DOI: 10.1002/adsc.201300341

Oxidative C–O Cross-Coupling of 1,3-Dicarbonyl Compounds and Their Heteroanalogues with *N*-Substituted Hydroxamic Acids and *N*-Hydroxyimides

Alexander O. Terent′ev,[a,*] Igor B. Krylov,[a] Vladimir P. Timofeev,[b] Zoya A. Starikova,[c] Valentina M. Merkulova,[a] Alexey I. Ilovaisky,[a] and Gennady I. Nikishin[a]

[a] N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky Prospekt 47, 119991 Moscow, Russian Federation
Fax: (+7)-499-135-5328; phone: (+7)-499-137-2944; e-mail: terentev@ioc.ac.ru
[b] V. A. Engelhardt Institute of Molecular Biology, Russian Academy of Sciences, 32 Vavilova st., 119991 Moscow, Russian Federation
[c] A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilova st., 119991 Moscow, Russian Federation

Received: April 22, 2013; Published online: ■■ ▮▮, 0000

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201300341.

Abstract: The oxidative C–O cross-coupling of 1,3-dicarbonyl compounds and their heteroanalogues, 2-substituted malononitriles and cyanoacetic esters, with *N*-substituted hydroxamic acids and *N*-hydroxyimides was realized. The best results were obtained with the use of manganese(III) acetate [$Mn(OAc)_3$] or the cobalt(II) acetate catalyst [$Co(OAc)_{2cat.}$]/potassium permanganate [$KMnO_4$] system as the oxidant. The synthesis can be scaled up to gram quantities of coupling products; yields are 30–94%. The reaction proceeds *via* a radical mechanism through the formation of nitroxyl radicals from *N*-substituted hydroxamic acids and *N*-hydroxyimides.

Keywords: cobalt; coupling; hydroxamic acids; hydroxyimides; manganese; oxidation

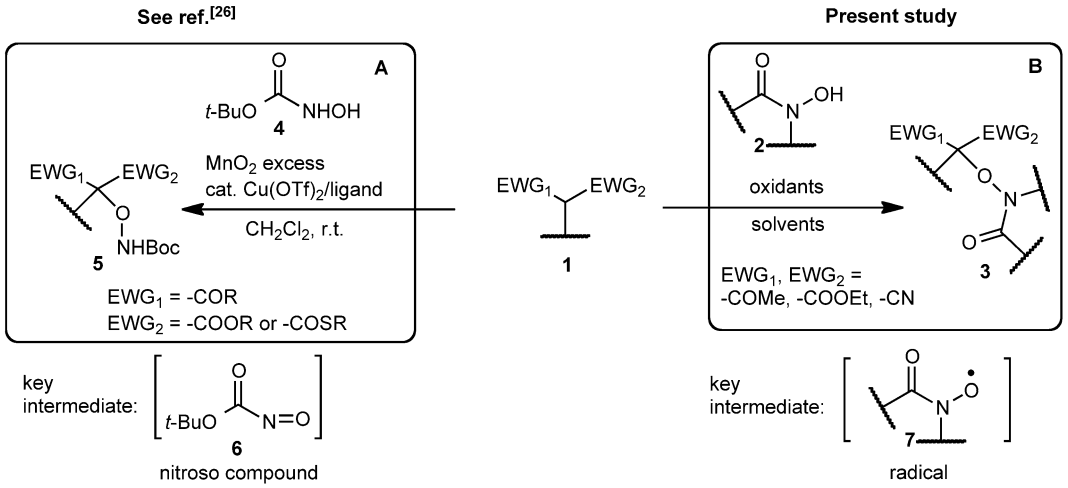
Introduction

The oxidative C–C cross-coupling with the involvement of 1,3-dicarbonyl compounds is one of the prominent fields of modern organic synthesis. Methods were developed for the coupling of 1,3-diketones, keto esters, diesters, and keto amides with a wide range of organic compounds, such as amines,[1–4] amides,[5] ethers,[4,6,7] thioethers,[4,8] alkanes,[9] indoles,[10] and compounds containing benzyl[1–4,6–8,11–16] or allyl[13,17] moieties. Peroxides, oxygen, or quinones combined with inexpensive transition metal salts (copper, iron, cobalt, and manganese salts) are generally used as oxidants, thus enabling the adaptation of these methods in laboratory practice.

Oxidative C–O coupling reactions were developed to a much lesser extent compared to the C–C cross-coupling. The development of these methods is limited by the ease of side oxidation reactions of the starting molecules giving alcohols, carbonyl compounds, and fragmentation products. The nucleophilic substitution is still the main method used for the introduction of OR groups into the molecules to form the C(sp^3)–OR moiety. The disadvantage of this approach is the necessity to introduce a leaving group (Hal, OH, OTs, and so on) into the molecule. Besides, nucleophilic substitution reactions are often accompanied by side elimination reactions.

Most of the known oxidative C–O coupling reactions with the participation of 1,3-dicarbonyl compounds were performed with the use of iodine-containing oxidants.[18–25] These reactions proceed *via* an ionic mechanism involving the attack of the electrophilic iodine atom on the enol of the dicarbonyl compound followed by the replacement of the iodine-containing moiety by a O-nucleophile to form a C–O coupling product.[18–21] Iodine compounds were used to perform the coupling reactions of dicarbonyl compounds with alcohols,[18,22,23] sulfonic acids,[18,19,21,22,24] carboxylic acids,[18,25] and phosphorus compounds.[18,20]

Our aim was to expand the scope of the oxidative C–O coupling. For this purpose, we performed for the



Scheme 1. Oxidative C–O cross-coupling of dicarbonyl compounds and their heteroanalogues **1** with *N*-substituted hydroxylamines **2** and **4**.

first time the oxidative C–O cross-coupling of *N*-substituted hydroxamic acids and *N*-hydroxyimides **2** with β-dicarbonyl compounds, diketones, keto esters, diesters, and 2-substituted malononitriles and cyanoacetic esters **1** (Scheme 1, reaction **B**). Under the optimized conditions, a wide variety of the previously unknown products **3** was synthesized, including sterically hindered compounds. Recently, structurally related products **5** have been synthesized by the enantioselective O-nitrosocarbonyl aldol reaction of β-keto esters and β-keto thioesters (Scheme 1, reaction **A**).[26]

The reaction **A** produces nitrosocarbonyl intermediate BocNO **6** from hydroxamic acid analogue BocNHOH **4**, and the N=O bond in this intermediate exhibits electrophilic properties in the reaction with dicarbonyl compound **1**. The nitrosocarbonyl intermediates can also be involved in the ene reaction[26–29] and the Diels–Alder cyclization.[26,30] *N*-Substituted hydroxamic acids and *N*-hydroxyimides **2**[31–33] used in the present study show a radically different reactivity. The reactions of these compounds with oxidizing agents produce nitroxyl radicals **7**.[33–35] The latter can add to the double bond,[36–42] abstract hydrogen atoms from the benzylic,[43–49] allylic,[47,50] or propargylic[44,51] positions, from the α-position of alcohols,[46,52] ethers,[46,47,53] and from tertiary and secondary carbon atoms of alkanes.[36,37,44,49,54]

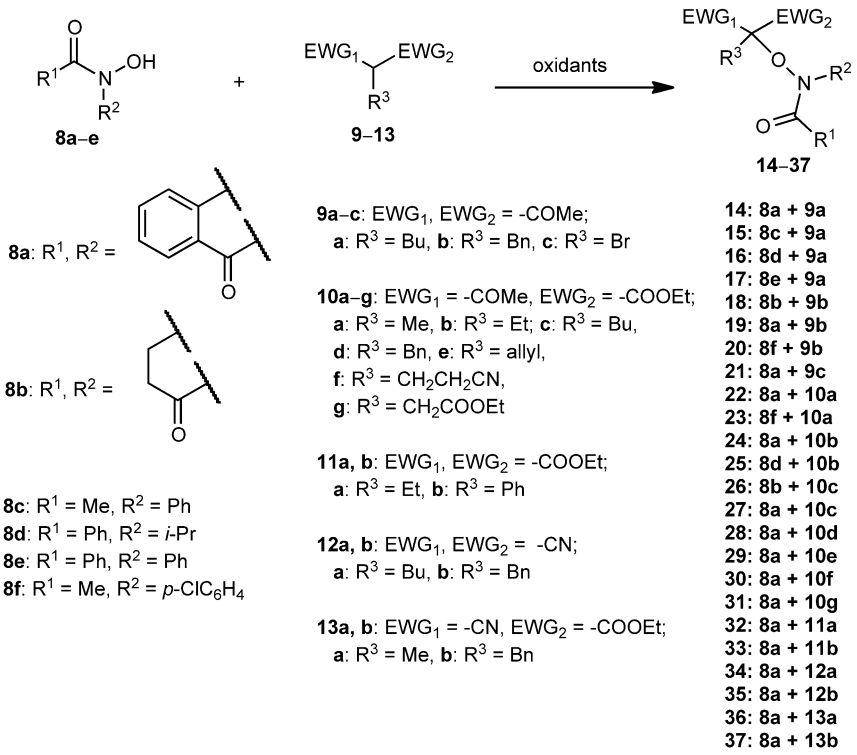
A few reactions with the involvement of dicarbonyl compounds, which are related to that investigated in the present study, were described in the literature: the oxidative coupling with stable 4-methoxy-2,6-diphenylphenoxyl radicals,[55] with *t*-BuOOH in the presence of transition metal salts,[56] with stable nitroxyl radical TEMPO (2,2,6,6-tetramethylpiperidine 1-oxyl) in the presence of a strong base and the oxidant $CuCl_2$ or $Fe(cp)_2PF_6$,[57,58] or under photocatalytic conditions.[59] To the best of our knowledge, only isolated examples of oxidative C–O[60] and C–C[1] coupling reactions with malononitrile and cyanoacetic ester derivatives are reported.

Target products **3** have attracted interest because of a wide range of biological activities of structurally related compounds.[61–67] The products of the coupling with *N*-hydroxyphthalimide (NHPI) are of special interest. Compounds containing the phthalimide *N*-oxyl moiety serve as convenient precursors of *O*-substituted hydroxylamines due to the ease of removal of the phthalic acid moiety. They are used in the synthesis of compounds having specific antagonistic,[68] inhibitory,[69,70] antiprotozoal,[71,72] and fungicidal[73–75] activities. This is why we have paid special attention to the coupling with NHPI and performed numerous experiments on these reactions. In turn, 1,3-dicarbonyl compounds, malononitrile and cyanoacetic ester derivatives are key intermediates in the synthesis of heterocyclic compounds.

Results and Discussion

The starting reagents used for the study were *N*-hydroxyphthalimide **8a**, *N*-hydroxysuccinimide **8b**, *N*-hydroxy-*N*-phenylacetamide **8c**, *N*-hydroxy-*N*-isopropylbenzamide **8d**, *N*-hydroxy-*N*-phenylbenzamide **8e**, and *N*-(4-chlorophenyl)-*N*-hydroxyacetamide **8f** combined with 2-substituted acetylacetones **9a–c**, acetoacetic esters **10a–g**, malonic esters **11a** and **b**, malononitriles **12a** and **b**, and cyanoacetic esters **13a** and **b** (Scheme 2).

In the first step, to find the optimal conditions, we studied the oxidative coupling of ethyl 2-acetylhexanoate **10c** with NHPI **8a** (Table 1). The reactions were performed in CH_3COOH, MeCN, EtOAc, and $CHCl_3$



Scheme 2. Oxidative C–O cross-coupling of dicarbonyl compounds **9**–**11** and their heteroanalogues **12** and **13** with *N*-hydroxyimides **8a** and **b** and *N*-substituted hydroxamic acids **8c–f**.

at temperatures from 25 to 80 °C with the use of different oxidants.

Manganese, cobalt, cerium, copper, lead, iron, and chromium salts (runs 1–24), metal-oxygen and metal-peroxide systems (runs 25–29), and peroxides (runs 30–32) were used as the oxidants.

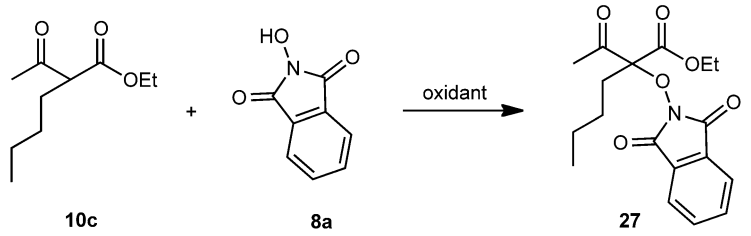
The best results were obtained with the use of the one-electron oxidants $Mn(OAc)_3$ (runs 1–3), CAN (run 19), and the $Co^{2+}_{cat.}/KMnO_4$ system (runs 12–15). We suppose that in the latter case, Co^{2+} is transformed into Co^{3+}, and the latter acts as the oxidant. The generation of phthalimide *N*-oxyl radicals (PINO) from NHPI in the presence of $Mn(OAc)_3$ was confirmed by ESR spectroscopy (see the Supporting information). It is known that CAN,[48] the Co^{2+}/oxidant system,[31–33,36,37,45,51–54] and $Pb(OAc)_4$[76,77] generate PINO radicals from NHPI. However, the reaction under study with $Pb(OAc)_4$ is characterized by a low conversion of **10c** and low selectivity (run 20). The yield of coupling product **27** in the reactions with the use of the $Co^{2+}/KMnO_4$ and $Co^{2+}/Pb(OAc)_4$ systems (runs 12–15 and 21) is substantially higher than that in the reactions with the oxidants $KMnO_4$ and $Pb(OAc)_4$ (runs 10, 11 and 20). The salts $Mn(OAc)_3$[78,79] and CAN[80,81] and the Co^{2+}/oxidant system[82–84] have found use in the oxidative addition of 1,3-dicarbonyl compounds to alkenes proceeding *via* the one-electron oxidation of the former. Therefore, the experimental results and the literature data suggest that the oxidant in the reaction under study is involved both in the one-electron oxidation of 1,3-dicarbonyl compounds and the oxidation of NHPI to form PINO.

Cobalt acetate catalyzes the oxidative coupling in the presence of oxygen (run 26) or peroxides (runs 28–29), but this reaction is accompanied by the hydroxylation of keto ester **10c** to form ethyl 2-acetyl-2-hydroxyhexanoate **38**. The reactions with the use of peroxides in the absence of metal salts are characterized by a low conversion of **10c**, and the target product was not detected (runs 30–32).

The optimal temperature for this reaction is 60 °C. Thus, the reduction of the temperature leads to a substantial decrease in the yield with retention of the complete conversion of keto ester **10c** (runs 4 and 5 *versus* run 1), whereas the yield remains unchanged as the temperature is raised to 80 °C (run 3). In runs 2 and 14 with the use of $Mn(OAc)_3 \cdot 2H_2O$ and $Co(OAc)_2/KMnO_4$ at 60 °C, the complete conversion of **10c** was achieved in 10 min. In runs 6–8 with $Mn(OAc)_3 \cdot 2H_2O$, the use of MeCN, EtOAc, or $CHCl_3$ instead of CH_3COOH leads to a decrease in the yield of **27** and the conversion of **10c**.

All reactions were carried out in air; the reaction performed under an argon atmosphere (run 15) afforded the target product in approximately the same yield.

Table 1. Effect of the nature of the oxidant, the solvent, the temperature, and the reaction time on the yield of oxidative coupling product **27**.[a]



10c **8a** **27**

Run	Oxidant (mole of the oxidant per mole of **10c**)	Temperature [°C]	Solvent	Conversion of **10c** [%]	Yield of **27** [%]
1	$Mn(OAc)_3{\cdot}2H_2O$ (2)	60	CH_3COOH	100	87
2[b]	$Mn(OAc)_3{\cdot}2H_2O$ (2)	60	CH_3COOH	100	87
3[b]	$Mn(OAc)_3{\cdot}2\,H_2O$ (2)	80	CH_3COOH	100	87
4	$Mn(OAc)_3{\cdot}2H_2O$ (2)	40	CH_3COOH	100	71
5	$Mn(OAc)_3{\cdot}2H_2O$ (2)	25	CH_3COOH	100	55
6	$Mn(OAc)_3{\cdot}2H_2O$ (2)	60	MeCN	92	48
7	$Mn(OAc)_3{\cdot}2H_2O$ (2)	60	EtOAc	45	16
8	$Mn(OAc)_3{\cdot}2H_2O$ (2)	60	$CHCl_3$	52	33
9	MnO_2 (1)	60	CH_3COOH	100	46
10	$KMnO_4$ (0.4)	60	CH_3COOH	100	39
11[c]	$KMnO_4$ (0.4)	60	CH_3COOH	100	63
12	$Co(NO_3)_2{\cdot}6H_2O$ (0.05); $KMnO_4$ (0.4)	60	CH_3COOH	100	80
13	$Co(OAc)_2{\cdot}4H_2O$ (0.05); $KMnO_4$ (0.4)	60	CH_3COOH	100	80
14[b]	$Co(OAc)_2{\cdot}4H_2O$ (0.05); $KMnO_4$ (0.4)	60	CH_3COOH	100	81
15[d]	$Co(OAc)_2{\cdot}4H_2O$, (0.05); $KMnO_4$, (0.4)	60	CH_3COOH	100	82
16	$Mn(OAc)_2{\cdot}4H_2O$ (0.05); $KMnO_4$ (0.4)	60	CH_3COOH	100	45
17	$Cu(OAc)_2{\cdot}H_2O$ (0.05); $KMnO_4$ (0.4)	60	CH_3COOH	100	44
18	$Fe(NO_3)_3{\cdot}9H_2O$ (0.05); $KMnO_4$ (0.4)	60	CH_3COOH	100	45
19	CAN (2)	60	CH_3COOH	100	74
20	$Pb(OAc)_4$ (1)	60	CH_3COOH	41	12
21	$Co(OAc)_2{\cdot}4H_2O$ (0.05); $Pb(OAc)_4$ (1)	60	CH_3COOH	86	61
22	$Cu(OAc)_2{\cdot}H_2O$ (2)	60	CH_3COOH	9	0
23	$FeCl_3$ (2)	60	CH_3COOH	13	0
24	$Co(OAc)_2{\cdot}4H_2O$ (0.05); $K_2Cr_2O_7$ (0.33)	60	CH_3COOH	100	50
25[e]	$Mn(OAc)_2{\cdot}4H_2O$ (0.05), O_2	60	CH_3COOH	28	0
26[e,f]	$Co(OAc)_2{\cdot}4H_2O$ (0.05), O_2	60	CH_3COOH	100	41
27	$Mn(OAc)_2{\cdot}4H_2O$ (0.05); $(NH_4)_2S_2O_8$ (1)	60	CH_3COOH	55	0
28[f]	$Co(OAc)_2{\cdot}4H_2O$ (0.05); $(NH_4)_2S_2O_8$ (1)	60	CH_3COOH	100	37
29[f]	$Co(OAc)_2{\cdot}4H_2O$ (0.05); H_2O_2 35% aq. (1.0)	60	CH_3COOH	100	35
30	MCPBA (1)	60	CH_3COOH	30	0
31	BzOOBz (1)	60	CH_3COOH	9	0
32	$(NH_4)_2S_2O_8$ (1)	60	CH_3COOH	5	0

[a] *General reaction conditions:* the oxidant was added with stirring for 30 s to a mixture of ethyl 2-acetylhexanoate **10c** (200 mg, 1.07 mmol), NHPI **8a** (175 mg, 1.07 mmol) and 5 mL of the solvent, which was heated to the specified temperature, and then the reaction mixture was stirred at the same temperature for 45 min. In runs 12–18, 21, 24, and 27–29, the salts $Co(OAc)_2{\cdot}4H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $Mn(OAc)_2{\cdot}4H_2O$, $Cu(OAc)_2{\cdot}H_2O$. or $Fe(NO_3)_3{\cdot}9H_2O$ were added 1 min before the addition of the oxidant.

[b] The reaction time was 10 min.

[c] $KMnO_4$ was added portionwise for 5 min.

[d] The reaction was performed under an argon atmosphere.

[e] Oxygen was bubbled through the reaction mixture (0.3 mL s^{-1}).

[f] Ethyl 2-acetyl-2-hydroxyhexanoate **38** was isolated as the by-product in 35–40 % yield.

Under the optimized conditions of the synthesis of **27** (Table 1, runs 2 and 14), we performed the oxidative coupling of *N*-hydroxyimides **8a** and **b** and *N*-substituted hydroxamic acids **8c–f** with 1,3-dicarbonyl compounds **9–11** and their heteroanalogues **12** and **13** (Table 2). Disadvantages of the oxidants $Mn(OAc)_3$ and CAN are their relatively high cost and large consumption. Thus, at least two moles of the oxidant are

Table 2. Oxidative coupling of *N*-hydroxyimides **8a** and **b** and *N*-substituted hydroxamic acids **8c–f** with 1,3-dicarbonyl compounds **9–11** and their heteroanalogues **12** and **13**.[a,b]

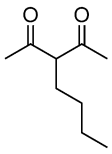
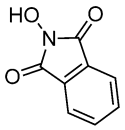
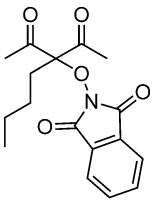
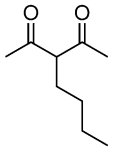
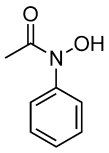
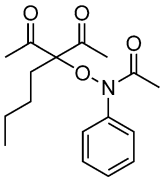
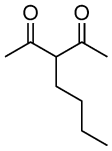
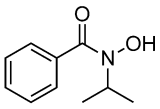
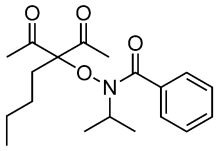
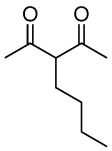
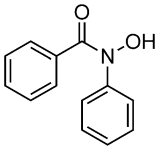
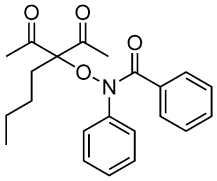
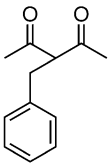
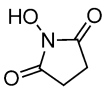
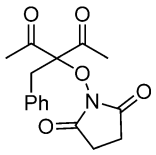
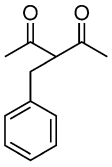
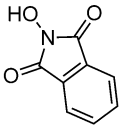
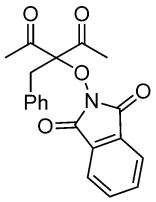
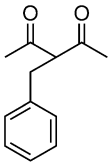
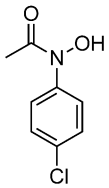
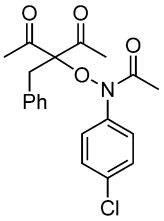
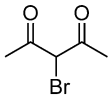
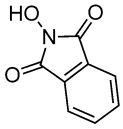
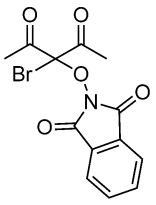
Run	C–H Reactant	N–OH Reactant	Products **14–37**	Yield [%] (conversion of **9–13** [%])
1	**9a** 	**8a** 	**14** 	77 (100)[b]
2	**9a** 	**8c** 	**15** 	72 (100),[a] 63 (100)[b]
3	**9a** 	**8d** 	**16** 	80 (100)[a]
4	**9a** 	**8e** 	**17** 	85 (100)[a]
5	**9b** 	**8b** 	**18** 	47 (100)[a]
6	**9b** 	**8a** 	**19** 	75 (100)[a]
7	**9b** 	**8f** 	**20** 	79 (100)[a]
8	**9c** 	**8a** 	**21** 	90 (100)[a]

Table 2. (Continued)

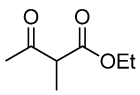
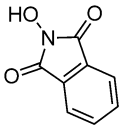
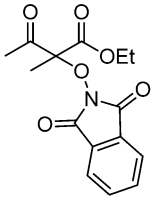
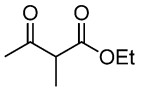
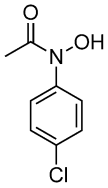
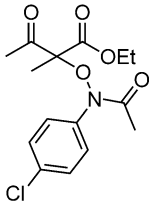
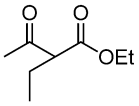
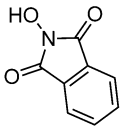
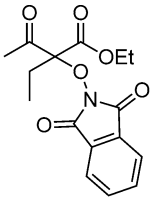
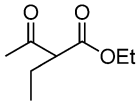
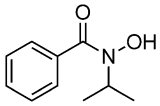
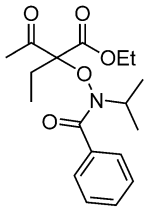
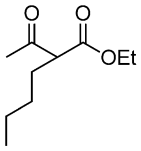
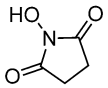
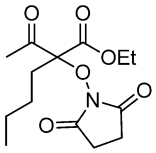
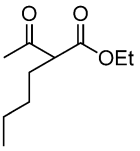
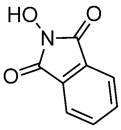
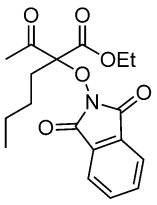
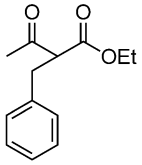
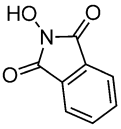
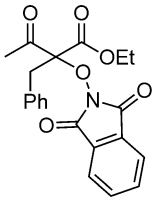
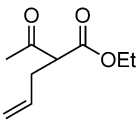
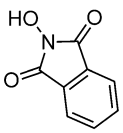
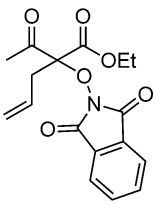
Run	C–H Reactant	N–OH Reactant	Products **14**–**37**	Yield [%] (conversion of **9**–**13** [%])
9	**10a** 	**8a** 	**22** 	90 (100)[b]
10	**10a** 	**8f** 	**23** 	78 (100),[a] 57 (78)[c]
11	**10b** 	**8a** 	**24** 	94 (100)[b]
12	**10b** 	**8d** 	**25** 	44 (100)[a]
13	**10c** 	**8b** 	**26** 	85 (100)[b]
14	**10c** 	**8a** 	**27** 	87 (100),[a] 81 (100),[b] 82 (100)[d]
15	**10d** 	**8a** 	**28** 	83 (100)[b]
16	**10e** 	**8a** 	**29** 	81 (100),[a] 77 (100)[b]

Table 2. (Continued)

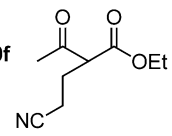
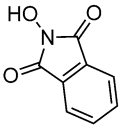
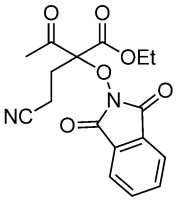
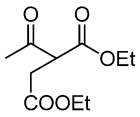
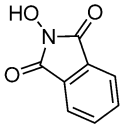
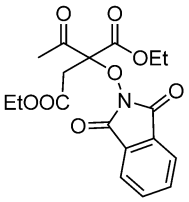
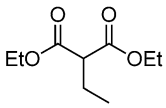
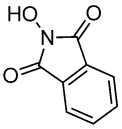
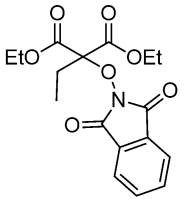
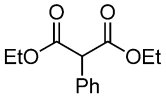
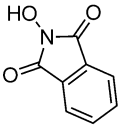
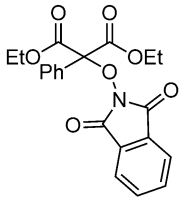
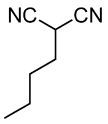
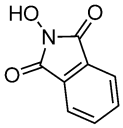
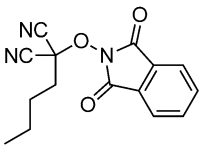
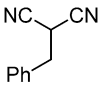
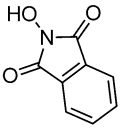
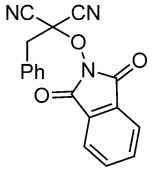
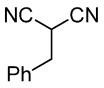
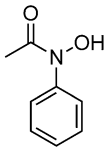
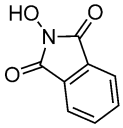
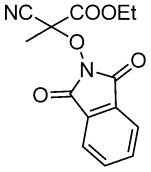
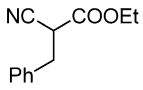
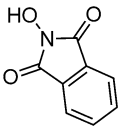
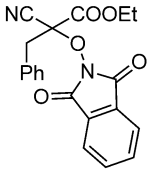
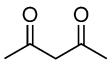
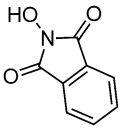
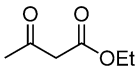
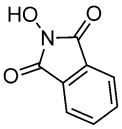
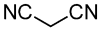
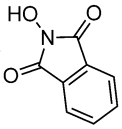
Run	C–H Reactant	N–OH Reactant	Products **14**–**37**	Yield [%] (conversion of **9**–**13** [%])
17	**10f** 	**8a** 	**30** 	90 (100)[b]
18	**10g** 	**8a** 	**31** 	93 (100),[a] 88 (100)[b]
19	**11a** 	**8a** 	**32** 	0 (5),[a or b] 30 (40),[e] 30 (59),[f] 30 (55)[g]
20	**11b** 	**8a** 	**33** 	50 (60),[a] 67 (81)[e]
21	**12a** 	**8a** 	**34** 	60 (82)[a]
22	**12b** 	**8a** 	**35** 	80 (96),[a] 55 (63)[b]
23	**12b** 	**8c** 		0 (4)[a]
24	**13a**	**8a** 	**36** 	51 (62)[a]

Table 2. (Continued)

Run	C–H Reactant	N–OH Reactant	Products **14**–**37**	Yield [%] (conversion of **9**–**13** [%])
25	**13b** 	**8a** 	**37** 	61 (70)[a]
26		**8a** 		0
27		**8a** 		0
28		**8a** 		0

[a] *Method A:* $Mn(OAc)_3 \cdot 2H_2O$ (0.453–1.62 g, 1.69–6.06 mmol, 2 moles per mole of the C-H reactant) was added with stirring for 30 s to a warm (60 °C) mixture of C–H reactant **9**–**13**, acetylacetone, acetoacetic ester or malononitrile (200 mg, 0.846–3.03 mmol), O–H reactant **8a–f** (121–493 mg, 0.846–3.03 mmol, 1 mole per mole of the C–H reactant), and CH_3COOH (4.2–15 mL, 5 mL per mmole of the C–H reactant), and then the mixture was stirred at 60°C for 10 min.

[b] *Method B:* $Co(OAc)_2 \cdot 4H_2O$ (11.3–17.3 mg, 45.4–69.3 μmol, 0.05 mole per mole of the C–H reactant) was added with stirring to a warm (60 °C) mixture of C–H reactant **9**–**12** (200 mg, 0.908–1.39 mmol), O–H reactant **8a**, **b**, or **c** (124–226 mg, 0.908–1.39 mmol, 1 mole per mole of the C–H reactant), and CH_3COOH (4.5–7 mL, 5 mL per mmole of the C–H reactant); after 1 min, $KMnO_4$ (57.4–87.7 mg, 0.363–0.555 mmol, 0.4 mole per mole of the C-H reactant) was added for 30 s, and then the mixture was stirred at 60°C for 10 min.

[c] The reaction was performed according to method A, but a double amount of *N*-(4-chlorophenyl)acethydroxamic acid **8f** was used.

[d] The synthesis was performed according to method B, but the amounts of the reactants were increased by a factor of 10.

[e] The reaction was performed according to method A but at 80 °C

[f] The reaction was performed according to method A but at 80 °C; the reaction time was 45 min.

[g] The reaction was performed according to method A but under reflux (111–113 °C), the reaction time was 4 min.

required for the formation of one mole of the product. From this point of view, the $Co(OAc)_{2cat.}/KMnO_4$ system has advantages, because it includes inexpensive potassium permanganate and only 0.4 mole of the oxidant is consumed per mole of the product. Further experiments were performed according to two procedures: with the use of $Mn(OAc)_3$ (method A) and the $Co(OAc)_{2cat.}/KMnO_4$ system (method B).

As can be seen from Table 2, the coupling reaction proceeds efficiently with the use of structurally different *N*-hydroxyimides, *N*-substituted hydroxamic acids, 1,3-keto esters, and 1,3-diketones (runs 1–18). The oxidative coupling of acetylacetone derivatives **9a–c** and acetoacetic ester derivatives **10a–g** afforded products **14**–**31** in high yields (up to 94%), despite the fact that the starting compounds contain bulky substituents near the reaction centers or the easily oxidizable benzyl and allyl moieties (runs 6, 15, 16), which can react with PINO.[36–38,43–50]

We also successfully performed the oxidative coupling with 2-substituted malonic esters, malononitriles, and cyanoacetic esters (runs 19–25). These reactants exhibit lower reactivity compared to 1,3-diketones and keto esters. Thus, the incomplete conversion of compounds **11**–**13** was observed, and the coupling occurred only with NHPI. The reaction of benzylmalo-

nodinitrile **12b** with NHPI afforded coupling product **35** in 80% yield (run 22). An attempt to perform the coupling of the same dinitrile with *N*-phenylacethydroxamic acid **8c** (run 23) resulted in the recovery of starting **12b**. This fact can be attributed to the lower reactivity of nitroxyl radicals generated from *N*-substituted hydroxamic acids compared to the PINO radical generated from NHPI.[85] Coupling product **32** was synthesized by the coupling of diethyl ethylmalonate **11a** with NHPI at 80 °C. At 60 °C, the reaction does not proceed (run 19). A further increase in the reaction temperature and time does not lead to an increase in the yield of **32** (run 19, footnotes [e]–[g]).

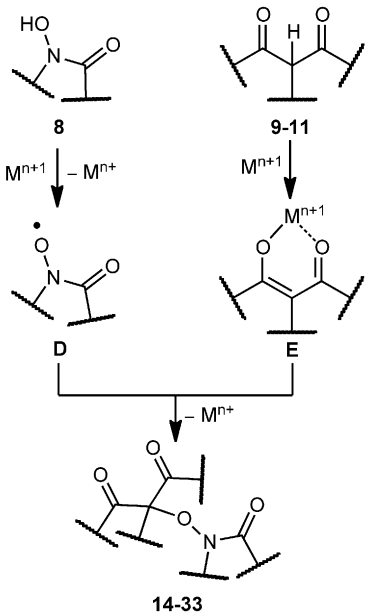
The investigation of the reaction of ethyl 2-methylacetoacetate **10a** with *N*-(4-chlorophenyl)acethydroxamic acid **8f** (run 10) showed that the doubling of the amount of hydroxamic acid **8f** leads to a decrease in the yield of coupling product **23** and the conversion of keto ester **10a** (run 10, footnote [c]). Apparently, in the presence of an excess of hydroxamic acid, $Mn(OAc)_3$ is consumed for its oxidation to the nitroxyl radical. This result additionally confirms the involvement of the oxidant not only in the generation of nitroxyl radicals but also in the oxidation of dicarbonyl compounds.

All β-dicarbonyl compounds and their heteroanalogues, which were successfully involved in the coupling reactions, contain a substituent in the α position. Coupling products are not obtained from compounds containing no substituents in this position (runs 26–28). Thus, the reaction of ethyl butyrylacetate **39** with NHPI in the presence of $Mn(OAc)_3$ gives phthalimide **40**, *N*-butyryloxyphthalimide **41**, and *N*-acetoxyphthalimide **42**. The probable pathway of the reaction yielding products **40**–**42** is shown in Scheme 3.

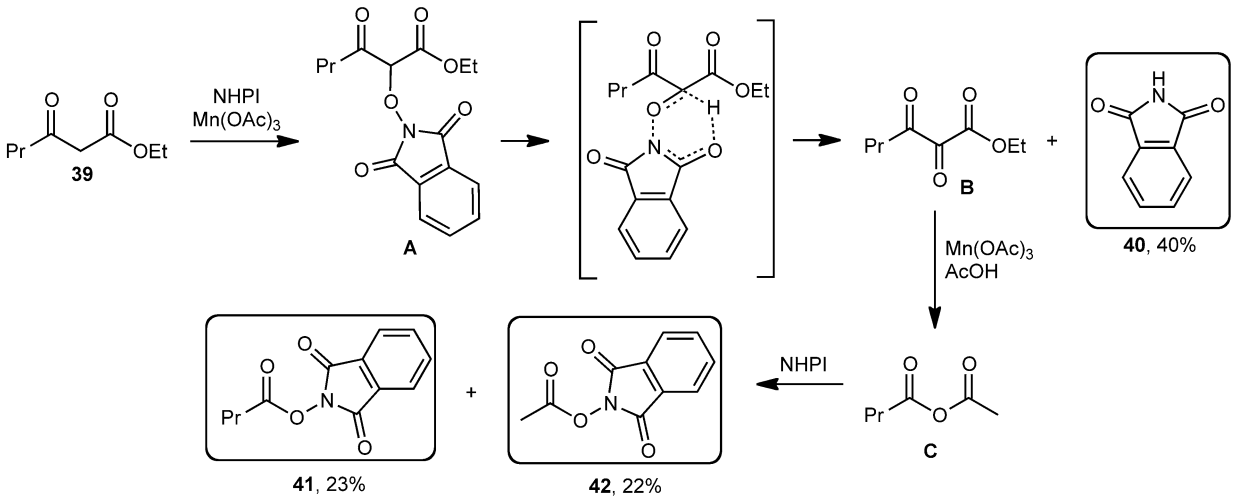
The initially formed target oxidative coupling product **A** undergoes the fragmentation under the reaction conditions to give phthalimide **40** and the tricarbonyl compound **B**. The latter transforms into anhydride **C**, which reacts with NHPI to form **41** and **42**. *N*-Alkoxyphthalimides undergo similar fragmentation at high temperatures[86] or at room temperature in the presence of a ruthenium-containing catalyst under visible light.[87]

The plausible pathway for the oxidative coupling of 1,3-dicarbonyl compounds with *N*-hydroxyimides and *N*-substituted hydroxamic acids is depicted in Scheme 4.

The nitroxyl radicals **D** are generated from hydroxylamine derivatives **8** in the presence of the oxidant. The reaction of the radical **D** with the enolate **E** af-



Scheme 4. Plausible pathway of the oxidative coupling of 1,3-dicarbonyl compounds with *N*-hydroxyimides and *N*-substituted hydroxamic acids.



Scheme 3. Plausible pathway of the reaction of ethyl butyrylacetate **39** with NHPI and $Mn(OAc)_3$.

fords coupling products **14**-**33**. In this step, the metal in the complex **E** is necessary for the one-electron oxidation of the dicarbonyl compound. The coupling with 2-substituted malononitriles **12a** and **b** and 2-substituted cyanoacetic esters **13a** and **b** apparently proceeds *via* a similar mechanism. The formation of the nitroxyl radicals **D** in the reaction mixture was confirmed by the ESR study of the coupling of NHPI with ethyl 2-acetylhexanoate (see the Supporting information).

To the best of our knowledge all oxidative coupling products **14**–**37** are new. All these products were characterized by ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy, elemental analysis, EI mass spectrometry, and HR-MS. The structure of compound **19** was additionally confirmed by X-ray diffraction (see the Supporting information).

Conclusions

The available approaches to the coupling of two organic molecules accompanied by the C–O bond formation are generally based on the substitution reactions with the use of O-nucleophiles. In this work, we propose a new oxidative C–O cross-coupling based on the reaction of 2-substituted 1,3-dicarbonyl compounds and their heteroanalogues with O-centered radicals generated *in situ* from *N*-substituted hydroxamic acids and *N*-hydroxyimides in the presence of metal-containing oxidants. The best results were obtained with the use of $Mn(OAc)_3$ or the $Co(OAc)_{2cat}$/$KMnO_4$ system.

The oxidative coupling occurs only with 1,3-dicarabonyl compounds containing a substituent at position 2. The coupling products generated from 2-unsubstituted 1,3-dicarbonyl compounds apparently undergo fragmentation under the reaction conditions.

The developed approach was used to synthesize a wide structural series of new multifunctionalized compounds, which can be used in the synthesis of hydroxylamine derivatives and heterocyclic compounds.

Experimental Section

The NMR spectra were recorded on a Bruker AM-300 spectrometer (300.13 MHz for ^{1}H and 75.48 MHz for ^{13}C) in $CDCl_3$. The IR spectra were recorded on a Bruker ALPHA FT-IR spectrometer. Mass spectra were recorded using Kratos MS 30 mass spectrometer. High resolution mass spectra (HR-MS) were measured on a Bruker maXis instrument using electrospray ionization (ESI).[88] The measurements were performed in a positive ion mode (interface capillary voltage was 4500 V); the mass range from *m*/*z* 50 to *m*/*z* 3000 Da; external calibration with Electrospray Calibrant Solution (Fluka). The syringe injection was used for all acetonitrile solutions (flow rate was 3 μL min^{-1}). Nitrogen was used as the dry gas; the interface temperature was set at 180 °C. The melting points were determined on a Köfler hot stage and are uncorrected.

Column chromatography was performed on SiO_2 (0.060–0.200 mm, 60 A, Acros). Commercial CH_2Cl_2, $CHCl_3$, ethyl acetate, MeCN, and acetic acid of high purity grade were used as is.

$Mn(OAc)_3{\cdot}2H_2O$ 98%, MnO_2 80–85%, $KMnO_4$ 99+%, $Co(NO_3)_2{\cdot}6H_2O$ 99+%, $Co(OAc)_2{\cdot}4H_2O$ 98–102%, $Mn(OAc)_2{\cdot}4H_2O$ 99+%, $Cu(OAc)_2{\cdot}H_2O$ 98+%, $Fe(NO_3)_3{\cdot}9H_2O$ 99+%, $(NH_4)_2Ce(NO_3)_6$ 99%, $Pb(OAc)_4$ 95% stabilized, $FeCl_3$ 98%, $K_2Cr_2O_7$ 99.5%, $(NH_4)_2S_2O_8$ 98+%, H_2O_2 (35% aqueous solution, stabilized), 3-chloroperoxybenzoic acid (MCPBA, 70–75%, balance 3-chlorobenzoic acid and water), dibenzoyl peroxide (BzOOBz, 75%, remainder water), *N*-hydroxyphthalimide 98%, *N*-hydroxysuccinimide 98+%, acetylacetone 99+%, ethyl acetoacetate 99+%, malononitrile 99%, ethyl 2-methylacetoacetate 95% (**10a**), diethyl acetylsuccinate 99% (**10g**), diethyl ethylmalonate 99% (**11a**), and diethyl phenylmalonate 98% (**11b**) were commercial reagents (Acros). $KMnO_4$ and $K_2Cr_2O_7$ were fine powders.

2-Substituted 1,3-dicarbonyl compounds **9a**,[89] **9b**,[90] **9c**,[91] **10b**,[92] **10c**,[93] **10d**,[94] **10e**,[95] **10f**,[96] 2-substituted malononitriles **12a**,[97] **12b**,[97] 2-substituted cyanoacetic esters **13a**,[98] **13b**,[99] and *N*-substituted hydroxamic acids **8c**,[100] **8d**,[101] **8f**[100] were synthesized according to the literature.

CCDC 930840 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Experiment to Table 1

The oxidant was added with stirring for 30 s [in run 11, $KMnO_4$ was added for 5 min; in runs 12–18, 21, 24, and 27–29, the salts $Co(OAc)_2{\cdot}4H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $Mn(OAc)_2{\cdot}4H_2O$, $Cu(OAc)_2{\cdot}H_2O$, or $Fe(NO_3)_3{\cdot}9H_2O$ were initially added, and after one min the oxidant given in the second place was added for 30 s; in runs 25 and 26, a stream of oxygen was bubbled through the reaction mixture at a rate of 0.3 mL s^{-1} until the synthesis was completed] to a mixture of ethyl 2-acetylhexanoate **10c** (200 mg, 1.07 mmol), NHPI **8a** (175 mg, 1.07 mmol) and the solvent (CH_3COOH, MeCN, EtOAc or $CHCl_3$; 5 mL) heated to a specified temperature (25, 40, 60, or 80 °C). Then the reaction mixture was stirred for 45 min (10 min in runs 2, 3, and 14) at the same temperature. Run 15 was performed under an argon atmosphere. The other experiments, except for runs 25 and 26 (where oxygen was used as the oxidant), were carried out in air.

The reaction mixture was cooled to room temperature. Then $CHCl_3$ (10 mL) and a solution of $Na_2S_2O_3{\cdot}5H_2O$ (200 mg) in H_2O (20 mL) were added, the mixture was shaken [when $Mn(OAc)_3{\cdot}2H_2O$, MnO_2, or $KMnO_4$ were used as the oxidants, the reaction mixture was dark-brown after the completion of the synthesis, and the mixture was shaken until the organic layer became completely or almost completely colorless], the organic layer was separated, and the aqueous layer was extracted with $CHCl_3$ (2 × 10 mL). All organic extracts were combined, successively washed with a saturated aqueous $NaHCO_3$ solution (15 mL) and H_2O

(20 mL), and dried with $MgSO_4$. The solvent was rotary evaporated. The products were isolated by column chromatography on silica gel using CH_2Cl_2/EtOAc as the eluent with an increasing gradient of the latter from 0 to 20%.

Experiment to Table 2

Method A: $Mn(OAc)_3 \cdot 2H_2O$ (0.453–1.62 g, 1.69–6.06 mmol, 2 moles per mole of the C–H reactant) was added with stirring for 30 s to a mixture of C–H reactant **9**–**13**, acetylacetone, acetoacetic ester or malononitrile (200 mg, 0.846–3.03 mmol), O–H reactant **8a**–**f** (121–493 mg, 0.846–3.03 mmol, 1 mole per mole of the C–H reactant), and CH_3COOH (4.2–15 mL, 5 mL per mmole of the C–H reactant), which was heated to 60 °C {80 °C in the runs with footnotes [e] and [f]; to boiling (111–113 °C) in the run with footnote [g]}. Then the mixture was stirred at the same temperature for 10 min (45 min in the run with footnote [f]; 4 min in the run with note [g]). The products were isolated according to the procedure described in the Experiment to Table 1.

In run 10 with footnote [c], a double amount of *N*-(4-chlorophenyl)acethydroxamic acid **8f** was used as compared to the general procedure (515 mg, 2.77 mmol, 2 moles per mole of **10a**).

Method B: $Co(OAc)_2 \cdot 4H_2O$ (11.3–17.3 mg, 45.4–69.3 μmol, 0.05 mole per mole of the C–H reactant) was added with stirring to a mixture of C–H reactant **9**–**12** (200 mg, 0.908–1.39 mmol), O–H reactant **8a**, **b**, **c** (124–226 mg, 0.908–1.39 mmol, 1 mole per mole of the C–H reactant), and CH_3COOH (4.5–7 mL, 5 mL per mmol of the C–H reactant) heated to 60°C. After 1 min, $KMnO_4$ (57.4–87.7 mg, 0.363–0.555 mmol, 0.4 mole per mole of the C–H reactant) was added for 30 s, and the reaction mixture was stirred at the same temperature for 10 min. The products were isolated according to the procedure described in the Experiment to Table 1.

Ethyl 2-Acetyl-2-(*N*-phthalimidyloxy)hexanoate 27 (Experiment with an increase in the amounts of the reactants by a factor of 10; Table 2, run 14, footnote [d])

$Co(OAc)_2 \cdot 4H_2O$ (134 mg, 0.537 mmol, 0.05 mole per mole of **10c**) was added to a mixture of ethyl 2-acetylhexanoate **10c** (2.00 g, 10.7 mmol), *N*-hydroxyphthalimide **8a** (1.75 g, 10.7 mmol, 1 mole per mole of **10c**), and CH_3COOH (10 mL) heated to 60 °C. After 1 min, $KMnO_4$ (679 mg, 4.30 mmol, 0.4 mole per mole of **10c**) was added for 30 s, and the reaction mixture was stirred at this temperature for 10 min.

The reaction mixture was cooled to room temperature, $CHCl_3$ (15 mL) and a solution of $Na_2S_2O_3 \cdot 5H_2O$ (200 mg) in H_2O (30 mL) were added, the reaction mixture was shaken, and the organic layer was separated. The aqueous layer was extracted with $CHCl_3$ (2×10 mL). All organic extracts were combined, successively washed with a saturated aqueous $NaHCO_3$ solution (15 mL) and H_2O (20 mL), and dried with $MgSO_4$. The solvent was removed on a rotary evaporator. Crude ethyl 2-acetyl-2-(*N*-phthalimidyloxy)hexanoate **27** was obtained as a viscous pale orange oil (see the ^1H and ^{13}C NMR spectra in the Supporting information); yield: 3.66 g. The product was purified by column chromatography on silica gel using CH_2Cl_2/EtOAc as the eluent with an increasing gradient of the latter from 0 to 20%. Ethyl 2-acetyl-2-(N-phthalimidyloxy)hexanoate **27** was obtained; yield: 3.06 g (8.81 mmol, 82%).

***N*-[(1,1-Diacetylpentyl)oxy]pthalimide (14):** Colorless crystals; mp 86–87 °C; ^1H NMR (300.13 MHz, $CDCl_3$): δ = 7.90–7.71 (m, 4H, ArH), 2.45 (s, 6H, $2CH_3$), 1.99–1.83 (m, 2H, CH_2), 1.32–1.11 (m, 4H, $2CH_2$), 0.80 (t, J = 7.3 Hz, 3H, CH_3); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 202.8 (C=O), 164.3 (NC=O), 135.0 (CH_{Ar}), 128.9 (C_{Ar}), 124.0 (CH_{Ar}), 98.1 (CON), 29.5 (CH_2), 27.3 ($2CH_3$), 25.4, 23.1 (CH_2), 13.7 (CH_3); IR (KBr): ν_{max} = 2965, 2938, 2903, 2882, 2858 (CH_2, CH_3), 1792, 1738, 1726 (C=O), 1372, 1357, 1186, 1131, 980, 876, 704 cm^{-1}; MS (70 eV): m/z (%) = 174 (24), 147 (100), 130 (26), 105 (46), 85 (83), 57 (48), 55 (46); HR-MS (ESI): m/z = 340.1144, calcd. for $C_{17}H_{19}NO_5 + Na^+$: 340.1155; elemental analysis calcd. (%) for $C_{17}H_{19}NO_5$: C 64.34, H 6.03, N 4.41; found: C 64.31, H 5.96, N 4.36.

***N*-[(1,1-Diacetylpentyl)oxy]-*N*-phenylacetamide (15):** Pale yellow oil; ^1H NMR (300.13 MHz, $CDCl_3$): δ = 7.49–7.36 (m, 3H, ArH), 7.36–7.28 (m, 2H, ArH), 2.13 (s, 6H, $2CH_3$), 2.04–1.92 (m, 2H, CH_2), 1.90 (s, 3H, $CH_3C(O)N$), 1.19–1.04 (m, 2H, CH_2), 1.04–0.88 (m, 2H, CH_2), 0.73 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 204.2 (2C=O), 171.5 (NC=O), 142.0 (C_{Ar}), 129.7 ($2CH_{Ar}$), 129.5 (CH_{Ar}), 127.7 ($2CH_{Ar}$), 97.2 (CON), 30.2, 27.3, 25.6, 23.1, 22.5, 13.8 (CH_2, CH_3); IR ($CHCl_3$): ν_{max} = 2963, 2931, 2874 (CH_2, CH_3), 1727, 1712 (C=O), 1358, 788, 698 cm^{-1}; MS (70 eV): m/z (%) = 305 (13) [M^+], 263 (23), 262 (42), 155 (26), 136 (33), 135 (100), 134 (61), 113 (73), 109 (48), 107 (29), 94 (60), 93 (58), 92 (52), 91 (35), 77 (42), 71 (28), 65 (85); HR-MS (ESI): m/z = 328.1522, calcd. for $C_{17}H_{23}NO_4 + Na^+$: 328.1519; elemental analysis calcd. (%) for $C_{17}H_{23}NO_4$: C 66.86, H 7.59, N 4.59; found: C 66.71, H 7.63, N 4.71.

***N*-[(1,1-Diacetylpentyl)oxy]-*N*-isopropylbenzamide (16):** Colorless oil; ^1H NMR (300.13 MHz, $CDCl_3$): δ = 7.56–7.45 (m, 3H, ArH), 7.45–7.33 (m, 2H, ArH), 4.08 (septet, J = 6.6 Hz, 1H, $CHMe_2$), 2.36 (s, 6H, $2CH_3C$=O), 2.09–1.93 (m, 2H, CH_2), 1.40–1.10 (m, 4H, $2CH_2$), 1.26 (d, J = 6.6 Hz, 6H, $2CH_3$), 0.87 (t, J = 7.1 Hz, 3H, CH_3); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 204.1 (C=O), 175.3 (NC=O), 134.8 (CAr), 131.7 (CHAr), 128.9 (2CHAr), 127.9 (2CHAr), 96.6 (CON), 55.9 (CHN), 30.6, 27.4, 26.0, 23.3, 19.9, 13.9 (CH_2, CH_3); IR ($CHCl_3$): ν_{max} = 2965, 2934, 2875 (CH_2, CH_3) 1729, 1712, 1673 (C=O), 1369, 1355, 1299, 1286, 1130, 704, 668 cm^{-1}; MS (70 eV): m/z (%) = 333 (1) [M^+], 290 (23), 164 (43), 163 (46), 162 (41), 149 (23), 148 (56), 148 (52), 146 (55), 113 (37), 106 (57), 105 (100), 104 (75), 84 (39), 77 (89), 76 (33), 71 (50), 55 (26); HR-MS (ESI): m/z = 356.1831, calcd. for $C_{19}H_{27}NO_4 + Na^+$: 356.1832; elemental analysis calcd. (%) for $C_{19}H_{27}NO_4$: C 68.44, H 8.16, N 4.20; found: C 68.41, H 8.18, N 4.26.

***N*-[(1,1-Diacetylpentyl)oxy]-*N*-phenylbenzamide (17):** Slightly yellow crystals; mp 47–49 °C; ^1H NMR (300.13 MHz, $CDCl_3$): δ = 7.46–7.36 (m, 2H, ArH), 7.36–7.11 (m, 8H, ArH), 2.24–2.07 (m, 2H, CH_2), 2.19 (s, 6H, $2CH_3$), 1.25–0.96 (m, 4H, $2CH_2$), 0.75 (t, J = 7.1 Hz, 3H, CH_3); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 204.4 (2C=O), 172.2 (NC=O), 142.3 (C_{Ar}), 133.8 (C_{Ar}), 131.1 (CH_{Ar}), 129.4 ($2CH_{Ar}$), 129.1 (CH_{Ar}), 128.7 ($2CH_{Ar}$), 128.4 ($2CH_{Ar}$), 128.2 ($2CH_{Ar}$), 97.6 (CON), 30.3, 27.3, 25.6, 23.1, 13.7 (CH_2,

CH_3); IR (KBr): ν_{max} = 3060 (CH_{Ar}), 2966, 2931, 2875 (CH_2, CH_3) 1730, 1705, 1688 (C=O), 1490, 1356, 1297, 1281, 1193, 701, 690 cm^{-1}; MS (70 eV): *m/z* (%) = 368 (28), 367 (10) [M^+], 366 (17), 198 (17), 196 (85), 168 (21), 107 (32), 106 (87), 105 (94), 104 (17), 93 (32), 78 (19), 77 (100), 65 (56); HR-MS (ESI): *m/z* = 390.1671, calcd. for $C_{22}H_{25}NO_4+Na^+$: 390.1676; elemental analysis calcd. (%) for $C_{22}H_{25}NO_4$: C 71.91, H 6.86, N 3.81; found: C 71.96, H 6.83, N 3.79.

***N*-(1-Acetyl-1-benzyl-2-oxopropoxy)succinimide (18):** Colorless crystals; mp 119–120 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.31–7.10 (m, 5H, ArH), 3.42 (s, 2H, $PhCH_2$), 2.60 (s, 4H, CH_2CH_2), 2.36 (s, 6H, $2CH_3$); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 202.5 (2C=O), 171.4 (NC=O), 133.7 (C_{Ar}), 130.4 ($2CH_{Ar}$), 128.5 ($2CH_{Ar}$), 127.3 (CH_{Ar}), 98.3 (CON), 37.4, 27.7, 25.4 (CH_2, CH_3); IR (KBr): ν_{max} = 1736, 1705 (C=O), 1362, 1193, 1084 cm^{-1}; MS (70 eV): *m/z* (%) = 261 (31), 189 (52), 119, (55), 100 (100), 92 (46), 91 (89); HR-MS (ESI): *m/z* = 326.1000, calcd. for $C_{16}H_{17}NO_5+Na^+$: 326.0999; elemental analysis calcd. (%) for $C_{16}H_{17}NO_5$: C 63.36, H 5.65, N 4.62; found: C 63.63, H 5.49, N 4.49.

***N*-(1-Acetyl-1-benzyl-2-oxopropoxy)phthalimide (19):** Colorless crystals; mp 142–143 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.88–7.73 (m, 4H, ArH), 7.18 (m, 5H, ArH), 3.51 (s, 2H, $PhCH_2$), 2.39 (s, 6H, $2CH_3$); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 202.6 (2C=O), 164.2 (NC=O), 135.1 (CH_{Ar}), 133.7 (C_{Ar}), 130.7 (CH_{Ar}), 128.9 (CH_{Ar}/C_{Ar}), 128.4 (CH_{Ar}), 127.2 (C_{Ar}/CH_{Ar}), 124.0 (CH_{Ar}), 98.4 (CON), 37.1 (CH_2), 27.8 ($2CH_3$); IR (KBr): ν_{max} = 3085, 3067, 3030 (CH_{Ar}), 2968, 2938, 2924 (CH_2, CH_3) 1792, 1738, 1717 (C=O), 1359, 1350, 1185, 1079, 981, 876, 705 cm^{-1}; MS (70 eV): *m/z* (%) = 148 (26), 91 (100); HR-MS (ESI): *m/z* = 374.0993, calcd. for $C_{20}H_{17}NO_5+Na^+$: 374.0999; elemental analysis calcd. (%) for $C_{20}H_{17}NO_5$: C 68.37, H 4.88, N 3.99; found: C 68.35, H 5.01, N 4.03.

***N*-(1-Acetyl-1-benzyl-2-oxopropoxy)-*N*-(4-chlorophenyl)-acetamide (20):** Slightly yellow crystals; mp 89–90 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 7.7 Hz, 2H, ArH), 7.29 (d, *J* = 7.7 Hz, 2H, ArH), 7.24–7.12 (m, 3H, ArH), 7.04–6.91 (m, 2H, ArH), 3.38 (s, 2H, $PhCH_2$), 2.09 (s, 6H, $2CH_3$), 1.89 [s, 3H, NC(O)CH_3]; ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 203.7 (2C=O), 172.2 (NC=O), 140.3, 135.8, 134.3 (C_{Ar}), 130.5 ($2CH_{Ar}$), 130.0 ($2CH_{Ar}$), 129.4 ($2CH_{Ar}$), 128.3 ($2CH_{Ar}$), 127.0 (CH_{Ar}) 97.3 (CON), 37.2 (CH_2), 27.7 ($2CH_3$), 22.5 [NC(O)CH_3]; IR (KBr): ν_{max} = 1717 (C=O), 1486, 1357, 1267, 1222, 1186, 1087, 832, 715, 562 cm^{-1}; MS (70 eV): *m/z* (%) = 373 (6) [M^+], 331 (28), 171 (34), 169 (100), 129 (39), 127 (60), 125 (60), 92 (34), 91 (54); HR-MS (ESI): *m/z* = 396.0964, calcd. for $C_{20}H_{20}ClNO_4+Na^+$: 396.0973; elemental analysis calcd. (%) for $C_{20}H_{20}ClNO_4$: C 64.26, H 5.39, Cl 9.48, N 3.75; found: C 64.13, H 5.31, Cl 9.58, N 3.71.

***N*-(1-Acetyl-1-bromo-2-oxopropoxy)phthalimide (21):** Colorless crystals; mp 139–139.5 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.94–7.75 (m, 4H, ArH), 2.65 (s, 6H, CH_3); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 195.0 (C=O), 162.6 (NC=O), 135.4 (CH_{Ar}), 128.5 (C_{Ar}), 124.3 (CH_{Ar}), 104.55 (CBr), 25.4 ($2CH_3$); IR (KBr): ν_{max} = 1791, 1743, 1723 (C=O), 1352, 1185, 697 cm^{-1}; MS (70 eV): *m/z* (%) = 174 (49), 161 (71), 148 (100), 105 (59), 104 (46), 90 (39); HR-MS (ESI): *m/z* = 361.9625, calcd. for $C_{13}H_{10}BrNO_5+Na^+$: 361.9635; elemental analysis calcd. (%) for $C_{13}H_{10}BrNO_5$: C 45.91, H 2.96, Br 23.49, N 4.12; found: C 46.02, H 2.63, Br 23.57, N 4.06.

Ethyl 2-(*N*-phthalimidyloxy)-2-methyl-3-oxobutanoate (22): Colorless crystals; mp 90–91 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.91–7.72 (m, 4H, ArH), 4.31 (q, *J* = 7.1 Hz, 2H, OCH_2), 2.54 (s, 3H, CH_3C=O), 1.61 (s, 3H, CH_3CON), 1.33 (t, *J* = 7.1 Hz, 3H, CH_3); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 202.5 (C=O), 167.4, 164.0 (NC=O, OC=O), 135.0 (CH_{Ar}), 128.84 (C_{Ar}), 124.0 (CH_{Ar}), 92.2 (CON), 62.7 (CH_2O), 26.1, 17.2, 14.0 (CH_2, CH_3); IR (KBr): ν_{max} = 1736 (C=O), 1356, 1275, 1237, 1138, 1111, 875, 703 cm^{-1}; MS (70 eV): *m/z* (%) = 305 (1) [M^+], 190 (70), 174 (63), 148 (64), 147 (100), 130 (87), 105 (64); HR-MS (ESI): *m/z* = 328.0786, calcd. for $C_{15}H_{15}NO_6+Na^+$: 328.0792; elemental analysis calcd. (%) for $C_{15}H_{15}NO_6$: C 59.01, H 4.95, N 4.59; found: C 59.08, H 4.97, N 4.49.

Ethyl 2-{[acetyl(4-chlorophenyl)amino]oxy}-2-methyl-3-oxobutanoate (23): Brownish crystals; mp 75–76 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.37 (d, *J* = 8.7 Hz, 2H, ArH), 7.27 (d, *J* = 8.7 Hz, 2H, ArH), 4.10–3.90 (m, 1H, OCH_2), 3.87–3.70 (m, 1H, OCH_2), 2.30 (s, 3H, CH_3C=O), 2.11 [s, 3H, CH_3C(O)N], 1.60 (s, 3H, CH_3CON) 1.08 (t, *J* = 7.1 Hz, 3H, CH_3); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 202.7 (C=O), 172.0, 167.9 (NC=O, OC=O), 139.7, 134.5 (C_{Ar}), 129.3, 128.1 (CH_{Ar}), 91.1 (CON), 62.1 (CH_2O), 25.8, 22.2, 17.6, 13.7 (CH_3); IR (KBr): ν_{max} = 3096, 3086, 3050 (CH_{Ar}), 2992, 2941, 2911 (CH_3, CH_2), 1741, 1726, 1695 (C=O), 1489, 1367, 1311, 1283, 1145, 1101, 1091, 852, 558 cm^{-1}; MS (70 eV): *m/z* (%) = 327 (4) [M^+], 285 (58), 144 (100), 127 (59), 98 (38); HR-MS (ESI): *m/z* = 350.0758, calcd. for $C_{15}H_{18}ClNO_5+Na^+$: 350.0766; elemental analysis calcd. (%) for $C_{15}H_{18}ClNO_5$: C 54.97, H 5.54, Cl 10.82, N 4.27; found: C 54.98, H 5.61, Cl 10.85, N 4.31.

Ethyl 2-(*N*-phthalimidyloxy)-2-ethyl-3-oxobutanoate (24): Colorless oil; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.89–7.66 (m, 4H, ArH), 4.24 (q, J_1 = 7.1 Hz, 2H, OCH_2), 2.48 (s, 3H, CH_3C=O), 2.19–1.98 (m, 2H, CH_2), 1.27 (t, J_1 = 7.1 Hz, 3H, CH_3) 1.00 (t, J_2 = 7.4 Hz, 3H, CH_3); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 202.2 (C=O), 166.9, 164.1 (NC=O, OC=O), 134.9 (CH_{Ar}), 128.9 (C_{Ar}), 123.8 (CH_{Ar}), 95.0 (CON), 62.4 (CH_2O), 27.3, 24.4, 13.9, 7.6 (CH_2, CH_3); IR ($CHCl_3$): ν_{max} = 2984, 2944 (CH_2, CH_3), 1797, 1745 (C=O), 1369, 1358, 1255, 1189, 1110, 977, 877, 705 cm^{-1}; MS (70 eV): *m/z* (%) = 319 (2) [M^+], 190 (88), 174 (85), 147 (81), 111 (80), 105 (100), 76 (79), 56 (66); HR-MS (ESI): *m/z* = 342.0945, calcd. for $C_{32}H_{47}NO_5+Na^+$: 342.0948; elemental analysis calcd. (%) for $C_{16}H_{17}NO_6$: C 60.18, H 5.37, N 4.39; found: C 60.06, H 5.33, N 4.33.

Ethyl 2-{[benzoyl(isopropyl)amino]oxy}-2-ethyl-3-oxobutanoate (25): Colorless oil; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.60–7.30 (m, 5H, ArH), 4.30–4.09 (m, 2H, OCH_2), 4.09–3.95 (m, 2H, CHN), 2.45 (s, 3H, CH_3C=O), 2.22–1.97 (m, 2H, CH_2), 1.37–1.14 (m, 9H, $3CH_3$), 0.95 (t, *J* = 7.3 Hz, CH_3); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 203.5 (C=O), 175.6, 168.3 (NC=O, OC=O), 134.9 (C_{Ar}), 131.7 (CH_{Ar}), 128.7 ($2CH_{Ar}$), 128.1 ($2CH_{Ar}$), 93.1 (CON), 61.8 (OCH_2), 56.1 (NCH), 27.0, 24.9, 19.8, 19.6, 14.0, 8.7 (CH_2, CH_3); IR ($CHCl_3$): ν_{max} = 2982, 2941 (CH_2, CH_3), 1741, 1725, 1671 (C=O), 1253, 1130, 703 cm^{-1}; MS (70 eV): *m/z* (%) = 335 (10) [M^+], 230 (30), 163 (21), 148 (30), 145 (48), 106 (53), 105 (70), 77 (100); HR-MS (ESI): *m/z* = 358.1621, calcd. for $C_{18}H_{25}NO_5+Na^+$: 358.1625; elemental analysis calcd. (%) for $C_{18}H_{25}NO_5$: C 64.46, H 7.51, N 4.18; found: C 64.61, H 7.61, N 4.20.

Ethyl 2-acetyl-2-(*N*-succinimidyloxy)hexanoate (26): Colorless crystals; mp 83–84 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 4.27–4.11 (m, 2H, OCH_2), 2.69 (s, 4H, CH_2CH_2), 2.42 (s, 3H, CH_3C=O), 2.03–1.78 (m, 2H, CH_2), 1.54–1.34 (m, 1H, CH_2), 1.34–1.14 (m, 6H, CH_2, CH_3), 0.85 (t, J = 7.0 Hz, 3H, CH_3); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 202.1 (C=O), 171.3, 168.8 (NC=O, OC=O), 94.1 (CON), 62.5 (OCH_2), 31.2, 27.2, 25.5, 24.9, 22.9, 13.9, 13.8 (CH_2, CH_3); IR (KBr): ν_{max} = 2969, 2939, 2877 (CH_2, CH_3), 1786, 1761, 1732 (C=O), 1469, 1365, 1356, 1308, 1273, 1260, 1214, 1191, 1150, 1133, 1073, 1003 cm^{-1}; MS (70 eV): m/z (%) = 299 (4) [M^+], 201 (27), 184 (24), 158 (100), 147 (24), 100 (45), 85 (70), 56 (34); HR-MS (ESI): m/z = 322.1251, calcd. for $C_{14}H_{21}NO_6$+Na^+: 322.1261; elemental analysis calcd. (%) for $C_{14}H_{21}NO_6$: C 56.18, H 7.07, N 4.68; found: C 56.13, H 7.01, N 4.69.

Ethyl 2-acetyl-2-(*N*-phthalimidyloxy)hexanoate (27): Colorless oil; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.88–7.67 (m, 4H, ArH), 4.25 (q, J = 7.1 Hz, 2H, OCH_2), 2.48 (s, 3H, CH_3C=O), 2.14–1.90 (m, 2H, CH_2), 1.64–1.43 (m, 1H, CH_2), 1.42–1.19 (m, 6H, CH_2, CH_3), 0.86 (t, J = 7.1 Hz, 3H, CH_3); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 202.4 (C=O), 167.0, 164.1 (OC=O, NC=O), 134.9 (CH_{Ar}), 129.0 (C_{Ar}), 123.9 (CH_{Ar}), 94.7 (CON), 62.5 (OCH_2), 31.1, 27.4, 25.0, 23.0, 13.9, 13.8 (CH_2, CH_3); IR ($CHCl_3$): ν_{max} = 2964, 2934, 2875 (CH_2, CH_3), 1743 (C=O), 1369, 1358, 1262, 1189, 705 cm^{-1}; MS (70 eV): m/z (%) = 347 (1) [M^+], 232 (38), 190 (75), 174 (62), 147 (90), 130 (73), 105 (49), 86 (41), 85 (100); HR-MS (ESI): m/z = 370.1257, calcd. for $C_{18}H_{21}NO_6$+Na^+: 370.1261; elemental analysis calcd. (%) for $C_{18}H_{21}NO_6$: C 62.24, H 6.09, N 4.03; found: C 62.22, H 6.11, N 3.97.

Ethyl 2-benzyl-2-(*N*-phthalimidyloxy)-3-oxobutanoate (28): Colorless crystals; mp 105–106 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.93–7.72 (m, 4H, ArH), 7.46–7.33 (m, 2H, ArH), 7.33–7.17 (m, 3H, ArH), 4.21–4.02 (m, 2H, OCH_2), 3.80 (d, J_1 = 14.3 Hz, 1H, CH_2), 3.52 (d, J_1 = 14.3 Hz, 1H, CH_2), 2.36 (s, 3H, CH_3C=O), 1.12 (t, J_2 = 7.1 Hz, 3H, CH_3); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 203.3 (C=O), 166.2, 164.0 (OC=O, NC=O), 135.0 (2CH_{Ar}), 134.0 (C_{Ar}), 130.9 (2CH_{Ar}), 128.9 (2C_{Ar}), 128.3 (2CH_{Ar}), 127.2 (CH_{Ar}), 123.9 (2CH_{Ar}), 95.6 (CON), 62.6 (OCH_2), 38.9 ($PhCH_2$), 28.1, 13.7 (CH_3); IR (KBr): ν_{max} = 2993 (CH_3), 1739 (C=O), 1365, 1351, 1286, 1264, 1185, 1115, 978, 876, 704 cm^{-1}; MS (70 eV): m/z (%) = 219 (83), 173 (39), 148 (33), 119 (48), 91 (100); HR-MS (ESI): m/z = 404.1125, calcd. for $C_{21}H_{19}NO_6$+Na^+: 404.1105; elemental analysis calcd. (%) for $C_{21}H_{19}NO_6$: C 66.13, H 5.02, N 3.67; found: C 66.17, H 5.01, N 3.68.

Ethyl 2-acetyl-2-(*N*-phthalimidyloxy)pent-4-enoate (29): Colorless oil; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.89–7.67 (m, 4H, ArH), 6.13–5.89 (m, 1H, =CH), 5.16–4.98 (m, 2H, =CH_2), 4.26 (q, J_1 = 7.1 Hz, 2H, OCH_2), 2.85 (d, J_2 = 7.0 Hz, 2H, CH_2), 2.47 (s, 3H, CH_3), 1.28 (t, J_1 = 7.1 Hz, 3H, CH_3); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 201.6 (C=O), 166.6, 164.1 (OC=O, NC=O), 135.0 (CH_{Ar}), 130.8 (=CH), 128.9 (C_{Ar}), 123.9 (CH_{Ar}), 119.9 (=CH_2), 94.2 (CON), 62.6 (OCH_2), 36.1 (CH_2), 27.3, 14.0 (CH_3); IR ($CHCl_3$): ν_{max} = 3084 (=CH_2, CH_{Ar}), 2986, 2925 (CH_2, CH_3), 1744 (C=O), 1189, 775, 705 cm^{-1}; MS (70 eV): m/z (%) = 331 (2) [M^+], 190 (73), 174 (72), 160 (49), 148 (57), 147 (98), 130 (64), 123 (73), 105 (62), 104 (55), 99 (83), 90 (79), 81 (51), 77 (43), 70 (100), 68 (90), 50 (45); HR-MS (ESI): m/z = 354.0950, calcd. for $C_{21}H_{19}NO_6$+Na^+: 354.0948; elemental analysis calcd. (%) for $C_{17}H_{17}NO_6$: C 61.63, H 5.17, N 4.23; found: C 61.59, H 5.21, N 4.25.

Ethyl 2-(2-cyanoethyl)-2-(*N*-phthalimidyloxy)-3-oxobutanoate (30): Colorless oil; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.89–7.74 (m, 4H, ArH), 4.24 (q, J = 7.1 Hz, 2H, OCH_2), 2.93–2.76 (m, 1H, CH_2), 2.65–2.33 (m, 3H, CH_2), 2.51 (s, 3H, CH_3C=O), 1.27 (t, J = 7.1 Hz, 3H, CH_3); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 200.9 (C=O), 165.6, 164.2 (OC=O, NC=O), 135.3 (CH_{Ar}), 128.8 (C_{Ar}), 124.2 (CH_{Ar}), 118.9 (CN), 92.5 (CON), 63.3 (OCH_2), 27.6, 27.4, 13.8, 11.8 (CH_2, CH_3); IR ($CHCl_3$): ν_{max} = 2987, 2941 (CH_2, CH_3), 2253 (CN), 1798, 1745, 1728 (C=O), 1369, 1359, 1264, 1189, 1076, 876, 706 cm^{-1}; MS (70 eV): m/z (%) = 344 (2) [M^+], 190 (82), 189 (49), 174 (100), 160 (83), 147 (58), 130 (40), 105 (90), 104 (63), 82 (46), 77 (48); HR-MS (ESI): m/z = 367.0899, calcd. for +Na^+: 367.0901; elemental analysis calcd. (%) for $C_{17}H_{16}N_2O_6$: C 59.30, H 4.68, N 8.14; found: C 59.23, H 4.71, N 8.13.

Diethyl 2-acetyl-2-(*N*-phthalimidyloxy)succinate (31): Slightly yellow oil; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.90–7.69 (m, 4H, ArH), 4.31–4.10 (m, 4H, OCH_2), 3.37 (d, J = 18.2 Hz, 1H, CH_2), 3.22 (d, J = 18.2 Hz, 1H, CH_2), 2.65 (s, 3H, CH_3C=O), 1.38–1.19 (m, 6H, CH_3); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 202.5 (C=O), 168.8, 165.8, 164.1 (OC=O, NC=O), 135.1 (CH_{Ar}), 129.0 (C_{Ar}), 124.0 (CH_{Ar}), 92.0 (CON), 63.1, 61.3 (OCH_2), 37.8, 27.1, 14.1, 13.8 (CH_2, CH_3); IR ($CHCl_3$): ν_{max} = 2987, 2941, 2909 (CH_2, CH_3), 1798, 1746 (C=O), 1372, 1350, 1286, 1243, 1189, 1062, 1034, 705 cm^{-1}; MS (70 eV): m/z (%) = 190 (76), 189 (61), 161 (39), 147 (100), 143 (41), 115 (92), 104 (44); HR-MS (ESI): m/z = 400.0996, calcd. for M+Na^+: 400.1003; elemental analysis calcd. (%) for $C_{18}H_{19}NO_8$: C 57.29, H 5.08, N 3.71; found: C 57.32, H 5.09, N 3.76.

Diethyl *N*-phthalimidyloxy(ethyl)malonate (32): Colorless oil; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.89–7.70 (m, 4H, ArH), 4.32 (q, J_1 = 7.1 Hz, 4H, 2OCH_2), 2.19 (q, J_2 = 7.4 Hz, 2H, CH_2), 1.32 (t, J_1 = 7.1 Hz, 6H, 2CH_3), 1.14 (t, J_2 = 7.4 Hz, 3H, CH_3); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 166.3, 164.1 (NC=O, OC=O), 134.8 (2CH_{Ar}), 129.2 (C_{Ar}), 123.8 (2CH_{Ar}), 90.6 (CON), 62.5 (OCH_2), 25.7, 14.1, 7.7 (CH_2, CH_3); IR ($CHCl_3$): ν_{max} = 2984, 2943 (CH_2, CH_3), 1799, 1745 (C=O), 1369, 1307, 1259, 1189, 1122, 11031028, 981, 877, 705, 669 cm^{-1}; MS (70 eV): m/z (%) = 349 (10) [M^+], 187 (100), 163 (55), 148 (54), 141 (62), 130 (51), 104 (86), 87 (70), 77 (47), 69 (83); HR-MS (ESI): m/z = 372.1050, calcd. for $C_{17}H_{19}NO_7$+Na^+: 372.1054; elemental analysis calcd. (%) for $C_{17}H_{19}NO_7$: C 58.45, H 5.48, N 4.01; found: C 58.47, H 5.32, N 3.99.

Diethyl *N*-phthalimidyloxy(phenyl)malonate (33): Colorless crystals; mp 81.5–83 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.84–7.57 (m, 6H, ArH), 7.42–7.25 (m, 3H, ArH), 4.49–4.25 (m, 4H, OCH_2), 1.30 (t, J = 7.1 Hz, 6H, CH_3); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 165.8, 163.3 (OC=O, NC=O), 134.6 (2CH_{Ar}), 132.1, 130.0 (CH_{Ar}/C_{Ar}), 129.4 (2CH_{Ar}), 128.8 (C_{Ar}/CH_{Ar}), 128.1 (2CH_{Ar}), 123.6 (2CH_{Ar}), 89.9 (CON), 62.9 (OCH_2), 14.0 (CH_3); IR (KBr): ν_{max} = 2995, 2982, 2941 (CH_2, CH_3), 1768, 1738 (C=O), 1278, 1227, 1211, 1029, 695 cm^{-1}; MS (70 eV): m/z (%) = 397 (2) [M+], 324 (39), 235 (91), 207 (88), 179 (48), 163 (49), 162 (58), 161 (100), 133 (72), 106 (39), 105 (51), 104 (81), 90 (66), 77 (77); HR-MS (ESI): m/z = 420.1056, calcd. for $C_{21}H_{19}NO_7$+Na^+:

420.1054; elemental analysis calcd. (%) for $C_{21}H_{19}NO_7$: C 63.47, H 4.82, N 3.52, found: C 63.40, H 4.71, N 3.51.

Butyl-(*N*-phthalimidyloxy)malononitrile (34): Colorless crystals; mp 96–96.5 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.13–7.70 (m, 4H, ArH), 2.62–2.29 (m, 2H), 1.94–1.73 (m, 2H), 1.66–1.34 (m, 2H), 1.01 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 163.0 (CON), 135.7 (CH_{Ar}), 128.8 (C_{Ar}), 124.7 (CH_{Ar}), 112.1 (CN), 75.80 (CON), 37.6, 26.0, 22.0, 13.7 (CH_2, CH_3); IR (KBr): ν_{max} = 2969, 2935, 2925, 2877 (CH_2, CH_3), 2251 (CN), 1806, 1754 (C=O), 1336, 1300, 1185, 1014, 995, 874, 721, 710, 689 cm^{-1}; MS (70 eV): m/z (%) = 283 (3) [M^+], 162 (72), 161 (92), 132 (92), 104 (100), 77 (68); HR-MS (ESI): m/z = 306.0843, calcd. for $C_{15}H_{13}N_3O_3+Na^+$: 306.0849; elemental analysis calcd. (%) for $C_{15}H_{13}N_3O_3$: C 63.60, H 4.63, N 14.83; found: C 63.38, H 4.49, N 14.84.

Benzyl-(*N*-phthalimidyloxy)malononitrile (35): Colorless crystals; mp 158–159 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.06–7.80 (m, 4H, ArH), 7.62–7.35 (m, 5H, ArH), 3.72 (s, 2H, CH_2); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 162.9 (NC=O), 135.7 (2CH_{Ar}), 130.8 (2CH_{Ar}), 129.5 (C_{Ar}/CH_{Ar}), 129.2 (2CH_{Ar}), 129.0, 128.8 (C_{Ar}/CH_{Ar}), 124.7 (2CH_{Ar}), 111.6 (2CN), 76.5 (CON), 43.5 (CH_2); IR (KBr): ν_{max} = 1799, 1749 (C=O), 1187, 1000, 965, 874, 713 cm^{-1}; MS (70 eV): m/z (%) = 163 (100), 132 (31), 104 (69), 91 (31), 76 (48); HR-MS (ESI): m/z = 340.0691, calcd. for $C_{18}H_{11}N_3O_3+Na^+$: 340.0693; elemental analysis calcd. (%) for $C_{18}H_{11}N_3O_3$: C 68.14, H 3.49, N 13.24; found: C 68.12, H 3.50, N 13.27.

Ethyl 2-cyano-2-(*N*-phthalimidyloxy)propanoate (36): White crystals; mp 120–121 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.98–7.68 (m, 4H, ArH), 4.37 (q, J = 7.0 Hz, 2H, OCH_2), 2.03 (s, 3H, CH_3C=O), 1.36 (t, J = 7.0 Hz, 3H, CH_3); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 163.6, 163.2 (OC=O, NC=O), 135.4 (CH_{Ar}), 128.7 (C_{Ar}), 124.2 (CH_{Ar}), 115.1 (CN), 81.3 (CON), 64.4 (OCH_2), 22.6, 13.9 (CH_3); IR (KBr): ν_{max} = 3107 (CH_{Ar}), 3005, 2979, 2940 (CH_2, CH_3), 1801, 1756, 1740 (C=O), 1469, 1351, 1299, 1185, 1161, 1145, 1015, 966, 874, 709 cm^{-1}; MS (70 eV): m/z (%) = 288 (12) [M^+], 163 (55), 147 (34), 132 (53), 105 (32), 104 (100), 90 (33), 76 (64); HR-MS (ESI): m/z = 311.0627, calcd. for $C_{14}H_{12}N_2O_5+Na^+$: 311.0638; elemental analysis calcd. (%) for $C_{14}H_{12}N_2O_5$: C 58.33, H 4.20, N 9.72; found: C 58.30, H 4.07, N 9.68.

Ethyl 2-cyano-2-(*N*-phthalimidyloxy)-3-phenylpropanoate (37): Colorless crystals; mp 126–127 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.98–7.71 (m, 4H, ArH), 7.53–7.26 (m, 5H, ArH), 4.31 (q, J = 7.1 Hz, 2H, OCH_2), 3.66 (s, 2H, CH_2), 1.27 (t, J = 7.1 Hz, CH_3); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 163.3, 163.1 (NC=O, OC=O), 135.3 (2CH_{Ar}), 130.74 (C_{Ar}/CH_{Ar}), 130.66 (2CH_{Ar}), 128.9 (2CH_{Ar}), 128.7, 128.6 (C_{Ar}/CH_{Ar}), 124.3 (2CH_{Ar}), 114.0 (2CN), 86.4 (CON), 64.2 (OCH_2), 41.6 (CH_2Ph), 13.9 (CH_3); IR (KBr): ν_{max} = 3036 (CH_{Ar}), 2987, 2937 (CH_2, CH_3), 1795, 1742 (C=O), 1466, 1351, 1320, 1223, 1187, 1077, 1051, 991, 876, 707 cm^{-1}; MS (70 eV): m/z (%) = 203 (46), 175 (44), 164 (54), 156 (43), 131 (41), 105 (58), 91 (100); HR-MS (ESI): m/z = 387.0944, calcd. for $C_{20}H_{16}N_2O_5+Na^+$: 387.0951; elemental analysis calcd. (%) for $C_{20}H_{16}N_2O_5$: C 65.93, H 4.43, N 7.69; found: C 65.91, H 4.39, N 7.71.

Ethyl 2-acetyl-2-hydroxyhexanoate (38):[102] Colorless oil; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 4.25 (q, J_1 = 7.2 Hz, 2H, OCH_2), 4.13 (s, 1H, OH), 2.27 (s, 3H, CH_3C=O), 2.17–2.00 (m, 1H, CH_2), 1.98–1.82 (m, 1H, CH_2), 1.43–1.14 (m, 7H, 2CH_2, CH_3), 0.89 (t, J_2 = 7.0 Hz, 3H, CH_3); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 205.2 (C=O), 171.1 (OC=O), 84.4 (COH), 62.7 (OCH_2), 35.1, 25.3, 24.8, 22.8, 14.2, 14.0 (CH_2, CH_3).

Reaction of Ethyl 3-Oxohexanoate 39 with NHPI 8a and Manganese Triacetate

$Mn(OAc)_3{\cdot}2H_2O$ (1.02 g, 3.80 mmol) was added with stirring to a solution (heated to 60 °C) of 3-oxohexanoate **39** (300 mg, 1.90 mmol), NHPI **8a** (309 mg, 1.90 mmol), and CH_3COOH (9 mL) for 30 s. Then the reaction mixture was stirred at this temperature for 45 min. The products were isolated according to the procedure described in the Experiment to Table 1. Phthalimide **40** (yield: 112 mg, 0.759 mmol, 40%), *N*-butyryloxyphthalimide **41** (yield: 102 mg, 0.436 mmol, 23%), and *N*-acetoxyphthalimide **42** (yield: 85.5 mg, 0.417 mmol, 22%) were obtained.

Phthalimide (40):[103,104] Colorless crystals; mp 234–235 °C, lit. mp 236 °C;[104] ^{1}H NMR (300.13 MHz, DMSO-d_6): δ = 11.31 (bs, 1H, NH), 7.82 (m, 4H, ArH); ^{13}C NMR (75.47 MHz, DMSO-d_6): δ = 169.2 (NC=O), 134.3 (CHAr), 132.6 (CAr), 122.9 (CHAr); IR (KBr): ν_{max} = 3199 (NH), 1775, 1752, 1730 (C=O), 1388, 1377, 1308, 1053, 716, 647, 534 cm^{-1}.

***N*-(Butyryloxy)phthalimide (41):** Colorless oil; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.94–7.83 (m, 2H, ArH), 7.83–7.70 (m, 2H, ArH), 2.64 (t, J_1 = 7.3 Hz, 2H, CH_2C=O), 1.91–1.73 (m, 2H, CH_2), 1.07 (t, J_2 = 7.4 Hz, 3H, CH_3); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 169.6, 162.1 (OC=O, NC=O), 134.8 (CH_{Ar}), 129.1 (C_{Ar}), 124.0 (CH_{Ar}), 32.9, 18.5, 13.5 (CH_2, CH_3); IR ($CHCl_3$): ν_{max} = 2971, 2920, 2879, 2851 (CH_2, CH_3), 1789, 1745 (C=O), 1062, 699, 670 cm^{-1}; elemental analysis calcd. (%) for $C_{12}H_{11}NO_4$: C 61.80, H 4.75, N 6.01; found: C 61.90, H 4.64, N 6.05.

***N*-(Acetoxy)phthalimide (42):**[105,106] Colorless crystals; mp 184–185 °C, lit. mp = 185 °C;[106] ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.93–7.83 (m, 2H, ArH), 7.83–7.72 (m, 2H, ArH), 2.40 (s, 3H, CH_3); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 166.7, 162.0 (OC=O, NC=O), 134.9 (CH_{Ar}), 129.1 (C_{Ar}), 124.1 (CH_{Ar}), 17.7 (CH_3); IR (KBr): ν_{max} = 1815, 1788, 1741, 1376, 1165, 1142, 969, 880, 697 cm^{-1}.

Acknowledgements

This work was supported by the Russian Foundation for Basic Research (Grant 12-03-31876) and the Ministry of Education and Science of the Russian Academy of Sciences (Grant No. 11.519.11.2038). High resolution mass spectra were recorded in the Department of Structural Studies of the Zelinsky Institute of Organic Chemistry (Moscow).

References

[1] Z. Li, C.-J. Li, *Eur. J. Org. Chem.* **2005**, 3173–3176.
[2] O. Baslé, C.-J. Li, *Green Chem.* **2007**, *9*, 1047–1050.
[3] A. Tanoue, W.-J. Yoo, S. Kobayashi, *Adv. Synth. Catal.* **2013**, *355*, 269–273.

[4] Z. Li, R. Yu, H. Li, *Angew. Chem.* **2008**, *120*, 7607–7610; *Angew. Chem. Int. Ed.* **2008**, *47*, 7497–7500.
[5] L. Zhao, C.-J. Li, *Angew. Chem.* **2008**, *120*, 7183–7186; *Angew. Chem. Int. Ed.* **2008**, *47*, 7075–7078.
[6] W.-J. Yoo, C. A. Correia, Y. Zhang, C. J. Li, *Synlett* **2009**, 138–142.
[7] Y. Zhang, C.-J. Li, *Angew. Chem.* **2006**, *118*, 1983–1986; *Angew. Chem. Int. Ed.* **2006**, *45*, 1949–1952.
[8] Z. Li, H. Li, X. Guo, L. Cao, R. Yu, H. Li, S. Pan, *Org. Lett.* **2008**, *10*, 803–805.
[9] Y. H. Zhang, C.-J. Li, *Eur. J. Org. Chem.* **2007**, 4654–4657.
[10] W. Wu, J. Xu, S. Huang, W. Su, *Chem. Commun.* **2011**, *47*, 9660–9662.
[11] Z. Li, L. Cao, C.-J. Li, *Angew. Chem.* **2007**, *119*, 6625–6627; *Angew. Chem. Int. Ed.* **2007**, *46*, 6505–6507.
[12] C. Guo, J. Song, S.-W. Luo, L.-Z. Gong, *Angew. Chem.* **2010**, *122*, 5690–5694; *Angew. Chem. Int. Ed.* **2010**, *49*, 5558–5562.
[13] D. Ramesh, U. Ramulu, S. Rajaram, P. Prabhakar, Y. Venkateswarlu, *Tetrahedron Lett.* **2010**, *51*, 4898–4903.
[14] Á. Pintér, A. Sud, D. Sureshkumar, M. Klussmann, *Angew. Chem.* **2010**, *122*, 5124–5128; *Angew. Chem. Int. Ed.* **2010**, *49*, 5004–5007.
[15] B. Zhang, Y. Cui, N. Jiao, *Chem. Commun.* **2012**, *48*, 4498–4500.
[16] C. A. Correia, C.-J. Li, *Tetrahedron Lett.* **2010**, *51*, 1172–1175.
[17] Z. Li, C.-J. Li, *J. Am. Chem. Soc.* **2006**, *128*, 56–57.
[18] J. Yu, J. Tian, C. Zhang, *Adv. Synth. Catal.* **2010**, *352*, 531–546.
[19] J. Hu, M. Zhu, Y. Xu, J. Yan, *Synthesis* **2012**, 1226–1232.
[20] R. M. Moriarty, C. Condeiu, A. Tao, O. Prakash, *Tetrahedron Lett.* **1997**, *38*, 2401–2404.
[21] J. S. Lodaya, G. F. Koser, *J. Org. Chem.* **1988**, *53*, 210–212.
[22] R. M. Moriarty, R. K. Vaid, V. T. Ravikumar, B. K. Vaid, T. E. Hopkins, *Tetrahedron* **1988**, *44*, 1603–1607.
[23] D. A. Price, S. Gayton, P. A. Stupple, *Synlett* **2002**, 1170–1172.
[24] U. S. Mahajan, K. G. Akamanchi, *Synlett* **2008**, 987–990.
[25] M. Uyanik, D. Suzuki, T. Yasui, K. Ishihara, *Angew. Chem.* **2011**, *123*, 5443–5446; *Angew. Chem. Int. Ed.* **2011**, *50*, 5331–5334.
[26] M. Baidya, K. A. Griffin, H. Yamamoto, *J. Am. Chem. Soc.* **2012**, *134*, 18566–18569.
[27] W. Adam, O. Krebs, *Chem. Rev.* **2003**, *103*, 4131–4146.
[28] C. P. Frazier, J. R. Engelking, J. R. deAlaniz, *J. Am. Chem. Soc.* **2011**, *133*, 10430–10433.
[29] D. Atkinson, M. A. Kabeshov, M. Edgar, A. V. Malkov, *Adv. Synth. Catal.* **2011**, *353*, 3347–3351.
[30] B. S. Bodnar, M. J. Miller, *Angew. Chem.* **2011**, *123*, 5746–5764; *Angew. Chem. Int. Ed.* **2011**, *50*, 5630–5647.
[31] S. Coseri, *Catal. Rev.* **2009**, *51*, 218–292.
[32] C. Galli, P. Gentili, O. Lanzalunga, *Angew. Chem.* **2008**, *120*, 4868–4874; *Angew. Chem. Int. Ed.* **2008**, *47*, 4790–4796.
[33] F. Recupero, C. Punta, *Chem. Rev.* **2007**, *107*, 3800–3842.
[34] A. R. Forrester, M. M. Ogilvy, R. H. Thomson, *J. Chem. Soc. C* **1970**, 1081–1083.
[35] V. N. Kalinin, V. I. Dzyuba, A. A. Duzhak, *J. Org. Chem. USSR (Engl. Transl.)* **1981**, *17*, 2270–2274; *Zh. Org. Khim.* **1981**, *17*, 2542–2546.
[36] T. Hara, T. Iwahama, S. Sakaguchi, Y. Ishii, *J. Org. Chem.* **2001**, *66*, 6425–6431.
[37] Y. Ishii, T. Iwahama, S. Sakaguchi, K. Nakayama, Y. Nishiyama, *J. Org. Chem.* **1996**, *61*, 4520–4526.
[38] S. Ozaki, T. Hamaguchi, K. Tsuchida, Y. Kimata, M. Masui, *J. Chem. Soc. Perkin Trans. 2* **1989**, 951–956.
[39] V. A. Schmidt, E. J. Alexanian, *Chem. Sci.* **2012**, *3*, 1672–1674.
[40] V. A. Schmidt, E. J. Alexanian, *J. Am. Chem. Soc.* **2011**, *133*, 11402–11405.
[41] V. A. Schmidt, E. J. Alexanian, *Angew. Chem.* **2010**, *122*, 4593–4596; *Angew. Chem. Int. Ed.* **2010**, *49*, 4491–4494.
[42] B. C. Giglio, V. A. Schmidt, E. J. Alexanian, *J. Am. Chem. Soc.* **2011**, *133*, 13320–13322.
[43] L. Melone, C. Gambarotti, S. Prosperini, N. Pastori, F. Recupero, C. Punta, *Adv. Synth. Catal.* **2011**, *353*, 147–154.
[44] Y. Amaoka, S. Kamijo, T. Hoshikawa, M. Inoue, *J. Org. Chem.* **2012**, *77*, 9959–9969.
[45] Y. Yoshino, Y. Hayashi, T. Iwahama, S. Sakaguchi, Y. Ishii, *J. Org. Chem.* **1997**, *62*, 6810–6813.
[46] C. Einhorn, J. Einhorn, C. Marcadal, J.-L. Pierre, *Chem. Commun.* **1997**, 447–448.
[47] S. M. Silvestre, J. A. R. Salvador, *Tetrahedron* **2007**, *63*, 2439–2445.
[48] A. O. Terent′ev, I. B. Krylov, M. Y. Sharipov, Z. M. Kazanskaya, G. I. Nikishin, *Tetrahedron* **2012**, *68*, 10263–10271.
[49] Y. Nishiwaki, S. Sakaguchi, Y. Ishii, *J. Org. Chem.* **2002**, *67*, 5663–5668.
[50] X. Tong, J. Xu, H. Miao, G. Yang, H. Ma, Q. Zhang, *Tetrahedron* **2007**, *63*, 7634–7639.
[51] S. Sakaguchi, T. Takase, T. Iwahama, Y. Ishii, *Chem. Commun.* **1998**, 2037–2038.
[52] T. Iwahama, Y. Yoshino, T. Keitoku, S. Sakaguchi, Y. Ishii, *J. Org. Chem.* **2000**, *65*, 6502–6507.
[53] K. Hirano, S. Sakaguchi, Y. Ishii, *Tetrahedron Lett.* **2002**, *43*, 3617–3620.
[54] T. Kagayama, M. Nakayama, R. Oka, S. Sakaguchi, Y. Ishii, *Tetrahedron Lett.* **2006**, *47*, 5459–5461.
[55] C. R. H. I. de Jonge, *Liebigs Ann. Chem.* **1986**, 299–304.
[56] A. O. Terent′ev, D. A. Borisov, I. A. Yaremenko, V. V. Chernyshev, G. I. Nikishin, *J. Org. Chem.* **2010**, *75*, 5065–5071.
[57] U. Jahn, P. Hartmann, I. Dix, P. G. Jones, *Eur. J. Org. Chem.* **2001**, 3333–3355.
[58] K. Molawi, T. Schulte, K. O. Siegenthaler, C. Wetter, A. Studer, *Chem. Eur. J.* **2005**, *11*, 2335–2350.
[59] H. Liu, W. Feng, C. W. Kee, Y. Zhao, D. Leow, Y. Pan, C.-H. Tan, *Green Chem.* **2010**, *12*, 953–956.
[60] A. O. Terent′ev, D. A. Borisov, V. V. Semenov, V. V. Chernyshev, V. M. Dembitsky, G. I. Nikishin, *Synthesis* **2011**, 2091–2100.

[61] P. González-Bulnes, A. González-Roura, D. Canals, A. Delgado, J. Casas, A. Llebaria, *Bioorg. Med. Chem.* **2010**, *18*, 8549–8555.
[62] P. González-Bulnes, A. M. Bobenchik, Y. Augagneur, R. Cerdan, H. J. Vial, A. Llebaria, C. B. Mamoun, *J. Biol. Chem.* **2011**, *286*, 28940–28947.
[63] T. Toyama, K. Nagamune, T. Horii, K. Tanabe, U.S. Patent 2010/0292472 A1, **2010**.
[64] D. Pal, S. Saha, *J. Adv. Pharm. Technol. Res.* **2012**, *3*, 92–99.
[65] J. Edelson, J. F. Douglas, B. J. Ludwig, *J. Pharm. Sci.* **1970**, *59*, 680–682.
[66] H. Kataoka, S. Horiyama, M. Yamaki, H. Oku, K. Ishiguro, T. Katagi, M. Takayama, M. Semma, Y. Ito, *Biol. Pharm. Bull.* **2002**, *25*, 1436–1441.
[67] H. Agarwal, O. P. Agarwal, R. Karnawat, I. K. Sharma, P. S. Verma, *Int. J. Appl. Biol. Pharm. Technol.* **2010**, *1*, 1293–1299.
[68] A. Alaninea, A. Boursonb, B. Büttelmanna, R. Gillb, M.-P. Heitza, V. Mutelb, E. Pinarda, G. Trubeb, R. Wylera, *Bioorg. Med. Chem. Lett.* **2003**, *13*, 3155–3159.
[69] A. High, T. Prior, R. A. Bell, P. K. Rangachari, *J. Pharmacol. Exp. Ther.* **1999**, *288*, 490–501.
[70] M. Bahta, G. T. Lountos, B. Dyas, S.-E. Kim, R. G. Ulrich, D. S. Waugh, T. R. Burke, *J. Med. Chem.* **2011**, *54*, 2933–2943.
[71] B. J. Berger, *Antimicrob. Agents Chemother.* **2000**, *44*, 2540–2542.
[72] L. Nieto, A. Mascaraque, F. Miller, F. Glacial, C. R. Martínez, M. Kaiser, R. Brun, C. Dardonville, *J. Med. Chem.* **2011**, *54*, 485–494.
[73] M.-Z. Wang, H. Xu, T.-W. Liu, Q. Feng, S.-J. Yu, S.-H. Wang, Z.-M. Li, *Eur. J. Med. Chem.* **2011**, *46*, 1463–1472.
[74] J.-X. Huang, Y.-M. Jia, X.-M. Liang, W.-J. Zhu, J.-J. Zhang, Y.-H. Dong, H.-Z. Yuan, S.-H. Qi, J.-P. Wu, F.-H. Chen, D.-Q. Wang, *J. Agric. Food Chem.* **2007**, *55*, 10857–10863.
[75] Y. Li, H.-Q. Zhang, J. Liu, X.-P. Yang, Z.-J. Liu, *J. Agric. Food Chem.* **2006**, *54*, 3636–3640.
[76] E. Lemaire, A. Rassat, *Tetrahedron Lett.* **1964**, *5*, 2245–2248.
[77] N. Koshino, B. Saha, J. H. Espenson, *J. Org. Chem.* **2003**, *68*, 9364–9370.
[78] B. B. Snider, *Chem. Rev.* **1996**, *96*, 339–363.
[79] A. S. Demir, M. Emrullahoglu, *Curr. Org. Synth.* **2007**, *4*, 223–237.
[80] V. Nair, A. Deepthi, *Chem. Rev.* **2007**, *107*, 1862–1891.
[81] T.-L. Ho, *Synthesis* **1973**, 347–354.
[82] J. Iqbal, T. K. P. Kumar, S. Manogaran, *Tetrahedron Lett.* **1989**, *30*, 4701–4702.
[83] P. Tarakeshwar, J. Iqbal, S. Manogaran, *Tetrahedron* **1991**, *47*, 297–304.
[84] J. Iqbal, B. Bhatia, N. K. Nayyar, *Tetrahedron* **1991**, *47*, 6457–6468.
[85] R. Amorati, M. Lucarini, V. Mugnaini, G. F. Pedulli, *J. Org. Chem.* **2003**, *68*, 1747–1754.
[86] A. M. Al-Etaibi, N. A. Al-Awadi, M. R. Ibrahim, Y. A. Ibrahim, *ARKIVOC (Gainesville, FL, U.S.A.)* **2010**, 149–162.
[87] M. Zlotorzynska, G. M. Sammis, *Org. Lett.* **2011**, *13*, 6264–6267.
[88] P. A. Belyakov, V. I. Kadentsev, A. O. Chizhov, N. G. Kolotyrkina, A. S. Shashkov, V. P. Ananikov, *Mendeleev Commun.* **2010**, *20*, 125–131.
[89] J. Bloomfield, *J. Org. Chem.* **1961**, *26*, 4112–4115.
[90] J. C. Jeffery, S. S. Kurek, J. A. McCleverty, E. Psillakis, R. M. Richardson, M. D. Ward, A. Wlodarczyk, *J. Chem. Soc. Dalton Trans.* **1994**, *17*, 2559–2564.
[91] L.-Z. Fang, Q.-H. Lv, F.-L. Yan, J.-M. Shen, *Asian J. Chem.* **2011**, *23*, 3425–3427.
[92] J. E. Beddow, S. G. Davies, K. B. Ling, P. M. Roberts, A. J. Russell, A. D. Smith, J. E. Thomson, *Org. Biomol. Chem.* **2007**, *5*, 2812–2825.
[93] W. B. Renfrow, A. Renfrow, *J. Am. Chem. Soc.* **1946**, *68*, 1801–1804.
[94] V. A. Martin, D. H. Murray, N. E. Pratt, Y.-B. Zhao, K. F. Albizati, *J. Am. Chem. Soc.* **1990**, *112*, 6965–6978.
[95] L. Bouissane, S. E. Kazzouli, E. M. Rakib, M. Khouili, A. Hannioui, M. Benchidmi, E. M. Essassi, G. Guillaumet, *Heterocycles* **2004**, *63*, 1651–1658.
[96] N. F. Albertson, *J. Am. Chem. Soc.* **1950**, *72*, 2594–2599.
[97] J. C. Dunham, A. D. Richardson, R. E. Sammelson, *Synthesis* **2006**, 680–686.
[98] X. Zhang, X. Jia, L. Fang, N. Liu, J. Wang, X. Fan, *Org. Lett.* **2011**, *13*, 5024–5027.
[99] K.-S. Shia, N.-Y. Chang, J. Yip, H.-J. Liu, *Tetrahedron Lett.* **1997**, *38*, 7713–7716.
[100] C. P. Brink, A. L. Crumbliss, *J. Org. Chem.* **1982**, *47*, 1171–1176.
[101] W. Przychodzeń, *Eur. J. Org. Chem.* **2005**, 2002–2014.
[102] J. Christoffers, T. Werner, S. Unger, W. Frey, *Eur. J. Org. Chem.* **2003**, 425–431.
[103] D. N. Sawant, Y. S. Wagh, K. D. Bhatte, B. M. Bhanage, *Eur. J. Org. Chem.* **2011**, 6719–6724.
[104] Q. Tao, J.-M. Chen, L. Ma, T.-B. Lu, *Cryst. Growth Des.* **2012**, *12*, 3144–3152.
[105] E. Malmström, R. D. Miller, C. J. Hawker, *Tetrahedron* **1997**, *53*, 15225–15236.
[106] M. Saljoughian, H. Morimoto, P. G. Williams, C. Than, S. J. Seligman, *J. Org. Chem.* **1996**, *61*, 9625–9628.

