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Use of acylphosphonates for the synthesis of α-chlorinated carboxylic and α,α′-dichloro dicarboxylic acids and their derivatives

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Abstract—α-Chloro acylphosphonates and α,α′-dichloro bisacylphosphonates were prepared in situ by chlorination of acylphosphonates and bisacylphosphonates, respectively, using sulfuryl chloride. Subsequently, they were cleaved to the corresponding α-chlorinated or α,α′-dichlorinated (di)carboxylic acids with a hydrogen peroxide–sodium bicarbonate system. Performing the cleavage with an alcohol or an amine yielded the corresponding α-chlorinated esters and α-chlorinated amides, respectively.

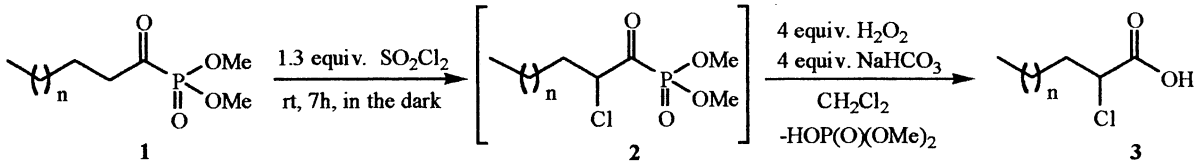
1. Introduction

The preparation of α-chloro carboxylic acids has been the subject of numerous industrial studies because of their importance in several domains, e.g. agrochemistry[1,2] and flotation chemistry.[3] Furthermore, α-chloro carboxylic acids and α,α′-dichloro dicarboxylic acids have been reported to stabilize photographical silver halide emulsions.[4] Several synthetic methods have been described, however most of them face the problem of free-radical chlorination in the alkyl chain. In contrast with the α-bromination in the Hell–Volhard–Zelinsky reaction, the α-chlorination with chlorine gas in the presence of phosphorus is less selective.[5,6] To suppress the radical chlorination, radical scavengers, e.g. oxygen and 7,7,8,8-tetracyanoquinodimethane are extensively used.[6–10] Some alternative procedures have been described, including: chlorination with thionyl chloride mediated by ultraviolet light;[11] chlorination with *N*-chlorosuccinimide in thionyl chloride at 90°C;[5] chlorination with sulfuryl chloride in the presence of benzoyl peroxide or pyridine at 70°C.[12] Except for some procedures for the α,α′-dichlorination of glutaric acid[13,14] and adipic acid,[15–17] no methods for longer dicarboxylic acids are described to our knowledge. Recently, our laboratory reported a new procedure to synthesize α-chloro carboxylic acids **3** at room temperature, without a competing chlorination in the aliphatic chain, starting from the corresponding dimethyl acylphosphonates **1** (Scheme 1).[18]

The convenience of the α-monochlorination, due to the activating phosphonate function, and the ease of the deprotection of the acid function, offers a perspective to establish a more general method for the synthesis of α,α′-dichloro dicarboxylic acids, α-chloro esters, α-chloro amides, α,α′-dichloro diesters and α,α′-dichloro diamides. In this paper, we want to disclose the expansion of this method to the α-chloro derivatives mentioned and to rediscuss the mechanism of the reaction which has now been proved experimentally.

2. Results and discussion

In an earlier report,[18] a mechanism was proposed for the



Scheme 1.

Keywords: acylphosphonates; monochlorination; Baeyer–Villiger oxidation.
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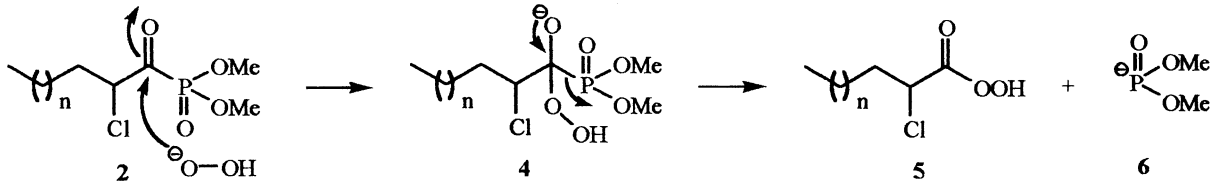
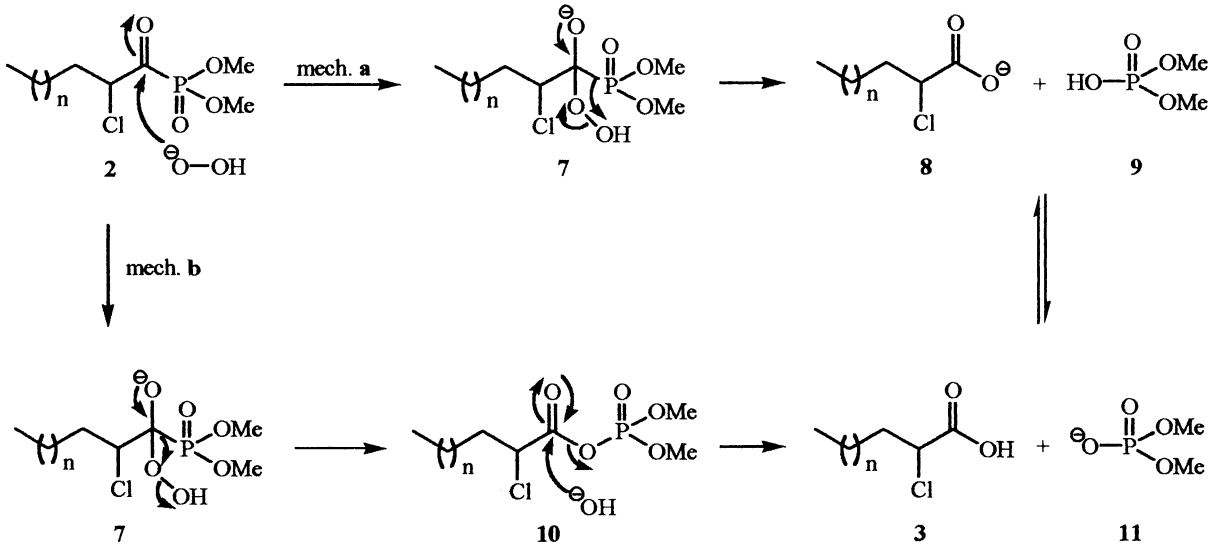


Scheme 2.



Scheme 3.

hydrolysis of the α-chloro acylphosphonate **2** to the corresponding α-chloro carboxylic acid **3** using hydrogen peroxide and sodium bicarbonate (Scheme 2). It was believed that after an addition–elimination step, the α-chloro peroxy acid **5** was formed. The liberated dimethyl phosphite **6** would then reduce the peroxy acid resulting in the formation of the α-chloro carboxylic acid **3**.

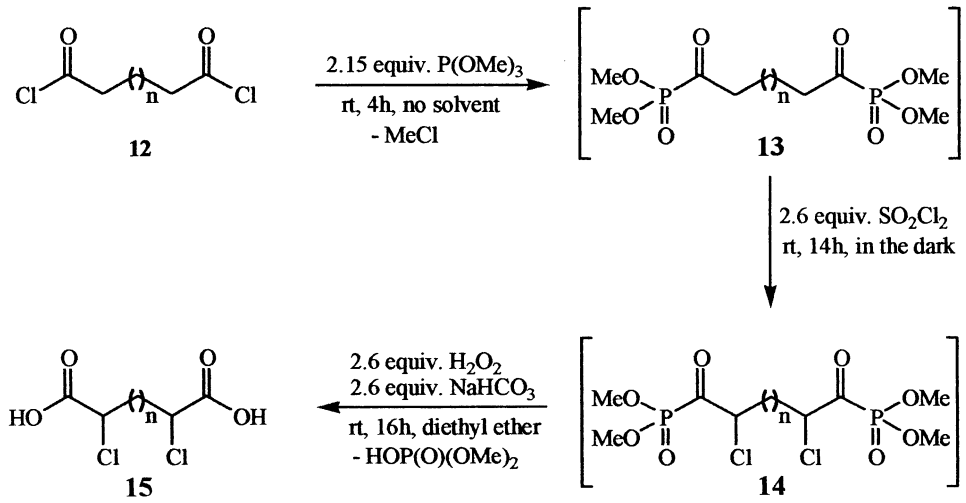
However, the proposed mechanism appears to be improbable since the hydrolysis is performed with an excess of hydrogen peroxide–sodium bicarbonate. Therefore, it seems more likely that dimethyl phosphite **6** is oxidized directly by the excess of hydrogen peroxide. The oxidation of **6** to dimethyl phosphate indeed proceeds very fast as observed in an experiment following the oxidation of **6** with hydrogen peroxide–sodium bicarbonate by ^{31}P NMR:

Table 1. Yields of α-chloro carboxylic acids **3** and α,α′-dichloro dicarboxylic acids **15**

Chlorinated carboxylic acid		Yield (%)
2-Chloro valeric acid	**3a** (n=1)	85
2-Chloro decanoic acid	**3b** (n=6)	55
2-Chloro tetradecanoic acid	**3c** (n=10)	65
2-Chloro hexadecanoic acid	**3d** (n=12)	78
2-Chloro octadecanoic acid	**3e** (n=14)	75
2,4-Dichloro glutaric acid	**15a** (n=1)	28
2,5-Dichloro adipic acid	**15b** (n=2)	67
2,7-Dichloro suberic acid	**15c** (n=4)	54
2,8-Dichloro azelaoic acid	**15d** (n=5)	69
2,11-Dichloro dodecanoic-1,12-diacid	**15e** (n=8)	79

the signal of **6** (δ: 10.77 ppm) is almost directly replaced by a signal attributable to the formation of dimethyl phosphate **9** (δ: 1.00 ppm). Accepting this mechanism, the α-chloro peroxy acid **5** should be formed because of the lack of reductants. A simple test,[19] however, proved that no peroxy acid was formed as the result of the reaction sequence (see experimental section). Since the α-chloro carboxylic acid **3** was formed, two alternative reaction mechanisms were suggested (Scheme 3).

Mechanism **a**, as well as mechanism **b**, starts with the addition of the hydrogen peroxide anion to **2**. A first possibility (mechanism **a**) involves a 4-center-mechanism leading to α-chloro carboxylic acid **8** and dimethyl phosphate **9**. Mechanism **b**, however, gives rise to the formation of dimethyl α-chloro acylphosphate **10** as an intermediate which is subsequently hydrolysed leading to **3** and **11**. Using ^{31}P NMR we were able to prove that mechanism **b** is the pathway by which the cleavage of **2** occurs. The ^{31}P NMR signal of **2** (δ: −1.54 ppm) gradually disappeared when hydrogen peroxide–sodium bicarbonate was added. Both mechanism **a** and mechanism **b** show the formation of adduct **7**, which was observed during the whole course of the reaction as a small signal (δ: 19.59 ppm). In mechanism **a**, **7** decomposes to the α-chloro carboxylic acid **8** and dimethyl phosphate **9** immediately. However, before **9** was perceived, a signal with a ^{31}P chemical shift of −5.75 ppm appeared at the expense of the signal of **2**. According to the literature,[20] the ^{31}P chemical shift of dimethyl acetylphosphate and dimethyl propionylphosphate is −5.90 and −5.70 ppm, respectively. Consequently, the



Scheme 4.

observed signal (δ: −5.75 ppm) was attributed to dimethyl α-chloro acylphosphate **10**. Essentially, **10** is formed by a Baeyer–Villiger oxidation of α-chloro acylphosphonate **2**. In accordance with mechanism **b**, this intermediate should be hydrolysed yielding **3** and **11**. Indeed, the signal of **10** slowly disappeared in favour of the signal of **11** (δ: 2.39 ppm). In addition, the same results were obtained repeating this procedure with an organic peroxide such as *tert*-butyl hydroperoxide in an organic solvent leading to the corresponding α-chloro *tert*-butyl ester **16c** (Table 2).

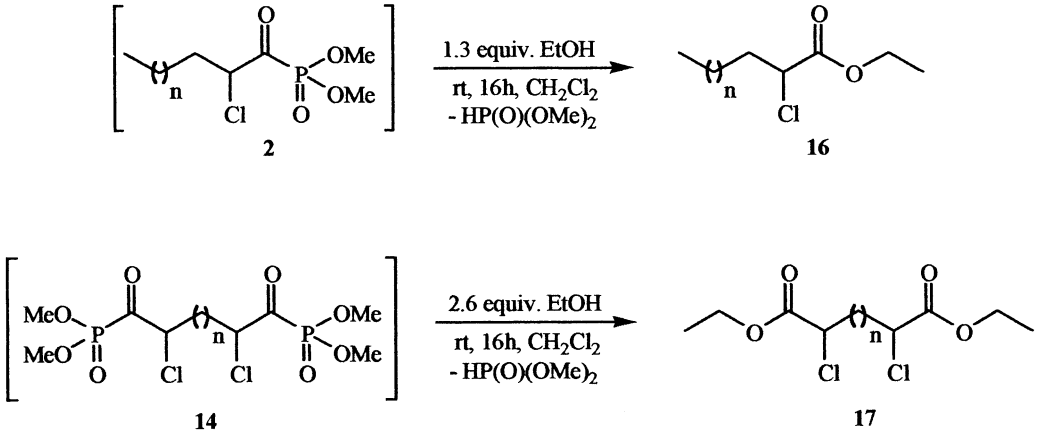
As reported earlier,[18] the procedure leads to the formation of α-chloro carboxylic acids **3** under mild conditions in good to very good yields (Table 1). Therefore, the procedure was evaluated to synthesize α,α′-dichloro dicarboxylic acids. In accordance with the original procedure, the scope of the reaction was broadened as shown in Scheme 4. These new results of the one-pot procedure are also listed in Table 1.

Because of the limited solubility of α,α′-dichloro dicarboxylic acids **15** in dichloromethane, the cleavage of **14** was performed in diethyl ether. During the work up of **14** only 2.6 equiv. of hydrogen peroxide and 2.6 equiv. of sodium bicarbonate were used. The dicarboxylic acids **15** were isolated after acidification of the reaction mixture with concentrated hydrogen chloride. The pure α,α′-dichloro dicarboxylic acids **15** were isolated after crystallization from the reaction mixture.

The yield of **15a** and **15b** are in the same order of magnitude of those reported in the literature.[13–15] The higher dicarboxylic acids **15c**, **15d** and **15e** are obtained in moderate to good yield under mild conditions. Except for compound **15c**, which was prepared from the corresponding acid, all α,α′-dichloro dicarboxylic acids **15** were prepared starting from the corresponding acid chloride **12**.

Acylphosphonates are not only very sensitive to hydrolysis,[21] the phosphorus–carbon (P–C) bond is also easily cleaved by a multitude of nucleophiles such as amines,[22] alcohols[23] and thiols[24] with the expulsion of phosphite. Consequently, the procedure was evaluated to synthesize α-chloro esters **16** and α,α′-dichloro diesters **17** by treatment of the corresponding chlorinated acylphosphonates **2** and **14**, respectively with ethanol (Scheme 5). The results are listed in Table 2.

The synthesis of the α-chloro esters **16** was successful. After an extraction of the crude reaction mixture, **16a** and **16b** were obtained as yellow oils with yields over 90%. The pure



Scheme 5.

Table 2. Yields of ethyl α-chloro esters **16**, diethyl α,α′-dichloro diesters **17**, *N*-alkyl α-chloro amides **18** and *N*,*N*′-diisopropyl α,α′-dichloro diamides **19**

Chlorinated ester		Yield (%)
Ethyl 2-chloro decanoate	**16a** (*n*=6)	78
Ethyl 2-chloro tetradecanoate	**16b** (*n*=10)	89
tert-Butyl 2-chloro decanoate	**16c** (*n*=6)	55
Diethyl 2,4-dichloro glutaroate	**17a** (*n*=1)	/[a]
Diethyl 2,5-dichloro adipoate	**17b** (*n*=2)	/[a]
Diethyl 2,11-dichloro dodecan-1,12-dioate	**17c** (*n*=8)	53
Chlorinated amide		
N-Isopropyl 2-chloro decanoylamide	**18a** (*n*=6)	72
N-Isopropyl 2-chloro tetradecanoylamide	**18b** (*n*=10)	72
N-Isopropyl 2-chloro octadecanoylamide	**18c** (*n*=14)	74
N-[(*S*)-1-Phenylethyl] 2-chloro decanoylamide	**18d** (*n*=6)	96 (26)[b]
N,*N*′-Diisopropyl 2,4-dichloro glutarylamide	**19a** (*n*=1)	4
N,*N*′-Diisopropyl 2,5-dichloro adipoylamide	**19b** (*n*=2)	3
N,*N*′-Diisopropyl 2,11-dichloro dodecanoyl-1,12-diamide	**19c** (*n*=8)	18

[a] The crude reaction product was a complex mixture from which the chlorinated ester could not be isolated.
[b] The crude mixture was purified by crystallization and this yield is given between brackets.

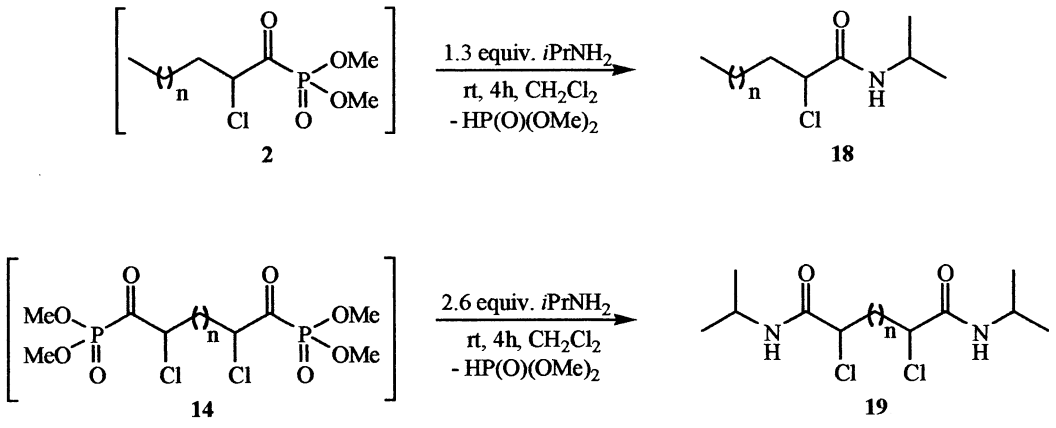
α-chloro esters **16** were isolated by means of flash chromatography using petroleum ether/ethyl acetate as eluent (Table 2). On the other hand, the preparation of α,α′-dichloro diesters **17** was less successful. Both ester **17a** and **17b** could not be isolated from the complex reaction mixtures although small amounts were formed. The chlorinated ester **17c**, however, was formed with a yield of 70% and could be isolated with a moderate yield after flash chromatography.

Analogous to the synthesis of the chlorinated esters, isopropyl amine was evaluated as a nucleophile to synthesize the corresponding chlorinated isopropyl amides (Scheme 6).

Isopropyl amine, as representative for the group of the amines, appeared to be an efficient nucleophile for the synthesis of α-chlorinated amides **18**. The amides **18** were isolated as yellow solids and purified by crystallization yielding the pure amides as a white powder. Comparable to the preparation of the diesters **17a** and **17b**, the synthesis of the α,α′-dichloro diamides **19a** and **19b** was rather unsuccessful and only very poor yields of pure product were obtained. A small amount of pure amide **19c** was isolated, but the residue still contained approximately 25% of the product.

Concerning the stereochemistry of the reaction, some aspects can be deduced from the reaction of a chlorinated acylphosphonate **2** with a chiral amine, e.g. (*S*)-1-phenylethyl amine. Using this chiral amine, a diastereomeric mixture of amide **18d** (50/50) was formed and could be separated by flash chromatography into the two diastereoisomers. The two diastereoisomers revealed a different ^{13}C NMR value for the CHCl carbon with a difference of 0.12 ppm which was also visible in the crude spectrum of the diastereomeric mixture. Therefore, it can be concluded that the diastereoisomers with the chiral centers close to each other, can be differentiated by the carbon NMR values of the CHCl carbon.

In the case of the synthesis of dichloro glutaric acid **15a**, the detection of single peaks in the carbon NMR thus reveals the synthesis of one diastereomeric pair of acids. Taking into account the steric interactions, it can be deduced that the *trans* enantiomers are formed. However, for higher homologues the steric interaction during the chlorination is negligible which results in mixtures of *cis* and *trans* isomers, which can not be differentiated through the carbon NMR-values because of the diminished interaction between the two chiral centers. Therefore, it can be concluded that during the chlorination, no stereoselectivity is determined except for the synthesis of short chain difunctionalised derivatives (low yield) where the *trans* isomers are favoured.



Scheme 6.

In general, this paper describes a straightforward and high yielding one-pot procedure for the synthesis of α-chloro acids and α,α′-dichloro diacids and their corresponding esters and amides. The procedure, however, is not applicable to the synthesis of the lower ($<C_7$) α,α′-dichlorinated diesters and diamides probably due to intramolecular reactions.

3. Experimental

3.1. General

^{1}H NMR spectra and ^{13}C NMR spectra were recorded at 270 and 68 MHz, respectively. The ^{31}P NMR spectra were recorded at 109 MHz (JEOL EX 270). $CDCl_3$, CD_3OD or acetone-d6 was used as solvent. Mass spectra were obtained on a Varian MAT 112 mass spectrometer (70 eV). IR spectra were recorded with a Fourier Transform spectrometer (Perkin–Elmer, Spectrum One). Diethyl ether was distilled from sodium/benzophenone ketyl and dichloromethane was distilled from calcium hydride.

3.2. Peroxy acid test

In a round bottom flask of 250 ml, 1.5 g of sodium iodide was dissolved in 50 ml of water, 5 ml of glacial acetic acid and 5 ml of chloroform. The assumed α,α′-dichloro dicarboxylic acid **5e** was added and the mixture was stirred. No colouring due to the formation of iodine was observed. Consequently, **5e** was not a peroxy acid and the procedure gives rise to the formation of carboxylic acids **3** and **5**. To check the validity of this test, *m*-chloro perbenzoic acid was added. After stirring the mixture, an intense colouring was noticed.

3.3. General procedure for the synthesis of α,α′-dichloro dicarboxylic acids 15

In a round bottom flask of 50 ml, 32.3 mmol of trimethyl phosphite was added to 15 mmol of diacid dichloride **12** under a nitrogen atmosphere at 0°C. After stirring the reaction mixture for four hours at room temperature, the excess of trimethyl phosphite and the remainder of methyl chloride was evaporated in vacuo. The flask was covered with aluminium foil and 39 mmol of sulfuryl chloride was added by syringe at 0°C. The reaction mixture was stirred for 14 h at room temperature. The chlorination was stopped by adding 5 ml of dry dichloromethane and leading nitrogen gas through the solution expelling the excess of sulfuryl chloride and the remaining hydrogen chloride and sulfur dioxide. The solution was then added to a mixture of 39 mmol of hydrogen peroxide (35% in water), 39 mmol of sodium bicarbonate and 10 ml of diethyl ether in a round bottom flask of 50 ml at 0°C. After stirring the reaction mixture for 16 h at room temperature, the mixture was poured in 20 ml of 0.1 M of hydrogen chloride and was extracted with 20 ml of diethyl ether. The organic layer was dried over magnesium sulfate, filtered and the diethyl ether was evaporated. Purification of the reaction mixture was performed by crystallization in dichloromethane and ethyl acetate yielding the pure α,α′-dichloro dicarboxylic acid **15** (yield: 28–79%).

3.4. Procedure for the synthesis of suberoyl chloride 12c

In a round bottom flask of 50 ml, 15 mmol of suberic acid was dissolved in 20 ml of dichloromethane and was treated with 39 mmol of thionyl chloride in the presence of 0.8 mmol of *N*,*N*-dimethyl formamide (DMF) as a catalyst. Under a nitrogen atmosphere, the reaction mixture was refluxed for two hours. The dichloromethane was evaporated and the synthesis of the corresponding acylphosphonate was started.

3.4.1. 2,4-Dichloro glutaric acid (15a) as yellowish solid. ^{1}H NMR (270 MHz, $(CD_3)_2$=O) δ: 2.64 (2H, dd, J=7.9 Hz, J=6.3 Hz, CH_2); 4.67 (2H, dd, J=7.9 Hz, J=6.3 Hz, 2×CHCl). ^{13}C NMR (68 MHz, CD_3OD) δ: 39.96 (CH_2); 55.02 (2×CHCl); 170.53 (2×C=O). MS: *m*/*z* (%): 200/02/04 (M^+, 0.2); 182 (26); 154 (30); 119 (26); 107 (29); 96 (53); 94 (100); 76 (52); 75 (44); 63 (27); 55 (53); 49 (29); 45 (88); 41 (43). IR (cm^{-1}) ν_{max}: 1753 (C=O); 1727 (C=O); 1203 (C–O); 1235 (C–O); 3406 (O–H). Mp=148–150°C. Calcd for $C_5H_6Cl_2O_4$: C 29.88, H 3.01. Found: C 30.04, H 2.98.

3.4.2. 2,5-Dichloro adipic acid (15b) as yellowish solid. ^{1}H NMR (270 MHz, CD_3OD) δ: 2.03 (2H, m, CH_2); 2.22 (2H, m CH_2); 4.44 (2H, m, 2×CHCl). ^{13}C NMR (68 MHz, $(CD_3)_2$=O) δ: 32.17 (2×CH_2); 57.61 (2×CHCl); 170.40 (2×C=O). MS: *m*/*z* (%): 214/16/18 (M^+, 0.7); 163 (35); 161 (95); 133 (53); 125 (47); 107 (63); 97 (60); 94 (31); 89 (26); 73 (49); 62 (86); 53 (89); 45 (100); 41 (81). IR (cm^{-1}) ν_{max}: 1713 (C=O); 1202 (C–O); 1248 (C–O); 3434 (O–H). Mp=135–137°C. Calcd for $C_6H_8Cl_2O_4$: C 33.51, H 3.75. Found: C 33.72, H 3.62.

3.4.3. 2,7-Dichloro suberic acid (15c) as yellowish solid. ^{1}H NMR (270 MHz, CD_3OD) δ: 1.50 (4H, m, 2×CH_2); 1.92 (2H, m, CH_2CHCl); 2.01 (2H, m, CH_2CHCl); 4.35 (2H, dd, J=7.3 Hz, J=6.3 Hz, 2×CHCl). ^{13}C NMR (68 MHz, CD_3OD) δ: 26.38 (2×CH_2CH$_2$CHCl); 35.81 (2×CH_2CHCl); 58.60 (2×CHCl); 172.88 (2×C=O). MS: *m*/*z* (%): 242/44/46 (M^+, 0.4); 151 (17); 149 (55); 131 (25); 113 (45); 96 (39); 94 (100); 81 (23); 79 (25); 67 (34); 55 (64); 45 (54); 41 (81). IR (cm^{-1}) ν_{max}: 1712 (C=O); 1228 (C–O). Mp=134–139°C. Calcd for $C_8H_{12}Cl_2O_4$: C 39.53, H 4.98. Found: C 39.67, H 4.79.

3.4.4. 2,8-Dichloro azelaoic acid (15d) as yellowish solid. ^{1}H NMR (270 MHz, $CDCl_3$) δ: 1.45 (6H, m, 3×CH_2); 1.89 (2H, m, CH_2CHCl); 1.98 (2H, m, CH_2CHCl); 4.35 (2H, dd, J=7.3 Hz, J=6.3 Hz, 2×CHCl). ^{13}C NMR (68 MHz, $CDCl_3$) δ: 26.65 (CH_2); 29.11 (2×CH_2); 35.70 (2×CH_2CHCl); 58.09 (2×CHCl); 171.71 (2×C=O). MS: *m*/*z* (%): no M^+, 164 (16); 144 (15); 110 (47); 109 (53); 87 (27); 74 (25); 59 (27); 57 (100); 55 (28); 43 (37); 41 (44). IR (cm^{-1}) ν_{max}: 1734 (C=O); 1210 (C–O); 1306 (C–O). Mp=104–107°C. Calcd for $C_9H_{14}Cl_2O_4$: C 42.04, H 5.49. Found: C 42.14, H 5.36.

3.4.5. 2,11-Dichloro dodecanoic-1,12-diacid (15e) as yellowish solid. ^{1}H NMR (270 MHz, CD_3OD) δ: 1.33 (8H, s, 4×CH_2); 1.43 (4H, m, 2×CH_2); 1.92 (4H, m, 2×CH_2CHCl); 4.33 (2H, dd, J=7.6 Hz, J=5.9 Hz, 2×CHCl). ^{13}C NMR (68 MHz, CD_3OD) δ: 27.29 (2×CH_2); 30.20 (2×

CH_2); 30.58 (2×CH_2); 36.39 (2×*C*H_2CHCl); 59.12 (2×CHCl); 173.37 (2×C═O). MS: *m*/*z* (%): 298/300/02 (0.4); 132 (28); 118 (48); 94 (67); 81 (35); 73 (40); 69 (45); 67 (36); 57 (32); 55 (100); 45 (34); 43 (34); 41 (97). IR (cm^{-1}) ν_{max}: 1711 (C═O); 1215 (C–O); 1239 (C–O). Mp=99–102°C. Calcd for $C_{12}H_{20}Cl_2O_4$: C 48.17, H 6.74. Found: C 48.09, H 6.82.

3.5. General procedure for the synthesis of α-chloro esters 16

In a round bottom flask of 50 ml, 5.8 mmol of trimethyl phosphite was added to 5 mmol of acid chloride under a nitrogen atmosphere at 0°C. After stirring the reaction mixture for four hours at room temperature, the excess of trimethyl phosphite and the remainder of methyl chloride was evaporated in vacuo. The flask was covered with aluminium foil and 6.5 mmol of sulfuryl chloride was added by syringe at 0°C. The reaction mixture was stirred for 14 h at room temperature. The reaction was quenched by addition of 5 ml of dry dichloromethane and nitrogen gas was led through the solution in order to remove the excess of sulfuryl chloride and the remaining hydrogen chloride and sulfur dioxide. The solution was added to 6.5 mmol of absolute ethanol dissolved in 10 ml of dry dichloromethane at 0°C. After stirring the reaction mixture for 16 h under a nitrogen atmosphere at room temperature, the mixture was poured in 20 ml of 0.1 M of hydrogen chloride and was extracted with 20 ml of dichloromethane. The organic layer was dried over magnesium sulfate, filtered and the dichloromethane was evaporated. Purification of the reaction mixture was performed by flash chromatography using petroleum ether and ethyl acetate as the eluent (yield: 78–89%).

3.5.1. Ethyl 2-chloro decanoate (16a) as yellow oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ: 0.88 (3H, t, J=6.6 Hz, CH_3); 1.31 (13H, m, C*H*$_3$C*H*$_2$O, 5×CH_2); 1.40 (2H, m, C*H*$_2$C*H*$_2$CHCl), 1.97 (2H, m, C*H*$_2$CHCl); 4.24 (3H, m, CH_2O, CHCl). ^{13}C NMR (68 MHz, $CDCl_3$) δ: 13.86 (CH_3); 13.89 (CH_3); 22.48 (CH_2); 25.81 (CH_2); 28.72 (CH_2); 28.99 (CH_2); 29.13 (CH_2); 31.65 (CH_2); 34.74 (*C*H_2CHCl); 57.23 (CH_2O); 61.67 (CHCl). 169.60 (C═O). MS: *m*/*z* (%): 234 (M^+, 2); 177 (17); 124 (32); 122 (100); 94 (20); 85 (51); 83 (82); 69 (19); 57 (19); 55 (21); 43 (23). IR (cm^{-1}) ν_{max}: 1747 (C═O). Flash chromatography: (PE/EtOAc:20/80): R_f=0.7. Calcd for $C_{12}H_{23}ClO_2$: C 61.39, H 9.87. Found: C 61.33, H 9.78.

3.5.2. Ethyl 2-chloro tetradecanoate (16b) as yellow oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ: 0.88 (3H, t, J=6.6 Hz, CH_3); 1.26 (23H, m, C*H*$_3$C*H*$_2$O, 10×CH_2); 1.95 (2H, m, C*H*$_2$CHCl); 4.24 (3H, m, CHCl, CH_2O). ^{13}C NMR (68 MHz, $CDCl_3$) δ: 13.91 (CH_3); 13.98 (CH_3); 22.59 (CH_2); 25.86 (CH_2); 28.77 (CH_2); 29.26 (2×CH_2); 29.38 (CH_2); 29.54 (3×CH_2); 31.83 (CH_2); 34.79 (*C*H_2CHCl); 57.27 (CH_2O); 61.73 (CHCl); 169.65 (C═O). MS: *m*/*z* (%): 290/92 (M^+, 0.8); 124 (9); 122 (28); 87 (12); 85 (66); 83 (100); 57 (7); 55 (7); 47 (16); 41 (6). IR (cm^{-1}) ν_{max}: 1747 (C═O). Flash chromatography: (PE/EtOAc:30/70): R_f=0.6. Calcd for $C_{16}H_{31}ClO_2$: C 66.07, H 10.74. Found: C 65.97, H 10.61.

3.6. Procedure for the synthesis of *tert*-butyl 2-chloro decanoate 16c

Except for the work up of the α-chloro acylphosphonate **2a**, the procedure is analogous to the synthesis of the α-chlorinated esters **16**. The α-chloro acylphosphonate **2a** was treated with 10 mmol of pyridine and 10 mmol of *tert*-butyl hydroperoxide (3 M in *iso*-octane) and the reaction mixture was stirred for 96 h under nitrogen atmosphere at room temperature. The reaction mixture was poured in 20 ml of 0.1 M of hydrogen chloride and was extracted with 20 ml of dichloromethane. The organic layer was dried over magnesium sulfate, filtered and the dichloromethane was evaporated. The chlorinated *tert*-butyl ester was isolated by flash chromatography using petroleum ether and ethyl acetate as eluent (yield: 55%).

3.6.1. *tert*-Butyl 2-chloro decanoate (16c) as yellow oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ: 0.88 (3H, t, J=6.4 Hz, CH_3); 1.27 (12H, s, 6×CH_2); 1.35 (9H, s, C(CH_3)$_3$); 2.00 (2H, m, C*H*$_2$CHCl); 4.27 (1H, m, CHCl). ^{13}C NMR (68 MHz, $CDCl_3$) δ: 13.95 (CH_3); 22.50 (CH_2); 25.77 (C(*C*H_3)); 25.86 (2×C(*C*H_3)); 28.66 (CH_2); 28.97 (CH_2); 29.02 (CH_2); 29.11 (CH_2); 31.65 (CH_2); 34.77 (*C*H_2CHCl); 54.38 (CHCl); 84.46 (*C*(CH_3)$_3$); 167.21 (C═O). MS: *m*/*z* (%): no M^+; 160 (3); 142 (4); 108 (6); 88 (12); 86 (68); 84 (100); 57 (14); 49 (14); 47 (18). IR (cm^{-1}) ν_{max}: 1046 (C–O); 1189 (C–O); 1786 (C═O). Flash chromatography: (PE/EtOAc:10/90): R_f=0.7. Calcd for $C_{14}H_{27}ClO_2$: C 63.98, H 10.35. Found: C 63.73, H 11.60.

3.7. Procedure for the synthesis of diethyl 2,11-dichloro dodecan-1,12-dioate 17c

The procedure is analogous to the synthesis of the α-chlorinated esters **16**. The following amounts of reagents were used: 5 mmol of dodecanoyl dichloride **12e**, 10.8 mmol of trimethyl phosphite and 13 mmol of sulfuryl chloride. The α,α′-dichloro bisacylphosphonate **14e** was added to a round bottom flask of 50 ml containing 13 mmol of absolute ethanol dissolved in 10 ml of dry dichloromethane at 0°C. The reaction mixture was stirred for four hours under a nitrogen atmosphere at room temperature. The mixture was poured in 20 ml of 0.1 M of hydrogen chloride and was extracted with 20 ml of dichloromethane. The organic layer was dried over magnesium sulfate, filtered and the dichloromethane was evaporated. The chlorinated ester **17c** was isolated by flash chromatography using petroleum ether and ethyl acetate as eluent (yield: 53%).

3.7.1. Diethyl 2,11-dichloro dodecan-1,12-dioate (17c) as yellow oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ: 1.31 (14H, m, 4×CH_2, 2×CH_3); 1.40 (4H, m, 2×C*H*$_2$C*H*$_2$CHCl); 1.97 (4H, m, 2×C*H*$_2$CHCl); 4.24 (6H, m, 2×CH_2O, 2×CHCl). ^{13}C NMR (68 MHz, $CDCl_3$) δ: 13.80 (2×CH_3); 25.64 (2×CH_2); 28.52 (2×CH_2); 28.88 (2×CH_2); 34.59 (2×*C*H_2CHCl); 57.16 (2×CH_2O); 61.65 (2×CHCl); 169.52 (2×C═O). MS: *m*/*z* (%): no M^+; 140 (16); 125 (17); 111 (14); 99 (10); 85 (62); 83 (100); 59 (16); 49 (11); 48 (17); 47 (30); 45 (15). IR (cm^{-1}) ν_{max}: 1747 (C═O). Flash chromatography: (PE/EtOAc:40/60): R_f=0.6. Calcd for $C_{16}H_{28}Cl_2O_4$: C 54.09, H 7.94. Found: C 53.91, H 8.00.

3.8. General procedure for the synthesis of α-chloro amides 18

The procedure is analogous to the synthesis of the α-chlorinated esters **16**. 5 mmol of acid chloride and 5.8 mmol of trimethyl phosphite were used for the synthesis of acylphosphonate **1** and the chlorination was performed with 6.5 mmol of sulfuryl chloride. The chlorinated acylphosphonate **2** was added to a round bottom flask of 50 ml containing 6.5 mmol of isopropyl amine (or (*S*)-1-phenylethyl amine) dissolved in 10 ml of dry dichloromethane at 0°C. The reaction mixture was stirred for four hours under a nitrogen atmosphere at room temperature. The reaction mixture was poured in 20 ml of 0.1 M of hydrogen chloride and was extracted with 20 ml of dichloromethane. After drying the organic layer over magnesium sulfate and filtration, the dichloromethane was evaporated and the pure α-chloro amide **18** was isolated by crystallization using dichloromethane and petroleum ether (yield: 72–74%).

3.8.1. *N*-Isopropyl 2-chloro decanoylamide (18a) as yellowish solid. ^{1}H NMR (270 MHz, $CDCl_3$) δ: 0.88 (3H, t, J=6.6 Hz, CH_3); 1.18 (3H, d, J=6.3 Hz, CH(CH_3)); 1.19 (3H, d, J=6.3 Hz, CH(CH_3)); 1.27 (10H, s, 5×CH_2); 1.45 (2H, s, CH_2); 1.92 (1H, m, CH_2CHCl); 2.07 (1H, m, CH_2CHCl); 4.07 (1H, m, CH(CH_3)$_2$); 4.31 (1H, dd, J=7.9 Hz, J=4.0 Hz, CHCl); 6.46 (1H, s, NH). ^{13}C NMR (68 MHz, $CDCl_3$) δ: 14.34 (CH_3); 22.70 (CH_3); 22.77 (CH_3); 22.90 (CH_3); 26.06 (CH_2); 29.13 (CH_2); 29.42 (CH_2); 29.60 (CH_2); 32.06 (CH_2); 35.83 (*C*H_2CHCl); 42.14 (NCH); 61.69 (CHCl); 168.39 (C═O). MS: *m/z* (%): 247/49 (M^+, 5); 232 (7); 212 (13); 137 (34); 135 (100); 100 (15); 86 (60); 83 (16); 55 (11); 44 (30); 43 (46). IR (cm^{-1}) ν_{max}: 1650 (C═O); 3295 (NH); 1551 (NH). Mp= 57–59°C. Calcd for $C_{13}H_{26}ClNO$: C 63.01, H 10.58. Found: C 63.22, H 10.72.

3.8.2. *N*-Isopropyl 2-chloro tetradecanoylamide (18b) as yellowish solid. ^{1}H NMR (270 MHz, $CDCl_3$) δ: 0.88 (3H, t, J=6.6 Hz, CH_3); 1.18 (3H, d, J=6.6 Hz, CH(CH_3)); 1.19 (3H, d, J=6.6 Hz, CH(CH_3)); 1.25 (18H, s, 9×CH_2); 1.45 (2H, s, CH_2); 1.91 (1H, m, CH_2CHCl); 2.08 (1H, m, CH_2CHCl); 4.07 (1H, m, CH(CH_3)$_2$); 4.31 (1H, dd, J=8.3 Hz, J=4.0 Hz, CHCl); 6.41 (1H, s, NH). ^{13}C NMR (68 MHz, $CDCl_3$) δ: 14.07 (CH_3); 22.43 (CH_3); 22.52 (CH_3); 22.64 (CH_2); 25.75 (CH_2); 28.81 (CH_2); 29.33 (CH_2); 29.47 (CH_2); 29.60 (4×CH_2); 31.88 (CH_2); 35.56 (*C*H_2CHCl); 41.85 (NCH); 61.57 (CHCl); 168.05 (C═O). MS: *m/z* (%): 303/05 (M^+, 10); 269 (24); 227 (6); 191 (6); 138 (28); 136 (82); 86 (64); 84 (100); 47 (17); 44 (14); 43 (25). IR (cm^{-1}) ν_{max}: 1650 (C═O); 3295 (NH); 1551 (NH). Mp=76–78°C. Calcd for $C_{17}H_{34}ClNO$: C 67.18, H 11.28. Found: C 67.30, H 11.10.

3.8.3. *N*-Isopropyl 2-chloro octadecanoylamide (18c) as yellowish solid. ^{1}H NMR (270 MHz, $CDCl_3$) δ: 0.88 (3H, t, J=6.6 Hz, CH_3); 1.18 (3H, d, J=6.6 Hz, CH(CH_3)); 1.19 (3H, d, J=6.6 Hz, CH(CH_3)); 1.25 (26H, s, 13×CH_2); 1.45 (2H, s, CH_2); 1.90 (1H, m, CH_2); 2.10 (1H, m, CH_2); 4.07 (1H, m, CH(CH_3)$_2$); 4.31 (1H, dd, J=8.3 Hz, J=4.0 Hz, CHCl); 6.39 (1H, s, NH). ^{13}C NMR (68 MHz, $CDCl_3$) δ: 14.14 (CH_3); 22.46 (CH_3); 22.57 (CH_3); 22.71 (CH_2); 25.80 (CH_2); 28.88 (CH_2); 29.40 (3×CH_2); 29.52 (2×CH_2); 29.70 (5×CH_2); 31.93 (CH_2); 35.62 (*C*H_2CHCl); 41.90 (NCH); 61.58 (CHCl); 168.10 (C═O). MS: *m/z* (%): 359/61 (M^+; 12); 346 (7); 326 (12); 191 (7); 149 (7); 138 (43); 136 (100); 87 (41); 55 (10); 43 (29). IR (cm^{-1}) ν_{max}: 1651 (C═O); 3295 (NH); 1553 (NH). Mp=76–82°C. Calcd for $C_{21}H_{42}ClNO$: C 70.06, H 11.76. Found: C 70.18, H 11.65.

3.8.4. *N*-[(*S*)-1-Phenylethyl] 2-chloro decanoylamide (18d). *Mixture of diastereoisomers*. (a) White solid. ^{1}H NMR (270 MHz, $CDCl_3$) δ: 0.88 (3H, t, J=6.6 Hz, CH_3); 1.28 (10H, s, 5×CH_2); 1.47 (2H, s, CH_2); 1.52 (3H, d, J=6.9 Hz, NCHCH_3); 1.94 (1H, m, CH_2CHCl); 2.11 (1H, m, CH_2CHCl); 4.33 (1H, dd, J=8.3 Hz, J=4.0 Hz, CHCl); 5.10 (1H, m, NCH); 6.81 (1H, d, J=7.3 Hz, NH); 7.33 (5H, m, C_6H_5). ^{13}C NMR (68 MHz, $CDCl_3$) δ: 14.07 (CH_3); 21.71 (CH_3); 22.61 (CH_2); 25.77 (CH_2); 28.82 (CH_2); 29.15 (CH_2); 29.31 (CH_2); 31.77 (CH_2); 35.54 (*C*H_2CHCl); 49.20 (NCH); 61.46 (CHCl); 126.04 (2×CH); 127.51 (CH); 128.73 (2×CH); 142.48 (C_{quat}); 168.10 (C═O). MS: *m/z* (%): 309/11 (M^+, 1.2); 212 (18); 157 (32); 150 (23); 136 (27); 125 (42); 122 (100); 121 (30); 119 (65); 108 (31); 94 (55); 85 (44); 83 (61); 76 (13); 55 (28); 43 (26). IR (cm^{-1}) ν_{max}: 1650 (C═O); 3288 (NH); 1545 (NH). Flash chromatography: (PE/EtOAc: 95/5): R_f=0.20. Mp=75–77°C. Calcd for $C_{19}H_{28}ClNO$: C 69.77, H 9.11. Found: C 69.54, H 9.01.

(b) White solid. ^{1}H NMR (270 MHz, $CDCl_3$) δ: 0.87 (3H, t, J=6.6 Hz, CH_3); 1.24 (10H, s, 5×CH_2); 1.41 (2H, s, CH_2); 1.52 (3H, d, J=6.9 Hz, NCHCH_3); 1.89 (1H, m, CH_2CHCl); 2.06 (1H, m, CH_2CHCl); 4.36 (1H, dd, J=8.3 Hz, J=4.0 Hz, CHCl); 5.10 (1H, m, NCH); 6.82 (1H, d, J=7.3 Hz, NH); 7.32 (5H, m, C_6H_5). ^{13}C NMR (68 MHz, $CDCl_3$) δ: 14.09 (CH_3); 21.74 (CH_3); 22.64 (CH_2); 25.77 (CH_2); 28.82 (CH_2); 29.13 (CH_2); 29.33 (CH_2); 31.82 (CH_2); 35.61 (*C*H_2CHCl); 49.22 (NCH); 61.58 (CHCl); 126.02 (2×CH); 127.51 (CH); 128.75 (2×CH); 142.67 (C_{quat}); 168.15 (C═O). MS: *m/z* (%): 309/11 (M^+, 1.2); 212 (18); 157 (32); 150 (23); 136 (27); 125 (42); 122 (100); 121 (30); 119 (65); 108 (31); 94 (55); 85 (44); 83 (61); 76(13); 55 (28); 43 (26). IR (cm^{-1}) ν_{max}: 1656 (C═O); 3292 (NH); 1557 (NH). Flash chromatography (PE/EtOAc: 95/5): R_f=0.25. Mp=75–77°C. Calcd for $C_{19}H_{28}ClNO$: C 69.77, H 9.11. Found: C 69.54, H 9.01.

3.9. General procedure for the synthesis of α,α-dichloro diamides 19

The procedure is analogous to the synthesis of the α-chlorinated amides **18**. The following amounts of reagents were used: 5 mmol of diacid dichloride, 10.8 mmol of trimethyl phosphite and 13 mmol of sulfuryl chloride. The α,α′-dichloro bisacylphosphonate **14** was added to a round bottom flask of 50 ml containing 13 mmol of isopropyl amine dissolved in 10 ml of dry dichloromethane at 0°C. The reaction was stirred for four hours under a nitrogen atmosphere at room temperature. The α,α′-dichloro amides **19a** and **19b** were isolated by dissolving the resulting brown oil in a small amount of methanol and placing this solution for 24 h at −18°C (yield: 3–4%). The chlorinated amide **19c** was isolated by extraction of the reaction mixture with 20 ml of dichloromethane and by crystallization using ethyl acetate and chloroform (yield: 18%).

3.9.1. *N,N′*-Diisopropyl 2,4-dichloro glutarylamide (19a) as yellowish solid. ^{1}H NMR (270 MHz, $CDCl_3$) δ: 1.18 (6H, d, J=6.3 Hz, 2×CH_3); 1.20 (6H, d, J=4.6 Hz, 2×CH_3); 2.64 (2H, m, CH_2); 4.07 (2H, m, 2×NCH); 4.54 (2H, m, 2×CHCl); 6.45 (2H, s, 2×NH). ^{13}C NMR (68 MHz, $CDCl_3$) δ: 22.41 (4×CH_3); 41.33 (CH_2); 42.16 (2×NCH); 57.70 (2×CHCl); 166.77 (2×C═O). MS: *m/z* (%): 282/84/86 (M^+, 10); 227 (41); 225 (67); 191 (34); 182 (22); 160 (29); 148 (37); 137 (32); 135 (100); 118 (36); 44 (34); 43 (49). IR (cm^{-1}) ν_{max}: 1651 (C═O); 3250 (NH); 1562 (NH). Mp=177–181°C. Calcd for $C_{11}H_{20}Cl_2N_2O_2$: C 46.65, H 7.12. Found: C 46.72, H 7.14.

3.9.2. *N,N′*-Diisopropyl 2,5-dichloro adipoylamide (19b) as yellowish solid. ^{1}H NMR (270 MHz, $CDCl_3$) δ: 1.19 (12H, d, J=6.6 Hz, 4×CH_3); 2.11 (2H, m, CH_2); 2.31 (2H, m, CH_2); 4.06 (2H, m, 2×NCH); 4.34 (2H, m, 2×CHCl); 6.41 (2H, s, 2×NH). ^{13}C NMR (68 MHz, $CDCl_3$) δ: 22.43 (2×CH_3); 22.54 (2×CH_3); 32.00 (2×CH_2); 42.09 (2×NCH); 60.20 (CHCl); 60.29 (CHCl); 167.19 (2×C═O). MS: *m/z* (%): 296/98/300 (M^+, 20); 198 (31); 165 (40); 163 (43); 149 (31); 114 (42); 113 (33); 96 (54); 69 (57); 67 (34); 57 (31); 55 (57); 52 (35); 44 (100); 43 (80). IR (cm^{-1}) ν_{max}: 1652 (C═O); 3287 (NH); 1556 (NH). Mp=209–212°C. Calcd for $C_{12}H_{22}Cl_2N_2O_2$: C 48.49, H 7.46. Found: C 48.43, H 7.39.

3.9.3. *N,N′*-Diisopropyl 2,11-dichloro dodecanoyl-1,12-diamide (19c) as yellowish solid. ^{1}H NMR (270 MHz, $CDCl_3$) δ: 1.18 (6H, d, J=6.6 Hz, 2×CH_3); 1.19 (6H, d, J=6.6 Hz, 2×CH_3); 1.29 (8H, s, 4×CH_2); 1.45 (4H, s, 2×CH_2); 1.91 (2H, m, CH_2CHCl); 2.08 (2H, m, CH_2CHCl); 4.08 (2H, m, 2×NCH); 4.31 (2H,dd, J=8.3 Hz, J=3.9 Hz, 2×CHCl); 6.41 (2H, d, J=6.6 Hz, 2×NH). ^{13}C NMR (68 MHz, $CDCl_3$) δ: 22.44 (2×CH_3); 22.55 (2×CH_3); 25.71 (2×CH_2); 28.75 (2×CH_2); 29.16 (2×CH_2); 35.54 (2×*C*H_2CHCl); 41.94 (2×NCH);61.49 (2×CHCl); 168.16 (2×C═O). MS: *m/z* (%): 380/82/84 (M^+, 2); 235 (84); 221 (59); 193 (100); 165 (52); 109 (28); 91 (26); 82 (78); 66 (86); 57 (69); 55 (57); 49 (75); 47 (82); 42 (43); 41 (55). IR (cm^{-1}) ν_{max}: 1652 (C═O); 3288 (NH); 1552 (NH). Mp=118–121°C. Calcd for $C_{18}H_{34}Cl_2N_2O_2$: C 56.69, H 8.99. Found: C 56.74, H 7.12.

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