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$Cu(OTf)_2$-catalyzed α-halogenation of ketones with 1,3-dichloro-5,5′-dimethylhydantoin and *N*-bromosuccinimide

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Copper(II) triflate catalyses efficiently the α-halogentaion of aryl or alkyl ketones with 1,3-dichloro-5,5′-dimethyl-hydantoin and *N*-bromosuccinimde to give the corresponding α,α-dichloroketones and α-bromoketones in high yield with excellent product selectivity.

Keywords: Lewis acid**,** copper (II), catalyst, chlorination, bromination, ketone

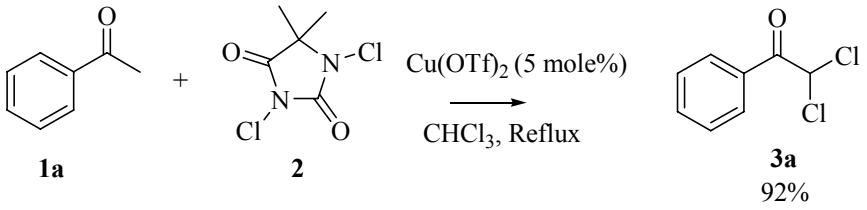
α-Halogenation of ketones to produce α-haloketones is a fundamental process in organic chemistry[1]. In particular, 1-aryl or alkyl-2,2-dichloroethanones **2** are versatile intermediates for the preparation of arylhydroxyacetic acids, arylglyoxals, their acetals, α-haloepoxides, α-haloketones[2a], etc. The two main preparative methods for the synthesis of α,α-dichloroketones are the chlorination of 1-arylethanones with chlorine in acetic acid[3], and Lewis acid-catalyzed acylation of arenes with dichloroacetyl chloride[2b,c]. Several approaches to 1-aryl-2,2-dichloroethanones have been reported[5], which include reactions of 1-arylethanones with copper(II) chloride[6] and benzyl-trimethylammonium tetrachloroiodate[7], phenyl-magnesium bromide with 1,2,2-trichloro-*N,N*-diethyleneamine[8], ozonolysis of 4,4-dichloro-3-phenylbut-2-enoic acid[9], arylacetylenes with hypo-chlorites[10] or *N*-chlorosuccinimide[11], and H_2O_2-HCl[12]. However, many of these methods make use of expensive and toxic reagents and solvents, long reaction times and high temperatures with poor product selectivity[5]. In addition, the *N*-bromo-succinimide (NBS) has been classically utilized for the α-bromination of ketones[13] *via* radical process promoted by radical initiators such as AIBN and benzoyl peroxide in CCl_4 (ref. 14) and Other methods for α-bromination of ketones include use of ionic liquids[5i], TMS·OTf[15], ammonium acetate[16], *p*-toluene sulphonic acid[17].

Results and Discussion

In continuation of the work[18] on $Cu(OTf)_2$-catalyzed transformations, it is interested in employing $Cu(OTf)_2$, being a mild Lewis acid catalyst, for α-chlorination of ketone using 1,3-dichloro-5,5′-dimethylhydantoin as electrophilic chlorine source[19]. Accordingly, acetophenone **1a** is subjected to $Cu(OTf)_2$-catalyzed chlorination with 1,3-dichloro-5,5′-dimethylhydantoin (**2**,1 equiv.), which produced 2,2-dichloro-1-phenylethanone **3a** in 92% yield **(Scheme I)**.

Encouraged by this result, other various Lewis acids such as Cu(OTf), $Cu(OAc)_2$, $CuCl_2$, CuCl, CuI, $Co(OAc)_2$ and $CoCl_2$ are screened for the chlorination of acetophenones with 1,3-dichloro-5,5′-dimethyl-hydantoin **2** as the chlorine source, which produced 2,2-dichloro-1-phenylethanone. Results of these studies are presented in **Table I**, which showed that $Cu(OTf)_2$ was found to be an effective catalyst compared to others for the synthesis of α,α-dichloroacetophenones with very high selectivity and excellent yields. For $Cu(OTf)_2$-catalyzed chlorination of acetophenone, out of solvents like CH_2Cl_2, CH_3CN, CH_3CO_2H and temperatures ranging from 25°C to reflux, it is found that $CHCl_3$ at reflux temperature is the best solvent system for the chlorination.

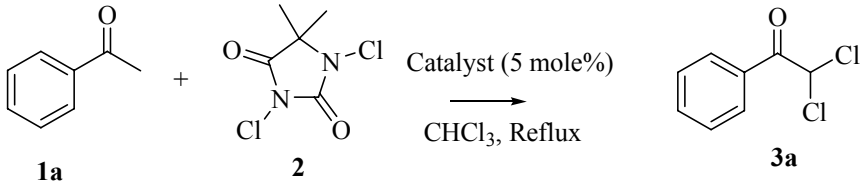
To generalize the scope of reaction, various aromatic ketones are used for α-chlorination. It is found that dichlorination of substituted



1a **2** **3a**
92%

Scheme I — (a) $Cu(OTf)_2$ (1mole%), $CHCl_3$, 80°C

Table I — Catalyst screening for dichlorination of acetophenone **1a** with 1,3-dichloro 5,5′-dimethylhydantoin **2**



1a **2** **3a**

No.	Catalyst	Yield of **3a** (%)[a]
1	$Cu(OTf)_2$	92
2	CuOTf	10
3	$Cu(OAc)_2$	23
4	$CuCl_2$	10
5	CuCl	0
6	CuI	0
7	$Co(OAc)_2$	0
8	$CoCl_2$	>5

Reaction conditions — Acetophenone (4 mmole), 1,3-dichloro-5,5′-dimethylhydantion (4.4 mmole), $Cu(OTf)_2$ (5 mole%),$CHCl_3$ (20 mL), reflux

acetophenones undergo smoothly giving high yields of α,α-dichloroketones with good yield and selectivity, the results of which are summarized in **Table II**. Remarkably, nuclear chlorination was not at all observed even in the activated aromatic ketones such as methoxyacetophenones **3g-h**. This can be explained from the fact that $Cu(OTf)_2$ is readily activating α-position of the ketone by enolization and thus deactivating the aromatic ring for electrophilic chlorination. Only in the case of 3,4,5-trimethoxyacetophenone **3i**, it is aromatic chlorination as well as monochlorination was observed at the *α*-position. As can be seen from **Table II**, substituted aromatic ketones (nitro, halide, CH_3 and OCH_3) underwent α,α-dichlorination to give the corresponding α,α-dichloroacetophenones **3a-l** in high yields.

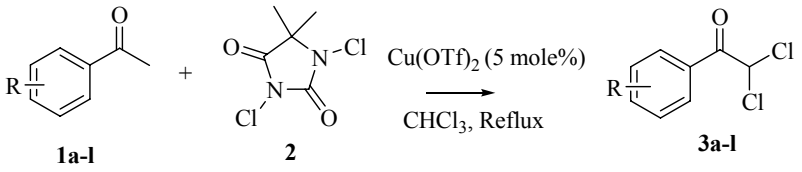
We were interested to examine aliphatic ketones as well as chalcones for dichlorination reaction. Thus, $Cu(OTf)_2$-catalyzed α-chlorination of aliphatic ketones **4a-c** were carried out with 1,3-dichloro-5,5′-dimethylhydantoin, which gave α,α'-dichloroketones **5a-c** in 67-76% yields (**Table III**).

In the case of substituted chalcones (R = H, Cl, OMe) **6a-c**, α,α-dichlorochalcones **7a-c** were obtained in 83-87% yields and interestingly the double bond was not at all affected under the reaction conditions (**Table IV**).

Next acetophenone was subjected to $Cu(OTf)_2$-catalyzed *α*-bromination with *N*-bromosuccinimide. It was observed that $Cu(OTf)_2$-catalyzed bromination of acetophenone with NBS (1 equiv.) gave α-bromoacetophenone **9a** in 82% yield

(**Table V**. entry 1). The compound α,α-dibromo-acetone was formed as a minor product (<5%) under the reaction conditions. A systematic study of various ketones was carried out, the results of which are presented in **Table V**.

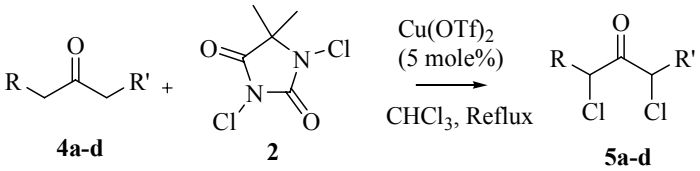
Table II — Cu-catalyzed α,α-dichlorination of substituted acetophenones[a]



Entry	R	Time (hr)	Yields of **3a-i** (%)[b]
a	H	8	92
b	4- O_2N	6	76
c	4-Br	7	77
d	4-Cl	7	71
e	4-F	8	73
f	4-CH_3	5	75
g	4-OCH_3	6	83
h	3,4-$(OCH_3)_2$	6	85
i	3,4,5-$(OCH_3)_3$	5	85[c]
j	Propiophenone	6	87
k	α-Tetralone	7	85
l	2-Acetyl naphthalene	6	86

[a]Reaction conditions — Arylketone (4 mmole), 1,3-dichloro 5,5′-dimethylhydantoin (4.4 mmole), $Cu(OTf)_2$ (5 mole%),$CHCl_3$ (20 mL), reflux
[b]Isolated yields after column chromatography
[c]2-chloro(2-chloro 3,4,5-trimethoxyphenyl)ethanone was obtained

Table III — Cu-catalyzed dichlorination of aliphatic ketones[a]



Entry	Ketone **4a-d**	Time (hr)	Yield of **5a-d** (%)[b]
a	2-methylcyclohexanone	6	67
b	2-butanone	7	67
c	2 -pentanone	7	76

[a]Reaction conditions — ketone (4 mmole), 1,3-dichloro 5,5′-dimethyl hydantoin (4.4 mmole), $Cu(OTf)_2$ (5 mole%),$CHCl_3$ (2 0 mL), reflux.
[b]Isolated yields after column chromatography

Conclusion

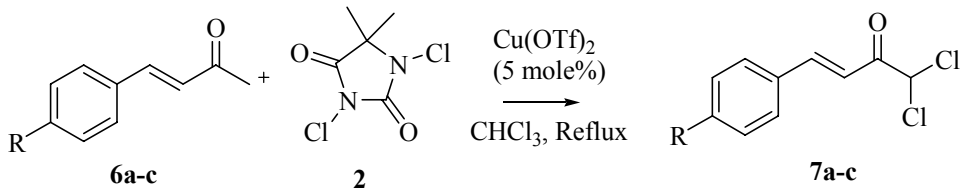
In conclusion for the first time Cu-catalyzed a simple and efficient method for the halogenation of ketones is devloped. In terms of handling and availability 1,3-dichloro-5,5′-dimethylhydantoin and *N*-bromosuccinimide is superior halogen sources. This method works very well with a variety of ketones and tolerates various functional groups.

Experimental Section

A general procedure for α,α-dichlorination of ketones

To a stirred solution of ketone (4 mmole) and $Cu(OTf)_2$ (2 mole%) in $CHCl_3$ (20 mL), was added 1,3-dichloro-5,5′-dimethyl hydration (4.4 mmole). Then, it was refluxed for 8 hr under nitrogen atmosphere. After completion of reaction (monitored

Table IV — Dichlorination of chalcones[a]

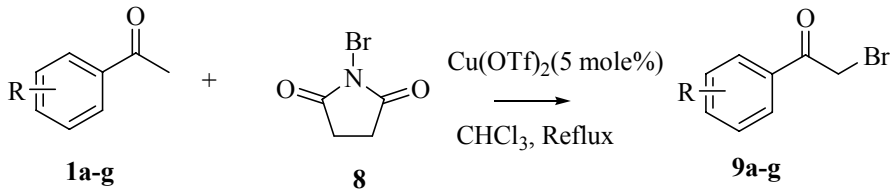


6a-c **2** **7a-c**

Entry	R **6a-c**	Time (hr)	Yield of **7a-c** (%)[b]
a	H	8	87
b	Cl	6	84
c	OMe	7	83

[a]Reaction conditions — Chalcone (4 mmole), 1,3-dichloro 5,5′-dimethyl hydantoin (4.4 mmole), $Cu(OTf)_2$ (5 mole%),$CHCl_3$ (20 mL), reflux
[b]Isolated yields after column chromatography

Table V — Cu-catalyzed α-bromination of ketones using NBS[a]



1a-g **8** **9a-g**

Entry	Ketone (R)	Time (hr)	Yield of **9a-i** (%)[b]
a	H	8	82
b	3-NO_2	6	89
c	4-NO_2	6	76
d	3,4-Cl	7	77
e	3,4-$(OCH_3)_2$	6	65
f	α-tetralone	7	85
g	2-acetyl-naphthalene	6	86
h	cyclohexanone	6	77
i	2-methyl-cyclohexanone	6	81

[a]Reaction conditions — ketone (4 mmole), NBS (4.4 mmole), $Cu(OTf)_2$ (5 mole%),$CHCl_3$ (20 mL), reflux
[b]Isolated yields after column chromatography

by TLC), the reaction-mixture was diluted with 20 mL chloroform. Organic phase was washed with a saturated sodium thiosulphate solution (20 mL) and brine (20 mL). The organic layer was dried over anhyd. Na_2SO_4, concentrated under reduced pressure to give the crude product. The crude product was purified by column chromatography [silica gel (60-120 mesh) and petroleum ether:ethyl acetate as eluent] to give dichloroketone in pure form.

2,2-Dichloro-1-phenylethanone, 3a. Yield: 92%, gum, IR ($CHCl_3$): 757, 990, 1093, 1402, 1590, 1712 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 6.63 (s, 1H), 7.51 (t, J = 7.3 Hz, 2H), 7.64 (t, J = 7.3 Hz, 1H), 8.09 (d, J = 7.3 Hz, 2H); ^{13}C NMR (50 MHz $CDCl_3$): δ 67.74, 128.76, 129.62, 131.20, 134.33, 185.45; Anal. Calcd. for $C_8H_6C_{l2}O$: C, 50.83; H, 3.20; Found: C, 50.80; H, 3.21%.

2,2-Dichloro-1-(4-nitrophenyl)ethanone, 3b. Yield: 76%, gum, IR ($CHCl_3$): 757, 990, 1093, 1335, 1402, 1450, 1590, 1711 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 6.55 (s, 1H), 8.34-8.35 (dd, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 67.71, 123.79, 130.85, 135.79,

150.70, 184.35; Anal. Calcd. for $C_8H_5Cl_2NO_3$: C, 41.06; H, 2.15; N, 5.98. Found: C, 40.87; H, 2.07; N, 5.82%.

1-(4-Bromophenyl)-2,2-dichloroethanone, 3c. Yield: 77%, gum, IR ($CHCl_3$): 669, 1011, 1075, 1215, 1274, 1400, 1586, 1712 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 6.58 (s, 1H), 7.66 (d, J = 8.7 Hz, 2H), 7.97 (d, J = 8.7 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 67.63, 129.74, 129.86, 131.05, 133.08, 184.80; Anal. Calcd. for $C_8H_5BrCl_2O$: C, 35.86; H, 1.88. Found: C, 35.71; H, 1.75%.

2,2-Dichloro-1-(4-chlorophenyl)ethanone, 3d. Yield: 71%; gum, IR ($CHCl_3$): 669, 850, 1094, 1216, 1274, 1402, 1590, 1712, 2400, 3019 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 6.53 (s, 1H), 7.49 (d, J = 8.5 Hz, 2H), 8.07 (d, J = 8.5 Hz, 2H); ^{13}C NMR (50MHz, $CDCl_3$): δ 67.79, 129.17, 129.41, 131.21, 141.09, 184.56; Anal. Calcd. for $C_8H_5Cl_3O$: C, 42.99; H, 2.26. Found: C, 42.76; H, 2.29%.

2,2-Dichloro-1-(4-fluorophenyl)ethanone, 3e. Yield: 73%; IR ($CHCl_3$): 767, 849, 1012, 1090, 1410 1592, 1714 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 6.58 (s, 1H), 7.15-7.26 (m, 2H), 8.13-8.21 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 67.75, 116.12 (d, J = 22.3 Hz), 127.44 (d, J = 2.9 Hz), 132.64 (d, J = 9.9 Hz), 166.31 (d, J = 258.4 Hz), 184.37; Anal. Calcd. for $C_8H_5Cl_2FO$: C, 46.41; H, 2.43. Found: C, 46.33; H, 2.39%.

2,2-Dichloro-1-*p*-tolylethanone, 3f. Yield: 75%; IR ($CHCl_3$): 669, 756, 1216, 1280, 1419, 1607, 1702, 2400, 3091 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 2.45 (s, 3H), 6.65 (s, 1H), 7.31(d, J = 8.3 Hz, 2H), 7.98 (d, J = 8.3 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.68, 67.71, 128.58, 129.48, 129.66, 145.63, 185.26; Anal. Calcd. for $C_9H_8OCl_2$: C, 53.23; H, 3.97. Found: C, 53.12; H, 3.82%.

2,2-Dichloro-1-(4-methoxyphenyl)ethanone, 3g. Yield: 83%; IR ($CHCl_3$): 857, 1410, 1620, 1711 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 3.90 (s, 3H), 6.61 (s, 1H), 6.97 (d, J = 8.9 Hz, 2H), 8.08 (d, J = 8.9 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 55.40, 67.71, 114.01, 123.67, 131.98, 164.42, 184.24; Anal. Calcd. for $C_9H_8Cl_2O_2$: C, 49.34; H, 3.68. Found: C, 49.21; H, 3.45%.

2,2-Dichloro-1-(3,4-dimethoxyphenyl)ethanone, 3h. Yield: 85%; IR ($CHCl_3$): 669, 756, 1092, 1215, 1326, 1491, 1611, 1697, 2399, 3019 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 3.95 (s, 3H), 3.98 (s, 3H), 6.66 (s, 1H), 6.92 (d, J = 8.6 Hz, 2H), 7.60 (d, J = 2.0 Hz, 2H), 7.75 (dd, J = 2.0, 8.6 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 55.56, 55.73, 67.33, 109.82, 111.25, 123.64, 124.11, 148.93, 154,19, 184,16. Analysis for $C_{10}H_{10}C_{l2}O_3$ requires C, 48.22; H, 4.05. Found: C, 48.11; H, 4.12%.

2-Chloro-1-(2-chloro-3,4,5-trimethoxyphenyl)-ethanone, 3i. Yield: 85%; IR ($CHCl_3$): 757, 823, 1410, 1614, 1711 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 3.89 (s, 3H), 3.91 (s, 3H), 3.95 (s, 3H), 4.75 (s, 2H), 6.96 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 48.68, 55.83, 60.70, 60.76, 108.15, 118.16, 130.83, 146.10, 149.69, 151.99, 192.58; Anal. Calcd. for $C_{11}H_{12}C_{l2}O_4$: C, 47.33; H, 4.33. Found: C, 47.21; H, 4.37%.

2,2-Dichloro-1-phenylpropan-1-one, 3j. Yield: 87%; IR ($CHCl_3$): 757, 1223, 1410, 1590, 1713 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 2.35 (s, 3H), 7.41-7.51 (m, 2H), 7.54-7.62 (m 1H), 8.29-8.34 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 35.91, 71.10, 127.93, 131.22, 133.38, 187.90; Anal. Calcd. for $C_9H_8Cl_2O$: C, 53.23; H, 3.97. Found: C, 53.17; H, 3.91%.

2,2-Dichloro-3,4-dihydronaphthalen-1(2*H*)-one, 3k. Yield: 85%; IR ($CHCl_3$): 746, 815, 879, 1123, 1217, 1291, 1425, 1598, 1702 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 2.96 (t, J = 5.9 Hz, 2H), 3.21 (t, J = 5.9 Hz, 2H), 7.25 (d, J = 7.6Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.54 (t, J = 7.5 Hz, 1H), 8.16 (d, J = 7.6 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 27.28, 43.08, 86.22, 127.39, 128.62, 129.68, 134.48, 142.02, 183.65; Anal. Calcd. for $C_{10}H_8Cl_2O$: C, 55.84; H, 3.75. Found: C, 55.65; H, 3.71%.

2,2-Dichloro-1-(naphthalen-4-yl)ethanone, 3l. Yield: 86%; IR ($CHCl_3$): 784, 846, 938, 1047, 1373, 1465, 1695, 2941 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 6.79 (s, 1H), 7.47-7.69 (m, 3H), 7.87-8.06 (m, 3H), 8.50 (d, J = 8.5 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 69.07, 123.89, 125.17, 126.80, 128.12, 128.54, 129.86, 130.76, 133.71,134.26, 188.08; Anal. Calcd. for $C_{12}H_8Cl_2O$: C, 60.28; H, 3.37. Found: C, 60.11; H, 3.21%.

2,6-Dichloro-2-methylcyclohexanone, 5[a]. Yield: 67%; ^1H NMR (200 MHz, $CDCl_3$): δ 1.71 (s, 3H), 1.78-2.00 (m, 3H), 2.18-2.40 (m, 2H), 2.49-2.64 (m, 1H), 5.23-5.33 (dd, J = 6.1, 6.7 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.10, 26.74, 38.39, 42.20, 60.31, 70.69, 196.92; Anal. Calcd. for $C_7H_{10}Cl_2O$: C, 46.43; H, 5.57. Found: C, 46.32; H, 5.51%.

1,3-Dichlorobutan-2-one, 5b. Yield: 67%; ^1H NMR (200 MHz, $CDCl_3$): δ 1.67 (d, J = 6.9 Hz, 3H), 4.46 (s, 2H), 4.64 (q, J = 6.9, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 19.84, 45.51, 55.57, 196.80; Anal. Calcd. for $C_4H_6Cl_2O$: C, 34.07; H, 4.29. Found: C, 34.23; H, 4.11%.

1,3-Dichloropentan-2-one, 5c. Yield: 76%; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.06 (t, *J* = 7.3 Hz, 3H), 1.89-2.13 (m, 2H), 4.36-4.56 (q, 1H), 4.44-4.46 (d, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 10.22, 26.79, 45.94, 62.25, 196.47; Anal. Calcd. for $C_5H_8Cl_2O$: C, 38.74; H, 5.20. Found: C, 38.66; H, 5.29%.

(*E*)-1,1-Dichloro-4-phenylbut-3-en-2-one, 7a. Yield: 87%; IR ($CHCl_3$): 746, 981, 1076, 1147, 1216, 1333, 1450, 1613, 1691, 2401, ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.97 (s, 1H), 7.20 (d, *J* = 15.9 Hz, 1H), 7.30-7.45 (m, 3H), 7.62-7.66 (m, 2H), 7.89 (d, *J* = 15.9 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 69.75, 117.43, 128.75, 128.92, 131.36, 133.67, 147.75, 185.35; Anal. Calcd. for $C_{10}H_8Cl_2O$: C, 55.84; H, 3.75. Found: C, 55.67; H, 3.79%.

(*E*)-1,1-Dichloro-4-(4-methoxyphenyl)but-3-en-2-one, 7b. Yield: 84%; ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.86 (s, 3H), 5.96 (s, 1H), 6.93 (d, *J* = 8.9 Hz, 2H), 7.06 (d, *J* = 15.7 Hz, 1H), 7.59 (d, *J* = 8.9 Hz, 2H), 7.85 (d, *J* = 15.7 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 55.19, 69.85, 114.37, 114.97, 126.42, 130.66, 147.51, 162.30, 185.39; Anal. Calcd. for $C_{11}H_{10}Cl_2O_2$: C, 53.90; H, 4.11. Found: C, 53.79; H, 4.19%.

(*E*)-1,1-Dichloro-4-(4-chlorophenyl)but-3-en-2-one, 7c. Yield: 83%; ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.96 (s, 1H), 7.18 (d, *J* = 15.9 Hz, 1H), 7.41 (d, *J* = 8.9 Hz, 2H), 7.58 (d, *J* = 8.9 Hz, 2H), 7.84 (d, *J* = 15.9 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 69.70, 117.86, 129.25, 129.89, 132.20, 137.37, 146.21, 185.21; Anal. Calcd. for $C_{10}H_7Cl_3O$: C, 48.14; H, 2.83. Found: C, 48.01; H, 2.89%.

A general procedure for α-bromination of ketones

To a stirred solution of ketone (4 mmole) and $Cu(OTf)_2$ (2 mole %) in $CHCl_3$ (20 mL), was added *N*-bromosuccinimide (4 mmole). Then it was refluxed for 8 hr under nitrogen atmosphere. After completion of reaction (monitored by TLC), the reaction- mixture was diluted with 20 mL chloroform. Organic phase was washed with a saturated sodium thiosulphate solution (20 mL) and brine (20 mL). The organic layer was dried over anhyd. Na_2SO_4, concentrated under reduced pressure to give the crude product. The crude product was purified by column chromatography [silica gel (60-120 mesh) and petroleum ether:ethyl acetate as eluent] to give α-bromoketone **9a-i** in pure form.

2-Bromo-1-phenylethanone, 9a. Yield: 82%; IR ($CHCl_3$): 759, 1234, 1374, 1462, 1592, 1691 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.47 (s, 2H), 7.46-7.62 (m, 3H), 7.99 (dt, *J* = 1.5, 7.0 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 31.15, 128.65, 129.28, 133.57, 134.76, 190.92; M/S: 200, 198, 105, 91, 77, 65, 51; Anal. Calcd. for C_8H_7BrO: C, 48.27; H, 3.54. Found: C, 48.22; H, 3.52%.

2-Bromo-1-(3-nitrophenyl)ethanone, 9b. Yield: 89%; IR ($CHCl_3$): 769, 1215, 1265, 1352, 1535, 1614, 1693 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.49 (s, 2H), 7.74 (t, *J* = 7.9 Hz, 1H), 8.34 (dd, *J* = 1.1, 7.9 Hz, 1H), 8.48 (dq, *J* = 1.1, 8.2 Hz, 1H), 8.82 (t, *J* = 1.9 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 30.22, 123.58, 127.94, 130.13, 134.35, 134.99, 148.30,189.32; Mass: *m/z*: 244, 242, 150, 134, 120, 104, 92, 76, 63, 40; Anal. Calcd. for $C_8H_6BrNO_3$: C, 39.37; H, 2.48; N, 5.74. Found: C, 39.33; H, 2.49; N, 5.77%.

2-Bromo-1-(4-nitrophenyl)ethanone, 9c. Yield: 76%; IR ($CHCl_3$): 757, 856, 1190, 1215, 1270, 1346, 1529, 1693 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.47 (s, 2H), 8.16 (d, *J* = 9.1 Hz, 2H), 8.35 (d, *J* = 9.1 Hz, 2H), ^{13}C NMR (50 MHz, $CDCl_3$): δ 30.36. 123.88, 129.92, 138.29, 150.51, 189.84; Anal. Calcd. for $C_8H_6BrNO_3$: C, 39.37; H, 2.48; N, 5.74. Found: C, 39.34; H, 2.43; N, 5.73%.

2-Bromo-1-(3,4-dichlorophenyl)ethanone, 9d. Yield: 77%; IR ($CHCl_3$): 756, 890, 1192, 1590, 1690 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.50 (s, 2H), 7.36 (dd, *J* =1.7, 8.3 Hz, 1H), 7.47 (d, *J* = 1.7 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 34.15, 127.23, 130.15, 131.07, 132.15, 133.78, 138.11, 192.07; Mass: *m/z*: 268, 173, 145, 124, 109, 95, 74, 62, 42; Anal. Calcd. for $C_8H_5BrCl_2O$: C, 35.86; H, 1.88.Found: C, 35.83; H, 1.85%.

2-Bromo-1-(3,4-dimethoxyphenyl)ethanone, 9e. Yield: 65%; IR ($CHCl_3$): 757, 890, 930, 1143, 1590, 1695 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.95 (s, 3H), 3.97 (s, 3H), 4.42 (s, 2H), 6.92 (d, *J* = 8.3 Hz, 1H), 7.54 (d, *J* = 2.0 Hz, 1H), 7.63 (dd, *J* = 2.0, 8.3 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 32.57, 55.87, 56.01, 110.03, 111.66, 123.20, 124.18, 149.15, 154.29, 184.61; Anal. Calcd. for $C_{10}H_{11}BrO_3$: C, 46.36; H, 4.28. Found: C, 46.32; H, 4.33%.

2-Bromo-3,4-dihydronaphthalen-1(2*H*)-one, 9f. Yield: 85%; IR (neat): 796, 887, 1195, 1303, 1598, 1681 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.43-2.54 (m, 2H), 2.86-2.99 (m, 1H), 3.25-3.41 (m, 1H), 4.74 (t, J = 4.1 Hz, 1H), 7.26-7.39 (m, 2H), 7.53 (dt, *J* = 1.5, 7.5Hz, 1H), 8.10 (dd, *J* = 1.2, 7.8 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 25.79, 31.59, 50.44, 126.70, 128.11, 128.51, 129.52, 133.79, 142.71,

190.07; Anal. Calcd. for $C_{10}H_9BrO$: C, 53.36; H, 4.03. Found: C, 53.31; H, 3.98%.

2-bromo-1-(naphthalen-4-yl)ethanone, 9g. Yield: 86%; IR ($CHCl_3$): 777, 1086, 1168, 1247, 1508, 1685 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 4.58 (s, 2H), 7.48-7.63 (m, 3H), 7.87-8.07 (m, 3H), 8.63 (d, J = 8.2 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 33.94, 124.03, 125.43, 126.56, 128.26, 128.36, 128.47, 130.34, 131.91, 133.70, 194.02; Mass: *m/z*: 250, 248,155, 141, 127, 115, 95, 77, 63, 42; Anal. Calcd. for $C_{12}H_9BrO$: C, 57.86; H, 3.64. Found: C, 57.82; H, 3.61%.

2-Bromocyclohexanone, 9h. Yield: 77%; IR (neat): 1176,1340, 1452, 1717 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.73-2.05 (m, 4H), 2.20-2.41 (m, 3H), 2.91-3.06 (m, 1H), 4.45 (dt, J = 1.2, 6.1Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 22.00, 26.50, 36.61, 37.77, 53.44, 203.05; Mass: *m/z*: 180, 176,132, 97, 82, 69, 55, 41; Anal. Calcd. for C_6H_9BrO: C, 40.71; H, 5.12. Found: C, 40.74; H, 5.09%.

2-Bromo-2-methylcyclohexanone, 9i. Yield: 81%; IR (neat): 1132, 1340, 1452, 1723 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.56-1.86 (m, 3H), 1.82 (s, 3H), 1.99-2.15 (m, 2H), 2.29-2.45 (m, 2H), 3.13-3.31 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 22.14, 26.69, 27.92, 36.53, 43.41, 65.71, 204.46; Anal. Calcd. for $C_7H_{11}BrO$: C, 44.00; H, 5.80. Found: C, 44.05; H, 5.82%.

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