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An expedient osmium(VI)/$K_3Fe(CN)_6$-mediated selective oxidation of benzylic, allylic and propargylic alcohols†

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A chemoselective osmium(VI) catalyzed oxidation of benzylic, allylic and propargylic alcohols using $K_3Fe(CN)_6$ as a secondary oxidant is described. This protocol is operationally simple and exhibits excellent chemoselectivity favouring the oxidation of benzylic alcohols over the aliphatic alcohols. A larger scale reaction was also found to be compatible.

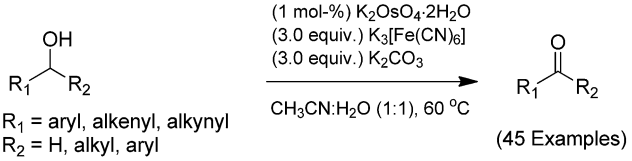
Introduction

Oxidation of alcohols is an important method for functional group transformations in synthetic organic chemistry[1] as well as in industry.[2] Many methods have been developed to accomplish this elementary reaction. Some of the notable methods involve the use of chromium reagents,[3] manganese(IV)oxide,[4] $(COCl)_2$/DMSO (Swern oxidation),[5] hypervalent iodine reagents,[6] TEMPO,[7] *etc.* An alternative and even more practical approach using metal complexes as catalyst in combination with terminal oxidants has been reported. Examples include Cu,[8] Pd,[9] Ru,[10] Au,[11] W,[12] Mn,[13] Fe,[14] Co,[15] V,[16] *etc.* An attractive alternative is the use of O_2 as primary oxidant in transition metal catalyzed alcohol oxidations.[17] In addition, Iwabuchi and co-workers reported an elegant method, in which the oxidation of various primary and secondary alcohols into corresponding carbonyl compounds is mediated by a novel alkoxyamine-type organocatalyst, 3-methyl-4-oxa-5-aza-homoadamantane with NaOCl as the primary oxidant.[18] However, the organocatalyst shows high reactivity and is not suitable for chemoselective oxidation of allylic, benzylic, and propargylic alcohols. Recently, Stahl and co-workers showed that Cu(I)/ABNO or TEMPO catalytic system exhibits high chemoselectivity for unhindered primary alcohols.[19] A few reports are documented to address the chemoselective oxidation of allylic and benzylic alcohols. Notable examples include DDQ/$NaNO_2$,[20] DDQ/$Mn(OAc)_3$,[21] NBS/thiourea,[22] vanadium complexes,[23] Pd-catalyst/α-bromo sulphoxide,[24] Pt black/H_2O_2,[25] Fe-catalyst/Na_2CO_3 [26] and *N*-hydroxyindole/CuCl.[27]

While many methods are known in literature for alcohol oxidation, the selectivity issue is still a concern and there is scope for developing newer methods, particularly for chemoselective oxidation of allylic, benzylic, and propargylic alcohols. Although osmium(IV) is frequently used for the dihydroxylation of olefins,[28] Beller and co-workers for the first time reported Os(IV)/DABCO catalyzed oxidation of alcohols using O_2 as a primary oxidant.[29] However, this protocol is not suitable for chemoselective oxidation of allylic and benzylic alcohols. Later Brown and co-workers achieved a practical Os/Cu co-catalyzed air oxidation of allylic and benzylic alcohols.[30] Recently Shah and co-workers developed osmium/chloramine-T catalyzed oxidation of allylic and benzylic alcohols.[31] Working on similar lines we explored the $K_2OsO_4 \cdot 2H_2O$/$K_3[Fe(CN)_6]$-mediated chemoselective oxidation of various allylic, benzylic and propargylic alcohols to carbonyl compounds in good to excellent yields. Primary and secondary unactivated alcohols are unreactive towards this oxidation system (Scheme 1).

Results and discussion

To begin this study, 4-methoxy benzyl alcohol (**1**) was chosen as a model substrate to optimize the reaction conditions (Table 1). Initially, **1** was added to a well stirred solution of $K_2OsO_4 \cdot 2H_2O$ (0.4 mol%), $K_3[Fe(CN)_6]$ (3.0 equiv.), K_2CO_3, (3.0 equiv.), pyridine (2.0 mol%), and $MeSO_2NH_2$ (2.0 equiv.) in a mixture of *t*BuOH : H_2O (1 : 1). The reaction was performed in a closed vessel and stirred for 72 h at room temperature. The desired product 4-methoxy benzaldehyde (**2a**) was isolated in 67% yield (Table 1, entry 1). When we increased the catalyst loading to 0.6 mol% and 0.8 mol% (Table 1, entries 2 and 3), after 48 h, under



Scheme 1 Oxidation of benzylic, allylic and propargylic alcohols.

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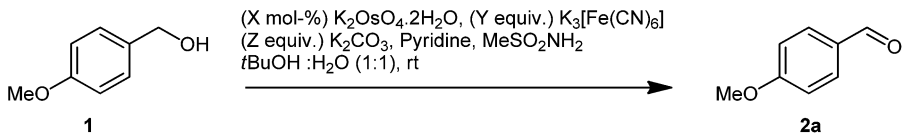
† Electronic supplementary information (ESI) available: Copies of ^1H and ^{13}C NMR spectra for all the compounds. See DOI: 10.1039/c4ra07500e

Table 1 Optimization of alcohol oxidation varying the amounts of Os catalyst, Fe complex, K_2CO_3 and additives[a]



1 2a

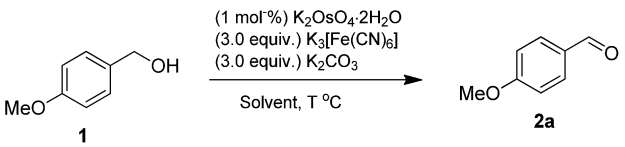
Entry	$K_2OsO_4\cdot 2H_2O$ (X mol%)	$K_3[Fe(CN)_6]$ (Y equiv.)	K_2CO_3 (Z equiv.)	Pyridine (mol%)	$MeSO_2NH_2$ (equiv.)	t (h)	Yield[b] (%)
1	0.4	3.0	3.0	2.0	2.0	72	67
2	0.6	3.0	3.0	2.0	2.0	48	73
3	0.8	3.0	3.0	2.0	2.0	48	78
4	0.8	6.0	6.0	2.0	2.0	48	87
5	1.0	6.0	6.0	2.0	2.0	13	Quant.
6	1.0	3.0	3.0	2.0	2.0	18	93
7	1.0	2.0	2.0	2.0	2.0	72	62
8	1.0	3.0	3.0	2.0	—	18	96
9	1.0	3.0	3.0	—	2.0	15	96
10	1.0	3.0	3.0	—	—	15	Quant.
11	—	3.0	3.0	—	—	15	NR
12	1.0	—	3.0	—	—	15	2
13	1.0	3.0	—	—	—	15	NR

[a] Reaction conditions: substrate (0.5 mmol), $K_2OsO_4\cdot 2H_2O$ (X mol%), $K_3[Fe(CN)_6]$ (Y equiv.), K_2CO_3 (Z equiv.), pyridine, $MeSO_2NH_2$, in tBuOH (1.5 mL) and H_2O (1.5 mL) at room temperature. [b] Isolated yields. NR = no reaction.

similar conditions the yield of **2a** was improved to 73% and 78% respectively. With the increase in the amount of secondary oxidant, $K_3[Fe(CN)_6]$ and K_2CO_3 to 6.0 equiv. each, 87% of **2a** was isolated (Table 1, entry 4). However to our delight, increasing the Os(VI) catalyst loading to 1.0 mol%, after 13 h, **2a** was obtained quantitatively (entry 5). To improve the oxidation efficiency, we kept the Os(VI) loading to 1 mol%, and decreased the amount of secondary oxidant and K_2CO_3 to 3.0 equiv. each. This resulted in **2a** in 93% yield (entry 6). Further decrease in the amount of oxidant and K_2CO_3 (2.0 equiv. each) required longer reaction time and gave lower yield (Table 1, entry 7). The requirement of additives like pyridine and $MeSO_2NH_2$ was further investigated. With no $MeSO_2NH_2$ added, the reaction was completed in 18 hours giving **2a** in 96% yield (entry 8). Similarly, with no pyridine added, **2a** was obtained also in 96% yield (entry 9). Gratifyingly, in the absence of both pyridine and $MeSO_2NH_2$, the reaction yielded **2a** quantitatively (entry 10). With no primary oxidant $K_2OsO_4\cdot 2H_2O$ there was no reaction (entry 11). Similarly, with no $K_3[Fe(CN)_6]$ or no K_2CO_3, the reaction did not work (entries 12 and 13). This strongly indicated the need of secondary oxidants.

Encouraged by these results, we carried out the screening of solvent and temperature conditions (Table 2) using the optimum requirement from Table 1, entry 10. Of the solvent mixtures (with water, Table 2, entries 1–7) tested we found $CH_3CN : H_2O$ (1 : 1) was the best combination which delivered aldehyde **2a** quantitatively, with substantially reduced reaction time (entry 6, 1.5 h). Further, from the temperature study (Table 2, entries 8–12) the reaction in $CH_3CN : H_2O$ (1 : 1) at 60 °C reduced the reaction time to just 15 min, producing aldehyde **2a** quantitatively. The oxidation of **1a** on gram scale (1 g, 7.23 mmol) gave **2a** without much change in reaction time and yield (98%, entry 13). Thus, with the optimized condition which include the use of $K_2OsO_4\cdot 2H_2O$ (1.0 mol%), $K_3[Fe(CN)_6]$ (3.0 equiv.), K_2CO_3 (3.0 equiv.) in $CH_3CN : H_2O$ (1 : 1) at 60 °C, we explored the scope and limitations of this oxidation protocol (Table 3).

Table 2 Optimization of alcohol oxidation varying solvent and temperature[a]



1 2a

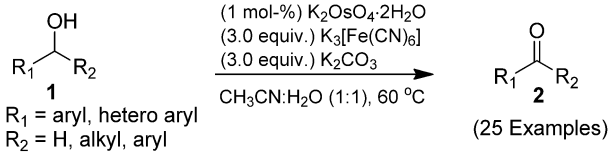
Entry	Solvent (1 : 1)	T °C	t	% yield[b]
1	tBuOH : H_2O	rt	15 h	Quant.
2	DMF : H_2O	rt	5 h	78
3	DMSO : H_2O	rt	4 h	88
4	THF : H_2O	rt	27 h	67
5	Toluene : H_2O	rt	15 h	73
6	$CH_3CN : H_2O$	rt	1.5 h	Quant.
7	$(CH_3)_2CO : H_2O$	rt	6 h	92
8	tBuOH : H_2O	45	13 h	97
9	tBuOH : H_2O	60	12 h	95
10	$CH_3CN : H_2O$	45	30 min	Quant.
11	$CH_3CN : H_2O$	60	15 min	Quant.
12	$CH_3CN : H_2O$	80	12 min	Quant.
13	$CH_3CN : H_2O$	60	20 min	98[c]

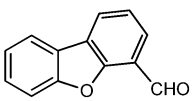
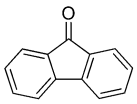
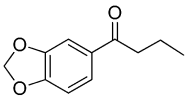
[a] Reaction conditions: substrate (0.5 mmol), $K_2OsO_4\cdot 2H_2O$ (0.005 mmol), $K_3[Fe(CN)_6]$ (1.5 mmol), K_2CO_3 (1.5 mmol) in solvent (1.5 mL) and H_2O (1.5 mL). [b] Isolated yields. [c] Reaction on 1 g, 7.23 mmol of **1**.

Various benzyl alcohols with aryl substitution involving electron donating and withdrawing groups like methoxy, methyl, nitro, chloro and hydroxyl were compatible with the reaction conditions, delivering the desired aryl aldehydes **2a–l** in good to quantitative yields within the short reaction times of 10–45 min (Table 3, entries 1–12). Benzyl alcohols with strong electron withdrawing nitro groups exhibited higher reactivity compared to benzyl alcohols having the electron donating groups (Table 3, *e.g.* entry 5 *vs.* 3). In some cases a mere filtration of the reaction mixture and concentration of the filtrate afforded virtually pure products. α-Hetero aryl methyl alcohols delivered the corresponding aldehydes **2m–u** (entries 13–21) in good yields with the exception of N-based heterocycles like **2p–t** obtained in moderate 36–51% yields (entries 16–20). It appears that N-based heterocycles are poor substrates with the exception of 1*H*-indole-3ylmethanol giving **2n** in good yields (78%, entry 14, Table 3). The dibenzofuran based aldehyde **2u** was obtained in good yield (73%, entry 21) after 4 h reaction. Secondary benzylic alcohols were also oxidized under the present oxidation protocol delivering aryl ketones **2v–y** in good to quantitative yields (entries 22–25).

The method was further explored towards oxidation of benzylic and/or allylic and propargylic alcohols (Table 4). With the optimized conditions, the primary allyl alcohols delivered the unsaturated aldehydes **4a** and **b** in good yields (Table 4, entries 1 and 2). The secondary allyl alcohols provided the unsaturated ketones **4c–f** in moderate to good yields (entries 3–6). Similarly, the primary propargyl alcohols afforded the

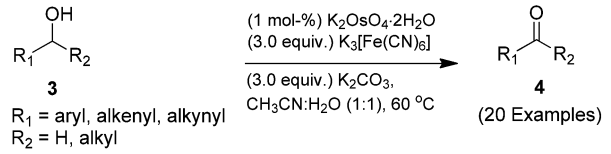
Table 3 Oxidation of various aryl alcohols by $K_2[OsO_4\cdot 2H_2O]/K_3[Fe(CN)_6]$ system[a]



Entry	Product		*t*	Yield[b] (%)
1	4-MeO-benzaldehyde	**2a**	15 min	Quant.
2	4-Me-benzaldehyde	**2b**	20 min	98
3	2,5-Dimethoxybenzaldehyde	**2c**	45 min	Quant.
4	3,4-Dimethoxybenzaldehyde	**2d**	30 min	Quant.
5	4-NO_2-benzaldehyde	**2e**	10 min	Quant.
6	3-NO_2-benzaldehyde	**2f**	15 min	98
7	4-Cl-benzaldehyde	**2g**	45 min	87
8	2-Cl-benzaldehyde	**2h**	45 min	81
9	α-Napthaldehyde	**2i**	20 min	96
10	Piperonal	**2j**	25 min	Quant.
11	2-OH-benzaldehyde	**2k**	45 min	65
12	4-OH-3-methoxy benzaldehyde	**2l**	45 min	88
13	Thiophene-2-carbaldehyde	**2m**	2 h	78
14	1*H*-Indole-3-carbaldehyde	**2n**	2 h	78
15	Furfural	**2o**	2 h	82
16	Pyridine-3-carbaldehyde	**2p**	6 h	36
17	Pyridine-2-carbaldehyde	**2q**	10 h	38
18	Quinoline-4-carbaldehyde	**2r**	18 h	40
19	3-Methyl-1-phenyl-1*H*-pyrazole-4-carbaldehyde	**2s**	18 h	42
20	1*H*-Imidazole-4-carbaldehyde	**2t**	18 h	51
21		**2u**	4 h	73
22	Acetophenone	**2v**	15 min	Quant.
23	Benzophenone	**2w**	15 min	Quant.
24		**2x**	30 min	Quant.
25		**2y**	8 h	91

[a] Reaction conditions: substrate (0.5 mmol), $K_2OsO_4\cdot 2H_2O$ (0.005 mmol), $K_3[Fe(CN)_6]$ (1.5 mmol), K_2CO_3 (1.5 mmol) in CH_3CN (1.5 mL) and H_2O (1.5 mL) at 60 °C. [b] Isolated yields.

Table 4 Oxidation of allylic, benzylic and propargylic alcohols[a]



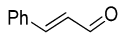
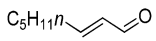
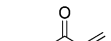
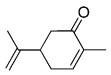
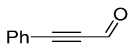
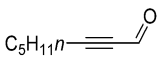
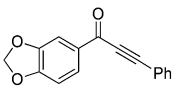
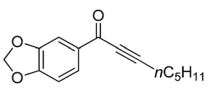
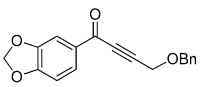
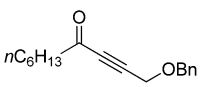
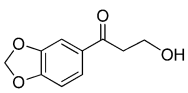
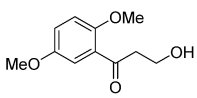
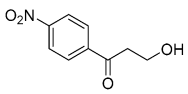
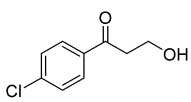
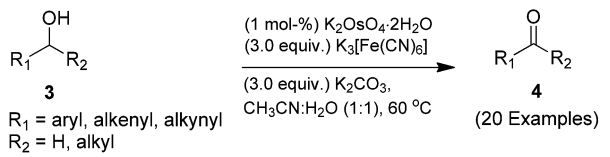
Entry	Product		T (h)	Yield[b] (%)
1		**4a**	3	87
2		**4b**	14	88
3		**4c**	18	77
4		**4d**	18	58
5		**4e**	18	47
6		**4f**	18	68
7		**4g**	3	85
8		**4h**	18	65
9		**4i**	10	88
10		**4j**	10	68
11		**4k**	10	76
12		**4l**	10	64
13		**4m**	10	84
14		**4n**	12	85
15		**4o**	12	69
16		**4p**	12	77
17	Dodecanal	**4q**	48	NF
18	Phenylacetaldehyde	**4r**	48	NF
19		**4s**	48	NF

Table 4 (*Contd.*)



Entry	Product		T (h)	Yield[b] (%)
20		**4t**	48	NF

[a] Reaction conditions: substrate (0.5 mmol), $K_2OsO_4 \cdot 2H_2O$ (0.005 mmol), $K_3[Fe(CN)_6]$ (1.5 mmol), K_2CO_3(1.5 mmol) in CH_3CN (1.5 mL) and H_2O (1.5 mL) at 60 °C. [b] Isolated yields. NF = not formed.

alkynals **4g** and **h** in good yields (entries 7 and 8). The benzylic and secondary propargyl alcohols gave the corresponding ketones **4i–l** in good to excellent yields (entries 9–12). The selective oxidation of benzylic over unactivated primary aliphatic alcohols resulted in only benzylic alcohol oxidation delivering the β-hydroxyalkyl aryl ketones **4m–p** in good yields (entries 13–16). The oxidation of unactivated primary or secondary alcohols failed to deliver the corresponding carbonyl compounds **4q–t** (entries 17–20) indicating that the present protocol is mild and selective towards oxidation of benzylic, allylic and propargylic alcohols.

Conclusions

In conclusion, we have developed an efficient method for the selective oxidation of benzylic, allylic and propargylic alcohols with catalytic Os(VI) and using $K_3[Fe(CN)_6]$ as secondary oxidant. The method is mild, operationally simple and can be carried out in a closed flask. High yields of aryl and unsaturated aldehydes and good chemoselectivity are other advantages of this method.

Experimental section

General information

Solvents and reagents were purified by standard methods. Thin-layer chromatography was performed on EM 250 Kieselgel 60 F254 silica gel plates. The spots were visualized by staining with $KMnO_4$ or under UV lamp. ^1H and ^{13}C NMR were recorded with a Bruker, AVANCE III 500 or 400 spectrometer and the chemical shifts are based on TMS peak at $\delta = 0.00$ pm for proton NMR and $CDCl_3$ peak at $\delta = 77.00$ ppm (t) in carbon NMR. IR spectra were obtained on Perkin Elmer Spectrum One 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 TOF method.

General procedure for oxidation of alcohols

To a well stirred solution of $K_2OsO_4 \cdot 2H_2O$ (1.8 mg, 0.005 mmol, 1.0 mol%), $K_3[Fe(CN)_6]$ (554 mg, 1.5 mmol, 3.0 equiv.), K_2CO_3, (207 mg, 1.5 mmol, 3.0 equiv.) in CH_3CN (1.5 mL) and H_2O (1.5 mL) was added the substrate alcohol (0.5 mmol) at room temperature. The reaction mixture was warmed to 60 °C and stirred for specified time (see Tables 3 and 4). It was then quenched with aq. saturated solution of. Na_2SO_3 (1.0 mL) and the solvent partially evaporated. The reaction mixture was then filtered through a small pad of silica gel and washed with EtOAc (3 × 10 mL). The filtrate was concentrated and the residue in some cases contained virtually pure compound and no further purification was necessary. In other cases the residue was purified by silica gel column chromatography using petroleum ether/EtOAc as an eluent to afford the carbonyl compounds.

4-Methoxybenzaldehyde (2a). Isolated yield of **2a**, (68 mg, quant.). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 9.89 (s, 1H), 7.84 (d, J = 8.8 Hz, 2H), 7.01 (d, J = 8.8 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 164.4, 131.8, 129.7, 114.1, 55.4.

4-Methylbenzaldehyde (2b). Isolated yield of **2b**, (59 mg, 98%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 9.96 (s, 1H), 7.77 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 7.8 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 145.4, 134.1, 129.7, 129.6, 21.7.

2,5-Dimethoxybenzaldehyde (2c). Isolated yield of **2c**, (83 mg, quant.). Yellow crystalline solid, mp 44–46 °C; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 10.43 (s, 1H), 7.32 (d, J = 3.3 Hz, 1H), 7.13 (dd, J = 9.0, 3.3 Hz, 1H), 6.93 (d, J = 9.0 Hz, 1H), 3.89 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.6, 156.7, 153.6, 124.9, 123.5, 113.3, 110.4, 56.1, 55.8.

3,4-Dimethoxybenzaldehyde (2d). Isolated yield of **2d**, (83.0 mg, quant.). White solid, mp 41–42 °C; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 9.84 (s, 1H), 7.45 (dd, J = 8.2, 2.0 Hz, 1H), 7.40 (d, J = 1.8 Hz, 1H), 6.97 (d, J = 8.2 Hz, 1H), 3.96 (s, 3H), 3.93 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 154.4, 149.6, 130.1, 126.8, 110.3, 108.9, 56.1, 56.0.

4-Nitrobenzaldehyde (2e). Isolated yield of **2e**, (75.5 mg, quant.). Yellow solid, mp 102–104 °C; ^{1}H NMR (500 MHz, $CDCl_3$/TMS) δ 10.16 (s, 1H), 8.40 (d, J = 8.6 Hz, 2H), 8.07 (d, J = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3, 151.1, 140.0, 130.5, 124.3.

3-Nitrobenzaldehyde (2f). Isolated yield of **2f**, (74 mg, 98%). Yellow solid, mp 54–56 °C; ^{1}H NMR (500 MHz, $CDCl_3$/TMS) δ 10.12 (s, 1H), 8.73–8.71 (m, 1H), 8.49 (d, J = 8.2 Hz, 1H), 8.24 (d, J = 7.6 Hz, 1H), 7.77 (t, J = 7.90 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.7, 148.7, 137.3, 134.6, 130.3, 128.5, 124.3.

4-Chlorobenzaldehyde (2g). Isolated yield of **2g**, (61.1 mg, 87%). White solid, mp 45–47 °C; ^{1}H NMR (500 MHz, $CDCl_3$/TMS) δ 9.98 (s, 1H), 7.83 (d, J = 8.6 Hz, 2H), 7.52 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 140.9, 134.6, 130.8, 129.4.

2-Chlorobenzaldehyde (2h). Isolated yield of **2h**, (56.9 mg, 81%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 10.50 (s, 1H), 7.93 (d, J = 7.7 Hz, 1H), 7.54–7.51 (m, 1H), 7.47–7.45 (m, 1H), 7.40 (t, J = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9, 137.9, 135.1, 132.3, 130.5, 129.3, 127.2.

1-Naphthaldehyde (2i). Isolated yield of **2i**, (75 mg, 96%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 10.41 (s, 1H), 9.26 (d, J = 8.6 Hz, 1H), 8.10 (d, J = 8.2 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 8.2 Hz, 1H), 7.72–7.70 (m, 1H), 7.68–7.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 138.9, 136.7, 135.3, 133.7, 131.4, 130.5, 129.1, 128.5, 126.9, 124.9.

Piperonal (2j). Isolated yield of **2j**, (75 mg, quant.). White solid, mp 35–37 °C; ^{1}H NMR (500 MHz, $CDCl_3$/TMS) δ 9.81 (s, 1H), 7.41 (d, J = 7.9 Hz, 1H), 7.33 (d, J = 1.5 Hz, 1H), 6.92 (d, J = 7.9 Hz, 1H), 6.07 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2, 153.0, 148.6, 131.8, 128.6, 108.3, 106.8, 102.0.

2-Hydroxybenzaldehyde (2k). Isolated yield of **2k**, (39.7 mg, 65%). Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$/TMS) δ 11.02 (s, 1H), 9.89 (s, 1H), 7.57–7.50 (m, 2H), 7.04–6.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 161.6, 137.0, 133.7, 120.6, 119.8, 117.6.

4-Hydroxy-3-methoxybenzaldehyde (2l). Isolated yield of **2l**, (66.9 mg, 88%). White solid, mp 81–82 °C; ^{1}H NMR (500 MHz, $CDCl_3$/TMS) δ 9.83 (s, 1H), 7.44–7.42 (m, 2H), 7.04 (d, J = 8.5 Hz, 1H), 6.21 (s, 1H), 3.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 151.8, 147.2, 129.7, 127.5, 114.4, 108.8, 56.0.

Thiophene-2-carbaldehyde (2m). Isolated yield of **2m**, (43.7 mg, 78%). Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 9.95 (s, 1H), 7.80–7.77 (m, 2H), 7.24–7.21 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 183.0, 144.0, 136.3, 135.1, 128.3.

1*H*-Indole-3-carbaldehyde (2n). Isolated yield of **2n**, (56.6 mg, 78%). Brown solid, mp 193–195 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.89 (s, 1H), 8.23 (s, 1H), 8.07 (d, J = 7.8 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.27–7.19 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 186.0, 139.2, 137.5, 124.4, 124.1, 122.8, 121.3, 118.6, 112.9.

Furfural (2o). Isolated yield of **2o**, (39.4 mg, 82%). Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$/TMS) δ 9.69 (s, 1H), 7.72–7.71 (m, 1H), 7.27 (d, J = 0.4 Hz, 1H), 6.63 (dd, J = 3.6, 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 152.8, 148.0, 121.0, 112.5.

Pyridine-3-carbaldehyde (2p). Isolated yield of **2p**, (19.3 mg, 36%). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 10.11 (s, 1H), 9.07 (d, J = 1.2 Hz, 1H), 8.84 (dd, J = 4.8, 1.4 Hz, 1H), 8.16 (td, J = 6.0, 2.0 Hz, 1H), 7.48 (dd, J = 7.8, 4.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7, 154.7, 152.0, 135.8, 131.4, 124.1.

Pyridine-2-carbaldehyde (2q). Isolated yield of **2q**, (20.4 mg, 38%). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 10.10 (s, 1H), 8.80 (d, J = 4.4 Hz, 1H), 7.97 (d, J = 7.7 Hz, 1H), 7.88 (td, J = 7.6, 0.7 Hz, 1H), 7.55–7.52 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 152.5, 149.9, 136.9, 127.7, 121.5.

Quinoline-4-carbaldehyde (2r). Isolated yield of **2r**, (31.4 mg, 40%). White solid, mp 45–47 °C; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 10.53 (s, 1H), 9.20 (d, 4.2 Hz, 1H), 9.02 (dd, J = 8.5, 1.0 Hz, 1H), 8.23 (d, J = 8.4 Hz, 1H), 7.85–7.80 (m, 2H), 7.74 (td, J = 7.7, 1.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 150.4, 149.2, 136.8, 130.2, 130.0, 129.4, 125.8, 124.4, 123.9.

3-Methyl-1-phenyl-1*H*-pyrazole-4-carbaldehyde (2s). Isolated yield of **2s**, (39.1 mg, 42%). White solid, mp 57–59 °C; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 9.99 (s, 1H), 8.34 (s, 1H), 7.68 (dd, J = 8.6, 1.1 Hz, 2H), 7.49 (t, J = 7.9 Hz, 2H), 7.38–7.34 (m, 1H), 2.59

(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.3, 151.9, 139.0, 131.7, 129.6, 127.6, 122.9, 119.5, 13.0.

1*H*-Imidazole-4-carbaldehyde (2t). Isolated yield of **2t**, (24.5 mg, 51%). Pale yellow solid, mp 174–176 °C; ^{1}H NMR (400 MHz, CD_3OD) δ 9.77 (s, 1H), 7.93 (s, 1H), 7.90 (s, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ 183.4, 138.8, 134.9, 129.5.

Dibenzo[*b*,*d*]furan-4-carbaldehyde (2u). Isolated yield of **2u**, (71.6 mg, 73%). White solid, mp 94–96 °C; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 10.6 (s, 1H), 8.21 (dd, J = 7.6, 1.2 Hz, 1H), 8.01–7.95 (m, 2H), 7.70 (d, J = 8.1 Hz, 1H), 7.54 (td, J = 7.8, 1.1 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.42 (t, J = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.4, 156.6, 155.9, 128.1, 127.5, 126.6, 126.0, 123.5, 122.9, 122.8, 121.2, 120.8, 112.1.

Acetophenone (2v). Isolated yield of **2v**, (60 mg, quant.). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 7.97–7.92 (m, 2H), 7.57–7.51 (m, 1H), 7.48–7.41 (m, 2H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 137.0, 133.0, 128.5, 128.2, 26.5.

Benzophenone (2w). Isolated yield of **2w**, (91.1 mg, quant.). White solid, mp 47–49 °C; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 7.81 (d, J = 7.0 Hz, 4H), 7.61–7.57 (m, 2H), 7.49 (t, J = 7.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 137.5, 132.4, 130.0, 128.2.

9*H*-Fluoren-9-one (2x). Isolated yield of **2x**, (90.1 mg, quant.). Yellow solid, mp 80–82 °C; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 7.66 (d, J = 7.4 Hz, 2H), 7.53–7.46 (m, 4H), 7.31–7.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 144.3, 134.5, 134.0, 128.9, 124.1, 120.2.

1-(Benzo[*d*][1,3]dioxol-5-yl)butan-1-one (2y). Isolated yield of **2y**, (87.5 mg, 91%). Colorless oil; IR ($CHCl_3$, cm^{-1}): ν 3079, 2964, 2928, 2906, 2873, 2784, 1674, 1605, 1504, 1488, 1443, 1359, 1303, 1248, 1141, 1114, 1089, 1039, 998, 935, 911, 807, 648, 620, 577; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 7.56 (dd, J = 8.2, 1.6 Hz, 1H), 7.44 (d, J = 1.7 Hz, 1H), 6.84 (d, J = 8.2 Hz, 1H), 6.03 (s, 2H), 2.86 (t, J = 7.3 Hz, 2H), 1.77–1.71 (m, 2H), 0.99 (t, J = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 151.3, 147.9, 131.7, 123.9, 107.54, 107.50, 101.6, 40.0, 17.7, 13.6; HRMS (ESI-TOF) calcd for $[C_{11}H_{12}O_3 + Na]^+$ 215.0679, found 215.0677.

Cinnamaldehyde (4a). Isolated yield of **4a**, (57.5 mg, 87%). Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$/TMS) δ 9.71 (d, J = 7.7 Hz, 1H), 7.57 (dd, J = 7.0, 2.4 Hz, 2H), 7.49 (d, J = 16.0 Hz, 1H), 7.45–7.43 (m, 3H), 6.57 (dd, J = 16.0, 7.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.7, 152.8, 134.0, 131.3, 129.1, 128.6, 128.5.

(*E*)-Oct-2-enal (4b). Isolated yield of **4b**, (55.5 mg, 88%). Colorless oil; IR ($CHCl_3$, cm^{-1}): ν 2956, 2930, 2862, 1688, 1635, 1465, 1382, 1146, 1097, 976, 909, 650; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 9.50 (d, J = 7.9 Hz, 1H), 6.89–6.81 (m, 1H), 6.15–6.08 (m, 1H), 2.36–2.30 (m, 2H), 1.55–1.47 (m, 2H), 1.36–1.25 (m, 4H), 0.90 (t, J = 6.9, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 159.1, 132.9, 32.7, 31.3, 27.5, 22.4, 13.9; HRMS (ESI-TOF) calcd for $[C_8H_{14}O + K]^+$ 165.0676, found 165.0681.

1-Phenylprop-2-en-1-one (4c). Isolated yield of **4c**, (50.9 mg, 77%). Colorless oil; IR ($CHCl_3$, cm^{-1}): ν 3065, 3020, 1733, 1672, 1609, 1580, 1448, 1404, 1286, 1233, 1180, 1072, 994, 698; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 7.95 (d, J = 7.1 Hz, 2H), 7.58–7.56 (m, 1H), 7.45 (t, J = 7.1 Hz, 2H), 7.16 (dd, J = 17.1, 10.6 Hz, 1H), 6.44 (dd, J = 17.1, 1.6 Hz, 1H), 5.94 (dd, J = 10.6, 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 137.2, 132.9, 132.3, 130.1, 128.6, 128.5; HRMS (ESI-TOF) calcd for $[C_9H_8O + Na]^+$ 155.0467, found 155.0473.

Dec-1-en-3-one (4d). Isolated yield of **4d**, (44.7 mg, 58%). Colorless oil; IR ($CHCl_3$, cm^{-1}): ν 2980, 2929, 2857, 1703, 1684, 1616, 1466, 1402, 1478, 1263, 1184, 1081, 985, 962, 911; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 6.35 (dd, J = 17.7, 10.5 Hz, 1H), 6.21 (dd, J = 17.6, 1.2 Hz, 1H), 5.81 (dd, J = 10.5 Hz, 1H), 2.57 (t, J = 7.5 Hz, 2H), 1.61–1.57 (m, 2H), 1.32–1.26 (m, 8H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.8, 136.4, 127.6, 39.5, 31.5, 29.0, 28.9, 23.8, 22.4, 13.9; HRMS (ESI-TOF) calcd for $[C_{10}H_{18}O + Na]^+$ 177.1250, found 177.1245.

2-Methyl-5-(prop-1-en-2-yl)cyclohex-2-enone (4e). Isolated yield of **4e**, (35.3 mg, 47%). Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$/TMS) δ 6.75–6.74 (m, 1H), 4.76 (d, J = 19.8 Hz, 2H), 2.71–2.63 (m, 1H), 2.59–2.54 (m, 1H), 2.46–2.07 (m, 3H), 1.77 (d, J = 1.2 Hz, 3H), 1.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 146.7, 144.7, 135.4, 110.4, 43.1, 42.4, 31.2, 20.5, 15.7.

Cyclohex-2-en-1-one (4f). Isolated yield of **4f**, (32.7 mg, 68%). Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$/TMS) δ 6.98 (td, J = 10.1, 4.2 Hz, 1H), 6.00 (td, J = 10.1, 2.0 Hz, 1H), 2.43–2.39 (m, 2H), 2.36–2.32 (m, 2H), 2.04–1.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 150.7, 129.9, 38.1, 25.6, 22.7.

3-Phenylpropiolaldehyde (4g). Isolated yield of **4g**, (55.3 mg, 85%). Colorless oil; IR ($CHCl_3$, cm^{-1}): ν 2926, 2855, 2738, 2240, 2189, 1660, 1596, 1489, 1444, 1388, 1283, 1260, 1178, 1160, 1070, 1027, 1002, 978, 922, 688, 617; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 9.41 (s, 1H), 7.59 (dd, J = 8.3, 1.1 Hz, 2H), 7.51–7.46 (m, 1H), 7.39–7.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 133.2, 131.2, 128.7, 119.3, 95.1, 88.4; HRMS (ESI-TOF) calcd for $[C_9H_6O + H]^+$ 131.0491, found 131.0494.

Oct-2-ynal (4h). Isolated yield of **4h**, (40.3 mg, 65%). Colorless oil; IR ($CHCl_3$, cm^{-1}): ν 3022, 2959, 2934, 2862, 2740, 2284, 2201, 1669, 1466, 1424, 1387, 1341, 1327, 1139, 1106, 1064, 1028, 976, 929, 908, 882, 812, 668; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 9.18 (s, 1H), 2.41 (t, J = 7.1 Hz, 2H), 1.62–1.57 (m, 2H), 1.42–1.33 (m, 4H), 0.91 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 99.4, 81.6, 30.9, 27.2, 22.0, 19.0, 13.8.

1-(Benzo[*d*][1,3]dioxol-5-yl)-3-phenylprop-2-yn-1-one (4i). Isolated yield of **4i**, (110 mg, 88%). Pale yellow solid, mp 92–93 °C; IR ($CHCl_3$, cm^{-1}): ν 3018, 2904, 2785, 2208, 1732, 1630, 1600, 1504, 1485, 1447, 1373, 1359, 1251, 1140, 1107, 1097, 1043, 1014, 997, 936, 908, 885, 822, 688, 668; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 7.90 (dd, J = 8.2, 1.6 Hz, 1H), 7.68–7.63 (m, 3H), 7.48–7.40 (m, 3H), 6.92 (d, J = 8.2 Hz, 1H), 6.09 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 152.8, 148.2, 132.9, 132.0, 130.6, 128.6, 127.2, 120.1, 108.2, 108.0, 102.1, 92.3, 86.7; HRMS (ESI-TOF) calcd for $[C_{16}H_{10}O_3 + Na]^+$ 273.0522, found 273.0523.

1-(Benzo[*d*][1,3]dioxol-5-yl)oct-2-yn-1-one (4j). Isolated yield of **4j**, (83.7 mg, 68%). Colorless oil; IR ($CHCl_3$, cm^{-1}): ν 3076, 2961, 2932, 2791, 2210, 1742, 1637, 1602, 1503, 1487, 1444, 1359, 1319, 1275, 1260, 1226, 1157, 1116, 1077, 1038, 934, 913, 888, 853, 806, 677, 648; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 7.79 (dd, J = 8.2, 1.7 Hz, 1H), 7.55 (d, J = 1.6 Hz, 1H), 6.87 (d, J = 8.1 Hz, 1H), 6.06 (s, 2H), 2.47 (t, J = 7.2 Hz, 2H), 1.67 (q, J = 7.3 Hz, 2H), 1.48–1.32 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 152.5, 147.9, 131.9, 126.9, 108.1,

107.7, 101.9, 95.9, 79.3, 30.9, 27.3, 21.9, 18.9, 13.7; HRMS (ESI-TOF) calcd for $[C_{15}H_{16}O_3 + Na]^+$ 267.0992, found 267.0991.

1-(Benzo[*d*][1,3]dioxol-5-yl)-4-(benzyloxy)but-2-yn-1-one (4k). Isolated yield of **4k**, (111.8 mg, 76%). Pale yellow solid, mp 69–70 °C; IR ($CHCl_3$, cm^{-1}): ν 3066, 3032, 2903, 2787, 2250, 2229, 1638, 1601, 1504, 1486, 1445, 1360, 1262, 1227, 1155, 1105, 1091, 1039, 932, 910, 857, 822, 806, 648, 605; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 7.82 (dd, J = 8.1, 1.7 Hz, 1H), 7.55 (d, J = 1.6 Hz, 1H), 7.40–7.31 (m, 5H), 6.88 (d, J = 8.2 Hz, 1H), 6.08 (s, 2H), 4.69 (s, 2H), 4.44 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 153.1, 148.3, 136.7, 131.6, 128.6, 128.1, 127.5, 126.8, 108.2, 108.0, 102.1, 89.3, 84.1, 72.2, 57.2; HRMS (ESI-TOF) calcd for $[C_{18}H_{14}O_4 + Na]^+$ 317.0784, found 317.0785.

1-(Benzyloxy)dec-2-yn-4-one (4l). Isolated yield of **4l**, (82.7 mg, 64%). Colorless oil; IR ($CHCl_3$, cm^{-1}): ν 3032, 2950, 2929, 2214, 1676, 1496, 1455, 1399, 1351, 1256, 1228, 1154, 1092, 1028, 907, 698; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 7.39–7.31 (m, 5H), 4.62 (s, 2H), 4.33 (s, 2H), 2.57 (t, J = 7.4 Hz, 2H), 1.69–1.57 (m, 2H), 1.34–1.27 (m, 6H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.4, 136.7, 128.4, 128.2, 128.0, 87.3, 85.3, 72.0, 56.8, 45.3, 31.4, 28.5, 23.8, 22.3, 13.9; HRMS (ESI-TOF) calcd for $[C_{17}H_{22}O_2 + Na]^+$ 281.1512, found 281.1509.

1-(Benzo[*d*][1,3]dioxol-5-yl)-3-hydroxypropan-1-one (4m). Isolated yield of **4m**, (81.6 mg, 84%). White solid, mp 85–87 °C; IR ($CHCl_3$, cm^{-1}): ν 3447, 3019, 2971, 2896, 1670, 1604, 1506, 1490, 1444, 1355, 1257, 1109, 1097, 1041, 936, 878, 669; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 7.57 (dd, J = 8.2, 1.7 Hz, 1H), 7.43 (d, J = 1.7 Hz, 1H), 6.86 (d, J = 8.2 Hz, 1H), 6.06 (s, 2H), 4.02–3.98 (m, 2H), 3.15 (t, J = 5.3 Hz, 2H), 2.71 (t, J = 6.4 Hz, *OH*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 152.0, 148.2, 131.4, 124.5, 107.9, 107.6, 101.9, 58.1, 40.0; HRMS (ESI-TOF) calcd for $[C_{10}H_{10}O_4 + Na]^+$ 217.0471, found 217.0472.

1-(2,5-dimethoxyphenyl)-3-hydroxypropan-1-one (4n). Isolated yield of **4n**, (89.3 mg, 85%). Colorless oil; IR ($CHCl_3$, cm^{-1}): ν 3436, 3000, 2946, 2906, 2837, 1669, 1610, 1582, 1496, 1465, 1443, 1414, 1358, 1280, 1223, 1182, 1165, 1049, 1017, 912, 815, 648; ^{1}H NMR (500 MHz, $CDCl_3$/TMS) δ 7.32 (d, J = 3.2 Hz, 1H), 7.05 (dd, J = 8.9, 3.2 Hz, 1H), 6.92 (d, J = 8.9 Hz, 1H), 3.97 (t, J = 5.3 Hz, 2H), 3.87 (s, 3H), 3.79 (s, 3H), 3.26 (t, J = 5.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.4, 153.3, 153.1, 127.2, 120.4, 113.5, 112.9, 58.1, 55.7, 55.5, 45.8; HRMS (ESI-TOF) calcd for $[C_{11}H_{14}O_4 + Na]^+$ 233.0784, found 233.0791.

3-Hydroxy-1-(4-nitrophenyl)propan-1-one (4o). Isolated yield of **4o**, (67.3 mg, 69%). Yellow solid, mp 88–90 °C; IR ($CHCl_3$, cm^{-1}): ν 3415, 2923, 2851, 1679, 1642, 1599, 1514, 1404, 1341, 1212, 1102, 1048, 912, 598; ^{1}H NMR (500 MHz, $CDCl_3$/TMS) δ 8.35 (d, J = 9.0 Hz, 2H), 8.15 (d, J = 8.9 Hz, 2H), 4.10 (q, J = 5.7 Hz, 2H), 3.30 (t, J = 5.3 Hz, 2H), 2.42 (t, J = 6.5 Hz, 1H, *OH*) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.6, 150.5, 140.9, 129.1, 123.9, 57.7, 41.1; HRMS (ESI-TOF) calcd for $[C_9H_9NO_4 + Na]^+$ 218.0424, found 218.0428.

1-(4-Chlorophenyl)-3-hydroxypropan-1-one (4p). Isolated yield of **4p**, (71.1 mg, 77%). Yellow oil; IR ($CHCl_3$, cm^{-1}): ν 3437, 2945, 2891, 1681, 1591, 1569, 1488, 1465, 1401, 1361, 1250, 1209, 1175, 1093, 1063, 1014, 998, 976, 909, 876, 818, 649; ^{1}H NMR (500 MHz, $CDCl_3$/TMS) δ 7.91 (d, J = 8.6 Hz, 2H), 7.45 (d, J = 8.6 Hz, 2H), 4.03 (t, J = 5.3 Hz, 2H), 3.20 (t, J = 5.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.8, 139.7, 134.8, 129.3, 128.8, 57.6, 40.4; HRMS (ESI-TOF) calcd for $[C_9H_9ClO_2 + Na]^+$ 207.0183, found 207.0190.

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