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Expedient Synthesis of Long-Chain ω-Substituted Fatty Acids and Esters from Cyclic Ketones Using Iodine and Hydrogen Peroxide

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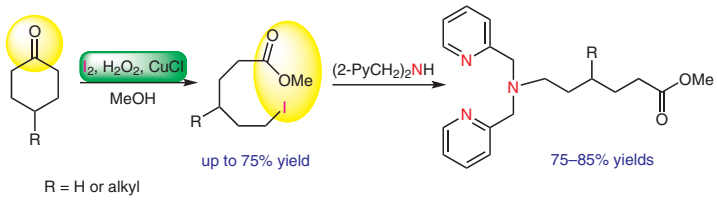

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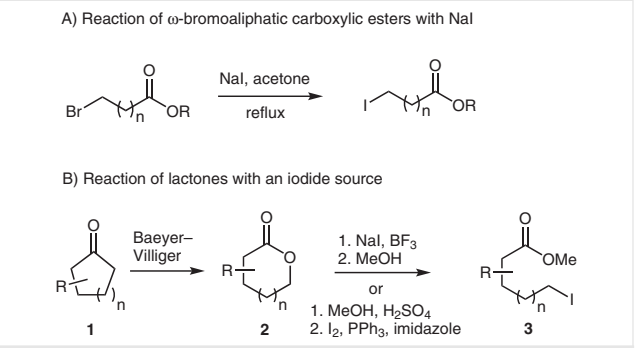
Abstract A simple and convenient synthesis of ω-iodoaliphatic carboxylic acids and esters by the reaction of cyclic ketones with iodine and hydrogen peroxide in the presence of catalytic CuCl has been developed. ω-Iodoaliphatic carboxylic esters were further used for the efficient preparation of di(2-pyridylmethylamino)alkanoic acids in excellent yields.

Key words cyclic ketones, ω-iodoaliphatic carboxylic acids, ω-iodoaliphatic carboxylic esters, ligands, di-(2-picolyl)amine, di-(2-pyridylmethylamino)alkanoic acids, chelating reagents

ω-Iodoaliphatic carboxylic acids and esters are useful building blocks in organic synthesis and they are important precursors in the synthesis of biologically active molecules.[1] Particularly noteworthy is the application of these compounds in the synthesis of ^{123}I-labeled derivatives, which are used as tracers for SPECT imaging.[2] However, existing methods for the preparation of these important compounds are limited to only two common procedures: (i) the nucleophilic substitution of bromine in ω-bromoaliphatic carboxylic esters by the action of NaI in acetone (Scheme 1, A),[1b,3] and (ii) the Baeyer–Villiger oxidation of cyclic ketones **1** to lactones **2** followed by their conversion into ω-iodoaliphatic carboxylic esters **3** by treatment with an iodide source, as illustrated in Scheme 1, B.[1a,4]

Both of the procedures shown in Scheme 1 have significant limitations. The first method requires initial preparation of ω-bromoaliphatic carboxylic esters from the corresponding carboxylic acids or hydroxycarboxylic acids.[5] Only some unbranched ω-bromoaliphatic carboxylic acids are commercial products, while the branched analogues are not readily available. The second method requires numerous synthetic steps involving isolation of intermediate products.



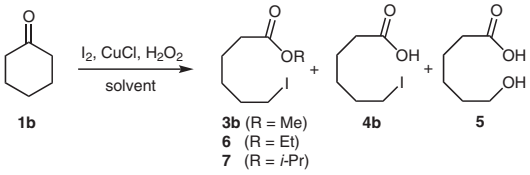
Scheme 1 Known procedures for the preparation of ω-iodoaliphatic carboxylic esters

We have developed a simple and convenient method for the preparation of ω-iodoaliphatic carboxylic acids and esters by the reaction of cyclic ketones with iodine and hydrogen peroxide at room temperature in the presence of catalytic CuCl. We assume that this reaction can be considered as an in situ modification of the Baeyer–Villiger (BV) oxidation. Hydrogen peroxide in the presence of metal salts[6] or iodine[7] as catalysts is a known oxidizing system for BV reactions; however, the formation of organic iodides in these reactions has not been previously reported.

Reaction conditions were optimized using cyclohexanone **1b** as the substrate. The nature of solvent had a particularly strong effect on the composition of products (Table 1). The reaction gave satisfactory yields of iodo-substituted products only when alcohols are used as solvents (Table 1, entries 1–4). The highest combined yield (99%) of iodo-sub-

stituted ester **3b** and acid **4b** was observed in methanol. The ratio of ester to acid **4b** strongly depends on the nature of the alcohol; sharply increasing from MeOH to *t*-BuOH. While the reactions in methanol and ethanol (entries 1 and 2) give esters **3b** and **6** as main products, the reactions in isopropanol and *t*-BuOH afforded 6-iodohexanoic acid **4b** as major product (entries 3 and 4). This result is probably explained by strong steric effect of the bulky alkyl groups on the ester formation. 6-Iodohexanoic acid **4b** was also isolated in low yields along with some 6-hydroxyhexanoic acid **5** when acetonitrile or tetrahydrofuran were used as solvents (entries 5 and 6). 6-Hydroxyhexanoic acid **5** was the only product observed in trace amounts for the reaction in water (entry 7).

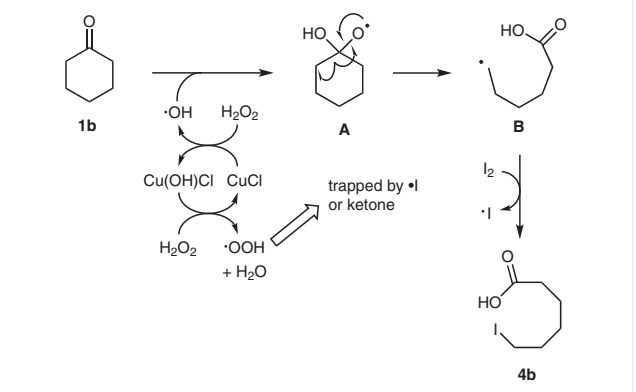
Table 1 Effect of Solvent on the Reaction of Cyclohexanone with Iodine and Hydrogen Peroxide in the Presence of Catalytic CuCl[a]



Entry	Solvent	Ester (%)[b]	**4b** (%)[b]	**5** (%)[b]
1	MeOH	**3b** (75)	24	0
2	EtOH	**6** (55)	40	0
3	*i*-PrOH	**7** (3)	75	0
4	*t*-BuOH	0	84	0
5	MeCN	0[c]	18	7
6	THF	0[c]	24	8
7	H_2O	0[c]	0	<1

[a] Reaction conditions: cyclohexanone (6 mmol), I_2 (3 mmol), CuCl (0.6 mmol), H_2O_2 (18 mmol), solvent, r.t., 8 h.
[b] Isolated yield.
[c] Unreacted cyclohexanone was also isolated.

A simplified mechanistic explanation for the formation of 6-iodohexanoic acid **4b** from cyclohexanone **1b**, hydrogen peroxide and iodine is provided in Scheme 2. Based on previous reports on Cu(I)-catalyzed oxidation using hydrogen peroxide or *tert*-butyl hydroperoxide,[8] Cu(I) complex reacts with H_2O_2 to generate hydroxyl radical along with Cu(II) complex, which is reconverted into Cu(I) by hydroperoxide. The addition of a hydroxyl radical to cyclic ketone **1b** results in the formation of O-centered radical **A**, which undergoes radical fragmentation leading to C-centered radical **B**. Finally, the latter is trapped with iodine to produce 6-iodohexanoic acid **4b**. In methanol, the hydroxyl radical can be expected to be converted into a methoxy radical through hydrogen absorption, thereby leading to methyl esters in a similar mechanism. On the other hand, the addition of the sterically hindered *tert*-butoxy radical cannot proceed, therefore only carboxylic acids were obtained in *tert*-butyl alcohol. The hydroperoxide radical, formed by regeneration of Cu(I) catalyst, may be trapped by starting ketone (one more equivalent) and/or iodine radical. This mechanistic scheme is similar to the previously reported cleavage of cyclohexanone with hydrogen peroxide and catalytic CuCl in the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO).[9]



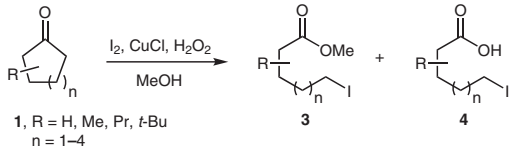
Scheme 2 Mechanistic explanation of the formation of 6-iodohexanoic acid from cyclohexanone, H_2O_2, CuCl and iodine

The data in Table 1 indicate that the outcome of this reaction can be changed by the solvent. In particular, the use of *t*-BuOH as solvent leads to exclusive formation of 6-iodohexanoic acid **4b**. This is a potentially important result taking into account that the hydrolysis of ω-iodoaliphatic carboxylic esters does not afford ω-iodoaliphatic carboxylic acids because of the low stability of organic iodides under reactions conditions.[10] In contrast, the reaction in methanol mainly affords methyl 6-iodohexanoate **3b**, which can be easily separated from the impurity of acid **4b** by chromatography.

ω-Iodoaliphatic carboxylic esters **3** are generally more useful than the corresponding acids **4** as synthetic precursors for the consequent synthetic steps and therefore we have further investigated the preparation of esters **3** from different cyclic ketones **1** (Table 2) using methanol or ethanol as the solvents. All these reactions afforded esters **3** as major products, which were isolated by column chromatography in generally high preparative yields.

The obtained methyl esters **3** of ω-iodoaliphatic carboxylic acids were further used for the preparation of di(2-pyridylmethylamino)alkanoic acids, which are applied as ligands for complexation of ^{99m}Tc and $^{186/188}$Re,[11] and also for the synthesis of coordination polymers.[12] A common procedure for the synthesis of di(2-pyridylmethylamino)alkanoic acids **10** is based on the reaction of ω-aminoaliphatic carboxylic acids **8** with 2-picolyl chloride or 2-picolyl bromide **9**.[11d,13] Another method relies on the reaction of ω-aminoaliphatic carboxylic acids **8** with pyridine-2-carbaldehyde **11** in the presence of sodium triacetoxyborohydride

Table 2 Preparation of ω-Iodoaliphatic Carboxylic Esters from Ketones[a]

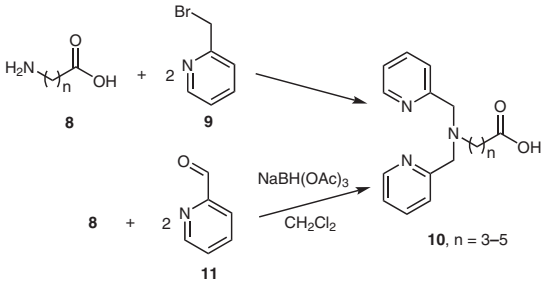


1, R = H, Me, Pr, *t*-Bu
n = 1–4

3 **4**

Entry	Ketone	Time (h)	**3** (%)[b]	**4** (%)[b]
1	cyclopentanone (**1a**)	8	**3a** (70)	**4a** (18)
2	cyclohexanone (**1b**)	8	**3b** (75)	**4b** (24)
3	3-methylcyclohexanone (**1c**)	14	**3c**[c] (57)	–[d]
4	4-methylcyclohexanone (**1d**)	14	**3d** (65)	**4d** (3)
5	4,4-dimethylcyclohexanone (**1e**)	16	**3e** (40)	**4e** (5)
6	4-propylcyclohexanone (**1f**)	14	**3f** (68)	0
7	4-*tert*-butylcyclohexanone (**1g**)	14	**3g** (75)	**4g** (10)
8	cycloheptanone (**1h**)	24	**3h** (68)	**4h** (5)
9	cyclooctanone (**1i**)	24	**3i** (58)	**4i** (2)
10	cyclooctanone (**1i**)[e]	36	**3i′** (55)[f]	**4i** (5)

[a] Reaction conditions: cyclohexanone (6 mmol), I_2 (3 mmol), CuCl (0.6 mmol), H_2O_2 (18 mmol), MeOH, r.t., 8–36 h.
[b] Isolated yield.
[c] Obtained as a 3:2 mixture of 6-iodo-3-methylhexanoate and 6-iodo-5-methylhexanoate.
[d] Obtained as an inseparable mixture of isomeric acids was formed.
[e] Ethanol was used as the solvent.
[f] Ethyl ester of 8-iodooctanoic acid was isolated.

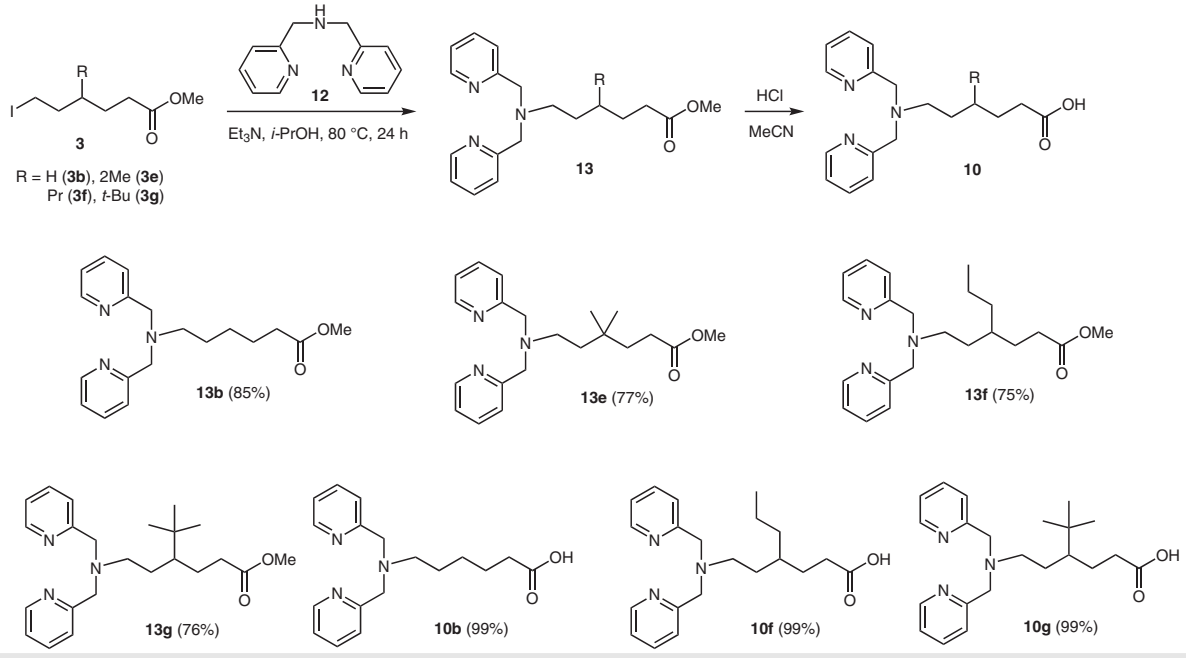


8 **9** **10**, n = 3–5 **11**

Scheme 3 Known procedures for the preparation of di(2-pyridylmethylamino)alkanoic acids **10**

(Scheme 3).[14] The short-chain derivatives of di(2-pyridylmethylamino)alkanoic acids can also be prepared from ω-bromoaliphatic carboxylic acids and di(2-picolyl)amine.[15]

We have developed a new approach to the synthesis of di(2-pyridylmethylamino)alkanoic acids based on the reaction of ω-iodoaliphatic carboxylic esters **3** with di(2-picolyl)amine **12** (Scheme 4). In the first step, a mixture of ester **3** with di(2-picolyl)amine **12** and Et_3N in *i*-PrOH is stirred at 80 °C for 24 hours to provide di(2-pyridylmethylamino)alkanoic esters **13**. Esters **13** are purified by column chromatography on silica gel and finally hydrolyzed to give di(2-pyridylmethylamino)alkanoic acids **10** in quantitative yield. Our procedure affords products **10** in higher yields and in a lower number of synthetic steps compared with the reported method starting from ω-bromoaliphatic carboxylic acids and di(2-picolyl)amine.[15]



Scheme 4 Synthesis of di(2-pyridylmethylamino)alkanoic esters **13** and acids **10** from ω-iodoaliphatic carboxylic esters **3**

In conclusion, we have developed a simple and convenient method for the preparation of ω-iodoaliphatic carboxylic acids and esters from commercially available cyclic ketones. Based on these compounds, we have synthesized di(2-pyridylmethylamino)alkanoic acids, which are used for the synthesis of coordination polymers and ligands for binding ^{99m}Tc and $^{186/188}$Re.

All reactions were performed under an air atmosphere. Commercially available reagents were used without further purification from freshly opened containers. NMR spectra were recorded at 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR). Chemical shifts (δ) are reported in parts per million. Melting points were determined with a Büchi M-560 apparatus. HRMS were measured in ESI mode and the mass analyzer of the HRMS was TOF.

Preparation of ω-Iodoaliphatic Carboxylic Esters 3 and Acids 4 from Ketones 1; General Procedure

To a solution of cyclic ketone **1** (6 mmol) and iodine (3 mmol) in appropriate solvent (10 mL), copper(I) chloride (0.6 mmol) was added, and then hydrogen peroxide solution (12 mmol, 0.638 g, 32% H_2O_2, d = 1.125 g/mL) in the same solvent (4 mL) was added dropwise during 2 h under stirring. The solution was then stirred at r.t. for 2–10 h, and then hydrogen peroxide (6 mmol, 0.319 g) was added dropwise during 4–24 h. An aqueous solution of Na_2SO_3 (1 mL) was added to the reaction mixture and the resulting solution was filtered. Dichloromethane (3 × 10 mL) was added to the filtrate and the organic layer was washed with saturated aqueous $NaHCO_3$ (15 mL) and dried with Na_2SO_4. The solvent was evaporated and the liquid product (**3a–i**) was dried in vacuum.

The aqueous extract was acidified with dilute hydrochloric acid until carbon dioxide evolution ceased, then dichloromethane (3 × 10 mL) was added and the mixture was extracted. The organic extracts were combined, dried with Na_2SO_4, the solvent was evaporated and a crystalline or liquid product **4b–i** was dried in vacuum.

Methyl 5-Iodopentanoate (3a) and 5-Iodopentanoic Acid (4a)

Cyclopentanone (**1a**) (489 mg, 5.8 mmol), iodine (739 mg, 2.9 mmol), and copper(I) chloride (57 mg, 0.58 mmol) were mixed in MeOH (10 mL), and then a solution of hydrogen peroxide (11.6 mmol, 0.617 g, 32% H_2O_2, d = 1.125 g/mL) in MeOH (4 mL) was added dropwise during 2 h with stirring. The solution was then stirred at r.t. for 2 h, and then hydrogen peroxide (5.8 mmol, 0.308 g) was added dropwise during 4 h. Workup according to the general procedure afforded product **3a** [493 mg; R_f 0.82 (hexane/ethyl acetate, 5:1)] and product **4a** [120 mg; R_f 0.12 (hexane/ethyl acetate, 5:1)].

Methyl 5-Iodopentanoate (3a)[16]

Yield: 0.493 g (70%); pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.67 (s, 3 H, OCH_3), 3.18 (t, *J* = 6.8 Hz, 2 H), 2.34 (t, *J* = 7.2 Hz, 2 H), 1.89–1.82 (m, 2 H), 1.77–1.70 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.68, 51.76, 32.99, 32.85, 25.91, 5.95.

5-Iodopentanoic Acid (4a)[17]

Yield: 0.120 g (18%); white solid; mp 57–58 °C (Lit.[15] 58.2 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.20 (t, *J* = 6.8 Hz, 2 H), 2.39 (t, *J* = 7.6 Hz, 2 H), 1.91–1.85 (m, 2 H), 1.79–1.72 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.28, 32.91, 32.69, 25.63, 5.80.

Methyl 6-Iodohexanoate (3b) and 6-Iodohexanoic Acid (4b)

Cyclohexanone (**1b**) (588 mg, 6 mmol), iodine (762 mg, 3 mmol), and copper(I) chloride (59 mg, 0.6 mmol) were mixed in MeOH (10 mL), then a solution of hydrogen peroxide (12 mmol, 0.638 g, 32% H_2O_2, d = 1.125 g/mL) in MeOH (4 mL) was added dropwise during 2 h under stirring. The solution was then stirred at r.t. for 2 h, and then hydrogen peroxide (6 mmol, 0.319 g) was added dropwise during 4 h. Workup according to the general procedure afforded product **3b** [606 mg (55%); R_f 0.82 (hexane/ethyl acetate, 5:1)] and product **4b** [158 mg (24%); R_f 0.12 (hexane/ethyl acetate, 5:1).

Methyl 6-Iodohexanoate (3b)[1b]

Yield: 0.606 g (55%); pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.67 (s, 3 H, OCH_3), 3.18 (t, *J* = 6.8 Hz, 2 H), 2.32 (t, *J* = 7.6 Hz, 2 H), 1.87–1.90 (m, 2 H), 1.67–1.61 (m, 2 H), 1.47–1.39 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.92, 33.92, 33.18, 30.00, 23.68, 6.57.

6-Iodohexanoic Acid (4b)[17]

Yield: 0.158 g (24%); white solid; mp 41 °C (Lit.[17] 41 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.18 (t, *J* = 6.8 Hz, 2 H), 2.37 (t, *J* = 7.6 Hz, 2 H), 1.86–1.82 (m, 2 H), 1.69–1.62 (m, 2 H), 1.49–1.43 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.92, 33.92, 33.18, 30.00, 23.68, 6.57.

Methyl 6-Iodo-3-methylhexanoate (3c) and Methyl 6-Iodo-5-methylhexanoate (3c′)

3-Methylcyclohexanone (**1c**) (654 mg, 5.8 mmol), iodine (741 mg, 2.92 mmol), and copper(I) chloride (58 mg, 0.59 mmol) were mixed in MeOH (10 mL), then a solution of hydrogen peroxide (12 mmol, 0.638 g, 32% H_2O_2, d = 1.125 g/mL) in MeOH (4 mL) was added dropwise during 2 h under stirring. The solution was then stirred at r.t. for 2 h, and then hydrogen peroxide (5.8 mmol, 0.308 g) was added dropwise during 8 h. Workup according to the general procedure afforded a mixture of product **3c** and **3c′** [3:2; 821 mg (57%); R_f 0.82 (hexane/ethyl acetate, 5:1)] as a pale-yellow oil.

Compound 2c

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.65 (s, 3 H, OCH_3,), 3.21–3.11 (m, 2 H), 2.32–2.25 (m, 2 H), 2.17–2.10 (m, 1 H), 1.90–1.77 (m, 2 H), 1.47–1.34 (m, 2 H), 0.93 (d, *J* = 6.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.49, 51.60, 41.53, 37.50, 31.13, 29.65, 20.57, 6.90.

Compound 2c′

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.65 (s, 3 H, OCH_3), 3.21–3.11 (m, 2 H), 2.32–2.25 (m, 2 H), 2.02–1.93 (m, 1 H), 1.65–1.56 (m, 2 H), 1.31–1.18 (m, 2 H), 0.97 (d, *J* = 6.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.01, 51.68, 35.93, 34.58, 34.10, 22.41, 19.79, 17.42.

Methyl 6-Iodo-4-methylhexanoate (3d) and 6-Iodo-4-methylhexanoic Acid (4d)

4-Methylcyclohexanone (**1d**) (677 mg, 5.98 mmol), iodine (670 mg, 3 mmol), and copper(I) chloride (59 mg, 0.6 mmol) were mixed in MeOH (10 mL), then a solution of hydrogen peroxide (11.6 mmol, 0.617 g, 32% H_2O_2, d = 1.125 g/mL) in MeOH (4 mL) was added dropwise during 2 h under stirring. The solution was then stirred at r.t. for 4 h, and then hydrogen peroxide (5.8 mmol, 0.308 g) was added dropwise during 8 h. Workup according to the general procedure afforded product **3d** [495 mg (65%); R_f 0.82 (hexane/ethyl acetate, 5:1)] and product **4d** [25 mg (3%); R_f 0.12 (hexane/ethyl acetate, 5:1)].

Methyl 6-Iodo-4-methylhexanoate (3d)[18]

Yield: 0.495 g (65%); pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.18 (t, *J* = 6.8 Hz, 2 H), 2.37 (t, *J* = 7.6 Hz, 2 H), 1.86–1.82 (m, 2 H), 1.69–1.62 (m, 2 H), 1.49–1.43 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.27, 51.76, 40.60, 33.54, 31.73, 31.18, 18.45, 4.75.

6-Iodo-4-methylhexanoic Acid (4d)[19]

Yield: 0.025 g (3%); pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.26–3.13 (m, 2 H), 2.43–2.34 (m, 2 H), 1.91–1.83 (m, 1 H), 1.71–1.58 (m, 3 H), 1.52–1.45 (m, 1 H), 0.90 (d, *J* = 6.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.40, 40.57, 33.47, 31.74, 30.85, 18.41, 4.58.

Methyl 6-Iodo-4,4-dimethylhexanoate (3e) and 6-Iodo-4,4-dimethylhexanoic Acid (4e)

4,4-Dimethylcyclohexanone (**1e**) (134 mg, 1.07 mmol), iodine (127 mg, 0.5 mmol), and copper(I) chloride (10 mg, 0.1 mmol) were mixed in MeOH (10 mL), then a solution of hydrogen peroxide (2.14 mmol, 0.116 g, 32% H_2O_2, d = 1.125 g/mL) in MeOH (4 mL) was added dropwise during 2 h under stirring. The solution was stirred at r.t. for 4 h, and then hydrogen peroxide (1.07 mmol, 0.080 g) was added dropwise during 10 h. Workup according to the general procedure afforded product **3e** [120 mg (40%); R_f 0.82 (hexane/ethyl acetate, 5:1)] and product **4e** [14 mg (5%); R_f 0.12 (hexane/ethyl acetate, 5:1)].

Methyl 6-Iodo-4,4-dimethylhexanoate (3e)[3a]

Yield: 0.120 g (40%); pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.66 (s, 3 H, OCH_3), 3.14 (m, 2 H), 2.25 (t, *J* = 8 Hz, 2 H), 1.89 (t, *J* = 8 Hz, 2 H), 1.58–1.54 (m, 2 H), 0.87 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.46, 51.81, 47.26, 36.04, 35.52, 29.35, 26.20, 0.51.

6-Iodo-4,4-dimethylhexanoic Acid (4e)

Yield: 0.014 g (5%); pale-yellow oil.

IR (film): 2925, 1702, 1411, 733 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.13 (t, *J* = 8.0 Hz, 2 H), 2.30 (t, *J* = 7.6 Hz, 2 H), 1.90 (t, *J* = 8.0 Hz, 2 H), 1.57 (t, *J* = 8.0 Hz, 2 H), 0.89 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.65, 47.22, 35.73, 35.72, 35.48, 29.37, 26.15, 0.40.

HRMS (TOF, ES^+): *m*/*z* [M + 2 Na – H]$^+$ calcd for $C_8H_{14}INa_2O_2$: 314.9828; found: 314.9826.

Methyl 6-Iodo-4-propylhexanoate (3f)

4-Propylcyclohexanone (**1f**) (841 mg, 6 mmol), iodine (762 mg, 3 mmol), and copper(I) chloride (60 mg, 0.61 mmol) were mixed in MeOH (10 mL), and then a solution of hydrogen peroxide (12 mmol, 0.638 g, 32% H_2O_2, d = 1.125 g/mL) in MeOH (4 mL) was added dropwise during 2 h under stirring. The solution was then stirred at r.t. for 4 h, and then hydrogen peroxide (6 mmol, 0.319 g) was added dropwise during 8 h. Workup according to the general procedure afforded product **3f** [608 mg (68%); R_f 0.82 (hexane/ethyl acetate, 5:1)].

Yield: 0.608 g (68%); pale-yellow oil.

IR (film): 2926, 2830, 1735, 1435, 1169 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.67 (s, 3 H, OCH_3), 3.19 (t, *J* = 7.6 Hz, 2 H), 2.30 (t, *J* = 7.6 Hz, 2 H), 1.81–1.79 (m, 2 H), 1.63–1.58 (m, 2 H), 1.48–1.66 (m, 1 H), 1.29–1.24 (m, 1 H), 0.89 (t, *J*=7.2 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.27, 51.74, 38.03, 37.88, 34.92, 31.39, 27.99, 19.51, 14.46, 4.60.

HRMS (TOF, ES^+): *m*/*z* [M + H]$^+$ calcd for $C_{10}H_{20}IO_2$: 299.0508; found: 299.0506.

Methyl 6-Iodo-4-*tert*-butylhexanoate (3g) and 6-Iodo-4-*tert*-butylhexanoic Acid (4g)

4-*tert*-Butylcyclohexanone (**1g**) (924 mg, 6 mmol), iodine (762 mg, 3 mmol), and copper(I) chloride (60 mg, 0.6 mmol) were mixed in MeOH (10 mL), and then a solution of hydrogen peroxide (12 mmol, 0.638 g, 32% H_2O_2, d = 1.125 g/mL) in MeOH (4 mL) was added dropwise during 2 h under stirring. The solution was then stirred at r.t. for 4 h, and then hydrogen peroxide (6 mmol, 0.319 g) was added dropwise during 8 h. Workup according to the general procedure afforded product **3g** [702 mg (75%); R_f 0.82 (hexane/ethyl acetate, 5:1)] and product **4g** [89 mg (10%); R_f 0.12 (hexane/ethyl acetate, 5:1)].

Methyl 6-Iodo-4-*tert*-butylhexanoate (3g)

Yield: 0.702 g (75%); pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.67 (s, 3 H, OCH_3), 3.29–3.23 (m, 1 H), 3.18–3.11 (m, 1 H), 2.45–2.30 (m, 2 H), 2.43–2.30 (m, 2 H), 2.08–2.01 (m, 1 H), 1.89–1.84 (m, 1 H), 1.66–1.60 (m, 1 H), 1.40–1.30 (m, 1 H), 0.98–0.95 (m,1 H), 0.88 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.11, 51.75, 49.64, 36.29, 34.24, 34.06, 27.75, 26.21, 6.79.

6-Iodo-4-*tert*-butylhexanoic Acid (4g)

Yield: 0.89 g (10%); pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.30–3.24 (m, 1 H), 3.20–3.13 (m, 1 H), 2.50–2.34 (m, 2 H), 2.12–2.03 (m, 1 H), 1.91–1.84 (m, 1 H), 1.67–1.57 (m, 1 H), 1.42–1.33 (m, 1 H), 1.05–0.98 (m,1 H), 0.90 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.73, 49.53, 36.21, 34.08, 33.95, 27.75, 25.93, 6.76.

Methyl 7-Iodoheptanoate (3h) and 7-Iodoheptanoic Acid (4h)

Cycloheptanone (**1h**) (684 mg, 6.1 mmol), iodine (775 mg, 3.05 mmol), and copper(I) chloride (60 mg, 0.61 mmol) were mixed in MeOH (10 mL), and then a solution of hydrogen peroxide (12.2 mmol, 0.641 g, 32% H_2O_2, d = 1.125 g/mL) in MeOH (4 mL) was added dropwise during 2 h under stirring. The solution was then stirred at r.t. for 10 h, and then hydrogen peroxide (6.1 mmol, 0.320 g) was added dropwise during 12 h. Workup according to the general procedure afforded product **3h** [560 mg (68%); R_f 0.82 (hexane/ethyl acetate, 5:1)] and product **4h** [37 mg (5%); R_f 0.12 (hexane/ethyl acetate, 5:1)].

Methyl 7-Iodoheptanoate (3h)[4c]

Yield: 0.560 g (68%); pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.66 (s, 3 H, OCH_3), 3.18 (t, *J* = 7.2 Hz, 2 H), 2.31 (t, *J* = 7.6 Hz, 2 H), 1.83–1.78 (m, 2 H), 1.65–1.61 (m, 2 H), 1.45–1.30 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.24, 51.66, 34.05, 33.34, 30.23, 28.13, 24.81, 7.18.

7-Iodoheptanoic Acid (4h)[4b]

Yield: 0.037 g (5%); pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.18 (t, *J* = 6.8 Hz, 2 H), 2.36 (t, *J* = 7.2 Hz, 2 H), 1.86–1.79 (m, 2 H), 1.68–1.61 (m, 2 H), 1.46–1.34 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.29, 34.05, 33.31, 30.22, 28.04, 24.52, 7.12.

Ethyl 8-Iodooctanoate (3i) and 8-Iodooctanoic Acid (4i)

Cyclooctanone (**1i**) (680 mg, 5.4 mmol), iodine (686 mg, 2.7 mmol), and copper(I) chloride (54 mg, 0.53 mmol) were mixed in MeOH (10 mL), and then a solution of hydrogen peroxide (10.8 mmol, 0.574 g, 32% H_2O_2, d = 1.125 g/mL) in MeOH (4 mL) was added dropwise during 2 h under stirring. The solution was then stirred at r.t. for 10 h, and then hydrogen peroxide (5.4 mmol, 0.287 g) was added dropwise during 24 h. Workup according to the general procedure afforded product **3i** [434 mg (55%); R_f 0.82 (hexane/ethyl acetate, 5:1)] and product **4i** [36 mg (5%); R_f 0.12 (hexane/ethyl acetate, 5:1)].

Ethyl 8-Iodooctanoate (3i)[3b]

Yield: 0.434 g (55%); pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.12 (q, *J* = 7.2 Hz, 2 H), 3.18 (t, *J* = 6.8 Hz, 2 H), 2.31 (t, *J* = 7.2 Hz, 2 H), 1.85–1.80 (m, 2 H), 1.65–1.59 (m, 2 H), 1.41–1.34 (m, 4 H), 1.25 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.81, 60.38, 34.36, 33.35, 30.24, 29.02, 28.13, 24.84, 14.40, 7.20.

8-Iodooctanoic Acid (4i)[20]

Yield: 0.036 g (5%); pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.19 (t, *J* = 6.8 Hz, 2 H), 2.39–2.35 (m, 2 H), 1.85–1.80 (m, 2 H), 1.67–1.62 (m, 2 H), 1.43–1.37 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.60, 33.84, 33.76, 33.34, 30.25, 28.07, 24.57, 7.12.

Preparation of Esters of Di(2-Pyridylmethylamino)alkanoic Acids 13; General Procedure

A mixture of ω-iodoaliphatic carboxylic ester **3** (1 mmol), di(2-picolyl)amine (1.2 mmol) and triethylamine (1.2 mmol) in isopropanol (10 mL) was stirred at 80 °C for 24 h. The reaction mixture was washed with saturated sodium bicarbonate solution and extracted with chloroform. The separated organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using CH_3OH/EtOAc (1:10) as eluent to provide the desired ester of di(2-pyridylmethylamino)alkanoic acid **13** as a viscous light-yellow syrup.

Methyl 6-(Bis(pyridin-2-ylmethyl)amino)hexanoate (13b)[21]

The reaction of methyl 6-iodohexanoate (**3b**) (606 mg, 2.37 mmol), di(2-picolyl)amine (**12**) (565 mg, 2.84 mmol) and triethylamine (286 mg, 2.84 mmol) in *i*-PrOH (10 mL) according to the general procedure afforded product **13b**.

Yield: 0.750 g (85%); viscous light-yellow syrup; R_f 0.7 (ethyl acetate/EtOH, 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (d, *J* = 4.8 Hz, 2 H), 7.64 (t, *J* = 7.6 Hz, 2 H), 7.52 (d, *J* = 7.6 Hz, 2 H), 7.13 (t, *J* = 6.4 Hz, 2 H), 3.79 (s, 4 H), 3.63 (s, 3 H, OCH_3), 2.53 (t, *J* = 7.2 Hz, 2 H), 2.25 (t, *J* = 7.6 Hz, 2 H), 1.57–1.50 (m, 4 H), 1.31–1.21 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.22, 159.96, 149.06, 136.47, 122.96, 122.00, 60.55, 54.31, 51.55, 34.11, 26.91, 26.85, 24.87.

Methyl 6-(Bis(pyridin-2-ylmethyl)amino)-4,4-dimethylhexanoate (13e)

The reaction of methyl 6-iodo-4,4-dimethylhexanoate (**3e**) (115 mg, 0.41 mmol), di(2-picolyl)amine (**12**) (81 mg, 0.41 mmol) and triethylamine (50 mg, 0.49 mmol) in *i*-PrOH (10 mL) according to the general procedure afforded product **13e**.

Yield: 0.109 g (77%); viscous light-yellow syrup; R_f 0.7 (ethyl acetate/hexane, 5:2).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.53 (d, *J* = 5.2 Hz, 2 H), 7.66 (t, *J* = 7.6 Hz, 2 H), 7.53 (d, *J* = 8 Hz, 2 H), 7.15 (t, *J* = 5.2 Hz, 2 H), 3.82 (s, 4 H), 3.63 (s, 3 H, OCH_3), 2.54 (t, *J* = 8 Hz, 2 H), 2.19 (t, *J* = 8 Hz, 2 H), 1.51–1.43 (m, 4 H), 0.78 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.81, 159.61, 148.96, 136.73, 123.08, 122.17, 60.32, 51.71, 49.69, 38.00, 36.57, 32.06, 29.40, 26.92.

HRMS (TOF, ES$^+$): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{32}N_3O_2$: 356.2338; found: 356.2331.

Methyl 6-(Bis(pyridin-2-ylmethyl)amino)-4-propylhexanoate (13f)

The reaction of methyl 6-iodo-4-propylhexanoate (**3f**) (614 mg, 2.06 mmol), di(2-picolyl)amine (**12**) (492 mg, 2.47 mmol) and triethylamine (250 mg, 2.47 mmol) in *i*-PrOH (10 mL) according to the general procedure afforded product **13f**.

Yield: 0.570 g (75%); viscous light-yellow syrup; R_f 0.7 (ethyl acetate/hexane, 5:2).

IR (film): 2926, 1736, 1589–1433, 1361, 759 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (d, *J* = 4.4 Hz, 2 H), 7.64 (t, *J* = 7.6 Hz, 2 H), 7.51 (d, *J* = 8 Hz, 2 H), 7.13 (t, *J* = 6 Hz, 2 H), 3.79 (s, 4 H), 3.61 (s, 3 H, OCH_3), 2.52 (t, *J* = 7.2 Hz, 2 H), 2.20 (t, *J* = 7.6 Hz, 2 H), 1.50–1.45 (m, 4 H), 1.34–1.29 (m, 1 H), 1.24–1.68 (m, 2 H), 1.12–1.08 (m, 2 H), 0.79 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.54, 159.97, 149.01, 136.53, 123.01, 122.03, 60.54, 51.90, 51.59, 35.52, 35.03, 31.49, 30.56, 28.70, 19.58, 14.47.

HRMS (TOF, ES$^+$): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{32}N_3O_2$: 370.2495; found: 370.2489.

Methyl 6-(Bis(pyridin-2-ylmethyl)amino)-4-*tert*-butylhexanoate (13g)

The reaction of methyl 6-iodo-4-*tert*-butylhexanoate (**3g**) (530 mg, 1.7 mmol), di(2-picolyl)amine (**12**) (398 mg, 2. mmol) and triethylamine (202 mg, 2 mmol) in *i*-PrOH (10 mL) according to the general procedure afforded product **13g**.

Yield: 0.488 g (75%); viscous light-yellow syrup; R_f 0.7 (ethyl acetate/hexane, 5:2).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 (d, *J* = 5.6 Hz, 2 H), 7.64 (t, *J* = 7.6 Hz, 2 H), 7.52 (d, *J* = 7.6 Hz, 2 H), 7.13 (t, *J* = 6.4 Hz, 2 H), 3.83 (s, 4 H), 3.61 (s, 3 H, OCH_3), 2.53–2.48 (m, 2 H), 2.27–2.23 (m, 1 H), 2.14–2.06 (m, 1 H), 1.81–1.70 (m, 2 H), 1.31–1.22 (m, 1 H), 0.79 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.32, 160.03, 149.12, 136.47, 123.06, 122.02, 60.64, 54.98, 51.49, 46.20, 34.04, 33.81, 28.49, 27.70, 26.91.

HRMS (TOF, ES$^+$): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{34}N_3O_2$: 384.2651; found: 384.2646.

Preparation of Di(2-pyridylmethylamino)alkanoic Acids 10; General Procedure

The ester of di(2-pyridylmethylamino)alkanoic acid **13** (1 mmol) was dissolved in CH_3CN (2 mL), and then HCl (36%, 50 μL) was added and the mixture was stirred at 80 °C for 2 h. The solvent was evaporated and the yellow viscous liquid product **10** was dried in vacuum.

6-(Bis(pyridin-2-ylmethyl)amino)hexanoic Acid (10b)[21]

The reaction of methyl 6-(bis(pyridin-2-ylmethyl)amino)hexanoate (**13b**) (442 mg, 1.35 mmol) and HCl (36%, 68 μL) in CH_3CN (2 mL) according to the general procedure afforded product **10b** as a yellow viscous liquid.

Yield: 0.419 g (99%); yellow viscous liquid; R_f 0.1 (ethyl acetate/ethanol, 10:1).

^{1}H NMR (400 MHz, D_2O): δ = 8.81 (d, *J* = 6 Hz, 2 H), 8.59 (t, *J* = 9.2 Hz, 2 H), 8.13 (d, *J* = 8 Hz, 2 H), 8.03 (t, *J* = 6.8 Hz, 2 H), 4.39 (s, 4 H), 2.75 (t, *J* = 7.6 Hz, 2 H), 2.36 (t, *J* = 7.2 Hz, 2 H), 1.60–1.56 (m, 4 H), 1.32–1.24 (m, 2 H).

^{13}C NMR (100 MHz, D_2O): δ = 178.82, 152.72, 147.01, 141.61, 127.12, 126.31, 55.69, 54.68, 33.55, 25.73, 25.03, 23.88.

6-(Bis(pyridin-2-ylmethyl)amino)-4-propylhexanoic Acid (10f)

The reaction of methyl 6-(bis(pyridin-2-ylmethyl)amino)-4-propylhexanoate (**13f**) (130 mg, 0.35 mmol) and HCl (36%, 25 μL) in CH_3CN (2 mL) according to the general procedure afforded product **10f**.

Yield: 0.124 g (99%); yellow viscous liquid; R_f 0.1 (ethyl acetate/EtOH, 10:1).

IR (film): 3400–2800, 1718, 1375, 1165, 764 cm^{-1}.

^{1}H NMR (400 MHz, D_2O): δ = 8.72 (d, *J* = 5.2 Hz, 2 H), 8.51 (t, *J* = 7.6 Hz, 2 H), 8.05 (d, *J* = 8 Hz, 2 H), 7.94 (t, *J* = 6.8 Hz, 2 H), 4.29 (s, 4 H), 2.63 (t, *J* = 6 Hz, 2 H), 2.21 (t, *J* = 7.6 Hz, 2 H), 1.43–1.37 (m, 4 H), 1.26–1.23 (m, 1 H), 1.13–1.04 (m, 4 H), 0.70 (t, J= 6.4 Hz, 2 H).

^{13}C NMR (100 MHz, D_2O): δ = 178.96, 152.65, 147.08, 141.41, 127.07, 126.28, 55.48, 52.25, 34.38, 34.05, 30.95, 28.56, 27.76, 18.69, 13.46.

HRMS (TOF, ES$^+$): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{30}N_3O_2$: 356.2338; found: 356.2337.

6-(Bis(Pyridin-2-ylmethyl)amino)-4-*tert*-butylhexanoic acid (10g)

The reaction of methyl 6-(bis(pyridin-2-ylmethyl)amino)-4-*tert*-butylhexanoate (**13g**) (201 mg, 0.52 mmol) and HCl (36%, 26 μL) in CH_3CN (2 mL) according to the general procedure afforded product **10g**.

Yield: 0.191 g (99%); yellow viscous liquid; R_f 0.1 (ethyl acetate/EtOH, 10:1).

^{1}H NMR (400 MHz, D_2O): δ = 8.75 (d, *J* = 6 Hz, 2 H), 8.53 (t, *J* = 8 Hz, 2 H), 8.08 (d, *J* = 8.4 Hz, 2 H), 7.96 (t, *J* = 6.8 Hz, 2 H), 4.33 (s, 4 H), 2.61 (t, *J* = 8.4 Hz, 2 H), 2.23–2.22 (m, 2 H), 1.76–1.58 (m, 2 H), 1.22–1.12 (m, 2 H), 0.72 (s, 10 H).

^{13}C NMR (100 MHz, D_2O): δ = 178.66, 152.71, 147.08, 141.48, 127.03, 126.30, 55.38, 54.71, 45.08, 33.29, 33.02, 26.58, 26.44, 25.97.

HRMS (TOF, ES$^+$): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{32}N_3O_2$: 370.2489; found: 370.2496.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1591598.

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