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IBX, AN EXCELLENT REAGENT FOR OXIDATION OF 2-FURYL CARBINOLS: A NEW AND GENERAL METHOD FOR PREPARATION OF FURYL KETONES

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An excellent method for the oxidation of various 2-furyl carbinols with o-iodoxybenzoic acid (IBX) has been described. This method provides a simple and efficient route to a variety of 2-furylketones which are not readily accessible otherwise.

Keywords: Furyl ketone; iodoxybenzoic acid (IBX); oxidation

2-Furyl ketones are important synthetic precursors and are present in many natural products.[1] Moreover, several furyl ketones possess important biological activities such as anti-AIDS activity.[2] However, their preparation is not as straightforward and easy as it may appear.[3a] In view of this, several indirect methods are employed for the preparation of furyl ketones,[3,4] including Friedel–Crafts acylation,[3b] reaction of organovanadium reagents with furfural,[3d] reaction of arylcopper reagents with anhydrides,[3f] Pd-catalyzed coupling of organomercurials with acyl halides,[3g] and Barbier reaction of furyl lithium.[3a] Wolf and associates also developed Pd-catalyzed coupling of furyl stannates with acyl chlorides to form furanyl ketones.[5a] Recently, Kerr and coworkers described a general method for the synthesis of ketones, which can be extended to furyl ketones.[5b] However, these methods involve multistep sequences and suffer from various types of limitations such as poor yields and use of heavy metals.

In principle, oxidation of the furyl carbinol could constitute one of the simplest and most versatile routes to furyl ketones. Some reagents such as Jones reagent, pyridinium chlorochromate (PCC), pyridinium dichromate (PDC), MnO_2, and tetrapropylammonium perruthenate (TPAP) have been used, but these reagents appear to be unsatisfactory.[6,7] PCC induces rearrangement,[6a,b] but PDC and MnO_2 give poor yields.[6c,7a] Similarly, Swern oxidation also does not appear to be a suitable method.[7c] Thus, there is a lack of mild and efficient methods for the oxidation of furyl carbinols.

In the context of a synthetic endeavour, we required furyl ketones **2a–d** and congeners (Fig. 1). Though these ketones have been prepared earlier, their

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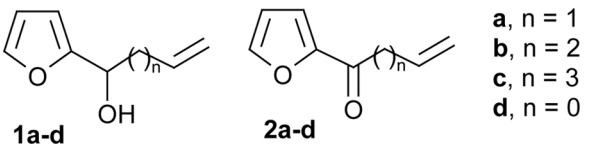


Figure 1. Furyl carbinols and furyl ketones.

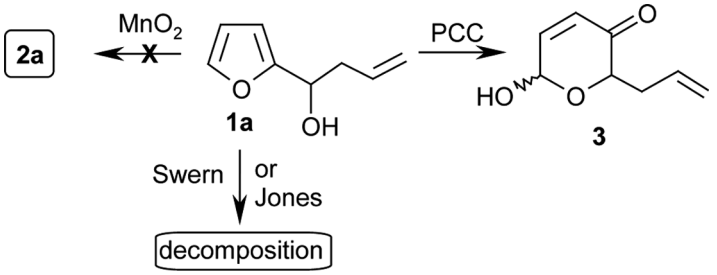
preparation involves complex procedures. For example, ketone **2a** has been prepared by the ytterbium- and indium-[8a,b] mediated addition of allyl halide to furyl oxocyanide, which is not readily accessible. Moreover, this and other related methods work only with allyl reagents. The compound **2b** has been prepared by Barbier type coupling[3a] as well as via a cyanohydrin–trimethylsilylether multistep route.[3c] The ketone **2c** has been prepared by a complicated sequence, employing bis (iodozincio) methane and α-sulfonyloxy ketone followed by the treatment with dilithium dichlorocyanocuprate and allyl bromide.[4a] Similarly, the compound **2d** has been prepared by addition of vinyl Grignard on Weinreb amide derived from 2-furoic acid.[4b]

Therefore, we considered devising a simple and general method by the oxidation of carbinols **1a–d**, which are readily accessible. While the oxidation of **1a** with MnO_2 was unsuccessful, Swern oxidation and oxidation with Jones reagent led to decomposition of the starting material. Treatment of **1a** with PCC gave the rearranged product **3**. Oxidation of **1a** with PDC gave a poor yield of the desired ketone (Scheme 1). It appears that the sensitivity of furan ring toward acidic and oxidizing reagents is one of the problems.

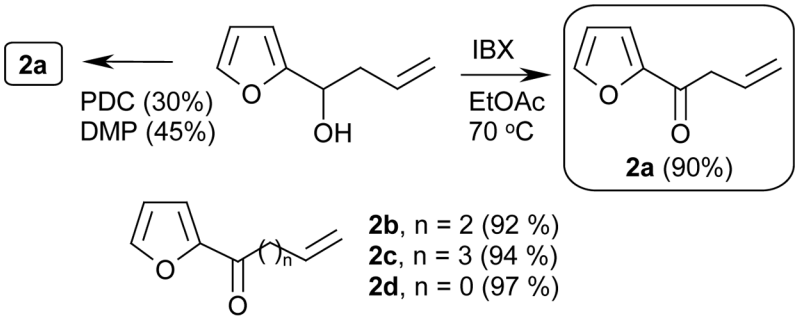
Therefore, we turned our attention to oxidizing agents based on hypervalent iodine.[9] Initially, the carbinol **1a** was treated with Dess–Martin periodinane. However, the reaction was slow and gave the ketone **2a** in poor yield (45%).

In view of these difficulties, we considered oxidizing **1a** with o-iodoxybenzoic acid (IBX) because it is a mild reagent.[9,10] Thus, a solution of the carbinol **1a** in ethyl acetate was heated with IBX at 70 °C. It was indeed gratifying to note that the oxidation occurred smoothly and gave the desired ketone **2a** in excellent yield (90%) without inducing oxidative rearrangement (Scheme 2). Encouraged by this observation, other carbinols **1b–d** were also treated with IBX to give the corresponding ketones in excellent yields.

To check the generality of this method, a more sensitive furyl ethynyl carbinol **6** was prepared, and its oxidation was examined. Thus, furfural **4** was added to



Scheme 1. Oxidation of 2-furyl carbinols.

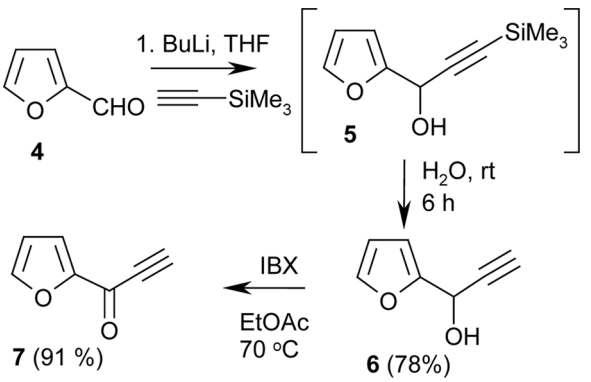


Scheme 2. Oxidation of 2-furyl carbinols to ketones.

trimethylsily acetylide, and the resulting alcohol **5** was treated with water to remove the trimethylsilyl moiety and give the propargyl alcohol **6**. The alcohol **6** was then subjected to oxidation with IBX, which gave the corresponding ketone **7** in excellent yield (91%) (Scheme 3). Though the compound **7** has been prepared earlier via acylation, yield was not mentioned.[11a]

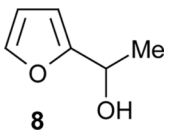
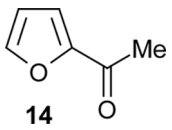
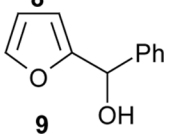
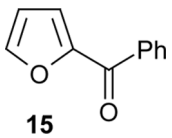
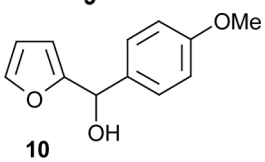
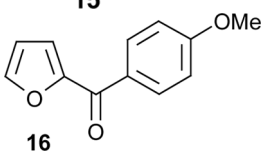
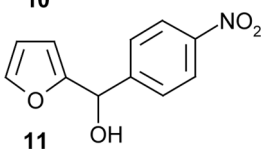
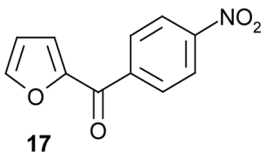
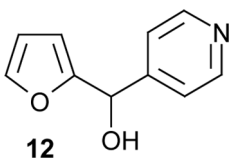
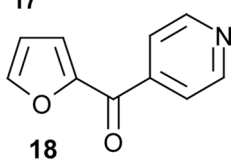
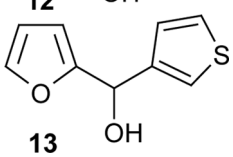
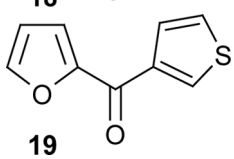
In addition, other furyl carbinols having alkyl and aryl moieties underwent smooth oxidation with IBX to furnish the corresponding ketones in excellent yields (Table 1). It may be noted that furyl-aryl carbinols **10** and **11,** having electron-donating and electron-withdrawing substituents respectively, underwent smooth oxidation (entries 3 and 4). Further, furyl-aryl carbinol **12,** having a pyridyl moiety, was also efficiently oxidized to give the corresponding ketone **18** in excellent yield. It is interesting to note that the carbinol **13**, having a sensitive thiophene moiety, also underwent smooth oxidation to give the ketone **19** in excellent yield (Table 1).

It may be worth mentioning that this oxidation protocol can easily be scaled up. [The oxidation of **1a** has been successfully carried out on a 5-g scale, and the product **2a** was obtained in excellent yield (90%).] The oxidant can be regenerated from the by-product and may be used for further oxidation. (The recycled IBX was used for the oxidation of the substrate **1b** on a 3.5-g scale without any apparent decrease



Scheme 3. Preparation of furyl ethynyl carbinol and its oxidation.

Table 1. Oxidation of furyl carbinols to ketones

Entry	Substrate	Product	Yield (%)[a]	Lit. yield (%)[ref.]
1	 **8**	 **14**	90	(76)[11b]
2	 **9**	 **15**	93	(92)[5a]
3	 **10**	 **16**	88	(67)[5b]
4	 **11**	 **17**	94	(2)[12]
5	 **12**	 **18**	91	(—[b])[13]
6	 **13**	 **19**	94	(14)[14]

[a]Isolated yield.
[b]Yield not reported.

in yield.) Further, the method is simple and does not require inert atmosphere and anhydrous solvents. The product of sufficient purity is obtained just by filtration of the solid residue.

In summary, we have shown that IBX is a reagent of choice for the oxidation of furyl carbinols, which provides a simple and efficient method for the preparation of a variety of 2-furanyl ketones. IBX does not induce rearrangement of furyl carbinols and gives the corresponding ketones in excellent yields.

EXPERIMENTAL

Caution! IBX is explosive at high temperatures (>200 °C) and under impact. Its preparation and reaction should be done with necessary precaution in an efficient fume hood.

The furyl carbinols **1a–d** were prepared by the addition of appropriate Grignard reagents to furfural. The acetylenic carbinol **6** was prepared by the addition of lithium–trimethysilylacetylide to furfural. The carbinols **9–13** were prepared by addition of 2-lithiofuran to the corresponding aldehydes. However, the complete data of **1c**, **1d** are not available. Similarly, though the carbinols **6** and **10–13** are known, their spectroscopic data are not available in the literature. Hence, the preparation of **1c**, **1d**, **6**, and **10–13** and their data are given here.

1-(Furan-2-yl)hex-5-en-1-ol 1c

A solution of freshly distilled furfural (1.4 mL, 17 mmol, in 10 mL THF) was added in a dropwise manner to a solution of 4-pentenylmagnesium bromide, prepared from 5-bromopent-1-ene (2.52 g) and magnesium (530 mg), in dry tetrahydrofuran (THF, 35 mL) at 0 °C. After stirring the reaction mixture at 0 °C for half an hour, it was allowed to warm to room temperature and further stirred for 6 h. A saturated solution of NH_4Cl (5 mL) was added to the reaction mixture, and it was filtered through a celite pad. The two layers were separated, and the aqueous layer was extracted with diethyl ether. The combined organic extract was washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the residue was chromatographed on silica gel [petroleum ether–ethyl acetate (80:20)] to give **1c** (2.45 g, 87%) as a colorless liquid. IR (film) ν_{max}: 3379, 1640 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.35 (dd, $J_1 = 1.6$ Hz, $J_2 = 0.4$ Hz, 1H), 6.30 (dd, $J_1 = 3.6$ Hz, $J_2 = 2.0$ Hz, 1H), 6.21–6.20 (m, 1H), 5.84–5.73 (m, 1H), 5.03–4.93 (m, 2H), 4.6 (br. s, 1H), 2.47 (br. s, 1H), 2.14–2.02 (m, 2H), 1.88–1.78 (m, 2H), 1.56–1.47 (m, 1H), 1.44–1.35 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 156.9, 141.9, 138.5, 114.8, 110.1, 105.8, 67.6, 35.0, 33.5, 24.8. HRMS: found 189.0888 $[M + Na]^+$; calcd. for $C_{10}H_{14}O_2Na$: 189.0891 $[M + Na]^+$.

1-(Furan-2-yl)prop-2-en-1-ol 1d

Vinyl magnesium bromide (50 mL, 1.0 M in THF, 50 mmol) was added to a solution of freshly distilled furfural (3.3 mL, 40 mmol) in anhydrous diethyl ether (25 mL) in a dropwise manner at 0 °C under nitrogen atmosphere. After stirring the reaction mixture at 0 °C for half an hour, it was allowed to warm to room temperature and further stirred for 3 h. Workup as described previously followed by chromatography [petroleum ether–ethyl acetate (80:20)] furnished **1d** (3.5 g, 71%) as a colorless liquid. IR (film) ν_{max}: 3399, 1647 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.40 (s, 1H), 6.34 (d, $J = 2.8$ Hz, 1H), 6.26 (d, $J = 2.8$ Hz, 1H), 6.17–6.02 (m, 1H), 5.45 (d, $J = 17.2$ Hz, 1H), 5.30 (d, $J = 10.0$ Hz, 1H), 5.24 (m,1H), 2.15 (d, $J = 5.2$ Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.1, 142.6, 136.9, 116.7, 110.4, 106.9, 68.7. HRMS: found 125.0600 $[M + H]^+$; calcd. for $C_7H_8O_2$: 125.0602 $[M + H]^+$.

1-(Furan-2-yl)prop-2-yn-1-ol 6

n-BuLi (6 mL, 1.6 M in hexane, 9.6 mmol) was added to a solution of trimethylsilyl acetylene (1.3 mL, 9.2 mmol) in anhydrous THF (15 mL) in a dropwise manner

at −78 °C under nitrogen. The resulting mixture was allowed to warm to room temperature and stirred for 1 h. It was cooled again to −78 °C, and a solution of furfural (0.6 mL, 700 mg, 7.3 mmol) in THF (5 mL) was slowly added. The reaction mixture was then allowed to warm to 0 °C, followed by addition of water (2.0 mL). The resulting mixture was further stirred at room temperature for 6 h. The two layers were then separated, and the aqueous layer was extracted with diethyl ether. The combined organic extract was washed with brine and dried over anhydrous Na_2SO_4. Removal of solvent followed by chromatography [petroleum ether–ethyl acetate (85:15)] furnished **6** (0.693 g, 78%) as a colorless liquid. IR (film) ν_{max}: 3292, 1010 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.43 (dd, $J_1 = 2.0$ Hz, $J_2 = 0.8$ Hz, 1H), 6.48 (d, $J = 3.2$ Hz, 1H), 6.36 (dd, $J_1 = 2.8$ Hz, $J_2 = 1.2$ Hz, 1H), 5.47 (dd, $J_1 = 6.4$ Hz, $J_2 = 2.0$ Hz, 1H), 2.63 (d, $J = 2.8$ Hz, 1H), 2.51 (d, $J = 6.8$ Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.6, 143.3, 110.6, 108.1, 81.1, 74.2, 58.1. HRMS: found 145.0267 $[M + Na]^+$; calcd. for $C_7H_6O_2$: 145.0265 $[M + Na]^+$.

Furan-2-yl(4-methoxyphenyl)methanol 10

n-BuLi (4 mL, 1.6 M in hexane, 6.4 mmol) was added to a solution of furan (0.7 mL, excess, freshly distilled) in anhydrous THF (7.5 mL) in a dropwise manner at −78 °C under an argon atmosphere. The resulting mixture was allowed to warm to 0 °C and stirred for 30 min. It was cooled again to −78 °C, and a solution of 4-methoxybenzaldehyde (560 mg, 4.12 mmol) in THF (5 mL) was added slowly. The reaction mixture was then allowed to warm to 0 °C, followed by addition of a saturated solution of NH_4Cl (2 mL). The two layers were separated, and the aqueous layer was extracted with diethyl ether. The combined organic extract was washed with brine and dried over anhydrous Na_2SO_4. Removal of solvent followed by chromatography [petroleum ether–ethyl acetate (85:15)] furnished **10** (0.622 g, 74%) as oil. IR (film) ν_{max}: 3394, 1610, 1515 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.38–7.32 (m, 3H), 6.91–6.87 (m, 2H), 6.30 (dd, $J_1 = 3.2$ Hz, $J_2 = 2.0$ Hz, 1H), 6.10 (d, $J = 0.8$ Hz, 1H), 5.75 (s, 1H), 3.79 (s, 3H), 2.55 (br. s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.2, 156.2, 142.2, 133.1, 127.8, 113.7, 110.0, 107.0, 69.6, 55.1. HRMS: found 227.0676 $[M + Na]^+$; calcd. for $C_{12}H_{12}O_3$: 227.0684 $[M + Na]^+$.

Furan-2-yl(4-nitrophenyl)methanol 11

The reaction of furan (0.7 mL, excess, freshly distilled) with n-BuLi (4 mL, 1.6 M in hexane, 6.4 mmol) and 4-nitrobenzaldehyde (600 mg, 4 mmol) as described previously, followed by chromatographic separation [petroleum ether–ethyl acetate (80:20)], furnished **11** (0.63 g, 72%), mp 110–113 °C. IR (film) ν_{max}: 3472, 1599, 1524, 1340 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.24–8.20 (m, 2H), 7.64–7.61 (m, 2H), 7.40 (dd, $J_1 = 1.6$ Hz, $J_2 = 0.8$ Hz, 1H), 6.34 (dd, $J_1 = 3.2$ Hz, $J_2 = 2.0$ Hz, 1H), 6.17 (d, $J = 3.6$ Hz, 1H), 5.94 (d, $J = 4.0$ Hz, 1H), 2.59 (d, $J = 4.0$ Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.6, 147.8, 147.7, 143.2, 127.4, 123.8, 110.6, 108.2, 69.2. HRMS: found 220.0618 $[M + H]^+$; calcd. for $C_{11}H_9O_4N$: 220.0610 $[M + H]^+$.

Furan-2-yl (4-pyridyl)methanol 12

The reaction of furan (3.2 mL, excess, freshly distilled) with n-BuLi (16 mL, 1.6 M in hexane, 30 mmol) and pyridine-4-carboxaldehyde (2.16 g, 21 mmol) as described previously, followed by purification of the crude product by charcoal treatment, furnished **12** (3.19 g, 90%), mp 83–85 °C. IR (film) ν_{max}: 3120, 1605, 1420, 1147, 1049 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.50–8.48 (m, 2H), 7.40–7.26 (m, 3H), 6.33 (dd, $J_1 = 2.0$ Hz, $J_2 = 1.2$ Hz, 1H), 6.16 (d, $J = 2.8$ Hz, 1H), 5.83 (s, 1H), 4.40 (brs, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.1, 151.1, 149.1, 142.8, 121.7, 110.4, 107.7, 68.3. HRMS: found 176.0706 $[M + H]^+$; calcd. for $C_{10}H_9O_2N$: 176.0712 $[M + H]^+$.

Furan-2-yl(3-thienyl)methanol 13

The reaction of furan (0.7 mL, excess, freshly distilled) with n-BuLi (4 mL, 1.6 M in hexane, 6.4 mmol) and 3-thiophenecarboxaldehyde (470 mg, 4.2 mmol) as described previously, followed by chromatography [petroleum ether–ethyl acetate (85:15)], furnished 600 mg of **13** (0.600 g, 86.6%) as a colorless liquid. IR (film) ν_{max}: 3368, 1011 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.40 (s, 1H), 7.32–7.30 (m, 2H), 7.11 (dd, $J_1 = 4.4$ Hz, $J_2 = 1.6$ Hz, 1H), 6.34–6.32 (m, 1H), 6.18 (d, $J = 3.2$ Hz, 1H) 5.89 (s, 1H), 2.47 (br. s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.7, 142.5, 142.3, 126.5, 126.1, 122.3, 110.3, 107.2, 66.4. HRMS: found 203.0151 $[M + Na]^+$; calcd. for $C_9H_8O_2SNa$: 203.0143 $[M + Na]^+$.

General Procedure for Oxidation with IBX

IBX (2.0 eq.) was added to a solution of the alcohol (1.0 eq.) in ethyl acetate (10 mL/mmol) at ambient temperature (~30 °C). The resulting heterogeneous mixture was immersed in a preheated oil bath at 70–75 °C. The reaction was monitored by thin-layer chromatography (TLC). On completion of the reaction (generally 2 h), the reaction mixture was cooled and filtered through a short pad of celite. It was washed with ethyl acetate (2 × 20 mL). The combined filtrate was concentrated under reduced pressure and chromatographed on silica gel to give the product. Some of the ketones are known, but their spectroscopic data are either not available or incomplete, so the spectral data of all the ketones are given here.

1-(Furan-2-yl)but-3-en-1-one 2a

The oxidation of alcohol **1a** (2.6 g, 18.8 mmol) with IBX (10.5 g, 37.5 mmol) according to the procedure described previously furnished 2.32 g (91%) of ketone **2a**. IR (film) ν_{max}: 1667, 1639, 1467 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.60–7.59 (m, 1H), 7.22 (dd, $J_1 = 3.6$ Hz, $J_2 = 0.4$ Hz, 1H), 6.55 (dd, $J_1 = 3.2$ Hz, $J_2 = 0.4$ Hz, 1H), 6.09–5.98 (m, 1H), 5.26–5.21 (m, 2H), 3.63–3.59 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 187.1, 152.4, 146.7, 130.5, 119.2, 118.5, 117.7, 112.5, 43.5. HRMS: found 137.0605 $[M + H]^+$; calcd. for $C_8H_8O_2$: 137.0603 $[M + H]^+$.

1-(Furan-2-yl)pent-4-en-1-one 2b

The oxidation of alcohol **1b** (3.0 g, 19.7 mmol) with IBX (11 g, 39.3 mmol) according to the procedure described previously gave **2b** (2.72 g, 92%). IR (film) ν_{max}: 1679, 1641, 1568, 1470 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.58 (dd, $J_1 = 1.6$ Hz, $J_2 = 0.8$ Hz, 1H), 7.19 (dd, $J_1 = 3.6$ Hz, $J_2 = 0.4$ Hz, 1H), 6.53 (dd, $J_1 = 3.6$ Hz, $J_2 = 1.6$ Hz, 1H), 5.92–5.82 (m, 1H), 5.10–4.98 (m, 2H), 2.96–2.90 (m, 2H), 2.51–2.45 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 188.9, 152.9, 146.4, 137.1, 116.9, 115.4, 112.2, 37.7, 28.1. HRMS: found 151.0764 $[M + H]^+$; calcd. for $C_9H_{10}O_2$: 151.0759 $[M + H]^+$.

1-(Furan-2-yl)hex-5-en-1-one 2c

The oxidation of alcohol **1c** (1.6 g, 9.6 mmol) with IBX (5.3 g, 19 mmol) according to the procedure described previously furnished ketone **2c** (1.45 g, 94%). IR (film) ν_{max}: 1672, 1569, 1468 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.58–7.57 (m, 1H), 7.18 (dd, $J = 4.0$ Hz, 1H), 6.54–6.52 (m, 1H), 5.88–5.74 (m, 1H), 5.07–4.97 (m, 2H), 2.83 (t, $J = 9.6$ Hz, 2H), 2.14 (q, $J = 9.2$ Hz, 2H), 1.88–1.78 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 189.6, 152.9, 146.3, 137.9, 116.9, 115.4, 112.2, 37.7, 32.2, 23.4. HRMS: found 165.0913 $[M + H]^+$; calcd. for $C_{10}H_{12}O_2$ 165.0916 $[M + H]^+$.

1-(Furan-2-yl)prop-2-en-1-one 2d

Oxidation of alcohol **1d** (400 mg, 3.2 mmol) with IBX (1.83 g, 6.5 mmol) according to the procedure described previously furnished **2d** (340 mg, 87%) as a colorless liquid. IR (film) ν_{max}: 1651, 1466 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.65–7.64 (m, 1H), 7.28 (dd, $J_1 = 3.6$ Hz, $J_2 = 0.8$ Hz, 1H), 7.11–7.04 (m, 1H), 6.59–6.53 (m, 2H), 5.88 (dd, $J_1 = 10.4$ Hz, $J_2 = 1.6$ Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.3, 153.1, 147.1, 131.5, 129.7, 118.5, 112.7. HRMS: found 123.0446 $[M + H]^+$; calcd. for $C_7H_6O_2$: 123.0446 $[M + H]^+$.

1-(Furan-2-yl)prop-2-yn-1-one 7

The oxidation of alcohol **6** (180 mg, 1.5 mmol) with IBX (852 mg, 3 mmol) according to the procedure described previously furnished ketone **7** (160 mg, 90%) as a colorless liquid. IR (film) ν_{max}: 3253, 3147, 2101, 1636, 1459, 1056 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.70–7.69 (m, 1H), 7.42 (dd, $J_1 = 3.6$ Hz, $J_2 = 0.8$ Hz, 1H), 6.61 (dd, $J_1 = 3.6$ Hz, $J_2 = 1.6$ Hz, 1H), 3.34 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.9, 152.9, 148.6, 122.0, 112.9, 79.8, 79.5. HRMS: found 121.0288 $[M + H]^+$; calcd. for $C_7H_4O_2$: 121.0290 $[M + H]^+$.

2-Acetylfuran 14

Oxidation of the alcohol **8** (500 mg, 4.5 mmol) with IBX (2.65 g, 9.5 mmol) as described previously furnished **14** (460 mg, 94%) as a liquid. IR (film) ν_{max}: 1678, 1570, 1470 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.57–7.56 (m, 1H), 7.25–7.16 (m, 1H), 6.52 (dd, $J_1 = 3.6$ Hz, $J_2 = 1.6$ Hz, 1H), 2.46 (s, 3H). ^{13}C NMR ($CDCl_3$,

100 MHz): δ 187.0, 152.9, 146.6, 117.4, 112.4, 26.1. HRMS: found 111.0449 $[M+H]^+$; calcd. for $C_6H_6O_2$: 111.0446 $[M+H]^+$.

Furan-2yl(phenyl)methanone 15

The oxidation of alcohol **9** (180 mg, 1 mmol) with IBX (568 mg, 2 mmol) according to the procedure described previously furnished **15** (172 mg, 93%) as a liquid. IR (film) ν_{max}: 1648, 1599, 1561, 1464 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.98–7.95 (m, 2H), 7.71–7.70 (m, 1H), 7.61–7.57 (m, 1H), 7.51–7.47 (m, 2H), 7.26–7.23 (m, 1H), 6.59 (dd, $J_1 = 3.6$ Hz, $J_2 = 1.6$ Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 182.7, 152.5, 147.2, 137.4, 132.7, 129.4, 128.5, 120.6, 112.3. HRMS: found 173.0598 $[M+H]^+$; calcd. for $C_{11}H_8O_2$: 173.0603 $[M+H]^+$.

Furan-2-yl(4-methoxyphenyl)methanone 16

The oxidation of alcohol **10** (208 mg, 1 mmol) with IBX (571 mg, 2 mmol) as described previously gave **16** (181 mg, 88%) as a solid, mp 60–62 °C (lit.[7a] mp 59–60 °C). IR (thin film) ν_{max}: 1638, 1601, 1571, 1464, 1260 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.05–8.01 (m, 2H), 7.68 (m, 1H), 7.23–7.22 (m, 1H), 6.99–6.96 (m, 2H), 6.58 (dd, $J_1 = 3.6$ Hz, $J_2 = 1.6$ Hz, 1H), 3.89 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 181.2, 163.5, 152.9, 146.6, 131.9, 130.0, 119.7, 113.9, 112.2, 55.6. HRMS: found 203.0709 $[M+H]^+$; calcd. for $C_{12}H_{10}O_3$: 203.0708 $[M+H]^+$.

Furan-2-yl (4-nitrophenyl)methanone 17

Oxidation of alcohol **11** (200 mg, 0.9 mmol) with IBX (562 mg, 2 mmol) as described previously furnished ketone **17** (186 mg, 94%) as a solid, mp 180–184 °C (lit.[13] mp 165–171 °C). IR (film) ν_{max}: 1638, 1601, 1518 cm^{-1}. ^1H NMR (400 MHz, CD_3OD): δ 8.1–8.38 (m, 2H), 8.18–8.15 (m, 2H), 7.97–7.96 (m, 1H), 7.44 (d, $J = 3.6$ Hz, 1H), 6.76 (dd, $J_1 = 3.6$ Hz, $J_2 = 1.6$ Hz, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 180.1, 150.9, 149.6, 149.5, 142.1, 130.3, 123.7, 122.5, 113.2. HRMS: found 218.0454 $[M+H]^+$; calcd. for $C_{11}H_7O_4N$: 218.0453 $[M+H]^+$.

Furan-2-yl(pyridine-4-yl)methanone 18

The oxidation of alcohol **12** (195 mg, 1.1 mmol) with IBX (592 mg, 2.1 mmol) gave **18** (176 mg, 91%) as a solid, mp 84–87 °C (lit.[13] mp 79–81 °C). IR (film) ν_{max}: 1649, 1548, 1408, 1032 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.81–8.80 (m, 2H), 7.76–7.64 (m, 3H), 7.31–7.30 (m, 1H), 6.63 (dd, $J_1 = 3.6$ Hz, $J_2 = 1.2$ Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 180.9, 151.9, 150.6, 148.0, 143.7, 122.5, 121.5, 112.6. HRMS: found 174.0553 $[M+H]^+$; calcd. for $C_{10}H_7O_2N$: 174.0555 $[M+H]^+$.

Furan-2-yl(thiophen-3-yl)methanone 19

The oxidation of alcohol **13** (182 mg, 1 mmol) with IBX (564 mg, 2 mmol) gave **19** (168 mg, 94%) as a liquid. IR (film) ν_{max}: 1633, 1566, 1465, 1284 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.40 (dd, $J_1 = 3.2$ Hz, $J_2 = 1.2$ Hz, 1H), 7.75 (dd, $J_1 = 5.2$ Hz,

$J_2 = 1.2$ Hz, 1H), 7.68–7.67 (m, 1H), 7.37–7.34 (m, 2H), 6.60 (dd, $J_1 = 3.6$ Hz, $J_2 = 16$ Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 175.5, 153.2, 146.5, 140.3, 133.5, 128.5, 125.9, 119.1, 112.5. HRMS: found 179.0163 $[M + H]^+$; calcd. for $C_9H_6O_2$ S: 179.0167 $[M + H]^+$.

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