Article

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Synthesis of β-Haloketones by β-Addition Reactions of α,β-Unsaturated Ketones with BX_3 (X = Br, Cl) as Halide Source

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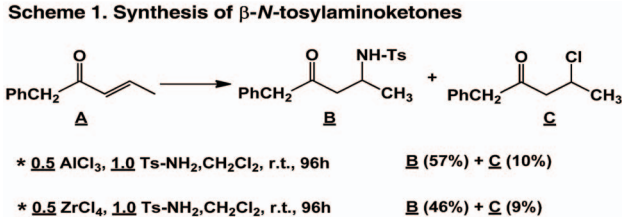
A series of β-bromoketones and β-chloroketones were synthesized by the addition reactions of α,β-unsaturated ketones under BX_3 (X = Br, Cl) and ethylene glycol reaction system. The α,β-unsaturated ester also was successfully converted to its corresponding β-bromoester under the reaction condition.

Keywords: β-Bromoketone; β-Chloroketone; α,β-Unsaturated ketone; β-Addition reaction; BBr_3; BCl_3.

INTRODUCTION

A β-substituted carbonyl compound is potentially biological active molecule and the important synthetic intermediate in organic synthesis.[1-4] Synthetic methodologies for synthesis of β-substituted carbonyl compounds are typically produced by the addition reactions such as Aldol-type reaction,[5,6] organocopper addition reaction[7,8] and Michael addition reaction.[9,10] Conjugate addition of organometallic reagent to α,β-unsaturated carbonyl compound is the commonly used method for specific introduction of a substituent to the β-position of carbonyl functionality.[11] Recently, our laboratory reported the synthesis of β-methoxyketones, β-aminoketones B, and β-amidoketones by a Lewis acids promoted β-addition reactions of α,β-unsaturated ketones under mild reaction conditions.[12,13] A contaminated β-chloroketone C was usually observed and characterized when Lewis acids such as $AlCl_3$ and $ZrCl_4$ were used for promotion of β-additional reaction of α,β-unsaturated ketone (Scheme 1). The formation of β-chloroketone as side product also was observed and reported by other addition reaction conditions.[14,15] Some synthetic applications[16-22] of β-halocarbonyl compounds such as β-bromoketone and β-bromoester have been reported in the literatures. To our knowledge, only a few direct preparation of β-chlorocarbonyl compounds which by reaction of α,β-unsaturated ketone with excess Me_3SiCl/H_2O reaction condition[23] and β-additional reaction of β-methylsulfonylester[24] with $AlCl_3$ have been reported in the literatures. The difficult preparations of β-halocarbonyl compounds restrict their further synthetic applications.[23-26] Thus, we expected that the preparation of β-chloroketone may be achieved by the Michael addition reaction of α,β-unsaturated ketone with Lewis acid $AlCl_3$ which serves as chloride source by introducing promotion agents.

Scheme 1. Synthesis of β-*N*-tosylaminoketones



RESULTS AND DISCUSSIONS

The first test of our approach was examined by reaction of 1-phenyl-pent-3-en-2-one A and Lewis acid $AlCl_3$ with 2 drops of ammonia solution as promoting reagent in CH_2Cl_2 and the reaction mixture was stirred at room temperature (Scheme 2). The reaction mixture was stirred at room temperature for 42 hours and the expected product β-chloroketone C (47%) was obtained with recovery of 1-phenyl-pent-3-en-2-one A (18%).

The higher yield of β-chloroketone C (84%) was achieved when promoter ethylene glycol (3 equivalents to $AlCl_3$) was used and much shorter reaction time also was observed. We think that BCl_3 may release chloride as nucleophile easier than $AlCl_3$ when ethylene glycol was introduced as promoter under the reaction condition. Therefore, a reaction mixture of 1-phenyl-pent-3-en-2-one A (1.0 equivalent), BCl_3 (1.0 equivalent) and ethylene glycol (1.0 equivalent) in CH_2Cl_2 was investigated and stirred at 0 ^oC. The experimental results showed that β-chloroketone C was afforded with 85% and the reaction time was shortened from 5 days to half an hour. The formation yield was dramatically improved to 96% when 1.2 equivalents of BCl_3

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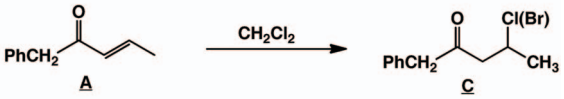
Scheme 2. Optimization of preparation of β-chloroketone



- 1.0 $AlCl_3$, 2drops NH_3, r.t., 42h — 47% (C) + 18% (A)
- 1.0 $AlCl_3$, 1.0 $HOCH_2CH_2OH$, r.t., 5 days — 55% (C) + 13% (A)
- 1.0 $AlCl_3$, 2.0 $HOCH_2CH_2OH$, r.t., 5 days — 72% (C) + 11% (A)
- 1.0 $AlCl_3$, 3.0 $HOCH_2CH_2OH$, r.t., 42 h — 84% (C)
- 1.0 BCl_3, 1.0 $HOCH_2CH_2OH$, 0 °C, 0.5 h — 85% (C)
- 1.2 BCl_3, 1.2 $HOCH_2CH_2OH$, 0 °C, 0.5 h — 96% (C)
- 1.2 BBr_3, 1.2 $HOCH_2CH_2OH$, 0 °C, 0.5 h — 96% (C)

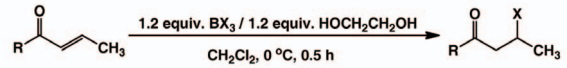
and $HOCH_2CH_2OH$ to substrate were used as the reaction system. Thus, we further investigated this method for the preparation of β-bromoketone by reaction of BBr_3 as bromide source with 1-phenyl-pent-3-en-2-one under the reaction condition. As shown in Scheme 2, β-bromoketone was also obtained with high yield (96%) under the reaction condition. Herewith, we wish to report the synthesis of β-haloketones by the β-additional reactions of α,β-unsaturated ketones with BX_3 (X = Br, Cl)/$HOCH_2CH_2OH$ reaction system.

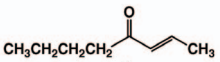
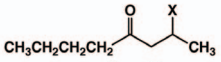
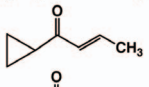
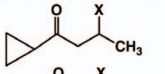
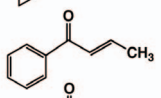
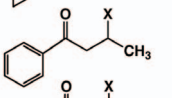
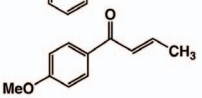
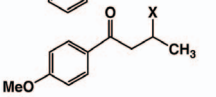
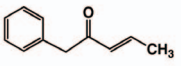
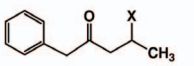
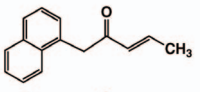
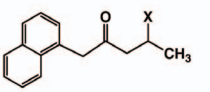
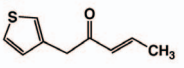
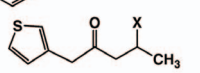
To understand and expand the scope for synthesis of β-haloketones by this reaction system BX_3 (X = Br, Cl)/$HOCH_2CH_2OH$, a series of α,β-unsaturated ketones was investigated and the results are shown in Table 1. The experimental results showed that alkyl and aryl α,β-unsaturated ketones were successfully converted to their corresponding β-bromoketones and β-chloroketones under the reaction condition.

A few previous reports showed that β-bromoester was used for synthesis of some synthetic intermediates and biologically active compounds.[16-21] Therefore, we further invetigated the reaction of α,β-unsaturated ester under this reaction condition. BBr_3 was added dropwise to a solution of methyl acrylate and ethylene glycol in CH_2Cl_2 at 0 °C and then the reaction mixture was stirred at room temperature for 24 hours. As shown in Scheme 3, a 96% yield of β-bromoester was obtained with longer reaction time which compared to α,β-unsaturated ketone under this reaction condition.

To understand and expand the synthetic applications of β-haloketones, we further investigated the reduction reaction of β-bromoketone by using AIBN/Bu_3SnH reducing

Table 1. Synthesis of β-bromoketones and β-chloroketones



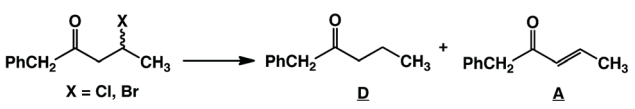
Entry	Substrate	Product	Yield (%) X = Cl	Yield (%) X = Br
1			88%	89%
2			78%	71%
3			74%	70%
4			82%	85%
5			96%	96%
6			76%	79%
7			80%	84%

Scheme 3. Synthesis of β-bromoester

- * 1.0 BBr_3, 1.0 HO⁓OH, CH_2Cl_2, 0 °C-r.t., 24 h — 87%
- * 1.2 BBr_3, 1.2 HO⁓OH, CH_2Cl_2, 0 °C-r.t., 24 h — 96%

agents.[28] The β-bromoketone C was introduced into AIBN (azobis(isobutyronitrile)) and Bu_3SnH (tributyltin hydride) in benzene and the reaction mixture was refluxed for 11 hours (Scheme 4).

Scheme 4. Reduction reactions of β-bromoketones



- X = Br — * 0.15 AIBN, 1.3 nBu_3SnH, PhH, reflux, 11 h — D (83%) + A (5%)
- X = Cl — * 0.15 AIBN, 1.3 nBu_3SnH, PhH, reflux, 6 h — D (64%) + A (4%)

The experimental results showed that β-bromoketone undergo dehalogenation reaction and which was converted to its corresponding hydrogenated product D (83%) with small amount of contaminated α,β-unsaturated ketone A (5%). β-Chloroketone also underwent this dehalogenation

reaction and a lower yield of product D (64%) was obtained with small amount of 1-phenyl-pent-3-en-2-one A (4%). This reaction scheme may provide an alternative method for hydrogenation reaction of α,β-unsaturated ketone to hydrogenated ketone.

As a conclusion, we demonstrate here a simple and an efficient method for the synthesis of β-bromoketones, β-chloroketones and β-bromoesters under $BX_3/HOCH_2CH_2OH$ reaction conditions.

EXPERIMENTAL

General. All reagents were purchased from Aldrich and Riedel-deHaen and all were used directly without further purification. All experiments were carried out under a nitrogen atmosphere which was dried primarily by passing through a column of potassium hydroxide (KOH) layered with calcium sulfate ($CaSO_4$). Thin-layer chromatography (TLC) analysis was performed on a plastic plate (or aluminum sheet) precoated with silica gel (Merck, 5554 Silica gel 60F254). Column chromatography was performed using silica gel (Merck 230-400 mesh) and ethyl acetate/hexane mixture as the eluent. The ^{1}H NMR (proton nuclear magnetic resonance) spectra were recorded at 300 MHz (Bruker-AC300P) with deuteriochloroform ($CDCl_3$, Aldrich 99.8 atom% D) as the solvent and the internal standard. The ^{13}C NMR (carbon nuclear magnetic resonance) spectra were recorded at 75.5 MHz (Bruker-AC300P) with $CDCl_3$ as the solvent and the internal standard. Mass spectra (MS) were recorded on JOEL SX-102A and VG 70-250S spectrophotometers and are reported in *m/z* units for the most abundant peaks. Infrared spectra (IR) were recorded on a Bruker Tensor 37 as a liquid film (neat).

A representative procedure for synthesis of β-bromoketone or β-chloroketone is as follows: BX_3 (X = Br, Cl) (1.2 mmol) was added dropwise to a solution of α,β-unsaturated ketone (1.0 mmol) and ethylene glycol (1.2 mmol) in CH_2Cl_2 (5 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 30 minutes and distilled water (10 mL) was added slowly and then the reaction mixture was extracted with ether (10 mL ×3). The combined organic layer was washed with brine (20 mL), dried with $MgSO_4$, filtered, and the organic solvent was removed under reduced pressure.

2-Chlorooctan-4-one (Table 1, Entry 1). ^{1}H-NMR: δ 0.85 (3H, H_8, t, J = 7.3), 1.20-1.30 (2H, H_7, m), 1.46-1.56 (2H, H_6, m), 1.48 (3H, H_1, d, J = 6.6), 2.38 (2H, H_5, t, J = 7.4), 2.66 (1H, H_3, dd, J = 16.8, 5.8), 2.90 (1H, H_3, dd, J = 16.8, 7.7), 4.40 (1H, H_2, ddq, J = 7.7, 7.4, 5.8); ^{13}C-NMR: δ 13.7, 22.2, 25.1, 25.5, 43.2, 52.4, 207.3); IR: (neat) 2960 (sp^3-CH, w), 2933 (sp^3-CH, w), 1715 (C=O, m), 1377 (m), 1132 (m), 616 (C-Cl, m).

2-Bromooctan-4-one (Table 1, entry 1). ^{1}H-NMR: δ 0.85 (3H, H_8, t, J = 7.4), 1.20-1.32 (2H, H_7, m), 1.46-1.56 (2H, H_6, m), 1.66 (3H, H_1, d, J = 6.6), 2.37 (2H, H_5, t, J = 7.4), 2.80 (1H, H_3, dd, J = 17.0, 6.0), 3.04 (1H, H_3, dd, J = 17.0, 7.7), 4.27 (1H, H_2, ddq, J = 7.7, 6.0, 6.); ^{13}C-NMR: δ 13.6, 22.1, 25.4, 26.1, 43.4, 53.0, 207.2; IR: (neat) 2961 (sp^3-CH, w), 2934 (sp^3-CH, w), 1716 (C=O, s), 1379 (m), 1132 (m).

3-Chloro-1-cyclopropylbutan-1-one (Table 1, entry 2). ^{1}H-NMR: δ 0.88-0.95 (2H, m), 1.05-1.10 (2H, m), 1.55 (3H, H_4, d, J = 6.6), 1.88-1.96 (1H, m), 2.88 (1H, H_2, dd, J = 16.8, 7.3), 3.10 (1H, H_2, dd, J = 16.8, 6.3), 4.48 (1H, H_3, ddq, J = 7.3, 6.6, 6.3); ^{13}C-NMR: δ 10.8, 20.9, 25.0, 52.2, 52.9, 206.9; IR: (neat) 2982 (sp^3-CH, w), 2931 (sp^3-CH, w), 1698 (C=O, m), 1388 (m), 1061 (m), 618 (C-Cl, m).

3-Bromo-1-cyclopropylbutan-1-one (Table 1, entry 2). ^{1}H-NMR: δ 1.65 (3H, H_4, d, J = 6.6), 2.01-2.10 (2H, m), 2.54 (2H, d, J = 7.0), 2.82 (1H, H_2, dd, J = 17.0, 5.6), 3.04 (1H, H_2, dd, J = 17.0, 8.1), 3.37 (2H, t, J = 6.6), 4.42 (1H, H_3, ddq, J = 8.1, 5.6, 6.6); ^{13}C-NMR: δ 25.9, 26.1, 32.9, 41.1, 42.8, 53.0, 205.5; IR: (neat) 2964 (sp^3-CH, w), 2922 (sp^3-CH, w), 1714 (C=O, s), 1375 (m), 1241 (m).

3-Chloro-1-phenylbutan-1-one (Table 1, entry 3). ^{1}H-NMR: δ 1.62 (3H, H_4, d, J = 6.6), 3.24 (1H, H_2, dd, J = 17.0, 6.6), 3.57 (1H, H_2, dd, J = 17.0, 6.6), 4.67 (1H, H_3, ddq, J = 6.6, 6.6, 6.6), 7.44-7.49 (2H, m), 7.55-7.60 (1H, m), 7.93-7.96 (1H, m); ^{13}C-NMR: δ 25.2, 48.5, 52.6, 128.0, 128.6, 133.4, 136.6, 196.5; HRMS: *m/z* 182.0492 (calcd. for $C_{10}H_{11}ClO$, 182.0498); MS: *m/z* 186 (6, M+4), 184 (3, M+2), 182 (6, M), 165 (1), 147 (15), 130 (8), 115 (8), 106 (7), 105 (base), 91 (6), 77 (43); IR: (neat) 3061 (sp^2-CH, w), 2982 (sp^3-CH, w), 2929 (sp^3-CH, w), 1683 (C=O, s), 1448 (m), 1217 (m), 753 (s), 688 (s), 616 (C-Cl, m).

3-Bromo-1-phenylbutan-1-one (Table 1, entry 3). ^{1}H-NMR: δ 1.81 (3H, H_4, d, J = 6.7), 3.38 (1H, H_2, dd, J = 17.3, 6.7), 3.71 (1H, H_2, dd, J = 17.3, 6.9), 4.69 (1H, H_3, ddq, J = 6.9, 6.7, 6.7), 7.44-7.49 (2H, m), 7.55-7.60 (1H, m), 7.93-7.96 (1H, m); ^{13}C-NMR: δ 26.4, 43.3, 49.3, 128.0, 128.6, 133.4, 136.4, 196.5; IR: (neat) 3061 (sp^2-CH, w), 2979 (sp^3-CH, w), 2922 (sp^3-CH, w), 1682 (C=O, m), 1448 (m), 1218 (m), 759 (m).

3-Chloro-1-(4-methoxyphenyl)butan-1-one (Table 1, entry 4). ^{1}H-NMR: δ 1.61 (3H, H_4, d, J = 6.6), 3.18 (1H, H_2, dd, J = 16.8, 6.6), 3.52 (1H, H_2, dd, J = 16.8, 6.7), 3.86 (3H, OMe, s), 4.65 (1H, H_3, ddq, J = 6.7, 6.6, 6.6), 6.94 (2H, d, J = 9.0), 7.93 (2H, d, J = 9.0); ^{13}C-NMR: δ 25.3, 48.2, 53.0, 55.5, 113.8, 130.0, 130.4, 163.8, 195.0; HRMS: *m/z* 212.0602 (calcd. for $C_{11}H_{13}ClO_2$, 212.0604); MS: *m/z* 215 (11, M+3), 214 (20, M+2), 213 (31, M+1), 212 (57, M), 177 (75), 134 (49), 135 (base), 107 (28); IR: (neat) 2973 (sp^3-CH, w), 2934 (sp^3-CH, w), 1674 (C=O, s), 1597 (s), 1167 (s), 1023 (m), 830 (s), 596 (C-Cl, m).

3-Bromo-1-(4-methoxyphenyl)butan-1-one (Table 1, entry 4). ^{1}H-NMR: δ 1.78 (3H, H_4, d, J = 6.7), 3.30 (1H, H_2, dd, J = 17.0, 6.8), 3.64 (1H, H_2, dd, J = 17.0, 7.0), 3.84 (3H, OMe, s), 4.68 (1H, H_3, ddq, J = 7.0, 6.8, 6.7), 6.91 (2H, d, J = 8.9), 7.91 (2H, d, J = 8.9); ^{13}C-NMR: δ 26.4, 43.8, 48.9, 55.4, 113.8, 129.5, 130.3, 163.7, 195.0; HRMS: *m/z* 256.0114 (calcd. for $C_{11}H_{13}BrO_2$, 256.0099); MS: *m/z* 259 (10, M+3), 258 (9, M+2), 257 (10, M+1), 256 (8, M), 177 (38), 176 (26), 136 (8), 135 (base); IR: (neat) 3006 (sp^2-CH, w), 2988 (sp^3-CH, w), 2923 (sp^3-CH, w), 1673 (C=O, m), 1597 (m), 1260 (m), 1166 (m), 764 (s).

4-Chloro-1-phenyl-pentan-2-one (Table 1, entry 5). ^{1}H-NMR: δ 1.48 (3H, H_5, d, J = 6.5), 2.74 (1H, H_3, dd, J = 17.0, 6.0), 3.00 (1H, H_3, dd, J = 17.0, 7.6), 3.72 (2H, H_1, s), 4.45 (1H, H_4, ddq, J = 7.6, 6.6, 6.0), 7.19-7.38(5H, m); ^{13}C-NMR: δ 25.0, 50.7, 51.5, 52.3, 127.2, 128.7, 129.4, 133.4, 204.5; MS: *m/z* 198 (4, M+2), 196 (12, M), 160 (8), 106 (21), 105 (71), 92 (18), 91 (base), 79 (10), 77 (52), 69 (64), 65 (28), 63 (10), 51 (6); IR: (neat) 3031 (sp^2-CH, w), 2982 (sp^3-CH, w), 1715 (C=O, s), 1127 (m), 699 (C-Cl, m).

4-Bromo-1-phenylpentan-2-one (Table 1, entry 5). ^{1}H-NMR: δ 1.67 (3H, H_5, d, J = 6.6), 2.88 (1H, H_3, dd, J = 17.2, 6.2), 3.13 (1H, H_3, dd, J = 17.2, 7.6), 3.71 (2H, H_1, s), 4.49 (1H, H_4, ddq, J = 7.6, 6.6, 6.2), 7.20-7.38(5H, m); ^{13}C-NMR: δ 26.0, 42.9, 50.4, 52.1, 127.1, 128.7, 129.4, 133.3, 204.4; HRMS: *m/z* 240.0149 (calcd. for $C_{11}H_{13}BrO$, 240.0150); MS: *m/z* 243 (9, M+3), 242 (4, M+2), 241 (9, M+1), 240 (4, M), 161 (13), 149 (13), 123 (22), 121 (25), 92 (20), 91 (base), 90 (20), 89 (0), 65 (55); IR: (neat) 3060 (sp^2-CH, w), 3029 (sp^2-CH, w), 2960 (sp^3-CH, w), 2927 (sp^3-CH, w), 1714 (C=O, m), 1668 (m), 1285 (m), 778 (s).

4-Chloro-1-(naphthalen-5-yl)pentan-2-one (Table 1, entry 6). ^{1}H-NMR: δ 1.43 (3H, H_5, d, J = 6.6), 2.67 (1H, H_3, dd, J = 17.1, 5.7), 2.98 (1H, H_3, dd, J = 17.1, 7.6), 4.16 (2H, H_1, dd, J = 22.1, 15.9), 4.45 (1H, H_4, ddq, J = 7.6, 6.6, 5.7), 7.38~7.56 (4H, m), 7.81~7.90 (3H, m); ^{13}C-NMR: δ 25.0, 49.1, 51.1, 52.4, 123.7, 125.6, 126.0, 126.6, 128.3, 128.4, 128.8, 130.2, 132.2, 134.0, 205.1; HRMS: *m/z* 246.0816 (calcd. for $C_{15}H_{15}ClO$, 246.0811); MS: *m/z* 249 (2, M+3), 248 (6, M+2), 247 (6, M+1), 246 (18, M), 210 (1), 144 (18), 141 (base), 139 (9), 115 (22); IR: (neat) 3047 (sp^2-CH, w), 2981 (sp^3-CH, w), 1714 (C=O, s), 1126 (m), 774 (C-Cl, s).

4-Bromo-1-(naphthalen-5-yl)pentan-2-one (Table 1, entry 6). ^{1}H-NMR: δ 1.62 (3H, H_5, d, J = 6.6), 2.82 (1H, H_3, dd, J = 17.3, 5.9), 3.13 (1H, H_3, dd, J = 17.3, 7.7), 4.15 (2H, H_1, dd, J = 22.4, 15.9), 4.49 (1H, H_4, ddq, J = 7.7, 6.6, 5.9), 7.39-7.57 (4H, m), 7.82-7.90 (3H, m); ^{13}C-NMR: δ 26.1, 43.0, 48.8, 51.8, 123.7, 125.5, 125.9, 126.6, 128.2, 128.4, 128.8, 130.1, 132.1, 133.9, 205.0; HRMS: *m/z* 290.0312 (calcd. for $C_{15}H_{15}BrO$, 290.0306); MS: *m/z* 293 (2, M+3), 292 (8, M+2), 291 (2, M+1), 290 (8, M), 210 (15), 142 (17), 141 (base), 139 (17), 115 (32), 69 (48); IR: (neat) 3045 (sp^2-CH, w), 2987 (sp^3-CH, w), 2902 (sp^3-CH, w), 1714 (C=O, m), 1126 (m), 775 (s).

4-Chloro-1-(thiophen-3-yl)pentan-2-one (Table 1, entry **7).** ^{1}H-NMR: δ 1.50 (3H, H_5, d, J = 6.6), 2.74 (1H, H_3, dd, J = 17.0, 5.7), 2.99 (1H, H_3, dd, J = 17.0, 7.6), 3.74 (2H, H_1, s), 4.44 (1H, H_4, ddq, J = 7.6, 6.6, 5.7), 6.95 (1H, dd, J = 4.9, 1.3), 7.11 (1H, dd, J = 2.9, 1.3), 7.31 (1H, dd, J = 4.9, 2.9); ^{13}C-NMR: δ 25.0, 44.9, 51.4, 52.3, 123.2, 126.1, 128.4, 133.0, 204.0; HRMS: *m/z* 203.0816 (calcd. for $C_{15}H_{15}ClO$, 203.0811); MS: *m/z* 205 (M+2, 4), 204 (M+1, 8), 203 (M, 56), 191 (10), 167 (20), 161 (4), 138 (16), 128 (6), 111 (52), 107 (32), 105 (base); IR: (neat) 3104 (sp^2-CH, w), 2980 (sp^3-CH, w), 1715 (C=O, s), 1126 (m), 776 (C-Cl, m).

4-Bromo-1-(thiophen-3-yl)pentan-2-one (Table 1, entry 7). ^{1}H-NMR: δ 1.68 (3H, H_5, d, J = 6.8), 2.88 (1H, H_3, dd, J = 17.2, 6.0), 3.13 (1H, H_3, dd, J = 17.2, 7.6), 3.73 (2H, H_1, s), 4.35 (1H, H_4, ddq, J = 7.6, 6.8, 6.0), 6.95 (1H, dd, J = 4.9, 1.0), 7.10 (1H, dd, J = 2.9, 1.0), 7.30 (1H, dd, J = 4.9, 2.9); ^{13}C-NMR: δ 26.0, 42.9, 44.7, 52.1, 123.1, 126.0, 128.4, 132.9, 204.0; HRMS: *m/z* 245.9430 (calcd. for $C_9H_{11}BrOS$, 245.9714); MS: *m/z* 248 (15, M+2), 247 (3, M+1), 246 (25, M), 245 (12), 166 (12), 151 (34), 147 (42), 131 (36), 97 (42), 69 (13), 43 (56), 28 (base); IR: (neat) 3051 (sp^2-CH, w), 2962 (sp^3-CH, w), 2928 (sp^3-CH, w), 1713 (C=O, m), 1264 (m), 731 (s), 702 (s).

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