

Synthesis of α -phenylselanyl and α -phenylsulfanyl nitriles from aldehyde *N,N*-dialkylhydrazones

Michaël Ternon, Xavier Pannecoucke, Francis Outurquin* and Claude Paulmier

Laboratoire de Synthèse Thio-et-Séléno-organique, IRCOF-UFR Sciences, Université de Rouen, F-76821, Mont Saint Aignan Cedex, France

In memoriam Professor Claude Paulmier who deceased on 28 November 2001

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Abstract—Phenylselenenylation of azaenolates, formed by LDA treatment of dimethylhydrazones **1** ($R^2=H$) and derived from linear aliphatic aldehydes, has led to α -phenylselanyl hydrazones **2**. α -Phenylselanyl nitriles **3** were, however, isolated when an excess of base and of PhSeX (X=Cl, Br) were used. Hydrazones **1** bearing an α -alkyl substituent ($R^2\neq H$) gave also nitriles **3**. SAMP-hydrazones **4** showed the same reactivity and the corresponding nitriles **3** were obtained in a racemic form. The use of PhSeCl, in the place of PhSeBr, has led to α -phenylsulfanyl nitriles **6** from hydrazones **1** derived from α -branched aldehydes ($R^2\neq H$). © 2002 Elsevier Science Ltd. All rights reserved.

Some years ago, we prepared, with modest enantiomeric excesses, (*R*)-2-arylselanyl-2-phenylpropanals by α -selenenylation of 2-phenylpropanal using chiral selenenamides, especially those derived from (*S*)-proline methyl ester.¹ In the search of a general method for the synthesis of enantiomerically enriched α -phenylselanyl carbonyl compounds,^{2–4} we were interested in the metalation–alkylation method of SAMP and RAMP-hydrazones developed by Enders and Eichenauer.⁶ After regeneration of the carbonyl group, α -alkyl carbonyl compounds were prepared with excellent ee. Optically active α -phenylsulfanyl aldehydes were prepared either by alkylation of the azaenolate formed from phenylsulfanylethanal SAMP-hydrazone^{5,7} or by sulfenylation of azaenolates derived from aldehyde or ketone SAMP-hydrazones.⁸

Using this method, good diastereoisomeric excesses were observed for the metalation–alkylation of phenylselanylethanal SAMP-hydrazone.⁹ In the course of the selenenylation of azaenolates, formed from dimethylhydrazones **1** ($R^2=H$) (LDA, 1.2 equiv., THF, 0°C then PhSeBr, 1.2 equiv.), the corresponding α -phenylselanyl hydrazones **2** were isolated with modest yields. (Scheme 1; Table 1, entries 1 and 2). To improve the yields, greater amounts of base and of PhSeBr (2.5 equiv.) were used. Surprisingly, the formation of the corresponding nitriles **3** ($R^2=H$) was observed (Table 1, entries 3 and 4). Similar results were obtained at -78°C and when PhSeCl or PhSeSePh were used as selenium reagent.

Keywords: hydrazone; SAMP; deprotonation; nitrile.

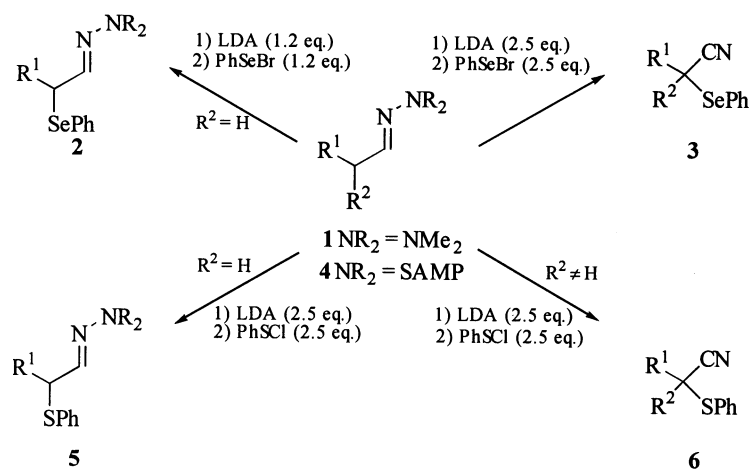
* Corresponding author. Fax: +33-2-35-52-29-59; e-mail: francis.outurquin@univ-rouen.fr

Dimethylhydrazones **1d–f**, formed from α -branched aldehydes, were also treated with excesses of LDA and PhSeBr. The corresponding α -phenylselanyl nitriles **3d–f** were obtained in good yields (entries 5, 7 and 9). With 1.2 equiv. of base and 1.2 equiv. of PhSeBr, the nitrile **3** could also be obtained, but with lower yields (entries 6 and 8).

The metalation–sulfenylation reaction (LDA, 2.5 equiv. and PhSeCl, 2.5 equiv.) was also carried out on dimethylhydrazones **1a** and **1b**. According to the work of Enders et al.,⁸ the α -phenylsulfanyl hydrazones **5a** and **5b** were isolated in correct yields but the α -phenylsulfanyl nitrile **6a** ($R^1=n\text{Bu}$, $R^2=H$) appeared also as a by-product (entries 10 and 11). Under the same experimental conditions, the α -alkyl hydrazones **1d–f** have led to the corresponding α -phenylsulfanyl nitriles **6d–6f** albeit in poorer yields than those observed for the selenium analogues (entries 12–14).

The metalation–selenenylation reaction of a 1/1 diastereoisomeric mixture of SAMP-hydrazone **4e** ($R^1=n\text{Pr}$, $R^2=Me$), using an excess of reagents, afforded the 2-methyl-2-phenylselanyl pentanenitrile **3e** in a racemic form (entry 15). 2*S*-enriched samples of SAMP-hydrazones **4e** and **4g** were also subjected to the reaction. The α -phenylselanyl nitriles **3e** and **3g**, respectively, were also obtained without optical activity (entries 16 and 17).

The synthesis of nitriles from aldehyde dialkylhydrazones is well documented. Nitriles could be synthesized by oxidation of the dialkylamino group followed by *syn*-elimination of dialkylhydroxylamine. H_2O_2 oxidation,^{10,11} oxone treatment



Scheme 1.

Table 1. α -Phenylselanyl hydrazones **2**, nitriles **3** and sulfur analogues **5** and **6**

Entry	Hydrazone no.	R ¹	R ²	PhYX	LDA and PhYX (<i>n</i> equiv.)	Yields (%)	
						Hydrazone	Nitrile
1	1a	<i>n</i> Bu	H	PhSeBr	1.2	2a (42)	–
2	1b	Bn	H	PhSeBr	1.2	2b (45)	–
3	1a	<i>n</i> Bu	H	PhSeBr	2.5	–	3a (43)
4	1c	<i>i</i> Pr	H	PhSeBr	2.5	–	3c (52)
5	1d	Me	Me	PhSeBr	2.5	–	3d (78)
6	1e	<i>n</i> Pr	Me	PhSeBr	1.2	–	3e (48)
7	1e	<i>n</i> Pr	Me	PhSeBr	2.5	–	3e (75)
8	1f	Et	Et	PhSeBr	1.2	–	3f (35)
9	1f	Et	Et	PhSeBr	2.5	–	3f (70)
10	1a	<i>n</i> Bu	H	PhSeBr	2.5	5a (50)	6a (10)
11	1b	Bn	H	PhSeBr	2.5	5b (57)	–
12	1d	Me	Me	PhSeBr	2.5	–	6d (48)
13	1e	<i>n</i> Pr	Me	PhSeBr	2.5	–	6e (51)
14	1f	Et	Et	PhSeBr	2.5	–	6f (62)
15	4e	<i>n</i> Pr	Me	PhSeBr	2.5	–	3e (60)
16	4e^a	<i>n</i> Pr	Me	PhSeBr	2.5	–	3e (72) ^b
17	4g^a	Et	Me	PhSeBr	2.5	–	3g (67) ^b

^a 2*R*-SAMP-hydrazone.

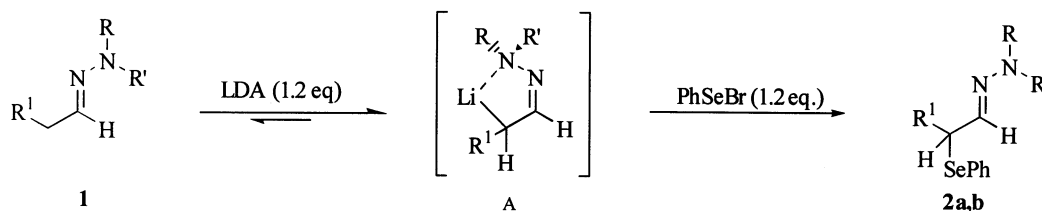
^b Racemic nitrile.

under microwave irradiation¹² have also been proposed. Enders et al. have used magnesium monoperoxyphthalate hexahydrate (MMPP) in the case of dimethylhydrazones¹³ and SAMP-hydrazones allowing the synthesis of nitriles with an α -asymmetric centre.¹⁴ The activation of the dialkyl-amino group can be also achieved by methylation^{15,16} or alkyl chloroformate addition.¹⁷ A subsequent basic treatment allows the formation of the nitrile group.

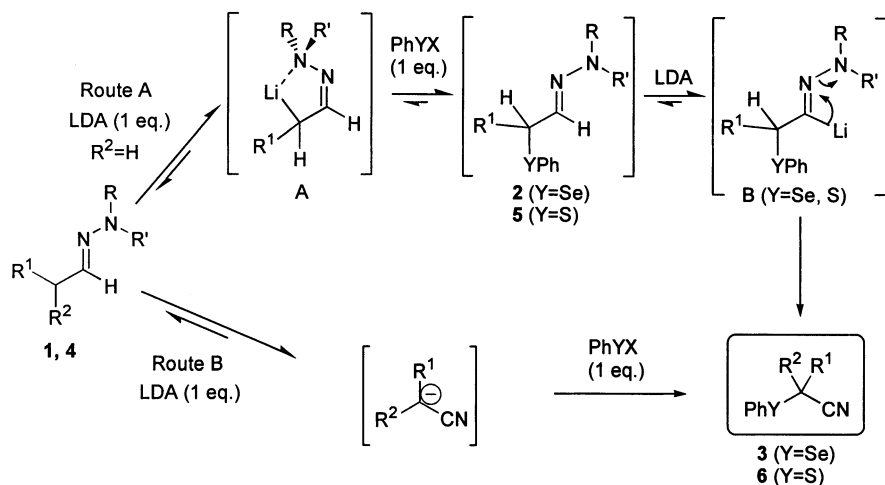
Some α -phenylselanyl nitriles have been prepared by different ways: Deprotonation–selenenylation of nitriles,¹⁸

deprotonation–alkylation of phenylselanyl acetonitrile,¹⁹ Bu₃P–PhSeCN treatment of aliphatic aldehydes,²⁰ phenylselenolate substitution of a α -mesyl nitrile,²¹ SnCl₄-activated reaction of Me₃SiCN with selenoacetals²² and conjugate addition of an enamine with α -phenylselanyl acrylonitrile.²³ α -Phenylsulfanyl nitriles have been prepared by reaction of Me₃SiCN with thioacetals²⁴ or α -(phenylsulfanyl) alkylbenzotriazoles.²⁵

Concerning the mechanistic aspect of this two-step reaction, we first observe that, when R²=H, the introduction of one



Scheme 2.



Scheme 3.

molar equivalent of base must lead to the lithium azaenolate A, stabilized by the chelating effect of the dialkylamino group. The reaction with the selenium electrophile affords the α -phenylselenyl hydrazones **2** (Scheme 2). The formation of the chelated intermediate A has been proposed to explain the excellent asymmetric induction observed when SAMP-hydrazones were used as substrates.²⁶

When $R^2=H$, in the presence of LDA and PhSeBr in excesses, the carbanionic species B must be formed and leads to the nitrile **3** ($R^2=H$) after loss of lithium dialkylamide (Table 1, entries 3 and 4, Scheme 3). The sulfur analogue is less prone to the elimination of LiNRR' and **6a** was only isolated as a by-product (Table 1, entries 10 and 11). Using stoichiometric amounts of reagents, Enders et al.⁸ have only observed the formation of α -phenylsulfanyl hydrazones **5**. In conclusion, when $R^2=H$, the α -chalcogenated nitriles **3a,c** were obtained probably through pathway A. This is in accordance with the fact that when 1.2 equiv. of LDA and PhSeBr were used, hydrazones **2** could be isolated in modest yields. But surprisingly, even varying the amount of base, with or without PhSeBr, we were not able to generate α -selenylated nitriles **3a,b** from hydrazones **2a,b**. Experiments are still under investigations to try to explain this result.

Starting from α -branched aldehyde hydrazones **1** or **4** ($R^2 \neq H$), α -chalcogenated nitriles **3d–g** (Y=Se) and **6d–f** (Y=S) were only isolated, even when 1.2 equiv. of LDA and 1.2 equiv. PhSeBr were used (Table 1). When 2*R*-SAMP hydrazones **4e** and **4g** were used, we could only isolate the racemic nitriles **3e** and **3g**, respectively (Table 1, entries 16 and 17). These two facts cannot be explained by the two-step pathway A.

In addition, Normant et al.²⁷ have observed the formation of α -alkyl hydrazones after metalation–alkylation of dimethylhydrazones, derived from linear aldehydes, in the presence of HMPA. Starting from α -branched aldehyde dimethylhydrazones, α -alkyl nitriles were only obtained. They suggested that the chelating effect of the cosolvent has favoured the displacement of the deprotonation site to the iminyl carbon.

The formation of the nitrile function must be accompanied by the regeneration of LDA. In a subsequent reaction, the α -metalation–chalcogenation of the nitrile (Scheme 3, route B) occurred as proposed in the literature.¹⁸ Starting from 2*R*-SAMP hydrazones, the isolation of racemic nitriles **3** is more easily explained by route B. The formation of the nitrile functional group must occur before α -chalcogenation as proposed by Normant et al.²⁷ Work is in progress to obtain more information regarding the regiocontrol of the deprotonation. Other bases and experimental conditions are being used.

We have described the synthesis of α -selenyl and α -sulfanyl nitriles, in a one-pot metalation–chalcogenation reaction, starting from aliphatic aldehyde dialkylhydrazones. α -Alkyl hydrazones were efficiently transformed into nitriles but those derived from linear aldehydes, needed excesses of LDA. α -Chalcogenated hydrazones could only be obtained from linear aldehyde hydrazones using 1 equiv. of LDA.

1. Experimental

Dimethylhydrazones²⁶ and SAMP-hydrazones⁶ were prepared as described. THF was distilled over sodium-benzophenone and diisopropylamine over NaOH. The chromatographic separations were achieved on silica gel (0.060–0.200 nm, pore diameter ca. 4 nm) available from ACROS. ¹H and ¹³C NMR spectrum were recorded on Bruker AC 200 and DPX 300 instruments and carried out in CDCl₃.

1.1. Preparation of α -phenylselenyl dimethylhydrazones **2**

The hydrazone **1** (1 mmol) in THF (10 ml) was added to a freshly prepared solution of LDA (1.2 mmol) at 0°C under argon. After 6 h at 0°C, a solution of PhSeBr (283 mg, 1.2 mmol) in THF (1 ml) was introduced. The mixture was stirred overnight at room temperature and then treated with a sat. aq. NaCl solution (10 ml). The organic layer was dried and the solvent eliminated. The hydrazones **2** were

purified by silica gel chromatography (eluent: cyclohexane–CH₂Cl₂, 8:2).

1.1.1. 2-Phenylselanylhexanal dimethylhydrazone 2a.

Oil, yield=42%. ¹H NMR, δ: 7.5 (m, 2H, Ph), 7.2 (m, 3H, Ph), 6.42 (d, 1H, H₁, *J*=8.1 Hz), 3.98 (q, 1H, H₂, *J*=8.1 Hz), 2.57 (s, 6H, N(CH₃)₂), 1.75 (q, 2H, CH₂, *J*=8.1 Hz), 1.39 (m, 4H, CH₂), 0.86 (t, 3H, CH₃, *J*=7.5 Hz). ¹³C NMR, δ: 137.5, 135.1, 128.6, 128.4, 127.3 (Ph, C₁), 46.3 (C₂), 42.8 (N(CH₃)₂), 32.9 (C₅), 30.1 (C₄), 22.1 (C₃), 13.7 (C₆). Anal. calcd for C₁₄H₂₂N₂Se: C, 56.56; H, 7.46; N, 9.42; found: C, 56.30; H, 7.73; N, 9.24%.

1.1.2. 3-Phenyl-2-phenylselanylpropanal dimethylhydrazone 2b.

Oil, yield=45%. ¹H NMR, δ: 7.5 (m, 2H, Ph), 7.2 (m, 8H, Ph), 6.47 (d, 1H, H₁, *J*=7 Hz), 4.26 (q, 1H, H₂, *J*=7.0 Hz), 3.15 (m, 2H, CH₂), 2.57 (s, 6H, N(CH₃)₂). ¹³C NMR, δ: 139.6, 136.5, 135.9, 129.8, 129.5, 129.3, 129.1, 128.1, 126.7 (C₁, Ph), 46.8 (C₂), 42.6 (N(CH₃)₂), 39.4 (C₃). Anal. calcd for C₁₇H₂₀N₂Se: C, 61.63; H, 6.08; N, 8.46; found: C, 61.71; H, 6.16; N, 8.55%.

1.2. Preparation of α-phenylselanylnitriles 3

The reaction was carried out as above using hydrazones **1** or **4** (1 mmol), LDA (2.5 mmol), PhSeBr (590 mg, 2.5 mmol). The nitriles **3** were purified by silica gel chromatography (eluent: cyclohexane–CH₂Cl₂, 8:2).

1.2.1. 2-Phenylselanylhexanenitrile 3a.

Oil, yield=43%. ¹H NMR, δ: 7.7 (m, 2H, Ph), 7.2 (m, 3H, Ph), 3.53 (t, 1H, H₂, *J*=7.3 Hz), 1.77 (q, 2H, H₃, *J*=7.3 Hz), 1.6 (m, 2H, H₄), 1.25 (m, 2H, H₅), 0.80 (t, 3H, H₆, *J*=7.3 Hz). ¹³C NMR, δ: 136.9, 130.5, 129.1, 125.6, 119.7, (Ph, C₁), 32.0 (C₃), 29.5 (C₄), 25.6 (C₂), 21.4 (C₅), 13.3 (C₆). MS (EI, 70 eV): 253 (M⁺, 90), 158 (100). Anal. calcd for C₁₂H₁₅NSe: C, 57.15; H, 5.99; N, 5.55; found: C, 57.48; H, 6.12; N, 5.65%.

1.2.2. 3-Methyl-2-phenylselanylbutanenitrile 3c.

Oil, yield=52%. ¹H NMR, δ: 7.7 (m, 2H, Ph), 7.2 (m, 3H, Ph), 3.45 (d, 1H, H₂, *J*=6.0 Hz), 2.01 (oct, 1H, H₃, *J*=6.0 Hz), 1.09 (d, 6H, H₄, *J*=6.0 Hz). ¹³C NMR, δ: 136.0, 131.3, 129.5, 121.7, 120.0 (Ph, C₁), 35.3 (C₂), 31.3 (C₃), 21.1, 19.8 (C₄). MS (EI, 70 eV): 239 (M⁺, 70), 170 (40), 157 (100), 82 (30), 77 (100). Anal. calcd for C₁₁H₁₃NSe: C, 55.47; H, 5.50; N, 5.88; found: C, 55.65; H, 5.86; N, 5.96%.

1.2.3. 2-Methyl-2-phenylselanylpropanenitrile 3d.²⁸

Oil, yield=78%. ¹H NMR, δ: 7.7 (m, 2H, Ph), 7.43–7.30 (m, 3H, Ph), 1.63 (s, 6H, CH₃). ¹³C NMR, δ: 137.4, 129.9, 129.2, 126.9 (Ph), 123.0 (C₁), 30.0 (C₂), 27.9 (C₃). MS (EI, 70 eV): 225 (M⁺, 40), 77 (90).

1.2.4. 2-Methyl-2-phenylselanylpentanenitrile 3e.

Oil, yield=75%. ¹H NMR, δ: 7.7 (m, 2H, Ph), 7.2 (m, 3H, Ph), 1.70 (m, 2H, H₃), 1.50 (m, 2H, H₄), 1.53 (s, 3H, H₆), 0.88 (t, 3H, H₅, *J*=7.3 Hz). ¹³C NMR, δ: 137.5, 129.7, 128.9, 125.8, 122.4 (Ph, C₁), 41.8 (C₃), 35.4 (C₂), 25.7 (C₆), 19.1 (C₄), 13.8 (C₅). MS (EI, 70 eV): 253 (M⁺, 60), 158 (100), 78 (50). Anal. calcd for C₁₂H₁₅NSe: C, 57.15; H, 5.99; N, 5.55; found: C, 57.56; H, 6.19; N, 5.87%.

1.2.5. 2-Ethyl-2-phenylselanylbutanenitrile 3f.

Oil, yield=70%. ¹H NMR, δ: 7.7 (m, 2H, Ph), 7.2 (m, 3H, Ph), 1.72 (q, 4H, H₃, *J*=7.3 Hz), 1.04 (t, 6H, H₄, *J*=7.3 Hz). ¹³C NMR, δ: 137.8, 129.9, 129.2, 125.7, 121.8 (Ph, C₁), 43.5 (C₂), 29.8 (C₃), 9.8 (C₄). MS (EI, 70 eV): 253 (M⁺, 70), 158 (100). Anal. calcd for C₁₂H₁₅NSe: C, 57.15; H, 5.99; N, 5.55; found: C, 57.56; H, 6.19; N, 5.87%.

1.2.6. 2-Methyl-2-phenylselanylbutanenitrile 3g.

Oil, yield=67%. ¹H NMR, 7.72–7.77 (m, 2H, Ph), 7.36–7.42 (m, 3H, Ph), 1.75–1.91 (m, 2H, CH₂), 1.59 (s, 3H, H₅), 1.13 (t, 3H, H₄, *J*=7.4 Hz). ¹³C NMR, δ: 137.7, 131.4, 129.9, 126.7, 122.5 (Ph, C₁), 36.5 (C₂), 33.2 (C₃), 25.2 (C₅), 10.2 (C₄). MS (CI, 200 eV): 240 (MH⁺, 100), 213 (60). Anal. calcd for C₁₁H₁₃NSe: C, 55.47; H, 5.50; N, 5.88; found: C, 55.81; H, 5.51; N, 5.81%.

1.3. Preparation of α-phenylsulfanyl dimethyl-hydrazones 5

The reaction was carried out as for the selenylated hydrazones **2** using hydrazones **1** (1 mmol), LDA (2.5 mmol), PhSCI (360 mg, 2.5 mmol). The hydrazones **5** were purified by silica gel chromatography (eluent: cyclohexane–CH₂Cl₂, 8:2).

1.3.1. 2-Phenylsulfanylhexanal dimethylhydrazone 5a.

Oil, yield=50%. ¹H NMR, δ: 7.7 (m, 2H, Ph), 7.2 (m, 3H, Ph), 6.27 (d, 1H, H₁, *J*=7.3 Hz), 3.77 (q, 1H, H₂, *J*=7.3 Hz), 2.55 (s, 6H, N(CH₃)₂), 1.65 (q, 2H, H₃, *J*=7.3 Hz), 1.2–1.4 (m, 4H, H₄, H₅), 0.82 (t, 3H, H₆, *J*=7.3 Hz). ¹³C NMR, δ: 137.2, 132.0, 129.1, 128.2, 126.4 (Ph, C₁), 50.4 (C₂), 42.9 (N(CH₃)₂), 32.8 (C₃), 28.2 (C₄), 22.3 (C₅), 13.8 (C₆). MS (CI, 200 eV): 251 (MH⁺, 20), 141 (100). Anal. calcd for C₁₄H₂₂N₂S: C, 67.15; H, 8.86; N, 11.19; found: C, 67.26; H, 9.12; N, 11.41%.

1.3.2. 3-Phenyl-2-phenylsulfanylpropanal dimethylhydrazone 5b.

Oil, yield=57%. ¹H NMR, δ: 7.10–7.40 (m, 10H, Ph), 6.32 (d, 1H, H₁, *J*=7.2 Hz), 4.07 (q, 1H, H₂, *J*=7.2 Hz), 2.92–3.10 (m, 2H, CH₂), 2.53 (s, 6H, N(CH₃)₂). ¹³C NMR, δ: 137.2, 134.5, 133.5, 131.3, 128.3, 128.0, 127.4, 125.9, 125.4, 51.4 (C₂), 42.6 (N(CH₃)₂), 39.4 (C₃). MS (CI, 200 eV): 285 (MH⁺, 20), 141 (175). Anal. calcd for C₁₇H₂₀N₂S: C, 71.79; H, 7.09; N, 9.85; found: C, 71.52; H, 7.02; N, 9.99%.

1.4. Preparation of α-phenylsulfanylnitriles 6

The reaction was carried out as above using hydrazones **1** (1 mmol), LDA (2.5 mmol), PhSCI (360 mg, 2.5 mmol). The nitriles **6** were purified by silica gel chromatography (eluent: cyclohexane–CH₂Cl₂, 8:2).

1.4.1. 2-Phenylsulfanylhexanenitrile 6a.²⁹

Oil, yield=57%. ¹H NMR, δ: 7.7 (m, 2H, Ph), 7.2 (m, 3H, Ph), 3.60 (t, 1H, H₂, *J*=7.4 Hz), 1.77 (q, 2H, H₃, *J*=7.4 Hz), 1.6 (m, 2H, H₄), 1.25 (m, 2H, H₅), 0.82 (t, 3H, H₆, *J*=7.4 Hz). ¹³C NMR, δ: 135.2, 130.8, 129.2, 125.6, 119.1, (Ph, C₁), 36.8 (C₂), 32.0 (C₃), 28.8 (C₄), 21.7 (C₅), 13.5 (C₆).

1.4.2. 2-Methyl-2-phenylsulfanylpropanenitrile 6d.²⁵

Oil, yield=48%. ¹H NMR, δ: 7.7 (m, 2H, Ph), 7.2 (m, 3H, Ph),

1.53 (s, 6H, H₃). ¹³C NMR, δ: 136.6, 130.1, 128.6, 124.1, 122.1 (Ph, C₁), 39.6 (C₂), 27.4 (C₃).

1.4.3. 2-Methyl-2-phenylsulfanylpentanenitrile 6e. Oil, yield=51%. ¹H NMR, δ: 7.7 (m, 2H, Ph), 7.2 (m, 3H, Ph), 1.55–1.75 (m, 4H, H₃, H₄), 1.44 (s, 3H, H₆), 0.90 (t, 3H, H₅, *J*=7.2 Hz). ¹³C NMR, δ: 136.8, 130.0, 129.1, 129.0, 121.7 (Ph, C₁), 44.3 (C₂), 41.55 (C₃), 25.2 (C₆), 18.4 (C₄), 13.7 (C₅). MS (EI, 70 eV): 205 (M⁺, 70), 110 (100). Anal. calcd for C₁₂H₁₅NS: C, 70.20; H, 7.36; N, 6.82; found: C, 70.27; H, 7.67; N, 7.13%.

1.4.4. 2-Ethyl-2-phenylsulfanylbutanenitrile 6f.²⁴ Oil, yield=62%. ¹H NMR, δ: 7.7 (m, 2H, Ph), 7.2 (m, 3H, Ph), 1.72 (q, 4H, H₃, *J*=7.3 Hz), 1.05 (t, 6H, H₄, *J*=7.3 Hz). ¹³C NMR, δ: 136.9, 130.0, 129.2, 129.1, 121.0 (Ph, C₁), 50.5 (C₂), 29.1 (C₃), 8.8 (C₄).

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