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Lanthanide-Catalyzed Oxyfunctionalization of 1,3-Diketones, Acetoacetic Esters, And Malonates by Oxidative C−O Coupling with Malonyl Peroxides

Alexander O. Terent'ev,*[,†] Vera A. Vil',[†] Evgenii S. Gorlov,[†] Gennady I. Nikishin,[†] Kasimir K. Pivnitsky,[†] and Waldemar Adam[‡,§]

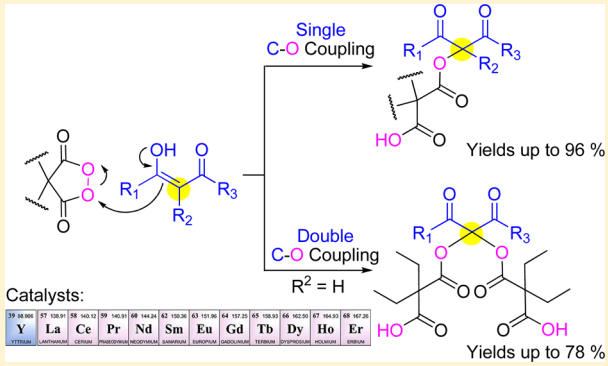
[†]N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prospekt, Moscow 119991, Russian Federation

[‡]Institute of Organic Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg, Germany

[§]Department of Chemistry, Facundo Bueso 110, University of Puerto Rico, Rio Piedras, Puerto Rico 00931, United States

Supporting Information

ABSTRACT: The lanthanide-catalyzed oxidative C−O coupling of 1,3-dicarbonyl compounds with diacyl peroxides, specifically the cyclic malonyl peroxides, has been developed. An important feature of this new reaction concerns the advantageous role of the peroxide acting both as oxidant and reagent for C−O coupling. It is shown that lanthanide salts may be used in combination with peroxides for selective oxidative transformations. The vast range of lanthanide salts (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Y) catalyzes oxidative C−O coupling much more efficiently than other used Lewis and Bronsted acids. This oxidative cross-coupling protocol furnishes mono and double C−O coupling products chemo-selectively in high yields with a broad substrate scope. The double C−O coupling products may be hydrolyzed to vicinal tricarbonyl compounds, which are otherwise cumbersome to prepare. Based on the present experimental results, a nucleophilic substitution mechanism is proposed for the C−O coupling process in which the lanthanide metal ion serves as Lewis acid to activate the enol of the 1,3-dicarbonyl substrate. The side reactions—chlorination and hydroxylation of the 1,3-dicarbonyl partners—may be minimized under proper conditions.



INTRODUCTION

The construction of chemical bonds by oxidative cross-coupling (cross-dehydrogenative coupling) is a promising and thriving field of modern organic chemistry. The formation of the new bond occurs with high atom efficiency, and no functional groups are required.[1] Oxidative C−C coupling reactions were studied most thoroughly; much literature has been amassed over the years.[2] Of the other types of coupling reactions (C−N, C−P, and C−O), the oxidative coupling to form the C−O bond between the partners is the more difficult.[3] One reason, unfortunately C−O coupling is generally accompanied by oxidation of the C partner into carbonyl products.[4]

Recently we communicated an efficient method for oxidative C−O coupling, in which one of the reagents, the diacyl peroxide, acts both as an O component and as the oxidizing agent of the double bond. The latter is contained in the 1,3-dicarbonyl partner through enolization.[5] Usually, in the oxidation of a double bond by peroxides, oxygen-atom transfer takes place.[6] The advantageous feature of the present reaction is the unusual chemical behavior of the peroxide: instead of oxygen-atom transfer by means of C−O bonding, the oxygen atom of the peroxide links together the two partners to afford the product. For emphasis, the present study embraces three aspects of modern synthetic chemistry: (1) the use of peroxides for the development of oxidative processes, (2) the selective oxyfunctionalization of 1,3-dicarbonyl substrates, and (3) the discovery of lanthanide to effect C−O coupling through Lewis-acid catalysis.

The 2-oxy-1,3-dicarbonyl fragment is widely represented in natural products and pharmaceuticals. Well-known examples are the azaphilones,[7] tetracycline antibiotics,[8] and barbituric acids.[9] Representatives of the extensive family of the azaphilones are analogues of chlorofusin, mitorubrin, and sclerotiorin. The isolation, modification, and synthesis of these natural products have received increased attention due to their antimicrobial,[10] antifungal,[11] and antiviral[12] activity. Tetracycline antibiotics, most of which contain a 2-hydroxy-1,3-dicarbonyl fragment, have been used worldwide for over 50 years in the treatment of infectious diseases.[13] The introduction of the RC(O)O substituent in the 5-position of the barbituric acid significantly increased the analgesic activity.[9] Thus, the

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development of a selective method for the efficient acyloxy-functionalization of the 1,3-dicarbonyl group comprises currently a desirable and timely task.

Cyclic diacyl peroxides have been prepared since the 1950s,[14] but only recently has this latent field of peroxide chemistry been rejuvenated, specifically for synthetic methodology. Significant current examples are the use of cyclic diacyl peroxides for the stereoselective dihydroxylation of alkenes,[15] arene oxidation catalyzed by hexafluoroisopropanol or trifluoroethanol,[16] selective arylation[17] and benzoyloxylation,[17d] and the [3 + 2] cycloaddition of arynes to azides resulting in benzotriazoles.[18]

The oxyfunctionalization of 1,3-dicarbonyl compounds and their hetero analogs was previously limited to hydroxylation,[19] peroxidation,[20] and the coupling of N−O fragments[21] and phenols.[22] In a number of studies, substituted 2-acyloxy-1,3-dicarbonyl products were synthesized by using hypervalent iodine compounds,[23] Bu_4NI/*t*-BuOOH,[24] manganese(III) acetate,[25] lead(IV) acetate,[26] and iron(III) salts.[27] To achieve the benzoyloxylation with the less reactive benzoyl peroxide as oxidant, the dicarbonyl substrates had to be previously activated by transformation into enamines,[28] copper complexes,[29] or enolates.[30] Unlike α-hydroxylation, methods for the intermolecular oxidative acyloxy-functionalization of 1,3-dicarbonyl compounds by diacyl peroxides appear not to have been reported. A detailed account of such an efficient single C−O coupling of 1,3-dicarbonyl substrates with malonyl peroxides is presented herein. It should be appreciated that the current method not only makes the α-hydroxylated 1,3-dicarbonyl substrates accessible by saponification of the single C−O coupling products prepared herein, but also the pendant carboxylic-acid functionality in the α-acyloxy substituent offers the opportunity for further functionalization and linking to biologically and pharmaceutically relevant targets. Furthermore, despite numerous attempts,[31] double 2-oxyfunctionalization of 1,3-dicarbonyl substrates is extremely rare because oxidative fragmentation and dimerization occur.[32] Our additional incentive for the present study was to develop methods double oxidative 2-oxyfunctionalization of 1,3-dicarbonyl substrates with the formation of polyfunctional products bearing carboxylic-acid groups for further synthetic modification. For example, double C−O coupling products containing six carbonyl groups offer promising perspectives for the complexation of diverse metal ions.[33] Similar 2-oxyfunctionalized 1,3-dicarbonyl compounds react with hydrazine, hydroxylamine, and amidrazones to form respectively the important heterocycles pyrazoles,[34] isoxazoles,[34a] 1,2,4-triazines,[35] and pyridines.[36]

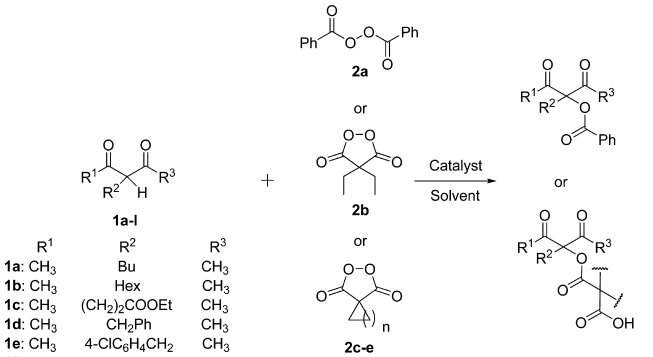
Synthetic strategy nowadays expects the use of catalysis to provide efficiency.[37] In view of our established interest in lanthanide catalysts, which have been widely used in biology, chemistry, material science, and medicine,[38] we demonstrated in our preliminary communication[5] that lanthanides are choice catalysts for our current purpose. (a) These mild but effective Lewis acids[39] do not decompose the diacyl peroxide, instead they activate them by increasing their electrophilic propensity. (b) Possibly, diacyl peroxides do not oxidize effectively anion in lanthanide salts. (c) In view of the high coordination capacity[40] of lanthanides, we anticipate that both the 1,3-dicarbonyl substrate and the diacyl-peroxide oxidant are ligated simultaneously to the lanthanum metal center, a desirable proximity for enhancing reactivity. Moreover, besides their favorable catalytic activity, the unique spectroscopic properties of lanthanide ions (long-lived excited-state lifetimes), lanthanide complexes have been employed as luminescent probes and biosensors for cellular imaging in MRI and immunoassay.[41] Also worthy of mention are the diverse systems for radiometric sensing and displacement assay of different chemical and biochemical substrates based on lanthanides.[42] In organic chemistry the lanthanides are used, among other applications, as mild Lewis acids. Of this fortunate property, we have made good use in the present study.[43]

In the present work we demonstrate that for reactive 1,3-dicarbonyl substrates, the oxidative C−O coupling is general with high catalytic efficiency for a variety of lanthanide (III) salts.

RESULTS AND DISCUSSION

The reaction panorama of the lanthanide-catalyzed C−O oxidative coupling process is displayed in Scheme 1, in which

Scheme 1. Single Oxidative C−O Coupling of Dicarbonyl Compounds 1 with Diacyl Peroxides 2 To Afford the C−O Coupling Products 3



	R^1	R^2	R^3
1a:	CH_3	Bu	CH_3
1b:	CH_3	Hex	CH_3
1c:	CH_3	$(CH_2)_2COOEt$	CH_3
1d:	CH_3	CH_2Ph	CH_3
1e:	CH_3	4-$ClC_6H_4CH_2$	CH_3
1f:	CH_3	CH_3	OEt
1g:		$-(CH_2)_3-$	OEt
1h:	CH_3	CH_2Ph	OEt
1i:	OEt	Et	OEt
1j:	OEt	Ph	OEt
1k:	CH_3	$CH_2CH_2C(O)CH_3$	CH_3
1l:	Ph	$CH_2CH_2C(O)CH_3$	CH_3

explicitly the reaction partners are specified: On the one hand, the dicarbonyl substrates **1** (C components) were selected, and on the other hand, the diacyl peroxides **2** partners (O components) afforded the coupling products **3**. The structure of the C components was varied to include the most reactive β-diketones **1a−e**, the moderately reactive β-oxoesters **1f−h**, and the toward oxidation persistent malonic esters **1i,j** and substrates **1k,l**. The latter contain an additional carbonyl function, but in the δ position remote from the reaction center. As oxidants (O components) we have chosen the diacyl peroxides **2**, including the industrially important noncyclic benzoyl peroxide **2a** and the cyclic diacyl peroxides **2b−e**. To clarify the codification of the coupling product **3**, the first letter index refers to the dicarbonyl substrate **1**, and the second letter index to the diacyl peroxide oxidant **2**; thus, the product **3hb** is obtained in the coupling of substrate **1h** with peroxide **2b**. The coupling was performed both in the presence and absence of transition-metal and nontransition-metal Lewis and Bronsted acid-type catalysts.

Our best results of the transition-metal-catalyzed C−O coupling are exhibited in Table 1, for which we have selected the moderately reactive dicarbonyl substrate 2-benzyl-3-oxobutanoate **1h** and the effective oxidant diethylmalonyl

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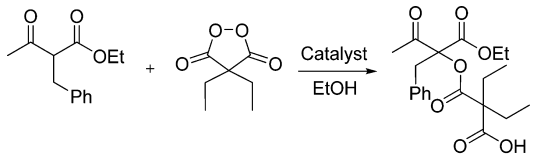
Table 1. Substrate Conversions and Product Yields in the Single Oxidative C−O Coupling of Substrate 1h with Diacyl Peroxide 2b Catalyzed by Transition-Metal Salts[a]

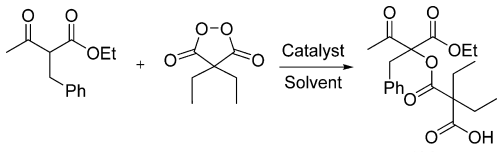


1h 2b 3hb

entry	catalyst	convn **1h**, %	yield **3hb**, %[b]
1	without catalyst	27	21 (25)
2	$LaCl_3{\cdot}7H_2O$	100	95 (97)
3	$CeCl_3{\cdot}7H_2O$	100	96 (97)
4	$PrCl_3{\cdot}6H_2O$	100	92 (96)
5	$NdCl_3{\cdot}6H_2O$	100	93 (98)
6	$SmCl_3{\cdot}6H_2O$	100	95 (97)
7	$GdCl_3{\cdot}6H_2O$	100	93 (96)
8	$TbCl_3{\cdot}6H_2O$	100	96 (98)
9	$DyCl_3{\cdot}6H_2O$	100	96 (98)
10	$HoCl_3{\cdot}6H_2O$	100	95 (97)
11	$Er(OAc)_3{\cdot}4H_2O$	100	93 (97)
12	$Eu(NO_3)_3{\cdot}6H_2O$	100	94 (96)
13	$La(NO_3)_3{\cdot}6H_2O$	100	96 (98)
14	$YCl_3{\cdot}6H_2O$	100	85 (90)

[a]General synthetic procedure: Catalyst (0.2 mol per mole of **1h**) was added with stirring to a solution of **1h** (500.0 mg, 2.27 mmol) in EtOH (10 mL). The reaction mixture was stirred at 20−25 °C for 5 min, then peroxide **2b** (538.5 mg, 3.41 mmol, molar ratio: 1.5 mol **2b**/1 mol oxoester **1h**) was added. The mixture was heated to 40 °C and stirred for 6 h. [b]Yields are based on isolated product; the values in parentheses were determined by ^{1}H NMR spectroscopy.

Table 2. Substrate Conversions and Product Yields in the Single Oxidative C−O Coupling of Substrate 1h with Diacyl Peroxide 2b Catalyzed by Nontransition-Metal Lewis and Bronsted Acids[a]



1h 2b 3hb

entry	catalyst (per mol **1h**)	solvent	convn **1h**, %	yield **3hb**, %[b]
1	$AlCl_3$ (0.2)	CH_2Cl_2	>99	71 (79)[c]
2	$SnCl_2{\cdot}2H_2O$ (0.2)	CH_2Cl_2	3	trace
3	$SnCl_4{\cdot}5H_2O$ (0.2)	CH_2Cl_2	8	trace
4[d]	I_2 (1)	CH_3CN	<5	0
5	phosphomolybdic acid (0.5)	EtOH	33	28 (31)
6	phosphotungstic acid (0.5)	EtOH	52	47 (50)
7	*p*-TsOH (0.5)	EtOH	32	25 (28)
8	H_2SO_4 (0.5)	EtOH	40	31 (34)
9	$HClO_4$ (0.5)	EtOH	42	34 (37)

[a]General synthetic procedure: Catalyst was added with stirring to a solution of **1h** (500.0 mg, 2.27 mmol) in solvent (10 mL). Then peroxide **2b** (538.5 mg, 3.41 mmol, molar ratio: 1.5 mol **2b**/1 mol **1h**) was added. The mixture was heated to 40 °C and stirred for 6 h. [b]Yields are based on isolated product; the values in parentheses were determined by ^{1}H NMR spectroscopy. [c]An inseparable mixture of undefined byproducts makes up the rest. [d]The mixture was stirred for 24 h at room temperature (20−25 °C).

peroxide **2b** as partner, in compliance with our previously communicated success.[5] Optimization of the reaction conditions by varying the reaction time, solvent, and temperature revealed that the C−O coupling reaction runs most efficiently in ethanol at 40 °C for 6 h (see Supporting Information for details).

In the absence of transition-metal salts, the C−O coupling of **1h** with **2b** results **3hb** in low yield (Table 1, entry 1). In contrast, excellent catalytic activity was achieved with all lanthanide salts, affording the coupling product **3hb** in high yields (92−96%), as shown in Table 1 (see entries 2−13). The counterion (acetate, chloride, or nitrate) in the lanthanide salt did not influence the high yields of coupling product **3hb** (compare entries 2−10 with 11−13 in Table 1). When the rare-earth salt yttrium chloride was used as catalyst, a slightly decreased yield of 85% was observed (Table 1, entry 14). It was found that the C−O coupling product **3hb** may be prepared in excellent yields under water-alcohol (7/3 volume ratio) conditions (see Supporting Information for details, Table S-1 entries 13−14).

The advantage and importance of lanthanide catalysis in the oxidative C−O coupling between the dicarbonyl substrate **1h** with diacyl peroxide **2b** are emphasized by the data of Table 2, in which we probed a number of nontransition-metal Lewis and Bronsted acids. These comprise the widely used Lewis acids $AlCl_3$ and the tin(II) and tin(IV) chlorides, which proved to be effective catalysts for the preparation of geminal bishydroperoxides[44] and cyclic triperoxides.[45] Also the aprotic I_2 was employed, which proved useful for the peroxidation of alkenes, enol esters, and acetals.[46] Moreover, we tested heteropoly acids—phosphomolybdic and phosphotungstic acids—which were previously shown to be effective catalysts for the peroxidation of carbonyl compounds.[47] The strong Bronsted acids *p*-TsOH, H_2SO_4, and $HClO_4$—traditional protic catalysts in preparative peroxidation chemistry[48]—were as well tried.

As the product data in Table 2 reveal, the oxidative C−O coupling with aluminum chloride afforded the target product **3hb** in 71% yield of isolated material (Table 2, entry 1), the best result in this list. The aprotic acids I_2, $SnCl_2{\cdot}2H_2O$, and $SnCl_4{\cdot}5H_2O$ were inefficient as catalysts (Table 2, entries 2−4). The heteropoly acids (Table 2, entries 5−6) and protic acids *p*-TsOH, H_2SO_4, and $HClO_4$ (Table 2, entries 7−9) gave **3hb** in yields between 25 and 47%. Thus, the nontransition-metal Lewis and Bronsted acids are considerably less effective catalysts for oxidative coupling compared to the lanthanides salts.

A variety of dicarbonyl compounds of differing nucleophilic reactivity were scrutinized with diethylmalonyl peroxide **2b**, to explore the scope of substrate structure in this oxidative C−O coupling. The results are summarized in Table 3 for the β-diketones **1a,c,e**, the β-oxoesters **1f−h**, the malonic esters **1i,j**, and the β,δ-triketones **1k,l**. The coupling reactions were carried out under the optimized conditions presented in Table 1 similar to those used without catalyst, with catalyst $LaCl_3{\cdot}7H_2O$, and catalyst $La(NO_3)_3{\cdot}6H_2O$. The experiments in Table 3 for substrates **1f−h**, **1i−l** without catalyst were carried out to accentuate the importance of lanthanide catalysis.

The high reactivity of β-diketones **1a,c,e** is evident in the first three entries of Table 3: Even without catalyst the expected coupling products **3ab**, **3cb**, and **3eb** were isolated in fair yields (57−65%) at nearly equal (63−72%) conversion of the substrates. Using the catalysts $LaCl_3{\cdot}7H_2O$ and $La(NO_3)_3{\cdot}$

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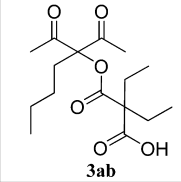
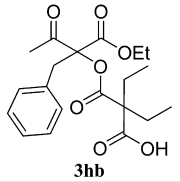
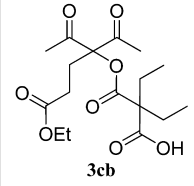
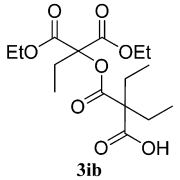
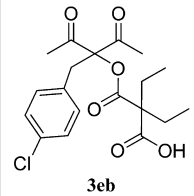
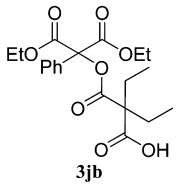
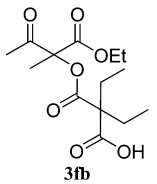
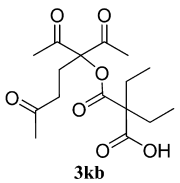
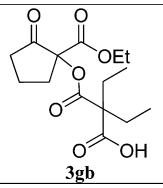
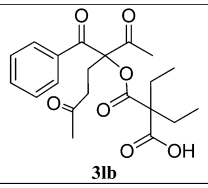
Table 3. Structures of the Coupling Products, Substrate Conversions, And Product Yields in the Single Oxidative C−O Coupling of Substrates 1 with Diacyl Peroxide 2b, Catalyzed by Lanthanum Chloride and Nitrate Salts[a]

C-O coupling products **3ab-lb**	Catalyst	Convn **1a-l**, %	Yield **3ab-lb**,%[b]	C-O coupling products **3ab-lb**	Catalyst	Convn **1a-l**, %	Yield **3ab-lb**,%[b]
 **3ab**	Without catalyst	69	61	 **3hb**	Without catalyst	27	21
	$LaCl_3·7H_2O$	84	77		$LaCl_3·7H_2O$	100	95
	$La(NO_3)_3·6H_2O$	79	62		$La(NO_3)_3·6H_2O$	100	96
 **3cb**	Without catalyst	63	57	 **3ib**	Without catalyst	10	7
	$LaCl_3·7H_2O$	97	85		$LaCl_3·7H_2O$	47	40
					$La(NO_3)_3·6H_2O$	23	20
 **3eb**	Without catalyst	72	65	 **3jb**	Without catalyst	13	9
	$LaCl_3·7H_2O$	98	83		$LaCl_3·7H_2O$	61	56
					$La(NO_3)_3·6H_2O$	46	44
 **3fb**	Without catalyst	25	24	 **3kb**	Without catalyst	83	76
	$LaCl_3·7H_2O$	91	75		$LaCl_3·7H_2O$	89	77
	$La(NO_3)_3·6H_2O$	73	61		$La(NO_3)_3·6H_2O$	91	71
 **3gb**	Without catalyst	23	19	 **3lb**	Without catalyst	12	9
	$LaCl_3·7H_2O$	96	84		$LaCl_3·7H_2O$	100	68[c]
					$La(NO_3)_3·6H_2O$	58	44

[a]General procedure: dicarbonyl compound (500.0 mg), catalyst $LaCl_3·7H_2O$ or $La(NO_3)_3·6H_2O$ (0.2 mol catalyst per mole of substrate), peroxide **2b** (1.5 mol peroxide/mol substrate), EtOH (10 mL), 40 °C, 6 h. [b]Yields are based on isolated product. [c]Additionally 21% 3-benzoyl-3-chloro-2,6-heptanedione (**7**).

$6H_2O$, however, the yields were upped appreciably to 77−85% of isolated products. The advantage of lanthanide catalysis is convincingly demonstrated for the less reactive β-oxoesters **1f−h**: Without a catalyst, low conversions (23−27%) of **1f−h** and poor yields (19−24%) of the coupling products **3fb**, **3gb**, and **3hb** were registered, whereas for the $LaCl_3·7H_2O$ or $La(NO_3)_3·6H_2O$ catalysts, the coupling products were isolated in a remarkably improved yields (61−96%) at nearly complete conversion of substrates. Nevertheless, coupling of the difficult-to-oxidize malonic esters **1i,j**[21a] was realized only in low yields (20−56%) even with the help of $LaCl_3·7H_2O$ or $La(NO_3)_3·6H_2O$ catalysts. Puzzling are the results for the β,δ-triketones **1k,l** (last two entries in Table 3): While substrate **1k** afforded the coupling product **3kb** in high yield (71−77%), irrespective of whether with or without lanthanide catalyst, for the related substrate **1l** the poor yield (9%) in the absence of lanthanide catalyst was significantly improved (68%) in the presence of $LaCl_3·7H_2O$ catalyst; additionally, the chlorination product 3-benzoyl-3-chloro-2,6-heptanedione (**7**) was isolated in 21% yield. As expected on the basis of enol nucleophicity, the reactivity of the substrate toward oxidation follows the β-diketones **1a−c** > β-oxoesters **1f−h** > malonic esters **1i,j** order, whereas the β,δ-triketones **1k,l** fall in between. For the oxoesters and malonic esters definitely, the lanthanide catalysis is essential, and the $LaCl_3·7H_2O$ is more effective than $La(NO_3)_3·6H_2O$.

The reactivity of the various diacyl peroxides, namely benzoyl peroxide **2a** and the malonyl peroxides **2c−e**, was tested with the β-diketones **1b,d,e** and β-oxoesters **1f,h**. The coupling was performed either in the absence of catalyst or in the presence of $LaCl_3·7H_2O$ or $La(NO_3)_3·6H_2O$, depending on the oxidative power of the peroxide (Table 4). The yields of C−O coupling product **3ba** for the poorly reactive benzoyl peroxide **2a** with the highly reactive β-diketone **1b** substrate are given in the first data block in Table 4. Clearly, without a catalyst, only a trace of product **3ba** was obtained, and with $LaCl_3·7H_2O$, a high yield (72%) was observed, but with $La(NO_3)_3·6H_2O$, the yield dropped to 6%. Similarly, for the combination of the less

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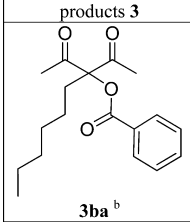
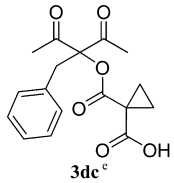
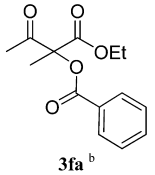
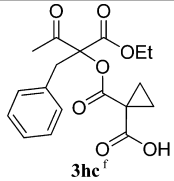
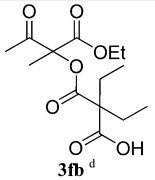
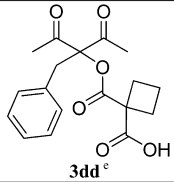
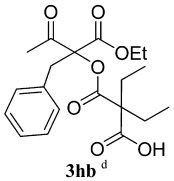
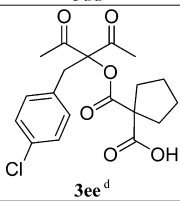
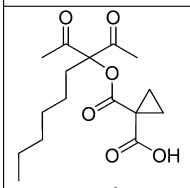
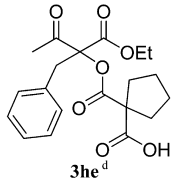
Table 4. Structures of C−O Coupling Products 3, Substrate Conversions, And Product Yields in the Single Oxidative C−O Coupling of Dicarbonyl Substrates 1 with Diacyl Peroxides 2 Catalyzed by Lanthanum Chloride and Nitrate Salts

C-O coupling products **3**	Catalyst	Convn **1**, %	Yield **3**, %[a]	C-O coupling products **3**	Catalyst	Convn **1**, %	Yield **3**, %[a]
 **3ba**[b]	Without catalyst	9	trace	 **3dc**[c]	Without catalyst	100	92
	$LaCl_3·7H_2O$	83	72				
	$La(NO_3)_3·6H_2O$	15	6				
 **3fa**[b]	Without catalyst	7	trace	 **3hc**[f]	$Eu(NO_3)_3·6H_2O$	27	23
	$LaCl_3·7H_2O$	100	26[c]		$LaCl_3·7H_2O$	23	17
	$La(NO_3)_3·6H_2O$	12	5		$La(NO_3)_3·6H_2O$	21	18
 **3fb**[d]	Without catalyst	25	24	 **3dd**[e]	Without catalyst	96	81
	$LaCl_3·7H_2O$	91	75				
	$La(NO_3)_3·6H_2O$	73	61				
 **3hb**[d]	Without catalyst	27	21	 **3ee**[d]	$LaCl_3·7H_2O$	94	70
	$LaCl_3·7H_2O$	100	95				
	$La(NO_3)_3·6H_2O$	100	96				
 **3bc**[e]	Without catalyst	97	90	 **3he**[d]	$LaCl_3·7H_2O$	100	38[g]
					$La(NO_3)_3·6H_2O$	100	34[h]

[a]Yields are based on isolated product. [b]Products **3ba**, **3fa**: dicarbonyl substrates **1b** or **1f** (500.0 mg), catalyst $LaCl_3·7H_2O$ or $La(NO_3)_3·6H_2O$ (0.2 mol catalyst per mole of **1b** or **1f**), peroxide **2a** (1.5 mol **2a**/ 1 mol **1b** or **1f**), MeOH (10 mL), 60 °C, 6 h. [c]Additionally 43% ethyl 2-chloro-2-methyl-3-oxobutanoate (**8**). [d]Products **3fb**, **3hb**, **3ee**, **3he**: dicarbonyl substrates **1e**, **1f**, or **1h** (500.0 mg), catalyst $LaCl_3·7H_2O$ or $La(NO_3)_3·6H_2O$ (0.2 mol catalyst per mole of **1e**, **1f**, or **1h**, peroxide **2e** or **2b** (1.5 mol peroxide/1 mol **1e**, **1f** or **1h**), EtOH (10 mL), 40 °C, 6 h. [e]Products **3bc**, **3dc**, **3dd**: dicarbonyl substrates **1b** or **1d** (500.0 mg), peroxide **2c** or **2d** (1.5 mol peroxide/1 mol **1b** or **1d**), $CHCl_3$ (10 mL), 40 °C, 6 h. [f]Product **3hc**: dicarbonyl substrate (500.0 mg), catalyst $Eu(NO_3)_3·6H_2O$ or $LaCl_3·7H_2O$ or $La(NO_3)_3·6H_2O$ (0.2 mol catalyst per mole of **1h**), peroxide **2c** (1.5 mol **2c**/1 mol **1h**), $CHCl_3$ (10 mL) [in the case of $LaCl_3·7H_2O$, 9:1 v/v $CHCl_3$/MeOH], 40 °C, 6 h. [g]Additionally 40% ethyl 2-benzyl-2-chloro-3-oxobutanoate (**9**). [h]Additionally 50% ethyl 2-benzyl-2-hydroxy-3-oxobutanoate (**10**).

reactive *β*-oxoesters **1f** with peroxide **2a** (see second data block in Table 4), only traces of product **3fa** were formed in the absence of catalyst; both $LaCl_3·7H_2O$ and $La(NO_3)_3·6H_2O$ catalysts led to the poor yields of 26% and 5%. A clarifying remark is in order in regard to the poor yields with the $La(NO_3)_3·6H_2O$ versus the $LaCl_3·7H_2O$ catalyst for the benzoyl peroxide (**2a**). Note that not only are the product yields very low but also the substrate conversions, namely 15% and 12% (see the first two data blocks in Table 4). This divergence in reactivity is only observed for the benzoyl peroxide (**2a**), the diacyl peroxide of marginal oxidative efficacy. Presumably, in such cases the differentiation in the catalytic activity of the lanthanide salt is more pronounced. Quite generally we found that $LaCl_3·7H_2O$ is more efficient than $La(NO_3)_3·6H_2O$, but the difference in substrate conversion and product yield is minor. For comparison we include in Table 4 our most reactive diethylmalonyl peroxide **2b** with the *β*-oxoesters **1f,h** substrates results, which were already given in Table 3. These data are displayed in the third and fourth data blocks of Table 4. The poor yields without catalyst (24%, 21%) are significantly improved with the $LaCl_3·7H_2O$ (75%, 95%) and $La(NO_3)_3·6H_2O$ (61%, 96%), which definitively emphasizes the advantage of lanthanide catalysis.

The next three data blocks in Table 4 deal with the spirocyclopropyl-substituted malonyl peroxide **2c**, of which the fifth and sixth data blocks refer to the coupling with the highly reactive *β*-diketones **1b** and **1d**. Even without catalyst, the respective coupling products **3bc** and **3dc** were obtained in high yields (90−92%), obviating the use of lanthanide salts. Nonetheless, as the seventh data block reveals, for the less reactive *β*-oxoester **1h**, the reaction with malonyl peroxide **2c** proceeds in low yields (17−23%) of coupling product **3hc**, independent of whether $Eu(NO_3)_3·6H_2O$, $LaCl_3·7H_2O$, or $La(NO_3)_3·6H_2O$ catalysts are employed. Analogous to the

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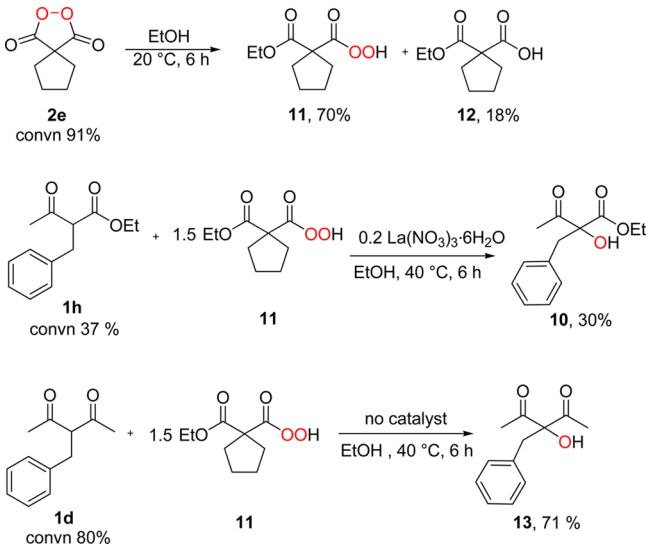
malonyl peroxide **2c**, the spirocyclobutyl-substituted malonyl peroxide **2d** affords the coupling product **3dd** with the highly reactive β-diketone **1d** in good yield (81%) without lanthanide catalyst (see eighth data block in Table 4). The last two entries in Table 4 refer to the least reactive malonyl peroxide **2e** (spirocyclopentyl substitution) with the β-dicarbonyl substrates **1e** and **1h**. As shown in the ninth data block, $LaCl_3{\cdot}7H_2O$ catalysis is essential to afford a high yield (70%) of coupling product **3ee**. Finally, the sluggish β-oxoester **1h** (last data block in Table 4) results in modest yields of coupling product **3he** even with the $LaCl_3{\cdot}7H_2O$ (38%) and $La(NO_3)_3{\cdot}6H_2O$ (34%) catalysts; the major byproducts are the respective 2-chlorinated **9** (40%) and 2-hydroxylated **10** (50%) derivatives.

This last entry in Table 4 for the $La(NO_3)_3{\cdot}6H_2O$-catalyzed reaction of the β-oxoester **1h** with the spirocyclopentylmalonyl peroxide **2e** is not only remarkable but also mechanistically puzzling: As major (50%) product ethyl 2-benzyl-2-hydroxy-3-oxobutanoate (**10**) and as minor (34%) product, the expected coupling product **3he** was obtained. A similar surprising result we already reported in our preliminary work[5] for the combination of 1,3-diketone **1d** with malonyl peroxide **2e** (in the preliminary work numbered **1a** for the substrate and **2c** for the peroxide) affording as major (35%) product the 3-benzyl-3-hydroxy-2,4-pentanedione. We showed previously[5] that the hydroxylated substrate is a primary product, that is, formed directly and not by solvolysis of the C−O coupling ester. What is responsible for this reaction dichotomy? Screening our earlier work on malonyl peroxide chemistry revealed that in alcohols, solvolysis takes place to afford a mixture of the corresponding peracid and carboxylic acid.[49] Indeed, in ethanol at 20 °C, the spiromalonyl peroxide **2e** leads to a mixture (see Scheme 2) of

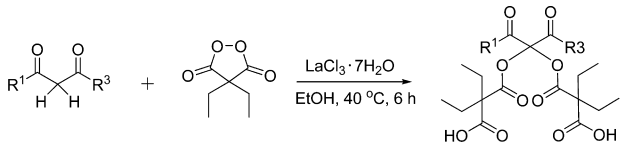
Scheme 2. Control Experiments for the Hydroxylation Side Reaction



peracid **11** (70%) and carboxylic acid **12** (18%). Treatment of the 1,3-dicarbonyl substrate **1h** with the isolated and purified peracid **11** was unproductive, but in the presence of $La(NO_3)_3{\cdot}6H_2O$ catalyst after 37% conversion of substrate **1h**, a 30% yield of the 2-hydroxy substrate **10** was confirmed (see Scheme 2). Moreover, when substrate **1d** (the one used in the preliminary work[5]) was treated with peracid **11**, the 2-hydroxy product **13** was obtained in 71% yield. Therewith the mechanistic mystery of the hydroxylation side reaction is unveiled.

As already shown in the abstract graphic and pointed out in the Introduction, β-dicarbonyl compounds with two enolizable hydrogen atoms (no α substitution), as in substrates **4a−f**, allow double oxyfunctionalization with malonyl peroxide **2b** to afford the novel double C−O coupling products **5a−f** (Scheme 3). Under $LaCl_3$ catalysis at 40 °C in EtOH within 6 h, good

Scheme 3. Double Oxidative C−O Coupling of Dicarbonyl Compounds 4a−f with Diacyl Peroxide 2b To Afford Products 5a−f

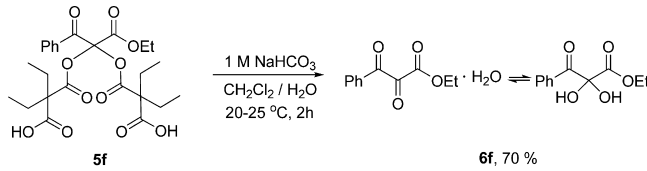


	R^1	R^3	Yield, %
5a:	CH_3	CH_3	58
5b:	Ph	CH_3	78
5c:	4-MeC_6H_4	CH_3	75
5d:	Ph	Ph	65
5e:	CH_3	OEt	68
5f:	Ph	OEt	56

yields (56−78%) of isolated material were obtained. The variation of α substitution in the double C−O coupling products **5a−f** is displayed by means of the structure matrix in Scheme 3.

The derivative **5f** of the double C−O coupling products was hydrolyzed to the vicinal 1,2,3-tricarbonyl compound **6f** (Scheme 4). Hydrolysis of **5f** was performed by 1 M $NaHCO_3$ at 20−25 °C for 2 h, leading to ethyl 2,3-dioxo-3-phenylpropanoate **6f** in good yield (70%), as shown in Scheme 4.

Scheme 4. Hydrolysis of the Double C−O Coupling Product 5f to the Vicinal Tricarbonyl Compound 6f



The results in Tables 3 and 4 manifest the following salient general trends in the oxidative C−O coupling reaction between the 1,3-dicarbonyl substrates **1** and malonyl peroxides **2**: (a) Toward the reactive substrates **1a−e**, the reactivity order of the diacyl peroxides **2a−e** is **2c** ≈ **2d** > **2b** ≫**2e** > **2a**; thus, the reaction of 1,3-diketones **1a−e** with peroxides **2b−d** affords the corresponding C−O coupling products **3** in high yields even without lanthanide catalysis. In contrast, the peroxides **2a,e** require the $LaCl_3{\cdot}7H_2O$ catalyst to achieve good yields. (b) Toward the less reactive β-oxoesters **1f−h**, the reactivity order of the diacyl peroxides is **2b** ≫ **2e**>**2a** ≈ **2c**, revealing that the diethyl-substituted malonyl peroxide **2b** is the more efficient partner for oxidative coupling. For the substrate **1h**, it is shown that a large variety of lanthanides serve as excellent catalysts (yields of C−O coupling product **3hb** better than 90%). (c) For the hard-to-oxidize malonic esters **1i−j**, even lanthanide catalysis performs only modestly. In such problematic cases, the chlorination of substrate **1** prevails when $LaCl_3{\cdot}7H_2O$ is employed as catalyst. Evidently, the peracid generated in situ from the malonyl peroxide **2** oxidizes the chloride ion to a

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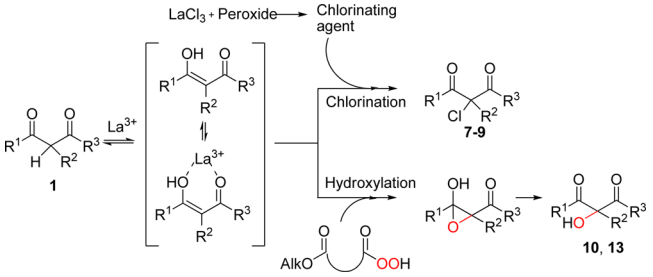
chlorinating agent,[50] presumably elemental chlorine. The latter in turn adds to the enol of the substrate **1** to afford the undesirable chlorination product (Scheme 5). Attempts to

Scheme 5. Suggested Mechanisms for the Chlorination and Hydroxylation Side Reactions



avoid this undesirable side reaction by employing $La(NO_3)_3 \cdot 6H_2O$ (no chloride ligands) as catalyst causes the hydroxylation of the 1,3-dicarbonyl substrate **1**. This alternative side reaction results from epoxidation of the enol derived from the substrate **1** by the in situ generated peracid[51] to afford the intermediary hydroxy epoxide; subsequent ring-opening affords the 2-hydroxy-1,3-dicarbonyl product (Scheme 5).

For the principal process, which constitutes the incentive for this study, namely the C−O coupling of the 1,3-dicarbonyl substrates **1** with the diacyl peroxides **2**, the mechanism in Scheme 6 is proposed.

Metal complexation with diacyl peroxide **2** is well documented.[52] The first step in the C−O coupling process is nucleophilic attack by the enol form of the substrate on the La-activated malonyl peroxide to form intermediate **I** by charge separation. The final C−O coupling product **3** is obtained through further reorganization by proton shift and dissociation of the lanthanide complex.

CONCLUSION

In summary, we have described a convenient and effective method for the oxidative C−O coupling of 1,3-diketones and 3-oxoesters with malonyl peroxides to afford hitherto unkown acyloxy-substituted products, but malonic esters are poorly reactive. It was shown that a wide range of lanthanide salts (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Y) are active catalysts for such oxidative acyloxylation. In comparison, poor catalytic activity was displayed by the common Lewis acids ($AlCl_3$, $SnCl_2$, $SnCl_4$), by the Bronsted acids (*p*-TsOH, H_2SO_4, $HClO_4$), and by phosphomolybdic and phosphotungstic acid, while elemental iodine was completely inactive. Numerous mono and some double C−O coupling products (altogether 24 examples) were synthesized in good to high yields. Double C−O coupling products **5a−f** containing six carbonyl groups offer promising perspectives for the complexation of diverse metal ions. What is particularly encouraging about our present research work is the symbiosis of the oxidizing power of diacyl peroxides with the catalytic activity of lanthanides.

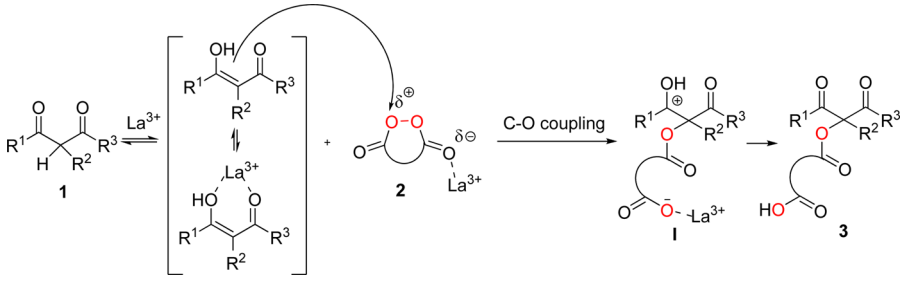
EXPERIMENTAL SECTION

Caution: Although we have encountered no difficulties in working with peroxides, precautions such as the use of safety shield, fume hood should be taken, the use of redox-active transition-metal salts, heating and vigorous shaking should be avoided!

NMR spectra were recorded on a commercial instrument (300.13 MHz for ^1H, 75.48 MHz for ^{13}C) in $CDCl_3$. IR spectra were recorded on a FT-IR spectrometer. High-resolution mass spectra (HRMS) were measured using electrospray ionization (ESI).[53] The measurements were done in a positive ion mode (interface capillary voltage 4500 V); the mass ratio was from *m*/*z* 50 to 3000 Da; external/internal calibration was done with Electrospray Calibrant Solution. A syringe injection was used for solutions in MeCN (flow rate 3 μL/min). Nitrogen was applied as a dry gas; interface temperature was set at 180 °C. The TLC analyses were carried out on standard silica-gel chromatography plates. The melting points were determined on a Kofler hot-stage apparatus. Chromatography was performed on silica gel (63−200 mesh).

2,4-Pentanedione (**4a**), 1-benzoylacetone (**4b**), dibenzoylmethane (**4d**), ethyl acetoacetate (**4e**), ethyl benzoylacetate (**4f**), ethyl 2-methylacetoacetate (**1f**), ethyl 2-oxocyclopentanecarboxylate (**1g**), diethyl ethylmalonate (**1i**), diethyl phenylmalonate (**1j**), benzoyl peroxide (**2a**, 75%, remainder water), diethyl 1,1-cyclopropanedicarboxylate, 1,1-cyclobutanedicarboxylic acid, AcOH, EtOH (96%), $AlCl_3$ (anhydrous), $SnCl_2 \cdot 2H_2O$, $SnCl_4 \cdot 5H_2O$, I_2, *p*-TsOH monohydrate, H_2SO_4, $HClO_4$ (70% solution in water), $NaHCO_3$, lanthanum(III) chloride heptahydrate ($LaCl_3 \cdot 7H_2O$), cerium(III) chloride heptahydrate ($CeCl_3 \cdot 7H_2O$), neodymium(III) chloride hexahydrate ($NdCl_3 \cdot 6H_2O$), samarium(III) chloride hexahydrate ($SmCl_3 \cdot 6H_2O$), gadolinium(III) chloride hexahydrate ($GdCl_3 \cdot 6H_2O$), terbium(III) chloride hexahydrate ($TbCl_3 \cdot 6H_2O$), dysprosium(III) chloride hexahydrate ($DyCl_3 \cdot 6H_2O$), holmium(III) chloride hexahydrate ($HoCl_3 \cdot 6H_2O$), lanthanum(III) nitrate hexahydrate ($La(NO_3)_3 \cdot 6H_2O$), yttrium(III) chloride hexahydrate ($YCl_3 \cdot 6H_2O$), praseodymium(III) chloride hexahydrate ($PrCl_3 \cdot 6H_2O$), erbium(III) acetate tetrahydrate ($Er(OAc)_3 \cdot 4H_2O$), europium(III) nitrate hexahydrate ($Eu(NO_3)_3 \cdot 6H_2O$), phosphomolybdic acid hydrate (formula weight: 1825.25 g/mol), phosphotungstic acid hydrate (formula weight: 2880.05 g/mol), and 2,2-diethyl malonic acid were purchased from commercial sources and was used as is. All solvents were distilled before use using standard procedures. Cyclopentane-1,1-dicarboxylic acid was synthesized according to literature.[15c] 3-Butyl-2,4-pentanedione (**1a**),[54] 3-hexyl-2,4-pentanedione (**1b**),[55] ethyl 4-acetyl-5-oxohexanoate (**1c**),[56] 3-benzyl-2,4-pentanedione (**1d**),[57] 3-(4-chlorobenzyl)-2,4-pentanedione (**1e**),[58] ethyl 2-benzyl-3-oxobutanoate (**1h**),[59] 3-acetyl-2,6-heptanedione (**1k**),[60] 3-benzoyl-2,6-heptanedione (**1l**),[60] and 1-(4-methyl-

Scheme 6. Mechanism for the C−O Coupling of 1,3-Dicarbonyl Substrates 1 with Diacyl Peroxides 2 To Afford the Oxyfunctionalized Product 3



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phenyl)-1,3-butanedione (**4c**)[61] were synthesized according to the literature.

Malonyl peroxides: spirocyclopropylmalonyl peroxide (**2c**),[62] spirocyclobutylmalonoyl peroxide (**2d**),[15c] spirocyclopentylmalonoyl peroxide (**2e**)[15c] were synthesized according to the literature.

Diethylmalonyl Peroxide (2b). Following the literature procedure,[15c] 2,2-diethyl malonic acid (8.0 g, 50.0 mmol) gave the title compound as a colorless oil (6.4 g, 40.5 mmol, 81%). ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 0.98 (t, J = 7.3 Hz, 6H), 1.95 (q, J = 7.3 Hz, 4H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 8.8, 28.7, 51.0, 174.0.

Spirocyclopropylmalonyl Peroxide (2c). Following the literature procedure,[62] diethyl 1,1-cyclopropanedicarboxylate (10.0 g, 54.0 mmol) gave the title compound as a white needle crystals (5.9 g, 46.0 mmol, 85%). White needle crystals, mp = 89−90 °C (lit. mp[62] = 90 °C). ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 2.11 (s, 4 H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 19.8, 23.6, 172.1.

Spirocyclobutylmalonoyl Peroxide (2d). Following the general procedure, 1,1-cyclobutanedicarboxylic acid (7.2 g, 50 mmol) gave the title compound as a white needle crystals (5.1 g, 36.0 mmol, 72%). White needle crystals, mp = 63−64 °C (lit. mp[15c] = 63 °C). ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 2.34 (quintet, J = 8.1 Hz, 2H), 2.69 (t, J = 8.1 Hz, 4H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 16.2, 28.9, 40.5, 173.9.

Spirocyclopentylmalonoyl Peroxide (2e). Following the general procedure, cyclopentane-1,1-dicarboxylic acid (7.9 g, 50.0 mmol) gave the title compound as a white crystalline solid (6.2 g, 39.5 mmol, 79%). White crystalline solid, mp = 39−40 °C (lit. mp[15c] = 41 °C). ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 1.96−2.01 (m, 4H), 2.22−2.27 (m, 4H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 26.6, 37.6, 46.8, 175.6.

General Procedure for Table 1, Entries 1−14. Transition-metal salt (molar ratio: 0.2 mol of salt per mole of **1h**) was added with stirring to a solution of ethyl 2-benzyl-3-oxobutanoate (**1h**) (500 mg, 2.27 mmol) in EtOH (10 mL) (in entry 1 catalyst was not used). The reaction mixture was stirred at 20−25 °C for 5 min. Then diethylmalonyl peroxide **2b** (538.5 mg, 3.41 mmol, molar ratio: 1.5 mol **2b**/1 mol oxoester **1h**) was added. The mixture was heated to 40 °C, stirred for 6 h, and cooled to 20−25 °C. The resulting mixture was diluted with $CHCl_3$ (70 mL), and the organic layer was washed with H_2O (3 × 10 mL), dried over Na_2SO_4, filtered, and concentrated under a water-jet vacuum. NMR yields were determined with 1,4-dinitrobenzene as the internal standard. The product **3hb** was isolated by column chromatography on SiO_2 with elution using PE-EtOAc in a linear gradient of latter from 30 to 90 vol %.

Detailed Experimental Procedure for Table 1, Entry 13. $La(NO_3)_3{\cdot}6H_2O$ (196.6 mg, 0.45 mmol, molar ratio: 0.2 mol of salt per mole of **1h**) was added with stirring to a solution of ethyl 2-benzyl-3-oxobutanoate (**1h**) (500 mg, 2.27 mmol) in EtOH (10 mL). The reaction mixture was stirred at 20−25 °C for 5 min. Then diethylmalonyl peroxide **2b** (538.5 mg, 3.41 mmol, molar ratio: 1.5 mol **2b**/1 mol oxoester **1h**) was added. The mixture was heated to 40 °C, stirred for 6 h, and cooled to 20−25 °C. The resulting mixture was diluted with $CHCl_3$ (70 mL), and the organic layer was washed with H_2O (3 × 10 mL), dried over Na_2SO_4, filtered, and concentrated under a water-aspirator vacuum. The conversion of **1h** (the characteristic signal is a doublet of the CH_2C_{arom} group at δ 3.12) and the yield of **3hb** (the characteristic signal is a two doublets of the CH_2C_{arom} group at δ 3.43 and δ 3.50) were determined from the ^{1}H NMR spectroscopic data. 1,4-Dinitrobenzene was used as the internal standard (the characteristic signal is a singlet of the four CH_{2arom} group at δ 8.38). Product **3hb** was isolated as described above. Yield of **3hb** was 96% (824.6 mg, 2.18 mmol).

2-{[1-Benzyl-1-(ethoxycarbonyl)-2-oxopropoxy]carbonyl}-2-ethylbutanoic Acid (3hb).[5] White solid, mp = 89−93 °C. R_f = 0.38 (PE:EtOAc = 5:1 + 2% AcOH). ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 0.83−0.90 (m, 6H), 1.14 (t, J = 7.3 Hz, 3H), 1.90−2.03 (m, 4H), 2.20 (s, 3H), 3.43 (d, J = 14.7 Hz, 1H, CH_2), 3.50 (d, J = 14.7 Hz, 1H, CH_2), 4.13 (q, J = 7.3 Hz, 2H), 7.05−7.12 (m, 2H), 7.17−7.25 (m, 3H), 10.32 (br.s., 1H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 8.2, 13.7, 25.4, 25.6, 27.6, 39.9, 58.6, 62.3, 88.6, 127.4, 128.2, 130.1, 133.4, 166.3, 170.6, 176.1, 201.2. HRMS (ESI) m/z [M + Na]$^+$: Calcd for $[C_{20}H_{26}NaO_7]^+$: 401.1571. Found: 401.1573. Anal. calcd for $C_{20}H_{26}O_7$ C: 63.48%, H: 6.93%. Found C: 63.44%, H: 6.90%. IR (KBr): 3423, 2975, 1764, 1710, 1355, 1312, 1258, 1234, 1128, 1060, 1014, 708, 516 cm^{-1}.

General Experimental Procedure for Table 2, Entries 1−3. $AlCl_3$ (60.5 mg, 0.45 mmol, molar ratio: 0.2 mol per mole of **1h**) or $SnCl_2{\cdot}2H_2O$ (101.5 mg, 0.45 mmol) or $SnCl_4{\cdot}5H_2O$ (157.8 mg, 0.45 mmol) was added with stirring to a solution of ethyl 2-benzyl-3-oxobutanoate **1h** (500 mg, 2.27 mmol) in CH_2Cl_2 (10 mL). Then diethylmalonyl peroxide **2b** (538.5 mg, 3.41 mmol, molar ratio: 1.5 mol **2b**/1 mol oxoester **1h**) was added. The mixture was heated to 40 °C and stirred for 6 h. The resulting mixture was diluted with $CHCl_3$ (70 mL), and the organic layer was washed with H_2O (3 × 10 mL), a 5% aqueous $NaHCO_3$ solution (2 × 10 mL), and again with H_2O (10 mL), dried over Na_2SO_4, filtered, and concentrated under a water-jet vacuum. NMR yields were determined with 1,4-dinitrobenzene as the internal standard. Product **3hb** was isolated as described above.

Experimental Procedure for Table 2, Entry 4. Molecular iodine (576.1 mg, 2.27 mmol, molar ratio: 1 mol of I_2 per mole of **1h**) was dissolved in solution of ethyl 2-benzyl-3-oxobutanoate **1h** (500 mg, 2.27 mmol) in CH_3CN (10 mL). Then diethyl malonyl peroxide (**2b**) (538.5 mg, 3.41 mmol, molar ratio: 1.5 mol **2b**/1 mol oxoester **1h**) was added. The mixture was stirred at 20−25 °C for 24 h. Target product **3hb** was not detected by TLC in the course of the reaction and after the synthesis.

General Experimental Procedure for Table 2, Entries 5−9. The diethylmalonyl peroxide (**2b**) (538.5 mg, 3.41 mmol, molar ratio: 1.5 mol **2b**/1 mol oxoester **1h**) was added with stirring to a solution of ethyl 2-benzyl-3-oxobutanoate **1h** (500 mg, 2.27 mmol) in EtOH (10 mL). Then acid (PMA, PTA, *p*-TsOH, H_2SO_4, $HClO_4$) (0.45 mmol, molar ratio: 0.2 mol per mole of **1h**) was added. The mixture was heated to 40 °C and stirred for 6 h. The resulting mixture was diluted with $CHCl_3$ (70 mL), and the organic layer was washed with H_2O (3 × 10 mL), a 5% aqueous $NaHCO_3$ solution (2 × 10 mL), and again with water (10 mL), dried over Na_2SO_4, filtered, and concentrated under a water-jet vacuum. NMR yields were determined with 1,4-dinitrobenzene as the internal standard. Product **3hb** was isolated as described above.

General Experimental Procedure for Table 3. $LaCl_3{\cdot}7H_2O$ (157.2−257.6 mg, 0.42−0.69 mmol, molar ratio: 0.2 mol of salt per mole of substrate **1**) or $La(NO_3)_3{\cdot}6H_2O$ (183.3−300.3 mg,0.42−0.69 mmol, molar ratio: 0.2 mol of salt per mole of substrate **1**) was added with stirring to a solution of 1,3-dicarbonyl compounds **1** (500.0 mg, 2.12−3.47 mmol) in EtOH (10 mL). The reaction mixture was stirred at 20−25 °C for 5 min. Then diethylmalonyl peroxide (**2b**) (502.0−822.7 mg, 3.17−5.20 mmol, molar ratio: 1.5 mol **2b**/1 mol 1,3-dicarbonyl compound **1**) was added. The mixture was heated to 40 °C and stirred for 6 h, cooled to 20−25 °C. The resulting mixture was diluted with $CHCl_3$ (70 mL), and the organic layer was washed with H_2O (3 × 10 mL), dried over Na_2SO_4, filtered, and concentrated under a water-jet vacuum. The yields of products were determined on isolated product by column chromatography on SiO_2 with elution using PE-EtOAc in a linear gradient of EtOAc from 30 to 90 vol %.

*2-{[(1,1-Diacetylpentyl)oxy]carbonyl}-2-ethylbutanoic Acid (**3ab**).* Yields: 61% (613.8 mg, 1.95 mmol, without catalyst), 77% (774.6 mg, 2.46 mmol, $LaCl_3$ catalyst), 62% (623.8 mg, 1.98 mmol, $La(NO_3)_3$ catalyst). Colorless oil. R_f = 0.41 (PE:EtOAc = 5:1 + 2% AcOH). ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 0.84 (t, J = 7.3 Hz, 3H), 0.93 (t, J = 7.3 Hz, 6H), 1.08−1.31 (m, 4H), 2.02 (q, J = 7.3 Hz, 4H), 2.17−2.30 (m, 8H), 10.35 (br, s, 1H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 8.2, 13.7, 22.5, 25.2, 25.3, 26.7, 32.9, 58.6, 95.1, 170.2, 176.9, 201.6. HRMS (ESI) m/z [M + Na]$^+$. Calcd for $[C_{16}H_{26}NaO_6]^+$: 337.1622. Found: 337.1625. Anal. calcd for $C_{16}H_{26}O_6$ C: 61.13%, H: 8.34%. Found C: 60.75%, H: 8.70%. IR (thin layer): 2699, 2942, 2879, 1739, 1715, 1457, 1418, 1357, 1228, 1206, 1126, 944 cm^{-1}.

*2-[(1,1-Diacetyl-4-ethoxy-4-oxobutoxy)carbonyl]-2-ethylbutanoic Acid (**3cb**).* Yields: 57% (510.1 mg, 1.42 mmol, without catalyst), 85% (760.7 mg, 2.12 mmol, $LaCl_3$ catalyst). Colorless oil. R_f = 0.43 (PE:EtOAc = 2:1+ 2% AcOH). ^{1}H NMR (300.13 MHz, $CDCl_3$, δ):

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0.93 (t, J = 7.3 Hz, 6H), 1.21 (t, J = 7.3 Hz, 3H), 2.01 (q, J = 7.3 Hz, 4H), 2.14−2.32 (m, 8H), 2.55−2.66 (m, 2H), 4.09 (q, J = 7.3 Hz, 2H), 9.45 (br.s., 1H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 8.2, 14.1, 25.1, 26.5, 28.0, 28.2, 58.5, 60.9, 93.5, 170.1, 172.0, 176.0, 201.0. HRMS (ESI) m/z [M + Na]$^+$. Calcd for $[C_{17}H_{26}NaO_8]^+$: 381.1520. Found: 381.1516. Anal. calcd for $C_{17}H_{26}O_8$ C: 56.97%, H: 7.31%. Found C: 56.90%, H: 7.28%. IR (thin layer): 2978, 2945, 2885, 1736, 1716, 1359, 1213, 1146, 1126 cm^{-1}.

*2-{[1-Acetyl-1-(4-chlorobenzyl)-2-oxopropoxy]carbonyl}-2-ethylbutanoic Acid (**3eb**).* Yields: 65% (565.2 mg, 1.71 mmol, without catalyst), 83% (760.0 mg, 2.18 mmol, $LaCl_3$ catalyst). White solid, mp = 113−115 °C. R_f = 0.35 (PE:EtOAc = 5:1 + 2% AcOH). ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 0.87 (t, J = 7.3 Hz, 6H), 1.97 (q, J = 7.3 Hz, 4H), 2.13 (s, 6H), 3.55 (s, 2H), 7.00 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 8.2 Hz, 2H), 10.92 (br.s., 1H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 8.2, 25.0, 27.3, 38.8, 58.6, 94.4, 128.6, 131.4, 132.0, 133.5, 170.4, 176.9, 201.6. HRMS (ESI) m/z [M + Na]$^+$. Calcd for $[C_{19}H_{23}ClNaO_6]^+$: 405.1075. Found: 405.1063. Anal. calcd for $C_{19}H_{23}O_6Cl$ C: 59.61%, H: 6.06%, Cl: 9.26%. Found C: 59.54%, H: 6.08%, Cl: 9.26%. IR (KBr): 3433, 2977, 2943, 2629, 1764, 1711, 1493, 1362, 1256, 1215, 1176, 1134 cm^{-1}.

*2-{[1-(Ethoxycarbonyl)-1-methyl-2-oxopropoxy]carbonyl}-2-ethylbutanoic Acid (**3fb**).* Yields: 24% (251.6 mg, 0.83 mmol, without catalyst), 75% (786.4 mg, 2.60 mmol, $LaCl_3$ catalyst), 61% (639.6 mg, 2.12 mmol, $La(NO_3)_3$ catalyst). Colorless oil. R_f = 0.31 (PE:EtOAc = 5:1 + 2% AcOH). ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 0.85−0.92 (m, 6H), 1.22 (t, J = 7.3 Hz, 3H), 1.68 (s, 3H), 1.91−2.04 (m, 4H), 2.29 (s, 3H), 4.19 (q, J = 7.3 Hz, 2H), 8.97 (br.s., 1H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 8.2, 8.3, 13.7, 19.1, 25.5, 25.6, 58.6, 62.4, 86.1, 166.9, 170.2, 176.1, 201.2. HRMS (ESI) m/z [M + Na]$^+$. Calcd for $[C_{14}H_{22}NaO_7]^+$: 325.1258. Found: 325.1261. Anal. calcd for $C_{14}H_{22}O_7$ C: 55.62%, H: 7.33%. Found C: 55.47%, H: 7.45%. IR (thin layer): 3197, 3095, 2979, 2945, 2885, 1739, 1450, 1358, 1267, 1232, 1113 cm^{-1}.

*2-({[1-(Ethoxycarbonyl)-2-oxocyclopentyl]oxy}carbonyl)-2-ethylbutanoic Acid (**3gb**).* Yields: 19% (191.2 mg, 0.61 mmol, without catalyst), 84% (845.3 mg, 2.69 mmol, $LaCl_3$ catalyst). Colorless oil. R_f = 0.59 (PE:EtOAc = 5:1 + 2% AcOH). ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 0.90 (t, J = 7.3 Hz, 6H), 1.24 (t, J = 7.3 Hz, 3H), 1.87−2.17 (m, 6H), 2.21−2.32 (m, 1H), 2.38−2.65 (m, 2H), 2.70−2.83 (m, 1H), 4.20 (q, J = 7.3 Hz, 2H), 10.84 (br.s., 1H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 8.4, 13.9, 18.4, 26.1, 33.0, 35.8, 58.5, 62.3, 84.4, 166.6, 170.9, 176.1, 207.2. HRMS (ESI) m/z [M + Na]$^+$. Calcd for $[C_{15}H_{22}NaO_7]^+$: 337.1258. Found: 337.1260. Anal. calcd for $C_{15}H_{22}O_7$ C: 57.32%, H: 7.05%. Found C: 57.29%, H: 7.14%. IR (thin layer): 2977, 2945, 2885, 1771, 1737, 1463, 1389, 1266, 1229, 1151, 1128, 1021 cm^{-1}.

*2-{[1,1-Bis(ethoxycarbonyl)propoxy]carbonyl}-2-ethylbutanoic Acid (**3ib**).* Yields: 7% (64.4 mg, 0.19 mmol, without catalyst), 40% (368.0 mg, 1.06 mmol, $LaCl_3$ catalyst), 20% (184.0 mg, 0.53 mmol, $La(NO_3)_3$ catalyst). Colorless oil. R_f = 0.34 (PE:EtOAc = 5:1 + 2% AcOH). ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 0.86−0.97 (m, 9H), 1.25 (t, J = 7.3 Hz, 6H), 1.94−2.08 (m, 4H), 2.22 (q, J = 7.3 Hz, 2H), 4.23 (q, J = 7.3 Hz, 4H), 9.46 (br.s., 1H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 7.7, 8.5, 13.9, 26.7, 28.1, 58.8, 62.3, 84.0, 166.1, 171.3, 175.4. HRMS (ESI) m/z [M + Na]$^+$: Calcd for $[C_{16}H_{26}NaO_8]^+$: 369.1520. Found: 369.1521. Anal. calcd for $C_{16}H_{26}O_8$ C: 55.48%, H: 7.57%. Found C: 55.48%, H: 7.62%. IR (thin layer): 2980, 2944, 2886, 1755, 1714, 1461, 1306, 1256, 1235, 1133, 1099, 1031 cm^{-1}.

*2-{[2-Ethoxy-1-(ethoxycarbonyl)-2-oxo-1-phenylethoxy]carbonyl}-2-ethylbutanoic Acid (**3jb**).* Yields: 9% (75.1 mg, 0.19 mmol, without catalyst), 56% (467.4 mg, 1.19 mmol, $LaCl_3$ catalyst), 44% (367.3 mg, 0.93 mmol, $La(NO_3)_3$ catalyst). Colorless oil. R_f = 0.55 (PE:EtOAc = 2:1 + 2% AcOH). ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 0.96 (t, J = 7.3 Hz, 6H), 1.19 (t, J = 7.3 Hz, 6H), 2.11 (q, J = 7.3 Hz, 4H), 4.21 (q, J = 7.3 Hz, 4H), 7.30−7.35 (m, 3H), 7.50−7.58 (m, 2H), 9.62 (br.s., 1H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 8.5, 13.7, 26.4, 58.8, 62.7, 83.0, 125.6, 128.6, 129.1, 133.7, 165.1, 171.1, 175.4. HRMS (ESI) m/z [M + Na]$^+$: Calcd for $[C_{20}H_{26}NaO_8]^+$: 417.1520. Found: 417.1517. Anal. calcd for $C_{20}H_{26}O_8$ C: 60.90%, H: 6.64%. Found C: 60.77%, H: 6.71%. IR (thin layer): 3070, 2981, 2944, 2885, 1757, 1711, 1464, 1451, 1368, 1248, 1124, 1055, 859, 735, 695 cm^{-1}.

*2-{[(1,1-Diacetyl-4-oxopentyl)oxy]carbonyl}-2-ethylbutanoic Acid (**3kb**).* Yields: 76% (733.1 mg, 2.23 mmol, without catalyst), 77% (742.7 mg, 2.26 mmol, $LaCl_3$ catalyst), 71% (684.8 mg, 2.09 mmol, $La(NO_3)_3$ catalyst). White solid, mp = 75−77 °C. R_f = 0.28 (PE:EtOAc = 2:1 + 2% AcOH). ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 0.92 (t, J = 7.3 Hz, 6H), 2.01 (q, J = 7.3 Hz, 4H), 2.09 (s, 3H), 2.24 (s, 6H), 2.35−2.43 (m, 2H), 2.48−2.56 (m, 2H), 9.75 (br.s., 1H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 8.2, 25.1, 26.5, 26.6, 29.7, 37.1, 58.5, 93.4, 170.0, 176.2, 201.2, 206.8. HRMS (ESI) m/z [M + Na]$^+$: Calcd for $[C_{16}H_{24}NaO_7]^+$: 351.1414. Found: 351.1414. Anal. calcd for $C_{16}H_{24}O_7$ C: 58.52%, H: 7.37%. Found C: 58.55%, H: 7.29%. IR (KBr): 3420, 3081, 2978, 1754, 1720, 1704, 1421, 1358, 1221, 1179, 1091, 919 cm^{-1}.

*2-{[(1-Acetyl-1-benzoyl-4-oxopentyl)oxy]carbonyl}-2-ethylbutanoic Acid (**3lb**).* Yields: 9% (75.6 mg, 0.19 mmol, without catalyst), 68% (571.5 mg, 1.46 mmol, $LaCl_3$ catalyst), 44% (369.8 mg, 0.95 mmol, $La(NO_3)_3$ catalyst). Colorless oil. R_f = 0.19 (PE:EtOAc = 2:1 + 2% AcOH). ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 0.58 (t, J = 7.3 Hz, 3H), 0.70 (t, J = 7.3 Hz, 3H), 1.77−1.92 (m, 4H), 2.10 (s, 3H), 2.32 (s, 3H), 2.45−2.83 (m, 4H), 7.37 (t, J = 7.3 Hz, 2H), 7.50 (t, J = 7.3 Hz, 1H), 7.75 (d, J = 8.1 Hz, 2H), 9.38 (br.s., 1H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 7.9, 8.0, 24.6, 24.7, 26.4, 26.5, 29.7, 37.2, 58.4, 93.2, 128.5, 128.8, 133.2, 134.7, 169.4, 176.0, 193.6, 200.8, 207.1. HRMS (ESI) m/z [M + Na]$^+$: Calcd for $[C_{21}H_{26}NaO_7]^+$: 413.1571. Found: 413.1563. Anal. calcd for $C_{21}H_{26}O_7$ C: 64.60%, H: 6.71%. Found C: 64.72%, H: 6.93%. IR ($CHCl_3$): 3468, 2976, 2944, 2617, 1724, 1449, 1360, 1124, 711, 703, 523 cm^{-1}.

Byproduct **7** was isolated additionally with C−O coupling product **3lb** in the case of $LaCl_3$ catalyst.

*3-Benzoyl-3-chloro-2,6-heptanedione (**7**).* Yield of **7** was 21% (120.0 mg, 0.45 mmo). Colorless oil. R_f = 0.81 (PE:EtOAc = 2:1 + 2% AcOH). ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 2.10 (s, 3H), 2.32 (s, 3H), 2.56−2.66 (m, 4H), 7.40 (t, J = 7.3 Hz, 2H), 7.53 (t, J = 7.3 Hz, 1H), 7.86 (d, J = 7.3 Hz, 2H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 26.2, 29.8, 30.4, 38.2, 78.6, 128.5, 129.6, 133.2, 133.6, 191.3, 200.7, 206.5. HRMS (ESI) m/z [M + Na]$^+$: Calculated for $[C_{14}H_{15}ClNaO_3]^+$: 289.0602. Found: 289.0603.

General Experimental Procedure for Table 4, Compounds 3ba, 3fa. $LaCl_3{\cdot}7H_2O$ (201.5−257.6 mg, 0.54−0.69 mmol, molar ratio: 0.2 mol/1 mol **1b**, **1f**) or $La(NO_3)_3{\cdot}6H_2O$ (235.0−300.3 mg, 0.54−0.69 mmol, molar ratio: 0.2 mol/1 mol **1b**, **1f**) was added with stirring to a solution of dicarbonyl compounds **1b**, **1f** (500.0 mg, 2.71−3.47 mmol) in MeOH (10 mL) at room temperature. The mixture was stirred at 20−25 °C for 5 min. Then benzoyl peroxide **2a** (1314.5−1680.2 mg, 4.07−5.20 mmol, molar ratio: 1.5 mol **2a**/1 mol **1b**, **1f**) was added. The reaction mixture was stirred at 60 °C for 6 h and cooled to 20−25 °C. The resulting mixture was diluted with $CHCl_3$ (70 mL), and the organic layer was washed with H_2O (3 × 10 mL), dried over Na_2SO_4, filtered, and concentrated under a water-jet vacuum. Product **3ba** or **3fa** was isolated by chromatography on SiO_2 eluting with PE-EtOAc in a linear gradient of the latter from 0 to 50 vol %.

*1,1-Diacetylheptyl Benzoate (**3ba**).* Yields: 0% (without catalyst), 72% (596.6 mg, 1.95 mmol, $LaCl_3$ catalyst), 6% (49.7 mg, 0.16 mmol, $La(NO_3)_3$ catalyst). Colorless oil. R_f = 0.58 (PE:EtOAc = 10:1). ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 0.84 (t, J = 6.6 Hz, 3H), 1.19−1.31 (m, 8H), 2.27−2.42 (m, 8H), 7.48 (t, J = 7.3 Hz, 2H), 7.62 (t, J = 7.3 Hz, 1H), 8.08 (d, J = 8.1 Hz, 2H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 13.9, 22.4, 23.5, 26.7, 29.2, 31.4, 33.5, 94.8, 128.6, 129.1, 129.9, 133.7, 165.2, 201.7. HRMS (ESI) m/z [M + Na]$^+$. Calcd for $[C_{18}H_{24}NaO_4]^+$: 327.1567. Found: 327.1563. Anal. calcd for $C_{18}H_{24}O_4$ C: 71.03%, H: 7.95%. Found C: 70.73%, H: 7.96%. IR (thin layer): 2957, 2930, 2859, 1717, 1453, 1356, 1281, 1179, 1106, 1097, 1070, 712 cm^{-1}.

*1-(Ethoxycarbonyl)-1-methyl-2-oxopropyl Benzoate (**3fa**).* Yields: 0% (without catalyst), 26% (239.2 mg, 0.90 mmol, $LaCl_3$ catalyst), 5% (46.0 mg, 0.17 mmol, $La(NO_3)_3$ catalyst). Colorless oil. R_f = 0.63 (PE:EtOAc = 5:1). ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 1.24 (t, J = 7.34 Hz, 3H), 1.83 (s, 3H), 2.43 (s, 3H), 4.24 (q, J = 7.34 Hz, 2H),

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7.46 (t, J = 7.33 Hz, 2H), 7.59 (t, J = 7.32 Hz, 1H), 8.06 (d, J = 8.07 Hz, 2H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 13.9, 19.8, 25.8, 62.2, 85.8, 128.5, 129.1, 129.8, 133.6, 164.9, 167.4, 201.1. HRMS (ESI) m/z $[M + Na]^+$. Calcd for $[C_{14}H_{16}NaO_5]^+$: 287.0890. Found: 287.0884. Anal. calcd for $C_{14}H_{16}O_5$ C: 63.63%, H: 6.10%. Found C: 63.71%, H: 6.07%. IR (thin layer): 2984, 2941, 1758, 1726, 1452, 1284, 1132, 1111, 1025, 712 cm^{-1}. Byproduct **8** was isolated additionally with C−O coupling product **3fa** in the case of $LaCl_3$ catalyst.

*Ethyl 2-chloro-2-methyl-3-oxobutanoate (**8**).*[63] Yield of **8** was 43% (266.5 mg, 1.49 mmol). Colorless oil. R_f = 0.78 (PE:EtOAc = 5:1). ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 1.28 (t, J = 7.3 Hz, 3H), 1.80 (s, 3H), 2.35 (s, 3H), 4.26 (q, J = 7.3 Hz, 2H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 13.8, 24.2, 25.2, 63.0, 70.7, 168.0, 198.7.

General Experimental Procedure for Table 4, Products 3fb, 3hb, 3ee, 3he. $LaCl_3{\cdot}7H_2O$ (165.3−257.6 mg, 0.45−0.69 mmol, molar ratio: 0.2 mol $LaCl_3{\cdot}7H_2O$/1 mol substrate **1**) or $La(NO_3)_3{\cdot}6H_2O$ (192.7−300.3 mg, 0.45−0.69 mmol, molar ratio: 0.2 mol of salt per mole of substrate **1**) was added with stirring to a solution of dicarbonyl compound **1f**, **1h**, **1e** (500.0 mg, 2.23−3.47 mmol) in EtOH (10 mL) at room temperature. The mixture was stirred at 20−25 °C for 5 min. Then malonyl peroxide **2b** or **2e** (521.2−822.7 mg, 3.34−5.20 mmol, molar ratio: 1.5 mol **2b** or **2e**/1 mol dicarbonyl compound) was added. The reaction mixture was stirred at 40 °C for 6 h, cooled to 20−25 °C. The resulting mixture was diluted with $CHCl_3$ (70 mL), and the organic layer was washed with H_2O (3 × 10 mL), dried over Na_2SO_4, filtered, and concentrated under a water-jet vacuum. Products **3fb**, **3hb**, **3ee**, **3he** were isolated by chromatography on SiO_2 eluting with PE-EtOAc in a linear gradient of the latter from 30 to 90 vol %.

*1-{[1-Acetyl-1-(4-chlorobenzyl)-2-oxopropoxy]carbonyl}-cyclopentanecarboxylic Acid (**3ee**).* Yield was 70% (593.2 mg, 1.56 mmol, $LaCl_3$ catalyst). White solid, mp = 85−86 °C. R_f = 0.42 (PE:EtOAc = 5:1 + 2% AcOH). ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 1.69−1.77 (m, 4H), 2.13 (s, 6H), 2.20−2.29 (m, 4H), 3.55 (s, 2H), 7.00 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 10.00 (br.s., 1H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 25.5, 27.1, 34.5, 38.8, 60.5, 94.6, 128.6, 131.4, 132.1, 133.5, 170.9, 177.7, 201.4. HRMS (ESI) m/z $[M + Na]^+$: Calcd for $[C_{19}H_{21}ClNaO_6]^+$: 403.0919. Found: 403.0908. Anal. calcd for $C_{19}H_{21}ClO_6$ C: 59.92%, H: 5.56%, Cl: 9.31%. Found C: 59.85%, H: 5.63%, Cl: 9.31%. IR (KBr): 3411, 2965, 2873, 1750, 1706, 1493, 1357, 1296, 1195, 1158 cm^{-1}.

*1-{[1-Benzyl-1-(ethoxycarbonyl)-2-oxopropoxy]carbonyl}-cyclopentanecarboxylic Acid (**3he**).* Yields: 38% (324.7 mg, 0.86 mmol, $LaCl_3$ catalyst), 34% (290.5 mg, 0.77 mmol, $La(NO_3)_3$ catalyst). White solid, mp = 68−69 °C. R_f = 0.48 (PE:EtOAc = 2:1 + 2% AcOH). ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 1.17 (t, J = 7.3 Hz, 3H), 1.63−1.75 (m, 4H), 2.11−2.30 (m, 7H), 3.47 (d, J = 13.9 Hz, 1H, CH_2), 3.54 (d, J = 13.9 Hz, 1H, CH_2), 4.08−4.20 (m, 2H), 7.03−7.15 (m, 2H), 7.18−7.26 (m, 3H), 10.47 (br.s., 1H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 13.7, 25.5, 27.4, 34.3, 34.4, 39.5, 60.3, 62.3, 88.8, 127.4, 128.3, 130.2, 133.6, 166.2, 170.6, 177.6, 201.5. HRMS (ESI) m/z $[M + Na]^+$: Calcd for $[C_{20}H_{24}NaO_7]^+$: 399.1414. Found: 399.1411. Anal. calcd for $C_{20}H_{24}O_7$ C: 63.82%, H: 6.43%. Found C: 63.54%, H: 6.48%. IR (thin layer): 2982, 2963, 2875, 1764, 1714, 1282, 1263, 1161, 1085, 1014, 704 cm^{-1}.

Byproduct **9** was isolated additionally with C−O coupling product **3he** in the case of $LaCl_3$ catalyst.

*Ethyl 2-benzyl-2-chloro-3-oxobutanoate (**9**).*[64] Yield of **9** was 40% (231.3 mg, 0.91 mmol). Colorless oil. R_f = 0.67 (PE:EtOAc = 10:1). ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 1.23 (t, J = 7.3 Hz, 3H), 2.24 (s, 3H), 3.43 (d, J = 14.7 Hz, 1H), 3.53 (d, J = 14.7 Hz, 1H), 4.15−4.27 (m, 2H), 7.16−7.30 (m, 5H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 13.8, 26.4, 42.2, 63.0, 75.2, 127.4, 128.2, 130.6, 134.0, 167.0, 198.8.

Byproduct **10** was isolated additionally with C−O coupling product **3he** in the case of $La(NO_3)_3$ catalyst.

*2-Benzyl-2-hydroxy-3-oxobutanoate (**10**).*[65] Yield of **10** was 50% (268.2 mg, 1.14 mmol). Colorless oil. R_f = 0.67 (PE:EtOAc = 5:1). ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 1.27 (t, J = 7.3 Hz, 3H), 2.26 (s, 3H), 3.17 (d, J = 14.1 Hz, 1H), 3.40 (d, J = 14.1 Hz, 1H), 4.06 (br.s., 1H), 4.21 (q, J = 7.3 Hz, 2H), 7.17−7.30 (m, 5H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 14.0, 25.1, 40.7, 62.8, 84.2, 127.1, 128.2, 130.1, 134.6, 170.5, 203.9.

General Procedure for Products 3bc, 3dc, 3dd. Malonyl peroxide **2c** or **2d** (504.9−560.3 mg, 3.94−4.07 mmol, 1.5 mol **2c or 2d**/1 mol substrate **1**) was added with stirring to a solution of diketone **1b** or **1d** (500.0 mg, 2.63−2.71 mmol) in $CHCl_3$ (10 mL) at room temperature. The reaction mixture was stirred at 40 °C for 6 h and cooled to 20−25 °C, and the solvent was removed using a water-jet vacuum pump. Products **3bc**, **3dc**, or **3dd** were isolated as described above.

*1-{[(1,1-Diacetylheptyl)oxy]carbonyl}cyclopropanecarboxylic Acid (**3bc**).* Yield was 90% (762.8 mg, 2.44 mmol). Colorless oil. R_f = 0.51 (PE:EtOAc = 2:1 + 2% AcOH). ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 0.85 (t, J = 7.3 Hz, 3H), 1.04−1.32 (m, 10H), 1.82−1.93 (m, 4H), 2.22 (s, 6H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 13.9, 21.7, 22.4, 23.4, 26.0, 26.4, 29.0, 31.3, 33.5, 96.1, 170.9, 173.3, 200.5. HRMS (ESI) m/z $[M + Na]^+$. Calcd for $[C_{16}H_{24}NaO_6]^+$: 335.1465. Found: 335.1465. Anal. calcd for $C_{16}H_{24}O_6$ C: 61.52%, H: 7.74%. Found C: 61.60%, H: 7.61%. IR (thin layer): 3412, 2958, 2931, 2861, 1740, 1716, 1417, 1359, 1332, 1187, 1154, 1131, 974, 527.

*1-[(1-Acetyl-1-benzyl-2-oxopropoxy)carbonyl]-cyclopropanecarboxylic Acid (**3dc**).* Yield was 92% (769.7 mg, 2.42 mmol). White solid, mp = 79−80 °C. R_f = 0.44 (PE:EtOAc = 2:1 + 2% AcOH). ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 1.53−1.59 (m, 2H), 1.75−1.80 (m, 2H), 2.14 (s, 6H), 3.61 (s, 2H), 6.95−7.01 (m, 2H), 7.24−7.28 (m, 3H), 10.87 (br.s., 1H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 21.7, 25.9, 26.8, 39.0, 95.6, 127.7, 128.7, 129.5, 133.2, 170.7, 173.1, 200.4. HRMS (ESI) m/z $[M + Na]^+$: Calcd for $[C_{17}H_{18}NaO_6]^+$: 341.0996. Found: 341.0994. Anal. calcd for $C_{19}H_{18}O_4$ C: 64.14%, H: 5.70%. Found C: 64.15%, H: 5.78%. IR (KBr): 3034, 3010, 2927, 1744, 1702, 1358, 1329, 1219, 1143, 919, 767, 719, 522 cm^{-1}.

*1-[(1-Acetyl-1-benzyl-2-oxopropoxy)carbonyl]-cyclobutanecarboxylic Acid (**3dd**).* Yield was 81% (707.5 mg, 2.13 mmol). Colorless oil. R_f = 0.27 (PE:EtOAc = 2:1 + 2% AcOH). ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 2.00 (quintet, J = 8.3 Hz, 2H), 2.14 (s, 6H), 2.57 (t, J = 8.3 Hz, 4H), 3.59 (s, 2H), 7.02−7.06 (m, 2H), 7.19−7.26 (m, 3H), 9.45 (br.s, 1H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 16.1, 27.1, 28.7, 39.4, 52.7, 94.7, 127.4, 128.4, 129.9, 133.6, 170.0, 176.7, 201.5. HRMS (ESI) m/z $[M + Na]^+$. Calcd for $[C_{18}H_{20}NaO_6]^+$: 355.1152. Found: 355.1148. Anal. calcd for $C_{18}H_{20}O_6$ C: 65.05%, H: 6.07%. Found C: 65.30%, H: 6.30%. IR (thin layer): 3065, 3004, 2957, 1741, 1714, 1417, 1358, 1280, 1201, 1134, 1109, 928, 705 cm^{-1}.

Experimental Procedure for 1-{[1-Benzyl-1-(ethoxycarbonyl)-2-oxopropoxy]carbonyl} cyclopropanecarboxylic Acid (3hc). $Eu(NO_3)_3{\cdot}6H_2O$ (200.7 mg, 0.45 mmol, molar ratio: 0.2 mol/1 mol oxoester **1h**) or $LaCl_3{\cdot}7H_2O$ (168.6 mg, 0.45 mmol, molar ratio: 0.2 mol/1 mol oxoester **1h**) or $La(NO_3)_3{\cdot}6H_2O$ (196.6 mg, 0.45 mmol, molar ratio: 0.2 mol/1 mol oxoester **1h**) was added with stirring to a solution of oxoester **1h** (500.0 mg, 2.27 mmol) in $CHCl_3$ or in 9:1 v/v $CHCl_3$/MeOH the case of $LaCl_3{\cdot}7H_2O$ (10 mL) at room temperature. The mixture was stirred at 20−25 °C for 5 min. Then cyclopropyl malonyl peroxide **2c** (436.1 mg, 3.4 mmol, molar ratio: 1.5 mol **2c**/1 mol oxoester **1h**) was added. The reaction mixture was stirred at 40 °C for 6 h, cooled to 20−25 °C. The resulting mixture was diluted with $CHCl_3$ (70 mL), and the organic layer was washed with H_2O (3 × 10 mL), dried over Na_2SO_4, filtered, and concentrated under a water-jet vacuum. Product **3hc** was isolated as described above. Yields: 23% (181.1 mg, 0.52 mmol, $Eu(NO_3)_3$ catalyst), 17% (134.4 mg, 0.39 mmol, $LaCl_3$ catalyst), 18% (142.35 mg, 0.41 mmol, $La(NO_3)_3$ catalyst). Colorless oil. R_f = 0.16 (PE:EtOAc= 2:1 + 2% AcOH). ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 1.20 (t, J = 7.3 Hz, 3H), 1.50−1.59 (m, 1H), 1.77−1.91 (m, 3H), 2.28 (s, 3H), 3.46 (s, 2H), 4.19 (q, J = 7.3 Hz, 2H), 6.98−7.07 (m, 2H), 7.24−7.32 (m, 3H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 13.8, 22.5, 25.4, 27.3, 39.7, 62.8, 89.2, 127.9, 128.6, 129.7, 132.9, 165.8, 169.8, 174.4, 199.4. HRMS (ESI) m/z $[M + Na]^+$: Calcd for $[C_{18}H_{20}NaO_7]^+$: 371.1101. Found: 371.1094. Anal. calcd for $C_{18}H_{20}O_7$ C: 62.06%, H: 5.79%. Found C: 62.01%, H: 5.93%. IR (KBr): 3118, 3066, 3033, 2985, 1760, 1739, 1699, 1417, 1368, 1270, 1186, 1150, 1086, 860, 703 cm^{-1}.

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Experimental Procedures for Scheme 2. *Alcoholysis of Spirocyclopentylmalonoyl Peroxide (**2e**).* Spirocyclopentylmalonoyl peroxide (**2e**) (500.0 mg, 3.20 mmol) was added with stirring to EtOH (5 mL) at room temperature. The reaction mixture was stirred at 20 °C for 6 h, and then it was concentrated under a water-aspirator vacuum. Products **11** and **12** were isolated by chromatography on SiO_2 with elution using PE-EtOAc in a linear gradient of EtOAc from 0 to 50 vol %. Yield of **11** was 70% (452.9 mg, 2.24 mmol, purity ≥95% based on ^1H and ^{13}C NMR), and the yield of **12** was 18% (107.0 mg, 0.57 mmol).

*1-(Ethoxycarbonyl)cyclopentanecarboperoxoic Acid (**11**).* Colorless oil. R_f = 0.39 (PE:EtOAc = 5:1). ^1H NMR (300.13 MHz, $CDCl_3$, δ): 1.24 (t, J = 7.3 Hz, 3H,), 1.65−1.77 (m, 4H), 2.18−2.29 (m, 4H), 4.18 (q, J = 7.3 Hz, 2H), 11.24 (br.s., 1H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 13.9, 25.3, 34.7, 58.5, 62.1, 170.9, 173.7. HRMS (ESI) m/z $[M + Na]^+$: Calculated for $[C_9H_{14}NaO_5]^+$: 225.0733. Found: 225.0729.

*1-(Ethoxycarbonyl)cyclopentanecarboxylic Acid (**12**).*[66] Colorless oil. R_f = 0.26 (PE:EtOAc = 5:1). ^1H NMR (300.13 MHz, $CDCl_3$, δ): 1.24 (t, J = 7.3 Hz, 3H), 1.64−1.75 (m, 4H), 2.15−2.25 (m, 4H), 4.18 (q, J = 7.3 Hz, 2H), 9.94 (br.s., 1H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 13.9, 25.5, 34.7, 60.3, 61.6, 172.3, 178.7.

*Hydroxylation of Oxoester **1h** by 1-(Ethoxycarbonyl)-cyclopentanecarboperoxoic Acid **11**.* $La(NO_3)_3{\cdot}6H_2O$ (97.5 mg, 0.23 mmol, molar ratio: 0.2 mol $La(NO_3)_3{\cdot}6H_2O$/1 mol oxoester **1h**) was added with stirring to a solution of oxoester **1h** (250.0 mg, 1.14 mmol) in EtOH (5 mL) at room temperature. The mixture was stirred at 20−25 °C for 5 min. Then 1-(ethoxycarbonyl)-cyclopentanecarboperoxoic acid **11** (345.8 mg, 1.71 mmol, molar ratio: 1.5 mol **11**/1 mol oxoester **1h**) was added. The reaction mixture was stirred at 40 °C for 6 h and cooled to 20−25 °C. The resulting mixture was diluted with $CHCl_3$ (40 mL), and the organic layer was washed with H_2O (3 × 5 mL), dried over Na_2SO_4, filtered, and concentrated under a water-jet vacuum. Product **10** was isolated by chromatography on SiO_2 with elution using PE-EtOAc in a linear gradient of latter from 0 to 50 vol %. Yield of **10** is 30% (80.3 mg, 0.34 mmol).

*Hydroxylation of Diketone **1d** by 1-(Ethoxycarbonyl)-cyclopentanecarboperoxoic Acid **11**.* 1-(Ethoxycarbonyl)-cyclopentanecarboperoxoic acid (**11**) (398.6 mg, 1.97 mmol, molar ratio: 1.5 mol **11**/1 mol diketone **1d**) was added with stirring to a solution of diketone **1d** (250.0 mg, 1.31 mmol) in EtOH (5 mL) at room temperature. The reaction mixture was stirred at 40 °C for 6 h and cooled to 20−25 °C. The resulting mixture was diluted with $CHCl_3$ (70 mL), and the organic layer was washed with H_2O (3 × 5 mL), dried over Na_2SO_4, filtered, and concentrated under a water-aspirator vacuum. Product **13** was isolated as described above. Yield of **13** is 71% (191.8 mg, 0.93 mmol).

*3-Benzyl-3-hydroxy-2,4-pentanedione (**13**).*[5] Colorless oil. R_f = 0.33 (PE:EtOAc= 10:1). ^1H NMR (300.13 MHz, $CDCl_3$, δ): 2.21 (s, 6H), 3.27 (s, 2H), 4.68 (s, 1H), 7.16−7.28 (m, 5H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 25.6, 41.8, 91.0, 127.2, 128.3, 130.0, 134.5, 206.6.

General Procedure for Scheme 3. $LaCl_3{\cdot}7H_2O$ (371.4−165.6 mg, 1.00−0.45 mmol, molar ratio: 0.2 mol $LaCl_3{\cdot}7H_2O$/1 mol substrate **4**) was added with stirring to a solution of substrate **4** (500.0 mg, 2.23−5.00 mmol) in EtOH (10 mL) at room temperature. The mixture was stirred at 20−25 °C for 5 min. Then diethylmalonyl peroxide **2b** (1410.5−3163.0 mg, 8.92−20.00 mmol, molar ratio: 4 mol **2b**/1 mol substrate **4**) was added. The reaction mixture was stirred at 40 °C for 6 h and cooled to 20−25 °C. The resulting mixture was diluted with $CHCl_3$ (70 mL), and the organic layer was washed with H_2O (3 × 10 mL), dried over Na_2SO_4, filtered, and concentrated under a water-jet vacuum. Products **5** were isolated by chromatography on SiO_2 with elution using PE- EtOAc in a linear gradient of EtOAc from 30 to 90 vol %.

*2,2′-[(2,4-Dioxopentane-3,3-diyl)bis(oxycarbonyl)]bis(2-ethylbutanoic Acid) (**5a**).* Yield was 58% (1206.2 mg, 2.90 mmol). White solid, mp = 116−120 °C. R_f = 0.22 (PE:EtOAc = 2:1 + 2% AcOH). ^1H NMR (300.13 MHz, $CDCl_3$, δ): 0.86−0.98 (m, 12H), 1.93−2.07 (m, 8H), 2.41 (s, 6H), 11.70 (br.s., 2H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 8.2, 25.8, 26.4, 58.6, 97.4, 168.7, 176.7, 198.9. HRMS (ESI) m/z $[M + Na]^+$: Calcd for $[C_{19}H_{28}NaO_{10}]^+$: 439.1575. Found: 439.1570. Anal. calcd for $C_{19}H_{28}O_{10}$ C: 54.80%, H: 6.78%. Found C: 54.91%, H: 6.97%. IR (KBr): 3400, 2981, 2969, 2885, 1776, 1724, 1458, 1422, 1353, 1241, 1205, 1119, 1054, 977 cm^{-1}.

*2,2′-[(1,3-Dioxo-1-phenylbutane-2,2-diyl)bis(oxycarbonyl)]bis(2-ethylbutanoic Acid) (**5b**).* Yield was 78% (1150.6 mg, 2.40 mmol). White solid, mp = 111−113 °C. R_f = 0.24 (PE:EtOAc = 2:1 + 2% AcOH). ^1H NMR (300.13 MHz, $CDCl_3$, δ): 0.84−0.97 (m, 12H), 1.88−2.07 (m, 8H), 2.52 (s, 3H), 7.39−7.44 (m, 2H), 7.49−7.56 (m, 1H), 7.91 (d, J = 7.3 Hz, 2H), 11.43 (br.s., 2H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 8.3, 8.4, 25.9, 26.5, 58.7, 98.7, 127.9, 129.7, 132.9, 134.9, 168.5, 176.7, 192.5, 198.9. HRMS (ESI) m/z $[M + Na]^+$: Calcd for $[C_{24}H_{30}NaO_{10}]^+$: 501.1731. Found: 501.1727. Anal. calcd for $C_{24}H_{30}O_{10}$ C: 60.24%, H: 6.32%. Found C: 60.18%, H: 6.30%. IR (thin layer): 3370, 3082, 2977, 2885, 2635, 1782, 1708, 1695, 1450, 1257, 1207, 1121, 1066, 902 cm^{-1}.

*2,2′-[(1,3-Dioxo-1-(4-methyl-phenyl)butane-2,2-diyl)bis-(oxycarbonyl)]bis(2-ethylbutanoic Acid) (**5c**).* Yield was 75% (1049.1 mg, 2.13 mmol). Colorless oil. R_f = 0.27 (PE:EtOAc = 2:1 + 2% AcOH). ^1H NMR (300.13 MHz, $CDCl_3$, δ): 0.84−1.03 (m, 12H), 1.88−2.10 (m, 8H), 2.39 (s, 3H), 2.50 (s, 3H), 7.21 (d, J = 8.1 Hz, 2H), 7.85 (d, J = 8.1 Hz, 2H), 11.38 (br.s., 1H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 8.3, 8.4, 21.7, 25.9, 26.4, 58.7, 99.1, 128.7, 130.0, 132.0, 144.1, 168.5, 176.5, 191.3, 198.8. HRMS (ESI) m/z $[M + Na]^+$: Calcd for $[C_{25}H_{32}NaO_{10}]^+$: 515.1888. Found: 515.1881. Anal. calcd for $C_{25}H_{32}O_{10}$ C: 60.97%, H: 6.55%. Found C: 60.81%, H: 6.59%. IR ($CHCl_3$): 3436, 2977, 2946, 2632, 1772, 1738, 1712, 1608, 1457, 1217, 1123, 1068, 906 cm^{-1}.

*2,2′-[(1,3-Dioxo-1,3-diphenylpropane-2,2-diyl)bis(oxycarbonyl)]-bis(2-ethylbutanoic Acid) (**5d**).* Yield was 65% (783.5 mg, 1.45 mmol). White solid, mp = 136−138 °C. R_f = 0.40 (PE:EtOAc = 2:1 + 2% AcOH). ^1H NMR (300.13 MHz, $CDCl_3$, δ): 0.75−0.83 (m, 12H), 1.87−1.95 (m, 8H), 7.35−7.46 (m, 4H), 7.50−7.55 (m, 2H), 8.03 (d, J = 7.33 Hz, 4H), 10.89 (br.s., 2H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 8.2, 25.5, 58.8, 100.2, 128.1, 129.9, 133.3, 134.5, 168.2, 176.9, 190.9. HRMS (ESI) m/z $[M + Na]^+$: Calcd for $[C_{29}H_{32}NaO_{10}]^+$: 563.1888. Found: 563.1892. Anal. calcd for $C_{29}H_{32}O_{10}$ C: 64.44%, H: 5.97%. Found C: 64.34%, H: 6.00%. IR (KBr): 3401, 3076, 2978, 1774, 1707, 1450, 1256, 1212, 1132, 1030, 930, 691 cm^{-1}.

*2,2′-[(1-Ethoxy-1,3-dioxobutane-2,2-diyl)bis(oxycarbonyl)]bis(2-ethylbutanoic Acid) (**5e**).* Yield was 68% (1165.8 mg, 2.61 mmol). White solid, mp = 100−102 °C. R_f = 0.43 (PE:EtOAc = 2:1 + 2% AcOH). ^1H NMR (300.13 MHz, $CDCl_3$, δ): 0.86−0.97 (m, 12H), 1.24 (t, J = 7.33 Hz, 3H), 1.93−2.02 (m, 8H), 2.43 (s, 3H), 4.23 (q, J = 7.32 Hz, 2H), 9.36 (br.s., 2H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 8.2, 13.6, 25.6, 25.7, 26.0, 58.6, 63.3, 94.2, 162.3, 168.8, 176.1, 197.2. HRMS (ESI) m/z $[M + Na]^+$. Calcd for $[C_{20}H_{30}NaO_{11}]^+$: 469.1680. Found: 469.1680. Anal. calcd for $C_{20}H_{30}O_{11}$ C: 53.81%, H: 6.77%. Found C: 53.78%, H: 6.71%. IR (KBr): 3084, 2980, 2887, 1787, 1710, 1458, 1259, 1104, 1070, 939, 568 cm^{-1}.

*2,2′-[(1-Ethoxy-1,3-dioxo-3-phenylpropane-2,2-diyl)bis-(oxycarbonyl)]bis(2-ethylbutanoic Acid) (**5f**).* Yield was 56% (740.7 mg, 1.46 mmol). White solid, mp = 120−122 °C. R_f = 0.45 (PE:EtOAc = 2:1 + 2% AcOH). ^1H NMR (300.13 MHz, $CDCl_3$, δ): 0.78−0.99 (m, 12H), 1.29 (t, J = 7.3 Hz, 3H), 1.85−2.06 (m, 8H), 4.33 (q, J = 7.3 Hz, 2H), 7.36−7.56 (m, 3H), 8.06 (d, J = 7.3 Hz, 2H), 11.75 (br.s., 2H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 8.1, 8.3, 13.8, 25.6, 58.9, 63.3, 96.2, 128.2, 129.5, 133.38, 133.45, 163.2, 168.3, 177.3, 188.0. HRMS (ESI) m/z $[M + Na]^+$. Calcd for $[C_{25}H_{32}NaO_{11}]^+$: 531.1837. Found: 531.1834. Anal. calcd for $C_{25}H_{32}O_{11}$ C: 59.05%, H: 6.34%. Found C: 59.05%, H: 6.53%. IR (KBr): 2978, 2885, 1782, 1756, 1703, 1450, 1273, 1133, 1090, 1054, 929 cm^{-1}.

Experimental Procedure for Scheme 4. One M $NaHCO_3$ (5 mL) was added with stirring to a solution of coupling product **5f** (508.5 mg, 1.0 mmol) in $CHCl_3$ (10 mL). The reaction mixture was stirred at 20−25 °C for 2 h. The 1 M HCl (5 mL) was added, and aqueous layer was extracted with chloroform (3 × 10 mL). The combined organic layers washed with H_2O (3 × 5 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure. Product **6f**

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was isolated by chromatography on SiO_2 with elution using PE-EtOAc in a linear gradient of EtOAc from 10 to 50 vol %. Yield of **6f** is 70% (157.0 mg, 0.70 mmol).

*Ethyl 2,3-dioxo-3-phenylpropanoate (**6f**).*[67] Yellow oil. R_f = 0.61 (PE:EtOAc = 2:1). Mixture of vicinal tricarbonyl compound and its hydrated form. ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 1.07 (t, J = 7.3 Hz, 1.8 H), 1.37 (t, J = 7.3 Hz, 1.2H), 4.20 (q, J = 7.3 Hz, 1.2H), 4.41 (q, J = 7.3 Hz, 0.8H), 5.35 (br.s., 0.8H), 7.42−7.71 (m, 3H), 7.96−8.12 (m, 2H). ^{13}C NMR (75.48 MHz, $CDCl_3$, δ): 13.6, 13.9, 63.2, 63.3, 91.6, 128.5, 128.7, 129.1, 130.0, 130.1, 131.4, 131.5, 133.7, 134.6, 135.5, 169.9, 183.8, 190.2, 191.6.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02233.

data about reaction conditions, ^{1}H and ^{13}C NMR spectra, HRMS and IR spectra of all new compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: terentev@ioc.ac.ru.

Notes

The authors declare no competing financial interest.

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