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

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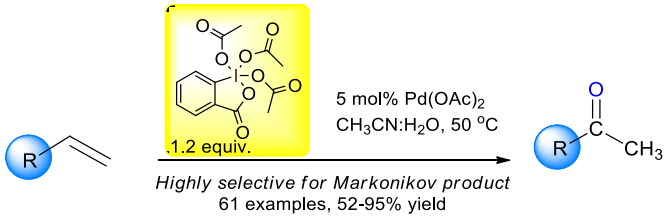


ABSTRACT: A mimic of Wacker process for C=O bond formation in terminal olefins can be initiated by a combination of Pd(II)/hypervalent iodine reagent, Dess-Martin periodinane (DMP) to generate methyl ketones. This operationally simple and scalable method offers Markonikov selectivity, has good functional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

INTRODUCTION

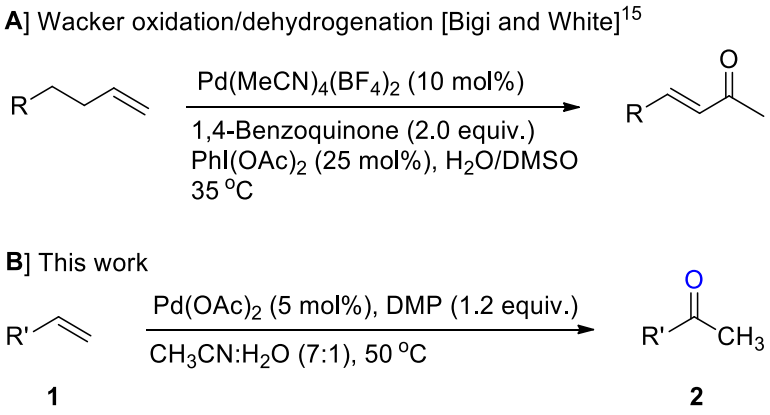
The chemistry of polyvalent iodine compounds has experienced an unprecedented growth during the last few decades. This rolling interest is mainly due to the remarkable oxidizing properties of hypervalent iodine reagents, their benign environmental nature and commercial availability. From the beginning of 1990s, the domain of oxidative transformation has witnessed a renaissance, in particular, the pioneering contributions by Dess and Martin has triggered confidence on 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-alkynyl propenals,[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 last few decades, substantial research interest has been focused on developing an alternative to the traditional re-oxidant $CuCl_2$ for Wacker oxidation, which mainly generates corrosive reaction media, chlorinated byproducts and isomerization of 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 the C-C=O bond. Despite the significant advances made in the greener side of the 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% of $PhI(OAc)_2$ (Scheme 1, **A**). 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 terminal oxidant. The information gathered during the course of development of terminal oxidants in Wacker process in our group[17] made 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 planned to study Wacker-type oxidation for C=O bond formation under N_2 atmosphere with

palladium catalyst and cyclic λ^5-iodanes (Scheme 1, **B**). The reaction system does not require oxygen or any other additives.

Scheme 1. Oxidation of Terminal Olefins to Methyl Ketones.

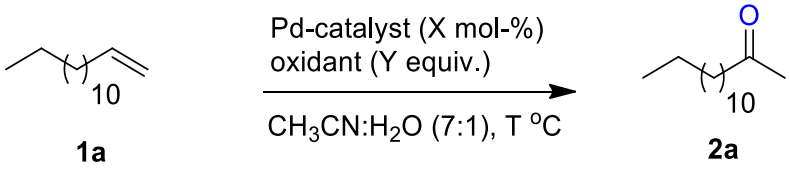


RESULTS AND DISCUSSION

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% of $Pd(OAc)_2$ in CH_3CN:H_2O (7:1) at 50 °C could produce tetradecane-2-one **2a** in 95% yield in 1 h reaction (Table 1, entry 2). However, lower yields were observed in the case of other oxidising agents such as 2-iodoxybenzoic acid (IBX) and (diacetoxyiodo)benzene [$PhI(OAc)_2$] (Table 1, entries 1 and 3, respectively). Oxidation in presence of granular iodine as well as mixture of I_2:*m*CPBA (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 that $Pd(OAc)_2$ to be the most suitable catalyst (entry 2). Various solvent combinations like 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 CH_3CN:H_2O mixture (7:1, entry 2). Effect of temperature on the reaction was studied (Table 1, entries 18-21), which confirmed that 50 ^oC was optimum requirement (entry 2). Higher temperatures may decompose DMP resulting in reduced yield. Screening of 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% of DMP required longer reaction time and delivered the methyl ketone product in lower yields although the starting olefin was consumed (entries 26 and 27). Lowering of $Pd(OAc)_2$ 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 over oxidation to unsaturated compounds like in the work by White et al.[15] (Scheme 1, **A**) was not observed indicating a good selectivity towards only Wacker oxidation with the reaction system in this work.

Table 1. Optimization of Reaction Conditions.[a]



Entry	Pd-catalyst (X mol %)	Oxidant (Y equiv.)	Solvent	Temp. (^oC)	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

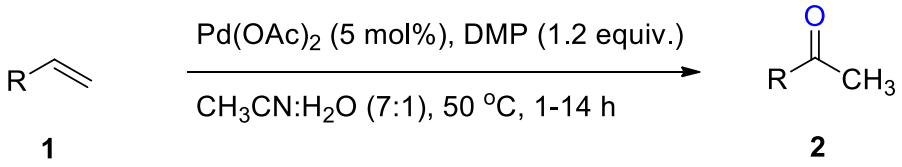
12	$[PdCl(allyl)]_2$ (5)	DMP (1.2)	$CH_3CN:H_2O$ (7:1)	50	1.5	31
13	Pd-C (5)	DMP (1.2)	$CH_3CN:H_2O$ (7:1)	50	12	NR[b]
14	$Pd(OAc)_2$(5)	DMP (1.2)	DMA:H_2O (7:1)	50	13	49
15	$Pd(OAc)_2$(5)	DMP (1.2)	DMF:H_2O (7:1)	50	10	53
16	$Pd(OAc)_2$(5)	DMP (1.2)	THF:H_2O (7:1)	50	10	24
17	$Pd(OAc)_2$(5)	DMP (1.2)	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%−2.0 equiv.), Pd-catalyst (1−5 mol%), at T °C in solvent (4 mL) under N_2.
[b] NR = No Reaction

The scope of the reaction was investigated by varying the olefins. Initially, various inactivated long chain olefins were tested under the optimized condition (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 alpha, omega-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%), **2h** (81%), benzoate **2i** (77%), MOM **2j** (65%), silyl **2k** (87%), esters **2l** (88%), **2m** (84%), aldehyde **2n** (80%) and acids **2o** (75%) and **2p** (77%) with complete Markonikov selectivity and in good yields (Table 2). Olefin bearing primary OH group failed to give the product

2q. There could be competing reactions from both olefin and OH groups which resulted in trail of spots on TLC. Lowering of DMP concentration resulted in unused starting material even after prolonged reaction time. However the secondary OH group containing olefin worked well giving **2r** in moderate 56% yield.

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

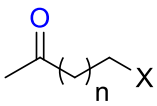


1 **2**

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]



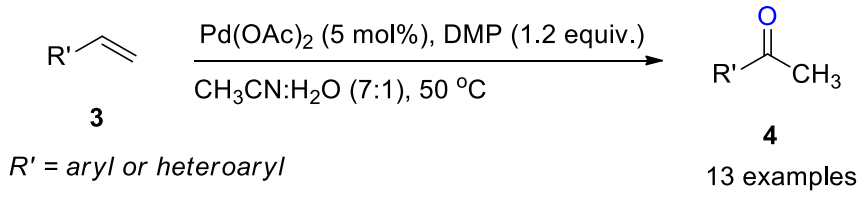
2g, X = Br, n = 7, 79%
2h, X = Br, n = 10, 81%
2i, X = OBz, n = 3, 77%
2j, X = OMOM, n = 8, 65%
2k, X = OTBDPS, n = 0, 87%
2l, X = CO_2Et, n = 0, 88%
2m, X = CO_2Me, n = 7, 84%
2n, X = CHO, n = 7, 80%
2o, X = CO_2H, n = 1, 75%
2p, X = CO_2H, n = 2, 77%
2q, X = OH, n = 8, complex mixt.
2r, X = CH(OH)-CH_3,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

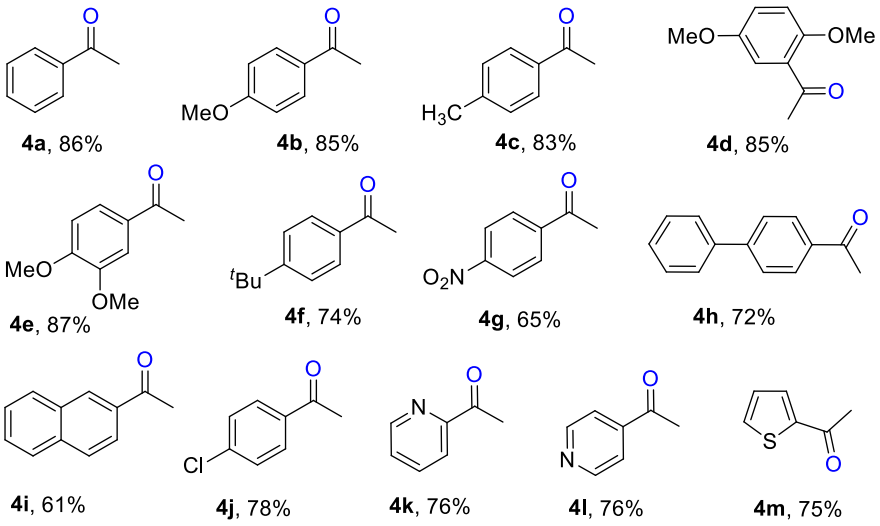
[a]Olefin **1** (0.5 mmol), $Pd(OAc)_2$ (5 mol%), DMP (1.2 equiv.), $CH_3CN:H_2O$ (7:1, 4 mL), 50 °C under N_2. [b]Substrate (0.5 mmol), $Pd(OAc)_2$ (10 mol %), DMP (2.4 equiv), $CH_3CN:H_2O$ (7:1, 4 mL), at 50 °C under N_2

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 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. With electron donor groups the yields of aryl methyl ketones was quite good: **4b** (85%), **4c** (83%), **4d** (85%), **4e** (87%) and **4f** (74%). Electron-withdrawing group

such as nitro which deactivates the ring was found to decrease the efficiency of the reaction considerably (**4g**, 65%). 4-Phenyl styrene and 2-vinyl naphthalene delivered the corresponding methyl ketones **4h** (72%) and **4i** (61%) in good yields. Notably, the tolerance of 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 ^{1}H NMR.

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



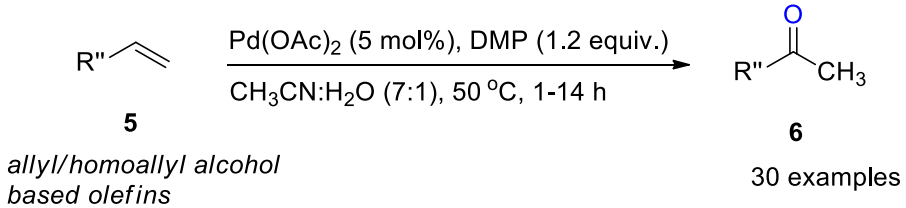


[a] Olefin **3** (0.5 mmol), $Pd(OAc)_2$ (5 mol%), DMP (1.2 equiv.), $CH_3CN:H_2O$ (7:1, 4 mL), 50 °C under N_2

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 co-ordination of the neighboring oxygen atom to the Lewis acidic palladium causing water attack through multiple pathways.[18] Substrates with tertiary alcohol functionality at the homoallylic position failed to deliver the methyl ketones **6a** and **6b**. *O*-Allyl salicylic acid delivered the methyl ketone **6c** in 77% yield. Similarly bis-allyl derivatives of salicylic acid (with ester and ether functionality) 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-methoxy phenyl (**6j**, 81%), 4-methylbenzoyl (**6k**, 87%) and nitrobenzoyl **6l** (64%) and **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 Markonikov 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). 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 delivered the ketones **6ab** and **6ac** in 66% yield each, respectively. Terminal unbranched allyl phthalimide offered methyl ketone **6ad** in a good yield of 79%.

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

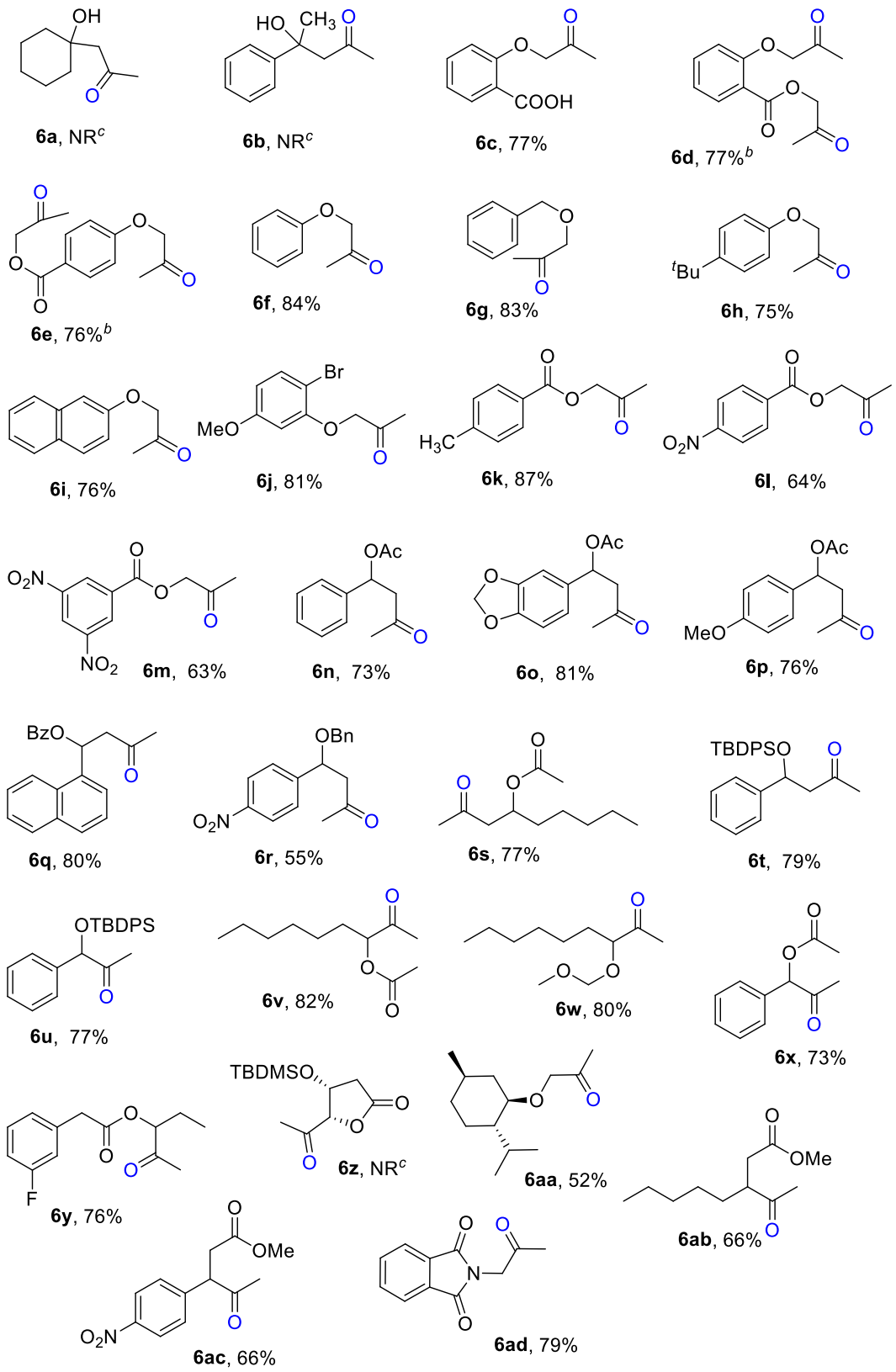


5

allyl/homoallyl alcohol based olefins

6

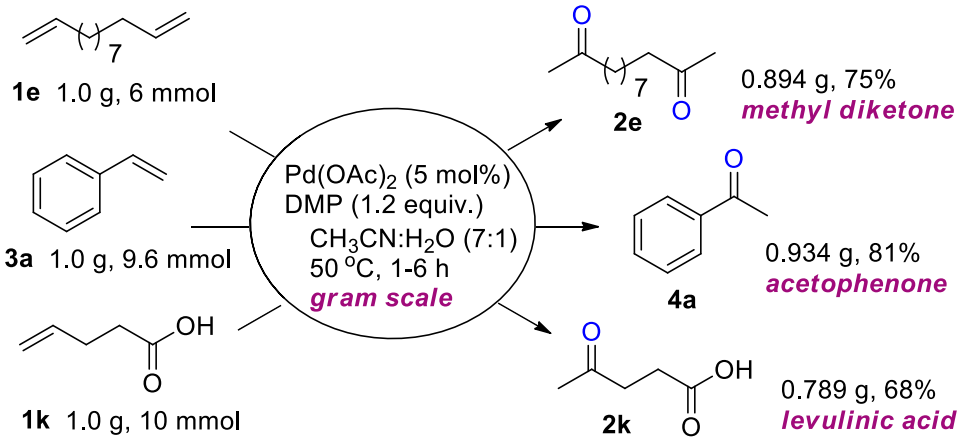
30 examples



[a] Reaction 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] 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.

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

Scheme 2. Gram Scale Reactions.



Iodine compounds in higher valence state are good oxidants.[14b] Similar to $CuCl_2$ acting as oxidant in the normal Wacker process we believe DMP serves as an oxidant for 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 revealed here an efficient and general method to synthesize methyl ketones employing 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, allyl and homoallyl alcohols with various protecting groups have been explored (61 examples). A wide spectrum of functional-group

tolerance, mild reaction conditions, Markonikov selectivity and 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 were recorded with a spectrometer operating at 500 or 400 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 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 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**).

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.

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.

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.

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.

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.

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.

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.

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.

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.

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 (ESITOF) calcd for $[C_{13}H_{26}O_3+Na]^+$ 253.1774, found 253.1778.

1-(tert-Butyldiphenylsilyloxy)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.

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 {^{1}H} NMR (100 MHz, $CDCl_3$): δ = 200.6, 167.1, 61.3, 50.1, 30.1, 14.0.

Methyl 10-oxo-undecanoate (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 cm1 ; ^{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 {^{1}H} 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.

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 {^{1}H} 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.

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 {^{1}H} NMR (100 MHz, $CDCl_3$): δ = 206.6, 178.2, 37.7, 29.8, 27.7.

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 {^{1}H} 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.

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}; ^1H 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.

Acetophenone (4a):[17b] Yield (51.7 mg, 86%). Pale yellow oil; ^1H 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.

4-Methoxyacetophenone (4b):[17b] Yield (63.8 mg, 85%). Colorless oil; ^1H 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).

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} ; ^1H 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.

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}; ^1H 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.

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}; ^1H 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.

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}; ^1H 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.

4-Nitroacetophenone (4g):[17b] Yield (53.7 mg, 65%). Pale yellow solid; mp 76−78 °C; ^1H 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.

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}; ^1H 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.

2-Acetylnapthalene (4i):[17b] Yield (52 mg, 61%). Colorless oil; ^1H 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.

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}; ^1H 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.

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}; ^1H 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.

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}; ^1H 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.

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}; ^1H 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.

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}; ^1H 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.

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}; ^1H 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 {^{1}H} NMR (100 MHz, $CDCl_3$): δ = 205.7, 201.7, 164.7, 157.6, 134.3, 132.4, 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.

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}; ^{1}H 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 {^{1}H} 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.

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}; ^{1}H 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 {^{1}H} 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.

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}; ^{1}H 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 {^{1}H} 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.

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}; ^{1}H 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 {^{1}H} 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.

1-(Napthalen-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.

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.

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.

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.

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.

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.

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.

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.

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.

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.

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, 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.

4-(tert-Butyldiphenylsilyloxy)-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.

1-(tert-Butyldiphenylsilyloxy)-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.

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.

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.

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.

2-Oxopentan-3-yl 2-(3-fluorophenyl)acetate (6y): Yield (90.5mg, 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 ppm; HRMS (ESI-TOF) calcd for $[C_{13}H_{15}FO_3+Na]^+$ 261.0897 found 261.0902.

1-[(1R,2S,5R)-2-Isopropyl-5-methylcyclohexyloxy]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.

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 {^{1}H} 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.

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}; ^{1}H 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 {^{1}H} 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.

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}; ^{1}H 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 {^{1}H} 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

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Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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