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Reactivity of *N*-Phenyl Silylated Ketenimines with Electrophilic Reagents

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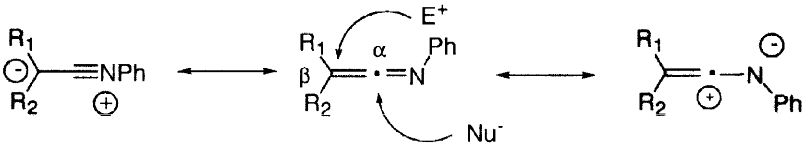
Abstract

We report the reactivity of new Cβ silylated ketenimines (**4**, **5**, **6**) and lithiated-silylated ketenimine **3** [easily generated from lithiated *S*-methyl-*N*-phenyl-trimethylsilylethanimidothioate **2**] toward electrophilic reagents. Reactions of these ketenimines with strong electrophilic reagents such as sulfanyl chloride (PhSCl) gave access to new sulfanylated ketenimines. With less reactive species [benzenesulfinyl chloride (PhS(O)Cl), p-toluenesulfonyl chloride, trimethylhalosilanes, diisopropyl chlorophosphate, acetyl chloride and propylene oxide] and **3**, the addition took place either on Cβ or on the nitrogen atom leading to relatively unstable functionalised ketenimines or new silylated ynamines respectively. © 1999 Elsevier Science Ltd. All rights reserved.

Keyword: Ketenimines, imidic derivatives, Silicon compounds, Sulfur compounds.

Introduction

Ketenimines are usually very reactive and unstable heterocumulenes when they are not substituted by stabilising substituents such as aryl,[1] phosphonium ylid,[2] *bis* (trifluoromethyl),[3] trimethylsilyl.[4-8] In accordance with the mesomeric structures drawn in scheme 1,[3, 9, 10] they can react with nucleophiles and electrophiles respectively on their central (Cα) and terminal (Cβ) carbons. The addition of electrophilic reagents to ketenimines has not been so much studied in comparison to that of nucleophilic reagents. Thus, studies have been limited to chlorine [11] and to benzenesulfanyl chloride with *bis* (trifluoromethyl) ketenimines,[12] triarylketenimines,[13] and with some more reactive alkylarylketenimines. [14]



scheme 1

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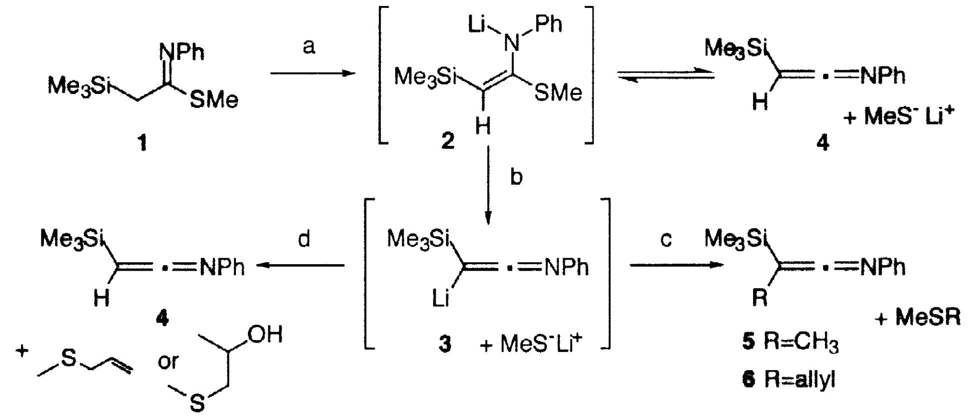
The stabilising effect of one or more trialkylsilyl substituents on heterocumulenes has been demonstrated for ketenes,[15-18] thioketenes [19] and ketenimines. [4, 5] This stabilisation has been discussed for ketenes and attributed to a hyperconjugative effect which, in particular, reduces the electrophilic character of the heterocumulene, a feature usually responsible for its instability.[16, 17] As far as the nucleophilicity is concerned, despite the steric effect of the silylated substituent, the well known β-stabilisation of carbocations by trialkylsilyl groups, and, in the case of ketenimines, the ability of amino groups to stabilise positive charge through their electron donating resonance effect, should favour the addition of electrophiles on the β-carbon [20, 21] of any C-silylated ketenimine.

In previous work, we have shown that lithiated *S*-methyl-*N*-phenyl imidothioesters, *via* elimination of lithium methylthiolate at temperatures above 0°C, led to the formation of a ketenimine (very probably in equilibrium with the starting lithiated imidothioester). The ketenimine could then react *in situ* with Grignard reagents (nucleophilic addition to the central carbon occurs). This procedure was used for the one pot synthesis of various imines and ketones [22-24] starting from a metallated imidothioester. More recently, we have described the synthesis of new stable mono C-silylated *N*-phenyl ketenimines from the *S*-methyl α-(trimethylsilyl)ethanimidothioate **1** (scheme 2).[25] Imidothioester **1**, upon treatment with two equivalents of n-butyllithium, in a mixture of THF/hexane, at -78°C followed by warming to +5°C, was converted to the β-lithiated-β-silylated ketenimine **3**, *via* the mono lithiated intermediate **2**. We observed that the very slow deprotonation of ketenimine **4** by n-BuLi became fast when catalytic MeSLi was added. This suggests that the key step is a second deprotonation of enaminate **2** which occurs with the assistance of the methylthio group just before or simultaneously to its elimination. The intermediate **3** can then be protonated (after addition of one equivalent of propylene oxide [1]), alkylated or allylated to lead to the new ketenimines **4**, **5** or **6**.



a) 2eq n-BuLi, THF/hexane, -78°C; b) +5°C; c) 2 RX, r.t.; d) 1) AllylBr or propylene oxide, -20°C; 2) H$^+$

scheme 2

Ketenimines **3** to **6**, stabilised by the trimethylsilyl substituent, are new functionalised heterocumulenes and we present herein our results related to their reactivity towards a

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[1] We have found that one equivalent of epoxide can advantageously replace the allyl bromide previously used to trap the lithium methylthiolate in the synthesis of **4**. This trapping increases the yield of the ketenimine [25]. The alkoxide resulting from the opening of the epoxide does not interfere in the reaction and gives, after protonation, an alcohol easily separated from the ketenimine.

selection of electrophilic reagents (benzenesulfanyl chloride, benzenesulfinyl chloride, *p*-toluenesulfonyl chloride, trimethylchlorosilane or trimethylbromosilane, diisopropyl chlorophosphate, acetyl chloride and propylene oxide).

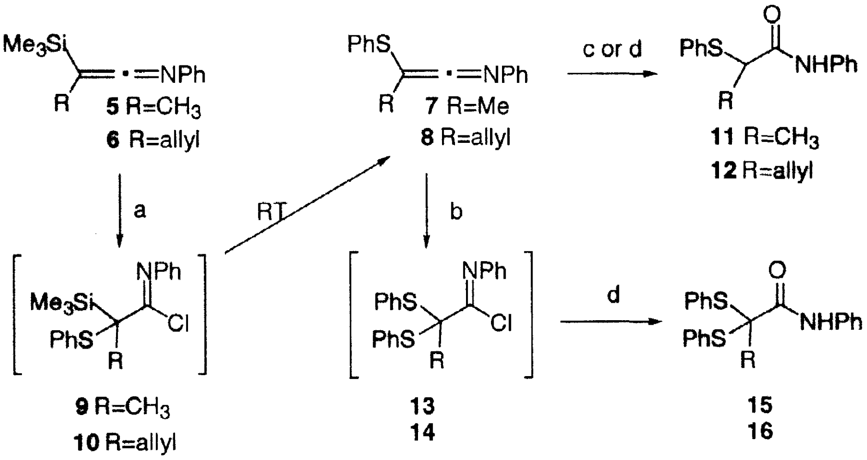
Results and discussion

a) Addition of benzenesulfanyl chloride

Depending on the substituent on Cβ (R, H or Li), silylated ketenimines have shown varied behaviour towards benzenesulfanyl chloride. In each case, the reaction was quantitative (NMR) and very fast, even at -78°C.

Addition of one equivalent of PhSCl at -78°C to ketenimine **5**, gave a new stable C-sulfanylated ketenimine **7** (66% yield after distillation).[26] The same kind of addition leading to ketenimine **8** was observed with the allylic ketenimine **6** (with no addition on the double bond of the allylic chain). The obtention of ketenimines **7** and **8**, which formally result from the substitution of the trimethylsilyl by the benzenesulfanyl group, can easily be explained by the formation of unstable imidoyl chlorides **9** and **10** followed by a spontaneous elimination of chlorotrimethylsilane. These two ketenimines, much less stabilised, slowly hydrolyse to the corresponding amides **11** and **12** when stored for a long time in a cold and moist atmosphere. This hydrolysis can also be performed quantitatively (on NMR basis) in a mixture of acetone/water or by chromatography on silica gel or neutral alumina (scheme 3).

When at least 2eq of PhSCl were added to ketenimine **5** or **6** at 0°C and the crude product immediately hydrolysed, the α,α-di(benzenesulfanyl)propanamide **15** and **16** were isolated respectively in 50% and 52% yield after chromatography. This double sulfanylation can be rationalised by the mono addition-elimination process leading first to the ketenimine **7** or **8**. Then addition of the second equivalent of PhSCl to **7** or **8** gives a disulfanylated imidoyl chloride **13** or **14** which was finally hydrolysed to the corresponding amides (scheme 3).

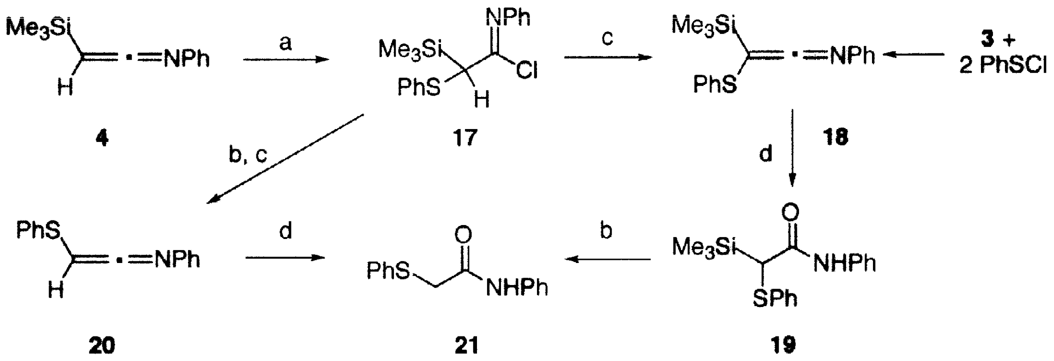


a) 1eq PhSCl, CH_2Cl_2, -78°C->r.t.; b) 1.1 eq PhSCl, CH_2Cl_2,, 0°C; c) Silica gel; d) 1:1-Acetone/Water

scheme 3

On the contrary, with non-alkylated ketenimine **4**, after addition of one equivalent of PhSCl, we did not observe the spontaneous elimination of chlorotrimethylsilane. Therefore, the relatively stable imidoyl chloride **17**, treated with an excess of triethylamine (2 eq), was dehydrochlorinated to give the new stable silylated and sulfanylated ketenimine **18** (55% after distillation).[11] As we anticipated from the *in situ* generated lithiated ketenimine **3**, the addition of two equivalents of PhSCl led to the same ketenimine **18** in 75% yield (the second equivalent reacting with MeSLi). Chromatography on silica gel column caused hydrolysis of **18**, without desilylation, and led to the α-silylated benzenesulfanylacetamide **19**. Thus, we found that chromatography of silylated ketenimines on silica gel was a good route to α-silylated amide nearly quantitatively and in good purity.

When crude imidoyl chloride **17**, was washed quickly with dilute HCl, before treatment with an excess of triethylamine (2 eq), the non-silylated and relatively unstable benzenesulfanylketenimine **20** was formed (scheme 4). This can be rationalised by a desilylation of **17** by HCl (without hydrolysis of the imidoyl function) followed by a dehydrochlorination by the tertiary amine.

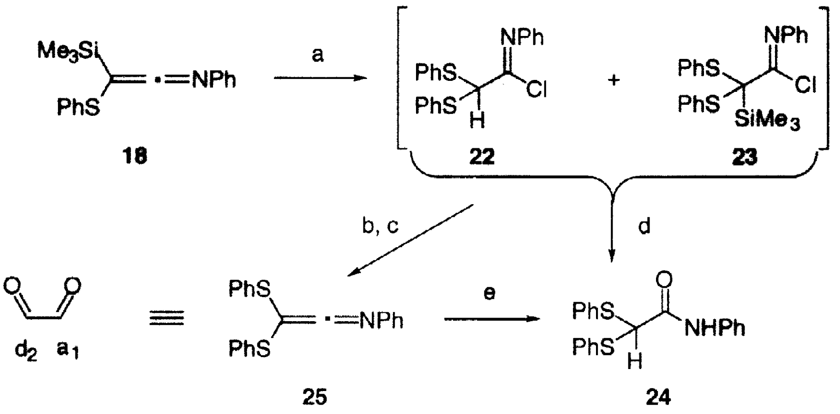


a) 1eq PhSCl, CH_2Cl_2, 0°C; b) diluted HCl; c) 2eq Et_3N, CH_2Cl_2,, r.t.; d) Silica gel or 1:1-Acetone/Water;

scheme 4

Ketenimine **20**, too unstable to be purified by distillation, was characterised by its hydrolysis on silica gel to the α-(benzenesulfanyl)acetamide **21** (65% yield) which was also obtained from the desilylation of amide **19** (scheme 4).

The reactivity of **18** towards PhSCl was examined also. Addition of 1.1eq of PhSCl at -10°C led, after warming to room temperature, to a mixture of imidoyl chlorides **22** and **23** which were not isolated but readily hydrolysed with a mixture acetone/water to amide **24** (yield: 41%). Moreover, after total desilylation of the crude mixture **22** and **23** (diluted HCl washing) and dehydrochlorination (with Et_3N, 2 eq), the ^{13}C NMR [77.3 (Cβ); 189.9 (Cα)] and IR (2010 cm^{-1}) data of the resulting crude product were in accordance with the formation of the new *bis* (benzenesulfanyl)ketenimine **25**. Attempts to purify this "masked dicarbonyl" were unsuccessful, but it was nevertheless characterised after hydrolysis to amide **24** (scheme 5).

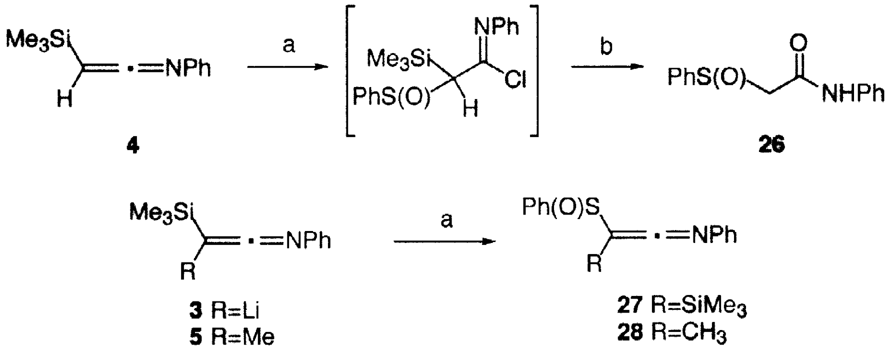


a) 1eq PhSCl, CH_2Cl_2, 0°C; b) diluted HCl; c) 2eq Et_3N, CH_2Cl_2, r.t.; d) Acetone/Water 50/50; e) Silica gel

scheme 5

b) Addition of benzenesulfinyl and *p*-toluenesulfonyl chlorides

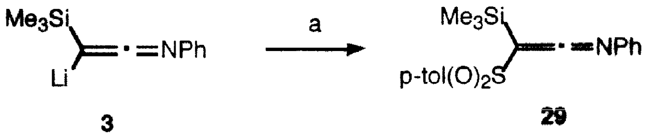
Benzenesulfinyl chloride was found to be very reactive with ketenimines **3**, **4** and **5** at -78°C to give unstable functionalised ketenimines. The isolation and characterisation of α-sulfinyl *N*-phenyl amide **26**, obtained from reaction of ketenimine **4** with PhS(O)Cl and subsequent hydrolysis, demonstrated that the addition on Cβ occurred. Moreover, the strong IR absorption bands observed at 1999 and 2005 cm^{-1} for the crude products obtained from the addition of PhS(O)Cl to the lithiated ketenimine **3** and methyl substituted ketenimine **5** were consistent with the formation of the corresponding ketenimines **27** and **28** (scheme 6). The unstability of these heterocumulenes did not allow any purification [27, 28] or further investigations.



a) 1 PhS(O)Cl, CH_2Cl_2, 0°C; b) Acetone/Water 50/50

scheme 6

The less reactive *p*-toluenesulfonyl chloride added to the lithiated ketenimine **3** only to give, after evaporation of the solvent, a crude silylated sulfonylketenimine **29** characterised by ^{13}C NMR (-1.8 (TMS); 80.2 (Cβ); 190.6 (Cα) and IR (1998 cm^{-1}) (scheme 7).



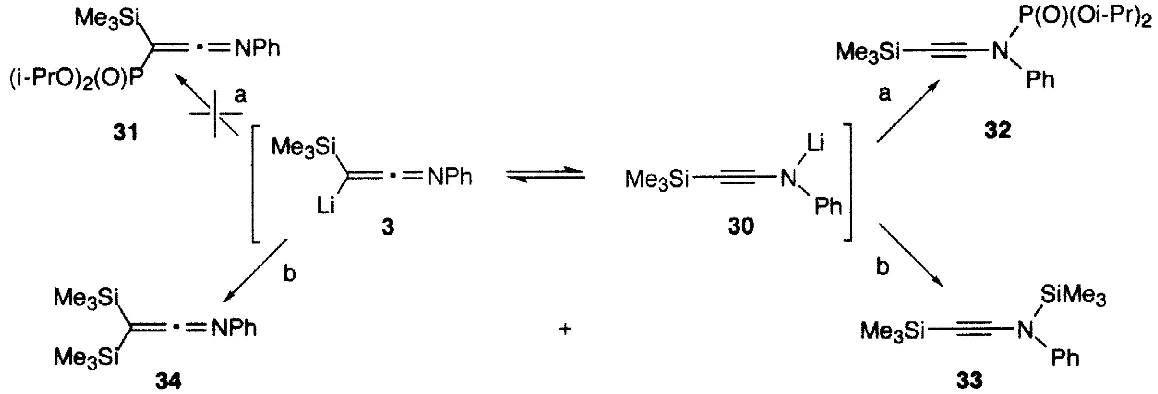
a) 1.9 *p*-tolSO$_2$Cl, THF/Hexane, -80°C
scheme 7

Although **29** seemed to be more stable than **27**, all our attempts to purify this oily product failed. This difficulty was previously encountered with a ketenimine monosubstituted by a sulfonyl group.[26] β,β'-disulfonylated (methyl, methyl)- or (methyl, phenyl)-ketenimines have however been isolated in pure form by recrystallisation.[29, 30]

c) Addition of other electrophilic reagents

Diisopropylchlorophosphate, acetyl chloride, trimethylchlorosilane or trimethylbromosilane and propylene oxide were found to be reactive only with the lithiated ketenimine **3** at room temperature.

The synthesis of stable C-phosphorylated [31, 32] and C-diphosphorylated [33] ketenimines has already been described. The reaction of diisopropyl chlorophosphate at the Cβ carbon of the in situ generated lithiated ketenimine **3** (in equilibrium with the N-lithiated ynamine **30**), would be an easy method for the preparation of new silylated and phosphorylated ketenimines such as **31**.[34] However, the phosphorylation occurred exclusively on nitrogen to give the new silylated and phosphorylated ynamine **32** (R = iPr, yield: 48%) [35] (scheme 8).

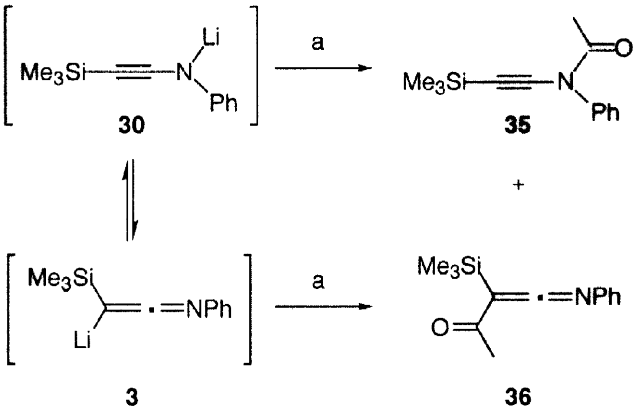


a) 2.5eq (*i*-PrO)$_2$P(O)Cl, THF/hexane, r.t., 3h; b) 3eq Me$_3$SiCl or Me$_3$SiBr, THF/hexane, r.t., 3h.

scheme 8

Chloro- and bromo-trimethylsilane added both on the terminal carbon and on the nitrogen of the lithiated ketenimine **3**. The crude product shows two IR absorption bands at 2146 and 2000 cm^{-1} corresponding to the presence of both the ynamine **33** and ketenimine **34**. After distillation only **34** [8] was recovered in 30% yield. Together with some thermal degradation, a thermal isomerisation of **33** into **34** is possible (scheme 8). Such a process has already been reported. [4, 36, 37]

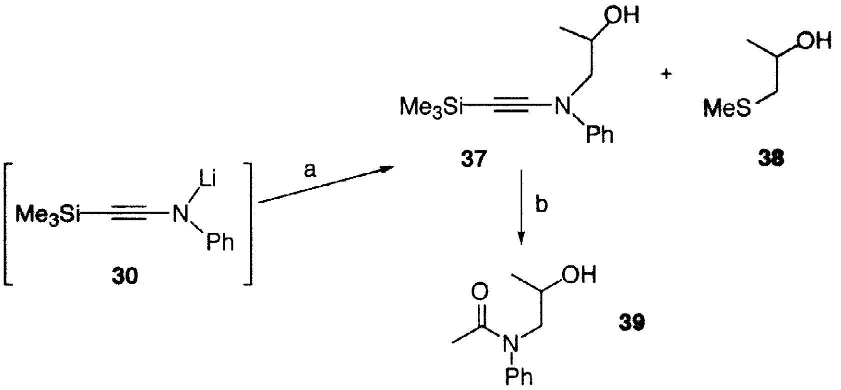
An excess of acetyl chloride reacted with **3** (in equilibrium with **30**) to lead to the new ynamine **35** isolated in 75% yield after distillation. When only two equivalents of acetyl chloride were used, the IR spectra of the crude product showed absorption bands at 2000 and 2150 cm^{-1} indicating the presence of both the ynamine **35** and the ketenimine **36** [38, 39] (scheme 9). However, after distillation, only ynamine **35** was recovered in low yield.[39]



a) 3eq AcCl, THF/Hexane, r.t., 3h

scheme 9

Addition of an excess of propylene oxide to **3** [2] gave a mixture of ynamine **37** and alcohol **38** (resulting from the addition of MeSLi to the epoxide); **37** could be distilled and isolated in good yield (80%). When purified by column chromatography on silica gel, hydration of the acetylenic bond was observed and acetamide derivative **39** was isolated in 50% yield [36] (scheme 10).



a) 3eq propylene oxide, THF/Hexane, r.t., 2h; b) Silica gel

scheme 10

Conclusion

The reaction of silylated ketenimines, readily generated from an α-silylated *N*-phenyl imidothioester, with electrophiles is an easy way for the preparation of new functionalised ketenimines or ynamines. It was found that benzenesulfanyl chloride is a powerful electrophile leading to new sulfanylated ketenimines or to relatively stable intermediate

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[2] see note 1

imidoyl chlorides. Less reactive electrophiles reacted, with variable regioselectivity, with the lithiated-silylated ketenimine only, either on the β-carbon (leading to ketenimines) or on the nitrogen (leading to ynamines). The functionalised ketenimines and ynamines obtained are new polyfunctional synthons which could allow further investigations into their reactivity and uses as building blocks in organic synthesis.

EXPERIMENTAL

All experiments were carried out under a nitrogen atmosphere, in flasks allowing the use of rubber septa. Tetrahydrofuran was distilled before use over sodium and benzophenone. Butyllithium (1.6M in hexane) was supplied by *Aldrich chemicals*. Other solvents were dried and purified by usual procedures. Silica gel (63-200µm) was purchased from Merck (Merck 60). Kügelrohr distillations were carried out with a Kügelrohr oven Büchi GRK 50 under vacuum. NMR spectra were recorded on a Brüker AC. 250 at 250 MHz for ^{1}H NMR, 62.9 MHz for ^{13}C. The chemical shifts are in ppm relative to tetramethylsilane as internal standard. Coupling constants (*J*) are given in hertz. Mentions of *ipso, o (ortho), m (meta), p (para)* are related to the *N*-phenyl and "prime" to the *S*-phenyl; C_α and C_β are related to the central and terminal carbon of the ketenimine. IR absorption (cm^{-1}) were recorded on a Perkin-Elmer684 or Perkin-Elmer16 PC FT-IR. Mass spectra (electronic impact at 70 eV) were recorded on a Nermag R10 RH. Melting points were measured with a Reichert melting point apparatus and are uncorrected. Benzenesulfanylchloride was prepared according to ref.[40] and after distillation, diluted in dichloromethane to give a 0.5M solution. This allows a better conservation.[41] Benzenesulfinylchloride was prepared according to ref.[42] Diisopropylchlorophosphate was prepared according to ref.[43].

Generation of lithiated ketenimine 3 from silylated imidothioester 1

Typical procedure I: To a stirred solution of **1** (1.5 g, 6.32 mmol) in THF/hexane (40/9 ml), cooled to -78°C, n-butyllithium (2.1 eq, 13.26 mmol, 8.3 ml) was added. Stirring was maintained for one hour in the cold bath and the temperature of the reaction mixture containing the lithiated imidothioester **2** was allowed to reach +5°C (flask outside the cold bath) in order to induce elimination of MeSLi and deprotonation leading to the lithiated ketenimine **3**.

Synthesis of ketenimine 4

To the stirred reaction mixture containing lithiated ketenimine **3** and MeSLi, propylene oxide (1.1 eq, 6.95 mmol, 0.49 ml) was added in order to trap MeSLi. Stirring was continued for an additional hour at room temperature, and the mixture was poured into a saturated NH_4Cl aqueous solution. The organic phase was separated and the aqueous layer was extracted twice with petroleum ether. Organic phases were then combined, washed with brine and dried over sodium sulfate. The solvent was removed under vacuum and the crude purified by kügelrohr distillation afford ketenimine **4** (900 mg, yield: 75 %).

***N*-Phenyl-(trimethylsilyl)ketenimine 4**:[25] yield: 75%; colourless liquid, bp (°C/mbar) = 60/10^{-3}; ^{1}H NMR: 0.19 [s, 9H, $(CH_3)_3Si$]; 3.33 (s, 1 H, =CH), 7.21 to 7.37 (m sharp, 5 H, Ph); ^{13}C NMR: 0.2 [$(CH_3)_3Si$)]; 37.4 (C_β); 123.1 (C*o*); 126.3 (C*p*); 129.3 (C*m*); 141.8 (C*ipso*); 181.1 (C_α); Anal. for $C_{11}H_{15}NSi$ (189.3 gmol^{-1}); Calcd. for C: 69.78; H: 7.98; N:7.39; Si:14.83; Found (%): C: 69.80; H:8.01; N: 7.46; Si: 14.93

Synthesis of ketenimine 5 and 6

Typical procedure II: To the stirred reaction mixture containing lithiated ketenimine **3** and MeSLi (procedure **I**), iodomethane (2.1 eq, 13.3 mmol, 0.85 ml) was added to trap MeSLi and methylate ketenimine **3**. Stirring was continued for an additional hour at room temperature. The mixture was poured into saturated NH_4Cl aqueous solution. The organic layer was removed. The aqueous layer was extracted twice with petroleum ether. Organic phases were then combined and washed with brine and dried over sodium sulfate. The solvent was removed under vacuum and the crude was purified by distillation to afford ketenimine **5** (1 g, yield: 79 %).

***N*-Phenyl-methyl-(trimethylsilyl)ketenimine** **5**:[25] yield: 79%; colourless liquid, bp (°C/mbar) = 60/10^{-3}; ^{1}H NMR: 0.17 [s, 9H, $(CH_3)_3Si$]; 1.70 (s, 3 H, CH_3), 7.16 to 7.36 (m sharp, 5 H, Ph); ^{13}C NMR: -1.3 [$(CH_3)_3Si$)];9.7 (CH_3); 46.9 (C_β); 123.2 (C_o); 126.2 (C_p); 129.4 (C_m); 143.4 (C_{ipso}); 183.6 (C_α); Anal. for $C_{12}H_{17}NSi$ (203.4 $gmol^{-1}$); Calcd. for C: 70.87; H: 8.43; N: 6.89; Si: 13.81; Found (%): C: 70.76; H: 8.55; N: 6.49; Si: 13.27

***N*-Phenyl-allyl-(trimethylsilyl)ketenimine** **6**:[25] yield: 65%; colourless liquid, bp (°C/mbar) = 65-70/10^{-3}, ^{1}H NMR: 0.17 (s, 9H, $(CH_3)_3Si$); 2.78 (td, J = 1.3, J =_6.6, 2 H, CH_2); 5.02 (ddd, J = 1.2, J = 3.2, J = 10.1, 1 H) and 5.13 (ddd, J = 1.6, J = 3.2, J = 16.9, 1 H) (CH_2); 5.90 (dddd, J = 6.5, J = 6.7, J = 10.1, J = 16.9, 1 H, CH); 7.20-7.36 (m,5H, Ph);); ^{13}C NMR: 0.01 [$(CH_3)_3Si$)]; 30.7 (CH_2); 52.8 (C_β); 116.3 (CH_2=); 124.0 (C_o); 127.2 (C_p); 130.2 (C_m); 143.8 (C_{ipso}); 138.2 (CH=); 183.9 (C_α); IR (NaCl): 1990 (C=C=N); 1615 (C=C); 1286; 842; 760 (CH_3Si); accurate mass: Calcd. for $C_{14}H_{19}NSi$: 229.1286; Found: 229.1276.

Addition of benzenesulfanyl chloride (1eq) to ketenimines 5 and 6:

Typical procedure III:To a stirred solution of *N*-Phenyl-methyl(trimethylsilyl) ketenimine **5** (202 mg, 10 mmol) in dry dichloromethane, cooled to -70°C, 1.8 ml of the 0.5M solution of benzenesulfanyle chloride (0.9 eq) in CH_2Cl_2 was added dropwise. Stirring was maintained for 30 min. and solvent was evaporated. Bulb to bulb distillation afforded *N*-Phenyl-methyl(benzenesulfanyl)ketenimine **8** (160 mg, yield: 66%).

***N*-Phenyl-methyl(benzenesulfanyl)ketenimine** **7**:[26] yield: 66%,.yellow liquid, bp (°C/mbar) = 100/10^{-3}; ^{1}H NMR: 2.01 (s, 3 H, CH_3); 7.16 to 7.48 (m, 10 $H_{arom.}$); ^{13}C NMR: 57.7 (C_β); 124.05; 126.1; 127.5; 127.6; 128.9; 129.6; 136.2; 140.9; 187.9 (C_α); mass m/z (%): 239 ($M^{+\cdot}$, 100); 224 (14.5); 109 (9.1); 77 (5.5); IR (NaCl): 2006 (C=C=N); 1438 (CH_3); 1592 (C=C); Anal. for $C_{15}H_{13}NS$ (239.3$gmol^{-1}$): Calcd. for S: 13.40; Found S: 13.49.

***N*-Phenyl-allyl(benzenesulfanyl)ketenimine** **8**: yield: 28% after distillation (some degradation occured), colourless liquid, bp (°C/mbar)=180/10^{-3}; ^{1}H NMR: 3.04 (dt, J = 1.2, J = 6.7, 2 H, CH_2); 5.08 to 5.29 (m, 2 H, =CH_2); 5.88 (ddt, J = 6.7, J_{cis} = 10.1, J_{trans} = 16.8, 1 H, =CH-); 7.16 to 7.57 (m, 10 $H_{arom.}$); ^{13}C NMR: 35.0 (-CH_2-); 61.5 (C_β); 117.7; 124.0; 126.2; 127.6; 127.8; 129.2; 129.3; 134.3; 136.4; 140.6; 186.9 (C_α); mass m/z (%): 265 ($M^{+\cdot}$, 19.7); 224 (6.7); 109 (12.8); 77 (14.5).

Generation of ketenimine 7 and 8 followed by *in situ* hydrolysis to the corresponding amides:

Typical procedure IV: To a stirred solution of *N*-Phenyl-trimethylsilylketenimine **5** (160 mg, 0.85 mmol)in dichloromethane (10 ml),cooled to -50°C, 1 eq of benzenesulfanyl chloride (136 mg) was added dropwise. The reaction was stirred for 3 h and then allowed to reach +4°C. Dichloromethane was removed under vacuum and replaced by a mixture acetone/water (9/1) and stirred at room temperature for 2 h. Column chromatography (eluent: Et_20/pentane, 1:1)on silica gel afforded 110 mg of **11** (yield: 51%).

Hydrolysis of **7** and **8** was also observed on silica gel or alumina.

***N*-Phenyl-2-benzenesulfanylpropanamide** **11**: yield: 51 %, white needles, mp = 110, Rf = 0.65 (silica-gel, Et_20/pentane, 1:1); ^{1}H NMR: 1.64 (d, J = 7.3, 3 H, CH_3); 3.92 (q, J = 7.3, 1 H, CH); 7.11 (t, J = 7.4, 1 $H_{arom.}$); 7.25 to 7.48 (m , 9 $H_{arom.}$); 8.41(broad s, 1 H, NCH); ^{13}C NMR: 18.3 (CH_3); 48.0 (CH); 119.9 (C_o); 124.7 (C_p); 127.8 ($C_{p'}$); 129.1 ($C_{m'}$); 129.5 (C_m); 130.8 ($C_{o'}$); 133.7 ($C_{ipso'}$); 137.5 (C_{ipso}); 170.1 (C=O); mass m/z: (%): 257 ($M^{+\cdot}$, 59.8); 137 (79.8); 120 (22.1); 109 (43.1); 93 (49.4); 77 (64.0); 69 (80.1); Anal. for $C_{15}H_{15}NOS$ (257.4 $gmol^{-1}$) Calcd. for S: 12.46; Found (%): S, 12.36.

***N*-Phenyl-2-benzenesulfanylpent-4-enamide** **12**: yield: 73%, white needles, mp = 110, Rf = 0.2 (alumina, petroleum ether/AcOEt: 90/10); ^{1}H NMR: 2.66 (dd, J = 14.5, J = 7.3, 1 H) et 2.86 (dd, J = 14.5, J = 7.3, 1 H) (CH_2); 3.86 (dd, J = 6.1, J = 7.3, 1 H, CH); 5.14 to 5.29 (m, 2 H, CH_2); 5.91 (dddd, J = 6.4, J =7, J_{cis}= 10.1, J_{trans}= 16.1, 1 H, =CH-); 7.11 (t, J = 7.3, 1H); 7.24 to 7.46 (m, 9 $H_{arom.}$); 8.38 (broad s, 1 H, NCH); ^{13}C NMR: 36.7 (CH_2); 53.5 (-CH-); 118.7 (CH_2=); 120.0 (C_o); 124.8 (C_p); 127.8 ($C_{p'}$); 129.1 (C_m); 129.5 ($C_{o'}$); 130.8 ($C_{m'}$); 133.3 (C_{ipso}); 133.8 (=CH); 137.4 ($C_{ipso'}$); 168.9 (C=O); mass m/z (%): 283 ($M^{\cdot+}$, 20.5); 174 (27.9); 172 (100); 109 (15.2); 93 (6.0).

Addition of two equivalents of benzenesulfanyl chloride to ketenimines 5 and 6 and *in situ* hydrolysis of the intermediate imidoyl chlorides 13 and 14:

Typical procedure V: To a solution of ketenimine **5** (150 mg, 0.75 mmol) in dichloromethane (10 ml), cooled to 0°C (ice bath), 3.3 ml (2.5 eq) of a 0.5 M solution of benzenesulfanyl chloride in dichloromethane was added dropwise. The reaction was then stirred at room temperature for 1h. Dichloromethane was removed under vacuum and the crude imidoyl chloride **13** was taken up in a mixture acetone/water (15/2). The solution was stirred for an additional hour and acetone was removed under vacuum before extraction of the aqueous phase with ether. The organic phase was dried over sodium sulfate. The solvent was removed under vacuum. Column chromatography (eluent: petroleum ether/AcOEt: 95/5) on silica gel afforded *N*-Phenyl-2.2-*bis*-(benzenesulfanyl)propanamide **15** (100 mg, yield: 40%).

***N*-Phenyl-2.2-*bis*(benzenesulfanyl)propanamide 15:** yield: 40 %, yellow oil, Rf_= 0.48 (Alumina, petroleum ether/AcOEt: 95/5); ^{1}H NMR: 1.74 (s, 3 H, CH_3); 7.11 (t, J = 6.9, 1 H); 7.24 to 7.40 (m, 11 H); 7.53 (dd, J = 1.2, J = 8, 4 $H_{arom.}$); ^{13}C NMR: 24.4 (CH_3); 63.3 (C_2); 119.7 (C_o); 124.6 (C_p); 129.1; 129.5; 130.0; 130.5; 136.1 ($C_{ipso'}$); 137.4 (C_{ipso}); 167.4 (C=O); mass m/z (%): 365 ($M^{\cdot+}$, 3.3); 255 (20.7); 146 (100); 109 (63.5); 92 (18.3); 77 (81.9); 65 (61.4); Anal. for $C_{21}H_{19}NOS_2$ (365.5 gmol^{-1}): Calcd. for S: 17.54; Found (%): S 17.31.

***N*-Phenyl-2.2-*bis*-(benzenesulfanyl)pent-4-enamide 16:** yield: 52 %, yellow crystals, mp_=_90, Rf = 0.57 (alumina, petroleum ether/AcOEt: 95/5); ^{1}H NMR: 2.87 (dt, J = 1.4, J = 6.7, 2 H, CH_2); 5.13 (dd, J = 1.5, J = 15.1, 1 H); 5.26 (dd, J =1.5, J =10.1, 1 H); 6.22 (ddt, J = 6.7, J_{cis}=10.4, J_{trans} = 17.1, 1 H, =CH); 7.07 to 7.14 (m, 1 $H_{arom.}$); 7.24 to 7.37 (m, 10 $H_{arom.}$); 7.48 to 7.51 (m, 4 $H_{arom.}$); ^{13}C NMR: 38.0 (CH_2); 67.2 [$C(S)_2$]; 119.4 (CH_2=); 119.7 (C_o); 124.6 (C_p); 129.1 ($C_{p'}$); 129.3 ($C_{m'}$); 129.8 (C_m); 132.2 ($C_{ipso'}$); 132.8 (=CH); 135.8 ($C_{o'}$); 137.2 (C_{ipso}); 167.1 (C=O); mass m/z (%): 391 ($M^{\cdot+}$, 12.2); 282 (53.0); 240 (60.0); 218 (70.5); 172 (100); 109 (20.0); 91 (8.7); 77 (4.3); Anal. for $C_{23}H_{21}NOS_2$ (391.5 g mol^{-1}); Calcd. for C: 70.55; H: 5.41; O: 4.09; S: 16.34; Found (%): C: 70.29; H: 5.49; O: 4.04; S: 16.79.

Addition of one equivalent of benzenesulfanyl chloride to ketenimine 4 or lithiated ketenimine 3:

To a solution of **4** (1.2 10 mmol, 230 mg) in dichloromethane (15 ml) cooled to -78°C, 2.4 ml of a 0.5 M solution of PhSCl in CH_2Cl_2 (1eq) was added dropwise. The reaction mixture was then stirred for one hour. The flask was then removed from the cold bath and triethylamine (2 eq, 2.4 10^{-3} mol, 340 μl) was added. The solution was maintained at room temperature for one hour and the solvent was removed under vacuum. Ammonium salts were precipitated with petroleum ether. Bulb to bulb distillation afforded **18** (190 mg, yield: 55%).

Ketenimine **18** was also obtained in a 75% yield from the mixture of lithiated ketenimine **3** and MeSLi generated according to procedure **I**, (addition and work up according to the typical procedure **II**, iodomethane being replaced by 2 eq of PhSCl)

***N*-Phenyl-2-trimethylsilyl-2-benzenesulfanyl-ethanimidoyl chloride 17 (crude oil):** ^{1}H NMR: 0.16 [s, 9H, $(CH_3)_3Si$]; 4.05 (s, 1 H, CH); 6.69 (d, J = 7.4, 1 H); 7.16 (dt, J = 7.2, J = 1.5, 1 H); 7.21 to 7.41 (m, 8 H); 7.58 to 7.51 (m, 1 H); ^{13}C NMR: -0.8 $(CH_3)_3Si$); 45.7 (CH); 120.2 (C_O); 124.1; 125.6; 127.4; 128.9; 129.6; 138.6 ($C_{ipso'}$); 146.7 (C_{ipso}); 179.5 (N=C-Cl); mass m/z (%): 336 ($M^{\cdot+}$+2, 2.1 (28)); 334 ($M^{\cdot+}$, 5.7 (72)); 243 (100); 226 (48.7); 224 (11.9); 166 (55.4); 109 (7.0); 77 (11.3).

***N*-Phenyl-trimethylsilyl(benzenesulfanyl)ketenimine 18:** yield: 55%, yellow oil, bp (°C/mbar) = 150/10^{-3}; ^{1}H NMR: 0.16 (s, 9 H, $Si(CH_3)_3$); 7.10 to 7.51(m, 10 $H_{arom.}$); ^{13}C NMR: -0.8 ($Si(CH_3)_3$); 46.7 (C_β); 124.0; 125.6; 127.2; 127.4; 127.6; 128.8; 129.2; 129.6; 138.6; 139.8 (Ph); 179.5 (C_α); mass m/z

(%): 297 (M$^{+\cdot}$, 87.3); 296 (58.2); 238 (100); 224 (14.5); 206 (7.3); 188 (7.3); IR (NaCl): 1998 (C=C=N); 1286; 842; 760 (CH$_3$Si); Anal. for C$_{17}$H$_{19}$NSSi (297.5 gmol^{-1}); Calcd. for C: 68.63; N: 4.71; S: 10.78; Found (%): C: 68.62; N: 4.66; S: 10.93.

Ketenimine **18** has also been synthesised in 75% yield following the procedure **II.**

***N*-Phenyl-2-trimethylsilyl-2-(benzenesulfanyl)acetamide 19:** white solid, ^{1}H NMR: 0.29 (s, 9H, (CH$_3$)$_3$Si); 3.52 (s, 1H, CH); 7.05 to 7.51 (m, 10 H$_{\text{arom.}}$); 8.57 (broad s , 1 H, NH).

***N*-Phenyl-2-benzenesulfanylacetamide 21** (resulting from the desilylation of **19**): yield: 52 %, white crystals, mp = 79°C, Rf = 0.5 (alumina, petroleum ether/AcOEt: 75/25); ^{1}H NMR: 3.76 (s, 2 H, CH$_2$); 7.09 to 7.49 (m, 10 H$_{\text{arom.}}$); 8.59 (broad s, 1 H, NH); ^{13}C NMR: 38.5 (CH$_2$); 120.0 (C_o); 124.9 (C_p); 127.2 ($C_{o'}$); 128.5; 129.2 ($C_{m'}$); 129.6; 134.2 ($C_{ipso'}$); 137.3 (C_{ipso}); 166.1 (C=O); mass m/z: (%): 243 (M$^{+\cdot}$, 9.7); 218 (20.2); 178 (6.1); 123 (43.0); 109 (52.6); 92 (14.9); 77 (29.0); Anal. for C$_{14}$H$_{13}$NOS (243.3 gmol^{-1}); Calcd. for C: 69.10; H: 5.38; O: 6.57; Found (%): C: 69.16; H: 5.38; O: 6.63.

Synthesis of *N*-Phenyl-benzenesulfanylketenimine 20:

To a stirred solution of **4** (120 mg, 6.3 10^{-4}mol) in dichloromethane (10 ml) cooled to 0°C, the solution of PhSCl (0.95 eq, 6 10^{-4}mol, 1.2 ml) was added dropwise. After 5 min, the mixture was pourred into an aqueous solution of acidified ammonium chloride (HCl) and rapidly extracted twice with ether. The organic layers were dried over Na2SO4, the solvent was evaporated and the residue was taken up in dichloromethane (10 ml) and triethylamine (3eq, 250 µl). The solution was stirred at room temperature for 1 h, concentrated under vacuum and ammonium salts were precipitated with petroleum ether. After filtration and evaporation of the solvent, the crude *N*-Phenyl benzenesulfanyl-ketenimine **20** was characterised by its spectra (NMR, IR) and by its conversion (in acetone-water or by passing through a silica gel column) into amide **22** (125mg, 65%).

***N*-Phenyl-benzenesulfanylketenimine 20 (crude):** yield: 65% (deduced from that of amide **22**); ^{1}H NMR: 4.84 (s, 1H, CH); 7.05 to 7.50 (m, 10 H$_{\text{arom.}}$); ^{13}C NMR: 46.8 (C$_\beta$); 124.5; 126.6; 126.8; 128.1; 128.4; 128.5; 129.2; 129.6; 138.6 et 139.5 (C_{ipso}); 184.5 (C$_\alpha$); IR (NaCl): 2014 (C=C=N); 728 (C=C)

Addition of PhSCl to ketenimine 18:

To a stirred solution of **18** (500 mg, 1.68 10 mmol) in dichloromethane (5ml) cooled to -10°C, the solution of PhSCl (1.1eq, 1.8 10^{-3}mol, 3.6 ml) was added dropwise. After 1h, the mixture was poured into an aqueous solution of acidified ammonium chloride (HCl) and rapidly extracted twice with ether. The organic layers were dried over Na2SO4. The solvent was removed and the residue was taken up by dichloromethane (10 ml) and triethylamine (2eq, 750 µl). The solution was stirred at room temperature for 2 h, and poured into a solution of ammonium chloride. The aqueous phase was extracted twice with ethyl acetate. The organic layers were combined, dried over sodium sulfate and concentrated under vacuum. The crude *N*-Phenyl-benzenesulfanylketenimine **25** was characterised by its spectra (NMR, IR) and by its conversion (in acetone-water or by passing through a silica gel column) into amide **24** (125mg, 65%).

***N*-Phenyl-*bis*(benzenesulfanyl)ketenimine 25 (crude oil):** ^{1}H NMR: 7.04 to 7.76 (m, H$_{\text{arom}}$); ^{13}C NMR: 77.3 (C$_\beta$); 119.7; 127.3; 127.7; 128.8; 129.2; 129.4; 129.5; 135.4; 146.2; 189.9 (C$_\alpha$); accurate mass: Calcd. for C$_{20}$H$_{15}$NS$_2$: 333.0634; Found: 333.0646 ; mass m/z (%): 333 (M$^{+\cdot}$, 100); 224 (17.9); 223 (53.8); 212 (23.1); 153 (20.5); 146 (10.3); 77 (41.0); IR (KBr): 2010 (C=C=N).

Intermediate unstable imidoyl chlorides **22** and **23** (precursors of **25**) were hydrolysed with a mixture acetone/water to lead to *N*-Phenyl-2,2-*bis*(benzenesulfanyl) acetamide **24** (yield: 41%, after chromatography on silica gel).

***N*-Phenyl-2.2-*bis*(benzenesulfanyl)acetamide 24:** yield: 66 % (from **18**), white crystals, mp = 140°C, Rf = 0.5 (alumina, petroleum ether/AcOEt: 95/5); ^{1}H NMR: 7.07 to 7.13 (m, 2 H$_{\text{arom.}}$); 7.20 to 7.36 (m, 6 H$_{\text{arom.}}$); 7.49 to 7.53 (m, 8 H$_{\text{arom.}}$); 8.11 (s large, 1H, NH); ^{13}C NMR: 118.7 (C_o); 123.8 (C_p); 127.7; 127.8; 128.3; 130.3 (C_m); 133.7 ($C_{ipso'}$); 135.5 (C_{ipso}); 163.5 (C=O); mass m/z (%): 351 (M$^{+\cdot}$, 3.8); 153 (13.6); 122 (11.2); 121 (18.1); 110 (100); 109 (38.8); 92 (17.4); 77 (23.3); 56 (33.3); 43 (69); Anal.

for $C_{20}H_{17}NOS_2$ (351.5 gmol^{-1}); Calcd. for C: 68.34; H: 4.87; N: 3.98; S: 18.25; Found (%): C: 67.96; H: 5.31; N: 3.74; S: 20.09.

Addition of benzenesulfinyl chloride to *N*-Phenyl-trimethylsilylketenimine 4 followed by hydrolysis:

To a stirred solution of *N*-Phenyl-trimethylsilylketenimine **4** (160 mg, 8.5 10^{-4} mol) in dichloromethane (10ml) cooled to -50°C, 1 eq of benzenesulfinyl chloride (136 mg) was added dropwise. The reaction was stirred for 3 h and then allowed to reach +4°C. Dichloromethane was removed under vacuum and the oily residue was taken up in a mixture of acetone/water (9/1) and stirred for 2h at room temperature. Acetone was removed under vacuum before extraction of the residue with diethyl ether. Chromatography on silica gel (petroleum ether/AcOEt: 75/25) afforded amide **26**.

***N*-Phenyl-2-benzenesulfinylacetamide 26**: dark orange crystals, mp = 114-118°C, Rf = 0.45 (silica, petroleum ether/AcOEt: 75/25); ^{1}H NMR: 3.61 (d, J = 14.1, 1 H) et 3.95 (d, J = 14.1, 1H) (CH_2); 7.08 (t, J=7.3, 1 H); 7.26 (t, J=0.8, 2 H); 7.34 to 7.47 (m, 5 $H_{arom.}$); 7.51 to 7.6 (m, 2 $H_{arom.}$); 9.11 (s large, 1 H, NH); ^{13}C NMR: 59.4 (CH_2); 120.4 (C_{o}); 124.1 ($C_{o'}$); 124.8 (C_{p}); 129.1 (C_{m}); 129.7 ($C_{m'}$); 131.9 ($C_{p'}$); 137.9 (C_{ipso}); 141.1 ($C_{ipso'}$); 161.8 (C=O); mass m/z (%): 259 ($M^{\cdot+}$, 28.4); 167 (16.8); 125 (14.7); 91 (36.8); 77 (100).

Addition of 1eq of *p*-toluenesulfonyl chloride to 3:

Procedure II was used, iodomethane being replaced by 2.1 eq of *p*-TolSO_2Cl:

***N*-Phenyl-trimethylsilyl(*p*-toluenesulfonyl)ketenimine 29 (crude)**; ^{1}H NMR: 0.25 (s, 9H, $(CH_3)_3Si$); 2.49 (s, 3H, CH_3); 7.26 to 7.42 (m, 8 $H_{arom.}$); 7.93 (d, J = 8.5, 1H); ^{13}C NMR: -1.8 $(CH_3)_3Si$); 22.2 (CH_3); 37.2 (C_β); 119.0; 124.0; 127.2; 128.1; 129.1; 129.6; 130.3; 142.1; 190.6 (C_α); IR (NaCl): 3064 (C_{Ar-H}); 1998 (C=C=N); 1592 (C=N); 844 (Si-C), [888, 762, 730, 690] (phenyl).

Addition of diisopropyl chlorophosphate, chloro- (or bromo-) trimethylsilane, acetyl chloride and propylene oxide:

These reactions were performed on the mixture of lithiated ketenimine **3** and MeSLi according to the typical procedure **II**, iodomethane being replaced by one of these electrophiles.

N*-Phenyl-*N*-(diisopropoxyphosphoryl)trimethylsilylethynamine 32:** (2.5 eq of diisopropyl chlorophosphate were used and the mixture was allowed to react for 3h at room temperature); yield: 48 % (purification: distillation and chromatography), colourless liquid, bp(°C/mbar) = 150/10^{-3}; Rf = 0.82 (Silica, petroleum ether/AcOEt: 50/50); ^{1}H NMR: 0.19 (s, 9 H, $(CH_3)_3Si$); 1.34 (d, J = 6.1, 6 H, CH(CH_3)2); 1.39 (d, J = 6.1, 6 H, CH$(CH_3)_2$); 4.77 [dd, J = 6.1, J = 8.6, 2 H, **C*H(CH_3)2]; 7.14 (tt, J < 1, J = 7.3, 1H, H_{p}); 7.33 (dd, J = J = 7.9, 2H, H_{m}); 7.54 (d, J = 7.6, 2 H, H_{o}); ^{13}C NMR: 0.18 (CH_3Si); 23.5 [d, J = 6.2, CH(CH_3)2]; 23.85 [d, J = 4.5, CH$(CH_3)_2$]; 60.7 (Si-C≡); 73.7 [d, J = 6.3, CH$(CH_3)_2$]; 97.65 (d, J = 3.6, ≡C-N); 121.8 (d, J = 2.7, C_{o}); 125.1 (s, C_{p}); 129.0 (s, C_{m}); 140.9 (d, J = 5.3, C_{ipso}); ^{31}P NMR ($CDCl_3$): -2.74; mass m/z (%): 353 ($M^{\cdot+}$, 32.3); 310 (9.1); 268 (34.3); 255 (25.2); 213 (12.8); 174 (26.0); 77 (29.0); IR (NaCl): 2166 (C≡C); 1008; [902, 844, 758, 716] phenyl; Anal. for $C_{17}H_{28}NO_3PSi$ (353.5 gmol^{-1}); Calcd. for C: 57.76; H: 7.98; P: 8.76; Found (%): C: 57.95; H: 8.05; P: 8.67.

***N*-Phenyl-*N*-(trimethylsilylethynyl)acetamide 35:** (3 eq of acetyl chloride were added and the mixture was left for 2h at r.t.); yield: 80 %, colourless liquid, bp (°C/mbar) = 125/10^{-3}); ^{1}H NMR: 0.20 [s, 9 H, $(CH_3)_3Si$]; 2.48 (s, 3 H, CH_3CO); 7.26 to 7.33 (m, 1 H); 7.39 to 7.43 (m, 4 H); ^{13}C NMR: 0.00 [$(CH_3)_3Si$]; 23.1 (CH_3); 125.1 (C_O); 127.30 (C_{p}); 129.0 (C_{m}); 138.7 (C_{ipso}); 171.6 (C=O); accurate mass: Calcd. for $C_{13}H_{17}NOSi$: 231.10794; Found: 231.09980 mass m/z (%): 231 ($M^{\cdot+}$, 9.1); 216 (13.1); 188 (13.1); 172 (100); 140 (15.7); 77 (18.5); 73 (8.5); 43 (76.4); IR (NaCl): 2165 (C≡C); 1710 (broad) (C=O).

N-Phenyl-[*N*-1-(2-hydroxypropyl)]-2-trimethylsilylethynamine 37: (2.5 eq of propylene oxide were added and the mixture was left for 2h at r.t.): yield: 75 %, colourless liquid, bp (°C/mbar) =

100/10^{-3}; ^{1}H NMR: 0.22 (s, 9 H, CH_3Si); 1.30 (d, J = 6.3, 3 H, CH_3); 2.25 (d, J = 3.5, 1 H, OH); 3.50 (d, J = 5.9, 2 H, CH_2); 4.32 (dq, J_1 = 3.7, J_2 = 6.1, 1H, CH); 6.94 (dt, J_1 = 7.3, 1 H, H_p); 7.13 (dd, J = 7.8, J <1, 2 H, H_o); 7.29 (dd, J = 7.9, J =1.2, 2 H, H_m); ^{13}C NMR: 0.73 (CH_3Si); 20.4 (CH_3); 58.0 (CH_2); 66.0 (CHOH); 101.7 (Si-C≡); 115.1 (C_o); 121.3 (C_p); 129.1 (≡C-N); 129.2 (C_m); 144 (C_{ipso}); mass m/z (%): 247 ($M^{·+}$, 29.7); 201 (100); 188 (22.7); 174 (28.1); 105 (27.1); 91 (18.9); 77 (22.6); IR (NaCl): 3402; 2962; 2154 (C≡C); 1598; 1498; 842; 750, 692; Anal. for $C_{14}H_{21}NOSi$ (247.4 gmol^{-1}); Calcd. for C: 67.96; H: 8.55; N: 5.66; Found (%): C: 66.91; H: 8.41; N: 5.52.

Purification by column chromatography on silica gel (eluting system: petroleum ether/AcOEt: 90/10), afforded acetamide **39** (resulting from the hydrolysis of silylated ynamine **37**).

***N*-Phenyl-[*N*-1-(2-hydroxypropyl)]acetamide 39:** yield: 50 %, colourless liquid, Rf = 0.27 (Silica, petroleum ether/AcOEt: 90/10); ^{1}H NMR: 1.30 (d, J = 6.4, 3 H, CH_3); 2.02 (s, 3 H, CH_3CO); 3.25 (broad s, 2 H, CH_2); 3.83 (s, 1 H, OH); 5.12 (ddq, J = 6.4, J = 4.9, J = 6.4, 1 H, CH); 6.61 (ddt, J = 0.9, J = 8.4, J =2.2, , 2 H, H_o); 6.70 (tt, J = 0.9, J = 7.3, 1 H, H_p); 7.16 (dd, J = 7.3, J = 8.5, H_m); ^{13}C NMR: 18.0 (CH_3); 21.3 (CH_3CO); 48.9 (CH_2); 69.9 (CHOH); 113.0 (C_o); 117.8 (C_p); 129.4 (C_m); 148 (C_{ipso}); 170.85 (C=O); accurate mass: Calcd. for $C_{11}H_{15}NO_2$: 193.11027; Found: 193.10741; mass m/z (%): 193 ($M^{·+}$, 36.1); 180 (13.1); 133 (14.10); 115 (11.8); 106 (100); 77 (44.6); 51 (12.1); 43 (30).

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