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Mitsunobu synthesis of symmetrical alkyl and polyfluoroalkyl secondary amines

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Abstract

Trifluoromethanesulfonamides (triflamides) having the structure $CF_3SO_2N[(CH_2)_3R]_2$ (R = C_nF_{2n+1} or C_nH_{2n+1}, n = 4, 6, 8, 10) are obtained in high yields, when $CF_3SO_2NH_2$ is reacted with 3-perfluoroalkyl-1-propanols or the parent aliphatic alcohols in a Mitsunobu reaction (Ph_3P/[*i*-$PrO_2CN{=}NCO_2$-*i*-Pr]/ether). Products are isolated easily by fluorous extraction, fluorous solid–organic liquid filtration or *n*-heptane/CH_3OH extraction. Consecutive deprotection of triflamides with $LiAlH_4$ in boiling ether or dioxane solution affords the title amines in good overall yields. Fluorous partition coefficients of the *F*-tagged amides and amines are determined and qualitatively analyzed.

Keywords: Amines; Fluorophilicity; Ideal separation; Mitsunobu reaction; Trifluoromethanesulfonamide

1. Introduction

Fluorous amines are important compounds that have been used as scavengers or precursors for the synthesis of fluorous reagents and catalysts [1]. Their synthesis usually involves several steps starting from perfluoroalkyl iodides [2]. The Mitsunobu reaction is a useful tool for the alkylation of an acidic pronucleophile (NuH) with a primary or secondary alcohol (ROH) to afford the coupled products (NuR) [3]. When NuH has a pK_a < 11, the use of Ph_3P/diethyl azodicarboxylate (DEAD) or diisopropyl azodicarboxylate (DIAD) reagent pairs resulted in good yields, while for alkylation of less acidic partners other mediators were introduced [4]. Due to the wide scope of the Mitsunobu reaction, several strategies were elaborated which provide quicker work-up procedures instead of using the time demanding 'classical' chromatographic methods for the separation of products and spent reagents (e.g. Ph_3PO, *i*-$PrO_2CNHNHCO_2$-*i*-Pr [$DIADH_2$]). Some of these methods rely on the application of orthogonal phases and of reagents with tuned phase affinities, thus providing ideal separations [5]. Fluorous Mitsunobu reactions have increasing scope since the introduction of novel fluorous azodicarboxylates (^{F}DEAD) and phosphines ($^F Ph_3P$) [6]. In its *reverse* fluorous versions, however, using fluorous substrates (^{F}NuH/ROH, NuH/^{F}ROH or ^{F}NuH/^{F}ROH) with the classical Ph_3P/DIAD couple, the fluorous products (^{F}NuR, NuR^F or ^{F}NuR^F) are easily separable from all other reaction components [7].

A series of long chain fluorous primary and secondary amines has been synthesized by reductive alkylation of $PhCH_2NH_2$ using one or two equivalents of perfluoroalkylalkanals and an excess of $NaBH(OAc)_3$, respectively, followed by the removal of the protecting benzyl-group [2a] or by the ammonolysis of perfluoroalkylpropyl iodides [2b]. Some syntheses of secondary amines that can be easily scaled up to the hundred gram scale rely on the alkylation of $ArSO_2NHR'$ and CF_3CONH_2 substrates and the consecutive deprotection of $ArSO_2NRR'$ (R, R' = alkyl) and CF_3CONR_2 (R = alkyl) intermediates formed, respectively [8].

2. Results and discussion

To devise more effective synthetic processes that can furnish easily secondary fluorous amines on the gram scale, we

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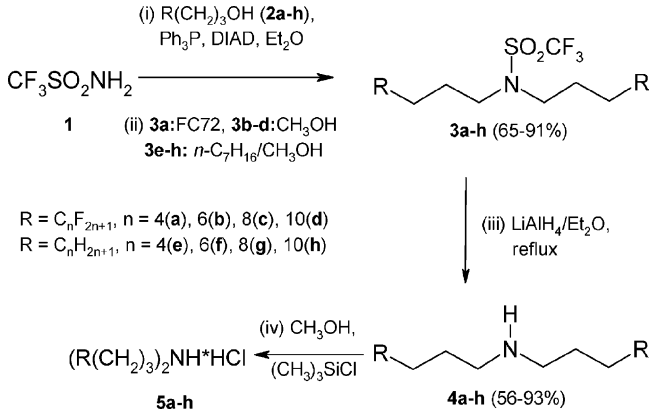

Scheme 1. Synthesis of symmetrical secondary amines.

considered using two-basic QSO_2NH_2 type NH-acids (Q = Ar, perfluoroalkyl) of appropriate pK_a [9] and fluorous alcohols under classical Mitsunobu conditions. We have found that the reaction of triflamide (**1**) and fluorous (**2a–d**) or fatty alcohols (**2e–h**) with slight excess of Ph_3P/DIAD in ether affords fluorophilic or lipophilic triflamides (**3a–h**, Scheme 1) in good yields.

These results are in accordance with literature precedents where CF_3SO_2NHR triflamides had been alkylated with alcohols using Ph_3P/DIAD or DEAD reagent pairs and the intermediates formed deprotected to afford *N*-alkyl benzylamines or some biologically active polyamines [9,10].

Our attempts to extend the scope of this reaction to secondary alcohols failed when (±)-2-octanol was tested. The use of $C_nF_{2n+1}(CH_2)_mOH$ ($m \geq 3$) as fluorous alcohols is justified by the fact, that the presence of at least an $(CH_2)_3$ spacer between the C_nF_{2n+1} and OH groups is necessary to mitigate the strong electron withdrawing effect of fluorine atoms on the reaction centers [7a]. Since triflamides **3** have non-polar character, they are easily separated from the reagent derived polar compounds (Ph_3PO, $DIADH_2$). Fluorous amides (**3a–d**) were isolated using fluorous extraction (**3a**) or fluorous solid (**3b–d**)–organic liquid filtration, while the lipophilic ones (**3e–h**) were isolated with *n*-heptane/CH_3OH extraction.

Consecutive deprotection [10] of triflamides **3** with an excess of $LiAlH_4$ in boiling ether or dioxane solutions afforded the secondary amines **4** in crystalline or liquid state following an extractive work-up procedure. The solids were obtained in high purity (≥98%), while most of the liquids can be purified further by precipitation of their crystalline hydrochlorides **5** from a methanol solution with an excess of HCl generated in situ (Scheme 1 and Section 4).

The amides **3** and amines **4** were assayed by GC and characterized by microanalysis (**e–h**) or HRMS (**a–d**) and ^1H, ^{13}C and ^{19}F NMR spectroscopy (**a–h**), as described in Section 4. The NMR properties showed numerous patterns, but usually of a routine nature. For example, the NCH_2CH_2 ^{13}C signals were grouped in ranges (triflamides **3a–h**, $\delta = 48.3$–48.6; secondary amines **4a–h**, $\delta = 48.1$–50.3; amine hydrochlorides **5a–h**, $\delta = 48.3$–48.6), always downfield of the $CH_2C_nF_{2n+1}$ signals (**3a–d**, **4a–d**, **5a–d**, $\delta = 26.9$–29.6).

Quantitative data on the fluorous phase affinities of the above polyfluoroalkyl amides and amines were sought.

Table 1
Fluorophilicities of some triflamides and amines

Entry	ln *P*
3a	0.77
4a	0.71
3b	2.25
4b	1.98
3c	3.56
4c	3.40[a]
3d	4.47
4d	4.08

[a] cf. Ref. [2a,b].

Accordingly, the perfluoro(methylcyclohexane) [$CF_3C_6F_{11}$]/toluene partition coefficients (*P*) were determined by GC as described in Section 4. Then, these values were converted to a free energy scale by taking their natural logarithm, and displayed as, $f = \ln P$, fluorophilicities (Table 1).

The results obtained are in agreement with predictable trends [7c,11], since compounds with larger calculated molar volume and lower estimated vaporization energy should have higher ln *P* values. Thus, the substitution of NH for NSO_2CF_3 (**3** → **4**) resulted in a decrease for each pairs (**4a** < **3a**, **4b** < **3b**, **4c** < **3c**, **4d** < **3d**), while the lengthening of fluorous ponytails increased the fluorophilicities in both series (**3**, **4**) in the **a** < **b** < **c** < **d** sequence.

3. Conclusions

Symmetrical secondary amides were synthesized effectively under Mitsunobu conditions using triflamide as a precursor. Their reductive deprotection afforded a series of novel polyfluoroalkyl amines and alkyl ones known in Refs. [15–19]. Workup procedures involved only simple separation processes and furnished the crude target products in relatively high purity. The *n*-heptane/CH_3OH liquid–liquid biphasic system was introduced for the ideal separation of lipophilic reaction products from classical Mitsunobu reaction mixtures (Section 4).

4. Experimental details

4.1. Solvents and reagents

Diethyl ether and dichloromethane (A.R. grade) were purchased from Reanal and distilled from P_2O_5 before use. Dioxane (A.R. grade) was purchased from Reanal, and distilled from sodium/benzophenone before use. Methanol, *n*-heptane and *iso*-octane (A.R. grades) were purchased from Reanal and used as received. FC-72 (mixture of perfluorohexanes) was purchased from Fluorochem Ltd. and used as received. Triflamide (**1**) [12] and fluorous alcohols **2a** [13] and **2b–d** [14] were prepared as reported and purified by fractional distillation under reduced pressure to afford **2a** (bp 64 °C/20 mmHg, GC: 98.0%), **2b** (bp 84–86 °C/20 mmHg, GC: 99.0%), **2c** (bp 82–83 °C/0.1 mmHg, mp 42 °C, GC: 99.1%) and **2d** (bp 110 °C/0.1 mmHg, mp 86–89 °C, GC: 98.1%). Alcohols **2e–h** (GC ≥ 98%, 98%, 99% and 97%) were

purchased from Aldrich and used as received. Ph_3P (≥98%) and DIAD (≥94%) were purchased from Aldrich and Fluka, respectively, and used as received.

4.2. General details

Fourier transformed infrared spectra were recorded neat, as a film or KBr disc as indicated, on a Bruker Equinox FTIR spectrophotometer, ν_{max} in cm^{-1}. The intensity of the bands were characterized as broad (br), strong (s), medium (m) or weak (w). ^1H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker Avance 250 spectrometer using a 5 mm inverse $^1H/^{13}C/^{31}P/^{19}F$ probehead at room temperature. The inverse gated proton decoupling sequence was applied for $^{13}C\{^1H\}$ and $^{19}F\{^1H\}$ measurements. Data are expressed as chemical shifts in ppm relative to residual chloroform (^1H δ 7.27), $CDCl_3$ (^{13}C δ 77.0) or an external standard for ^{19}F ($CFCl_3$, $\delta = 0$). The multiplicity of each signal is designated by s, singlet; d, doublet; dd, doublet of doublets; t, triplet; q, quartet; p, pentet; m, multiplet; br, broad. Coupling constants J are given in Hz. NMR samples were prepared in $CDCl_3$ (**3e–h**, **4e–h**), acetone-d_6 (**3a–c**, **4a–c**), acetone-d_6/$CClF_2CCl_2F$ = 1:1 (v/v) mixture (**3d**, **4d**) or CF_3CO_2H/with acetone-d_6 insert (**5a–h**). Mass spectra were determined on a VG ZAB2-SEQ tandem mass spectrometer using electron impact (70 eV) for ionization and direct probe for sample introduction at a source temperature of 180–250 °C. Mass range (m/z) from 25 to 1500 was considered. The accuracy of the HRMS is described by the formula: $(M_{found} - M_{calcd})/M_{calcd} < \pm 5 \times 10^{-6}$. Melting points were determined on a Boetius micro melting point apparatus, and are uncorrected. All the reaction steps were monitored by gas chromatography (Hewlett-Packard 5890 Series II, PONA [crosslinked methylsilicone gum] 50 m × 0.2 mm × 0.5 μm column, H_2 carrier gas, FID detection). Elemental analyses were performed by the Microanalytical Laboratory of the Eötvös Loránd University.

4.3. GC determination of fluorous partition coefficients

In a 2-ml volumetric flask the given compounds (**3a–d**, **4a–d**, 10 mg) were extracted in a 1.00–1.00-ml mixture of pre-equilibrated perfluoro(methylcyclohexane) and toluene. The closed vessel was first immersed in a water bath (50 °C) for 30 min with frequent shaking, then allowed to cool to 25 °C. After standing overnight or longer at this temperature 300 ± 3 μl aliquots of the separated upper and lower phases were withdrawn and diluted with 300 ± 3 μl benzotrifluoride, which served as an internal standard during GC analysis. An average of 7–11 injections for each run of three independent determinations resulted in the ln P values listed (Table 1).

4.4. N,N-Bis(4,4,5,5,6,6,7,7,7-nonafluoro-heptyl) trifluoromethanesulfonamide (3a)

Note: Ph_3P was used here in a slight excess to DIAD, to allow its complete coversion to $DIADH_2$, since DIAD unlike to $DIADH_2$ is partially soluble in boiling FC72.

To a stirred solution of **1** (1.49 g, 10 mmol), **2a** (5.56 g, 20 mmol) and Ph_3P (6.82 g, 26 mmol) in ether (50 ml) was added a solution of DIAD (≥94%, 5.0 g, ≥23 mmol) in ether (25 ml) with ice cooling over a period of 30 min. The mixture was strirred at RT overnight. The ether was then evaporated (Rotavap) and the residue extracted with boiling FC-72 (3× 25 ml). These extracts were filtered and the FC-72 was recovered by atmospheric distillation. The crude product was purified by short-path distillation (16 mmHg, bath: 180 °C) from Raschig rings to provide **3a** (5.42 g, 81%) as a colorless oil (98% GC purity). ^1H NMR: δ 3.70 (2 × 2H, t, $^3J_{HH}$ = 7.4 Hz, H-1), 2.37 (2 × 2H, m, H-3), 2.09 (2 × 2H, p, $^3J_{HH}$ = 7.4 Hz, H-2); ^{13}C NMR (partial): δ 48.3 (s, C-1), 27.7 (t, $^2J_{CF}$ = 22 Hz, C-3), 20.0 (s, C-2); ^{19}F NMR: δ −77.18 (3F, s, CF_3SO_2), −82.6 (6F, t, $^3J_{FF}$ = 12 Hz, 2 × CF_3), −115.4 (4F, m, 2 × CF_2), −125.6 (4F, m, 2 × CF_2), −127.3 (4F, m, 2 × CF_2); IR (neat): 2959w, 1393m, 1358m, 1228s, 1199s, 1134s, 720m; HRMS (EI) calcd. for $C_{15}H_{12}F_{21}NO_2S$ (M^+): 669.0253. Found: 669.0273.

4.5. General procedure for the preparation of fluorophilic amides (3b–d)

To a stirred solution of **1** (1.49 g, 10 mmol), the F-propanols **2b–d** (20 mmol) and Ph_3P (6.29 g, 24 mmol) in ether (60 ml) was added DIAD (≥94%, 5.4 g, ≥25 mmol) in ether (50 ml) with ice-cooling over a period of 1 h. The mixture was strirred at RT overnight then the ether evaporated in vacuum (Rotavap). The solid residue obtained was refluxed with methanol (50 ml) for 10 min and first allowed to cool to RT then cooled further in a freezer (−20 °C). The crystalline product was filtered and washed with cold methanol (4× 10 ml), and then dried in vacuum over P_2O_5 to provide the appropriate amides in a pure state.

4.6. N,N-Bis(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-nonyl)trifluoromethanesulfonamide (3b)

Yield: 7.22 g (83%) white crystals, mp 56–57 °C, GC purity: 99%. ^1H NMR: δ 3.70 (2 × 2H, t, $^3J_{HH}$ = 7.5 Hz, H-1), 2.37 (2 × 2H, m, H-3), 2.09 (2 × 2H, p, $^3J_{HH}$ = 7.4 Hz, H-2); ^{13}C NMR (partial): δ 48.4 (s, C-1); 27.7 (t, $^2J_{CF}$ = 22 Hz, C-3), 20.1 (s, C-2); ^{19}F NMR: δ −77.2 (3F, s, CF_3SO_2), −82.5 (6F, t, $^3J_{FF}$ = 12 Hz, 2 × CF_3), −115.2 (4F, m, 2 × CF_2), −123.1 (4F, m, 2 × CF_2), −124.1 (4F, m., 2 × CF_2), −124.7 (4F, m, 2 × CF_2), −127.5 (4F, m, 2 × CF_2); IR (KBr): 2979w, 1399m, 1368m, 1228s, 1192s, 1144s, 699s; HRMS (EI) calcd. for $C_{19}H_{12}F_{29}NO_2S$ (M^+): 869.0126. Found: 869.0167.

4.7. N,N-Bis(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro-undecyl)trifluoromethane sulfonamide (3c)

Yield: 9.74 g (91%) white crystals, mp 81–82 °C, GC purity: 99%. ^1H NMR: δ 3.69 (2 × 2H, t, $^3J_{HH}$ = 7.3 Hz, H-1), 2.37 (2 × 2H, m, H-3), 2.09 (2 × 2H, p, $^3J_{HH}$ = 7.4 Hz, H-2); ^{13}C NMR (partial): δ 48.4 (s, C-1), 27.9 (t, $^2J_{CF}$ = 22 Hz, C-3), 20.2 (s, C-2); ^{19}F NMR: δ −77.2 (3F, s, CF_3SO_2), −82.5 (6F, t, $^3J_{FF}$ = 12 Hz, 2 × CF_3), −115.2 (4F, m, 2 × CF_2), −123.1

(12F, br, three peaks overlap, 2 × 3CF_2), −123.9 (4F, m, 2 × CF_2), −124.7 (4F, m, 2 × CF_2), −127.5 (4F, m, 2 × CF_2); IR (KBr): 2980w, 1400m, 1373m, 1252s, 1226s, 1148s, 658s; HRMS (EI) calcd. for $C_{23}H_{13}F_{37}NO_2S$ ($M + H^+$): 1070.0076. Found: 1070.0098.

4.8. N,N-Bis(4,4,5,5,6,6,7,7,8,8,9,9,10,10, 11,11,12,12,13,13,13-heneicosafluoro-tridecyl) trifluoromethanesulfonamide (**3d**)

Yield: 10.5 g (83%) white crystals, mp 110–111 °C, GC purity: 98%. ^{1}H NMR: δ 3.73 (2 × 2H, t, $^3J_{HH}$ = 7.3 Hz, H-1), 2.39 (2 × 2H, m, H-3), 2.15 (2 × 2H, m, H-2); ^{19}F NMR: δ −77.1 (3F, s, CF_3SO_2), −82.3 (6F, t, $^3J_{FF}$ = 12 Hz, 2 × CF_3), −115.2 (4F, m, 2 × CF_2), −122.8 (20F, five peaks overlap, 2 × 5CF_2), −123.8 (4F, m, 2 × CF_2), −124.5 (4F, m, 2 × CF_2), −127.4 (4F, m, 2 × CF_2); IR (KBr): 2960w, 1400m, 1375w, 1227s, 1152s, 663 m; HRMS (EI) calcd. for $C_{27}H_{13}F_{45}NO_2S$ ($M + H^+$): 1269.9948. Found: 1269.9908.

4.9. General procedure for the preparation of lipophilic amides (**3e–h**)

To a stirred solution of **1** (1.49 g, 10 mmol), the alcohols **2e–h** (20 mmol) and Ph_3P (6.29 g, 24 mmol) in ether (25 ml) was added DIAD (≥94%, 5.6 g, ≥26 mmol) in ether (10 ml) with ice-cooling during 1 h. The mixture was then stirred at RT overnight, and the ether evaporated. The residue obtained was mixed with methanol (50 ml), extracted with *n*-heptane (3× 50 ml) and the combined *n*-heptane layers with methanol (3× 25 ml). Then, the *n*-heptane extracts were evaporated and dried in vacuum (16 mmHg, bath: 90 °C for 2 h) to afford the appropriate amides.

4.10. N,N-Bis(heptyl)trifluoromethanesulfonamide (**3e**)

Yield: 3.00 g (87%) colorless oil, GC purity: 98%. ^{1}H NMR: δ 3.32 (2 × 2H, t, $^3J_{HH}$ = 7.4 Hz, H-1), 1.61 (2 × 2H, p, $^3J_{HH}$ = 7.4 Hz, H-2), 1.28–1.29 (2 × 8H, overlap), 0.88 (2 × 3H, t, $^3J_{HH}$ = 7.1 Hz, H-7); ^{13}C NMR: δ 120.3 (q, $^1J_{CF}$ = 324 Hz, *C*F_3SO_2), 48.6 (s, C-1), 31.9, 29.0, 28.6, 26.6, 22.7 (C-6), 14.2 (C-7); ^{19}F NMR: δ −76.4 (3F, s, CF_3SO_2); IR (neat): 2931s, 2860m, 1390s, 1226s, 1186s, 1133s. Anal. calcd. for $C_{15}H_{30}F_3NO_2S$ (345.47): C, 52.2; H, 8.8; N, 4.1; S, 9.3. Found: C, 52.4; H, 8.9; N, 4.2; S, 9.1.

4.11. N,N-Bis(nonyl)trifluoromethanesulfonamide (**3f**)

Yield: 2.61 g (65%) colorless oil, GC purity: 97%. ^{1}H NMR: δ 3.32 (2 × 2H, t, $^3J_{HH}$ = 7.4 Hz, H-1), 1.61 (2 × 2H, p, $^3J_{HH}$ = 7.4 Hz, H-2), 1.27–1.28 (2 × 12H, overlap), 0.88 (2 × 3H, t, $^3J_{HH}$ = 7.1 Hz, H-9); ^{13}C NMR: δ 120.3 (q, $^1J_{CF}$ = 324 Hz, *C*F_3SO_2), 48.6 (s, C-1), 32.0, 29.6, 29.4, 29.3, 28.6, 26.7, 22.8 (C-8), 14.2 (C-9); ^{19}F NMR: δ −76.3 (3F, s, CF_3SO_2); IR (neat): 2928s, 2857m, 1391s, 1226s, 1186s, 1133m. Anal. calcd. for $C_{19}H_{38}F_3NO_2S$ (401.58): C, 56.8; H, 9.5; N, 3.5; S, 8.0. Found: C, 56.6; H, 9.7; N, 3.5; S, 7.8.

4.12. N,N-Bis(undecyl)trifluoromethanesulfonamide (**3g**)

Yield: 3.11 g (68%) colorless oil, GC purity: 99.6%. ^{1}H NMR: δ 3.32 (2 × 2H, t, $^3J_{HH}$ = 7.4 Hz, H-1), 1.61 (2 × 2H, p, $^3J_{HH}$ = 7.4 Hz, H-2), 1.27–1.28 (2 × 16H, overlap), 0.88 (2 × 3H, t, $^3J_{HH}$ = 7.1 Hz, H-11); ^{13}C NMR: δ 120.3 (q, $^1J_{CF}$ = 324 Hz, *C*F_3SO_2), 48.6 (C-1), 32.1, 29.8, 29.7, 29.7, 29.5, 29.3, 28.6, 26.6, 22.9 (C-10), 14.3 (C-11); ^{19}F NMR: δ −76.3 (3F, s, CF_3SO_2); IR (neat): 2926s, 2856m, 1391s, 1226s, 1186s, 1134m. Anal. calcd. for $C_{23}H_{46}F_3NO_2S$ (457.69): C, 60.4; H, 10.1; N, 3.1; S, 7.0. Found: C, 60.6; H, 10.3; N, 3.2; S, 6.8.

4.13. N,N-Bis(tridecyl)trifluoromethanesulfonamide (**3h**)

Yield: 4.32 g (84%) colorless oil, GC purity: 97%. ^{1}H NMR: δ 3.32 (2 × 2H, t, $^3J_{HH}$ = 7.4 Hz, H-1), 1.61 (2 × 2H, p, $^3J_{HH}$ = 7.4 Hz, H-2), 1.27 (2 × 20H, overlap), 0.88 (2 × 3H, t, $^3J_{HH}$ = 6.9 Hz, H-13); ^{13}C NMR: δ 120.3 (q, $^1J_{CF}$ = 324 Hz, *C*F_3SO_2), 48.6 (C-1), 32.1, 29.9 (two peaks overlap), 29.8, 29.7, 29.6, 29.3, 28.6, 26.7, 22.9 (C-12), 14.3 (C-13); ^{19}F NMR: δ −76.3 (3F, s, CF_3SO_2); IR (neat): 2926s, 2855s, 1392s, 1226s, 1186s, 1134m. Anal. calcd. for $C_{27}H_{54}F_3NO_2S$ (513.80): C, 63.1; H, 10.6; N, 2.7; S, 6.2. Found: C, 63.3; H, 10.5; N, 2.9; S, 6.0.

4.14. General procedure for the synthesis of amines (**4a–h**)

Triflic amides **3a–h** (2.40 mmol) and $LiAlH_4$ (1.0 g, 26 mmol) in ether (170 ml, for **3a–d**) or dioxane (50 ml, for **3e–h**) was stirred and refluxed for 17 h (**a–c**), 58 h (**d**) or 4–8 h (**e–h**), respectively. The exccess of $LiAlH_4$ was carefully decomposed by the slow addition of water (4 ml) and 20% NaOH (20 ml). The ether or dioxane rich phases were separated, the aqueous ones extracted with ether (3× 50 ml) and the combined organics washed with water (3× 50 ml) and dried (Na_2SO_4). Consecutive evaporation of solvent afforded amines **4a–h** in crude state (GC assay ≥95%). They could be purified further with short-path distillation or recrystallization. Liquid samples were stored in closed vials under an argon atmosphere to exclude moisture and CO_2.

4.15. Bis(4,4,5,5,6,6,7,7,7-nonafluoro-heptyl)amine (**4a**)

Yield: 1.02 g (79%) colorless oil, GC purity: 99.5%; following short-path distillation from Raschig rings (16 mmHg, bath: 150 °C). ^{1}H NMR: δ 2.72 (2 × 2H, t, $^3J_{HH}$ = 6.5 Hz, H-1), 2.32 (2 × 2H, tt, $^3J_{HH}$ = 7.9 Hz, $^3J_{HF}$ = 20 Hz, H-3), 1.76 (2 × 2H, m, $^3J_{HH}$ = 6.5 Hz, H-2), no NH proton observed; ^{13}C NMR (partial): δ 48.2 (s, C-1), 28.6 (t, $^2J_{CF}$ = 23 Hz, C-3), 20.8 (s, C-2); ^{19}F NMR: δ -82.7 (6F, t, $^3J_{FF}$ = 12 Hz, 2 × CF_3), −115.6 (4F, m, 2 × CF_2), −125.7 (4F, m, 2 × CF_2), −127.3 (4F, m, 2 × CF_2); IR (neat): 2835w, 1357m, 1232s, 1133s, 719m; HRMS (EI) calcd. for $C_{14}H_{12}F_{18}N$ ($M - H^+$): 536.0683. Found: 536.0707.

*4.16. Bis(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-nonyl)amine (**4b**)*

Yield: 0.99 g (56%) colorless oil, GC purity: 99%; following short-path distillation from Raschig rings (16mmHg, bath: 190 °C). ^{1}H NMR: δ 2.72 (2 × 2H, t, $^3J_{HH}$ = 6.5 Hz, H-1), 2.32 (2 × 2H, tt, $^3J_{HH}$ = 7.8 Hz, $^3J_{HF}$ = 20 Hz, H-3), 1.76 (2 × 2H, m, $^3J_{HH}$ = 6.9 Hz, H-2), no NH proton observed; ^{13}C NMR (partial): δ 48.2 (s, C-1), 28.6 (t, $^2J_{CF}$ = 23 Hz, C-3), 20.8 (s, C-2); ^{19}F NMR: δ −82.5 (6F, t, $^3J_{FF}$ = 12 Hz, 2 × CF_3), −115.4 (4F, 2 × CF_2), −123.1 (4F, m, 2 × CF_2), −124.1 (4F, m, 2 × CF_2), −124.8 (4F, m, 2 × CF_2), −127.5 (4F, m, 2 × CF_2); IR (neat): 2835w, 1365m, 1240s, 1206s, 708m; HRMS (EI) calcd. for $C_{18}H_{12}F_{26}N$ ($M - H^+$): 736.0555. Found: 736.0527.

*4.17. Bis(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro-undecyl)amine (**4c**)*

Yield: 2.07 g (92%) of white crystals, GC: 99% pure, mp 42–43 °C/*iso*-octane, Ref. [2a] mp 43–44 °C. ^{1}H, ^{13}C, ^{19}F NMR and IR spectra are in agreement with the reported ones [2b]: ^{1}H NMR: δ 2.72 (2 × 2H, t, $^3J_{HH}$ = 6.5 Hz, H-1), 2.32 (2 × 2H, m, $^3J_{HH}$ = 7.8 Hz, $^3J_{HF}$ = 20 Hz, H-3), 1.76 (2 × 2H, m, $^3J_{HH}$ = 6.5 Hz, H-2), no NH proton observed; ^{13}C NMR (partial): δ 48.1 (s, C-1), 28.6 (t, $^2J_{CF}$ = 23 Hz, C-3), 20.8 (s, C-2); ^{19}F NMR: δ −82.4 (6F, t, $^3J_{FF}$ = 12Hz, 2 × CF_3), −115.4 (4F, m, 2 × CF_2), −123.0 (12F, m, three peaks overlap, 2 × 3CF_2), −123.9 (4F, m, 2 × CF_2), −124.8 (4F, m, 2 × CF_2), −127.4 (4F, m, 2 × CF_2); IR (KBr): 2830w, 1355m, 1203s, 1149s, 656s; HRMS (EI) calcd. for $C_{18}H_{12}F_{26}N$ ($M - H^+$): 936.0427. Found: 936.0402.

*4.18. Bis(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-heneicosafluoro-tridecyl)amine (**4d**)*

Yield: 2.29 g (84%) white crystals, mp 80–82 °C/*iso*-octane, GC purity: 99%. ^{1}H NMR: δ 2.74 (2 × 2H, t, $^3J_{HH}$ = 6.5 Hz, H-1), 2.31 (2 × 2H, m, $^3J_{HH}$ = 7.6 Hz, $^3J_{HF}$ = 20 Hz, H-3,), 1.78 (2 × 2H, m, $^3J_{HH}$ = 6.5 Hz, H-2), no NH proton observed; ^{13}C NMR (partial): δ 49.0 (s, C-1), 29.6 (t, $^2J_{CF}$ = 22.1 Hz, C-3), 21.6 (s, C-2); ^{19}F NMR: δ −82.5 (6F, t, $^3J_{FF}$ = 10 Hz, 2 × CF_3), −115.5 (4F, m, 2 × CF_2), −122.9 (20F, m, five peaks overlap, 2 × 5CF_2), −123.9 (4F, m, 2 × CF_2), −124.8 (4F, m, 2 × CF_2), −127.4 (4F, m, 2 × CF_2); IR (KBr): 2832w, 1355m, 1226s, 1151s, 644s; HRMS (EI) calcd. for $C_{26}H_{13}F_{42}N$ (M^+): 1137.0377. Found: 1137.0374.

*4.19. Diheptyl amine (**4e**)*

Yield: 476 mg (93%) colorless oil, GC purity: 98%, after ether evaporated (Rotavap). Ref. [15] mp 32–33 °C {with $3H_2O$} and bp 147–148 °C/15 mmHg. ^{1}H NMR: δ 3.32 (2 × 2H, t, $^3J_{HH}$ = 7.5 Hz, H-1), 1.61 (2 × 2H, p, $^3J_{HH}$ = 6.8 Hz, H-2), 1.28–1.29 (2 × 8H, overlap), 0.87 (2 × 3H, t, $^3J_{HH}$ = 6.8 Hz, H-7), no NH proton observed; ^{13}C NMR: δ 48.6 (C-1), 31.8, 29.0, 28.6, 26.6, 22.7 (C-6), 14.1 (C-7); IR (neat): 2926s, 2855s. Anal. calcd. for $C_{14}H_{31}N$ (213.41): C, 78.8; H, 14.6; N, 6.6. Found: C, 79.0; H, 14.8; N, 6.4.

*4.20. Dinonyl amine (**4f**)*

Yield: 498 mg (77%) white crystals, mp 35–36 °C, GC purity: 96%, after ether evaporated (Rotavap). Ref. [16] mp 32–33 °C and Ref. [17] bp 188 °C/12 mmHg. ^{1}H NMR: δ 2.54 (2 × 2H, t, $^3J_{HH}$ = 7.5 Hz, H-1), 1.44 (2 × 2H, p, $^3J_{HH}$ = 6.5 Hz, H-2), 1.22 (2 × 12H overlap), 0.83 (2 × 3H, t, $^3J_{HH}$ = 6.8 Hz, H-9), no NH proton observed; ^{13}C NMR: δ 50.3 (s, C-1), 32.0, 30.3, 29.8, 29.7, 29.5, 27.6, 22.8 (C-8), 14.2 (C-9); IR (KBr): 3277w, 2924s, 2853s. Anal. calcd. for $C_{18}H_{39}N$ (269.52): C, 80.2; H, 14.6; N, 5.2. Found: C, 80.0; H, 14.4; N, 5.0.

*4.21. Diundecyl amine (**4g**)*

Yield: 688 mg (88%) white crystals, mp 43–44 °C, GC purity: 95%, after ether evaporated (Rotavap). Ref. [18] mp 51.5–52.5 °C/C_6H_6-EtOH. ^{1}H NMR: δ 2.56 (2 × 2H, t, $^3J_{HH}$ = 6.8 Hz, H-1), 1.46 (2 × 2H, br p, H-2), 1.24 (2 × 16H overlap), 0.85 (2 × 3H, t, $^3J_{HH}$ = 6.8Hz, H-11), no NH proton observed; ^{13}C NMR: δ 50.3 (C-1), 32.1, 30.3, 29.8 (three peaks overlap), 29.78, 29.5, 27.6, 22.9 (C-10), 14.3 (C-11); IR (KBr): 3268w, 2916s, 2849s. Anal. calcd. for $C_{22}H_{47}N$ (325.63): C, 81.2; H, 14.6; N, 4.3. Found: C, 81.3; H, 14.6; N, 4.1.

*4.22. Ditridecyl amine (**4h**)*

Yield: 834 mg (91%) white crystals, mp 47–48 °C, GC purity: 96%, after ether evaporated (Rotavap). Ref. [19] mp 56.5 °C/C_6H_6-EtOH. ^{1}H NMR: δ 2.56 (2 × 2H, t, $^3J_{HH}$ = 7.1 Hz, H-1), 1.46 (2 × 2H, br m, H-2), 1.24 (2 × 20H overlap), 0.86 (2 × 3H, t, $^3J_{HH}$ = 6.8 Hz, H-13), no NH proton observed; ^{13}C NMR: δ 50.3 (C-1), 32.1, 30.4, 29.8 (six peaks overlap), 29.6, 27.6, 22.9 (C-12), 14.3 (C-13); IR (KBr): 3266w, 2919s, 2850s. Anal. calcd. for $C_{26}H_{55}N$ (381.73): C, 81.8; H, 14.5; N, 3.7. Found: C, 81.6; H, 14.3; N, 3.6.

*4.23. General procedure for the synthesis of amine hydrochlorides (**5a–h**)*

The liquid or melted amines **4a–h** (1.5 mmol) were dissolved in methanol (5–10 ml), then mixed with trimethylchlorosilane (1–2 ml, 8–16 mmol) and stirred at RT for 1 h. Then, the crystalline precipitate formed was filtered, washed with cold ether (3× 5 ml) and dried over KOH pellets in vacuum to afford the appropriate hydrochlorides. GC assays: 5 mg of the hydrochloride was shaken with 5% NaOH (2 ml) and ether (3 ml) for 2 min, then the ether phase was separated and dried (Na_2SO_4) and 0.1 μl injected to the column.

*4.24. Bis(4,4,5,5,6,6,7,7,7-nonafluoro-heptyl)amine hydrochloride (**5a**)*

Yield: 0.68 g (79%) white crystals, mp 180 °C, GC purity: 99.5%. ^{1}H NMR: δ 6.74 (2H, br, $^+NH_2$), 2.62 (2 × 2H, br, H-1),

1.49 (2 × 4H overlap, H-2 and H-3); ^{13}C NMR (partial): δ 47.5 (s, C-1), 26.9 (t, $^{2}J_{CF}$ = 23 Hz, C-3), 17.0 (t, $^{3}J_{CF}$ = 4.8 Hz, C-2); ^{19}F NMR: δ −84.5 (6F, t, $^{3}J_{FF}$ = 10 Hz, 2 × CF_3), −117.3 (4F, p, $^{3}J_{FF}$ = 14 Hz, 2 × CF_2), −127.3 (4F, br, 2 × CF_2), −128.9 (4F, m, 2 × CF_2); IR (KBr): 2784m, 1358m, 1247s, 1130s, 719s; HRMS (EI) calcd. for free base $C_{14}H_{13}F_{18}N$ (M^+): 537.0761. Found: 537.0769.

4.25. Bis(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-nonyl)amine hydrochloride (**5b**)

Yield: 1.09 g (94%) white crystals, mp 195 °C, GC purity: 99.9%. ^{1}H NMR: δ 7.33 (2H, br, $^{+}NH_2$), 3.22 (2 × 2H, br, H-1), 2.04 (2 × 4H, m, H-2 and H-3); ^{13}C NMR (partial): δ 48.2 (s, C-1), 27.6 (t, $^{2}J_{CF}$ = 23 Hz, C-3), 17.6 (t, $^{3}J_{CF}$ = 4.8 Hz, C-2); ^{19}F NMR: δ −83.73 (6F, t, $^{3}J_{FF}$ = 10 Hz, 2 × CF_3), −116.5 (4F, br m, 2 × CF_2), −123.8 (4F, br, 2 × CF_2), −124.9 (4F, br, 2 × CF_2), −125.6 (4F, br, 2 × CF_2), −128.5 (4F, m, 2 × CF_2); IR (KBr): 2783m, 1367m, 1200s, 1142s, 711m; HRMS (EI) calcd. for free base $C_{18}H_{13}F_{26}N$ (M^+): 737.0633. Found: 737.0645.

4.26. Bis(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro-undecyl)amine hydrochloride (**5c**)

Yield: 1.34 g (92%) white crystals, mp 211 °C, GC purity: 98%. ^{1}H NMR: δ 7.34 (2H, s, $^{+}NH_2$), 3.21 (2 × 2H, br, H-1), 2.04 (2 × 4H, m, H-2 and H-3); ^{13}C NMR (partial): δ 48.1 (s, C-1), 27.6 (t, $^{2}J_{CF}$ = 23 Hz, C-3), 17.6 (t, $^{3}J_{CF}$ = 4.8 Hz, C-2); ^{19}F NMR: δ −83.72 (6F, t, $^{3}J_{FF}$ = 10 Hz, 2 × CF_3), −116.4 (4F, br, 2 × CF_2), −123.8 (12F, br, three peaks overlap, 2 × 3CF_2), −124.7 (4F, br, 2 × CF_2), −125.6 (4F, br, 2 × CF_2), −128.4 (4F, br, 2 × CF_2); IR (KBr): 2771m, 1334m, 1202s, 1149s, 660m; HRMS (EI) calcd. for free base $C_{22}H_{13}F_{34}N$ (M^+): 937.0505. Found: 937.0473.

4.27. Bis(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-heneicosafluoro-tridecyl)amine hydrochloride (**5d**)

Yield: 1.62 g (92%) white crystals, mp 235–236 °C, GC purity: 99%. ^{1}H NMR: δ 7.35 (2H, s, $^{+}NH_2$), 3.21 (2 × 2H, t, H-1), 2.04 (2 × 4H, m, H-2 and H-3); ^{13}C NMR (partial): δ 48.1 (C-1), 27.6 (t, $^{2}J_{CF}$ = 23 Hz, C-3), 17.6 (t, $^{3}J_{CF}$ = 4.8 Hz, C-2); ^{19}F NMR: δ −83.72 (6F, t, $^{3}J_{FF}$ = 10 Hz, 2 × CF_3), −116.5 (4F, br, 2 × CF_2), −123.7 (20F, br, five peaks overlap, 2 × 5CF_2), −124.7 (4F, br, 2 × CF_2), −125.6 (4F, br, 2 × CF_2), −128.4 (4F, br, 2 × CF_2); IR (KBr): 2727m, 1344m, 1212s, 1151s, 665m; HRMS (EI) calcd. for free base $C_{22}H_{12}F_{42}N$ ($M - H^+$): 1136.0299. Found: 1136.0291.

4.28. Diheptylamine hydrochloride (**5e**)

At −25 °C white needles were deposited, which after filtration and washing with cold ether afforded 105 mg (28%) of **5e**, mp 254–255 °C, Ref. [15] mp 255 °C.

4.29. Dinonylamine hydrochloride (**5f**)

At −25 °C white needles were deposited, which after filtration and washing with cold ether afforded 82 mg (18%) of **5f**, mp 230–232 °C, Ref. [17a] mp 230–232 °C.

4.30. Diundecylamine hydrochloride (**5g**)

Yield: 510 mg (94%) white crystals, mp 204–206 °C, GC purity: 99%. ^{1}H NMR: δ 9.42 (2H, br, $^{+}NH_2$), 2.88 (2 × 2H, br, H-1), 1.87 (2 × 2H, br, H-2), 1.24 (2 × 16H overlap), 0.86 (2 × 3H, t, $^{3}J_{HH}$ = 6.8 Hz, H-11); ^{13}C NMR: δ 48.0 (C-1), 32.1, 29.9, 29.76, 29.7, 29.6, 29.3, 27.1, 26.1, 22.9 (C-10), 14.3 (C-11); IR (KBr): 2921s, 2851s. Anal. calcd. for $C_{22}H_{48}ClN$ (362.09): C, 73.0; H, 13.4; Cl, 9.8; N, 3.9. Found: C, 72.8; H, 13.3; Cl, 9.7; N, 3.8.

4.31. Ditridecylamine hydrochloride (**5h**)

Yield: 577 mg (92%) white crystals, mp 202–204 °C, GC purity: 99%. ^{1}H NMR: δ 9.39 (2H, br, $^{+}NH_2$), 2.87 (2 × 2H, t, $^{3}J_{HH}$ = 8.0 Hz, H-1), 1.87 (2 × 2H, br, H-2), 1.22 (2 × 20H overlap), 0.85 (2 × 3H, t, $^{3}J_{HH}$ = 6.8 Hz, H-13); ^{13}C NMR: δ 48.0 (C-1), 32.1, 29.9, 29.80 (two overlapping peaks), 29.74, 29.68, 29.5, 29.3, 27.1, 26.1, 22.8 (C-12), 14.3 (C-13); IR (KBr): 3430w, 2921s, 2851m. Anal. calcd. for $C_{26}H_{56}ClN$ (418.20): C, 74.7; H, 13.5; Cl, 8.5; N, 3.4. Found: C, 74.5; H, 13.7; Cl, 8.3; N, 3.1.

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References

[1] (a) W. Zhang, Tetrahedron 59 (2003) 4475–4489;
(b) S. Werner, D.P. Curran, Org. Lett. 5 (2003) 3293–3296;
(c) C.W. Lindsley, W.H. Leister, in: J.A. Gladysz, D.P. Curran, I.T. Horváth (Eds.), Handbook of Fluorous Chemistry, Wiley–VCH, Weinheim, 2004, pp. 236–246.
[2] (a) C. Rocaboy, W. Bauer, J.A. Gladysz, Eur. J. Org. Chem. 14 (2000) 2621–2628;
(b) Z. Szlávik, G. Tárkányi, Á. Gömöry, G. Tarczay, J. Rábai, J. Fluorine Chem. 108 (2001) 7–14;
(c) J. Rábai, in: J.A. Gladysz, D.P. Curran, I.T. Horváth (Eds.), Handbook of Fluorous Chemistry, Wiley–VCH, Weinheim, 2004, pp. 156–174;
(d) A. Abulikemu, G. Halász, A. Csámpai, Á. Gömöry, J. Rábai, J. Fluorine Chem. 125 (2004) 1143–1146.
[3] (a) O. Mitsunobu, Synthesis (1981) 1–28;
(b) D.L. Hughes, Org. Prep. Proced. Int. 28 (1996) 127–164;
(c) D.L. Hughes, Org. React. 42 (1992) 335–365.
[4] (a) S. Itô, T. Tsunoda, Pure Appl. Chem. 71 (1999) 1053–1057;
(b) E.J. Kim, S.Y. Ko, E.K. Dziadulewicz, Tetrahedron Lett. 46 (2005) 631–633.
[5] (a) R. Dembinski, Eur. J. Org. Chem. (2004) 2763–2772;
(b) S. Dandapani, D.P. Curran, Chem. Eur. J. 10 (2004) 3130–3138.

[6] (a) E.G. Hope, A.M. Stuart, J. Fluorine Chem. 100 (1999) 75–83;
(b) A.P. Dobbs, C. McGregor-Johnson, Tetrahedron Lett. 43 (2002) 2807–2810;
(c) R. Dembinski, in: J.A. Gladysz, D.P. Curran, I.T. Horváth (Eds.), Handbook of Fluorous Chemistry, Wiley–VCH, Weinheim, 2004, pp. 190–202;
(d) S. Dandapani, D.P. Curran, J. Org. Chem. 69 (2004) 8751–8757;
(e) D.P. Curran, X. Wang, Q. Zhang, J. Org. Chem. 70 (2005) 3716–3719.
[7] (a) J. Rábai, D. Szabó, E.K. Borbás, I. Kövesi, I. Kövesdi, A. Csámpai, Á. Gömöry, V.E. Pashinnik, Yu.G. Shermolovich, J. Fluorine Chem. 114 (2002) 199–207;
(b) M.W. Markowicz, R. Dembinski, Org. Lett. 4 (2002) 3785–3787;
(c) D. Szabó, A.-M. Bonto, I. Kövesdi, Á. Gömöry, J. Rábai, J. Fluorine Chem. 126 (2005) 641–652.
[8] (a) G. Spielberger, in: Methoden der Organische Chemie (Houben-Weyl), Band XI/1, Georg Thieme, Stuttgart, 1957, pp. 98–102;
(b) F. Möller, in: Methoden der Organische Chemie (Houben-Weyl), Band XI/1, Georg Thieme, Stuttgart, 1957, pp. 941–948;
(c) P.A. Harland, P. Hodge, W. Maughan, E. Wildsmith, Synthesis (1984) 941–943.
[9] (a) M.L. Edwards, D.M. Stemerick, J.R. McCarthy, Tetrahedron 150 (1994) 5579–5590;
(b) K.E. Bell, D.W. Knight, M.B. Gravestock, Tetrahedron Lett. 36 (1995) 8681–8684;
(c) R.D. Trepka, J.K. Harrington, J.W. Belisle, J. Org. Chem. 39 (1974) 1094–1098.
[10] J.B. Hendrickson, R. Bergeron, D.D. Sternbach, Tetrahedron 31 (1975) 2517–2521.
[11] J.G. Gladysz, C. Emnet, J. Rábai, Partition coefficients involving fluorous solvents, in: J.A. Gladysz, D.P. Curran, I.T. Horváth (Eds.), Handbook of Fluorous Chemistry, Wiley–VCH, Weinheim, 2004, pp. 56–100, Chapter 6.
[12] B.H. Thomas, G. Shafer, J.J. Ma, M.-H. Tu, D.D. DesMarteau, J. Fluorine Chem. 125 (2004) 1231–1240.
[13] N.O. Brace, J. Fluorine Chem. 20 (1982) 313–328.
[14] (a) Z. Szlávik, G. Tárkányi, Gy. Tarczay, Á. Gömöry, J. Rábai, J. Fluorine Chem. 98 (1999) 83–87;
(b) For an optimized procedure for the preparation of alcohol **2c**, see: J. Rábai, I. Kövesi, A.-M. Bonto, in: J.A. Gladysz, D.P. Curran, I.T. Horváth (Eds.), Handbook of Fluorous Chemistry, Wiley–VCH, 2004, pp. 419–420.
[15] H. King, T.S. Work, J. Chem. Soc. (1940) 1307–1314.
[16] B.N. Sudarikov, Yu.G. Frolov, V.A. Il'ichev, A.A. Pushkov, O.I. Zakharov-Nartsissov, A.V. Ochkin, Tr. Mosk. Khim.-Tekhnol. Inst. im D. I. Mendeleeva 43 (1963) 21–28.
[17] (a) E.T. Borrows, B.M.C. Hargreaves, J.E. Page, J.C.L. Resuggan, F.A. Robinson, J. Chem. Soc. (1947) 197–202;
(b) F. DeAngelis, I. Grgurina, R. Nicoletti, Synthesis (1979) 70–71;
(c) E. Hadicke, W. Schlenk Jr., Liebigs Ann. Chem. 764 (1972) 103–111.
[18] J.B. Wright, R.C. Elderfield, J. Org. Chem. 11 (1946) 111–122.
[19] C.W. Hoerr, H.J. Harwood, A.W. Ralston, J. Org. Chem. 11 (1946) 199–206.