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Hypervalent Iodine as a Terminal Oxidant in Wacker-Type Oxidation of Terminal Olefins to Methyl Ketones

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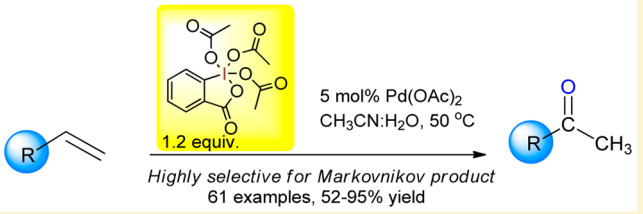
Supporting Information

ABSTRACT: A mimic of the Wacker process for C=O bond formation in terminal olefins can be initiated by a combination of the Pd(II) and hypervalent iodine reagent, Dess–Martin periodinane to generate methyl ketones. This operationally simple and scalable method offers Markovnikov selectivity, has good functional group compatibility, and is mild and high yielding.

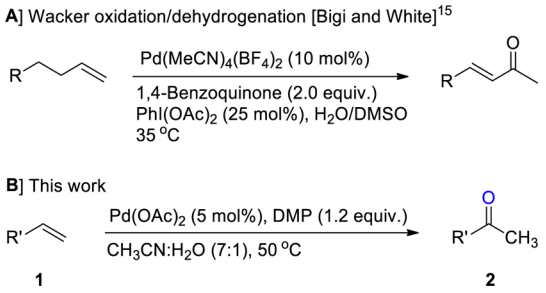


INTRODUCTION

The chemistry of polyvalent iodine compounds has experienced an unprecedented growth during the past few decades. This rolling interest is mainly due to the remarkable oxidizing properties of hypervalent iodine reagents and their benign environmental nature and commercial availability. From the beginning of the 1990s, the domain of oxidative transformation has witnessed a renaissance; in particular, the pioneering contributions by Dess and Martin has triggered confidence in the potential use of Dess–Martin periodinane (DMP) as an oxidizing agent for the selective transformation of alcohols to carbonyl compounds.[1] DMP has emerged as a powerful and selective oxidant that affects a plethora of oxidative transformations in synthetic organic chemistry. These include construction of an array of *p*-quinones from a variety of anilide systems,[2] deoximation of aldoximes/ketoximes,[3] oxidation of the Baylis–Hillman adducts to *α*-methylene *β*-keto esters,[4] synthesis of 2-alkynylpropenals,[5] oxidation of fluoroalkyl-substituted carbinols,[6] and acceleration of the Dess–Martin oxidation of alcohols by water.[7]

The selective transformation of terminal olefins into polar functional groups late in synthetic sequences is a challenge, and the outcome in most cases is substrate dependent.[8] Over the past few decades, substantial research interest has been focused on developing an alternative to the traditional reoxidant $CuCl_2$ for Wacker oxidation, which mainly generates corrosive reaction medium, chlorinated byproducts, and isomerization of the double bond.[9] The basis of this process popularized by several research groups lies in the C=C bond activation to generate methyl ketones.[10−12] In most of the cases, a terminal olefin has been used as feedstock material where a C=C bond gets oxidized to a C—C=O bond. Despite the significant advances made on the greener side of hypervalent iodine chemistry,[13,14] the application in approaches involving C=O bond formation from olefins is far less realized. A good example to convert terminal olefins to *α,β*-unsaturated ketones was recently reported by Bigi and White[15] employing 2.0 equiv of benzoquinone and 25 mol % $PhI(OAc)_2$ (Scheme 1A). Use of benzoquinone in Wacker oxidation was well established before,[10a,12b,16] and here too they realized that it is responsible for Wacker oxidation catalyzed by a palladium source. The role of $PhI(OAc)_2$ was therefore concluded to be that in dehydrogenation and not as a terminal oxidant. The information gathered during the course of development of terminal oxidants in the Wacker process in our group[17] led us to hypothesize about additional modes of reactivity that could be revealed through further explorations of DMP toward Wacker-type oxidation. These assumptions proved fruitful, and herein we report the direct oxidation of terminal olefins into methyl ketones. We studied Wacker-type oxidation for C=O bond formation under a N_2 atmosphere with a palladium catalyst and cyclic λ^5-iodanes (Scheme 1B). The reaction system does not require oxygen or any other additives.

Scheme 1. Oxidation of Terminal Olefins to Methyl Ketones



RESULTS AND DISCUSSION

1-Tetradecene (**1a**) was chosen as a model substrate to optimize the reaction conditions (Table 1). We chose $Pd(OAc)_2$ (5 mol %) and tested several iodine-based oxidants (Table 1, entries 1−7). The use of 1.2 equiv of DMP with 5 mol % $Pd(OAc)_2$ in CH_3CN/H_2O (7:1) at 50 °C could

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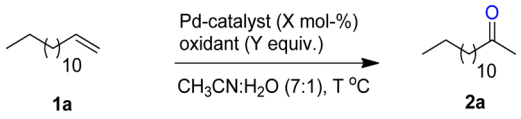
Table 1. Optimization of the Reaction Conditions[a]

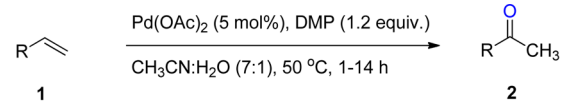


1a 2a

entry	Pd catalyst (concn, mol %)	oxidant (amt, equiv)	solvent	temp (°C)	time (h)	yield (%)
1	$Pd(OAc)_2$(5)	IBX (1.2)	CH_3CN/H_2O (7:1)	50	1.5	68
2	$Pd(OAc)_2$(5)	DMP (1.2)	CH_3CN/H_2O (7:1)	50	1	95
3	$Pd(OAc)_2$(5)	$PhI(OAc)_2$ (1.2)	CH_3CN/H_2O (7:1)	50	6	58
4	$Pd(OAc)_2$(5)	I_2 (1.2)	CH_3CN:H_2O (7:1)	50	1	NR[b]
5	$Pd(OAc)_2$(5)	I_2/*m*CPBA (1:2; 1.5)	CH_3CN/H_2O (7:1)	50	1	NR[b]
6	$Pd(OAc)_2$(5)	PhIO (1.2)	CH_3CN/H_2O (7:1)	50	72	12
7	$Pd(OAc)_2$(5)	PIFA (1.2)	CH_3CN/H_2O (7:1)	50	23	36
8	$Pd(OTFA)_2$ (5)	DMP (1.2)	CH_3CN/H_2O (7:1)	50	1	48
9	$PdCl_2$ (5)	DMP (1.2)	CH_3CN/H_2O (7:1)	50	1	79
10	$Pd(dba)_2$ (5)	DMP (1.2)	CH_3CN/H_2O (7:1)	50	1	72
11	$PdCl_2(CH_3CN)_2$ (5)	DMP (1.2)	CH_3CN/H_2O (7:1)	50	1.5	42
12	$[PdCl(allyl)]_2$ (5)	DMP (1.2)	CH_3CN/H_2O (7:1)	50	1.5	31
13	Pd−C (5)	DMP (1.2)	CH_3CN/H_2O (7:1)	50	12	NR[b]
14	$Pd(OAc)_2$(5)	DMP (1.2)	DMA/H_2O (7:1)	50	13	49
15	$Pd(OAc)_2$(5)	DMP (1.2)	DMF/H_2O (7:1)	50	10	53
16	$Pd(OAc)_2$(5)	DMP (1.2)	THF/H_2O (7:1)	50	10	24
17	$Pd(OAc)_2$(5)	DMP (1.2)	$DMSO/H_2O$ (7:1)	50	23	14
18	$Pd(OAc)_2$(5)	DMP (1.2)	CH_3CN/H_2O (7:1)	rt	1.2	70
19	$Pd(OAc)_2$(5)	DMP (1.2)	CH_3CN/H_2O (7:1)	40	1.2	86
20	$Pd(OAc)_2$(5)	DMP (1.2)	CH_3CN/H_2O (7:1)	65	1	80
21	$Pd(OAc)_2$(5)	DMP (1.2)	CH_3CN/H_2O (7:1)	85	1	59
22	$Pd(OAc)_2$(5)	DMP (0.5)	CH_3CN/H_2O (7:1)	50	2	63
23	$Pd(OAc)_2$(5)	DMP (1.0)	CH_3CN/H_2O (7:1)	50	1.5	88
24	$Pd(OAc)_2$(5)	DMP (1.5)	CH_3CN/H_2O (7:1)	50	1	95
25	$Pd(OAc)_2$(5)	DMP (2.0)	CH_3CN/H_2O (7:1)	50	1	94
26	$Pd(OAc)_2$(5)	DMP (10 mol %)	CH_3CN/H_2O (7:1)	50	12	21
27	$Pd(OAc)_2$(5)	DMP (20 mol %)	CH_3CN/H_2O (7:1)	50	7	39
28	$Pd(OAc)_2$(1)	DMP (1.2)	CH_3CN/H_2O (7:1)	50	18	12
29	$Pd(OAc)_2$(2)	DMP (1.2)	CH_3CN/H_2O (7:1)	50	12	23
30	$Pd(OAc)_2$(5)		CH_3CN/H_2O (7:1)	50	12	NR[b]
31		DMP (1.2)	CH_3CN/H_2O (7:1)	50	12	NR[b]

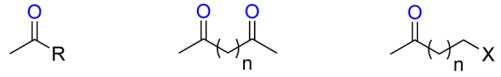
[a]All reactions were performed with olefin **1a** (0.5 mmol), oxidant (10 mol % to 2.0 equiv), and Pd catalyst (1−5 mol %), at *T* °C in solvent (4 mL) under N_2. [b]NR = no reaction.

Table 2. Wacker-Type Oxidation of Aliphatic Terminal Olefins[a]



1 2

Aliphatic terminal olefins 18 examples



2a, R = $C_{12}H_{25}$, 95%
2b, R = C_6H_{13}, 74%
2c, R = C_3H_7, 72%
2d, R = C_8H_{17}, 79%

2e, n = 6, 78%[b]
2f, n = 8, 80%[b]

2g, X = Br, n = 7, 79%
2h, X = Br, n = 10, 81%
2i, X = OBz, n = 3, 77%
2j, X = OMOM, n = 8, 65%
2k, X = OTBDPS, n = 0, 87%
2l, X = CO_2Et, n = 0, 88%
2m, X = CO_2Me, n = 7, 84%
2n, X = CHO, n = 7, 80%
2o, X = CO_2H, n = 1, 75%
2p, X = CO_2H, n = 2, 77%
2q, X = OH, n = 8, complex mixt.
2r, X = CH(OH)-CH_3, n = 12, 56%

[a]Reactions conditions: olefin **1** (0.5 mmol), $Pd(OAc)_2$ (5 mol %), DMP (1.2 equiv), CH_3CN/H_2O (7:1; 4 mL), 50 °C, under N_2. [b]Reactions conditions: substrate (0.5 mmol), $Pd(OAc)_2$ (10 mol %), DMP (2.4 equiv), CH_3CN/H_2O (7:1; 4 mL), at 50 °C, under N_2.

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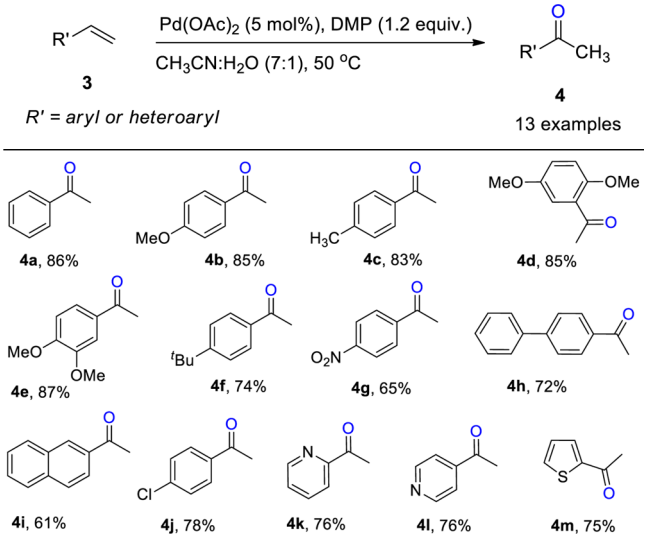
produce tetradecane-2-one (**2a**) in 95% yield in a 1 h reaction (Table 1, entry 2). However, lower yields were observed in the case of other oxidizing agents such as 2-iodoxybenzoic acid (IBX) and (diacetoxyiodo)benzene [$PhI(OAc)_2$] (Table 1, entries 1 and 3, respectively). Oxidation in the presence of granular iodine as well as an I_2/*m*CPBA mixture (1:2; 1.5 equiv) (Table 1, entries 4 and 5, respectively) failed to deliver the methyl ketone, indicating molecular iodine to be unfit for this oxidation. Iodosobenzene (PhIO) did not support the system and could produce only 12% of the product **2a** (entry 6). [Bis(trifluoroacetoxy)iodo]benzene (PIFA) could lead to the product **2a** in 36% yield (Table 1, entry 7). The performance of different Pd catalysts was tested using DMP (1.2 equiv; Table 1, entries 8−13), which showed $Pd(OAc)_2$ to be the most suitable catalyst (entry 2). Various solvent combinations such as DMA, DMF, THF, and DMSO with water were examined (Table 1, entries 14−17). These solvent combinations did not improve the yields in comparison to the CH_3CN/H_2O mixture (7:1; entry 2). The effect of temperature on the reaction was studied (Table 1, entries 18−21), which confirmed that 50 °C was the optimum requirement (entry 2). Higher temperatures may decompose DMP, resulting in a reduced yield. Screening of the DMP concentration (Table 1, entries 22−27) showed that 1.2 equiv of DMP (entry 2) was optimum. The catalytic version using 10−20 mol % DMP required a longer reaction time and delivered the methyl ketone product in lower yields, although the starting olefin was consumed (entries 26 and 27). Lowering of the $Pd(OAc)_2$ concentration from 5 mol % to lower values also did not favor the reaction yields (entries 28 and 29). The reactions without Pd catalyst or the oxidant did not work (entries 30 and 31). In all cases, overoxidation to unsaturated compounds such as in the work by White et al.[15] (Scheme 1A) was not observed, indicating a good selectivity toward only Wacker oxidation with the reaction system in this work.

The scope of the reaction was investigated by varying the olefins. Initially, various inactivated long-chain olefins were tested under the optimized conditions (Table 2). 1-Tetradecene, 1-octene, 1-pentene, and 1-decene delivered the corresponding methyl ketones **2a−d** in 72−95% yields (Table 2). Terminal α,ω-dienes also reacted well with excellent selectivity, giving diketones **2e** (78%) and **2f** (80%). Methyl ketone synthesis was compatible with diverse functional groups such as bromides **2g** (79%) and **2h** (81%), benzoate **2i** (77%), MOM **2j** (65%), silyl **2k** (87%), esters **2l** (88%) and **2m** (84%), aldehyde **2n** (80%), and acids **2o** (75%) and **2p** (77%) with complete Markovnikov selectivity and in good yields (Table 2). Olefins bearing a primary OH group failed to give the product **2q**. There could be competing reactions from both the olefin and OH groups which resulted in a trail of spots on TLC. Lowering of the DMP concentration resulted in unused starting material even after a prolonged reaction time. However, the secondary OH group containing olefin worked well, giving **2r** in a moderate 56% yield.

Styrenes are masked precursors for aryl methyl ketone synthesis via olefin oxidation. However, the olefinic bond is an activated system to be investigated for issues of regioselectivity. A number of aryl-substituted styrenes were screened for oxidation under the present protocol (Table 3). Simple styrene proved to be an excellent substrate for the generation of acetophenone (**4a**) (86%). Varying the substituents on the aromatic unit suggested that electronic parameters are contributing factors in the Wacker-type oxidation reaction.

Table 3. Wacker-Type Oxidation of Styrenes[a]



[a]Reactions conditions: olefin **3** (0.5 mmol), $Pd(OAc)_2$ (5 mol %), DMP (1.2 equiv), CH_3CN/H_2O (7:1; 4 mL), 50 °C, under N_2.

With electron donor groups the yields of aryl methyl ketones were quite good: **4b** (85%), **4c** (83%), **4d** (85%), **4e** (87%), and **4f** (74%). An electron-withdrawing group such as nitro which deactivates the ring was found to decrease the efficiency of the reaction considerably (**4g**, 65%). 4-Phenylstyrene and 2-vinylnaphthalene delivered the corresponding methyl ketones **4h** (72%) and **4i** (61%) in good yields. Notably, the tolerance of a halo substituent (**4j**, 78%) and heteroaromatic compounds **4k** (76%), **4l** (76%), and **4m** (75%) allowed this protocol to be viable for heteroaryl methyl ketone synthesis. In a couple of cases traces of aldehydes were observed, but the amount was well below 2% by ^1H NMR.

We next investigated different substrates with substituents at the allylic or homoallylic positions, such as cycloalkyl, tertiary alcohols, aryl ethers, esters, silyl, acetates, MOM, phthalimide, and menthyl groups (Table 4). Many of these substrates show possible coordination of the neighboring oxygen atom to the Lewis acidic palladium, causing water attack through multiple pathways.[18] Substrates with a tertiary alcohol functionality at the homoallylic position failed to deliver the methyl ketones **6a** and **6b**. *O*-Allylsalicylic acid delivered the methyl ketone **6c** in 77% yield. Similarly bisallyl derivatives of salicylic acid (with ester and ether functionalities) gave the diketones **6d** and **6e** in 77% and 76% yields, respectively. Primary allyl alcohols with various protecting groups delivered methyl ketones in good yields: phenyl (**6f**, 84%), benzyl (**6g**, 83%), 4-*tert*-butylphenyl (**6h**, 75%), 2-naphthyl (**6i**, 76%), 2-bromo-5-methoxyphenyl (**6j**, 81%), 4-methylbenzoyl (**6k**, 87%), and nitrobenzoyl (**6l**, 64%; **6m**, 63%). Homoallyl alcohols with acetate, benzoate, and benzyl protections delivered the methyl ketones **6n** (73%), **6o** (81%), **6p** (76%), **6q** (80%), **6r** (55%), **6s** (77%), and **6t** (79%) in good yields and complete Markovnikov selectivity. The acyloin products **6u** (77%), **6v** (82%), **6w** (80%), and **6x** (73%) were obtained in good yields without the formation of competitive aldehydes (by heteroatom-directed effects). The fluorine substituent at the *meta* position in **5y** worked well and offered the methyl ketone **6y** in 76% yield. TBS-protected β-hydroxy-γ-lactone **5z** failed to deliver the ketone **6z** under this protocol. Menthyl allyl ether was a sluggish substrate and gave **6aa** in 52% yield. γ,δ-Unsaturated ester worked efficiently and

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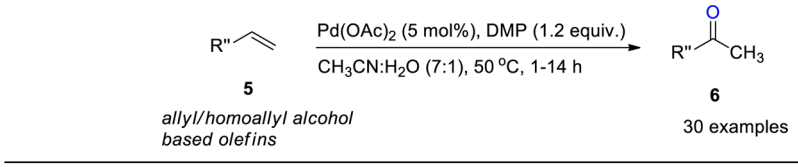
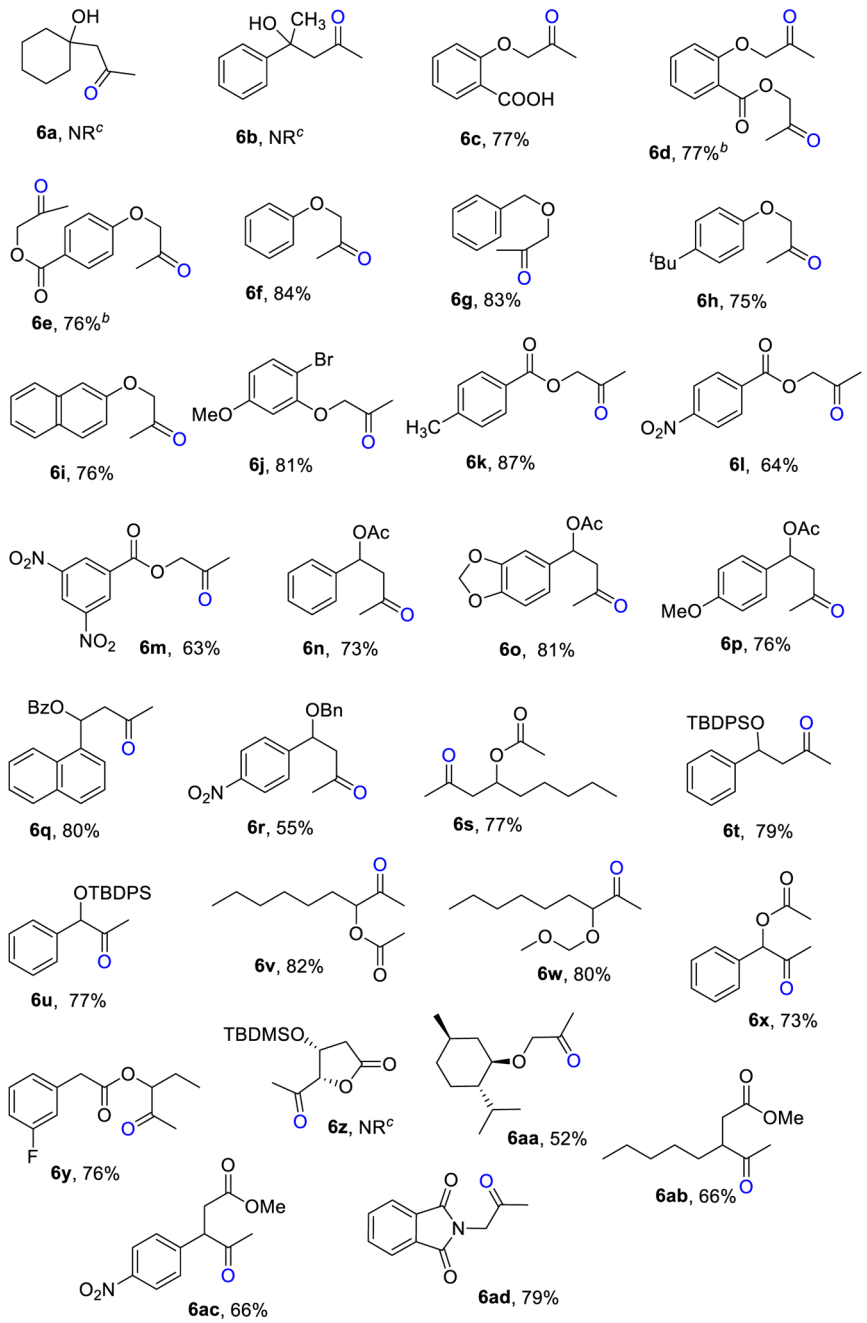
Table 4. Synthesis of Methyl Ketones from Substituted Allylic and Homoallylic Compounds[a]





[a]Reactions conditions: substrate (0.5 mmol), $Pd(OAc)_2$ (5 mol %), DMP (1.2 equiv), CH_3CN/H_2O (7:1; 4 mL), at 50 °C, under N_2. [b]Reactions conditions: substrate (0.5 mmol), $Pd(OAc)_2$ (10 mol %), DMP (2.4 equiv), CH_3CN/H_2O (7:1; 4 mL), at 50 °C, under N_2. [c]NR = no reaction.

delivered the ketones **6ab** and **6ac** in 66% yield each. Terminal unbranched allylphthalimide offered methyl ketone **6ad** in a good yield of 79%.

The scale-up experiments on a gram scale were attempted on terminal α,ω-diene **1f**, styrene (**3a**), and 4-pentenoic acid (**1o**) (Scheme 2). The reactions on a 1 g scale of each delivered results comparable to those in Tables 1 and 2 for these substrates, giving **2f**, **4a**, and **2o** (levulinic acid) in 75%, 81%, and 68% isolated yields, respectively.

Iodine compounds in a higher valence state are good oxidants.[14b] Similar to $CuCl_2$ acting as an oxidant in the normal Wacker process, we believe DMP serves as an oxidant for

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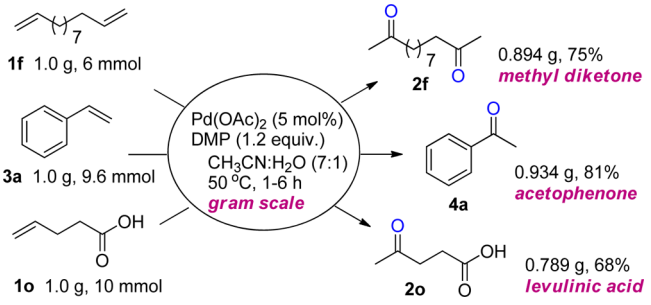
Scheme 2. Gram-Scale Reactions



regeneration of Pd(II) from Pd(0), although we could not ascertain the exact fate of DMP in the process. In comparison, the iodine(III) reagents also worked as oxidants but delivered lower yields of the methyl ketones (Table 1). We could not isolate iodine(III) compounds or iodobenzoic acid after the reaction.

CONCLUSION

In conclusion, we have revealed here an efficient and general method to synthesize methyl ketones employing the cyclic λ^5-iodane (Dess–Martin periodinane) reagent, mimicking the Wacker process.[19] The objective to promote a direct and operationally simple oxidation process was achieved. Various long-chain terminal olefins, dienes, substituted styrenes, and allyl and homoallyl alcohols with various protecting groups have been explored (61 examples). A wide spectrum of functional group tolerance, mild reaction conditions, and Markovnikov selectivity and the use of commercially available Dess–Martin periodinane as the sole oxidant are key features of this methodology. Since it is a process with operational simplicity and exclusive ketone delivery, we expect this method to find broad applications in synthetic chemistry.

EXPERIMENTAL SECTION

General Information. ^{1}H and ^{13}C NMR spectra were recorded with a spectrometer operating at 500 or 400 MHz and 125 or 100 MHz for proton and carbon nuclei, respectively. IR spectra were obtained on an FT-IR spectrometer, and samples were prepared by evaporation from $CHCl_3$ on CsBr plates. High-resolution mass spectra (HRMS) were obtained using positive electrospray ionization by the TOF method.

General Procedure for Wacker-Type Oxidation of Terminal Olefins to Methyl Ketones. To a stirred solution of olefin (0.5 mmol, 1.0 equiv) in CH_3CN (3.5 mL) and H_2O (0.5 mL) were added $Pd(OAc)_2$ (5.7 mg, 0.025 mmol, 5 mol %) and DMP (255 mg, 0.6 mmol, 1.2 equiv) at room temperature. The reaction mixture was warmed to 50 °C and stirred for a specified time under a nitrogen atmosphere. The reaction mixture was then filtered through a small pad of silica gel and washed with EtOAc, and the filtrate was concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc as the eluent to afford the methyl ketones. $Pd(OAc)_2$ (11.4 mg, 0.05 mmol, 10 mol %) and DMP (518 mg, 0.1.22 mmol, 2.4 equiv) were used for terminal olefins bearing two active olefin sites (compounds **1e**, **1f**, **5d**, and **5e**).

*Data for tetradecan-2-one (**2a**):*[17b] yield 101 mg (95%); colorless oil; IR ($CHCl_3$) ν_{max} = 3017, 2916, 1704, 1406, 1379, 1284, 1165, 1131, 1018, 949, 717, 667 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ = 2.42 (t, J = 7.5 Hz, 2H), 2.14 (s, 3H), 1.58–1.55 (m, 4H), 1.36–1.19 (m, 16H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 209.3, 43.7, 31.8, 29.7, 29.6, 29.53, 29.5, 29.4, 29.3, 29.25, 29.1, 23.7, 22.6, 14.0.

*Data for octan-2-one (**2b**):*[17b] yield 47.4 mg (74%); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ = 2.41 (t, J = 7.5 Hz, 2H), 2.13 (s, 3H), 1.59–1.52 (m, 2H), 1.32–1.21 (m, 6H), 0.87 (t, J = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 209.5, 43.8, 31.6, 29.8, 28.8, 23.8, 22.5, 14.0.

*Data for pentan-2-one (**2c**):*[20] yield 31.0 mg (72%); colorless oil; IR ($CHCl_3$) ν_{max} = 2966, 2928, 1723, 1385, 1259, 1034, 699, 549 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ = 2.37 (t, J = 7.5 Hz, 2H), 2.09 (s, 3H), 1.59–1.52 (m, 2H), 0.87 (t, J = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 209.4, 45.6, 29.8,17.2, 13.6.

*Data for decan-2-one (**2d**):*[17b] yield 61.7 mg (79%); colorless oil; IR ($CHCl_3$) ν_{max} = 3020, 2950, 2928, 1715, 1465, 1401, 1361, 1163, 667 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ = 2.40 (t, J = 7.5 Hz, 2H), 2.11 (s, 3H), 1.55–1.52 (m, 2H), 1.30–1.22 (m, 10H), 0.86 (t, J = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 209.4, 43.8, 31.8, 29.8, 29.3, 29.14, 29.1, 23.8, 22.6, 14.1; HRMS (ESI-TOF) calcd for $[C_{10}H_{20}O + Na]^+$ 179.1406, found 179.1409.

*Data for decane-2,9-dione (**2e**):*[17b] yield 66.4 mg (78%); colorless oil; IR ($CHCl_3$) ν_{max} = 3019, 2933, 2858, 1717, 1409, 1363, 1168, 1048, 967, 927, 667 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ = 2.41 (t, J = 7.4 Hz, 4H), 2.12 (s, 6H), 1.61–1.52 (m, 4H), 1.31–1.25 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 209.2, 43.6, 29.9, 28.9, 23.5; HRMS (ESI-TOF) calcd for $[C_{10}H_{18}O_2 + Na]^+$ 193.1199, found 193.1198.

*Data for dodecane-2,11-dione (**2f**):*[17b] yield 79.3 mg (80%); colorless oil; IR ($CHCl_3$) ν_{max} = 3017, 2916, 1704, 1406, 1379, 1284, 1165, 1131, 1018, 949, 717, 667 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ = 2.40 (t, J = 7.4 Hz, 4H), 2.12 (s, 6H), 1.63–1.51 (m, 4H), 1.28–1.2 (m, 8H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 209.2, 43.6, 29.7, 29.1, 28.9, 23.6; HRMS (ESI-TOF) calcd for $[C_{12}H_{22}O_2 + Na]^+$ 221.1512, found 221.1512.

*Data for 10-bromodecan-2-one (**2g**):*[17b] yield 93 mg (79%); colorless oil; IR ($CHCl_3$) ν_{max} = 2927, 2850, 1715, 1466, 1361, 1220, 1163, 1037, 910, 726 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ = 3.39 (t, J = 6.8 Hz, 2H), 2.41 (t, J = 7.4 Hz, 2H), 2.13 (s, 3H), 1.87–1.78 (m, 2H), 1.59–1.51 (m, 2H), 1.42–1.38 (m, 2H), 1.29–1.23 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 209.3, 43.7, 34.0, 32.7, 29.8, 29.2, 29.0, 28.5, 28.0, 23.7; HRMS (ESI-TOF) calcd for $[C_{10}H_{19}BrO + Na]^+$ 257.0511, found 257.0511.

*Data for 13-bromotridecan-2-one (**2h**):*[21] yield 118.2 mg (81%); colorless oil; IR ($CHCl_3$) ν_{max} = 2927, 2850, 1715, 1466, 1361, 1220, 1163, 1037, 1024, 910, 736 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ = 3.39 (t, J = 6.8 Hz, 2H), 2.41 (t, J = 7.4 Hz, 2H), 2.12 (s, 3H), 1.87–1.78 (m, 2H), 1.59–1.51 (m, 2H), 1.42–1.38 (m, 2H), 1.29–1.23 (m, 12H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 209.5, 43.8, 34.0, 32.8, 29.8, 29.7, 29.4, 29.36, 29.1, 28.7, 28.1, 23.8; HRMS (ESI-TOF) calcd for $[C_{13}H_{25}BrO + Na]^+$ 299.0981, found 299.0977.

*Data for 5-oxohexyl benzoate (**2i**):*[17b] yield 85 mg (77%); colorless oil; IR ($CHCl_3$) ν_{max} = 2956, 2918, 2950, 1718, 1602, 1584, 1452, 1410, 1361, 1315, 1176, 1165, 1119, 1071, 1027, 963, 905, 807, 714, 688, 675 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ = 8.04–8.02 (m, 2H), 7.58–7.53 (m, 1H), 7.46–7.40 (m, 2H), 4.36 (t, J = 6.1 Hz, 2H), 2.51 (t, J = 6.9 Hz, 2H), 2.15 (s, 3H), 1.82–1.70 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 208.5, 166.6, 132.9, 130.3, 129.5, 128.3, 64.5, 43.0, 29.9, 28.1, 20.2; HRMS (ESI-TOF) calcd for $[C_{13}H_{16}O_3 + Na]^+$ 243.0992, found 243.0989.

*Data for 11-(methoxymethoxy)undecan-2-one (**2j**):*[17b] yield 75 mg (65%); colorless oil; IR ($CHCl_3$) ν_{max} = 3014, 2929, 2856, 1716, 1465, 1410, 1361, 1145, 1111, 1043, 919, 667 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ = 4.61 (s, 2H), 3.51 (t, J = 6.6 Hz, 2H), 3.35 (s, 3H), 2.41 (t, J = 7.5 Hz, 2H), 2.13 (s, 3H), 1.60–1.54 (m, 2H), 1.28–1.27 (m, 12H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 209.3, 96.3, 67.8, 55.0, 43.7, 29.8, 29.7, 29.3, 29.1, 26.1, 23.8; HRMS (ESI-TOF) calcd for $[C_{13}H_{26}O_3 + Na]^+$ 253.1774, found 253.1778.

*Data for 1-[(tert-butyldiphenylsilyl)oxy]propan-2-one (**2k**):*[17b] yield 136 mg (87%); colorless oil; IR ($CHCl_3$) ν_{max} = 3071, 3050, 2933, 2893, 2859, 1736, 1717, 1589, 1473, 1428, 1391, 1354, 1231, 1189, 1113, 940, 824, 703, 615 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ = 7.65 (dd, J = 7.2, 0.7 Hz, 4H), 7.44–7.38 (m, 6H), 4.16 (s, 2H), 2.20 (s, 3H), 1.10 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 208.5, 135.5, 132.6, 130.0, 127.8, 69.9, 26.7, 26.3, 19.2; HRMS (ESI-TOF) calcd for $[C_{19}H_{24}O_2Si + Na]^+$ 335.1438, found 335.1437.

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*Data for ethyl 3-oxobutanoate (**2l**):*[17b] yield 57.3 mg (88%); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ = 4.16 (q, J = 7.2 Hz, 2H), 3.40 (s, 2H), 2.23 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 200.6, 167.1, 61.3, 50.1, 30.1, 14.0.

*Data for methyl 10-oxoundecanoate (**2m**):*[17a] yield 90 mg (84%); colorless oil; IR ($CHCl_3$) ν_{max} = 2931, 2857, 1740, 1717, 1459, 1437, 1362, 1197, 1171, 1103, 1017, 882, 669 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ = 3.65 (s, 3H), 2.40 (t, J = 7.4 Hz, 2H), 2.28 (t, J = 7.5 Hz, 2H), 2.12 (s, 3H), 1.61−1.52 (m, 4H), 1.34−1.22 (m, 8H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 209.3, 174.3, 51.4, 43.7, 34.0, 29.8, 29.1, 29.03, 29.0, 24.9, 23.7; HRMS (ESI-TOF) calcd for $[C_{12}H_{22}O_3 + Na]^+$ 237.1461, found 237.1461.

*Data for 10-oxoundecanal (**2n**):*[22] yield 73.7 mg (80%); colorless oil; IR ($CHCl_3$) ν_{max} = 2931, 2856, 2722, 1718, 1463, 1412, 1362, 1167, 1020, 758 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ = 9.71 (s, 1H), 2.40−2.35 (m, 4H), 2.09 (s, 3H), 1.61−1.48 (m, 4H), 1.31−1.18 (m, 8H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 209.2, 202.8, 43.8, 43.6, 29.8, 29.0, 28.95, 23.7, 21.9; HRMS (ESI-TOF) calcd for $[C_{11}H_{20}O_2 + Na]^+$ 207.1356, found 207.1350.

*Data for 4-oxopentanoic acid (**2o**):*[17b] yield 43.5 mg (75%); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ = 2.73 (t, J = 7.2 Hz, 2H), 2.61 (t, J = 7.2 Hz, 2H), 2.18 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 206.6, 178.2, 37.7, 29.8, 27.7.

*Data for 5-oxohexanoic acid (**2p**):*[17a] yield 50.1 mg (77%); colorless oil; IR ($CHCl_3$) ν_{max} = 3501, 3020, 2920, 2851, 1715, 1416, 1373, 1161, 1070, 1049, 955, 668 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ = 2.53 (t, J = 7.2 Hz, 2H), 2.39 (t, J = 7.2 Hz, 2H), 2.15 (s, 3H), 1.94−1.84 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 208.0, 178.7, 42.3, 32.8, 29.9, 18.5; HRMS (ESI-TOF) calcd for $[C_6H_{10}O_3 + Na]^+$ 153.0522, found 153.0525.

*Data for 16-hydroxyheptadecane-2-one (**2r**):*[17b] yield 75.7 mg (56%); white solid; mp 55−57 °C; IR ($CHCl_3$) ν_{max} = 3402, 2916, 2849, 1709, 1464, 1372, 1163, 1124, 1038, 910, 667 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$/TMS) δ = 3.78−3.75 (m, 1H), 2.38 (t, J = 7.4 Hz, 2H), 2.10 (s, 3H), 1.55−1.51 (m, 2H), 1.39−1.38 (m, 2H), 1.35−1.22 (m, 20H), 1.15 (d,J = 6.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 209.4, 68.1, 43.8, 39.3, 29.8, 29.6, 29.59, 29.56, 29.5, 29.4, 29.3, 29.1, 25.7, 23.8, 23.4; HRMS (ESI-TOF) calcd for $[C_{17}H_{34}O_2 + Na]^+$ 293.2451, found 293.2455.

*Data for acetophenone (**4a**):*[17b] yield 51.7 mg (86%); pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ = 7.98−7.92 (m, 2H), 7.60−7.51 (m, 1H), 7.50−7.42 (m, 2H), 2.60 (s, 3H).$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 198.1, 137.0, 133.0, 128.5, 128.2, 26.5.

*Data for 4-methoxyacetophenone (**4b**):*[17b] yield 63.8 mg (85%); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ = 7.94 (d, J = 8.6 Hz, 2H), 6.94 (d, J = 8.6 Hz, 2H), 3.87 (s, 3H), 2.56 (s, 3H).

*Data for 4-methylacetophenone (**4c**):*[17a] yield 55.7 mg (83%); colorless oil; IR ($CHCl_3$) ν_{max} = 3032, 3005, 2961, 2924, 2857, 1682, 1607, 1569, 1429, 1407, 1358, 1269, 1182, 1019, 954, 912, 815, 734 cm^{-1} ; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ = 7.86 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 2.58 (s, 3H), 2.41 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 197.9, 143.9, 134.7, 129.2, 128.4, 26.5, 21.6; HRMS (ESI-TOF) calcd for $[C_9H_{10}O + Na]^+$ 157.0624, found 157.0623.

*Data for 2,5-dimethoxyacetophenone (**4d**):*[17b] yield 76.6 mg (85%); colorless oil; IR ($CHCl_3$) ν_{max} = 3014, 2929, 2856, 1716, 1465, 1410, 1361, 1145, 1111, 1043, 919, 667 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ = 7.28 (d, J = 3.2 Hz, 1H), 7.02 (dd, J = 8.6, 3.6 Hz, 1H), 6.90 (d, J = 9.0 Hz, 1H), 3.87 (s, 3H), 3.78 (s, 3H), 2.61 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 199.4, 153.5, 153.4, 128.3, 120.4, 113.8, 113.2, 56.0, 55.8, 31.8; HRMS (ESI-TOF) calcd for $[C_{10}H_{12}O_3 + Na]^+$ 203.0679, found 203.0682.

*Data for 3,4-dimethoxyacetophenone (**4e**):*[17a] yield 78.4 mg (87%); colorless oil; IR ($CHCl_3$) ν_{max} = 3080, 3005, 2962, 2938, 2840, 1673, 1588, 1513, 1463, 1417, 1358, 1334, 1270, 1224, 1175, 1150, 1135, 1079, 1023, 976, 915, 878, 808, 732, 645 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ = 7.58 (dd, J = 8.4, 2.0 Hz, 1H), 7.55 (d, J = 2.0 Hz, 1H), 6.89 (d, J = 8.4 Hz, 1H), 3.95 (s, 3H), 3.94 (s, 3H), 2.57 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 196.7, 153.1, 148.8, 130.3, 123.2, 109.9, 109.8, 55.9, 55.8, 26.1; HRMS (ESI-TOF) calcd for $[C_{10}H_{12}O_3 + H]^+$ 181.0859, found 181.0862.

*Data for 4-tert-butylacetophenone (**4f**):*[17b] yield 65.2 mg (74%); colorless oil; IR ($CHCl_3$) ν_{max} = 2965, 2907, 2871, 1719, 1685, 1607, 1407, 1363, 1271, 1114, 1015, 958, 838, 777, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ = 7.90 (d, J = 8.7 Hz, 2H), 7.48 (d, J = 8.7 Hz, 2H), 2.58 (s, 3H), 1.34 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 197.9, 156.8, 134.5, 128.3, 125.5, 35.1, 31.0, 26.5; HRMS (ESI-TOF) calcd for $[C_{12}H_{16}O + H]^+$ 177.1274, found 177.1276.

*Data for 4-nitroacetophenone (**4g**):*[17b] yield 53.7 mg (65%); pale yellow solid; mp 76−78 °C; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ = 8.32 (d, J = 8.8 Hz, 2H), 8.11 (d, J = 8.8 Hz, 2H), 2.68 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 196.3, 150.7, 141.6, 129.3, 123.9, 27.0.

*Data for 4-phenylacetophenone (**4h**):*[17b] yield 70.6 mg (72%); white solid; mp 115−117 °C; IR ($CHCl_3$) ν_{max} = 3019, 2923, 1679, 1599, 1404, 1359, 1267, 1119, 1078, 1044, 957, 927, 842, 694, 669 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ = 8.04 (d, J = 8.6 Hz, 2H), 7.69 (d, J = 8.6 Hz, 2H), 7.63 (d, J = 7.0 Hz, 2H), 7.50−7.41 (m, 3H), 2.65 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 197.8, 145.8, 139.9, 135.8, 128.94, 128.9, 128.2, 127.3, 127.2, 26.6; HRMS (ESI-TOF) calcd for $[C_{14}H_{12}O + Na]^+$ 219.0780, found 219.0783.

*Data for 2-acetylnaphthalene (**4i**):*[17b] yield 52 mg (61%); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ = 8.48 (s, 1H), 8.04 (dd, J = 8.7, 1.7 Hz, 1H), 7.97 (d, J = 8.2 Hz, 1H), 7.92−7.86 (m, 2H), 7.66−7.53 (m, 2H), 2.73 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 198.2, 135.6, 134.5, 132.5, 130.2, 129.5, 128.6, 128.5, 127.8, 126.8, 123.9, 26.7.

*Data for 4-chloroacetophenone (**4j**):*[17a] yield 60.3 mg (78%); colorless oil; IR ($CHCl_3$) ν_{max} = 3018, 2927, 2855, 1687, 1590, 1572, 1488, 1429, 1397, 1358, 1261, 1095, 1013, 958, 831, 668 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ = 7.89 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.7 Hz, 2H), 2.58 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 196.8, 139.5, 135.4, 129.7, 128.9, 26.5.

*Data for 2-acetylpyridine (**4k**):*[23] yield 46 mg (76%); colorless oil; IR ($CHCl_3$) ν_{max} = 3010, 1700, 1584, 1437, 1358, 1283, 1239, 1101, 1044, 955, 591 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ = 8.68−8.66 (m, 1H), 8.04−8.02 (m, 1H), 7.83−7.78 (m, 1H), 7.48−7.43 (m, 1H), 2.72 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 200.0, 153.5, 148.9, 136.8, 127.0, 121.6, 25.7.

*Data for 4-acetylpyridine (**4l**):*[24] yield 46 mg (76%); colorless oil; IR ($CHCl_3$) ν_{max} = 3048, 1697, 1557, 1409, 1363, 1267, 1221, 1063, 1020, 992, 962, 818, 600, 588 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ = 8.76 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 2.52 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 197.1, 150.7, 142.7, 121.2, 26.5.

*Data for 2-acetylthiophene (**4m**):*[25] yield 47.3 mg (75%); brown oil; IR ($CHCl_3$) ν_{max} = 3091, 1663, 1518, 1415, 1357, 1275, 1035, 934, 858, 676, 592 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ = 7.69 (dd, J = 5.0, 1.4 Hz, 1H), 7.63 (dd, J = 3.5, 1.4 Hz, 1H), 7.12 (dd, J = 5.0, 3.5 Hz, 1H), 2.56 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 190.7, 144.5, 133.7, 132.4, 128.1. 26.8.

*Data for 2-(2-oxopropoxy)benzoic acid (**6c**):*[17b] yield 74.8 mg (77%); colorless oil; IR ($CHCl_3$) ν_{max} = 3212, 2919, 1781, 1717, 1600, 1485, 1458, 1418, 1341, 1295, 1252, 1184, 1165, 1095, 1058, 1036, 958, 862, 829, 684, 646 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ = 8.18 (dd, J = 7.8, 1.4 Hz, 1H), 7.53 (t, J = 7.2 Hz, 1H), 7.18 (t, J = 7.6 Hz, 1H), 6.91 (d, J = 8.2 Hz, 1H), 4.89 (s, 2H), 2.30 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 201.2, 165.4, 156.3, 134.8, 134.1, 123.0, 118.9, 113.0, 73.7, 26.1; HRMS (ESI-TOF) calcd for $[C_{10}H_{10}O_4 + Na]^+$ 217.0471, found 217.0472.

*Data for 2-oxopropyl 2-(2-oxopropoxy)benzoate (**6d**):*[17b] yield 96.3 mg (77%); white solid; mp 62−64 °C; IR ($CHCl_3$) ν_{max} = 3020, 2928, 2846, 1728, 1603, 1586, 1491, 1457, 1420, 1364, 1306, 1253, 1180, 1168, 1134, 1097, 1060, 1012, 964, 884, 828, 703, 668 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ = 7.96 (dd, J = 7.8, 1.8 Hz, 1H), 7.51−7.48 (m, 1H), 7.1 (td, J = 7.6, 0.8 Hz, 1H), 6.84 (d, J = 8.3 Hz, 1H), 4.88 (s, 2H), 4.60 (s, 2H), 2.35 (s, 3H), 2.23 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 205.7, 201.7, 164.7, 157.6, 134.3, 132.4,

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121.5, 119.5, 113.6, 73.9, 68.6, 26.9, 26.2; HRMS (ESI-TOF) calcd for $[C_{13}H_{14}O_5 + Na]^+$ 273.0733, found 273.0700.

*Data for 2-oxopropyl 4-(2-oxopropoxy)benzoate (**6e**):*[17b] yield 95.1 mg (76%); white solid; mp 80−82 °C; IR ($CHCl_3$) ν_{max} = 3021, 2928, 1721, 1607, 1583, 1509, 1420, 1371, 1314, 1276, 1170, 1115, 1070, 1008, 966, 883, 848, 696, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ = 8.03 (d, J = 9.0 Hz, 2H), 6.91 (d, J = 9.0 Hz, 2H), 4.82 (s, 2H), 4.61 (s, 2H), 2.28 (s, 3H), 2.21 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 204.3, 201.9, 165.3, 161.7, 132.1, 122.6, 114.3, 72.8, 68.6, 26.5, 26.2; HRMS (ESI-TOF) calcd for $[C_{13}H_{14}O_5 + Na]^+$ 273.0733, found 273.0734.

*Data for 1-phenoxypropan-2-one (**6f**):*[17b] yield 63.1 mg (84%); colorless oil; IR ($CHCl_3$) ν_{max} = 3043, 3065, 2919, 2849, 1733, 1599, 1590, 1496, 1457, 1433, 1359, 1305, 1295, 1228, 1172, 1155, 1085, 1067, 967, 888, 817, 806, 782, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ = 7.33−7.28 (m, 2H), 7.02−6.98 (m, 1H), 6.91−6.88 (m, 2H), 4.54 (s, 2H), 2.28 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 205.9, 157.6, 129.6, 121.7, 114.4, 72.9, 26.6; HRMS (ESI-TOF) calcd for $[C_9H_{10}O_2 + Na]^+$ 173.0573, found 173.0573.

*Data for 1-(benzyloxy)propan-2-one (**6g**):*[17b] yield 68.1 mg (83%); colorless oil; IR ($CHCl_3$) ν_{max} = 3067, 3032, 2868, 1729, 1603, 1584, 1497, 1455, 1376, 1357, 1276, 1226, 1167, 1118, 1074, 1028, 1013, 939, 868, 699, 682 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ = 7.38−7.25 (m, 5H), 4.58 (s, 2H), 4.07 (s, 2H), 2.16 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 206.6, 137.1, 128.5, 128.0, 127.8, 75.2, 73.3, 26.4; HRMS (ESI-TOF) calcd for $[C_{10}H_{12}O_2 + Na]^+$ 187.0730, found 187.0729.

*Data for 1-[4-(tert-butyl)phenoxy]propan-2-one (**6h**):*[17b] yield 77.4 mg (75%); colorless oil; IR ($CHCl_3$) ν_{max} = 3041, 2963, 2906, 2869, 1724, 1610, 1583, 1514, 1480, 1464, 1435, 1364, 1297, 1255, 1234, 1185, 1066, 829, 809, 682 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ = 7.32 (d, J = 8.9 Hz, 2H), 6.82 (d, J = 8.9 Hz, 2H), 4.52 (s, 2H), 2.28 (s, 3H), 1.30 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 206.4, 155.5, 144.5, 126.5, 114.0, 73.2, 34.1, 31.5, 26.6; HRMS (ESI-TOF) calcd for $[C_{13}H_{18}O_2 + Na]^+$ 229.1199, found 229.1199.

*Data for 1-(naphthalen-2-yloxy)propan-2-one (**6i**):*[17b] yield 76.1 mg (76%); white solid; mp 64−66 °C; IR ($CHCl_3$) ν_{max} = 3028, 3056, 2924, 2850, 1732, 1631, 1600, 1509, 1470, 1432, 1390, 1358, 1272, 1259, 1222, 1173, 1122, 1071, 978, 950, 908, 875, 838, 819, 638 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ = 7.79 (d, J = 8.8 Hz, 2H), 7.72 (d, J = 8.2 Hz, 1H), 7.48−7.44 (m, 1H), 7.39−7.35 (m, 1H), 7.22 (dd, J = 9.0, 2.6 Hz, 1H), 7.03 (d, J = 2.5 Hz, 1H), 4.66 (s, 2H), 2.33 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 205.9, 155.6, 134.2, 129.9, 129.3, 127.7, 126.8, 126.6, 124.2, 118.5, 106.9, 73.0, 26.7; HRMS (ESI-TOF) calcd for $[C_{13}H_{12}O_2 + Na]^+$ 223.0730, found 223.0729.

*Data for 1-(2-bromo-5-methoxyphenoxy)propan-2-one (**6j**):*[17a] yield 105 mg (81%); white solid; mp 68−70 °C; IR ($CHCl_3$) ν_{max} = 2939, 1721, 1586, 1488, 1462, 1432, 1359, 1307, 1283, 1263, 1201, 1169, 1067, 1024, 910, 832, 649 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ = 7.45 (d, J = 8.7 Hz, 1H), 6.46 (dd, J = 8.7, 2.7 Hz, 1H), 6.35 (d, J = 2.7 Hz, 1H), 4.52 (s, 2H), 3.78 (s, 3H), 2.38 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 205.6, 160.1, 154.7, 133.5, 107.1, 102.7, 101.0, 73.6, 55.6, 27.0; HRMS (ESI-TOF) calcd for $[C_{10}H_{11}BrO_3 + Na]^+$ 280.9784, found 280.9783.

*Data for 2-oxopropyl 4-methylbenzoate (**6k**):*[17b] yield 83.6 mg (87%); colorless oil; IR ($CHCl_3$) ν_{max} = 3036, 3006, 2927, 1735, 1719, 1611, 1577, 1509, 1420, 1374, 1279, 1177, 1112, 1022, 962, 841, 691, 639 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ = 7.97 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.1 Hz, 2H), 4.86 (s, 2H), 2.40 (s, 3H), 2.22 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 202.1, 165.9, 144.2, 129.9, 129.2, 126.3, 68.6, 26.2, 21.6; HRMS (ESI-TOF) calcd for $[C_{11}H_{12}O_3 + Na]^+$ 215.0679, found 215.0675.

*Data for 2-oxopropyl 4-nitrobenzoate (**6l**):*[17b] yield 71.4 mg (64%); white solid; mp 102−104 °C; IR ($CHCl_3$) ν_{max} = 3115, 3081, 3060, 2977, 2934, 2855, 1742, 1721, 1607, 1524, 1421, 1367, 1320, 1274, 1184, 1120, 1106, 1011, 964, 883, 855, 720, 623 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ = 8.28 (d, J = 9.1 Hz, 2H), 8.23 (d, J = 9.1 Hz, 2H), 4.97 (s, 2H), 2.23 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 200.3, 164.0, 150.7, 134.6, 131.0, 123.6, 69.1, 26.1; HRMS (ESI-TOF) calcd for $[C_{10}H_9O_5N + Na]^+$ 246.0373, found 246.0379.

*Data for 2-oxopropyl 3,5-dinitrobenzoate (**6m**):*[17b] yield 84.5 mg (63%); white solid; mp 139−141 °C; IR ($CHCl_3$) ν_{max} = 3093, 3020, 2923, 1735, 1630, 1599, 1547, 1462, 1418, 1345, 1285, 1157, 1075, 1035, 923, 905, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ = 9.27−9.25 (m, 1H), 9.24−9.20 (m, 2H), 5.05 (s, 2H), 2.27 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 199.1, 161.9, 148.7, 132.9, 129.7, 122.8, 69.6, 25.9; HRMS (ESI-TOF) calcd for $[C_{10}H_8O_7N_2 + Na]^+$ 291.0224, found 291.0230.

*Data for 3-oxo-1-phenylbutyl acetate (**6n**):*[17b] yield 75.3 mg (73%); colorless oil; IR ($CHCl_3$) ν_{max} = 3064, 3032, 2927, 2853, 1736, 1721, 1608, 1495, 1454, 1373, 1239, 1163, 1043, 950, 917, 871, 701, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ = 7.37−7.28 (m, 5H), 6.18 (dd, J = 8.7, 4.9 Hz, 1H), 3.12 (dd, J = 16.6, 8.7 Hz, 1H), 2.82 (dd, J = 16.7, 4.9 Hz, 1H), 2.15 (s, 3H), 2.04 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 204.7, 169.8, 139.6, 128.6, 128.2, 126.4, 71.6, 49.8, 30.4, 21.0; HRMS (ESI-TOF) calcd for $[C_{12}H_{14}O_3 + Na]^+$ 229.0835, found 229.0835.

*Data for 1-(benzo[d][1,3]dioxol-5-yl)-3-oxobutyl acetate (**6o**):*[17a] yield 101.4 mg (81%); colorless oil; IR ($CHCl_3$) ν_{max} = 2919, 2852, 1773, 1736, 1660, 1625, 1600, 1503, 1489, 1448, 1359, 1239, 1178, 1103, 1037, 977, 929, 804, 788 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ = 6.84−6.75 (m, 3H), 6.09 (dd, J = 8.5, 5.1 Hz, 1H), 5.94 (s, 2H), 3.27 (dd, J = 16.6, 8.5 Hz, 1H), 2.80 (dd, J = 16.6, 5.2 Hz, 1H), 2.14 (s, 3H), 2.02 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 204.7, 169.8, 147.8, 147.5, 133.4, 120.3, 108.3, 106.9, 101.1, 71.4, 49.8, 30.4, 21.1; HRMS (ESI-TOF) calcd for $[C_{13}H_{14}O_5 + Na]^+$ 273.0733, found 273.0735.

*Data for 1-(4-methoxyphenyl)-3-oxobutyl acetate (**6p**):*[17b] yield 89.8 mg (76%); colorless oil; IR ($CHCl_3$) ν_{max} = 3003, 2960, 2936, 2840, 1740, 1729, 1612, 1516, 1464, 1424, 1372, 1303, 1177, 1033, 948, 835, 657 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ = 7.29 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 6.13 (dd, J = 8.5, 5.3 Hz, 1H), 3.78 (s, 3H), 3.10 (dd, J = 16.5, 8.5 Hz, 1H), 2.81 (dd, J = 16.5, 5.3 Hz, 1H), 2.14 (s, 3H), 2.01 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 204.8, 169.9, 159.5, 131.6, 128.0, 113.9, 71.3, 55.2, 49.6, 30.4, 21.1; HRMS (ESI-TOF) calcd for $[C_{13}H_{16}O_4 + Na]^+$ 259.0941, found 259.0948.

*Data for 1-(naphthalen-1-yl)-3-oxobutyl benzoate (**6q**):*[17b] yield 127.4 mg (80%); colorless oil; IR ($CHCl_3$) ν_{max} = 3062, 3009, 2925, 2854, 1719, 1601, 1584, 1510, 1492, 1451, 1417, 1398, 1363, 1315, 1270, 1176, 1110, 1070, 1058, 1026, 975, 938, 862, 798, 713, 686 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ = 8.25 (d, J = 8.4 Hz, 1H), 8.10−8.07 (m, 2H), 7.88 (d, J = 7.6 Hz, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.64−7.42 (m, 7H), 7.21 (dd, J = 9.0, 4.0 Hz, 1H), 3.40 (dd, J = 16.9, 8.6 Hz, 1H), 3.13 (dd, J = 16.9, 4.1 Hz, 1H), 2.23 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 204.6, 165.3, 135.6, 133.9, 133.1, 129.9, 129.8, 129.6, 129.0, 128.9, 128.7, 126.6, 125.8, 125.3, 123.7, 122.9, 69.9, 49.6, 30.4; HRMS (ESI-TOF) calcd for $[C_{21}H_{18}O_3 + Na]^+$ 341.1148, found 341.1148.

*Data for 4-(benzyloxy)-4-(4-nitrophenyl)butan-2-one (**6r**):*[17b] yield 82.3 mg (55%); colorless oil; IR ($CHCl_3$) ν_{max} = 3066, 3032, 3008, 2865, 1716, 1606, 1521, 1497, 1415, 1347, 1162, 1096, 1075, 1028, 884, 857, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ = 8.15 (d, J = 8.8 Hz, 2H), 7.48 (d, J = 8.7 Hz, 2H), 7.27−7.21 (m, 5H), 4.93 (dd, J = 8.4, 4.6 Hz, 1H), 4.32 (d, J = 11.3 Hz, 1H), 4.27 (d, J = 11.3 Hz, 1H), 2.99 (dd, J = 16.5, 8.5 Hz, 1H), 2.57 (dd, J = 16.5, 4.6 Hz, 1H), 2.10 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 205.3, 148.9, 147.6, 137.2, 128.4, 127.9, 127.9, 127.5, 123.9, 76.5, 71.5, 51.5, 31.0; HRMS (ESI-TOF) calcd for $[C_{17}H_{17}NO_4 + Na]^+$ 322.1050, found 322.1049.

*Data for 2-oxononan-4-yl acetate (**6s**):*[17b] yield 77.1 mg (77%); colorless oil; IR ($CHCl_3$) ν_{max} = 3011, 2950, 2932, 2861, 1736, 1717, 1677, 1628, 1459, 1424, 1364, 1248, 1166, 1023, 981, 960, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ = 5.22−5.16 (m, 1H), 2.70 (dd, J = 16.2, 7.4 Hz, 1H), 2.57 (dd, J = 16.2, 5.3 Hz, 1H), 2.13 (s, 3H), 2.01 (s, 3H), 1.54−1.51 (m, 2H), 1.32−1.21 (m, 6H), 0.86 (t, J = 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 205.8, 170.5, 70.3,

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48.0, 34.1, 31.5, 30.4, 24.8, 22.5, 21.1, 14.0; HRMS (ESI-TOF) calcd for $[C_{11}H_{20}O_3 + Na]^+$ 223.1305, found 223.1307.

*Data for 4-[(tert-butyldiphenylsilyl)oxy]-4-phenylbutan-2-one (**6t**):*[17a] yield 159 mg (79%); colorless oil; IR ($CHCl_3$) ν_{max} = 3070, 2999, 2931, 2894, 2858, 1716, 1589, 1472, 1454, 1427, 1391, 1361, 1309, 1259, 1190, 1161, 1111, 1028, 1007, 956, 912, 855, 822, 701, 613 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/ TMS) δ = 7.65−7.63 (m, 2H), 7.44−7.40 (m, 3H), 7.38−7.32 (m, 3H), 7.25−7.18 (m, 7H), 5.15 (t, J = 6.5 Hz, 1H), 2.92 (dd, J = 15.2, 6.5 Hz, 1H), 2.71 (dd, J = 15.2, 6.4 Hz, 1H), 1.90 (s, 3H), 1.01 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 206.4, 143.5, 135.8, 133.7, 133.2, 129.7, 129.5, 128.1, 127.5, 127.4, 127.3, 126.2, 72.3, 54.1, 31.1, 26.9, 19.2; HRMS (ESI-TOF) calcd for $[C_{26}H_{30}O_2Si + Na]^+$ 425.1907, found 425.1904.

*Data for 1-[(tert-Butyldiphenylsilyl)oxy]-1-phenylpropan-2-one (**6u**):*[17b] yield 149.6 mg (77%); colorless oil; IR ($CHCl_3$) ν_{max} = 3070, 2961, 2932, 2894, 2859, 1717, 1589, 1492, 1472, 1428, 1391, 1351, 1307, 1190, 1113, 1070, 1028, 910, 855, 823, 701, 648 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/ TMS) δ = 7.66−7.64 (m, 2H), 7.47−7.42 (m, 3H), 7.40−7.32 (m, 5H), 7.31−7.27 (m, 5H), 5.08 (s, 1H), 2.02 (s, 3H), 1.13 (m, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 207.7, 138.2, 135.7, 135.6, 132.8, 132.6, 130.0, 129.8, 128.5, 128.1, 127.8, 127.6, 126.2, 81.7, 26.9, 24.3, 19.3; HRMS (ESI-TOF) calcd for $[C_{25}H_{28}O_2Si + Na]^+$ 411.1751, found 411.1755.

*Data for 2-oxononan-3-yl acetate (**6v**):*[17b] yield 82.1 mg (82%); colorless oil; IR ($CHCl_3$) ν_{max} = 3027, 2956, 2929, 2851, 1744, 1731, 1462, 1429, 1376, 1239, 1122, 1072, 1046, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ = 4.98 (dd, J = 8.2, 4.6 Hz, 1H), 2.16 (s, 3H), 2.15 (s, 3H), 1.76−1.71 (m, 2H), 1.54−1.25 (m, 8H), 0.88 (t, J = 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 205.5, 170.7, 78.7, 31.5, 30.2, 28.9, 26.1, 25.1, 22.5, 20.7, 14.0.

*Data for 3-(methoxymethoxy)nonan-2-one (**6w**):*[17a] yield 80.9 mg (80%); colorless oil; IR ($CHCl_3$) ν_{max} = 3019, 2956, 2928, 2857, 1719, 1466, 1355, 1153, 1122, 1104, 1037, 921, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ = 4.64 (s, 2H), 3.97 (t, J = 6.3 Hz, 1H), 3.38 (s, 3H), 2.17 (s, 3H), 1.66−1.62 (m, 2H), 1.41−1.32 (m, 8H), 0.87 (t, J = 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 210.1, 96.4, 82.8, 56.0, 32.0, 31.6, 29.0, 25.9, 25.1, 22.5, 14.0; HRMS (ESI-TOF) calcd for $[C_{11}H_{22}O_3 + Na]^+$ 225.1461, found 225.1459.

*Data for 2-oxo-1-phenylpropyl acetate (**6x**):*[17b] yield 70.1 mg (73%); colorless oil; IR ($CHCl_3$) ν_{max} = 3065, 3030, 2925, 2854, 1745, 1733, 1678, 1626, 1603, 1496, 1455, 1428, 1373, 1234, 1169, 1124, 1081, 1051, 961, 941, 914, 866, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ = 7.44−7.38 (m, 5H), 5.97 (s, 1H), 2.20 (s, 3H), 2.12 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 201.7, 170.3, 133.1, 129.4, 129.1, 128.1, 80.9, 26.1, 20.7; HRMS (ESI-TOF) calcd for $[C_{11}H_{12}O_3 + Na]^+$ 215.0679, found 215.0676.

*Data for 2-oxopentan-3-yl 2-(3-fluorophenyl)acetate (**6y**):* yield 90.5 mg (76%); colorless oil; IR ($CHCl_3$) ν_{max} = 2921, 2850, 1742, 1731,1613, 1593, 1490, 1452, 1265, 1144, 1114 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ = 7.31−7.27 (m, 1H), 7.11−6.95 (m, 3H), 4.96 (dd, J = 7.8, 4.6 Hz, 1H), 3.71 (s, 2H), 2.09 (s, 3H), 1.83−1.72 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 204.8, 170.6, 164.02, and 161.58 ($J_{C,F}$ = 244 Hz), 135.81 and 135.74 ($J_{C,F}$ = 7.0 Hz), 130.08 and 130.0 ($J_{C,F}$ = 8.0 Hz), 125.04 and 125.01 ($J_{C,F}$ = 3.0 Hz), 116.49 and 116.27 ($J_{C,F}$ = 22.0 Hz), 114.35 and 114.14 ($J_{C,F}$ = 21.0 Hz), 80.15, 40.68, and 40.67 ($J_{C,F}$ = 1.0 Hz), 26.2, 23.6, 9.4; HRMS (ESI-TOF) calcd for $[C_{13}H_{15}FO_3 + Na]^+$ 261.0897, found 261.0902.

*Data for 1-[[(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl]oxy]-propan-2-one (**6aa**):*[17b] yield 55.2 mg (52%); colorless oil; $[\alpha]_D^{25}$ = −73.3 (c = 1.0, $CHCl_3$); IR ($CHCl_3$) ν_{max} = 3020, 2958, 2928, 2872, 1720, 1457, 1370, 1116, 1015, 938, 842, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ = 4.14 (d, J = 16.8 Hz, 1H), 3.93 (d, J = 16.8 Hz, 1H), 3.11 (td, J = 10.6, 4.1 Hz, 1H), 2.28−2.24 (m, 1H), 2.18 (s, 3H), 2.06−2.00 (m, 1H), 1.68−1.61 (m, 2H), 1.37−1.28 (m, 2H), 1.01−0.84 (m, 8H), 0.78 (d, J = 7.0 Hz, 4H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 208.0, 80.3, 74.3, 48.0, 40.0, 34.4, 31.4, 26.6, 25.6, 23.2, 22.2, 20.9, 16.1; HRMS (ESI-TOF) calcd for $[C_{13}H_{24}O_2 + Na]^+$ 235.1669, found 235.1666.

*Data for methyl 3-acetyloctanoate (**6ab**):*[26] yield 66.1 mg (66%); colorless oil; IR ($CHCl_3$) ν_{max} = 2959, 2931, 2864, 1740, 1718, 1459, 1439, 1356, 1205, 1165, 1068, 1021, 898, 600 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ = 3.58 (s, 3H), 3.01−2.94 (m, 1H), 2.78−2.69 (m, 1H), 2.38−2.29 (m, 1H), 2.22 (s, 3H), 1.59−1.50 (m, 1H), 1.39−1.21 (m, 7H), 0.87 (t, J = 6.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 210.9, 173.0, 51.7, 47.9, 35.0, 31.7, 31.3, 29.5, 26.5, 22.4, 13.9; HRMS (ESI-TOF) calcd for $[C_{11}H_{20}O_3 + Na]^+$ 223.1306, found 223.1305.

*Data for methyl 3-(4-nitrophenyl)-4-oxopentanoate (**6ac**).* yield 82.9 mg (66%); light yellow solid; mp 108−110 °C; IR ($CHCl_3$) ν_{max} = 3020, 1720, 1525, 1349, 1216, 1018, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ = 8.21 (dd, J = 6.8, 2.0 Hz, 2H), 7.42 (dd, J = 6.8, 2.0 Hz, 2H), 4.34−4.30 (m, 1H), 3.6 (s, 3H), 3.27−3.20 (m, 1H), 2.57 (dd, J = 17.0, 5.4 Hz, 1H), 2.15 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 205.2, 171.8, 144.52, 129.2, 124.8, 54.4, 52.0, 36.6, 29.7; HRMS (ESI-TOF) calcd for $[C_{12}H_{13}NO_5 + Na]^+$ 274.0686, found 274.0686.

*Data for 2-(2-oxopropyl)isoindoline-1,3-dione (**6ad**):*[27] yield 80.3 mg (79%); white solid; mp 110−112 °C; IR ($CHCl_3$) ν_{max} = 2925, 1771, 1724, 1416, 1369, 1307, 1190, 1018, 725, 714 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ = 7.85 (dd, J = 5.4, 2.7 Hz, 2H), 7.72 (dd, J = 5.4, 2.7 Hz, 2H), 4.48 (s, 2H), 2.25 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 199.7, 167.6, 134.1, 131.9, 123.4, 47.0, 26.9; HRMS (ESI-TOF) calcd for $[C_{11}H_9NO_3 + Na]^+$ 226.0475, found 226.0474.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00137.

^1H and ^{13}C NMR spectra for all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4155. (b) Dess, D. B.; Martin, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 7277.

(2) (a) Nicolaou, K. C.; Sugita, K.; Baran, P. S.; Zhong, Y.-L. *Angew. Chem., Int. Ed.* **2001**, *40*, 207. (b) Nicolaou, K. C.; Sugita, K.; Baran, P. S.; Zhong, Y.-L. *J. Am. Chem. Soc.* **2002**, *124*, 2221.

(3) Chaudhari, S. S.; Akamanchi, K. G. *Synthesis* **1999**, 760.

(4) Lawrence, N. J.; Crump, J. P.; McGown, A. T.; Hadfield, J. A. *Tetrahedron Lett.* **2001**, *42*, 3939.

(5) Thongsornkleeb, C.; Danheiser, R. L. *J. Org. Chem.* **2005**, *70*, 2364.

(6) Linderman, R. J.; Graves, D. M. *J. Org. Chem.* **1989**, *54*, 661.

(7) Meyer, S. D.; Schreiber, S. L. *J. Org. Chem.* **1994**, *59*, 7549.

(8) (a) Weiner, B.; Baeza, A.; Jerphagnon, T.; Feringa, B. L. *J. Am. Chem. Soc.* **2009**, *131*, 9473. (b) Keith, J. A.; Henry, P. M. *Angew. Chem., Int. Ed.* **2009**, *48*, 9038. (c) Michel, B. W.; McCombs, J. R.; Winkler, A.; Sigman, M. S. *Angew. Chem., Int. Ed.* **2010**, *49*, 7312. (d) Dong, J. J.; Browne, W. R.; Feringa, B. L. *Angew. Chem., Int. Ed.* **2015**, *54*, 734.

(9) Aguado, J.; Serrano, D. P.; Van Grieken, R.; Escola, J. M.; García, R.; Carretero, S. Modified Wacker of long chain terminal olefins. In

DOI: 10.1021/acs.joc.6b00137
J. Org. Chem. 2016, 81, 2113−2121

Book of Extended Abstracts of the Fourth World Congress on Oxidation Catalysis; Berlin, Potsdam, Germany, 2001; pp 493−497.
(10) (a) Clement, W. H.; Selwitz, C. M. *J. Org. Chem.* **1964**, *29*, 241. (b) Tsuji, J. *Synthesis* **1984**, 369. (c) Tsuji, J.; Nagashima, H.; Hori, K. *Chem. Lett.* **1980**, *9*, 257. (d) Roussel, M.; Mimoun, H. *J. Org. Chem.* **1980**, *45*, 5387. (e) Mimoun, H.; Charpentier, R.; Mitschler, A.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1980**, *102*, 1047. (f) Miller, D. G.; Wayner, D. D. *J. Org. Chem.* **1990**, *55*, 2924. (g) Tang, H.-G.; Sherrington, D. C. *J. Catal.* **1993**, *142*, 540.
(11) (a) ten Brink, G.-J.; Arends, I. W. C. E.; Papadogianakis, G.; Sheldon, R. A. *Appl. Catal., A* **2000**, *194-195*, 435. (b) Jiang, H.; Jia, L.; Li, J. *Green Chem.* **2000**, *2*, 161. (c) Namboodiri, V. V.; Varma, R. S.; Sahle-Demessie, E.; Pillai, U. R. *Green Chem.* **2002**, *4*, 170. (d) Wang, Z.-Y.; Jiang, H.-F.; Qi, C.-R.; Wang, Y.-G.; Dong, Y.-S.; Liu, H.-L. *Green Chem.* **2005**, *7*, 582. (e) Cornell, C. N.; Sigman, M. S. *Inorg. Chem.* **2007**, *46*, 1903 and references therein. (f) Wang, J.-Q.; Cai, F.; Wang, E.; He, L.-N. *Green Chem.* **2007**, *9*, 882. (g) Michel, B. W.; Camelio, A. M.; Cornell, C. N.; Sigman, M. S. *J. Am. Chem. Soc.* **2009**, *131*, 6076. (h) Wang, J.-L.; He, L.-N.; Miao, C.-X.; Li, Y.-N. *Green Chem.* **2009**, *11*, 1317.
(12) (a) Kulkarni, M. G.; Shaikh, Y. B.; Borhade, A. S.; Chavhan, S. W.; Dhondge, A. P.; Gaikwad, D. D.; Desai, M. P.; Birhade, D. R.; Dhatrak, N. R. *Tetrahedron Lett.* **2013**, *54*, 2293. (b) Zhang, G.; Xie, X.; Wang, Y.; Wen, X.; Zhao, Y.; Ding, C. *Org. Biomol. Chem.* **2013**, *11*, 2947. (c) Wang, Y.-F.; Gao, Y.-R.; Mao, S.; Zhang, Y.-L.; Guo, D.-D.; Yan, Z.-L.; Guo, S.-H.; Wang, Y.-Q. *Org. Lett.* **2014**, *16*, 1610.
(13) (a) Thottumkara, A. P.; Bowsher, M. S.; Vinod, T. K. *Org. Lett.* **2005**, *7*, 2933. (b) Nicolai, S.; Erard, S.; González, D. F.; Waser, J. *Org. Lett.* **2010**, *12*, 384. (c) Lovick, H. M.; Michael, F. E. *J. Am. Chem. Soc.* **2010**, *132*, 1249. (d) Zhu, Y.-P.; Jia, F.-C.; Liu, M.-C.; Wu, A.-X. *Org. Lett.* **2012**, *14*, 4414. (e) Zhang, B.; Studer, A. *Org. Lett.* **2013**, *15*, 4548. (f) Purohit, V. C.; Allwein, S. P.; Bakale, R. P. *Org. Lett.* **2013**, *15*, 1650. (g) Hong, K. B.; Johnston, J. N. *Org. Lett.* **2014**, *16*, 3804.
(14) For reviews see: (a) Dong, D.-Q.; Hao, S.-H.; Wang, Z.-L.; Chen, C. *Org. Biomol. Chem.* **2014**, *12*, 4278 and references therein. (b) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2002**, *102*, 2523. (c) Romero, R. M.; Woste, T. H.; Muniz, K. *Chem. - Asian J.* **2014**, *9*, 972. (d) Singh, F. V.; Wirth, T. *Chem. - Asian J.* **2014**, *9*, 950. (e) Wirth, T. *Angew. Chem., Int. Ed.* **2005**, *44*, 3656.
(15) Bigi, M. A.; White, M. C. *J. Am. Chem. Soc.* **2013**, *135*, 7831.
(16) Teo, P.; Wickens, Z. K.; Dong, G.; Grubbs, R. H. *Org. Lett.* **2012**, *14*, 3237.
(17) (a) Fernandes, R. A.; Bethi, V. *Tetrahedron* **2014**, *70*, 4760. (b) Fernandes, R. A.; Chaudhari, D. A. *J. Org. Chem.* **2014**, *79*, 5787.
(18) (a) Michel, B. W.; Camelio, A. M.; Cornell, C. N.; Sigman, M. S. *J. Am. Chem. Soc.* **2009**, *131*, 6076. (b) Muzart, J. *Tetrahedron* **2007**, *63*, 7505.
(19) A provisional process patent on this work has been filed, application no. 2965/MUM/2015.
(20) Erdogan, G.; Grotjahn, D. B. *Org. Lett.* **2014**, *16*, 2818.
(21) Zhang, W.-C.; Li, C.-J. *J. Org. Chem.* **2000**, *65*, 5831.
(22) Mitsudo, K.; Kaide, T.; Nakamoto, E.; Yoshida, K.; Tanaka, H. *J. Am. Chem. Soc.* **2007**, *129*, 2246.
(23) Lauber, M. B.; Stahl, S. S. *ACS Catal.* **2013**, *3*, 2612.
(24) Pascanu, V.; Gomez, A. B.; Ayats, C.; Platero-Prats, A. E.; Carson, F.; Su, J.; Yao, Q.; Pericas, M. À.; Zou, X.; Martín-Matute, B. *ACS Catal.* **2015**, *5*, 472.
(25) Bindu, P.; Naini, S. R.; Shanmukha Rao, K.; Dubey, P. K.; Pal, S. *J. Heterocyclic Chem.* **2014**, *51*, 586.
(26) Kato, K.; Teraguchi, R.; Kusakabe, T.; Motodate, S.; Yamamura, S.; Mochida, T.; Akita, H. *Synlett* **2007**, 63.
(27) Lei, A.; Wu, S.; He, M.; Zhang, X. *J. Am. Chem. Soc.* **2004**, *126*, 1626.

DOI: 10.1021/acs.joc.6b00137
J. Org. Chem. 2016, 81, 2113−2121