

New Coupling Reactions of Some Acyl Chlorides with Samarium Diiodide in the Presence of Samarium: Carbinols from Three Acyl Units

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A mixture of samarium(II) iodide and samarium can induce a coupling reaction of *three* molecules of alkanoyl halide to give trialkylcarbinols of 2-hydroxy-1,3-diones. When aliphatic, unbranched alkanoyl chlorides are used, this new coupling reaction provides trimeric products as the main re-

action products. Tetrahydropyran (THP) proved superior as the solvent because no ring-opening and subsequent reaction with the alkanoyl halides was observed under the reaction conditions, unlike when THF was used.

Introduction

Samarium(II) iodide has proven to be a powerful one-electron reducing agent, which has been widely applied since its first preparation by Kagan.^[1] Reactions of samarium(II) iodide include a variety of radical processes such as reductions of halides, ring-closure and reductive coupling reactions.^[2–6] In the context of our research concerning dianionic oxy-Cope rearrangements,^[7–10] we had a need for some 1,2-diones. Among other ways, these can be conveniently prepared by coupling reactions of acyl chlorides with the aid of samarium diiodide.^[11–14] While the coupling of aromatic acyl chlorides gives the corresponding 1,2-diketones directly,^[12] coupling of aliphatic acyl halides usually affords α -hydroxy ketones, which can be oxidized to the respective 1,2-diketones. An advantage of this method is the variety of acyl chlorides available. The technique using nickel(II) iodide as a catalyst is preferred, because it usually results in the highest yields and only a few side products.^[14] Samarium(II) iodide is prepared by treatment of 1,2-diiodoethane or diiodomethane^[15] with samarium in THF. It is normally used as a metal-free, dark blue solution in THF.^[1,16]

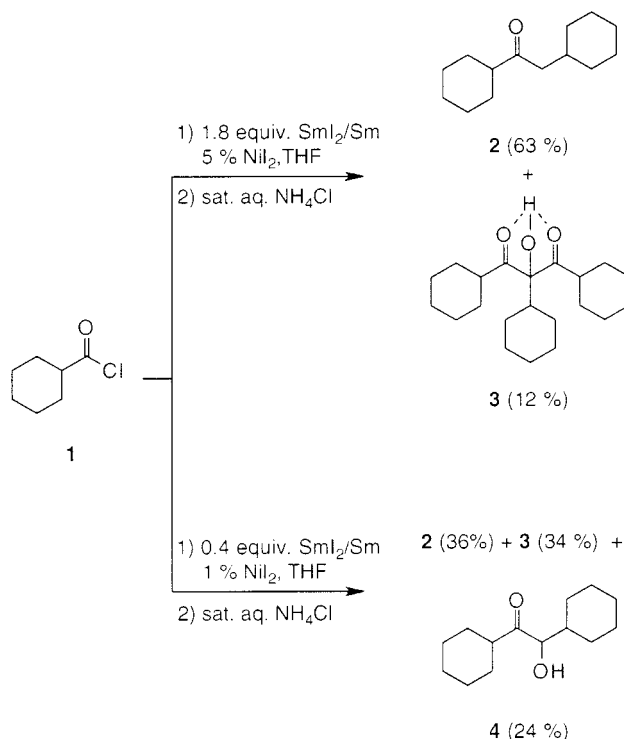
Samarium(II) iodide/samarium is known to be an effective coupling reagent for acid amides, giving enediamines and showing enhanced reactivity in reduction of alkyl halides.^[17,18] Here we report our observation that couplings of acyl chlorides induced by samarium(II) iodide in the presence of samarium powder can provide coupling products incorporating *three* acyl units.

Results and Discussion

Cyclohexylmethanoyl chloride (**1**) was treated with 1.8 equiv. of a solution of SmI₂ in THF, containing elemental samarium and 5 mol-% of NiI₂ as catalyst. The expected α -

hydroxy ketone was not obtained; further reduction led to the formation of 1,2-dicyclohexylethanone (**2**) in 63% yield, in addition to a side product which was identified as 1,2,3-tricyclohexyl-2-hydroxy-1,3-propanedione (**3**, 12%). Compound **3** was characterized by its mass spectrum and its IR carbonyl absorption at $\tilde{\nu} = 1688\text{ cm}^{-1}$. The ¹³C NMR spectrum was in agreement with **3**; the ¹H NMR spectrum was less diagnostic.

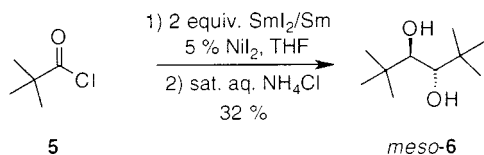
A modification of the reaction conditions resulted in a shift of the product distribution. Use of only 0.4 equiv. of SmI₂ and only 1% NiI₂ caused the yield of **2** to decrease to 36%, whereas that of **3** increased significantly to 34%. In addition, 27% of α -hydroxy ketone **4** was isolated; this would have been the product expected in the absence of elemental samarium. The overall yield of the reaction was



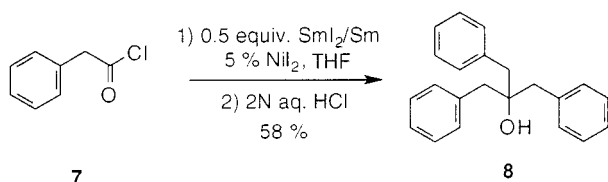
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94%. When elemental samarium was replaced by magnesium as the reducing agent, only 10% of **3** and 5% of **4** were obtained.

Next, 2,2-dimethylpropanoyl chloride (**5**) was subjected to the same reaction conditions. Here, presumably for steric reasons, only the *meso*-diol *meso*-**6**, identified by comparison with literature data,^[19,20] was obtained, in 32% yield.

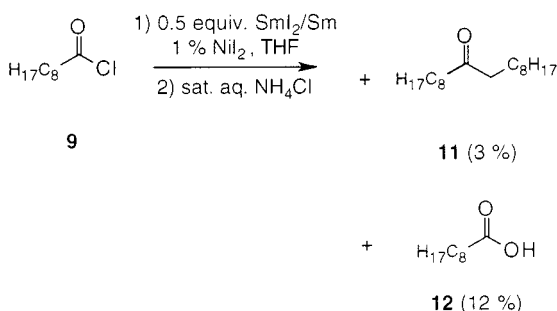
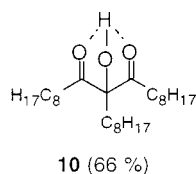


When phenylacetyl chloride (**7**) was treated with 0.5 equiv. of samarium(II) iodide in the presence of 5% NiI₂ and elemental samarium, the known tertiary alcohol **8**^[21–24] was obtained as the only reaction product, in 58% yield. Obviously, in addition to the coupling of three molecules of **7**, decarbonylation had occurred first; this is a known characteristic of the phenylacetyl radical.^[12,25,26]

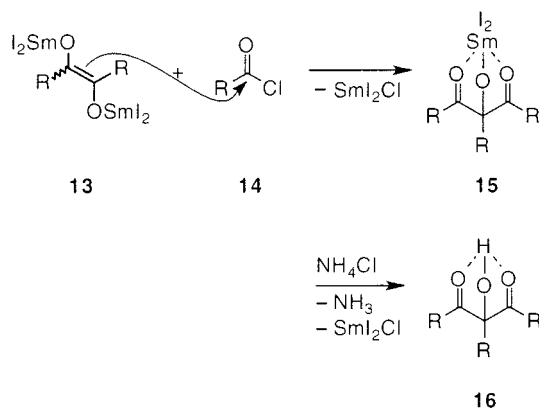


Next, linear aliphatic acyl halides were tested. When nonanoyl chloride (**9**) was used, three molecules of **9** coupled to give 10-hydroxy-10-octylnonadecane-9,11-dione (**10**) as the main reaction product, in 66% yield. In addition, 9-octadecanone^[27] (**11**, 3%) and 12% of nonanoic acid^[28,29] (**12**), presumably formed from unchanged starting material **9** during the hydrolytic workup, were also found. No α -hydroxy ketone was obtained.

The formation of three-component coupling products like **10** can be explained by expanding on the accepted reac-

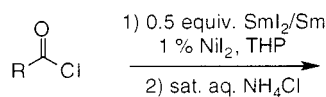


tion mechanism that leads to α -hydroxy ketones.^[13] In this mechanism, **13** is an intermediate. It might undergo nucleophilic attack on a third molecule of alkanoyl halide **14**, with elimination of SmI₂Cl and formation of **15**, which is then hydrolyzed to product **16**. The use of samarium metal is thought to allow a synproportionation with the Sm^{III} formed in situ to generate Sm^{II}, thus allowing the use of a smaller amount of SmI₂.

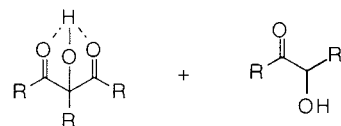


An important side reaction appears to be the formation of 4-iodobutylalkanoates, as a result of a ring-opening reaction of the THF solvent in the presence of a Lewis acid such as SmI₃.^[30,31] Such products were obtained in poor yields when *rac*-2-chloro-2-phenylacetyl chloride, acetyl chloride or dichloroacetyl chloride were tested.

In order to avoid the side reaction, tetrahydropyran (THP) was tried as the solvent. THP does not undergo a ring-opening reaction under the conditions applied. With this solvent but under otherwise unchanged reaction conditions, the trimerization was found to be the main reaction path. Propanoyl chloride (**17**) gave a 68% yield of **18** in



17: R = C₂H₅
21: R = C₅H₁₁
26: R = C₁₇H₃₅



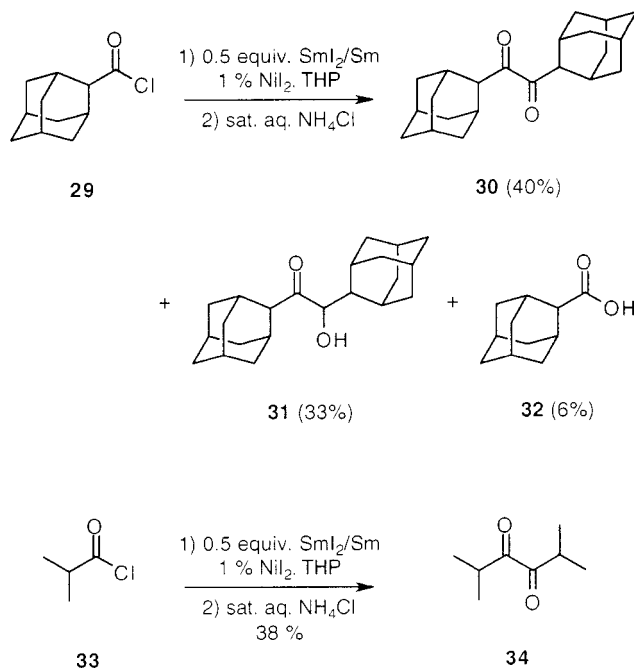
18: R = C₂H₅ (68%)
22: R = C₅H₁₁ (72%)
27: R = C₁₇H₃₅ (34%)

19: R = C₂H₅ (10%)
23: R = C₅H₁₁ (6%)

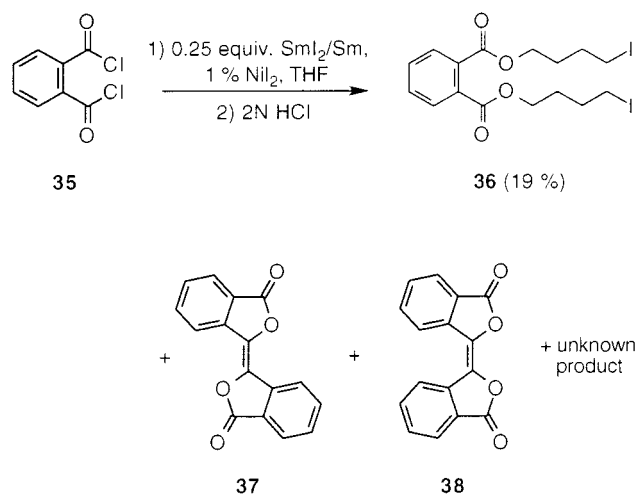
20: R = C₂H₅ (6%)
25: R = C₅H₁₁ (7%)
28: R = C₁₇H₃₅ (57 %)

addition to minor quantities of **19** and **20**. Hexanoyl chloride (**21**) afforded 72% of trimer **22** in addition to side products **23–25**. Stearic acid chloride (**26**) gave trimer **27** in 34% yield in addition to a substantial amount of stearic acid (**28**, 57%) possibly indicating reduced reactivity of the halide.

Adamantanoyl chloride (**29**), presumably for steric reasons, did not undergo the trimerization but reacted to give the known 1,2-di-(1-adamantyl)ethanedione (**30**) in 40% yield, as well as 33% of 1,2-di-(1-adamantyl)-2-hydroxyethanone (**31**) and 6% of adamantylcarboxylic acid (**32**). Similarly, the reaction of 2-methylpropanoyl chloride (**34**) gave a 30% yield of 2,5-dimethyl-3,4-hexanedione (**35**).

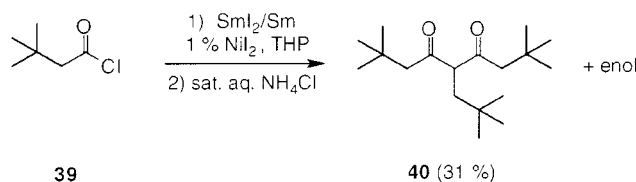


When the reaction was tested with phthaloyl dichloride (**33**), di(4-iodobutyl) phthalate (**34**) was obtained as the main product in 19% yield. In addition to some unidentified, possibly oligomeric, product, known dimers **35** and **36** were isolated as a 4:1-mixture (from NMR, 2%).^[32] When

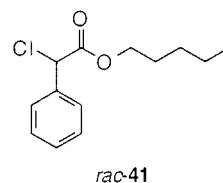


THP was used as the solvent, a 6% yield of **37** and **38** was obtained, together with formation of the unidentified product. As expected, no **36** was formed when THP was used.

Another case of partial deoxygenation was found in the reaction of 3,3-dimethylbutanoyl chloride (**39**) with SmI_2/Sm . Unexpectedly, the reaction gave a 31% yield of diketone **40**, which was obtained as an approximately 4:1 mixture of the diketone and an enol.^[33] Compound **40** was characterized spectroscopically and its constitution was confirmed by a ^{13}C , ^1H COSY spectrum.



Some experiments were performed in an attempt to replace the expensive samarium by Sm_2Co_7 alloy, which is industrially manufactured for use in permanent magnets and therefore comparatively cheap. However, when benzoyl chloride was treated with 1,2-diiodoethane and Sm_2Co_7 in THF, only the corresponding 4-iodobutyl and 4-(4-iodobutoxy)butyl esters were obtained, in 81% and 13% yield, respectively. The reaction with 2,2-dimethylpropanoyl chloride (**5**) gave 4-iodobutyl 2,2-dimethylpropanoate in 49% yield. Apparently these reactions are a function of the reactivity of the acyl halides and not of the presence of the cobalt samarium alloy. When *rac*-2-chloro-2-phenylacetyl chloride was treated with NaI in THF,^[30] *rac*-4-iodobutyl 2-chloro-2-phenyl acetate (*rac*-**39**) was obtained in 88% yield as well.



Conclusion

In conclusion, SmI_2/Sm can induce a coupling reaction between three acyl halide molecules, to provide carbinols and 2-hydroxy-1,3-diones as the main reaction products. This reaction path is most active when aliphatic, unbranched alkanoyl halides are used. With some, albeit not all, branched substrates, the usual coupling products obtained were 1,2-diketones or 2-hydroxy ketones. As solvent, THP is superior to THF, as competing ring-opening reactions do not take place.

Experimental Section

General: All operations were carried out under an argon atmosphere, using standard Schlenk techniques. THF and tetrahydropy-

ran (THP) were dried over NaK/benzophenone and were distilled under argon before use. ^1H NMR: Bruker AM 400 (400.1 MHz), WP 200 SY (200.1 MHz). ^{13}C NMR: Bruker AM 400 (100.6 MHz), WP 200 SY (50.3 MHz). Signal multiplicities were determined by APT or DEPT technique, “+” indicating secondary (CH_2) or quaternary (C_q), “−” indicating primary (CH_3) or tertiary (CH) carbon atoms. Chemical shifts refer to $\delta_{\text{TMS}} = 0$ or to residual solvent signals as internal standard. – IR: Perkin–Elmer FT-IR spectrometers 580 and 1710. – MS: Finnigan MAT 112 and 312. HRMS: Finnigan MAT 312 and VG Autospec, FAB-MS in 4-nitrobenzyl alcohol. – Melting points (m.p.): Büchi (Dr. Tottoli), uncorr. values. – Column chromatography: Silica gel (J. T. Baker, $\varnothing$ 40 μm), flash chromatography.^[34,35] Samarium powder was obtained from Rhône-Poulenc GmbH, Frankfurt, and Sm_2Co_7 was obtained from Elektro-Thermit GmbH, Essen.

Treatment of Cyclohexylmethanoyl Chloride (1) with SmI_2/Sm : Anhydrous NiI_2 (0.236 g, 0.8 mmol) was added to a solution of SmI_2 , which had been obtained from samarium (14.900 g, 99.1 mmol), 1,2-diiodoethane (12.000 g, 42.7 mmol) and THF (430 mL). The mixture was heated at reflux until it became dark blue. At 40 °C, cyclohexylmethanoyl chloride (**1**) (3.20 mL, 3.430 g, 23.6 mmol) was added dropwise. The mixture was stirred for 2 h at 25 °C and then cooled to 0 °C. After addition of 100 mL of satd aq solution of NH_4Cl , the mixture was stirred for 14 h. After threefold extraction, each time with 100 mL of TBME, the combined organic layers were washed with 100 mL of satd aq solutions of Na_2CO_3 and brine, then dried over Na_2SO_4 . Column filtration (length 10 cm, $\varnothing$ 5.0 cm, petroleum ether).

Fraction I: 1,2,3-Tricyclohexyl-2-hydroxy-1,3-propanedione (**3**) (0.309 g, 0.1 mmol, 12%) as a colorless solid (m.p. 115 °C): IR (KBr): $\tilde{\nu} = 3436\text{ cm}^{-1}$ (m, br, OH), 2928 (s, CH), 2852 (s, CH), 1688 (s, CO), 1448 (m), 1364 (w), 1328 (m), 1260 (w), 1240 (w), 1172 (w), 1144 (m, C–O), 1133 (m), 1104 (w), 1064 (m), 1028 (w), 996 (m), 965 (w), 941 (w), 892 (w), 804 (w), 745 (w), 632 (w), 516 (w), 484 (w), 416 (w). – ^1H NMR (400.1 MHz, CDCl_3): $\delta = 1.06\text{--}1.35$ (m, 16 H), $1.50\text{--}1.81$ (m, 14 H), 2.47 (m, 1 H, 1''-H), 3.08 (m, 2 H, 1'-H), 4.63 (s, 1 H, OH). – ^{13}C NMR (100.6 MHz, CDCl_3 , DEPT): $\delta = 25.48$ (CH_2), 25.54 (CH_2), 25.7 (CH_2), 26.1 (CH_2), 27.1 (CH_2), 28.7 (CH_2), 44.69 (CH, C-1' or C-1''), 44.72 (CH, C-1' or C-1''), 94.5 (C_q , C-2), 213.3 [C_q , C-1(3)]. – MS (70 eV, 80 °C): m/z (%) = 334 (2) [M^+], 225 (15), 224 (100) [$\text{M}^+ - \text{CO} - \text{C}_6\text{H}_{11}$], 123 (5), 112 (3), 111 (33) [C_6H_{11}](CO) $^+$], 95 (4), 84 (7), 83 (98) [$\text{C}_6\text{H}_{11}^+$], 81 (5), 69 (3), 67 (5). – HRMS ($\text{C}_{21}\text{H}_{34}\text{O}_3$): calcd. 334.250795; found 334.249573. – $\text{C}_{21}\text{H}_{34}\text{O}_3$ (334.50): calcd. C 75.41, H 10.25; found C 74.78, H 10.06.

Fraction II: 1,2-Dicyclohexylethanone (**2**)^[36,37] (1.560 g, 7.5 mmol, 63%) as a yellow oil. IR (CHCl_3): $\tilde{\nu} = 2924\text{ cm}^{-1}$ (s), 2852 (s), 1708 (s, C=O), 1448 (s), 1404 (w), 1372 (m), 1348 (w), 1308 (w), 1292 (w), 1243 (w), 1144 (m), 1100 (w), 1060 (w), 1004 (m), 964 (w), 894 (w). – ^1H NMR (400.1 MHz, CDCl_3): $\delta = 0.83\text{--}0.97$ (m, 2 H, 4'-H), $1.04\text{--}1.39$ (m, 8 H), $1.59\text{--}1.90$ (m, 11 H), 2.29 (d, $^3J_{2,1'} = 6.4\text{ Hz}$, 3 H, 2-H + 1'-H). – ^{13}C NMR (100.6 MHz, CDCl_3 , DEPT): $\delta = 25.6$ (CH_2), 25.8 (CH_2) 26.0 (CH_2), 26.1 (CH_2), 28.2 (CH_2), 33.2 [CH_2 , C-2'(6')], 33.5 (CH, C-1'), 48.3 (CH_2 , C-2), 51.1 (CH, C-1'), 213.8 (C_q , C-1). – MS (70 eV, 25 °C): m/z (%) = 209 (5) [$\text{M}^+ + 1$], 208 (30) [M^+], 165 (2), 153 (3), 127 (47), 126 (51), 125 (55) [C_6H_{11}](CO) CH_2^+], 112 (29) [C_6H_{11}](CO) H^+], 109 (7), 108 (4), 98 (7), 97 (79) [C_6H_{11}] CH_2^+], 85 (7), 84 (8), 83 (100) [$\text{C}_6\text{H}_{11}^+$], 82 (9), 81 (8), 80 (7), 79 (5), 71 (19), 69 (6), 68 (8), 67 (15). – HRMS ($\text{C}_{14}\text{H}_{24}\text{O}_1$): calcd. 208.182716; found 208.182907.

Treatment of 2,2-Dimethylpropanoyl Chloride (5) with SmI_2/Sm : Anhydrous NiI_2 (0.128 g, 0.4 mmol) was added to a solution of

SmI_2 , which had been obtained from samarium (14.700 g, 97.8 mmol), 1,2-diiodoethane (11.270 g, 40.0 mmol) and THF (100 mL). 2,2-Dimethylpropanoyl chloride (**5**) (2.60 mL, 2.550 g, 19.7 mmol) was added dropwise at 25 °C. The mixture was stirred for 14 h at 25 °C and then cooled to 0 °C. After addition of 100 mL of a satd aq solution of NH_4Cl , the mixture was extracted three times, each time with 100 mL of diethyl ether. The combined organic layers were dried over Na_2SO_4 . Column filtration (length 10 cm, $\varnothing$ 5.0 cm, petroleum ether/TBME 3:1) afforded 0.543 g (3.1 mmol, 32%) of *meso*-2,2,5,5-tetramethyl-3,4-hexanediol (*meso*-**6**).^[19,20]

Treatment of Phenylacetyl Chloride (7) with SmI_2/Sm : Anhydrous NiI_2 (0.031 g, 0.1 mmol) was added to a solution of SmI_2 , which had been obtained from samarium (3.310 g, 22.0 mmol), 1,2-diiodoethane (2.820 g, 10.0 mmol) and THF (100 mL). Phenylacetyl chloride (**7**) (2.72 mL, 3.180 g, 20.6 mmol) was added dropwise at 25 °C. The mixture was stirred for 15 min at 25 °C and then cooled to 0 °C. After addition of 50 mL of 2 N HCl, the mixture was extracted three times, each time with 100 mL of TBME. The collected organic layers were washed with a satd aq $\text{Na}_2\text{S}_2\text{O}_3$ solution and then dried over Na_2SO_4 . Column filtration (length 15 cm, $\varnothing$ 5.0 cm, petroleum ether/TBME 3:1) afforded 1.210 g (4.0 mmol, 58%) of 2-benzyl-1,3-diphenyl-2-propanol (**8**).^[21–23]

Treatment of Nonanoyl Chloride (9) with SmI_2/Sm : Anhydrous NiI_2 (0.030 g, 0.1 mmol) was added to a solution of SmI_2 , which had been obtained from samarium (1.654 g, 11.0 mmol), diiodomethane^[15] (1.339 g, 5.0 mmol) and THF (50 mL). Nonanoyl chloride (**9**) (1.40 mL, 1.729 g, 10.1 mmol) was added dropwise at 25 °C. The mixture was stirred for 2 h at 25 °C and then cooled to 0 °C. After addition of 50 mL of a satd aq solution of NH_4Cl , the mixture was extracted six times, each time with 50 mL of TBME. The combined organic layers were washed with satd aq solutions of NaHCO_3 , $\text{Na}_2\text{S}_2\text{O}_3$ and brine, and dried over Na_2SO_4 . Column chromatography (length 12 cm, $\varnothing$ 5.0 cm, petroleum ether/TBME 29:1).

Fraction I: 10-Hydroxy-10-octylnonadecane-9,11-dione (**10**) (0.946 g, 2.2 mmol, 66%) as a yellowish oil. IR (film): $\tilde{\nu} = 3448$ (m, sharp, -OH with intramolecular H bridge) cm^{-1} , 2956 (s, CH), 2925 (s, CH), 2855 (s, CH), 1738 (m, C=O), 1701 (s, α -hydroxy ketone), 1465 (m, CH), 1376 (m), 1136 (s, C–O), 1105 (s, C–O). – ^1H NMR (400.1 MHz, CDCl_3): $\delta = 0.87$ [t, $J = 6.7\text{ Hz}$, 9 H, 1(19)-H, 27-H], 1.25 [m, 32 H, 2–6(14–18)-H, 21–26-H], 1.50 [m, 4 H, 7(13)-H], 1.93 (m, 2 H, 20-H), 2.25–2.75 [m, 4 H, 8(12)-H], 4.68 (s, 1 H, 28-H). – ^{13}C NMR (100.6 MHz, CDCl_3 , APT): $\delta = 14.08$ [–, CH_3 , C-1(19), 27], 14.09 [–, CH_3 , C-1(19), 27], 22.7 (+, CH_2) 23.23 (+, CH_2), 23.4 (+, CH_2), 29.13 (+, CH_2), 29.16 (+, CH_2), 29.21 (+, CH_2), 29.4 (+, CH_2), 29.7 (+, CH_2), 31.85 (+, CH_2), 31.86 (+, CH_2), 36.6 (+, CH_2 , C-20), 37.2 [+ , CH_2 , C-8(12)], 91.1 (+, C_q , C-10), 209.7 [+ , C_q , C-9(11)]. – MS (70 eV, 90 °C): m/z (%) = 424 (1) [M^+], 312 (1) [$\text{M}^+ - \text{C}_8\text{H}_{17}$], 285 (83) [$\text{M}^+ - \text{C}_9\text{H}_{17}\text{O}$], 270 (10) [285 – CH_3], 256 (1) [285 – CH_2], 141 (100) [$\text{C}_9\text{H}_{17}\text{O}^+$], 113 (1) [$\text{C}_8\text{H}_{17}^+$], 71 (19) [$\text{C}_5\text{H}_{11}^+$]. – HRMS ($\text{C}_{27}\text{H}_{52}\text{O}_3$): calcd. 424.391646, found 424.391602 – $\text{C}_{27}\text{H}_{52}\text{O}_3$: calcd. C 76.36, H 12.34, found C 76.22, H 12.44.

Fraction II: 9-Octadecanone (**11**) (0.037 g, 0.2 mmol, 3%).^[38]

Fraction III: Nonanoic acid (**12**) (0.189 g, 1.2 mmol, 12%).^[39]

Treatment of Propanoyl Chloride (17) with SmI_2/Sm : Anhydrous NiI_2 (0.030 g, 0.1 mmol) was added to a solution of SmI_2 , which had been obtained from samarium (1.654 g, 11.0 mmol), diiodomethane (1.339 g, 5.0 mmol) and THP (10 mL). Propanoyl chloride

(17) (0.90 mL, 0.959 g, 10.4 mmol) was added dropwise at 25 °C. The mixture was stirred for 1 h at 25 °C and then cooled to 0 °C. After addition of 50 mL of a satd aq solution of NH_4Cl , the mixture was extracted six times, each time with 50 mL of TBME. The combined organic layers were washed with solutions of NaHCO_3 , $\text{Na}_2\text{S}_2\text{O}_3$ and brine, and dried over Na_2SO_4 . Column chromatography (length 13 cm, $\varnothing$ 3.5 cm, petroleum ether/TBME 10:1).

Fraction I: 4-Hydroxy-4-ethylheptane-3,5-dione (18) (0.407 g, 2.36 mmol, 68%) as a yellowish oil. IR (ATR): $\tilde{\nu}$ = 3454 (m, sharp, -OH with intramolecular H bridge) cm^{-1} , 2979 (s, CH), 2941 (s, CH), 2881 (m, CH), 1703 (vs, α -hydroxy ketone), 1460 (m, CH). – ^1H NMR (400.1 MHz, CDCl_3): δ = 0.80 (t, $^3J_{8,9}$ = 7.3 Hz, 3 H, 9-H), 1.02 [t, $^3J_{1(7),2(6)}$ = 7.4 Hz, 6 H, 1(7)-H], 2.00 (q, 2 H, 8-H), 2.60 (m, 2J = -19.0 Hz, 4 H, 2(6)-H], 4.66 (s, br, weak, oH). – ^{13}C NMR (100.6 MHz, CDCl_3 , APT): δ = 7.37 (–, C-9), 7.44 [–, C-1(7)], 29.8 [+ , C-8], 30.6 [+ , C-2(6)], 90.9 (+, C-4), 210.2 [+ , C-3(6)]. – MS (70 eV, 25 °C): m/z (%) = 172 (1) [M^+], 116 (100) [M^+ – $\text{C}_3\text{H}_5\text{O}^+$], 101 (33) [116 – CH_3], 87 (2) [101 – CH_2], 69 (87 – H_2O). – HRMS ($\text{C}_9\text{H}_{16}\text{O}_3$): calcd. 172.109945, found 172.109940.

Fraction II: 4-Hydroxyhexan-3-one (3) (0.076 g, 0.5 mmol, 10%).^[40]

Fraction III: Propionic acid (4) (0.043 g, 0.6 mmol, 6%).^[39]

Treatment of Hexanoyl Chloride (21) with SmI_2/Sm : Anhydrous NiI_2 (0.030 g, 0.1 mmol) was added to a solution of SmI_2 , which had been obtained from samarium (1.654 g, 11.0 mmol), diiodomethane (1.339 g, 5.0 mmol) and THP (10 mL). Hexanoyl chloride (21) (1.60 mL, 1.541 g, 11.4 mmol) was added dropwise at 25 °C. The mixture was stirred for 1 h at 25 °C and then cooled to 0 °C. After addition of 50 mL of a satd aq solution of NH_4Cl , the mixture was extracted six times, each time with 50 mL of TBME. The combined organic layers were washed with satd aq solutions of NaHCO_3 , $\text{Na}_2\text{S}_2\text{O}_3$ and brine, and dried over Na_2SO_4 . Column chromatography (length 14 cm, $\varnothing$ 3.5 cm, petroleum ether/TBME 29:1).

Fraction I: 7-Hydroxy-7-pentyltridecane-6,8-dione (22) (0.812 g, 2.72 mmol, 72%) as a yellowish oil. IR (ATR): $\tilde{\nu}$ = 3447 cm^{-1} (m, sharp, -OH with intramolecular H bridge), 2958 (s, CH), 2930 (s, CH), 2861 (s, CH), 1700 (s, α -hydroxy ketone), 1466 (m, CH), 1402 (m), 1378 (m), 1261 (m), 1095 (m), 1021 (m). – ^1H NMR (400.1 MHz, CDCl_3): δ = 0.85–0.90 [m, 9 H, 1(13)-H, 18-H], 1.25 [m, 12 H, 2(12)-H, 3(11)-H, 15-H, 16-H, 17-H], 1.51 [m, 4 H, 4(10)-H], 1.94 (m, 2 H, 14-H), 2.38–2.73 [m, J = 7.3 Hz, 2J = -18.1 Hz, 4 H, 5(9)-H], 4.30–4.80 (s, br, oH). – ^{13}C NMR (100.6 MHz, CDCl_3 , APT): δ = 13.87 [–, C-1(13) or C-18], 13.93 [–, C-1(13) or C-18], 22.4 [+ , C-2(12)], 22.9 (+, C-17), 23.11 [+ , C-3(11) or C-16], 23.13 [+ , C-3(11) or C-16], 31.3 [+ , C-4(10)], 31.9 (+, C-15), 36.6 (+, C-14), 37.2 [+ , C-5(9)], 91.1 (+, C-7), 209.8 [+ , C-6(8)]. – MS (70 eV, 25 °C): m/z (%) = 299 (2) [M^+], 200 (100) [M^+ – $\text{C}_6\text{H}_{11}\text{O}^+$], 184 (3) [200 – O], 156 (2) [184 – CO], 143 (11), 114 (2) [$\text{C}_9\text{H}_{17}\text{O}^+$], 99 (55) [$\text{C}_6\text{H}_{11}\text{O}^+$], 85 (2), 71 (21). – HRMS ($\text{C}_{18}\text{H}_{34}\text{O}_3$): calcd. 298.250795, found 298.250824.

Fraction II: 6-Dodecanone (23) (0.094 g, 0.5 mmol, 9%).^[41]

Fraction III: 6-Hydroxy-7-dodecanone (8) (0.076 g, 0.4 mmol, 6%).^[42]

Fraction IV: Hexanoic acid (25) (0.059 g, 0.8 mmol, 7%).^[39]

Treatment of Stearoyl Chloride (26) with SmI_2/Sm : Anhydrous NiI_2 (0.015 g, 0.05 mmol) was added to a solution of SmI_2 , which had been obtained from samarium (0.827 g, 5.50 mmol) and diiodomethane (0.652 g, 2.50 mmol) in THP (10 mL). Stearoyl chloride

(1.9 mL, 1.711 g, 5.60 mmol) was added dropwise at 25 °C. The mixture was stirred for 2 h at 25 °C and then cooled to 0 °C. After addition of 50 mL of a satd aq solution of NH_4Cl , the mixture was extracted six times, each time with 50 mL of TBME. The combined organic layers were washed with satd aq solutions of NaHCO_3 , $\text{Na}_2\text{S}_2\text{O}_3$ and brine, and dried over Na_2SO_4 . Column chromatography (length 100 cm, $\varnothing$ 3 cm, first petroleum ether, then petroleum ether/TBME 30:1).

Fraction I (petroleum ether): 19-Hydroxy-19-heptadecylheptatriacontane-18,20-dione (27) (512 mg, 0.64 mmol, 34%), colorless solid (m.p. 51 °C). – IR (ATR): $\tilde{\nu}$ = 3437 (w, sharp, -OH with intramolecular H bridge) cm^{-1} , 2957 (s, CH), 2917 (s, CH), 2850 (s, CH), 1701 (m, α -hydroxy ketone), 1467 (m, CH), 1401 (m), 1376 (m), 1093 (m), 804 (m). – ^1H NMR (400.1 MHz, TMS, CDCl_3): δ = 0.87 [t, 9 H, 3J = 6.5 Hz, 1(37)-H, 54-H], 1.26 [s br, 86 H, 2–15(23–36)-H, 39–53-H], 1.51 [m, 4 H, 3J = 7.3 Hz, 16(22)-H], 1.94 (m, 2 H, 38-H), 2.25–2.75 [m, 4 H, 3J = 7.3 Hz, 17(21)-H], 4.69 (s, br, weak, 1 H, 55-H). – ^{13}C NMR (100.6 MHz, CDCl_3 , TMS, APT): δ = 14.1 [–, C-1(37), C-54], 22.7 [+ , C-2(36), C-53], 23.4 (+, CH_2), 29.1 (+, CH_2), 29.4 (+, CH_2), 29.65 (+, CH_2), 29.72 (+, CH_2), 29.73 (+, CH_2), 29.76 (+, CH_2), 32.0 [+ , C-3(35), C-52], 36.6 (+, C-38), 37.2 [+ , C-17(21)], 91.0 (+, C-19), 209.8 [+ , C-18(20)]. – FAB-MS: m/z = 803 (M^+ + H), 776, 757, 729, 702, 536, 509, 480, 403, 356, 307, 267, 239.

Fraction II (petroleum ether/TBME 30:1): Stearic acid (28) (900 mg, 3.2 mmol, 57%), identified by comparison with authentic material.

Treatment of 1-Adamantoyl Chloride (29) with SmI_2/Sm : Anhydrous NiI_2 (0.030 g, 0.1 mmol) was added to a solution of SmI_2 , which had been obtained from samarium (1.654 g, 11.0 mmol), diiodomethane (1.339 g, 5.0 mmol), and THP (10 mL). 1-Adamantanoyl chloride (2.186 g, 11.0 mmol) in THP (10 mL) was added dropwise at 25 °C. The mixture was stirred for 1 h at 25 °C and then cooled to 0 °C. After addition of 50 mL of a satd aq solution of NH_4Cl , the mixture was extracted six times, each time with 50 mL of TBME. The combined organic layers were washed with satd aq solutions of NaHCO_3 , $\text{Na}_2\text{S}_2\text{O}_3$ and brine, and dried over Na_2SO_4 . Column chromatography (length 14 cm, $\varnothing$ 3.5 cm, petroleum ether/TBME 10:1).

Fraction I: 1,2-Di-(1-adamantyl)ethanedione (30) (0.720 g, 2.2 mmol, 40%), as a yellow solid.^[43,44]

Fraction II: 1,2-Di-(1-adamantyl)-2-hydroxyethanone (31) (0.601 g, 1.8 mmol, 33%), colorless solid.^[2,44]

Fraction III: Adamantanoic acid (32) (0.120 g, 0.7 mmol, 6%), colorless solid.^[39]

Treatment of 2-Methylpropanoyl Chloride with SmI_2/Sm : Anhydrous NiI_2 (0.030 g, 0.10 mmol) was added to a solution of SmI_2 , which had been obtained from samarium (1.654 g, 11.0 mmol), diiodomethane (1.339 g, 5.0 mmol), and THP (10 mL). 2-Methylpropanoyl chloride (33) (1.20 mL, 1.220 g, 11.5 mmol) was added dropwise at 25 °C. The mixture was stirred for 1 h at 25 °C and then cooled to 0 °C. After addition of 50 mL of a satd aq solution of NH_4Cl , the mixture was extracted six times, each time with 50 mL of TBME. The collected organic layers were washed with satd aq solutions of NaHCO_3 , $\text{Na}_2\text{S}_2\text{O}_3$ and NaCl and then dried over Na_2SO_4 . Column chromatography (length 50 cm, $\varnothing$ 3 cm, petroleum ether/TBME 10:1) gave 0.312 g (2.2 mmol, 38%) of 2,5-dimethyl-3,4-hexanedione (34) as a bright yellow liquid.^[45]

Treatment of Phthaloyl Dichloride (35) with SmI₂/Sm: a) Anhydrous NiI₂ (0.060 g, 0.2 mmol) was added to a solution of SmI₂, which had been obtained from samarium (3.308 g, 22.0 mmol), diiodomethane (1.339 g, 5.0 mmol)^[15] and THF (50 mL). Phthaloyl dichloride (35) (3.0 mL, 2.144 g, 20.8 mmol) was added dropwise at 25 °C. The mixture was stirred for 2 h at 25 °C and then cooled to 0 °C. After addition of 50 mL of 2N HCl, the mixture was extracted six times, each time with 50 mL of trichloromethane. The combined organic layers were washed with satd aq solutions of NaHCO₃, Na₂S₂O₃ and brine, and dried over Na₂SO₄. The solvents were removed at reduced pressure, and the residue was dissolved in acetone. The insoluble material was separated by filtration and washed with acetone to give 0.050 g (0.2 mmol, 2%) of an unseparated mixture of **37** and **38** (1:4).^[46,47]

Compound 37: ¹³C NMR (100.6 MHz, Cl₂CDCDCl₂, APT): δ = 164.7 [+, C-1(1')], 135.8 [+, C-1a(1a')], 135.1 [–, C-6(6')], 133.2 [+, C-2(2')], 130.9 [+, C-5(5')], 126.9 [–, C-3(3')], 125.3 [–, C-4(4')].

Compound 38: ¹³C NMR (100.6 MHz, Cl₂CDCDCl₂, APT): δ = 166.0 [+, C-1(1')], 137.0 [+, C-1a(1a')], 135.3 [–, C-6(6')], 133.5 [+, C-2(2')], 130.7 [+, C-5(5')], 125.9 [–, C-3(3')], 123.3 [–, C-4(4')].

Acetone was removed from the filtrate under reduced pressure, and the residue was dissolved in TBME. Insoluble material was removed by filtration, and the filtrate was purified by column chromatography (length 14 cm, Ø = 5 cm, petroleum ether/TBME 2:1).

Fraction I: Di(4-iodobutyl) phthalate (**39**) (2.105 g, 4.0 mmol, 19%) as a viscous yellow oil. IR (CHCl₃): $\tilde{\nu}$ = 3033 (w) cm^{–1}, 2961 (m), 1723 (s, C=O), 1601 (w), 1287 (s, C–O), 1131 (m, C–O), 1074 (m), 994 (w). – ¹H NMR (200.1 MHz): δ = 1.7–2.1 [m, 8 H, 2'-H, 3'-H], 3.24 (t, ³J = 6.7 Hz, 4 H, 4'-H), 4.35 (t, ³J = 6.2 Hz, 4 H, 1'-H), 7.63 [m, AA'BB', 4 H, 3-H, 4-H]. – MS (70 eV, 140 °C): *m/z* (%) = 530 (1) [M⁺], 404 (43) [M⁺ – I], 332 (1), 264 (14), 183 (100), 167 (82), 149 (68) [C₈H₅O₃⁺], 132 (4) [C₈H₄O₂⁺], 76 (15) [C₆H₄⁺].

Fraction II: 0.265 g of an unidentified orange-yellow solid. IR (KBr): $\tilde{\nu}$ = 3041 (w) cm^{–1}, 2958 (w), 1784 (s), 1725 (s, C=O), 1599 (s), 1467 (s), 1285 (s, C–O), 1073 (m), 991 (m), 761 (m), 735 (m), 692 (m). – ¹H NMR (400.1 MHz, [D₆]acetone): δ = 1.29 (t, 4 H, ³J = 7.2 Hz), 3.17 (q, 3 H, ³J = 7.2 Hz), 4.30 (m, 2 H), 7.3–8.4 (m, br, 28 H). – ¹³C NMR (100.6 MHz, BB): δ = 8.8, 27.2, 46.7, 49.3, 64.9, 65.2, 123–135 (m, br), 168.2, 168.6. – MS-FAB: *m/z* = 832, 744, 678, 624, 570, 463, 399, 366, 327, 289, 249, 207 (100%).

b) Anhydrous NiI₂ (0.030 g, 0.1 mmol) was added to a solution of SmI₂, which had been obtained from samarium (1.654 g, 11.0 mmol), diiodomethane^[15] (1.339 g, 5.0 mmol) and THP (40 mL). Phthaloyl dichloride (**26**) (1.5 mL, 2.114 g, 10.4 mmol) was added dropwise at 25 °C. The mixture was stirred for 1 h at 25 °C and then cooled to 0 °C. After addition of 50 mL of 2 N HCl, the mixture was extracted six times, each time with 50 mL of trichloromethane. The combined organic layers were washed with satd aq solutions of NaHCO₃, Na₂S₂O₃ and brine, and dried over Na₂SO₄. The solvents were removed under reduced pressure, and the residue was dissolved in acetone. The insoluble material was separated by filtration and washed with acetone to afford 0.080 g (0.3 mmol, 6%) of a mixture of **37** and **38** as a yellow solid, identified by comparison with authentic material.

Acetone was removed at reduced pressure from the filtrate, and the residue was dissolved in TBME. Insoluble material was removed

by filtration, and the TBME was removed to afford 0.605 g of the same unidentified orange-yellow solid that had also been obtained in a).

Treatment of 3,3-Dimethylbutanoyl Chloride (39) with SmI₂/Sm: Anhydrous NiI₂ (0.030 g, 0.10 mmol) was added to a solution of SmI₂, which had been obtained from samarium (1.654 g, 11.0 mmol), diiodomethane (1.339 g, 5.0 mmol) and THP (10 mL). 3,3-Dimethylbutanoyl chloride (1.50 mL, 1.454 g, 10.8 mmol) was added dropwise at 25 °C. The mixture was stirred for 2 h at 25 °C and then cooled to 0 °C. After addition of 50 mL of a satd. aqueous solution of NH₄Cl, the mixture was extracted six times, each time with 50 mL of TBME. The collected organic layers were washed with a satd aq solution of NaHCO₃, Na₂S₂O₃ and NaCl and then dried over Na₂SO₄. Column chromatography (length 90 cm, Ø 3 cm, petroleum ether, then petroleum ether/TBME 20:1) gave 315 mg (1.1 mmol, 31%) of 2,2,8,8-tetramethyl-5-(2,2-dimethylpropyl)-nonane-4,6-dione (**40**), colorless solid (m.p. 93 °C).

Compound 40: enol form 4:1. – IR (ATR): $\tilde{\nu}$ = 3150 cm^{–1} (very weak, br, enol -OH), 2953 (s, CH), 2906 (m, CH), 2869 (m, CH), 1726 (s, β-diketone), 1699 (m, C=O), 1477 (m, CH), 1466 (m, CH), 1388 (m), 1364 (m), 1242 (m), 1091 (m), 1021 (m). – ¹H NMR (400.1 MHz, TMS, C₆D₆): δ = 0.76 (s, 9 H, 12-H), 1.01 [s, 18 H, 1(9)-H], 1.82 (d, 2 H, ³J_{10,5} = 5.7 Hz, 10-H), 2.27 + 2.28 [2s, 4 H, 3(7)-H], 3.56 (t, 1 H, ³J_{10,5} = 5.7 Hz, 5-H). – ¹³C NMR (100.6 MHz, C₆D₆, TMS, APT): δ = 29.4 (–, C-12), 29.5 [–, C-1(9)], 30.4 [+, C-2(8)], 30.8 (+, C-11), 40.7 (+, C-10), 53.3 [+, C-3(7)], 67.9 (–, C-5), 204.5 [+, C-4(6)]. The constitution of **40** was confirmed by a C,H COSY spectrum. – MS (70 eV, 25 °C): *m/z* (%) = 284 (2) [M⁺ + 1], 283 (7) [M⁺], 211 (3) [M⁺ – C₅H₁₁⁺], 184 (39), 167 (1), 127 (43), 99 (100) [C₆H₁₁O⁺], 71 (19) [C₅H₁₁⁺]. – HRMS (C₁₈H₃₄O₂): calcd. 282.255881, found 282.255829.

Enol Form:^[33] ¹H NMR (400.1 MHz, TMS, C₆D₆): δ = 0.86 (s, 9 H), 0.89 (s, 9 H), 1.07 (s, 9 H), 2.16 (d, 2 H, *J* = 10.3 Hz), 2.20 (s, 2 H), 5.07 (dd, 1 H, *J* = 10.4, 2.0 Hz), 6.13 (s, 1 H). – ¹³C NMR (100.6 MHz, C₆D₆, TMS, APT): δ = 29.4 (–), 29.7 (–), 29.8 (–), 30.5 (+), 30.9 (+), 31.8 (+), 47.6 (+), 55.3 (+), 77.1 (–), 138.5 (–), 171.5 (+), 204.6 (+).

Treatment of Benzoyl Chloride with 1,2-Diiodoethane/Sm₂Co₇: Sm₂Co₇ alloy (7.740 g, 10.8 mmol) and 1,2-diiodoethane (2.770 g, 9.8 mmol) in THF (100 mL) were heated at reflux for 72 h. After cooling to 25 °C, the green-blue solution was separated from the alloy. After dropwise addition of benzoyl chloride (0.57 mL, 0.690 g, 4.9 mmol), the resulting solution was stirred for 24 h at 25 °C. Then 25 mL of 2N HCl and 25 mL of a satd aq solution of Na₂S₂O₃ were added, and the mixture was extracted three times, each time with 30 mL of diethyl ether. The combined organic layers were washed with 50 mL of satd aq solutions of Na₂CO₃ and brine, and dried over Na₂SO₄. Column chromatography (length 16 cm, Ø 3.5 cm, petroleum ether/diethyl ether 6:1).

Fraction I: 4-Iodobutyl benzoate (1.210 g, 4.0 mmol, 81%), yellow liquid.^[31,48]

Fraction II: 4-(4-Iodobutoxy)butyl benzoate (0.248 g, 0.7 mmol, 13%) as a yellow oil. IR (KBr): $\tilde{\nu}$ = 3060 cm^{–1} (w, arom. CH), 2940 (m, CH), 2860 (m, CH), 2796 (w, CH), 1716 (s, CO), 1600 (w, arom. C=C), 1584 (w, arom. C=C), 1448 (m), 1372 (w), 1312 (m), 1272 (s), 1224 (m), 1176 (m), 1112 (s, C–O), 1068 (m), 1024 (m), 956 (w), 712 (s), 688 (w). – ¹H NMR (400.1 MHz, CDCl₃): δ = 1.60–1.78 (m, 4 H, 13-H + 14-H), 1.82–1.96 (m, 4 H, 9-H + 10-H), 3.22 (t, ³J_{15,14} = 6.9, Hz 2 H, 15-H), 3.44 (t, ³J_{12,13} = 6.3 Hz, 2 H, 12-H), 3.47 (t, ³J_{11,10} = 6.3 Hz, 2 H, 11-H), 4.35 (t, ³J_{8,9} =

6.4 Hz, 2 H, 8-H), 7.44 [m, 2 H, 4(6)-H], 7.56 (tt, $^3J_{5,4(6)} = 7.5$ Hz, $^4J_{5,3(7)} = 1.3$ Hz, 1 H, 5-H), 8.04 [m, 2 H, 3(7)-H]. – ^{13}C NMR (100.6 MHz, CDCl_3 , DEPT): $\delta = 6.9$ (CH_2 , C-15), 25.6 (CH_2 , C-13 or C-14), 26.3 (CH_2 , C-13 or C-14), 30.4 (CH_2 , C-9 or C-10), 30.6 (CH_2 , C-9 or C-10), 64.8 (CH_2 , C-8), 69.6 (CH_2 , C-11 or C-12), 70.3 (CH_2 , C-11 or C-12), 128.3 [CH , C-3(7) or C-4(6)], 129.5 [CH , C-3(7) or C-4(6)], 130.4 (C_q , C-2), 132.8 (CH , C-5), 166.6 (C_q , C-1). – MS (70 eV, 90 °C): m/z (%) = 249 (2) [$\text{M}^+ - \text{I}$], 226 (3), 183 (30) [$\text{C}_4\text{H}_8\text{I}^+$], 178 (9), 177 (69) [$\text{M}^+ - \text{I} - \text{C}_4\text{H}_8\text{O}$], 155 (3), 127 (3), 123 (12), 122 (3), 106 (8), 105 (100), 91 (4), 85 (4), 79 (3), 78 (3), 77 (29), 73 (3), 71 (10). – HRMS ($\text{C}_{15}\text{H}_{21}\text{O}_3$): calcd. 249.149070; found 249.148911. – $\text{C}_{15}\text{H}_{21}\text{IO}_3$ (376.23): calcd. C 47.89, H 5.63; found C 48.31, H 5.39.

Treatment of 2,2-Dimethylpropanoyl Chloride with 1,2-Diiodoethane/ Sm_2Co_7 : Sm_2Co_7 alloy (8.630 g, 12.1 mmol) and 1,2-diiodoethane (2.720 g, 9.6 mmol) in THF (200 mL) were heated at reflux for 120 h. After cooling to 25 °C, the green-blue solution was separated from the alloy. After dropwise addition of 2,2-dimethylpropanoyl chloride (**5**) (0.59 mL, 0.579 g, 4.8 mmol) to the solution, the resulting mixture was stirred for 15 min at 25 °C. Then 25 mL of 2 N HCl was added, and the solution was extracted three times, each time with 40 mL of diethyl ether. The combined organic layers were washed with 50 mL of satd aq solution of Na_2CO_3 and brine, and dried over Na_2SO_4 . Column chromatography (length 18 cm, $\varnothing$ 3.5 cm, petroleum ether/diethyl ether 5:1) afforded 4-iodobutyl 2,2-dimethylpropanoate (0.665 g, 2.3 mmol, 49%) as a bright yellow oil.^[49]

Treatment of *rac*-2-Chloro-2-Phenylacetyl Chloride with Sodium Iodide: *rac*-2-Chloro-2-phenylacetyl chloride (5.0 mL, 6.515 g, 34.5 mmol) was added dropwise at 25 °C under exclusion of light to a suspension of NaI (7.500 g, 50 mmol) in THF (50 mL). The solution turned brown. After 2 h at 25 °C, 50 mL of 1 N HCl was added. The mixture was extracted four times, each time with 50 mL of TBME. The combined organic layers were washed with 50 mL each of satd aq solutions of NaHCO_3 , $\text{Na}_2\text{S}_2\text{O}_3$, and brine, and dried over Na_2SO_4 . Column chromatography (length 12 cm, $\varnothing$ 5 cm, petroleum ether/TBME 5:1) afforded *rac*-4-iodobutyl 2-chloro-2-phenyl acetate (*rac*-**41**) (10.695 g, 30.3 mmol, 88%) as an orange oil. – IR (film): $\tilde{\nu} = 3030$ (w) cm^{-1} , 2957 (w), 1752 (s), 1600 (w), 1495 (w), 1454 (m), 1277 (s), 1227 (s), 1161 (s), 725 (s), 696 (s). – ^1H NMR (400.1 MHz, CDCl_3): $\delta = 1.75$ [m, 4 H, 2'(3')-H], 3.11 (t, $J = 6.5$ Hz, 2 H, 4'-H), 4.18 (t, $J = 5.9$ Hz, 2 H, 1'-H), 5.35 (s, 1 H, 2-H), 7.30 (d, 1 H, arom. H), 7.38 (m, 2 H, arom. H), 7.48 (m, 2 H, arom. H). – ^{13}C NMR (100.6 MHz, CDCl_3 , APT): $\delta = 5.5$ (–, C-4'), 29.2 (+, CH_2 , C-3'), 29.6 (+, CH_2 , C-2'), 59.0 (–, CH, C-2), 65.1 (+, CH_2 , C-1'), 127.8 (–, CH), 128.8 (–, CH), 129.3 (–, CH), 135.7 (+, C_q , C-3), 168.2 (+, C_q , C-1). – MS (70 eV, 25 °C): m/z (%) = 354 (3) [M^+ , ^{37}Cl], 352 (7) [M^+ , ^{35}Cl], 318 (7) [$\text{M}^+ - \text{Cl}$], 227 (10), 225 (22) [$\text{M}^+ - \text{I}$], 191 (20) [225 – Cl], 127 (21), 125 (67) [PhCHCl^+], 105 (62), 91 (100) [PhCH_2^+], 77 (24) [Ph^+]. – $\text{C}_{12}\text{H}_{14}\text{ClIO}_2$ (352.59): Calcd. C 40.88, H 4.00; found C 41.54, H 4.00.

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