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IBX/*n*-Bu_4NBr/CH_2Cl_2–H_2O: a new mild system for selective oxidation of secondary alcohols

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Abstract—A new alternative system for the chemoselective oxidation of secondary hydroxyl group to ketone with IBX/*n*-Bu_4NBr in CH_2Cl_2–H_2O has been developed. Under the reaction conditions, the secondary hydroxyl group was highly chemoselectively oxidized to the corresponding ketone, in moderate to good yields at rt, in the presence of primary hydroxyl group within the same molecule.

1. Introduction

The oxidation of alcohols to carbonyl compounds is a fundamental reaction in organic chemistry and several methods covering a wide variety of reagents have been developed for this important synthetic transformation.[1] Desired experimental conditions include high yields, mild conditions, high chemoselectivity, readily available non-toxic reagent, and compatibility with functional groups present in the substrates. In the synthesis of naturally occurring compounds, one usually faces the manipulation of compounds containing several types of hydroxyl functional groups, and it is necessary to selectively oxidize a single hydroxyl group (primary or secondary alcohol) within the same molecules. Thus, selective transformation of hydroxyl group has been a challenging target for synthetic chemists since it offers an alternative to synthesis via selective protection and deprotection. Many oxidizing reagents are known to promote selective oxidation of secondary alcohols in the presence of primary alcohols, including halogen-based oxidants, for example, *N*-bromoacetamide,[2] *N*-chloro/bromosuccinimide,[3] Cl_2/pyridine,[4] Br_2/HMPA/$NaHCO_3$,[5] $(Bu_3Sn)_2O/Br_2$,[6] $NOCl/CH_3CO_2H$,[7] $NaBrO_3/NaHSO_3$,[8] and $Ce(SO_4)_2/NaBrO_3$.[9] The other important oxidizing agents are peroxides/metal system,[10] dimethyldioxiranes,[11] DMSO-based reagents,[12] and Oppenauer oxidation variations.[13] Despite these readily available procedures, development of a better selective oxidation system is still desirable.

As part of our ongoing efforts in the development of newer applications of hypervalent iodine (V) compounds, we wish to report a new application of 2-iodoxybenzoic acid (IBX) with catalytic amount of tetrabutylammonium bromide (*n*-Bu_4NBr) for selective oxidation of secondary hydroxyl group. Chemoselective oxidation of sulfides to sulfoxides in the presence of an alcohol functional group using IBX/tetraethylammonium bromide (Et_4NBr) has been documented in the literature.[14] To our knowledge, there is no previous study that was directed toward selective oxidation of secondary hydroxyl group in the presence of primary hydroxyl within the same molecule using IBX as an oxidizing reagent.

2. Results and discussion

To begin with, a monofunctional alcohol, benzyl alcohol, was chosen as a substrate for investigating reaction conditions. Thus, it was subjected to the oxidation by IBX in the presence of a collection of phase transfer catalysts, that is *n*-Bu_4NBr, Et_4NCl, Et_4NBr, Et_4NI, $BnMe_3NBr$, and $BnEt_3NCl$ (Table 1). It should be noted that the type of halide anion of the catalyst has considerable effect on the oxidation reaction (Table 1, entries 2–4). The tetraethylammonium bromide (Et_4NBr) catalyzed the reaction more effectively than the corresponding iodide and chloride, respectively. The *n*-Bu_4NBr gave the best conversion of 89% (Table 1, entry 1). Tetrabutylammonium bromide was therefore, chosen as a catalyst of choice for further investigating optimum reaction conditions (Table 2).

From the results as shown in Table 2, for the oxidation using IBX alone in dichloromethane, moderate conversion of

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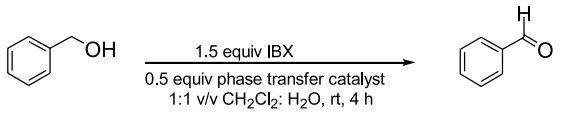
Table 1. Phase transfer catalyst optimization



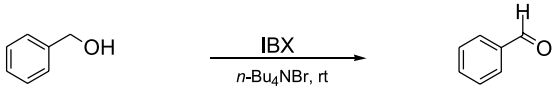
Entry	Phase transfer catalyst	Conversion (%)[a]
1	*n*-Bu_4NBr	89
2	Et_4NCl	22
3	Et_4NBr	62
4	Et_4NI	37
5	$BnMe_3NBr$	18
6	$BnEt_3NCl$	30

[a] Conversion (%) was calculated from ^1H NMR (300 MHz) integration.

mechanisms previously reported for the phase transfer catalyzed IBX oxidation of sulfides to sulfoxides.[14]

Comparative studies of our method (Method A) with those reported in the literature for IBX oxidation of alcohols (Methods B[15] and C[16]) were conducted. The selectivity and efficiency of our method are clearly demonstrated as shown in Table 4. A control experiment was also carried out with the 2,2,4-trimethyl-1,3-pentanediol substrate using the conditions described in Table 4 (Method A) without the *n*-Bu_4NBr. The oxidation gave all the possible products, that is the corresponding hydroxyketone (31%), hydroxyaldehyde (4%), dicarbonyl (2%), and recovered starting material (37%). The results seem to suggest that the origin of

Table 2. Optimization of reaction conditions



Entry	H_2O:CH_2Cl_2 (v/v)	IBX (equiv)	*n*-Bu_4NBr (equiv)	Time (h)	Conversion (%)[a]
1	0:100	1.5	—	4	45
2	1:1	1.5	—	7	31
3	0:100	1.5	0.5	2	88
4	1:3	1.5	0.5	4	92
5	1:1	1.5	0.5	4	89
6	1:1	1.5	0.1	4	70
7	1:1	1.5	1.0	4	60

[a] Conversion (%) was calculated from ^1H NMR (300 MHz) integration.

benzyl alcohol to benzaldehyde was obtained (Table 2, entry 1). A similar result was obtained when water was used as a co-solvent, even with prolonged reaction time (Table 2, entry 2). Reaction in the presence of 0.5 equiv of *n*-Bu_4NBr proceeded with shorter reaction time and provided better conversion (Table 2, entries 3–5). The v/v ratio of CH_2Cl_2:H_2O employed can be as low as 1:1. When either a lesser or stoichiometric amount of *n*-Bu_4NBr was employed, lower conversions were obtained (Table 2, entries 6–7). Therefore, the 1:1 v/v of H_2O:CH_2Cl_2 solvent system will be used in the standard conditions.

According to Tables 1 and 2, even though the oxidation reaction of monofunctional alcohols proceeded efficiently with as few as 1.5 equiv of IBX, an increased reaction rate was observed with excess oxidant. For the oxidation of diols, it was found that the use of 3 equiv of IBX afforded the best results; very small amounts of dicarbonyls or lactones were obtained. Based on this observation, 3 equiv of IBX were selected to examine the chemoselective oxidation of a variety of diols. The results are summarized in Table 3.

The observed transformations were chemoselective when both the primary and the secondary hydroxyl functional groups were present within the same molecules (Table 3). The ketones with the primary alcohol untouched were obtained in moderate to good yields. The dicarbonyl compounds as well as some lactones in cases leading to five- or six-membered ring lactones were also formed as minor products. The exact mechanism of selective oxidation is still unclear, but we propose that it should follow those chemoselectivity of IBX oxidation of diols under a bi-phasic solvent system in our study stems from the choice of solvent. The role of the bromide anion was believed to follow the previously suggested mechanism for Et_4NBr catalyzed IBX oxidation of sulfides to sulfoxides by causing a polarization of the I=O bond and leading to a reaction rate acceleration.[14]

3. Conclusion

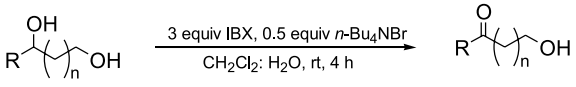
In conclusion, a selective and efficient new alternative method has been developed for the oxidation of secondary hydroxyl groups to ketones, in moderate to good yields, in the presence of primary hydroxyl groups within the same molecule. The reaction conditions do not involve moisture sensitive and environmentally unfriendly agents. We anticipate that this protocol will, to some extent, be of broad interest and use to the chemistry community.

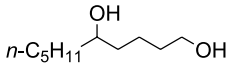
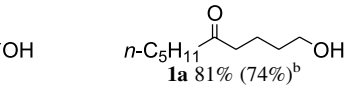
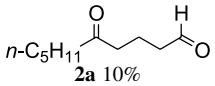
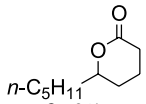
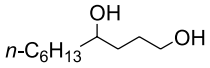
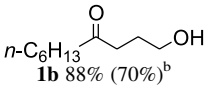
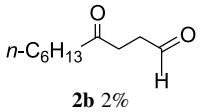
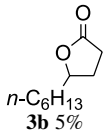
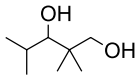
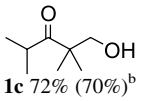
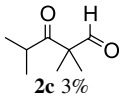
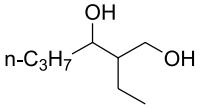
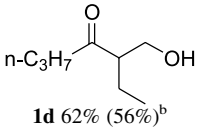
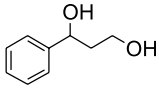
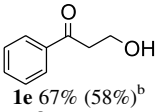
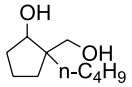
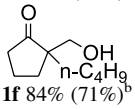
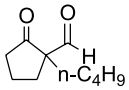
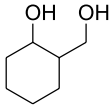
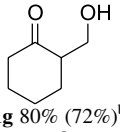
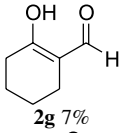
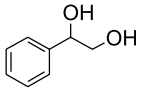
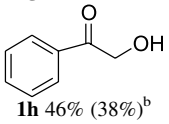
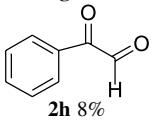
4. Experimental

4.1. General

Melting points (uncorrected) were determined on an Electrothermal 9100 Apparatus. Reagents were obtained from commercial sources and used as received. Column chromatography was performed using silica gel 60 (70–230 mesh). Analytical TLC was performed with silica gel 60 PF_{254} aluminium sheet with 0.2 mm layer of silica gel. ^1H NMR spectra were recorded at 300 MHz in $CDCl_3$ solution with tetramethylsilane as an internal standard. ^{13}C NMR

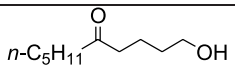
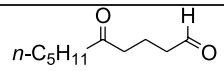
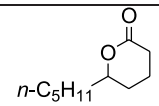
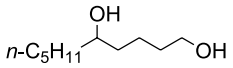
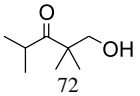
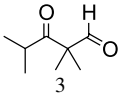
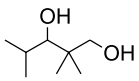
Table 3. Selective oxidation of secondary hydroxyls using IBX/*n*-Bu_4NBr in 1:1 v/v of H_2O:CH_2Cl_2



Entry	Substrate	Product (% yield)[a]		
1		 **1a** 81% (74%)[b]	 **2a** 10%	 **3a** 3%
2		 **1b** 88% (70%)[b]	 **2b** 2%	 **3b** 5%
3		 **1c** 72% (70%)[b]	 **2c** 3%	
4		 **1d** 62% (56%)[b]		
5		 **1e** 67% (58%)[b]		
6		 **1f** 84% (71%)[b]	 **2f** 8%	
7		 **1g** 80% (72%)[b]	 **2g** 7%	
8		 **1h** 46% (38%)[b]	 **2h** 8%	

[a] GC yields.
[b] Yields (%) given in parentheses are isolated yields after purification by column chromatography.

Table 4. Comparison of the oxidation of diols by IBX under other conditions

Substrate	Method[a]	Product (% yield)[b]		
				
	**A**[c]	81	10	3
	B	[d]	83	16
	C	[d]	76	23
				
	**A**[e]	72	3	
	B	[d]	77	
	C	[d]	86	

[a] Method **A**: 3 equiv IBX, 0.5 equiv *n*-Bu_4NBr, CH_2Cl_2:H_2O (1:1), rt, 4 h; Method **B**: 3 equiv IBX, DMSO, rt, 4 h; Method **C**: 3 equiv IBX, EtOAc, 80 °C, 4 h.
[b] GC yields.
[c] Starting material was recovered (6%).
[d] Not detected by GC.
[e] Starting material was recovered (21%).

spectra were recorded at 75 MHz with residual non-deuterated solvent peak as an internal standard. IR spectra were recorded on a GX FT-IR system (Perkin Elmer) spectrometer. Elemental analyses were determined on a Perkin Elmer Elemental Analyzer 2400 CHN. High resolution mass spectra were obtained on a Micromass model VQ-TOF2 mass spectrometer.

4.2. General procedure for the oxidation

To a stirred suspension of IBX (3.0 equiv) in H_2O:CH_2Cl_2 (v/v=1:1, 0.25 M based on starting alcohol) was added *n*-Bu_4NBr (0.5 equiv) followed by the addition of alcohol (1.0 equiv) in one portion. The mixture was stirred at rt for 4 h. The residual solids were filtered off and washed thoroughly with diethyl ether. The combined filtrate was washed successively with 8% sodium thiosulfate (15 mL), water (2×15 mL) and brine (1×15 mL). The organic layer was dried over anhydrous sodium sulfate, filtered, and evaporated (aspirator). The crude product was subsequently examined by gas chromatography for determining product conversion. Purification of the crude product by column chromatography (SiO_2) provided the isolated yield of the ketone.

4.2.1. Preparation of 1-hydroxy-5-decanone (1a). According to the general procedure, oxidation of 1,5-decanediol (174 mg, 1 mmol) gave 1-hydroxy-5-decanone, after column chromatography on silica gel (18×1.5 cm, 8:2 *n*-hexane/ethyl acetate as eluent), 127 mg (isolated yield; 74%) as colorless liquid: analytical TLC on silica gel, 7:3 *n*-hexane/ethyl acetate, R_f=0.17. IR (neat, cm^{-1}) 3423, O–H; 1712, C=O. 300 MHz ^{1}H NMR ($CDCl_3$, ppm) δ 3.57 (2H, br s) 2.55–2.10 (4H, m) 1.70–1.10 (11H, m) 0.82 (3H, t, J=6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 211.6, 62.1, 42.7, 42.1, 32.0, 31.3, 23.5, 22.4, 19.6, 13.8. Molecular ion (M+H) calcd for $C_{10}H_{21}O_2$: 173.1542; found (ESI-TOF) m/e=173.1536, error=3 ppm.

4.2.2. Preparation of 1-hydroxy-4-decanone (1b). According to the general procedure, oxidation of 1,4-decanediol (174 mg, 1 mmol) gave 1-hydroxy-4-decanone, after column chromatography on silica gel (18×1.5 cm, 8:2 *n*-hexane/ethyl acetate as eluent), 120 mg (isolated yield; 70%) as colorless liquid:[17] analytical TLC on silica gel, 7:3 *n*-hexane/ethyl acetate, R_f=0.16. IR (neat, cm^{-1}) 3422, O–H; 1707, C=O. 300 MHz ^{1}H NMR ($CDCl_3$, ppm) δ 3.64 (2H, t, J=6.1 Hz) 2.55–2.30 (4H, m) 2.00–1.66 (2H, m) 1.65–1.44 (2H, m) 1.40–1.17 (7H, m) 0.88 (3H, t, J=6.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 212.1, 62.1, 42.9, 39.4, 31.5, 28.8, 26.4, 23.8, 22.4, 14.0.

4.2.3. Preparation of 1-hydroxy-2,2,4-trimethyl-3-pentanone (1c). According to the general procedure, oxidation of 2,2,4-trimethyl-1,3-pentanediol (146 mg, 1 mmol) gave 1-hydroxy-2,2,4-trimethyl-3-pentanone, after column chromatography on silica gel (18×1.5 cm, 8:2 *n*-hexane/diethyl ether as eluent), 101 mg (isolated yield; 70%) as colorless liquid:[12a] analytical TLC on silica gel, 8:2 *n*-hexane/diethyl ether, R_f=0.12. IR (neat, cm^{-1}) 3479, O–H; 1699, C=O. 300 MHz ^{1}H NMR ($CDCl_3$, ppm) δ 3.56 (2H, s) 3.18–3.02 (1H, m) 2.85 (1H, br d, J=7.4 Hz) 1.18 (6H, s) 1.06 (6H, d, J=6.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 221.5, 69.3, 49.6, 34.5, 21.0, 19.8.

4.2.4. Preparation of 3-hydroxymethyl-4-heptanone (1d). According to the general procedure, oxidation of 2-ethyl-1,3-hexanediol (185 mg, 1.27 mmol) gave 3-hydroxymethyl-4-heptanone, after column chromatography on silica gel (18×1.5 cm, 7:3 *n*-hexane/diethyl ether as eluent), 103 mg (isolated yield; 56%) as colorless liquid:[10c] analytical TLC on silica gel, 7:3 *n*-hexane/diethyl ether, R_f=0.05. IR (neat, cm^{-1}) 3422, O–H; 1705, C=O. 300 MHz ^{1}H NMR ($CDCl_3$, ppm) δ 3.80 (1H, dd, ABX, J=11.0, 7.4 Hz) 3.70 (1H, dd, ABX, J=11.0, 4.1 Hz) 2.70–2.57 (1H, m) 2.48 (2H, t, J=7.3 Hz) 2.14 (1H, br s) 1.75–1.39 (4H, m) 0.93 (3H, t, J=7.5 Hz) 0.92 (3H, t, J=7.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 215.1, 62.4, 54.9, 44.8, 21.2, 16.8, 13.7, 11.8.

4.2.5. Preparation of 3-hydroxy-1-phenyl-1-propanone (1e). According to the general procedure, oxidation of 3-hydroxy-1-phenyl-1-propanol (152 mg, 1 mmol) gave 3-hydroxy-1-phenyl-1-propanone, after column chromatography on silica gel (18×1.5 cm, 8.5:1.5 *n*-hexane/ethyl acetate as eluent), 86.9 mg (isolated yield; 58%) as a colorless liquid:[18] analytical TLC on silica gel, 7:3 *n*-hexane/ethyl acetate, R_f=0.29. IR (neat, cm^{-1}) 3412, O–H; 1681, C=O. 300 MHz ^{1}H NMR ($CDCl_3$, ppm) δ 7.97 (2H, d, J=7.3 Hz) 7.59 (1H, t, J=7.4 Hz) 7.48 (2H, t, J=7.5 Hz) 4.05 (2H, t, J=5.4 Hz) 3.24 (2H, t, J=5.4 Hz) 2.85 (1H, br s). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 200.4, 136.6, 133.4, 128.6, 128.0, 58.0, 40.3.

4.2.6. Preparation of 2-butyl-2-hydroxymethylcyclopentanone (1f). According to the general procedure, oxidation of 2-butyl-2-hydroxymethylcyclopentanol (221 mg, 1.28 mmol) gave 2-butyl-2-hydroxymethylcyclopentanone, after column chromatography on silica gel (18×1.5 cm, 8:2 *n*-hexane/ethyl acetate as eluent), 156 mg (isolated yield; 71%) as a pale yellow liquid: analytical TLC on silica gel, 7:3 *n*-hexane/ethyl acetate, R_f=0.32. IR (neat, cm^{-1}) 3448, O–H; 1731, C=O. 300 MHz ^{1}H NMR ($CDCl_3$, ppm) δ 3.62 (1H, d, J=11.0 Hz) 3.47 (1H, d, J=11.0 Hz) 2.36 (1H, br s) 2.31–2.17 (2H, m) 2.01–1.80 (4H, m) 1.55–1.01 (6H, m) 0.88 (3H, t, J=7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 224.7, 65.7, 53.4, 38.8, 32.2, 30.5, 26.2, 23.2, 19.1, 13.8. Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.29; H, 10.45.

4.2.7. Preparation of 2-hydroxymethylcyclohexanone (1g). According to the general procedure, oxidation of 2-hydroxymethylcyclohexanol (130 mg, 1 mmol) gave 2-hydroxymethylcyclohexanone, after column chromatography on silica gel (18×1.5 cm, 8:2 *n*-hexane/ethyl acetate as eluent), 91.8 mg (isolated yield; 72%) as a colorless liquid:[19] analytical TLC on silica gel, 6:4 *n*-hexane/ethyl acetate, R_f=0.25. IR (neat, cm^{-1}) 3421, O–H; 1702, C=O. 300 MHz ^{1}H NMR ($CDCl_3$, ppm) δ 3.81–3.68 (1H, m) 3.68–3.54 (1H, m) 2.79 (1H, br s) 2.61–1.36 (9H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 214.6, 62.5, 52.1, 42.1, 30.0, 27.4, 24.6.

4.2.8. Preparation of 2-hydroxy-1-phenylethanone (1h). According to the general procedure, oxidation of 1-phenyl-

1,2-ethanediol (138 mg, 1 mmol) gave 2-hydroxy-1-phenyl-ethanone, after column chromatography on silica gel (18× 1.5 cm, 8:2 *n*-hexane/ethyl acetate as eluent), 52.4 mg (isolated yield; 38%) as a white solid:[20] mp 84.6–85.2 °C (Aldrich chemicals 86–89 °C); analytical TLC on silica gel, 7:3 *n*-hexane/ethyl acetate, R_f=0.31. IR (neat, cm^{-1}) 3428, O–H; 1682, C=O. 300 MHz ^{1}H NMR ($CDCl_3$, ppm) δ 7.93 (2H, d, J=7.6 Hz) 7.63 (1H, t, J=7.4 Hz) 7.51 (2H, t, J=7.7 Hz) 4.89 (2H, s) 2.98 (1H, br s). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 198.4, 134.3, 133.4, 128.9, 127.7, 65.4.

4.3. Characterization data for dicarbonyl compounds 2

4.3.1. 5-Oxodecanal (2a). Colorless liquid:[21] analytical TLC on silica gel, 6:4 *n*-hexane/ethyl acetate, R_f=0.52. IR (neat, cm^{-1}) 1709, C=O. 300 MHz ^{1}H NMR ($CDCl_3$, ppm) δ 9.75 (1H, s) 2.55–2.43 (4H, m) 2.39 (2H, t, J=7.4 Hz) 1.97–1.80 (2H, m) 1.65–1.47 (2H, m) 1.40–1.16 (4H, m) 0.89 (3H, t, J=6.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 210.3, 201.8, 42.8, 42.6, 41.1, 31.2, 23.3, 22.2, 15.8, 13.7.

4.3.2. 4-Oxodecanal (2b). Colorless liquid:[22] analytical TLC on silica gel, 6:4 *n*-hexane/ethyl acetate, R_f=0.47. IR (neat, cm^{-1}) 1712, C=O. 300 MHz ^{1}H NMR ($CDCl_3$, ppm) δ 9.80 (1H, s) 2.80–2.67 (4H, m) 2.47 (2H, t, J=7.5 Hz) 1.65–1.50 (2H, m) 1.40–1.18 (6H, m) 0.88 (3H, t, J=6.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 208.8, 200.4, 42.6, 37.3, 34.5, 31.4, 28.7, 23.7, 22.3, 13.9.

4.3.3. 2,2,4-Trimethyl-3-oxopentanal (2c). Colorless liquid:[23] analytical TLC on silica gel, 8:2 *n*-hexane/diethyl ether, R_f=0.45. IR (neat, cm^{-1}) 1736, 1702, C=O; 300 MHz ^{1}H NMR ($CDCl_3$, ppm) δ 9.64 (1H, s) 3.03–2.97 (1H, m) 1.35 (6H, s) 1.06 (6H, d, J=6.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 213.5, 200.9, 60.7, 36.5, 19.2, 19.0.

4.3.4. 1-Butyl-2-oxocyclopentanecarbaldehyde (2f). Colorless liquid: analytical TLC on silica gel, 7:3 *n*-hexane/diethyl ether, R_f=0.55. IR (neat, cm^{-1}) 1745, 1713, C=O; 300 MHz ^{1}H NMR ($CDCl_3$, ppm) δ 9.41 (1H, s) 2.66–1.07 (12H, m) 0.90 (3H, t, J=7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 215.3, 199.0, 67.5, 38.6, 32.7, 27.7, 26.6, 22.9, 19.2, 13.7. Molecular ion (M+H) calcd for $C_{10}H_{17}O_2$: 169.1229; found (ESI-TOF) m/e=169.1223, error=3 ppm.

4.3.5. 2-Hydroxy-1-cyclohexenecarbaldehyde (2g). Orange liquid;[24] analytical TLC on silica gel, 8:2 *n*-hexane/ethyl acetate, R_f=0.48. IR (neat, cm^{-1}) 3421, O–H; 1715, C=O; 1603, C=C. 300 MHz ^{1}H NMR ($CDCl_3$, ppm) δ 14.40 (1H, br s) 8.64 (1H, s) 2.47–2.25 (4H, m) 1.80–1.59 (4H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 187.5, 184.9, 108.8, 31.2, 23.1, 22.5, 21.2.

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