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# A simple, mild, and efficient method for the preparation of α,α-dichloroketones with DCDMH catalyzed by ammonium chloride

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ABSTRACT

New process that can selectively prepare α,α-dichloro ketones from various ketones with 1,3-dichloro-5,5-dimethylhydantoin (DCDMH) using ammonium chloride as a catalyst is reported. The effects of ammonium salts, solvents, DCDMH, and reaction temperature were investigated. Under the optimal condition, most of α,α-dichlorinated products were selectively obtained in 86–98% yield.



## 1. Introduction

Chlorinated organic compounds are highly versatile starting materials and intermediates in organic and organometallic chemistry and their production has been under constant investigation.[1,2] In particular, α,α-dichloroketones have received much attention because they are important intermediates for the synthesis of heterocycles,[3,4] unsaturated acids, and ynols,[5] and also useful in cyclopropanation reactions.[6,7] Main preparative methods for the synthesis of α,α-dichloroketones are the Lewis acid-catalyzed acylation of arenes with dichloroacetyl chloride,[8] and oxyhalogenation of alkynes.[9–11] Several approaches have been described for preparation α,α-dichloroketones from chlorination of ketones,[12] employing compounds, such as molecular chlorine,[13] thionyl chloride,[14,15] sulfuryl chloride,[16] copper(II) chloride,[17] benzyltrimethylammonium tetrachloroiodate,[18] *N*-chlorosuccinimide (NCS),[19,20] or $H_2O_2$–HCl.[21] However, most of the studies are limited to the preparation of α,α-dichloroketones and they also suffer for one or more disadvantages, such as high temperature, poor yields and selectivity, use of hazardous reagents, work up procedures, cost of metallic or strongly acids as catalyst. Hence, studies for the development of more safer, 'greener' and efficient method for chlorination of ketones into α,α-dichloroketones at reduced cost are highly desirable.

1,3-Dichloro-5,5-dimethylhydantoin (DCDMH) is disinfecting agent and bleaching agent that has been extensively employed in industrial and domestic water and fruit storage.[22] Application of DCDMH in chlorination of ketones to prepare α-monochloroketones have been reported[23,24] and α,α-dichloroketones were always found trace as by-products in the system.[23]

Ammonium salts have been extensively applied as fertilizers in agricultural production with low-price, which could be used to substitute metallic or strongly acidic as neutral catalysts. Das et al. had been reported the deprotection of aromatic acetates using $NH_4OAc$ as a catalyst.[25] Tanemura et al. reported α-monobrominations of various cyclic ketones using NBS catalyzed by ammonium salt in good yields.[26]

Herein, we report a simple, mild, and efficient method for the preparation of α,α-dichloroketones in good yields by the reaction of various ketones with 1,3-dichloro-5,5-dimethylhydantoin (DCDMH) in the presence of ammonium salts as catalysts in acetonitrile.

## 2. Results and discussion

In the preliminary experiments, our initial objective was identified are appropriate catalyst for regioselective α,α-dichloroketones with DCDMH. For this propose, acetophenone **1a** was chose as a molder for the reaction with 1.5 equiv DCDMH in acetonitrile catalyzed by various ammonium salts and the results are presented in Table 1 (entries 1–9). In the above study, best results were observed with ammonium halides. For example, using $NH_4Cl$

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**Table 1**
Effects of various catalysts and solvents on dichlorination of acetophenone **1a** with DCDMH[a]

| Entry | Ammonium salt | Solvent | Selectivity (**3a**/**4a**/**1a**)[b] |
|---|---|---|---|
| 1 | $NH_4Cl$ | $CH_3CN$ | 97/3/0 |
| 2 | $NH_4Br$ | $CH_3CN$ | 89/4/0[c] |
| 3 | $NH_4NO_2$ | $CH_3CN$ | 79/21/0 |
| 4 | $(NH_4)_2SO_4$ | $CH_3CN$ | 70/30/0 |
| 5 | $(NH_4)_2CO_3$ | $CH_3CN$ | 3.5/0.6/95.9 |
| 6 | $(COONH_4)_2$ | $CH_3CN$ | 1.6/0.4/98 |
| 7 | $(NH_4)_2HPO_4$ | $CH_3CN$ | 3/1/96 |
| 8 | $(NH_4)_3PO_4$ | $CH_3CN$ | — |
| 9 | $NH_4OAc$ | $CH_3CN$ | — |
| 10 | $NH_4Cl$ | THF | 9/80/11 |
| 11 | $NH_4Cl$ | $Et_2O$ | 8/76/16 |
| 12 | $NH_4Cl$ | $CH_2Cl_2$ | 3/22/75 |
| 13 | $NH_4Cl$ | $CH_3OH$ | 40/60/0 |

[a] The reaction was performed with 5 mmol of acetophenone (**1a**), 7.5 mmol of DCDMH, 2.5 mmol of ammonium salt, 10 mL of solvent at room temperature for 16 h.
[b] The ratio of **3a**/**4a**/**1a** determined by GC.
[c] 7% of 2-bromo-1-phenylethanone was observed.

as catalyst, the selectivity of **3a** could reach 97:3 (entry 1, Table 1); when $NH_4Br$ was used, the selectivity of **3a** was 89:4 (entry 2, Table 1), however, 7% of 2-bromo-1-phenylethanone as by-product was observed. When the salts of weak acid, such as $(NH_4)_3PO_4$, $NH_4OAc$ were used, the chlorination did not proceed that might be attributed to their property.[26]

The effects of different solvents on the selectivity of dichlorination of acetophenone **1a** were also examined, and the results were summarized in Table 1 (entries 10–13). When tetrahydrofuran (THF), $Et_2O$, were used as solvent, the reaction completed within 1 h to give a mixture of α-chloroacetophenone and α,α-dichloroacetophenone (**3a**) and the ratio determined by GC were 80:9 and 76:8 (entries 10 and 11, Table 1); prolonged the reaction time to 16 h, the selectivity of **3a** was not improved at all. When methanol was used as a solvent, moderate selectivity was observed (entry 13, Table 1). In this study, we found that acetonitrile is the best solvent (entry 1, Table 1) for maximum selectivity of the desired product **3a** (97:3) at room temperature.

Next, the effect of $NH_4Cl$ on the dichlorination of acetophenone **1a** was investigated (entries 1–6, Table 2). In this system, when 1.5 mmol of $NH_4Cl$ was used, **3a** was obtained with only 32% yield (entry 2, Table 2), whereas 2.5 mmol of $NH_4Cl$ resulted in an increase of the yield of **3a** to 95% (entry 4, Table 2). It seems that the larger amount of $NH_4Cl$ added to the reaction system was not so helpful to the process (entries 5 and 6, Table 2). When the process was without $NH_4Cl$ at room temperature, the chlorination that was determined by GC could not take place any more (entry 1, Table 2).

**Table 2**
Effects of $NH_4Cl$ and DCDMH on dichlorination of acetophenone **1a** with DCDMH[a]

| Entry | $NH_4Cl$ (mmol) | DCDMH (mmol) | Isolated yield (%) |
|---|---|---|---|
| 1 | 0 | 7.5 (1.5 equiv) | 0 |
| 2 | 1.5 (0.3 equiv) | 7.5 (1.5 equiv) | 32 |
| 3 | 2.0 (0.4 equiv) | 7.5 (1.5 equiv) | 74 |
| 4 | 2.5 (0.5 equiv) | 7.5 (1.5 equiv) | 95 |
| 5 | 3.0 (0.6 equiv) | 7.5 (1.5 equiv) | 96 |
| 6 | 4.0 (0.8 equiv) | 7.5 (1.5 equiv) | 96 |
| 7 | 2.5 (0.5 equiv) | 5.0 (1.0 equiv) | 80 |
| 8 | 2.5 (0.5 equiv) | 5.5 (1.1 equiv) | 85 |
| 9 | 2.5 (0.5 equiv) | 6.5 (1.3 equiv) | 91 |
| 10 | 2.5 (0.5 equiv) | 8.5 (1.7 equiv) | 92 |
| 11 | 2.5 (0.5 equiv) | 12.5 (2.5 equiv, NCS) | 62[b] |

[a] The reaction was performed with 5 mmol of acetophenone (**1a**), 10 mL of acetonitrile at room temperature for 16 h.
[b] 12.5 mmol of NCS was added, α,α-dichloroacetophenone (**3a**) and α-chloroacetophenone were obtained with 62% and 38% yields, respectively, after 24 h.

So we thought $NH_4Cl$ as the catalyst was necessary and helpful for selectivity.

The effect of DCDMH on the dichlorination of acetophenone **1a** was also investigated. When 5.0 mmol (1.0 equiv) of DCDMH was added to the reaction mixture, **3a** and monochlorination product were obtained with 80% and 20% yields (entry 7, Table 2), respectively. Increased the amount of DCDMH to 7.5 mmol (1.5 equiv) could result in an increase of the yield of **3a** to 95% (entry 4, Table 2). When larger amount of DCDMH was added to the reaction system, more by-products were occurred (entry 9, Table 2). When NCS was used, α,α-dichloroacetophenone (**3a**) and α-chloroacetophenone were obtained with 62% and 38%, respectively.

Temperature also affects the reaction (Table 3). Higher temperature resulted lower yields of **3a**; it may contribute to the volatility of molecular chlorine. So, the optimum temperature is 35 °C to obtain highest yields of desired products within a short period of time (entry 2, Table 3).

**Table 3**
Effect of temperature on the dichlorination of acetophenone **1a** using $NH_4Cl$ as catalyst[a]

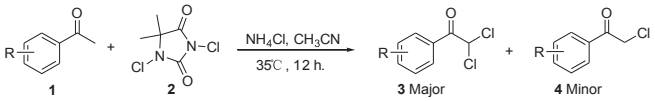
| Entry | Temperature (°C) | Time (h) | Isolated yield (%) |
|---|---|---|---|
| 1 | rt | 16 | 95 |
| 2 | 35 | 12 | 95 |
| 3 | 45 | 10 | 95 |
| 4 | 55 | 10 | 92 |
| 5 | Reflux | 8 | 91 |

[a] The reaction was performed with 5 mmol of acetophenone (**1a**), 7.5 mmol of DCDMH, 2.5 mmol of $NH_4Cl$, 10 mL of acetonitrile.

The optimal reaction condition for yield generation requires 5 mmol of **1a**, 7.5 mmol of DCDMH, 2.5 mmol of $NH_4Cl$, and 10 mL of acetonitrile at 35 °C for 12 h. To examine the scope of this protocol, the optimized conditions were then applied to the synthesis of a variety of substituted acetophenone, ethyl acetoacetate, diethyl malonate, propiophenone, and 3,3-dimethylbutanone. The results are listed in Table 4. Most of the substrates could be converted to the dichloro products in good yields. When **1b** with an electron-donating group on the benzene ring and **1d** to **1f**, with a halogen atom were investigated, **3b**, **3d**–**f** were obtained with 94–98% yields (entries 2 and 4–6, Table 4). However, when **1c** with a strong electron-donating group was used as substrate, 2, 2-dichloro-1-(3-chloro-4-methoxyphenyl)ethanone was found with the product **3c**, and the ratio of these two compounds determined by GC was 5:1 (entry 3, Table 4). Transformation of **1g**–**i** with strong electron-withdrawing groups to the dichloro products had been also accomplished with 91%, 86%, and 90% yields (entries 7–9, Table 4), respectively. When the same process was used to prepare **3j** and **3k** from the low solubility of **1j** and **1k** with bulky groups on the benzene ring, the volume of solvent must increased from 10 mL to 50 mL, the yields could reach 92% and 93% (entries 10 and 11, Table 4), respectively. Furthermore, the yield of the tested ethyl acetoacetate (**1l**) were 98% (entry 12, Table 4), which result may contribute to the relative stability of the enol form of **1l**. However, the yield diethyl malonate (**1m**) and propiophenone (**1n**) was not desirable (entries 13 and 14, Table 4) in the proposed system, monochloroproducts (**4m**, **4n**) were obtained as the main products and the isolation yields were 58% and 93%, which were similar to the result of a previous report.[27] In the case of aliphatic ketone **1o**, α,α-dichloropinacolone **3o** as a pure and white solid was obtained in 92% yield.

Samant et al.[28] suggested the mechanism of keto–enol tautomerism in the process of the bromination of substituted acetophenones using NBS and we thought the mechanism of our processes was possibly similar to the one that Samantet et al.

**Table 4**
α-Chlorinations of ketones with DCDMH catalyzed by ammonium chloride[a]




| Entry | Substrate | Product | Isolated yield (%) |
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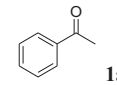
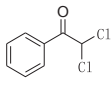
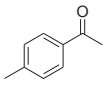
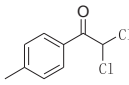
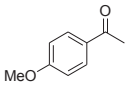
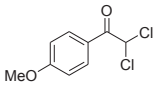
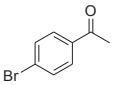
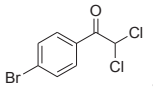
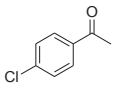
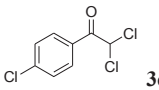
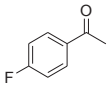
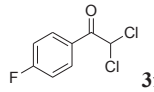
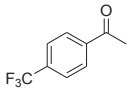
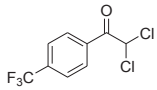
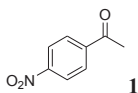
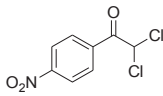
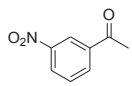
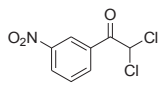
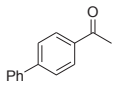
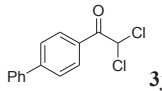
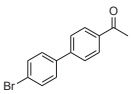
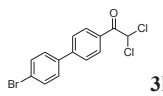
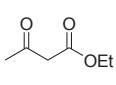
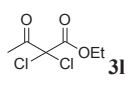
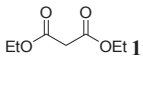
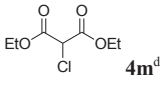
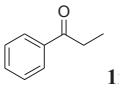
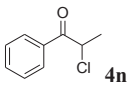
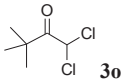
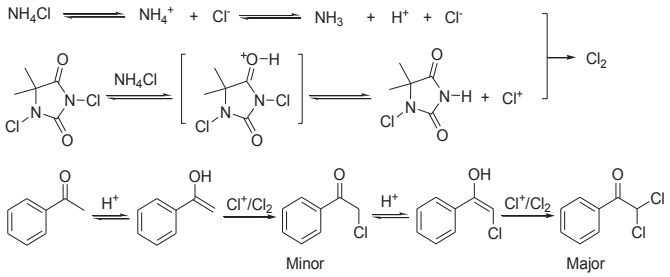
| 1 |  1a |  3a | 95 |
| 2 |  1b |  3b | 98 |
| 3 |  1c |  3c | —[b] |
| 4 |  1d |  3d | 95 |
| 5 |  1e |  3e | 98 |
| 6 |  1f |  3f | 94 |
| 7 |  1g |  3g | 91 |
| 8 |  1h |  3h | 86 |
| 9 |  1i |  3i | 90 |
| 10 |  1j |  3j[c] | 92 |
| 11 |  1k |  3k[c] | 93 |
| 12 |  1l |  3l | 98 |
| 13 |  1m |  4m[d] | 58 |
| 14 |  1n |  4n | 93 |

**Table 4** (*continued*)

| Entry | Substrate | Product | Isolated yield (%) |
|---|---|---|---|
| 15 |  1o |  3o | 92 |

[a]The reaction was performed with 5 mmol of ketone, 7.5 mmol of DCDMH, 2.5 mmol of $NH_4Cl$, 10.0 mL of acetonitrile at 35 °C for 12 h.
[b]A mixture of 2, 2-dichloro-1-(3-chloro-4-methoxy)ethanone and (**3e**) was obtained and the ratio determined by GC was 5:1.
[c]50.0 mL of acetonitrile was added.
[d]Diethyl 2-chloromalonate (**4m**) was obtained as the major product.

mentioned. Analogously, DCDMH may undergo protonation at the carbon oxygen resulting in the generation of chlorination in the presence of $NH_4Cl$. Since $NH_4Cl$ is a salt, which consists of a strong acid and a weak base, the behavior of $NH_4Cl$ in acetonitrile may be dissociated into $NH_4^+$ and $Cl^-$, and proton transfer from $NH_4^+$ affords $H^+$.[26] So the presence of $NH_4Cl$ was helpful to the generation of $Cl^+$ and keto–enol tautomerism. On the other hand, $Cl^+$, which was emitted from DCDMH could react with $Cl^-$ from $NH_4Cl$ for generation of trace molecular chlorine. This may result in the higher activity of $NH_4Cl$ than others (Scheme 1).




**Scheme 1.**

## 3. Conclusion

Using $NH_4Cl$ as a catalyst, various ketones were successfully dichlorinated by DCDMH at mild conditions with high selectivity for α,α-dichlorination. The new process has many advantages, such as the low price of the raw materials and catalyst, the wide range of substrates, the ease and safety of the operation, and high selectivity obtained, among others, thus confirming its value.

## 4. Experimental

### 4.1. General

All required chemicals were used directly without purification unless mentioned. Melting points (mp) were recorded on a Yanano MP500 apparatus and are uncorrected. $^1H$ NMR spectra were recorded on a Varian INOVA-500 (500 MHz) spectrometer with $CDCl_3$ as the solvent and TMS as the internal standard. Capillary GC was performed on GC2014 with a RTX-1 (Restek, ø 0.25 mm–30 m) column (Inj. 250 °C, Det. 250 °C). Analytical thin-layer chromatography (TLC) was carried out on precoated plates (silica gel 60 $F_{254}$), and spots were visualized with ultraviolet (UV) light. Flash column chromatography was carried out with silica gel (300–350 mesh).

### 4.2. General procedure for preparation of α,α-dichloroacetophenone

A mixture of 2.5 mmol of $NH_4Cl$, 5.0 mmol of substrate, and 10.0 mL of acetonitrile was stirred for 5 min, and then 7.5 mmol of

DCDMH was added by five times in 1 h, and the mixture was stirred 12 h at 35 °C. Afterward, solvent was distilled under reduced pressure; 20 mL of ethyl acetate was added to the residue. Next, the ethyl acetate layer was washed twice with water (20 mL), and dried over anhydrous $Na_2SO_4$. After filtration, the solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate=20/1, v/v) to give the product.

*4.2.1. 2, 2-Dichloro-1-phenylethanone (**3a**).*[19] Yield: 95%; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 6.69 (s, 1H, $CHCl_2$), 7.52–7.53 (m, 2H, ArH), 7.64–7.66 (m, 1H, ArH), 8.08–8.10 (m, 2H, ArH); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 67.7, 128.8, 129.6, 131.2, 134.3, 185.5.

*4.2.2. 2, 2-Dichloro-1-(4-methylphenyl)ethanone (**3b**).*[29] Yield: 98%; white solid; mp: 52–54 °C (Lit.: 54–56 °C); $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 2.39 (s, 3H, $CH_3$), 6.68 (s, 2H, $CHCl_2$), 7.20 (d, $J$=8.1 Hz, 2H, ArH), 7.94 (d, $J$=8.1 Hz, 2H, ArH); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 22.0, 67.7, 128.7, 129.1, 131.7, 145.3, 184.9.

*4.2.3. 2, 2-Dichloro-1-(4-methoxyphenyl)ethanone (**3c**).*[19] Yield: 14%; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 3.80 (s, 3H, $OCH_3$), 6.67 (s, 2H, $CHCl_2$), 6.97 (d, $J$=8.2 Hz, 2H, ArH), 7.85 (d, $J$=8.1 Hz, 2H, ArH); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 55.4, 67.7, 114.0, 123.7, 131.9, 164.4, 184.2.

*4.2.4. 2, 2-Dichloro-1-(3-chloro-4-methoxyphenyl)ethanone.*[19-] Yield: 76%; white solid; mp: 99–101 °C (Lit.: 99.8–100.9 °C); $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 4.00 (s, 3H, $OCH_3$), 6.57 (s, 1H, $CHCl_2$), 7.02 (d, $J$=8.8 Hz, 1H, ArH), 8.05 (dd, $J$=8.8 Hz, $J$=2.3 Hz, 1H, ArH), 8.14 (d, $J$=2.3 Hz, 1H, ArH); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 70.0, 114.3, 124.6, 127.0, 132.5, 133.1, 161.9, 185.7.

*4.2.5. 2, 2-Dichloro-1-(4-bromophenyl)ethanone (**3d**).*[21] Yield: 95%; white solid; mp: 59–61 °C (Lit.: 61–62 °C); $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 6.68 (s, 2H, $CHCl_2$), 7.60 (d, $J$=8.50 Hz, 2H, ArH), 7.88 (d, $J$=8.5 Hz, 2H, ArH). $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 67.6, 129.7, 129.9, 131.1, 133.1, 184.8.

*4.2.6. 2, 2-Dichloro-1-(4-chlorophenyl)ethanone (**3e**).*[21] Yield: 98%; white solid; mp: 56–58 °C (Lit.: 58–59 °C); $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 6.71 (s, 2H, $CHCl_2$), 7.40 (d, $J$=8.4 Hz, 2H, ArH), 7.92 (d, $J$=8.4 Hz, 2H, ArH); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 67.8, 129.2, 129.4, 131.2, 141.1, 184.6.

*4.2.7. 2, 2-Dichloro-1-(4-fluorophenyl)ethanone (**3f**).*[12] Yield: 94%; colorless oil, $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 6.58 (s, 1H, $CHCl_2$), 7.15–7.26 (m, 2H, ArH), 8.13–8.21 (m, 2H, ArH); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 67.8, 116.1, 127.4, 132.6, 166.3, 184.4.

*4.2.8. 2,2-Dichloro-1-(4-(trifluoromethyl)phenyl)ethanone (**3g**).*[9] Yield: 91%; colorless oil, $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 6.71 (s, 1H, $CHCl_2$), 7.31 (d, $J$=8.3 MHz, 2H), 7.98 (d, $J$=8.3 MHz, 2H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 67.7, 125.8, 130.1, 134.0, 135.3, 135.7, 184.1.

*4.2.9. 2, 2-Dichloro-1-(4-nitrophenyl)ethanone (**3h**).*[12] Yield: 86%; colorless oil (Lit.: 26.8–27.8 °C). $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 6.72 (s, 2H, $CHCl_2$), 8.16 (d, $J$=8.2 Hz, 2H, ArH), 8.55 (d, $J$=8.2 Hz, 2H, ArH); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 67.7, 123.8, 130.9, 135.8, 150.7, 184.3.

*4.2.10. 2, 2-Dichloro-1-(3-nitrophenyl)ethanone (**3i**).*[21] Yield: 90%; white solid; mp: 50–51 °C (Lit.: 52.5–54 °C). $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 6.73 (s, 2H, $CHCl_2$), 7.72–7.74 (m, 1H, ArH), 8.45–8.47 (m, 1H, ArH), 8.52–8.53 (m, 1H, ArH), 8.99–9.01 (m, 1H, ArH).

*4.2.11. 2,2-Dichloro-1-(biphenyl-4-yl)ethanone (**3j**).*[9] Yield: 92%; white solid; mp 86–88 °C (Lit.[2] 85–87 °C); $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 6.68 (s, 1H, $CHCl_2$), 7.50–7.41 (m, 3H, ArH), 7.64–7.61 (m, 2H, ArH), 7.72 (d, $J$=8.4 Hz, 2H, ArH), 8.17 (d, $J$=8.4 Hz, 2H, ArH); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 67.8, 127.2, 127.4, 128.6, 129.0, 130.3, 139.3, 147.2, 185.5.

*4.2.12. 2,2-Dichloro-1-(4′-bromobiphenyl-4-yl)ethanone (**3k**).* Yield: 93%; white solid; mp 144–145 °C; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 6.70 (s, 1H, $CHCl_2$), 7.52 (d, $J$=8.5 Hz, 2H, ArH), 7.64 (d, $J$=8.5 Hz, 2H, ArH), 7.72 (d, $J$=8.5 Hz, 2H, ArH), 8.20 (d, $J$=8.5 Hz, 2H, ArH); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 67.9, 123.2, 127.3, 128.9, 129.3, 130.5, 132.3, 138.3, 146.0, 185.5. Element Analysis: found: C, 48.71%; H, 2.70%. Calculated for $C_{14}H_9BrCl_2O$ (344.03): C, 48.83%; H, 2.62%.

*4.2.13. Ethyl 2, 2-dichloroacetoacetate (**3l**).*[30] Yield: 98%; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 1.30 (t, $J$=7 Hz, 3H, $CH_3$), 2.45 (s, 3H, $CH_3CO$), 4.28 (q, $J$=7 Hz, 2H, $CO_2CH_2$); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 14.0, 23.6, 64.8, 82.0, 163.5, 191.5.

*4.2.14. Diethyl 2-chloromalonate (**4m**).*[27] Yield: 58%; colorless oil; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 1.33 (t, $J$=7 Hz, 6H, $CH_3$), 4.31 (q, $J$=7 Hz, 4H, $OCH_2$), 4.85 (s, 1H, CHCl); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 13.9, 55.6, 63.2, 164.5.

*4.2.15. 2-Chloropropiophenone (**4n**).* Yield: 93%; colorless oil; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 1.76 (d, $J$=7 Hz, 3H, $CH_3$), 5.28 (q, $J$=7 Hz, 1H, CHCl), 7.49–7.53 (m, 2H, ArH), 7.60–7.63 (m, 1H, ArH), 8.02–8.04 (m, 2H, ArH); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 20.0, 55.6, 128.8, 129.0, 133.8, 134.1, 193.7.

*4.2.16. 1, 1-Dichloro-3,3-dimethylbutanone (**3o**).*[24] Yield: 92%; white solid; mp: 50–51 °C (Lit.: 50–51). $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 1.28 (s, 9H, $CH_3$), 6.45 (s, 1H, $CHCl_2$); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 26.5, 44.1, 52.8, 201.2.

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## Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2014.11.004. These data include MOL files and InChiKeys of the most important compounds described in this article.

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