	0/15	r.t./20	2-$MeOC_6H_4C(O)SNHPh$ (**13ea**)	59
26	4-$MeOC_6H_4$	$PhNH_2$	1:1	CH_2Cl_2	0/15	r.t./20	4-$MeOC_6H_4C(O)SNHPh$ (**13fa**)	47

[a]At 0 ˚C for 15 min. [b]At 15–24 ˚C for 20 min. [c]Isolated yield.

Table S31 Physical properties and spectral data of *S*-acylsulfenamides **13**

RC(O)SNR'R" **13**	m.p. / ˚C	i.r[a]/cm^{-1}. νC=O	^{1}H NMR[b] δ/ ppm	^{13}C NMR[c] δ/ ppm
$C_6H_5C(O)SNHCH_2Ph$ (**13aa**)	48-50	1659	3.21-3.52 (br. s, H, N*H*), 4.13 (s, 2H, CH_2), 7.10-8.06 (m, 10H, arom)	184.6 (*C*=O), 46.1 (N*C*H_2), 127.4-140.3 (arom)
$C_6H_5C(O)SNHEt$	oil	1660	0.95 (t, 7.8 Hz, 3H, CH_3), 2.73 (q, 7.8 Hz, 2H, CH_2), 2.8-3.4 (br, 1H, N*H*), 7.1-8,1 (m, 5H, arom)	184.2 (*C*=O), 45.5 (N*C*H_2), 15.5 *C*H_3), 126.4-130.2 (arom)
$[C_6H_5C(O)S]_2NEt$	39	1680	0.96 (t, 7.9 Hz, 3H, CH_3), 2.71-3.41 (q, 7.9 Hz, 2H, CH_2), 7.21-8.14 (m, 10H, arom)	184.3 (*C*=O), 45.6 (N*C*H_2), 16.0 *C*H_3), 127.4-141.0 (arom)
$C_6H_5C(O)SNHCH_2CH_2SSC(O)C_6H_5$ (**13ac**)	oil	1662	3.56 (d, 7.7 Hz, 2H, NCH_2), 3.78 (d, 7.7 Hz, 2H, SCH_2), 3.88 (br. s, 1H, N*H*), 7.22-8.10 (m, 10H, arom)	184.6 (*C*=O), 185.3 (*C*=O), 44.4 (N*C*H_2), 54.2 (S*C*H_2), 128.7-130.8 (arom)
$C_6H_5C(O)SNHPr$-*n* (**13ad**)	oil	1669	0.96 (t, 7.8 Hz, 3H, CH_3), 2.7-3.3 (m, 4H, NH*C*H_2*C*H_2), 7.22-8.01 (m, 5H, arom)	184.5 (*C*=O), 42.1 (N*C*H_2), 25.8 (*C*H_2), 11.1 *C*H_3), 127.4-132.6 (arom)
$C_6H_5C(O)SN(Pr$-*i*$)_2$ (**13ae**)	oil	1668	1.17 (d, 7.8 Hz, 6H, CH_3), 2.9-3.3 (m, 1H, NC*H*), 7.21-8.10 (m, 5H, arom)	184.6 (*C*=O), 44.3 (N*C*H), 25.7 (*C*H_3), 127.4-130.5 (arom)
$C_6H_5C(O)SNHBu$-*n* (**13af**)	oil	1660	0.7-1.9 (m, 7H, C_3H_7), 2.8-3.5 (m, 3H, N*H*, CH_2), 7.12-8.10 (m, 5H, arom)	184.5 (*C*=O), 42.1 (N*C*H_2), 36.1 (*C*H_2), 25.8 (*C*H_2), 11.1 (*C*H_3), 127.4-132.6 (arom)
$C_6H_5C(O)SNHBu$-*t* (**13ag**)	oil	1668	1.20 (s, 9H, C_4H_9), 3.0-3.2 (br. s, 1H, N*H*), 7.20-8.03 (m, 5H, arom)	184.5 (*C*=O), 48.3 (N*C*), 32.5 (*C*H_3), 127.8-131.1 (arom)
$C_6H_5C(O)SNHPh$ (**13ak**)	95-101	1660	4.80-5.31 (br. s, 1H, N*H*), 6.62-8.07 (m, 10H, arom)	184.4 (*C*=O), 127.4-130.1 (arom)
$C_6H_5C(O)SNHC_6H_4$Me-2	75-77	1660	2.32 (s, 3H, CH_3), 4.82-5.14 (br. s, 1H, N*H*), 6.63-8.07 (m, 9H, arom)	184.1 (*C*=O), 17.4 (2-*C*H_3Ar), 117.4-138.8 (arom)
$C_6H_5C(O)SNHC_6H_4$Me-4 (**13am**)	82-84	1663	2.23 (s, 3H, CH_3), 4.81-5.11 (br. s, 1H, N*H*), 6.72-8.08 (m, 9H, arom)	184.4 (*C*=O), 22.3 (*C*H_3Ar), 127.6-131.2 (arom)
$C_6H_5C(O)SNHC_6H_4$OMe-4 (**13an**)	62-64	1668	3.65 (s, 3H, OCH_3), 4.80-5.12 (br. s, 1H, N*H*), 6.52-7.92 (m, 9H, arom)	184.2 (*C*=O), 34.2 (O*C*H_3), 127.6-131.2 (arom)
$C_6H_5C(O)SNHC_6H_4$Cl-4	99-102	1676	4.91-5.20 (br. s, 1H, N*H*), 6.50-8.04 (m, 9H, arom)	184.2 (*C*=O), 127.6-135.2 (arom)

[a]Neat (KBr). [b]90 MHz, $CDCl_3$; internal standard: Me_4Si. [c]270 MHz, $CDCl_3$; internal standard: Me_4Si.

Table S32 Physical properties and spectral data of *S*-acylsulfenamides **13** (continued 1)

RC(O)SNR'R" **13**	m.p. / °C	i.r. [a]/cm^{-1} νC=O	^{1}H NMR[b] δ/ ppm	^{13}C NMR[c] δ/ ppm
4-MeC_6H_4C(O)SNHCH_2Ph (**13da**)	36-38	1656	2.28 (s, 3H, CH_3), 3.18-3.50 (br. s, H, N*H*), 4.03 (s, 2H, CH_2), 7.20-8.20 (m, 9H, arom)	184.6 (*C*=O), 46.4 (N*C*H$_2$), 21.4 (*C*H$_3$Ar), 128,3-130.7 (arom)
4-MeC_6H_4C(O)SN(Me)Ph (**13dg**)	76-78	1668	2.39 (s, 3H, CH_3), 3.48 (s, 3H, NCH_3), 6.7-8.0 (m, 9H, arom)	184.5 (*C*=O), 51.1 (N*C*H$_3$), 22.5 (*C*H$_3$Ar), 127.4-132.6 (arom)
4-MeC_6H_4C(O)SN(Et)Ph	oil	1673	1.36 (t, 7.9 Hz, 3H, CH_3), 2.42 (s 3H, ArCH_3), 3.38 (q, 7.9 Hz, 2H, CH_2), 6.7-8.0 (m, 9H, arom)	184.6 (*C*=O), 58.1 (N*C*H$_2$), 22.2 (*C*H$_3$Ar), 16.3 *C*H$_3$), 127.4-130.5 (arom)
4-MeC_6H_4C(O)SNEt$_2$	oil	1659	1.19 (t, 7.9 Hz, 6H, CH_3), 2.38 (s 3H, CH_3), 3.26 (q, 7.9 Hz, 4H, CH_2), 7.1-8.0 (m, 4H, arom)	184.5 (*C*=O), 49.3 (N*C*H$_2$), 22.4 (*C*H$_3$Ar), 15.6 *C*H$_3$), 127.8-130.0 (arom)
4-MeC_6H_4C(O)SN(Pr-*n*)$_2$ (**13dc**)	oil	1668	0.89 (t, 7.8 Hz, 6H, CH_3), 1.56 (sept, 7.8 Hz, 4H, CH_2), 2.34 (s, 3H, CH_3), 3.10 (t, 7.8 Hz, 4H, CH_2), 7.0-8.0 (m, 4H, arom)	184.6 (*C*=O), 57.3 (N*C*H$_2$), 24.1 (*C*H$_2$), 22.3 (*C*H$_3$Ar), 11.7 *C*H$_3$), 127.4-130.7 (arom)
4-MeC_6H_4C(O)SNHPr-*n* (**13db**)	oil	1659	0.93 (t, 7.8 Hz, 3H, CH_3), 1.57 (sex, 7.8 Hz, 2H, CH_2), 2.38 (s, 3H, CH_3), 3.12 (t, 7.8 Hz, 2H, CH_2), 5.27 (br. s, 1H, N*H*), 7.11-7.96 (m, 4H, arom)	184.6 (*C*=O), 40.1 (N*C*H$_2$), 36.1 (*C*H$_2$), 21.1 (*C*H$_3$Ar), 13.5 (*C*H$_3$), 128.1-130.0 (arom)
4-MeC_6H_4C(O)SNHPr-*i*	oil	1659	1.16 (d, 7.7 Hz, 6H, CH_3), 3.52 (hept, 7.7 Hz, 1H, C*H*), 3.42 (br. s, 1H, N*H*), 7.11-7.96 (m, 4H, arom)	184.4 (*C*=O), 47.3 (N*C*H), 22.4 (*C*H$_3$Ar), 18.3 *C*H$_3$), 127.4-130.8 (arom)
4-MeC_6H_4C(O)SN(Pr-*i*)$_2$ (**13dh**)	oil	1658	1.13 (d, 7.7 Hz, 6H, CH_3), 2.38 (s, 3H, CH_3), 3.39 (hept, 7.7 Hz, 1H, C*H*), 7.11-7.96 (m, 4H, arom)	184.6 (*C*=O), 44.4 (N*C*H), 21.4 (*C*H$_3$Ar), 18.2 (*C*H$_3$), 128,7-130.8 (arom)
4-MeC_6H_4C(O)SNHBu-*n*	oil	1653	2.38 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 0.93 (t, 7.7 Hz, 3H, CH_3), 1.57 (q, 7.7 Hz, 2H, CH_2), 5.27 (br. s, 1H, N*H*), 2.38 (s, 3H, CH_3), 7.11-7.96 (m, 4H, arom)	184.6 (*C*=O), 42.4 (N*C*H$_2$), 25.4 (*C*H$_2$), 23.3 (*C*H$_2$), 22.2 (*C*H$_3$Ar), 11.9 (*C*H$_3$), 128,7-130.8 (arom)
4-MeC_6H_4C(O)SNHBu-*t*	oil	1647	1.12 (s, 9H, CH_3), 2.34 (s, 3H, CH_3Ar), 2.9-3.2 (br. s, 1H, N*H*), 7.0-7.9 (m, 4H, arom)	184.2 (*C*=O), 48.5 (N*C*), 32.3 *C*H$_3$), 22.1 (*C*H$_3$Ar), 127.4-130.2 (arom)
4-MeC_6H_4C(O)SNHC$_6$H$_{11}$-*cyclo*	oil	1659	0.8-3.3 (m, 12H, N*H*C$_6$*H*$_{11}$), 2.38 (s, 3H, CH_3), 3.26 (q, 7.7 Hz, 4H, CH_2), 7.1-8,0 (m, 4H, arom)	184.3 (*C*=O), 50.2 (N*C*), 37.3 (*C*H$_2$), 25.3 (*C*H$_2$), 25.1 (*C*H$_3$), 22.1 (*C*H$_3$Ar), 127.4-31.0 (arom)

[a]KBr. [b]90 MHz, $CDCl_3$; internal standard: Me_4Si. [c]270 MHz, $CDCl_3$; internal standard: Me_4Si.

Table 33 Physical properties and spectral data of *S*-acylsulfenamides **13** (continued 2)

RC(O)SNR'R" **13**	m.p. / °C	i.r.[a]/ cm^{-1} ν C=O	^{1}H NMR[b] δ/ ppm	^{13}C NMR[c] δ/ ppm
4-MeC_6H_4C(O)S  (**13dd**)	oil	1660	1.40–2.20 (m, 4H, CH_2), 2.37 (s, 3H, CH_3Ar), 2.80–3.81 (m, 4H, NCH_2); 7.02–7.86 (m, 4H, arom)	184.4 (*C*=O), 48.3 (N*C*H$_2$), 25.5 (*C*H$_2$), 22.3 (*C*H$_3$Ar), 127.6-131.2 (arom)
4-MeC_6H_4C(O)S  (**13de**)	84-86	1657	1.21-1.93 (m, 6H, CH_2), 2.35 (s, 3H, CH_3Ar), 3.21-3.72 (m, 4H, CH_2), 7.06-8.05 (m, 4H, arom)	184.2 (*C*=O), 55.5 (N*C*H$_2$), 46.0 (*C*H$_2$), 25.1 (*C*H$_2$), 22.2 (*C*H$_3$Ar), 127.6-131.2 (arom)
4-MeC_6H_4C(O)S  (**13df**)	76-78	1668	2.39 (s, 3H, CH_3), 3.31-3.92 (m, 8H, CH_2), 7.12-7.87 (m, 4H, arom)	184.2 (*C*=O), 66.5 (O*C*H$_2$), 54.1 (N*C*H$_2$), 22.2 (*C*H$_3$Ar), 127.6-131.2 (arom)
4-MeC_6H_4C(O)SNPh$_2$	161-163	1664	2.41 (s, 3H, CH_3), 6.84-8.11 (m, 14H, arom)	185.1 (*C*=O), 21.5 (*C*H$_3$Ar), 128.1-130.6 (arom)
4-MeC_6H_4C(O)SNHC_6H_4Me-2	73-75	1661	2.21 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 4.81-5.13 (br. s, 1H, N*H*), 6.80-7.88 (m, 8H, arom)	186.4 (*C*=O), 28.6 (*C*H$_3$Ar), 17.6 (*C*H$_3$Ar),128.2-131.2 (arom)
4-MeC_6H_4C(O)SNHC_6H_4Me-4 (**13di**)	87-89	1688	2.38 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 4.81 -5.14 (br. s, 1H, N*H*), 6.81-7.93 (m, 8H, arom)	185.1 (*C*=O), 21.7 (*C*H$_3$Ar), 20.9 (*C*H$_3$Ar), 127.9-130.1 (arom)
4-MeC_6H_4C(O)SNHC_6H_4OMe-4	61-64	1663	2.36 (s, 3H, CH_3), 3.66 (s, 3H, OCH_3), 4.80-5.11 (br. s, 1H, N*H*), 6.63-7.90 (m, 8H, arom)	186.3 (*C*=O), 34.2 (*C*H$_3$OAr), 21.4 (*C*H$_3$Ar), 128.1-132.1 (arom)
4-MeC_6H_4C(O)SNHC_6H_4Cl-4 (**13dj**)	96-98	1673	2.40 (s, 3H, CH_3), 5.01-5.44 (br. s, 1H, N*H*), 7.10-8.20 (m, 8H, arom)	186.3 (*C*=O), 22.0 (*C*H$_3$Ar), 128.1-132.7 (arom)
2-MeOC_6H_4C(O)SNHPh (**13ea**)	100-102	1663	4.00 (s, 3H, OCH_3), 5.12-5.43 (br. s, 1H, N*H*), 6.83-8.01 (m, 9H, arom)	186.4 (*C*=O), 55.6 (ArO*C*H$_3$), 128.2-155.2 (arom)
4-MeOC_6H_4C(O)SNHPh (**13fa**)	118-120	1660	3.82 (s, 3H, CH_3O); 5.11–5.32 (br. s, 1H, N*H*); 6.82–8.06 (m, 9H, arom)	184.1 (*C*=O), 35.3 (*C*H$_3$OAr); 127.9–160.1 (arom)
4-ClC_6H_4C(O)SNHPh (**13ia**)	110-112	1660	4.92-5.13 (br. s, 1H, N*H*), 6.72-7.92 (m, 9H, arom)	185.3 (*C*=O), 128.9-135.6 (arom)
4-ClC_6H_4C(O)SNHC_6H_4Me-4 (**13ib**)	85-87	1679	2.39 (s, 3H, CH_3Ar), 5.03-5.32 (br. s, 1H, N*H*), 6.80-8.01 (m, 8H, arom)	186.4 (*C*=O), 21.4 (*C*H$_3$Ar), 128.1-132.1 (arom)

[a]KBr. [b]90 MHz, $CDCl_3$; internal standard: Me_4Si. [c]270 MHz, $CDCl_3$; internal standard: Me_4Si.

Table S34 Yields and physical properties of silver carbothioates **2a**

M(SC(O)R) **2a** M	R	compd no.	method	yield[a] / %	m,p. / °C	i.r./ cm^{-1} [b] νC=O	colour	recryst. solv.
Ag	C_6H_5	**2aa**	A[c]	81	136-138 (dec)[32]	1605,1575	colourless	MeOH/CH_2Cl_2 (1:2)
Ag	C_6H_5	**2aa**	B[d]	92				
Ag	C_6H_5	**2aa**	C[e]	90				
Ag	2-MeC_6H_4	**2ab**	B	74	106-109 (dec)	1608,1588	colourless	MeOH/CH_2Cl_2 (1:2)
Ag	3-MeC_6H_4	**2ac**	A	68	139-141 (dec)[32]	1613,1576	colourless	MeOH/CH_2Cl_2 (1:2)
Ag	4-MeC_6H_4	**2ad**	B	63	145-152 (dec)[32]	1608,1570	colourless	MeOH/CH_2Cl_2 (1:2)
Ag	2-$MeOC_6H_4$	**2ae**	B	78	128-130 (dec)	1610,1677	colourless	MeOH/CH_2Cl_2 (1:2)
Ag	4-$MeOC_6H_4$	**2af**	A	71	144-146 (dec)[32]	1603,1565	colourless	MeOH/CH_2Cl_2 (1:2)
Ag	4-$MeOC_6H_4$	**2af**	B	71				
Ag	2-ClC_6H_4	**2ag**	B	66	110-113 (dec)[32]	1605,1570	colourless	MeOH/CH_2Cl_2 (1:2)
Ag	3-ClC_6H_4	**2ah**	B	88	156-158 (dec)[32]	1604,1566	colourless	MeOH/CH_2Cl_2 (1:2)
Ag	4-ClC_6H_4	**2ai**	A	79	108-111 (dec)[32]	1595,1560	colourless	MeOH/CH_2Cl_2 (1:2)
Ag	4-ClC_6H_4	**2ai**	B	90				
Ag	2-$NO_2C_6H_4$	**2aj**	B	86	125-127 (dec)[32]	1567	colourless	MeOH/CH_2Cl_2 (1:2)
Ag	3-$NO_2C_6H_4$	**2ak**	B	92	127-130 (dec)[32]	1609,1605	colourless	MeOH/CH_2Cl_2 (1:2)
Ag	4-$NO_2C_6H_4$	**2al**	C	92	130-133 (dec)[32]	1598	colourless	MeOH/CH_2Cl_2 (1:2)
Ag	Me	**2am**	A	-	-	-		
Ag	*tert*-Bu	**2an**	A	-	-	-		
Ag	*n*-$CH_3(CH_2)_{16}$	**2ao**	A	-	-	-		

[a]Isolated yields. [b]KBr. [c]Method A: $AgNO_3$ + RCOSH. [d]Method B: $AgNO_3$+ K(SC(O)R). [e]Method C: $AgNO_3$ + piperidinium carbothioate.

Table S35 Yields and physical properties of zinc di(carbothioates) **2b**

$M(SC(O)R)_2$ **2b** M	R	compd no.	method	yield[a] / %	m.p. / °C	i.r./ cm^{-1} [b] νC=O	colour	recrystal. solv.
Zn	C_6H_5	**2ba**	A[c]	90	97-99	1530	colourless	MeOH/$CHCl_3$ (1:2)
Zn	C_6H_5	**2ba**	B[d]	94	97-99			
Zn	C_6H_5	**2ba**	C[e]	80	97-99			
Zn	2-MeC_6H_4	**2bb**	-	-	-			
Zn	3-MeC_6H_4	**2bc**	B	96	128-130	1520	colourless	MeOH/$CHCl_3$ (1:2)
Zn	4-MeC_6H_4	**2bd**	A	96	102-104	1527	colourless	MeOH/$CHCl_3$
Zn	4-MeC_6H_4	**2bd**	B	94	102-104			(1:2)
Zn	2-$MeOC_6H_4$	**2be**	-	-	-			
Zn	4-$MeOC_6H_4$	**2bf**	A	74	153-155	1539	colourless	MeOH/$CHCl_3$
Zn	4-$MeOC_6H_4$	**2bf**	B	87	153-155			(1:2)
Zn	3-ClC_6H_4	**2bg**	B	91	103-105	1552	colourless	MeOH/$CHCl_3$ (1:2)
Zn	4-ClC_6H_4	**2bi**	A	94	108-110	1588	colourless	MeOH/$CHCl_3$ (1:2)
Zn	4-ClC_6H_4	**2bi**	B	93	108-110			
Zn	3-$NO_2C_6H_4$	**2bk**	B	56	98-100	1520	colourless	MeOH/$CHCl_3$ (1:2)
Zn	4-$NO_2C_6H_4$	**2bl**	B	97	105-107	1520	colourless	MeOH/$CHCl_3$ (1:2)

[a]Isolated yields. [b]KBr. [c]Method A: $ZnCl_2$ + K(SC(O)R). [d]Method B: $Zn(OOCMe)_2$ + RCOSH. [e]Method C: $ZnCl_2$ + Piperidinium carbothioate.

Table S36 Yields and physical properties of cadmium di(carbothioates) **2c**

M(SC(O)R)$_2$ **2c**		compd	method	yield[a]	m,p.	i.r./ cm^{-1} [b]	colour	recrystal.
M	R	no.		/ %	/ °C	νC=O		solv.
Cd	C_6H_5	**2ca**	A[c]	92	102-107	1652	colourless	MeOH/CH_2Cl_2 (1:1)
Cd	C_6H_5	**2ca**	B[d]	84				
Cd	C_6H_5	**2ca**	C[e]	78				
Cd	2-$CH_3C_6H_4$	**2cb**	B	-	-			
Cd	3-$CH_3C_6H_4$	**2cc**	B	75	138-140	1584	colourless	MeOH/CH_2Cl_2 (1:1)
Cd	4-$CH_3C_6H_4$	**2cd**	B	94	176-178	1569	colourless	MeOH/CH_2Cl_2 (1:1)
Cd	4-$CH_3OC_6H_4$	**2cf**	B	88	198-200	1578	colourless	MeOH/CH_2Cl_2 (1:1)
Cd	4-$CH_3OC_6H_4$	**2cf**	C	74				
Cd	2-ClC_6H_4	**2cg**	B	92	189-191	1540	colourless	MeOH/CH_2Cl_2 (1:1)
Cd	3-ClC_6H_4	**2ch**	B	95	199-201	1544	colourless	MeOH/CH_2Cl_2 (1:1)
Cd	4-ClC_6H_4	**2ci**	B	92	156-158	1542	colourless	MeOH/CH_2Cl_2 (1:1)
Cd	2-$NO_2C_6H_4$	**2cj**	B	-				
Cd	4-$NO_2C_6H_4$	**2cl**	B	93	177-179	1540	colourless	MeOH/CH_2Cl_2 (1:1)

[a]Isolated yields. [b]KBr. [c]Method *A*: $Cd(OOCMe)_2$ + 2 RCOSH. [d]Method *B*: $CdCl_2$ + 2 K(SC(O)R). [e]Method *C*: $CdCl_2$ + 2 piperidinium carbothioate.

Table S37 Yields, physical and spectral data of *S*-triphenylgermanium carbothioates **3a**

MSC(O)R **3a**		compd.	yield[a]	m.p.	i.r. /cm^{-1}[b]	^{1}H NMR[c]	^{13}C NMR[d]
M	R	no.	/ %	/ °C	νC=O	/ δ	/ δ
Ph_3Ge[e]	C_6H_5	**3aa**	80	134-136	1652	7.38-8.05 (m, 20H, arom)	128.4-138.2 (arom) 192.2 (*C*=O)
Ph_3Ge	2-MeC_6H_4	**3ab**	74	119-121	1610	2.27 (s, 3H, CH_3), 7.05-7.88 (m, 19H, arom)	21.7 (*C*H$_3$), 127.9-137.1 (arom) 191.1 (*C*=O)
Ph_3Ge	4-MeC_6H_4	**3ac**	85	110-112	1651	2.24 (s, 3H, CH_3), 7.06-7.84 (m, 19H, arom)	21.6 (*C*H$_3$), 128.5-144.2 (arom) 191.7 (*C*=O)
Ph_3Ge	2-$MeOC_6H_4$	**3ad**	75	105-108	1634	3.75 (s, 3H, CH_3), 6.82-7.68 (m, 19H, arom)	55.9 (*C*H$_3$O), 112.0-157.5 (arom) 191.3 (*C*=O)
Ph_3Ge	4-$MeOC_6H_4$	**3ae**	81	103-105	1643	3.75 (s, 3H, CH_3O), 6.78-7.94 (m, 19H, arom)	55.5 (*C*H$_3$O), 113.5-163.8 (arom) 190.6 (*C*=O)
Ph_3Ge	3-ClC_6H_4	**3af**	58	97-99	1648	7.37-8.05 (m, 19H, arom)	128.2-154.0 (arom) 194.4 (*C*=O)
Ph_3Ge	4-ClC_6H_4	**3ag**	75	110-112	1650	7.35-7.96 (m, 19H, arom)	128.5-139.8 (arom) 191.1 (*C*=O)
Ph_3Ge	4-$NO_2C_6H_4$	**3ah**	61	135-137	1579	7.43-8.12 (m, 19H, arom)	130.9-157.3 (arom) 194.4 (*C*=O)
Ph_3Ge[f]	Me	**3ai**	73	96-98	1672	2.42 (s, 3H, CH_3), 7.41-7.61 (m, 15H, arom)	33.9 (*C*H$_3$). 128.5-134.7 (arom) 196.6 (*C*=O)
Ph_3Ge[f]	*tert*-Bu	**3aj**	76	87-89	1669	1.14 (s, 18H, CH_3), 7.27-7.54 (m, 15H, arom)	27.8 (*C*H$_3$), 48.3 (*C*CH$_3$), 128.4-135.1 (arom) 207.1 (*C*=O)

[a]Isolated yields. [b]KBr. [c]90 MHz, $CDCl_3$; internal standard: Me_4Si. [d]270 MHz, $CDCl_3$; internal standard: Me_4Si. [e]Ph_3GeCl + RCOSH. [f]Ph_3GeCl + K(SC(O)R).

Table S38 Yields, physical and spectral data of *S*-diphenylgermanium di(carbothioates) **3b**

$M(SC(O)R)_2$ **3b**		compd	yield[a]	m.p.	i.r. / cm^{-1} [b]	^1H NMR[c]	^{13}C NMR[d]
M	R	no.	/ %	/ °C	νC=O	/ δ	/ δ
Ph_2Ge[e]	C_6H_5	**3ba**	86	139-141	1647,1634	7.39-7.99 (m, 20H, arom)	128.4-137.5 (arom) 192.6 (*C*=O)
Ph_2Ge	2-MeC_6H_4	**3bb**	77	109-111	1617	2.39 (s, 6H, CH_3) 680-7.98 (m, 18H, arom)	21.9 (CH_3), 125.1-142.8 (arom), 193.3 (*C*=O)
Ph_2Ge	4-MeC_6H_4	**3bc**	85	158-160	1649,1628	2.37 (s, 6H, CH_3) 7.17-7.92 (m, 18H, arom)	21.7 (CH_3), 128.6-144.6 (arom), 192.2 (*C*=O)
Ph_2Ge	2-$MeOC_6H_4$	**3bd**	87	138-140	1652,1616	3.77 (s, 6H, CH_3O) 6.87-7.98 (m, 18H, arom)	55.8 (CH_3O), 112.0-158.0 (arom), 191.3 (*C*=O)
Ph_2Ge	4-$MeOC_6H_4$	**3be**	81	161-163	1640	3.77 (s, 6H, CH_3O) 6.83-7.97 (m, 18H, arom)	55.5 (CH_3O), 113.5-164.0 (arom), 190.9 (*C*=O)
Ph_2Ge	3-ClC_6H_4	**3bf**	61	122-124	1610	7.25-7.76 (m, 18H, arom)	128.5-157.6 (arom), 194.4 (*C*=O)
Ph_2Ge	4-ClC_6H_4	**3bg**	83	134-136	1657,1637	7.31-7.94 (m, 18H, arom)	128.6-164.0 (arom), 191.3 (*C*=O)
Ph_2Ge	4-$NO_2C_6H_4$	**3bh**	76	155-157	1606,1587	7.36-8.01 (m, 18H, arom)	129.5-161.3 (arom), 203.1 (*C*=O)
Ph_2Ge[f]	Me	**3bi**	80	oil	1688	33.3 (s, 6H, CH_3) 7.37-7.80 (m, 10H, arom)	33.3 (CH_3), 128.4-133.7 (arom), 206.2 (*C*=O)
Ph_2Ge[f]	*tert*-Bu	**3bj**	88	56-58	1674,1664	1.22 (s, 18H, CH_3) 7.37-7.78 (m, 10H, arom)	27.6 (CH_3) 48.2 (CCH_3), 128.4-134.7 (arom), 207.5 (*C*=O)

[a]Isolated yields. [b]KBr. [c]90 MHz, $CDCl_3$; internal standard: Me_4Si. [d]270 MHz, $CDCl_3$; internal standard: Me_4Si. [e]Ph_2GeCl_2 + 2 RCOSH. [f]Ph_2GeCl_2 + 2 K(SC(O)R).

Table S39 Yields, physical and spectral data of *S*-triphenyltin carbothioates **3c**

MSC(O)R **3c**		compd	yield[a]	m.p.	i.r./ cm^{-1} [b]	^1H NMR[c]	^{13}C NMR[c]	^{119}Sn NMR[d]
M	R	no.	/ %	/ °C	νC=O	/ δ	/ δ	/ δ
Ph_3Sn[e]	C_6H_5	**3ca**	83	106-108	1624	7.11-7.95 (m, 20H, arom)	196.5 (*C*=O)	-96.6 $^1J_{119Sn-13C}$=594 Hz
Ph_3Sn	2-MeC_6H_4	**3cb**	77	94-96	1575	2.38 (s, 3H, CH_3) 7.10-7.98 (m, 19H, arom)	21.9 (CH_3) 193.2 (*C*=O)	-98.1 $^1J_{119Sn-13C}$=589 Hz
Ph_3Sn	4-MeC_6H_4	**3cc**	83	233-235	1621	2.37 (s, 3H, CH_3), 7.11-7.95 (m, 19H, arom)	21.7 (CH_3) 196.0 (*C*=O)	-97.7 $^1J_{119Sn-13C}$=594 Hz
Ph_3Sn	2-$MeOC_6H_4$	**3cd**	92	170-172	1607	3.74 (s, 3H, CH_3), 6.80-7.71 (m, 19H, arom)	55.8 (CH_3O) 195.5 (*C*=O)	-102.5 $^1J_{119Sn-13C}$=589 Hz
Ph_3Sn	4-$MeOC_6H_4$	**3ce**	85	115-116	1616	3.75 (s, 3H, CH_3O), 6.83-8.04 (m, 19H, arom)	55.5 (CH_3O) 194.8 (*C*=O)	-99.2 $^1J_{119Sn-13C}$=591 Hz
Ph_3Sn	3-ClC_6H_4	**3cf**	69	94-96	1573	7.35-8.05 (m, 19H, arom)	191.7 (*C*=O)	-95.4 $^1J_{119Sn-13C}$=595 Hz
Ph_3Sn	4-ClC_6H_4	**3cg**	83	166-168	1610	7.34-7.99 (m, 19H, arom)	195.3 (*C*=O)	-94.8 $^1J_{119Sn-13C}$=594 Hz
Ph_3Sn	4-$NO_2C_6H_4$	**3ch**	59	137-139	1564	7.33-8.01 (m, 19H, arom)	196.4 (*C*=O)	-100.3 $^1J_{119Sn-13C}$=596 Hz
Ph_3Sn[f]	Me	**3ci**	95	154-156	1651	2.47 (s, 3H, CH_3) 7.38-7.71 (m, 15H, arom)	32.9 (CH_3) 201.0 (*C*=O)	-94.6 $^1J_{119Sn-13C}$=592 Hz
Ph_3Sn[f]	*tert*-Bu	**3cj**	78	oil	1646	1.11 (s, 9H, CH_3) 7.22-7.95 (m, 15H, arom)	28.1 (CH_3) 47.5 (CCH_3) 211.8 (*C*=O)	-97.3 $^1J_{119Sn-13C}$=591 Hz

[b]KBr. [b]90 MHz, $CDCl_3$; internal standard: Me_4Si. [c]270 MHz, $CDCl_3$; internal standard: Me_4Si. [d]270 MHz, $CDCl_3$; external standard: Me_4Sn. [e]Ph_3SnCl +piperidinium (SC(O)R). [f]Ph_3SnCl + K(SC(O)R).

Table S40 Yields, physical and spectral data of *S*-diphenyltin di(carbothioates) **3d**

$M(SC(O)R)_2$ **3d**		compd	yield[a]	m.p.	i.r. cm^{-1} [b]	^1H NMR[c]	^{13}C NMR[d]	^{119}Sn NMR[e]
M	R	no.	/ %	/ °C	νC=O	/ δ	/ δ	/ δ
Ph_2Sn[f]	C_6H_5	**3da**	95	154-116	1609	7.11-7.95 (m, 20H, arom)	200.1 (*C*=O)	-200.1 $^1J_{119Sn-13C}$=809 Hz
Ph_2Sn	2-MeC_6H_4	**3db**	88	131-133	1577	2.38 (s, 3H, CH_3) 7.10-7.98 (m, 18H, arom)	21.9 (CH_3) 193.2 (*C*=O)	-197.8 $^1J_{119Sn-13C}$=808 Hz
Ph_2Sn	4-MeC_6H_4	**3dc**	91	169-171	1611	2.37 (s, 3H, CH_3), 7.11-7.95 (m, 18H, arom)	21.7 (CH_3) 199.6 (*C*=O)	-201.8 $^1J_{119Sn-13C}$=809Hz
Ph_2Sn	2-$MeOC_6H_4$	**3dd**	91	171-173	1617	3.74 (s, 3H, CH_3), 6.80-7.71 (m, 18H, arom)	55.9 (CH_3O) 198.4 (*C*=O)	-199.9 $^1J_{119Sn-13C}$=796 Hz
Ph_2Sn	4-$MeOC_6H_4$	**3de**	83	163-166	1611	3.75 (s, 3H, CH_3O), 6.83-8.04 (m, 18H, arom)	55.6 (CH_3O) 198.4 (*C*=O)	-207.2 $^1J_{119Sn-13C}$=812 Hz
Ph_2Sn	3-ClC_6H_4	**3df**	67	101-103	1564	7.35-8.05 (m, 18H, arom)	191.7 (*C*=O)	-200.3 $^1J_{119Sn-13C}$=798 Hz
Ph_2Sn	4-ClC_6H_4	**3dg**	89	166-168	1617	7.34-7.99 (m, 18H, arom)	199.0 (*C*=O)	-199.4 $^1J_{119Sn-13C}$=799 Hz
Ph_2Sn	4-$NO_2C_6H_4$	**3dh**	72	155-157	1572	7.33-8.01 (m, 18H, arom)	196.8 (*C*=O)	-202.5 $^1J_{119Sn-13C}$=707 Hz
Ph_2Sn[g]	Me	**3di**	87	76-78	1651	2.47 (s, 6H, CH_3), 7.38-7.71 (m, 19H, arom)	32.9 (CH_3) 204.6 (*C*=O)	-169.1 $^1J_{119Sn-13C}$=706 Hz
Ph_2Sn[g]	*t*-Bu	**3dj**	82	oil	1646	1.11 (s, 18H, CH_3) 7.22-7.95 (m, 10H, arom)	28.3 (CH_3) 47.5 (CCH_3) 215.9 (*C*=O)	-181.6 $^1J_{119Sn-13C}$=782 Hz

[a]Isolated yields. [b]KBr. [c]90 MHz, $CDCl_3$, internal standard: Me_4Si. [d]270 MHz, $CDCl_3$, internal standard: Me_4Si. [e]270 MHz, CDCl, external standard: Me_4Sn. [f]Ph_2SnCl_2 + 2 piperidinium (SC(O)R). [g]Ph_2SnCl_2 + 2 K(SC(O)R).

Table S41 Yields, physical properties and spectral data of *S*-triphenyllead carbothioates **3e**

MSC(O)R **3e**		compd	yield[a]	m.p.	i.r./ cm^{-1} [b]	^1H NMR[c]	^{13}C NMR[d]
M	R	no.	/ %	°C	νC=O	/ δ	/ δ
Ph_3Pb[e]	C_6H_5	**3ea**	95	94-96	1619	7.29-8.09 (m, 20H, arom)	128.3-*154.0* (arom) $^1J_{13C-207Pb}$=547 Hz 196.9 (*C*=O)
Ph_3Pb	2-MeC_6H_4	**3eb**	72	93-95	1586	2.37 (s, 3H, CH_3) 7.10-7.98 (m, 19H, arom)	21.6 (CH_3), 128.2-*154.8* (arom) $^1J_{13C-207Pb}$=546 Hz, 197.2 (*C*=O)
Ph_3Pb	4-MeC_6H_4	**3ec**	98	106-108	1618	2.30 (s, 3H, CH_3), 7.12-7.99 (m, 19H, arom)	21.5 (CH_3), 128.8-*154.0* (arom) $^1J_{13C-207Pb}$=545 Hz, 196.4 (*C*=O)
Ph_3Pb	2-$MeOC_6H_4$	**3ed**	85	79-81	1607	3.77 (s, 3H, CH_3) 6.86-7.90 (m, 19H, arom)	56.8 (CH_3O), 111.9-*154.0* (arom) $^1J_{13C-207Pb}$=540 Hz, 200.7(*C*=O)
Ph_3Pb	4-$MeOC_6H_4$	**3ee**	89	104-106	1614	3.66 (s, 3H, CH_3O) 6.73-7.97 (m, 19H, arom)	55.4(CH_3O), 113.3-*154.1* (arom) $^1J_{13C-207Pb}$=547 Hz, 195.8 (*C*=O)
Ph_3Pb	3-ClC_6H_4	**3ef**	69	98-101	1579	7.35-8.03 (m, 19H, arom)	128.2-*156.0* (arom), $^1J_{13C-207Pb}$=549 Hz, 195.8 (*C*=O)
Ph_3Pb	4-ClC_6H_4	**3eg**	87	74-76	1618	7.28-7.99 (m, 19H, arom)	128.4-*154.0* (arom), $^1J_{13C-207Pb}$=547 Hz, 195.8 (*C*=O)
Ph_3Pb	4-$NO_2C_6H_4$	**3eh**	76	125-127	1567	7.33-8.11 (m, 19H, arom)	128.2-*154.0* (arom), $^1J_{13C-207Pb}$=550 Hz, 202.2 (*C*=O)
Ph_3Pb[f]	Me	**3ei**	97	90-93	1622	2.37 (s, 3H, CH_3) 7.37-7.83 (m, 15H, arom)	33.7 (CH_3), 130.1-*157.2* (arom), $^1J_{13C-207Pb}$= 540 Hz, 206.3 (*C*=O)
Ph_3Pb[f]	*tert*-Bu	**3ej**	91	75-77	1638	1.22 (s, 18H, CH_3) 7.36-7.81 (m, 15H, arom)	28.6 (CH_3), 48.21 (CCH_3), 129.2-*153.8* (arom), $^1J_{13C-207Pb}$ = 544 Hz, 212.1 (*C*=O)

[a]Isolated yields. [b]KBr. [c]90 MHz, $CDCl_3$, internal standard: Me_4Si. [d]270 MHz, $CDCl_3$, internal standard: Me_4Si. The italilc numbers of aromatic carbon show coupling with ^{207}Pb atom. [e]Ph_3PbCl + RCOSH. [f]Ph_3PbCl + K(SC(O)R).

Table S42 Yields, physical and spectral data of *S*-diphenyllead di(carbothioates) **3f**

$M(SOCR)_2$ **3f**		compd	yield[a]	m.p.	i.r./ cm^{-1} [b]	^1H NMR[c]	^{13}C NMR[d]
M	R	no.	/ %	/ °C	νC=O	/ δ	/ δ
Ph_2Pb[e]	C_6H_5	**3fa**	79	173-175	1616	7.33-8.09 (m, 20H, arom)	128.3-*157.8* (arom), $^1J_{13C\text{-}207Pb}$ = 859 Hz, 201.7 (*C*=O)
Ph_2Pb	2-MeC_6H_4	**3fb**	83	93-95	1617	2.40 (s, 6H, CH_3), 7.10-7.98 (m, 19H, arom)	21.8 (CH_3), 128.3-*157.3* (arom), $^1J_{13C\text{-}207Pb}$ = 859 Hz, 197.2 (*C*=O)
Ph_2Pb	4-MeC_6H_4	**3fc**	82	163-165	1618	2.39 (s, 6H, CH_3), 7.21-7.98 (m, 18H, arom)	21.7 (CH_3), 128.9-*157.8* (arom), $^1J_{13C\text{-}207Pb}$ = 857 Hz, 201.2 (*C*=O)
Ph_2Pb	2-$MeOC_6H_4$	**3fd**	85	155-157	1612	3.87 (s, 6H, CH_3), 6.94-8.01 (m, 18H, arom)	56.0 (CH_3O), 112.2-*157.6* (arom), $^1J_{13C\text{-}207Pb}$ = 852 Hz, 200.7 (*C*=O)
Ph_2Pb	4-$MeOC_6H_4$	**3fe**	95	166-168	1611	3.77 (s, 6H, CH_3O) 6.85-8.05 (m, 18H, arom)	55.5 (CH_3O), 113.3-*157.9* (arom), $^1J_{13C\text{-}207Pb}$ = 859 Hz, 199.9 (*C*=O)
Ph_2Pb	3-ClC_6H_4	**3ff**	57	176-178	1610	7.25-7.95 (m, 18H, arom)	127.9-*157.6* (arom), $^1J_{13C\text{-}207Pb}$ = 849 Hz, 194.4 (*C*=O)
Ph_2Pb	4-ClC_6H_4	**3fg**	90	170-172	1618	7.28-7.97 (m, 18H, arom)	128.3-*157.8* (arom), $^1J_{13C\text{-}207Pb}$ = 846 Hz, 200.6 (*C*=O)
Ph_2Pb	4-$NO_2C_6H_4$	**3fh**	77	124-126	1608	7.36-8.01 (m, 18H, arom)	128.5-*158.9* (arom), $^1J_{13C\text{-}207Pb}$ = 859 Hz, 203.3 (*C*=O)
Ph_2Pb[f]	Me	**3fi**	59	93-95	1629	2.37 (s, 6H, CH_3), 7.36-7.82 (m, 10H, arom)	33.6 (CH_3), 130.0-*157.1* (arom), $^1J_{13C\text{-}207Pb}$ = 816 Hz, 206.2 (*C*=O)
Ph_2Pb[f]	*tert*-Bu	**3fj**	58	oil	1701	1.22 (s, 18H, CH_3), 7.36-7.81 (m, 10H, arom)	28.4 (CH_3) 48.2 (CCH_3), 129.9-*157.2* (arom), $^1J_{13C\text{-}207Pb}$ = 831 Hz, 217.4 (*C*=O)

[a]Isolated yields. [b]KBr. [c]90 MHz, $CDCl_3$, internal standard: MeSi. [d]270 MHz, $CDCl_3$, internal standard: MeSi. The italilc numbers of aromatic carbon show coupling with ^{207}Pb atom. [e]Ph_2PbCl_2 + 2 RCOSH. [f]Ph_2PbCl_2 + 2 K(SC(O)R).

Table S43. Energies of **1a** and **1m**, corresponding to Table 3 in the text, calculated with MP2/S-TZPsp without considering the solvent effect

Species (symm)	E_{ES}/au	ΔE_{ES}/au	ΔE_{ES}/unit[a]	E_{ZP}/au	ΔE_{ZP}/au	ΔE_{ES}/unit[a]	n*[b]
PhCOSI (**1a**$_{syn}$: C_1)	-7659.8997	(0.0000)	(0.0)	-7659.7983	(0.0000)	(0.0)	0
PhCOSI (**1a**$_{syn}$: C_s)	-7659.8995	(0.0002)	(0.6)	-7659.7981	(0.0001)	(0.3)	1
PhCOSI (**1a**$_{anti}$: C_1)	-7659.8937	(0.0061)	(15.9)	-7659.7924	(0.0058)	(15.3)	0
MeCOSI (**1m**$_{syn}$: C_1)	-7468.6581	(0.0000)	(0.0)	-7468.6096	(0.0000)	(0.0)	0
MeCOSI (**1m**$_{syn}$: C_s)	-7468.6578	(0.0004)	(1.0)	-7468.6094	(0.0003)	(0.7)	1
MeCOSI (**1m**$_{anti}$: C_s)	-7468.6549	(0.0033)	(8.6)	-7468.6062	(0.0035)	(9.1)	0

[a] kJ mol^{-1}. [b] The number of the imaginary frequency.

Table S44. Energies of the species appeared in Figs. S1 and S2 and the related ones, calculated without considering the solvent effect under MP2/S-TZPsp.

Species (sym)	E_{ES} au	ΔE_{ES} au	ΔE_{ES} kJ mol^{-1}	E_{ZP} au	ΔE_{ZP} au	ΔE_{ES} kJ mol^{-1}	n*[a]
Reaction of **14m** with CH_2=CH_2							
MeSI (**14m**$_s$: C_1)	-7355.5477			-7355.5082			0
CH_2CH_2 (D_{2h})	-78.3624			-78.3109			0
I^- (O_h)	-6918.1575			-6918.1575			0
II$^+$ (C_s)	-515.55797			-515.4846			0
14m$_{s:C1}$ + C_2H_4	-7433.9100	as 0.0000	as 0.0	-7433.8192	as 0.0000	as 0.0	(0)
I (C_s)	-7433.8875	0.0226	59.1	-7433.7921	0.0271	71.2	0
II$^+$ + I^-	-7433.7372	0.1728	453.7	-7433.6421	0.1771	465.0	0
IIIA	-7433.9486	-0.0386	-101.3	-7433.8526	-0.0334	-87.7	0
IIIA'	-7433.9464	-0.0364	-95.6	-7433.8503	-0.0311	-81.7	0
IA (TS1: C_1)	-7433.8869	0.0232	60.6	-7433.7932	0.0260	68.3	1
IC (TS2: C_1)	-7433.8716	0.0385	100.8	-7433.7772	0.0420	110.2	1
IF (TS4: C_1)	-7433.8447	0.0653	171.4	-7433.7511	0.0681	178.8	1
Reaction of **1m** with CH_2=CH_2							
MeCOSI (**1m**$_s$: C_1)	-7468.6581			-7468.6096			0
CH_2CH_2 (D_{2h})	-78.3624			-78.3109			0
I^- (O_h)	-6918.1575			-6918.1575			0
II$^+$ (C_s)	-628.6825			-628.5788			0
1m$_{s:C1}$ + C_2H_4	-7547.0205	as 0.0000	as 0.0	-7546.9206	as 0.0000	as 0.0	(0)
I (C_s)	-7546.9892	0.0313	82.0	-7546.8850	0.0356	93.4	0
II$^+$ + I^-	-7546.8400	0.1804	473.8	-7546.7364	0.1842	483.7	0
IIIA	-7547.0641	-0.0436	-114.6	-7546.9585	-0.0380	-99.6	0
IIIA'	-7547.0629	-0.0424	-111.2	-7546.9573	-0.0401	-105.4	0
IC (TS2: C_1)	-7546.9715	0.0489	128.5	-7546.8686	0.0519	136.4	1
IF (TS4: C_1)	-7546.9610	0.0595	156.1	-7546.8582	0.0621	163.0	1

[a] The number of the imaginary frequency.

Table S45. Energies of the species appeared in Scheme 5 and Figs. 4 and 5 of the text, calculated considering the solvent effect of acetonitrile under MP2/S-TZPsp.

Species (sym)	E_{ES} au	ΔE_{ES} au	ΔE_{ES} kJ mol^{-1}	E_{ZP} au	ΔE_{ZP} au	ΔE_{ES} kJ mol^{-1}	n*[b]
Reaction of **1m** with CH_2=CH_2							
MeCOSI (**1m**$_s$: C_1)	-7468.6632	(0.0000)	(0.0)	7468.6148	(0.0000)	(0.0)	0
CH_2CH_2 (D_{2h})	-78.3636			-78.3123			0
I^- (O_h)	-6918.2511			-6918.2511	---	---	---
II$^+$ (C_s)	-628.7634			-628.6594			0
1m$_{s:C1}$ + C_2H_4	-7547.0268	as 0.0000	as 0.0	-7546.9271	as 0.0000	as 0.0	(0)
I (C_s)	-7547.0261	0.0007	1.8	-7546.9221	0.0050	13.1	0
ID (C_1)	-7547.0229	0.0039	10.2	-7546.9190	0.0081	21.3	0
II$^+$ + I^-	-7547.0145	0.0123	32.4	-7546.9105	0.0166	43.6	0
IIIA	-7547.0699	-0.0431	-113.1	-7546.9645	-0.0374	-98.2	0
IIIA'	-7547.0689	-0.0421	-110.3	-7546.9635	-0.0364	-95.6	0
IA (TS1: C_1)	-7547.0066	0.0202	53.1	-7546.9044	0.0227	59.6	1
IC (TS2: C_1)	-7547.0219	0.0049	13.1	-7546.9180	0.0091	23.9	1
IE (TS3: C_1)	-7547.0189	0.0079	20.9	-7546.9154	0.0117	30.7	1
IF (TS4: C_1)	-7546.9836	0.0433	113.7	-7546.8806	0.0465	122.1	1
Reaction of **14m** with CH_2=CH_2							
MeSI (**14m**$_s$: C_1)	-7355.5505			-7355.5111			0
CH_2CH_2 (D_{2h})	-78.3636			-78.3123			0
I^- (O_h)	-6918.2511			-6918.2511	---	---	---
II$^+$ (C_s)	-515.6646			-515.5693			0
14m$_{s:C1}$ + C_2H_4	-7433.9141	as 0.0000	as 0.0	-7433.8234	as 0.0000	as 0.0	(0)
I (C_s)	-7433.9273	-0.0131	-34.5	-7433.8316	0.0082	-21.6	0
ID (C_1)	-7433.9237	-0.0096	-25.2	-7433.8282	-0.0048	-12.6	0
II$^+$ + I^-	-7433.9157	-0.0016	-4.2	-7433.8204	0.0030	7.8	0
IIIA	-7433.9535	-0.0394	-103.5	-7433.8574	-0.0340	-89.4	0
IIIA'	-7433.9525	-0.0384	-100.8	-7433.8564	-0.0330	-86.6	0
IA (TS1: C_1)	-7433.9010	0.0131	34.4	-7433.8074	0.0160	42.0	1
IC (TS2: C_1)	-7433.9230	-0.0089	-23.3	-7433.8276	-0.0042	-10.9	1
IE (TS3: C_1)	-7433.9143	-0.0002	-0.4	-7433.8194	0.0040	10.4	1
IF (TS4: C_1)	-7433.8739	0.0402	105.7	-7433.7797	0.0437	114.6	1

[a] The number of the imaginary frequency.

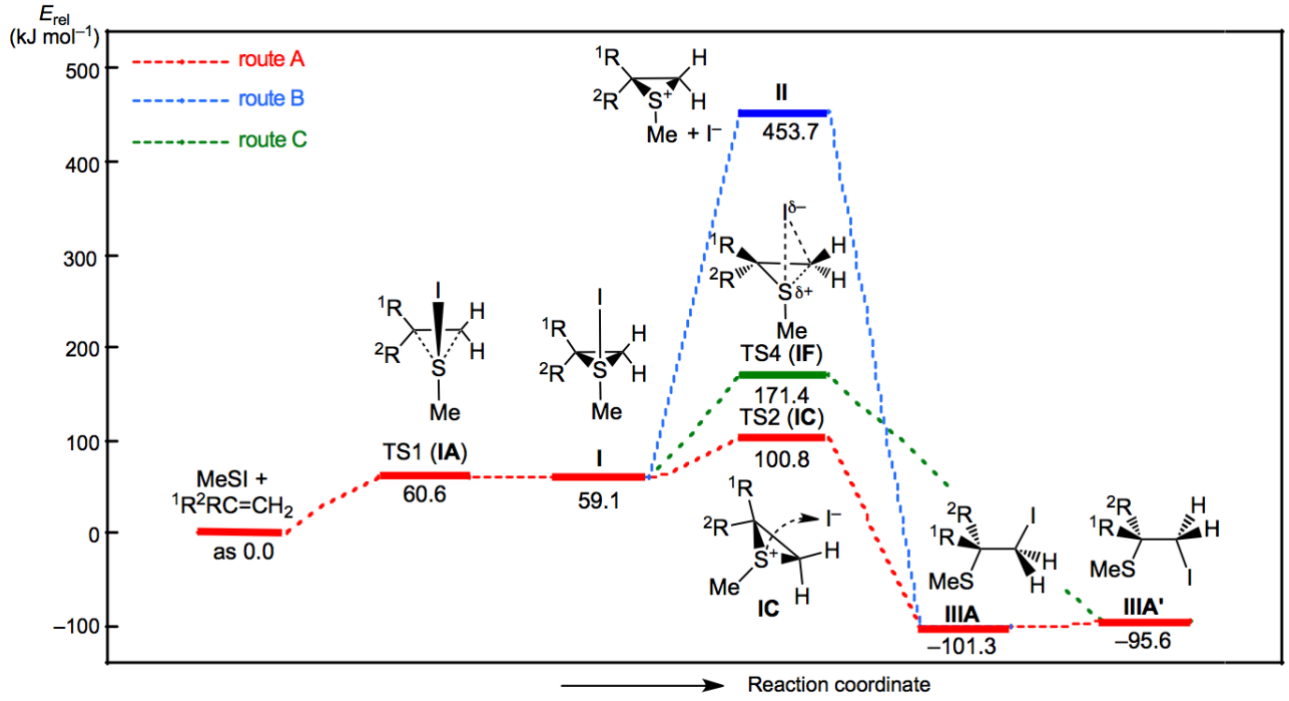


Fig. S1. Energy profile for the reaction of **14m** with CH_2=CH_2, calculated without considering the solvent effect under MP2/S-TZPsp.

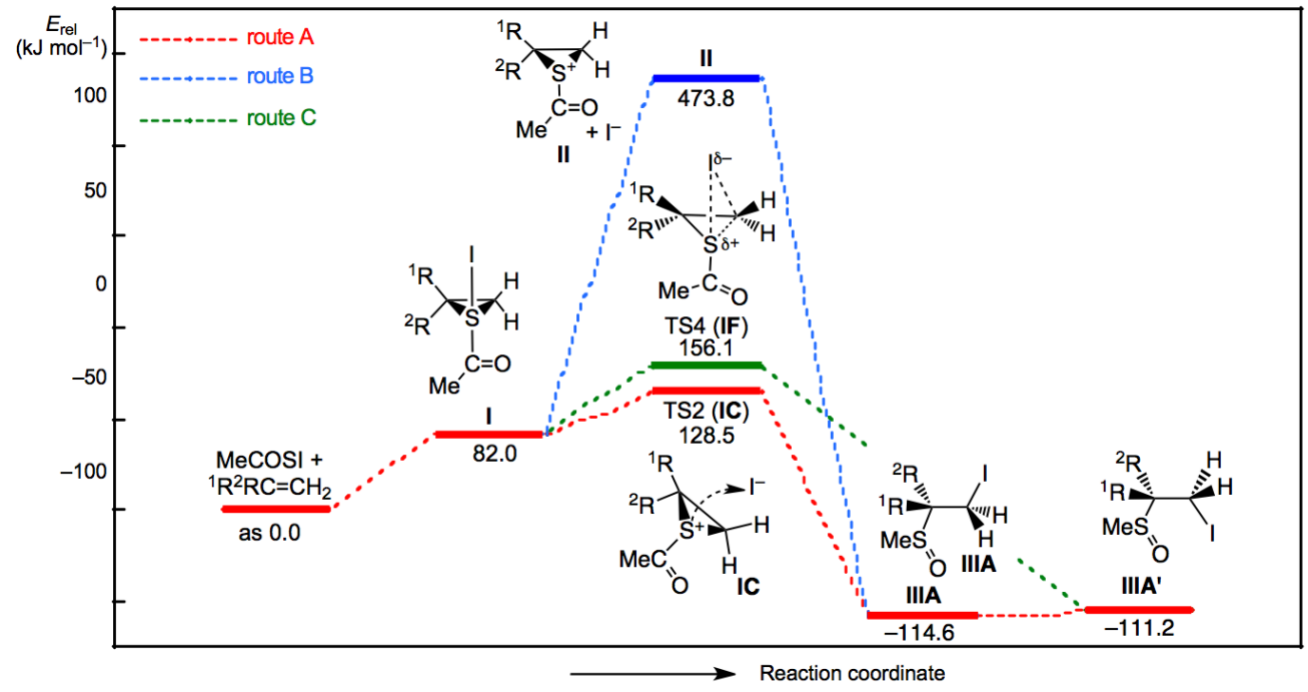


Fig. S2. Energy profile for the reaction of **1m** with CH_2=CH_2, calculated without considering the solvent effect under MP2/S-TZPsp.

Optimized structures given by Cartesian coordinates

Calculations were performed using the Gaussian 09 software package under nonrelativistic conditions. The basis sets of the (7433211/743111/7411/2+1s1p) form for I, the (63211/6111/31/2+1s1p) form for S and the (6211/311/21/2+1s1p) form for C and O with the (211/21/2) form for H were used for the calculations, as implemented in the Sapporo Basis Set Factory. The forms correspond to the Sapporo-TZP basis sets with the 1s1p diffusion functions, which are abbreviated by S-TZPsp, in this study. The Møller-Plesset second-order energy correlation (MP2) level was applied for the calculations (MP2/S-TZPsp). The species in question were optimized, and the optimized structures were confirmed by frequency analysis. An optimized structure containing only one imaginary frequency was assigned to a transition state (TS), while that with all real (positive) frequencies was assigned to the minimum structure.

The calculations were performed under the solvent effect of acetonitrile with SCRF (Self-Consistent Reaction Field) method (IEFPCM (polarizable continuum model using the integral equation formalism variant)) starting from the structures optimized without considering the solvent effect.

Optimized structures given by Cartesian coordinates for examined molecules, together with the total energies calculated with the MP2/BSS-A method of the Gaussian 09 program package.

MP2/S-TZPsp (no solvent effects)
Species **1a**$_{syn}$
Symmetry C_1
energy MP2 = –7659.899740 au
Standard orientation

6	0	-0.565671	0.524309	0.123628
8	0	-0.117076	1.624042	0.358237
16	0	0.465497	-0.915491	-0.277563
53	0	2.608843	0.016811	0.006135
6	0	-2.017751	0.197918	0.073566
6	0	-2.502480	-1.102901	0.263757
6	0	-2.906139	1.253783	-0.170347
6	0	-3.874962	-1.342579	0.203513
6	0	-4.274246	1.003309	-0.236431
6	0	-4.760867	-0.293779	-0.050792
1	0	-1.820679	-1.913481	0.485700
1	0	-2.509889	2.250858	-0.306767
1	0	-4.251389	-2.344395	0.360670
1	0	-4.960758	1.816202	-0.431904
1	0	-5.824599	-0.485018	-0.099107

MP2/S-TZPsp (no solvent effects)
Species **1a**$_{syn}$ (TS)
Symmetry C_s
energy MP2 = –7659.899530 au
Standard orientation

6	0	0.000000	0.759503	0.000000
8	0	-1.138151	1.172619	0.000000
16	0	0.405072	-1.014133	0.000000
53	0	-1.764108	-1.924870	0.000000
6	0	1.207798	1.633475	0.000000
6	0	2.512789	1.123821	0.000000

6	0	0.994851	3.018480	0.000000
6	0	3.597468	1.999212	0.000000
6	0	2.083960	3.886142	0.000000
6	0	3.386267	3.379663	0.000000
1	0	2.689000	0.055955	0.000000
1	0	-0.020509	3.390259	0.000000
1	0	4.604524	1.604483	0.000000
1	0	1.918932	4.955286	0.000000
1	0	4.231060	4.055512	0.000000

MP2/S-TZPsp (no solvent effects)
Species **1a**$_{anti}$
Symmetry C_1
energy MP2 = –7659.893674 au
Standard orientation

6	0	-0.544153	1.765618	0.100720
8	0	-0.877772	2.920444	-0.062838
16	0	1.225790	1.504590	0.436400
53	0	1.709722	-0.728986	-0.201404
6	0	-1.471224	0.608440	0.090752
6	0	-1.440711	-0.350912	1.109031
6	0	-2.429930	0.538067	-0.926382
6	0	-2.379054	-1.381031	1.108123
6	0	-3.342814	-0.515077	-0.937795
6	0	-3.320110	-1.472590	0.079413
1	0	-0.706831	-0.273499	1.900409
1	0	-2.447941	1.300077	-1.694511
1	0	-2.371974	-2.114716	1.903020
1	0	-4.074773	-0.584165	-1.731285
1	0	-4.036234	-2.283507	0.073890

MP2/S-TZPsp (no solvent effects)
Species **1m**$_{syn}$
Symmetry C_1
energy MP2 = –7468.658142 au
Standard orientation

6	0	3.363327	-0.141805	0.020069
1	0	3.924989	0.384983	-0.748546
1	0	3.435026	-1.215544	-0.137570
1	0	3.787962	0.107948	0.991445
6	0	1.934148	0.350706	-0.009713
8	0	1.602073	1.510500	-0.016560
16	0	0.782657	-1.043133	-0.014187
53	0	-1.288150	0.076893	0.003623

MP2/S-TZPsp (no solvent effects)
Species **1m**$_{syn}$ (TS)
Symmetry C_s
energy MP2 = –7468.657763 au
Standard orientation

6	0	-0.063949	-3.366538	0.000000
1	0	-0.961726	-3.978005	0.000000
1	0	0.535823	-3.585715	0.882076
1	0	0.535823	-3.585715	-0.882076
6	0	-0.471878	-1.911060	0.000000
8	0	-1.605459	-1.499356	0.000000
16	0	0.996795	-0.843869	0.000000

53	0	0.000000	1.288901	0.000000

MP2/S-TZPsp (no solvent effects)
Species **1m**$_{anti}$
Symmetry C_s
energy MP2 = –7468.654857 au
Standard orientation

6	0	1.706107	-1.711081	0.000000
1	0	2.305949	-2.616838	0.000000
1	0	1.930997	-1.108414	0.878317
1	0	1.930997	-1.108414	-0.878317
6	0	0.260845	-2.114086	0.000000
8	0	-0.153319	-3.252016	0.000000
16	0	-1.046444	-0.857352	0.000000
53	0	0.000000	1.273933	0.000000

MP2/S-TZPsp (no solvent effects)
Species **14m**
Symmetry C_s
energy MP2 = –7355.547689 au
Standard orientation

6	0	-1.011358	-2.234509	0.000000
1	0	-0.820251	-3.307536	0.000000
1	0	-1.567050	-1.962948	0.893071
1	0	-1.567050	-1.962948	-0.893071
16	0	0.626406	-1.458651	0.000000
53	0	0.000000	0.829790	0.000000

MP2/S-TZPsp (no solvent effects)
Species **4** (CH_2=CH_2)
Symmetry D_{2h}
energy MP2 = –78.362351 au
Standard orientation

6	0	0.000000	0.000000	0.667050
1	0	0.000000	0.922948	1.229276
1	0	0.000000	-0.922948	1.229276
6	0	0.000000	0.000000	-0.667050
1	0	0.000000	-0.922948	-1.229276
1	0	0.000000	0.922948	-1.229276

MP2/S-TZPsp (no solvent effects)
Species I^-
Symmetry O_h
energy MP2 = –6918.157547 au
Standard orientation

53	0	0.000000	0.000000	0.000000

MP2/S-TZPsp (no solvent effects)
Species TS2 (**IC**): **1m** + **4**
Symmetry C_1
energy MP2 = –7546.971548 au
Standard orientation

6	0	-4.792833	-0.353082	-0.000014
1	0	-5.587433	0.387165	0.000001
1	0	-4.864627	-0.991485	-0.880755

1	0	-4.864627	-0.991524	0.880699
6	0	-3.467857	0.338246	-0.000002
8	0	-3.223255	1.505525	0.000001
16	0	-2.038670	-0.923707	0.000009
53	0	2.523663	0.015810	-0.000002
6	0	-0.696279	0.194137	-0.723602
1	0	0.080910	-0.400430	-1.194728
1	0	-1.137439	1.026581	-1.255824
6	0	-0.696294	0.194144	0.723613
1	0	0.080893	-0.400407	1.194762
1	0	-1.137466	1.026594	1.255815

MP2/S-TZPsp (no solvent effects)
Species TS4 (**IF**): **1m** + **4**
Symmetry C_1
energy MP2 = –7546.961032 au
Standard orientation

6	0	1.323910	2.293070	-0.341223
1	0	0.262062	2.178692	-0.577675
1	0	1.472980	3.111727	0.356639
1	0	1.876560	2.459690	-1.265668
6	0	1.748734	1.012554	0.291856
8	0	2.035841	0.789965	1.433616
16	0	1.777614	-0.362904	-0.977373
53	0	-1.690624	0.005778	0.004426
6	0	2.138801	-1.739403	0.182226
1	0	2.511217	-2.571278	-0.404088
1	0	2.794695	-1.396699	0.974558
6	0	0.714901	-1.722752	0.459547
1	0	0.048421	-2.381083	-0.074605
1	0	0.350503	-1.281378	1.370837

MP2/S-TZPsp (no solvent effects)
Species **I**: **1m** + **4**
Symmetry C_s
energy MP2 = –7546.989243 au
Standard orientation

6	0	3.109498	2.284237	0.000000
1	0	3.624343	3.240428	0.000000
1	0	3.386488	1.699728	0.878353
1	0	3.386488	1.699728	-0.878353
6	0	1.627111	2.501068	0.000000
8	0	1.041481	3.548798	0.000000
16	0	0.719672	0.788873	0.000000
53	0	-0.840188	-1.887481	0.000000
6	0	-0.840188	1.464608	0.732337
1	0	-1.345662	0.642868	1.224495
1	0	-0.680001	2.405697	1.240311
6	0	-0.840188	1.464608	-0.732337
1	0	-1.345662	0.642868	-1.224495
1	0	-0.680001	2.405697	-1.240311

MP2/S-TZPsp (no solvent effects)
Species **II**$^+$: [MeC(=O)S + **4**]$^+$
Symmetry C_s
energy MP2 = –628.682476 au
Standard orientation

6	0	-0.022196	-2.394867	0.000000
1	0	0.789421	-3.117399	0.000000
1	0	-0.650767	-2.517572	0.882882
1	0	-0.650767	-2.517572	-0.882882
6	0	0.543646	-1.023551	0.000000
8	0	1.630378	-0.574034	0.000000
16	0	-0.986710	0.320159	0.000000
6	0	-0.022196	1.715636	0.732952
1	0	-0.673123	2.397419	1.262488
1	0	0.870176	1.375151	1.241902
6	0	-0.022196	1.715636	-0.732952
1	0	-0.673123	2.397419	-1.262488
1	0	0.870176	1.375151	-1.241902

MP2/S-TZPsp (no solvent effects)
Species **IIIA**: **1m** + **4**
Symmetry C_1
energy MP2 = –7547.064141 au
Standard orientation

6	0	4.426634	-0.595205	0.276388
1	0	4.620544	-1.531683	0.793422
1	0	4.988552	-0.590891	-0.657629
1	0	4.750601	0.248520	0.881312
6	0	2.957030	-0.512390	-0.056164
8	0	2.272350	-1.471054	-0.355146
16	0	2.316192	1.155796	-0.011345
53	0	-2.211478	-0.127741	0.000418
6	0	0.615349	0.804374	-0.536891
1	0	0.211102	1.743329	-0.910754
1	0	0.661390	0.084357	-1.351423
6	0	-0.199173	0.267518	0.621798
1	0	-0.262094	0.981865	1.436633
1	0	0.201333	-0.675291	0.978188

MP2/S-TZPsp (no solvent effects)
Species **IIIA'**: **1m** + **4**
Symmetry C_1
energy MP2 = –7547.062854 au
Standard orientation

6	0	3.705948	-1.169534	-0.466650
1	0	3.338546	-1.791443	-1.282969
1	0	4.681917	-0.777638	-0.742754
1	0	3.780529	-1.779571	0.430553
6	0	2.748901	-0.017106	-0.283784
8	0	2.755596	0.984614	-0.975058
16	0	1.571682	-0.283337	1.028086
53	0	-1.888180	-0.248291	-0.118217
6	0	0.612875	1.236634	0.834908
1	0	0.084015	1.382362	1.775275
1	0	1.328137	2.048310	0.694475
6	0	-0.343918	1.213206	-0.342809
1	0	0.175614	0.984173	-1.267042
1	0	-0.849723	2.170486	-0.440920

MP2/S-TZPsp (no solvent effects)
Species TS2 (**IC**): **14m** + **4**
Symmetry C_1

energy MP2 = –7433.871553 au
Standard orientation

6	0	-4.073542	0.517083	0.000001
1	0	-3.667395	1.524704	-0.000001
1	0	-4.670546	0.347718	-0.891772
1	0	-4.670559	0.347728	0.891768
16	0	-2.717247	-0.681323	0.000017
53	0	1.909838	0.003083	-0.000006
6	0	-1.319168	0.309718	0.730030
1	0	-1.672847	1.168808	1.283138
1	0	-0.559992	-0.319475	1.185367
6	0	-1.319170	0.309699	-0.730027
1	0	-1.672849	1.168775	-1.283156
1	0	-0.559993	-0.319506	-1.185348

MP2/S-TZPsp (no solvent effects)
Species TS4 (**IF**): **14m** + **4**
Symmetry C_1
energy MP2 = –7433.844714 au
Standard orientation

6	0	-3.485627	-0.611132	-0.222175
1	0	-3.737039	0.170719	-0.939418
1	0	-3.716927	-1.578662	-0.661701
1	0	-4.048545	-0.467919	0.698062
16	0	-1.693314	-0.597544	0.103850
53	0	1.510653	-0.118742	-0.006110
6	0	-1.589517	1.141059	0.697282
1	0	-2.598229	1.513653	0.851099
1	0	-0.933784	1.227665	1.553566
6	0	-0.975262	1.420192	-0.589754
1	0	-1.625065	1.413899	-1.456418
1	0	-0.009532	1.873961	-0.695097

MP2/S-TZPsp (no solvent effects)
Species **I**: **14m** + **4**
Symmetry C_s
energy MP2 = –7433.887468 au
Standard orientation

6	0	1.918112	-2.925322	0.000000
1	0	2.960418	-2.619799	0.000000
1	0	1.696302	-3.510112	0.889293
1	0	1.696302	-3.510112	-0.889293
16	0	0.773841	-1.484123	0.000000
53	0	-1.158555	1.025886	0.000000
6	0	1.918112	-0.254772	-0.738912
1	0	2.740520	-0.711428	-1.271372
1	0	1.330943	0.523030	-1.212661
6	0	1.918112	-0.254772	0.738912
1	0	2.740520	-0.711428	1.271372
1	0	1.330943	0.523030	1.212661

MP2/S-TZPsp (no solvent effects)
Species **II**$^+$: [MeCS + **4**]$^+$
Symmetry C_s
energy MP2 = –515.579667 au
Standard orientation

6	0	-0.392377	1.637757	0.000000

1	0	-1.434027	1.329250	0.000000
1	0	-0.155202	2.209521	0.893391
1	0	-0.155202	2.209521	-0.893391
16	0	0.681800	0.181526	0.000000
6	0	-0.392377	-1.112512	-0.738245
1	0	-1.240178	-0.702397	-1.269041
1	0	0.189384	-1.862153	-1.256721
6	0	-0.392377	-1.112512	0.738245
1	0	-1.240178	-0.702397	1.269041
1	0	0.189384	-1.862153	1.256721

MP2/S-TZPsp (no solvent effects)
Species **IIIA**: **14m** + **4**
Symmetry C_1
energy MP2 = –7433.948634 au
Standard orientation

6	0	3.357369	1.154015	-0.144169
1	0	2.788555	1.793079	0.526731
1	0	4.415859	1.276085	0.073837
1	0	3.173591	1.440076	-1.178117
16	0	2.970492	-0.596208	0.102872
53	0	-1.708505	0.050401	-0.033263
6	0	1.236081	-0.591096	-0.428215
1	0	1.154850	-0.066529	-1.380429
1	0	0.967221	-1.632881	-0.597824
6	0	0.335329	0.026623	0.622362
1	0	0.591960	1.061332	0.825598
1	0	0.358179	-0.540313	1.547352

MP2/S-TZPsp (no solvent effects)
Species **IIIA'**: **14m** + **4**
Symmetry C_1
energy MP2 = –7433.946449 au
Standard orientation

6	0	2.619639	-0.910565	0.869136
1	0	1.732417	-1.291666	1.370962
1	0	3.292241	-1.742404	0.672816
1	0	3.131613	-0.187910	1.503364
16	0	2.209807	-0.184288	-0.733542
53	0	-1.351609	-0.170146	-0.048183
6	0	1.346127	1.301387	-0.173728
1	0	2.062168	1.959084	0.327121
1	0	1.011584	1.798610	-1.083982
6	0	0.177508	1.076746	0.770333
1	0	-0.302034	2.022443	1.010091
1	0	0.490726	0.602762	1.695550

MP2/S-TZPsp (solvent effects: acetonitrile)
Species **1m**
Symmetry C_1
energy MP2 = –7468.663243 au
Standard orientation

6	0	-3.365265	-0.144667	0.000008
1	0	-3.862707	0.249674	0.884437
1	0	-3.428189	-1.229916	-0.000061
1	0	-3.862770	0.249797	-0.884330
6	0	-1.940475	0.348706	-0.000003

8	0	-1.605895	1.511169	-0.000007
16	0	-0.787063	-1.037940	-0.000006
53	0	1.291099	0.075923	0.000001

MP2/S-TZPsp (solvent effects: acetonitrile)
Species **14m**
Symmetry C_s
energy MP2 = –7355.550528 au
Standard orientation

6	0	-1.009137	-2.245702	0.000000
1	0	-0.805936	-3.316141	0.000000
1	0	-1.564054	-1.977629	0.893987
1	0	-1.564054	-1.977629	-0.893987
16	0	0.624304	-1.459898	0.000000
53	0	0.000000	0.832151	0.000000

MP2/S-TZPsp (solvent effects: acetonitrile)
Species **4** (CH_2=CH_2)
Symmetry D_{2h}
energy MP2 = –78.363605 au
Standard orientation

6	0	0.000000	0.000000	0.667663
1	0	0.000000	0.923470	1.229746
1	0	0.000000	-0.923470	1.229746
6	0	0.000000	0.000000	-0.667663
1	0	0.000000	-0.923470	-1.229746
1	0	0.000000	0.923470	-1.229746

MP2/S-TZPsp (solvent effects: acetonitrile)
Species I^-
Symmetry O_h
energy MP2 = –6918.251147 au
Standard orientation

53	0	0.000000	0.000000	0.000000

MP2/S-TZPsp (solvent effects: acetonitrile)
Species TS1 (**IA**): **1m** + **4**
Symmetry C_1
energy MP2 = –7547.006607 au
Standard orientation

6	0	0.873199	2.057888	-0.847999
1	0	1.818759	2.238613	-1.363526
1	0	0.156747	1.659349	-1.556241
1	0	0.521857	2.994692	-0.422610
6	0	1.166049	1.087228	0.260257
8	0	1.613821	1.364845	1.339428
16	0	0.901983	-0.724023	-0.205531
53	0	-1.704489	-0.172433	0.022083
6	0	3.108730	-0.735658	-0.743027
1	0	3.144901	-1.383376	-1.606456
1	0	3.397553	0.297613	-0.877182
6	0	2.880396	-1.250718	0.523567
1	0	2.778352	-2.316704	0.667728
1	0	3.007212	-0.638051	1.404175

MP2/S-TZPsp (solvent effects: acetonitrile)
Species TS2 (**IC**): **1m** + **4**
Symmetry C_1
energy MP2 = –7547.021868 au
Standard orientation

6	0	4.998514	-0.173292	-0.000006
1	0	5.743790	0.615633	-0.000008
1	0	5.101456	-0.805318	0.881909
1	0	5.101453	-0.805318	-0.881922
6	0	3.641832	0.429270	-0.000003
8	0	3.265122	1.552531	0.000000
16	0	2.285717	-0.989986	-0.000003
53	0	-2.724395	0.041605	-0.000001
6	0	0.911274	0.012625	0.729735
1	0	0.203620	-0.623559	1.240038
1	0	1.284646	0.884575	1.248853
6	0	0.911263	0.012631	-0.729710
1	0	0.203600	-0.623548	-1.240004
1	0	1.284622	0.884587	-1.248825

MP2/S-TZPsp (solvent effects: acetonitrile)
Species TS3 (**IE**): **1m** + **4**
Symmetry C_1
energy MP2 = –7547.018900 au
Standard orientation

6	0	4.426115	-0.698761	-0.470535
1	0	5.072839	-0.027153	0.093263
1	0	4.781232	-1.721715	-0.395873
1	0	4.421991	-0.369226	-1.509121
6	0	3.040744	-0.615278	0.075825
8	0	2.363675	-1.475923	0.558041
16	0	2.359388	1.139690	-0.068324
53	0	-2.359228	-0.146251	-0.051307
6	0	0.812464	0.876860	0.891840
1	0	0.923898	0.054053	1.585849
1	0	0.473547	1.816657	1.305528
6	0	0.412445	0.554202	-0.461719
1	0	0.510795	-0.455064	-0.824976
1	0	0.044564	1.323971	-1.118991

MP2/S-TZPsp (solvent effects: acetonitrile)
Species TS4 (**IF**): **1m** + **4**
Symmetry C_1
energy MP2 = –7546.983556 au
Standard orientation

6	0	1.638609	2.294796	-0.275682
1	0	0.610744	2.386758	-0.629914
1	0	1.840299	3.049577	0.478517
1	0	2.308530	2.411376	-1.126018
6	0	1.780786	0.934594	0.330400
8	0	1.834019	0.661129	1.504478
16	0	1.847183	-0.363115	-0.953756
53	0	-1.694918	0.065736	-0.023014
6	0	1.980336	-1.821102	0.168253
1	0	2.342089	-2.632681	-0.454273
1	0	2.616124	-1.563392	1.006865
6	0	0.565832	-1.855604	0.440098
1	0	-0.089434	-2.438919	-0.186839

1	0	0.181836	-1.492028	1.377264

MP2/S-TZPsp (solvent effects: acetonitrile)
Species **I**: **1m** + **4**
Symmetry C_1
energy MP2 = –7547.026112 au
Standard orientation

6	0	3.885200	-1.545108	0.000003
1	0	4.967415	-1.464098	-0.000003
1	0	3.536265	-2.083107	0.881515
1	0	3.536250	-2.083128	-0.881489
6	0	3.285415	-0.185352	-0.000006
8	0	3.782208	0.893795	-0.000018
16	0	1.339012	-0.323816	0.000004
53	0	-2.315159	-0.152881	-0.000002
6	0	1.008897	1.337683	0.731660
1	0	0.052226	1.317799	1.235009
1	0	1.873393	1.729340	1.249125
6	0	1.008889	1.337685	-0.731640
1	0	0.052213	1.317809	-1.234980
1	0	1.873381	1.729343	-1.249111

MP2/S-TZPsp (solvent effects: acetonitrile)
Species **ID**: **1m** + **4**
Symmetry C_1
energy MP2 = –7547.022919 au
Standard orientation

6	0	-4.600585	0.760823	-0.000038
1	0	-4.930911	1.794510	-0.000028
1	0	-4.967292	0.235649	-0.881625
1	0	-4.967348	0.235613	0.881503
6	0	-3.116683	0.716108	0.000007
8	0	-2.293685	1.569228	0.000044
16	0	-2.507830	-1.145612	-0.000002
53	0	2.492447	0.143100	-0.000004
6	0	-0.827010	-0.818327	-0.727559
1	0	-0.471742	-1.691079	-1.254701
1	0	-0.794007	0.133279	-1.237679
6	0	-0.827024	-0.818343	0.727588
1	0	-0.471765	-1.691106	1.254717
1	0	-0.794029	0.133252	1.237729

MP2/S-TZPsp (solvent effects: acetonitrile)
Species **II**: $[MeC(=O)S + \mathbf{4}]^+$
Symmetry C_s
energy MP2 = –628.763351 au
Standard orientation

6	0	-0.024596	-2.376512	0.000000
1	0	0.794022	-3.088995	0.000000
1	0	-0.651506	-2.503772	0.882338
1	0	-0.651506	-2.503772	-0.882338
6	0	0.522899	-0.998437	0.000000
8	0	1.622765	-0.564772	0.000000
16	0	-0.970248	0.303901	0.000000
6	0	-0.024596	1.708342	0.732237
1	0	-0.687731	2.379582	1.257503
1	0	0.865812	1.371367	1.244379

6	0	-0.024596	1.708342	-0.732237
1	0	-0.687731	2.379582	-1.257503
1	0	0.865812	1.371367	-1.244379

MP2/S-TZPsp (solvent effects: acetonitrile)
Species **IIIA**: **1m** + **4**
Symmetry C_1
energy MP2 = –7547.069918 au
Standard orientation

6	0	4.409672	-0.613039	0.291262
1	0	4.563419	-1.481061	0.928290
1	0	4.971562	-0.757530	-0.631419
1	0	4.769486	0.285091	0.786523
6	0	2.948124	-0.514584	-0.059508
8	0	2.256706	-1.469560	-0.368375
16	0	2.318886	1.152057	-0.017329
53	0	-2.205371	-0.133096	0.001540
6	0	0.613936	0.825960	-0.541252
1	0	0.224625	1.770883	-0.914852
1	0	0.650276	0.105259	-1.355215
6	0	-0.200189	0.307497	0.625637
1	0	-0.283505	1.041629	1.420274
1	0	0.203708	-0.621633	1.012208

MP2/S-TZPsp (solvent effects: acetonitrile)
Species **IIIA'**: **1m** + **4**
Symmetry C_1
energy MP2 = –7547.068873 au
Standard orientation

6	0	3.698055	-1.191730	-0.435836
1	0	3.343410	-1.813159	-1.258332
1	0	4.686441	-0.814674	-0.687620
1	0	3.743152	-1.797317	0.465849
6	0	2.751643	-0.029749	-0.284488
8	0	2.766566	0.957217	-1.000452
16	0	1.572780	-0.247798	1.031129
53	0	-1.886791	-0.254131	-0.113173
6	0	0.607893	1.264349	0.809140
1	0	0.083885	1.428362	1.748761
1	0	1.316268	2.078422	0.652588
6	0	-0.351357	1.216637	-0.364620
1	0	0.159415	0.970593	-1.289147
1	0	-0.867056	2.166723	-0.473576

MP2/S-TZPsp (solvent effects: acetonitrile)
Species TS1 (**IA**): **14m** + **4**
Symmetry C_1
energy MP2 = –7433.901026 au
Standard orientation

6	0	-1.221906	1.590055	0.000000
1	0	-2.265566	1.888396	-0.000002
1	0	-0.726070	1.962058	0.890308
1	0	-0.726063	1.962061	-0.890304
16	0	-1.123141	-0.238335	-0.000004
53	0	1.537291	-0.090043	0.000001
6	0	-3.257755	-0.419150	-0.691088
1	0	-3.436893	0.483439	-1.256655

1	0	-3.245066	-1.352128	-1.234998
6	0	-3.257761	-0.419150	0.691092
1	0	-3.436901	0.483439	1.256658
1	0	-3.245075	-1.352130	1.234997

MP2/S-TZPsp (solvent effects: acetonitrile)
Species TS2 (**IC**): **14m** + **4**
Symmetry C_1
energy MP2 = –7433.923024 au
Standard orientation

6	0	-4.276846	0.590012	-0.000001
1	0	-3.826555	1.577467	0.000023
1	0	-4.872560	0.433382	-0.893766
1	0	-4.872580	0.433347	0.893745
16	0	-2.982300	-0.667489	-0.000010
53	0	2.096977	0.011097	-0.000001
6	0	-1.559468	0.229780	0.735628
1	0	-1.860629	1.118519	1.270686
1	0	-0.877716	-0.443583	1.233282
6	0	-1.559459	0.229801	-0.735603
1	0	-1.860608	1.118557	-1.270639
1	0	-0.877700	-0.443548	-1.233266

MP2/S-TZPsp (solvent effects: acetonitrile)
Species TS3 (**IE**): **14m** + **4**
Symmetry C_1
energy MP2 = –7433.914292 au
Standard orientation

6	0	-3.516816	1.147231	0.099145
1	0	-2.682949	1.838688	0.018112
1	0	-4.258370	1.372177	-0.661614
1	0	-3.960040	1.194625	1.088938
16	0	-2.953201	-0.544883	-0.205401
53	0	1.832222	0.068104	-0.000099
6	0	-1.415504	-0.556723	0.788520
1	0	-1.420684	0.214657	1.547330
1	0	-1.201589	-1.550664	1.157871
6	0	-0.874142	-0.217377	-0.518471
1	0	-0.869506	0.802728	-0.862652
1	0	-0.624667	-1.002397	-1.211470

MP2/S-TZPsp (solvent effects: acetonitrile)
Species TS4 (**IF**): **14m** + **4**
Symmetry C_1
energy MP2 = –7433.873888 au
Standard orientation

6	0	1.791593	-1.521993	0.688625
1	0	0.797853	-1.326721	1.087989
1	0	1.803054	-2.512480	0.237553
1	0	2.563975	-1.453188	1.449806
16	0	2.147592	-0.389740	-0.664111
53	0	-1.463791	-0.034898	-0.027721
6	0	2.404463	1.194185	0.249449
1	0	2.924412	1.006260	1.181462
1	0	2.950594	1.836432	-0.433663
6	0	0.997443	1.498806	0.346442
1	0	0.489019	1.423015	1.291078

1	0	0.529551	2.086140	-0.426350

MP2/S-TZPsp (solvent effects: acetonitrile)
Species **I**: **14m** + **4**
Symmetry C_s
energy MP2 = –7433.927278 au
Standard orientation

6	0	1.966491	-3.231042	0.000000
1	0	3.005344	-2.916678	0.000000
1	0	1.734728	-3.803406	0.893002
1	0	1.734728	-3.803406	-0.893002
16	0	0.877391	-1.786116	0.000000
53	0	-1.212526	1.245459	0.000000
6	0	1.966491	-0.511692	-0.737554
1	0	2.803093	-0.937778	-1.271128
1	0	1.373903	0.247062	-1.228847
6	0	1.966491	-0.511692	0.737554
1	0	2.803093	-0.937778	1.271128
1	0	1.373903	0.247062	1.228847

MP2/S-TZPsp (solvent effects: acetonitrile)
Species **ID**: **14m** + **4**
Symmetry C_1
energy MP2 = –7433.923742 au
Standard orientation

6	0	-3.684160	1.187735	0.000036
1	0	-2.814716	1.837589	0.000032
1	0	-4.281644	1.337387	-0.893823
1	0	-4.281638	1.337390	0.893898
16	0	-3.148577	-0.536236	0.000037
53	0	2.007656	0.065029	-0.000027
6	0	-1.462236	-0.409273	0.733559
1	0	-1.311647	0.520538	1.260555
1	0	-1.187718	-1.317668	1.248118
6	0	-1.462239	-0.409275	-0.733494
1	0	-1.311653	0.520534	-1.260493
1	0	-1.187724	-1.317672	-1.248052

MP2/S-TZPsp (solvent effects: acetonitrile)
Species **II**: $[MeS + \mathbf{4}]^+$
Symmetry C_s
energy MP2 = –515.664590 au
Standard orientation

6	0	-0.393791	1.627430	0.000000
1	0	-1.432242	1.311314	0.000000
1	0	-0.159096	2.196734	0.893966
1	0	-0.159096	2.196734	-0.893966
16	0	0.683992	0.179279	0.000000
6	0	-0.393791	-1.104442	-0.737846
1	0	-1.236313	-0.684369	-1.266604
1	0	0.183706	-1.857897	-1.252062
6	0	-0.393791	-1.104442	0.737846
1	0	-1.236313	-0.684369	1.266604
1	0	0.183706	-1.857897	1.252062

MP2/S-TZPsp (solvent effects: acetonitrile)

Species **IIIA**: **14m** + **4**
Symmetry C_1
energy MP2 = –7433.953540 au
Standard orientation

6	0	3.364145	1.151446	-0.149929
1	0	2.801573	1.791663	0.523975
1	0	4.424997	1.266361	0.059051
1	0	3.169766	1.430860	-1.183067
16	0	2.967764	-0.596421	0.106943
53	0	-1.708889	0.049797	-0.033003
6	0	1.232688	-0.598826	-0.425303
1	0	1.158371	-0.087778	-1.384840
1	0	0.963808	-1.643560	-0.573613
6	0	0.339720	0.042311	0.616855
1	0	0.591188	1.082662	0.794127
1	0	0.357882	-0.506288	1.552691

MP2/S-TZPsp (solvent effects: acetonitrile)
Species **IIIA'**: **14m** + **4**
Symmetry C_1
energy MP2 = –7433.952537 au
Standard orientation

6	0	2.716998	-0.846033	0.881117
1	0	1.863829	-1.214100	1.445966
1	0	3.397103	-1.673455	0.693436
1	0	3.238788	-0.076394	1.446717
16	0	2.211180	-0.209802	-0.734346
53	0	-1.368258	-0.172233	-0.039250
6	0	1.334466	1.285044	-0.216785
1	0	2.048930	1.959898	0.260713
1	0	0.989265	1.754333	-1.137276
6	0	0.181191	1.077274	0.747262
1	0	-0.294161	2.026830	0.976830
1	0	0.499093	0.610354	1.673823

Appendix

QTAIM Dual Functional Analysis (QTAIM-DFA)

The bond critical point (BCP; ∗) is an important concept in QTAIM. The BCP of $(\omega, \sigma) = (3, -1)$[SA1] is a point along the bond path (BP) at the interatomic surface, where charge density $\rho(\boldsymbol{r})$ reaches a minimum. It is donated by $\rho_b(\boldsymbol{r}_c)$, so are other QTAIM functions, such as the total electron energy densities $H_b(\boldsymbol{r}_c)$, potential energy densities $V_b(\boldsymbol{r}_c)$ and kinetic energy densities $G_b(\boldsymbol{r}_c)$ at the BCPs. A chemical bond or interaction between A and B is denoted by A–B, which corresponds to the BP between A and B in QTAIM. We will use A-∗-B for BP, where the asterisk emphasizes the presence of a BCP in A–B.

The sign of the Laplacian $\rho_b(\boldsymbol{r}_c)$ ($\nabla^2\rho_b(\boldsymbol{r}_c)$) indicates that $\rho_b(\boldsymbol{r}_c)$ is depleted or concentrated with respect to its surrounding, since $\nabla^2\rho_b(\boldsymbol{r}_c)$ is the second derivative of $\rho_b(\boldsymbol{r}_c)$. $\rho_b(\boldsymbol{r}_c)$ is locally depleted relative to the average distribution around $\boldsymbol{r}_c$ if $\nabla^2\rho_b(\boldsymbol{r}_c) > 0$, but it is concentrated when $\nabla^2\rho_b(\boldsymbol{r}_c) < 0$. Total electron energy densities at BCPs ($H_b(\boldsymbol{r}_c)$) must be a more appropriate measure for weak interactions on the energy basis.[SA1–SA8] $H_b(\boldsymbol{r}_c)$ are the sum of kinetic energy densities ($G_b(\boldsymbol{r}_c)$) and potential energy densities ($V_b(\boldsymbol{r}_c)$) at BCPs, as shown in eqn (SA1). Electrons at BCPs are stabilized when $H_b(\boldsymbol{r}_c) < 0$, therefore, interactions exhibit the covalent nature in this region, whereas they exhibit no covalency if $H_b(\boldsymbol{r}_c) > 0$, due to the destabilization of electrons at BCPs under the conditions.[SA1] Eqn (SA2) represents the relation between $\nabla^2\rho_b(\boldsymbol{r}_c)$ and $H_b(\boldsymbol{r}_c)$, together with $G_b(\boldsymbol{r}_c)$ and $V_b(\boldsymbol{r}_c)$, which is closely related to the virial theorem.

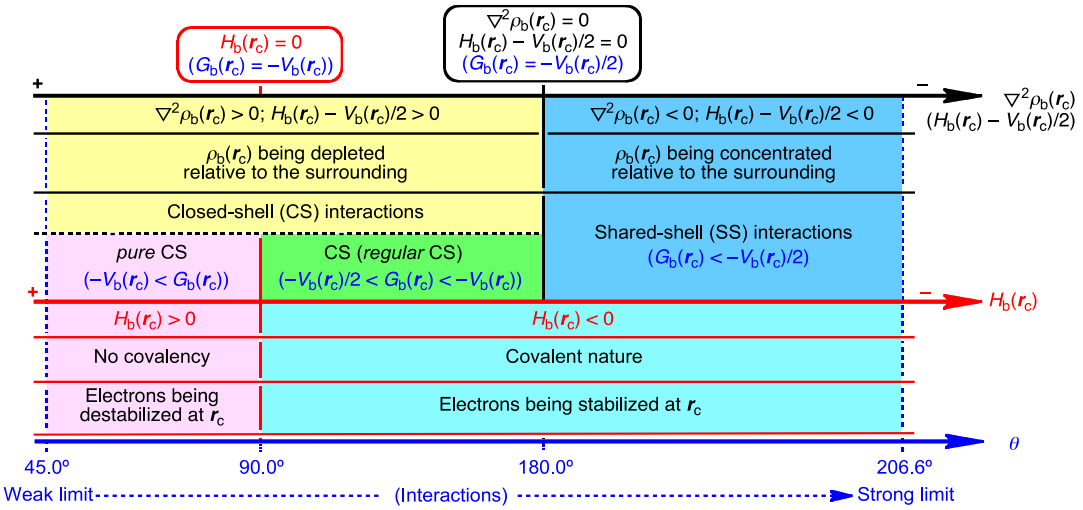
$$H_b(\boldsymbol{r}_c) = G_b(\boldsymbol{r}_c) + V_b(\boldsymbol{r}_c) \quad \text{(SA1)}$$

$$(\hbar^2/8m)\nabla^2\rho_b(\boldsymbol{r}_c) = H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2 \quad \text{(SA2)}$$

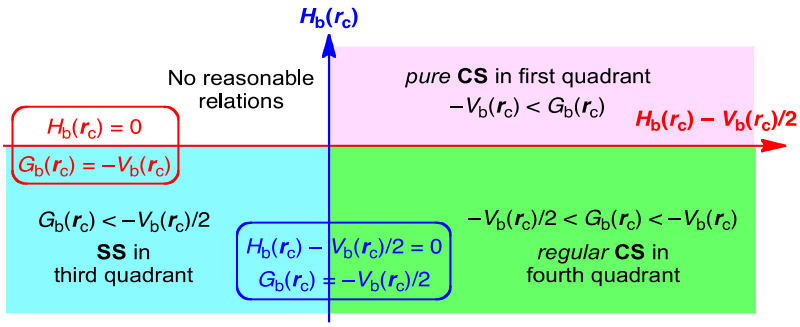
$$= G_b(\boldsymbol{r}_c) + V_b(\boldsymbol{r}_c)/2 \quad \text{(SA2')}$$

Interactions are classified by the signs of $\nabla^2\rho_b(\boldsymbol{r}_c)$ and $H_b(\boldsymbol{r}_c)$. Interactions in the region of $\nabla^2\rho_b(\boldsymbol{r}_c) < 0$ are called shared-shell (SS) interactions and they are closed-shell (CS) interactions for $\nabla^2\rho_b(\boldsymbol{r}_c) > 0$. $H_b(\boldsymbol{r}_c)$ must be negative when $\nabla^2\rho_b(\boldsymbol{r}_c) < 0$, since $H_b(\boldsymbol{r}_c)$ are larger than $(\hbar^2/8m)\nabla^2\rho_b(\boldsymbol{r}_c)$ by $V_b(\boldsymbol{r}_c)/2$ with negative $V_b(\boldsymbol{r}_c)$ at all BCPs (eqn (SA2)). Consequently, $\nabla^2\rho_b(\boldsymbol{r}_c) < 0$ and $H_b(\boldsymbol{r}_c) < 0$ for the SS interactions. The CS interactions are especially called *pure* CS interactions for $H_b(\boldsymbol{r}_c) > 0$ and $\nabla^2\rho_b(\boldsymbol{r}_c) > 0$, since electrons at BCPs are depleted and destabilized under the conditions.[SA1a] Electrons in the intermediate region between SS and *pure* CS, which belong to CS, are locally depleted but stabilized at BCPs, since $\nabla^2\rho_b(\boldsymbol{r}_c) > 0$ but $H_b(\boldsymbol{r}_c) < 0$.[SA1a] We call the interactions in this region *regular* CS,[SA4,SA5] when it is necessary to distinguish from *pure* CS. The role of $\nabla^2\rho_b(\boldsymbol{r}_c)$ in the classification can be replaced by $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$, since $(\hbar^2/8m)\nabla^2\rho_b(\boldsymbol{r}_c) = H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ (eqn (SA2)). Scheme SA1 summarizes the classification.

We proposed QTAIM-DFA by plotting $H_b(\boldsymbol{r}_c)$ versus $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ (= $(\hbar^2/8m)\nabla^2\rho_b(\boldsymbol{r}_c)$),[SA4a] after the proposal of $H_b(\boldsymbol{r}_c)$ versus $\nabla^2\rho_b(\boldsymbol{r}_c)$.[SA4b] Both axes in the plot of the former are given in energy unit, therefore, distances on the (x, y) (= $(H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2, H_b(\boldsymbol{r}_c))$ plane can be expressed in the energy unit, which provides an analytical development. QTAIM-DFA incorporates the classification of interactions by the signs of $\nabla^2\rho_b(\boldsymbol{r}_c)$ and $H_b(\boldsymbol{r}_c)$. Scheme SA2 summarizes the QTAIM-DFA treatment. Interactions of *pure* CS appear in the first quadrant, those of *regular* CS in the fourth quadrant and SS interactions do in the third quadrant. No interactions appear in the second one.



Scheme SA1. Classification of interactions by the signs of $\nabla^2\rho_b(\boldsymbol{r}_c)$ and $H_b(\boldsymbol{r}_c)$, together with $G_b(\boldsymbol{r}_c)$ and $V_b(\boldsymbol{r}_c)$.



Scheme SA2. QTAIM-DFA: Plot of $H_b(\boldsymbol{r}_c)$ versus $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ for Weak to Strong Interactions.

In our treatment, data for perturbed structures around fully optimized structures are also employed for the plots, together with the fully optimized ones (see Fig. SA1).[SA4–SA8] We proposed the concept of the "dynamic nature of interaction" originated from the perturbed structures. The behavior of interactions at the fully optimized structures corresponds to "the static nature of interactions", whereas that containing perturbed structures exhibit the "dynamic nature of interaction" as explained below. The method to generate the perturbed structures is discussed later. Plots of $H_b(\boldsymbol{r}_c)$ versus $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ are analyzed employing the polar coordinate (R, θ) representation with (θ_p, κ_p) parameters.[SA4a,SA5–SA8] Fig. SA1 explains the treatment. R in (R, θ) is defined by eqn. (SA3) and given in the energy unit. Indeed, R does not correspond to the usual interaction energy, but it does to the local energy at BCP, expressed by $[(H_b(\boldsymbol{r}_c))^2 + (H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2)^2]^{1/2}$ in the plot (cf: eqn. (SA3)), where $R = 0$ for the enough large interaction distance. The plots show a spiral stream, as a whole. θ in (R, θ) defined by eqn (SA4), measured from the y-axis, controls the spiral stream of the plot. Each plot for an interaction shows a specific curve, which provides important information of the interaction (see Fig. SA1). The curve is expressed by θ_p and κ_p. While θ_p, defined by eqn (SA5) and measured from the y-direction, corresponds to the tangent line of a plot, where θ_p is calculated employing data of the perturbed structures with a fully-optimized structure and κ_p is the curvature of the plot (eqn (SA6)). While (R, θ) correspond to the static nature, (θ_p, κ_p) represent the dynamic nature of interactions. We call (R, θ) and (θ_p, κ_p) QTAIM-DFA parameters, whereas $\rho_b(\boldsymbol{r}_c)$, $\nabla^2\rho_b(\boldsymbol{r}_c)$, $G_b(\boldsymbol{r}_c)$, $V_b(\boldsymbol{r}_c)$, $H_b(\boldsymbol{r}_c)$ and $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ belong to QTAIM functions. $k_b(\boldsymbol{r}_c)$, defined by eqn (SA7), is QTAIM function but it will be treated as if it were QTAIM-DFA parameter, if suitable.

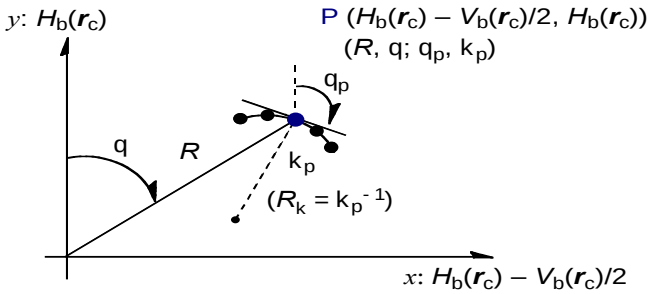


Fig. SA1 Polar (R, θ) coordinate representation of $H_b(\boldsymbol{r}_c)$ versus $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$, with ($\theta_p$, κ_p) parameters.

$$R = (x^2 + y^2)^{1/2} \quad \text{(SA3)}$$

$$\theta = 90^\circ - \tan^{-1}(y/x) \quad \text{(SA4)}$$

$$\theta_p = 90^\circ - \tan^{-1}(dy/dx) \quad \text{(SA5)}$$

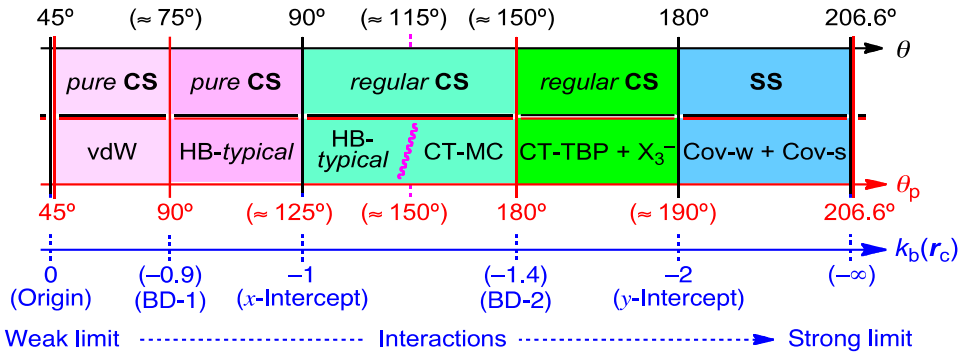
$$\kappa_p = |d^2y/dx^2| / [1 + (dy/dx)^2]^{3/2} \quad \text{(SA6)}$$

$$k_b(\boldsymbol{r}_c) = V_b(\boldsymbol{r}_c)/G_b(\boldsymbol{r}_c) \quad \text{(SA7)}$$

where $(x, y) = (H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2, H_b(\boldsymbol{r}_c))$

Criteria for Classification of Interactions: Behavior of Typical Interactions Elucidated by QTAIM-DFA

$H_b(\boldsymbol{r}_c)$ are plotted versus $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ for typical interactions in vdW (van der Waals interactions), HBs (hydrogen bonds), CT-MCs (molecular complexes through charge transfer), X_3^- (trihalide ions), CT-TBPs (trigonal bipyramidal adducts through charge-transfer), Cov-w (weak covalent bonds) and Cov-s (strong covalent bonds).[SA4–SA8] Rough criteria are obtained by applying QTAIM-DFA, after the analysis of the plots for the typical interactions according to eqns (SA3)–(SA7). Scheme SA3 shows the rough criteria, which are accomplished by the θ and θ_p values, together with the values of $k_b(\boldsymbol{r}_c)$. The criteria will be employed to discuss the nature of interactions in question, as a reference.



Scheme SA3. Rough classification and characterization of interactions by θ and θ_p, together with $k_b(\boldsymbol{r}_c)$ ($= V_b(\boldsymbol{r}_c)/G_b(\boldsymbol{r}_c)$).

Characterization of interactions

The characterization of interactions is explained employing $[^1Cl\text{-}^2Cl\text{-}^3Cl]^-$. The wide range of the perturbed structures were generated by partially optimizing $r(^2Cl\text{-}^3Cl)$ in $[^1Cl\text{-}^2Cl\text{-}^3Cl]^-$, assuming the $C_{\infty v}$ symmetry, with $r(^1Cl\text{-}^2Cl)$ being fixed in the wide range. The partial optimization method is called POM.[SA4b,SA5] The QTAIM functions, such as $V_b(\boldsymbol{r}_c)$, $G_b(\boldsymbol{r}_c)$, $H_b(\boldsymbol{r}_c)$, $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ are calculated at BCPs for the wide varieties of the perturbed structures of $[^1Cl\text{-}^2Cl\text{-}^3Cl]^-$. $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ and $H_b(\boldsymbol{r}_c)$ are

plotted versus the interaction distances $r(^1\text{Cl-}^2\text{Cl})$ in the perturbed structures of $[^1\text{Cl-}^2\text{Cl-}^3\text{Cl}]^-$, in the wide range. Fig. SA2 shows the plots. Each plot is analyzed using a regression curve of the ninth function and the first derivative of each regression curve is obtained. As shown in Fig. SA2, the maximum value of $H_b(\boldsymbol{r}_c)$ ($d(H_b(\boldsymbol{r}_c)/dr = 0$) is defined as the borderline between vdW and t-HB interactions. Similarly, the maximum value of $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ ($d(H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2)/dr = 0$) does to the borderline between CT-MC and CT-TBP. However, it seems difficult to find a characteristic point corresponding to the borderline between *t*-HB and CT-MC in nature. Therefore, the borderline is tentatively given by $\theta_p = 150^o$ based on the expectation form the experimental results, where θ_p is defined by $[90^o - \tan^{-1}[dH_b(\boldsymbol{r}_c)/d(H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2)]]$ in the plot of $H_b(\boldsymbol{r}_c)$ versus $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$. The proposed classification and characterization of interactions, by means of the QTAIM functions of $H_b(\boldsymbol{r}_c)$, $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$, $G_b(\boldsymbol{r}_c)$ and/or $V_b(\boldsymbol{r}_c)$, are summarized in Table SA1. The plot of $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ versus w in Fig. SA2 is essentially the same as that of $\nabla^2\rho_b(\boldsymbol{r}_c)$ versus d(H---F) in X–H---F–Y, presented by Espinosa and co-workers.[SA9]

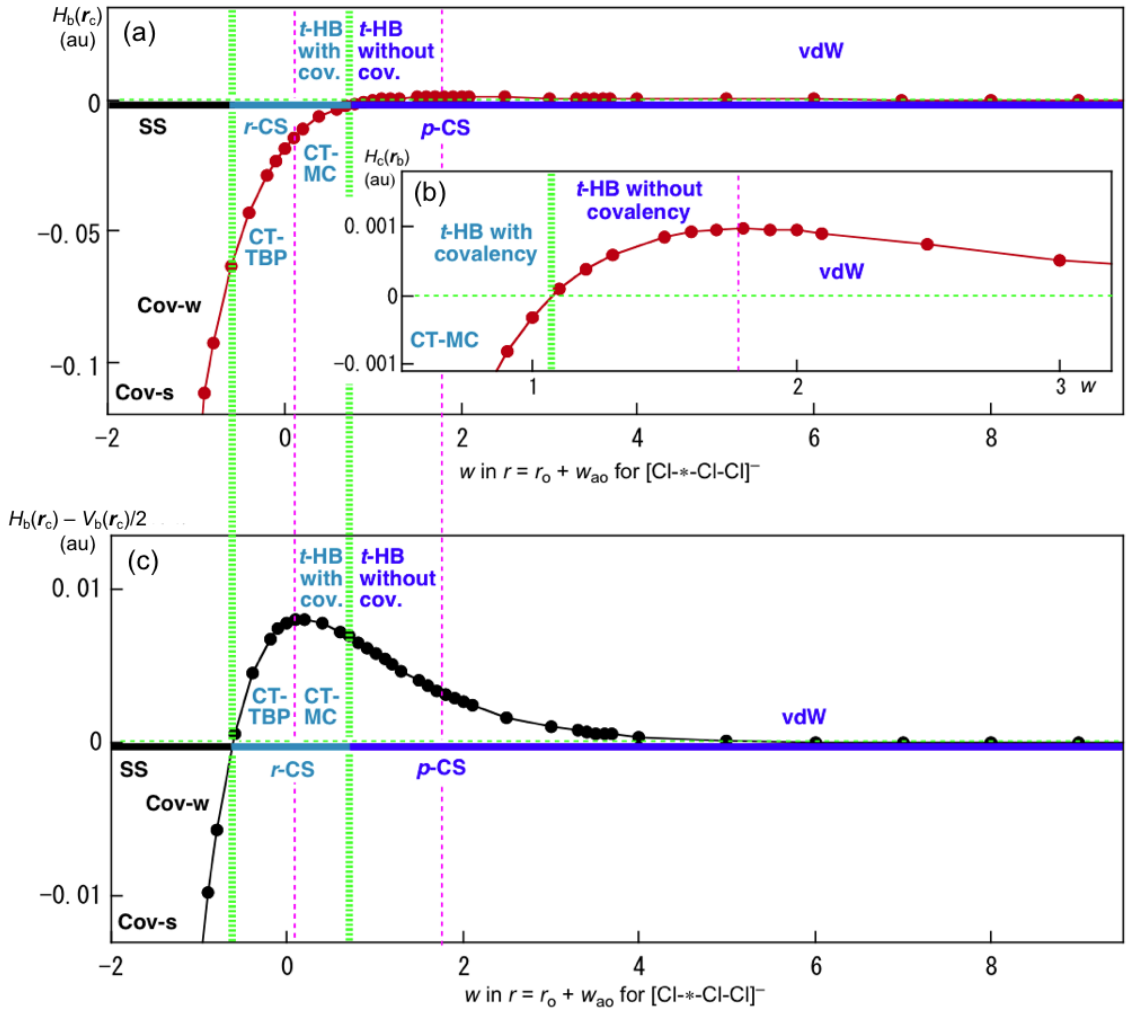


Fig. SA2 Plot of $H_b(\boldsymbol{r}_c)$ versus w in $r(^1\text{Cl-}^2\text{Cl}) = r_o(^1\text{Cl-}^2\text{Cl}) + wa_o$ for $^1\text{Cl-}^2\text{Cl-}^3\text{Cl}^-$ (a) with the magnified picture of (a) (b) and that of $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ versus w (c). Typical hydrogen bonds without covalency and typical hydrogen bonds with covalency are abbreviated as *t*-HB without cov. and *t*-HB with cov., respectively, whereas Cov-w and Cov-s stand for weak covalent bonds and strong covalent bonds, respectively.

Table SA1. Proposed definitions for the classification and characterization of interactions by the signs $H_b(\boldsymbol{r}_c)$ and $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ and their first derivatives, together with the tentatively proposed definitions by the characteristic points on the plots of $H_b(\boldsymbol{r}_c)$ versus $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$. The tentatively proposed definitions are shown by italic. The requirements for the interactions are also shown.

ChP/Interaction	Requirements by $H_b(\boldsymbol{r}_c)$ and $V_b(\boldsymbol{r}_c)$	Requirements by $G_b(\boldsymbol{r}_c)$ and $V_b(\boldsymbol{r}_c)$
Origin	$H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2 = 0$; $H_b(\boldsymbol{r}_c) = 0$	$G_b(\boldsymbol{r}_c) = 0$; $V_b(\boldsymbol{r}_c) = 0$
vdW	$H_b(\boldsymbol{r}_c) > 0$; $dH_b(\boldsymbol{r}_c)/d(-r) > 0$	$G_b(\boldsymbol{r}_c) > -V_b(\boldsymbol{r}_c)$; $dG_b(\boldsymbol{r}_c)/d(-r) > -dV_b(\boldsymbol{r}_c)/d(-r)$
Borderline (BD-1)	$H_b(\boldsymbol{r}_c) > 0$; $dH_b(\boldsymbol{r}_c)/d(-r) = 0$	$G_b(\boldsymbol{r}_c) > -V_b(\boldsymbol{r}_c)$; $dG_b(\boldsymbol{r}_c)/d(-r) = -dV_b(\boldsymbol{r}_c)/d(-r)$
t-HB$_{\text{with no covalency}}$	$H_b(\boldsymbol{r}_c) > 0$; $dH_b(\boldsymbol{r}_c)/d(-r) < 0$	$G_b(\boldsymbol{r}_c) > -V_b(\boldsymbol{r}_c)$; $dG_b(\boldsymbol{r}_c) < -dV_b(\boldsymbol{r}_c)$
Borderline (x-intercept)	$H_b(\boldsymbol{r}_c) = 0$ ($\theta_p{}^a = 125^o$)	$G_b(\boldsymbol{r}_c) = -V_b(\boldsymbol{r}_c)$ ($\theta_p{}^a = 125^o$)
t-HB$_{\text{with covalency}}$	$H_b(\boldsymbol{r}_c) < 0$; ($125^o <$) $\theta_p{}^a < 150^o$	$G_b(\boldsymbol{r}_c) < -V_b(\boldsymbol{r}_c)$; ($125^o <$) $\theta_p{}^b < 150^o$
Borderline (Tentative)	*$\theta_p{}^a = 150^o$*	*$\theta_p{}^b = 150^o$*
CT-MC	$d(H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2)/d(-r) > 0$; $150^o < \theta_p{}^a < 180^o$	$dG_b(\boldsymbol{r}_c) > dV_b(\boldsymbol{r}_c)/2$; $150^o < \theta_p{}^a < 180^o$
Borderline (BD-2)	$d(H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2)/d(-r) = 0$ ($H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2 > 0$; $H_b(\boldsymbol{r}_c) < 0$)	$2dG_b(\boldsymbol{r}_c)/d(-r) = -dV_b(\boldsymbol{r}_c)/d(-r)$ ($-V_b(\boldsymbol{r}_c)/2 < G_b(\boldsymbol{r}_c) < -V_b(\boldsymbol{r}_c)$)
CT-TBP with X_3^-	$d(H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2)/d(-r) < 0$ ($H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2 > 0$; $H_b(\boldsymbol{r}_c) < 0$)	$2dG_b(\boldsymbol{r}_c)/d(-r) < -dV_b(\boldsymbol{r}_c)/d(-r)$ ($-V_b(\boldsymbol{r}_c)/2 < G_b(\boldsymbol{r}_c) < -V_b(\boldsymbol{r}_c)$)
Borderline (y-intercept)	$H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2 = 0$ ($H_b(\boldsymbol{r}_c) < 0$)	$G_b(\boldsymbol{r}_c) = -V_b(\boldsymbol{r}_c)/2$ ($G_b(\boldsymbol{r}_c) < -V_b(\boldsymbol{r}_c)$)
Cov-w	$H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2 < 0$; *$R^c < 0.15$ au*	$G_b(\boldsymbol{r}_c) < -V_b(\boldsymbol{r}_c)/2$; *$R^c < 0.15$ au*
Borderline (Tentative)	*$R^c = 0.15$ au*	*$R^d = 0.15$ au*
Cov-s	$H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2 < 0$; *$R^c > 0.15$ au*	$G_b(\boldsymbol{r}_c) < -V_b(\boldsymbol{r}_c)/2$; *$R^d > 0.15$ au*

[a] $\theta_p = 90^o - \tan^{-1}[dH_b(\boldsymbol{r}_c)/d(H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2)]$, $\theta_p = 125^o$ is tentatively given for $\theta = 90^o$, where θ is defined by $90^o - \tan^{-1}[H_b(\boldsymbol{r}_c)/(H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2)]$ with $H_b(\boldsymbol{r}_c) = 0$. [b] $\theta_p = 90^o - \tan^{-1}[d(G_b(\boldsymbol{r}_c) + V_b(\boldsymbol{r}_c))/d(G_b(\boldsymbol{r}_c) + V_b(\boldsymbol{r}_c)/2)]$, $\theta_p = 125^o$ is tentatively given for $\theta = 90^o$, where θ is defined by $90^o - \tan^{-1}[(G_b(\boldsymbol{r}_c) + V_b(\boldsymbol{r}_c))/(G_b(\boldsymbol{r}_c) + V_b(\boldsymbol{r}_c)/2)]$ with $(G_b(\boldsymbol{r}_c) + V_b(\boldsymbol{r}_c)) = 0]$. [c] $R = [(H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2)^2 + (H_b(\boldsymbol{r}_c))^2]^{1/2}$. [d] $R = [(G_b(\boldsymbol{r}_c) + V_b(\boldsymbol{r}_c)/2)^2 + (G_b(\boldsymbol{r}_c) + V_b(\boldsymbol{r}_c))^2]^{1/2}$.

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