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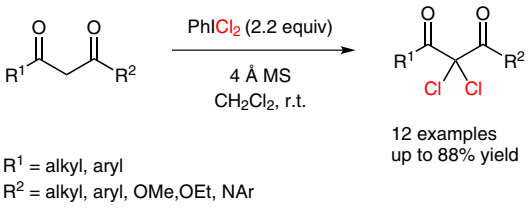
Iodobenzene Dichloride Mediated Sequential C–Cl Bond Formation: A Safe, Convenient and Efficient Method for the Direct α,α-Dichlorination of β-Dicarbonyl Compounds

Xiyan Duan*
Huiyun Zhou
Xinlei Tian
Jianwei Liu
Junying Ma*

School of Chemical Engineering & Pharmaceutics, Henan University of Science and Technology, Luoyang 471003, Henan, P. R. of China
duanxiyan@tju.edu.cn
majy379@163.com



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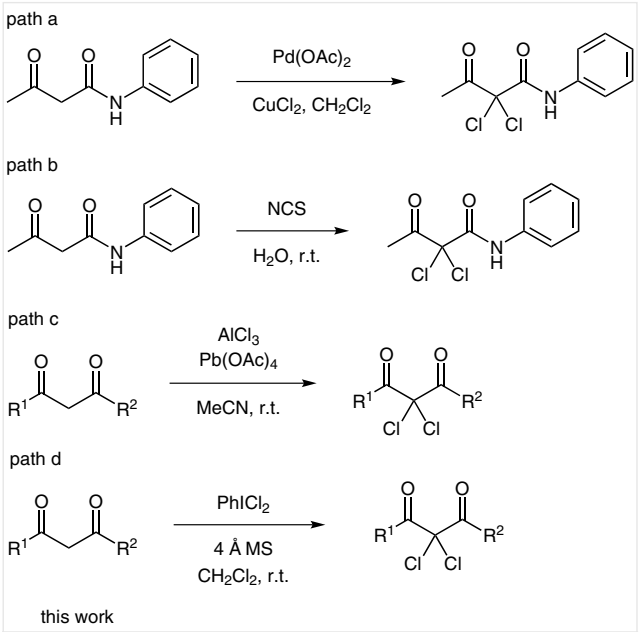
Abstract Various β-keto esters, 1,3-diketones, and β-oxo amides are directly converted into their corresponding α,α-dichloro-β-keto esters, 2,2-dichloro-1,3-diketones, and α,α-dichloro-β-oxo amides, respectively, in moderate to high yields, using iodobenzene dichloride in dichloromethane in the presence of 4 Å molecular sieves at room temperature. This process is postulated to proceed via the iodobenzene dichloride mediated sequential oxidative α-chlorination of the β-dicarbonyl substrates.

Key words iodobenzene dichloride, α,α-dichlorination, β-dicarbonyl compounds, hypervalent iodine, C–Cl bond formation

Carbon–chlorine bond formation is a valuable and fundamental transformation in organic chemistry, and has gained significant attention due to the occurrence of this type of bond in many biological and pharmaceutical molecules.[1] In particular, α,α-dichloro dicarbonyl compounds are important and valuable synthetic intermediates in organic synthesis and medicinal chemistry. For example, the antibiotic drugs, chloramphenicol[2] and fluorothiamphenicol,[3] have a wide spectrum of applications in the pharmaceutical and agrochemical industries. Existing methods for the formation of α,α-dichloro dicarbonyl compounds can be summarized as three general approaches: (1) palladium(II)-catalyzed sequential C–Cl bond formation (Scheme 1, path a);[4] (2) dichlorination of dicarbonyl compounds by reaction with *N*-chlorosuccinimide (NCS) (Scheme 1, path b);[5] (3) reaction with aluminum chloride/lead(IV) acetate [$AlCl_3$/$Pb(OAc)_2$] (Scheme 1, path c).[6] However, these methods suffer from drawbacks which include the use of hazardous reagents, harsh reaction conditions or long reaction times. In view of the cost as well as environmental concerns of employing heavy metals in chlorine substitution, the development of metal-free systems for dichlorination reactions are worthwhile.



Scheme 1 General methods for the α,α-dichlorination of β-dicarbonyl compounds

Significant advances have been made in the development of hypervalent iodine chemistry. Due to their ready availability and low toxicity in comparison with classic heavy-metal oxidants, hypervalent iodine reagents have been applied in a large number of diverse and useful chemical transformations.[7] Specifically, iodobenzene dichloride ($PhICl_2$), a hypervalent organoiodine(III) reagent of low toxicity, has been widely used as an oxidant as well as a halo-

gen source in organic reactions.[8] A literature study revealed that iodobenzene dichloride has been employed for the chlorination of alkenes, aromatic rings, allylic alcohols and ketones.[9] Herein, we report a method for the synthesis of 2,2-dichloro dicarbonyl compounds starting from β-dicarbonyl compounds, via direct dichlorination processes in the presence of iodobenzene dichloride and molecular sieves in dichloromethane at room temperature (Scheme 1, path d).

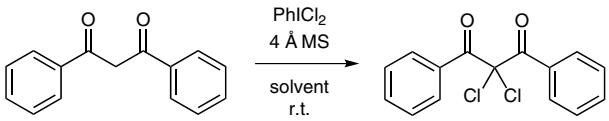
We utilized 1,3-diphenylpropane-1,3-dione (**1a**) as a model 1,3-dicarbonyl compound in order to optimize the reaction conditions. Selected data are listed in Table 1. Initially, the amount of iodobenzene dichloride was investigated. Increasing the number of equivalents of iodobenzene dichloride (from 1.2 to 2.2) resulted in complete consumption of the 1,3-dicarbonyl compound **1a** and α,α-dichloro dicarbonyl compound **2a** was obtained in 75% yield, a two-fold increase compared to the original yield (Table 1, entries 1 and 2). The addition of 4 Å molecular sieves led to an increased yield of 88% (Table 1, entry 3). Solvent-screening experiments revealed that the reaction occurred in polar as well as nonpolar solvents (Table 1, entries 3–8), but the reaction in dichloromethane gave the best yield within a relatively short period of time (Table 1, entry 3).

We next tested different additives in this system, and observed that trifluoroacetic acid (TFA) was effective, affording the desired product, 2,2-dichloro-1,3-diphenylpropane-1,3-dione (**2a**), in 83% yield (Table 1, entry 9). When acetic acid (AcOH) or trimethylsilyl trifluoromethanesulfonate (TMSOTf) were used, the desired product **2a** was obtained in moderate yields (Table 1, entries 10 and 11). In the presence of sodium *tert*-butoxide (*t*-BuONa), the reaction proceeded smoothly to afford **2a** in 78% yield (Table 1, entry 12). An examination of other bases as additives revealed that 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and potassium carbonate (K_2CO_3) gave decreased yields of **2a** (Table 1, entries 13 and 14).

Our investigations of the reaction conditions revealed that C–Cl bond formation took place in the absence of additives (acid or base). We assume this is due to the fact that β-dicarbonyl compounds, especially β-diketones, exist in solution as a mixture of keto and enol tautomers.[10] ^{1}H NMR spectroscopic analysis showed that substrates **1e** and **1f** (in $CDCl_3$) exist in the enol form (see the Supporting Information).

Under the optimum conditions (Table 1, entry 3), various 1,3-dicarbonyl compounds were examined to probe the scope and generality of this method, and the results are given in Table 2. The dichlorination of the β-keto esters, methyl 3-oxo-3-phenylpropanoate (**1b**) and ethyl 3-oxo-3-phenylpropanoate (**1c**), gave the dichlorinated products **2b** and **2c** in 77% and 70% yields, respectively (Table 2, entries 2 and 3). Substrate **1d** with an electron-donating group at the *para* position of the benzene moiety afforded the corresponding dichlorinated product **2d** in 60% yield (Table 2, entry 4). Replacing the ester group in **1d** with a keto carbonyl group (substrate **1e**) gave the corresponding α,α-dichloro dicarbonyl product **2e** in 48% yield. The use of **1d** and **1e** substrates bearing electron-donating groups at the *para* position of the benzene moiety gave reduced yields. Dicarbonyl compound **1f**, without an electron-donating group at the *para* position of the benzene ring, gave a higher yield (72%) of the corresponding product **2f**. Next, various β-oxo-*N*-amides (**1g**–**l**) were converted into the corresponding products **2g**–**l** in yields of 70–86% (Table 2, entries 7–12). The reaction conditions appeared to be quite tolerant of 3-oxo-*N*-amides with respect to the electronic nature of the substituents (electron-withdrawing or electron-donating groups) and their position on the aryl ring. Next, several simple substituted ketones were evaluated by applying the optimized conditions, however, no reactions occurred in these cases (Table 3, entries 1–4).

Table 1 Optimization of the Reaction Conditions for the Conversion of β-Dicarbonyl Compound **1a** into α,α-Dichloro Dicarbonyl Product **2a**[a]

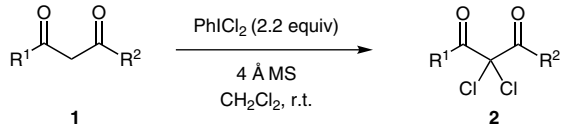


1a **2a**

Entry	$PhICl_2$ (equiv)	Additive	Solvent	Time (h)	Yield (%)[b]
1[c]	1.2	–	CH_2Cl_2	0.5	33
2[c]	2.2	–	CH_2Cl_2	0.25	75
3	2.2	–	CH_2Cl_2	0.25	88
4	2.2	–	DCE	0.25	72
5	2.2	–	MeCN	2	82
6	2.2	–	THF	3	33
7	2.2	–	1,4-dioxane	2	78
8	2.2	–	EtOH	3	59
9[d]	2.2	TFA	CH_2Cl_2	3	83
10[d]	2.2	AcOH	CH_2Cl_2	3	55
11[d]	2.2	TMSOTf	CH_2Cl_2	3	70
12[d]	2.2	*t*-BuONa	CH_2Cl_2	3	78
13[d]	2.2	DBU	CH_2Cl_2	3	35
14[d]	2.2	K_2CO_3	CH_2Cl_2	3	39

[a] Reaction conditions: **1a** (1 mmol), $PhICl_2$ (2.2 mmol), 4 Å MS (50 mg), CH_2Cl_2 (2 mL), r.t.
[b] Yield of isolated product.
[c] The reaction was carried out in the absence of molecular sieves.
[d] Reaction conditions: **1a** (1 mmol), $PhICl_2$ (2.2 mmol), 4 Å MS (50 mg), additive (1.0 equiv), CH_2Cl_2 (2 mL), r.t.

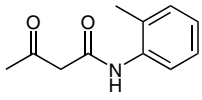
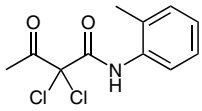
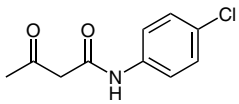
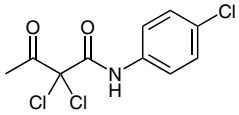
Table 2 Investigation of the Scope of the Procedure[a]



1 **2**

Entry	Substrate	Product	Time (min)	Yield (%)[b]
1	**1a**	**2a**	15	88
2	**1b**	**2b**	20	77
3	**1c**	**2c**	15	70
4	**1d**	**2d**	15	60
5	**1e**	**2e**	30	48
6	**1f**	**2f**	30	72
7	**1g**	**2g**	30	86
8	**1h**	**2h**	20	70
9	**1i**	**2i**	30	74
10	**1j**	**2j**	30	72

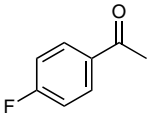
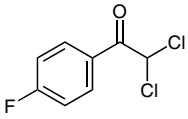
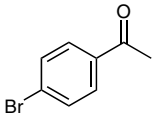
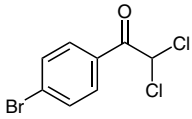
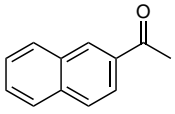
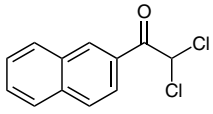
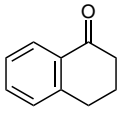
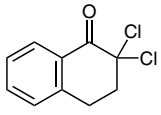
Table 2 (continued)

Entry	Substrate	Product	Time (min)	Yield (%)[b]
11	**1k**	 **2k**		25	63
12	**1l**	 **2l**		30	83

[a] Reaction conditions: **1** (1 mmol), $PhICl_2$ (2.2 mmol), 4 Å MS (50 mg), CH_2Cl_2 (2 mL), r.t.
[b] Yield of isolated product.

Table 3 Attempted Direct α,α-Dichlorination of Simple Ketones Using Iodobenzene Dichloride

3 **4**

Entry	Substrate	Product	Yield (%)
1	**3a** 	**4a** 	0
2	**3b** 	**4b** 	0
3	**3c** 	**4c** 	0
4	**3d** 	**4d** 	0

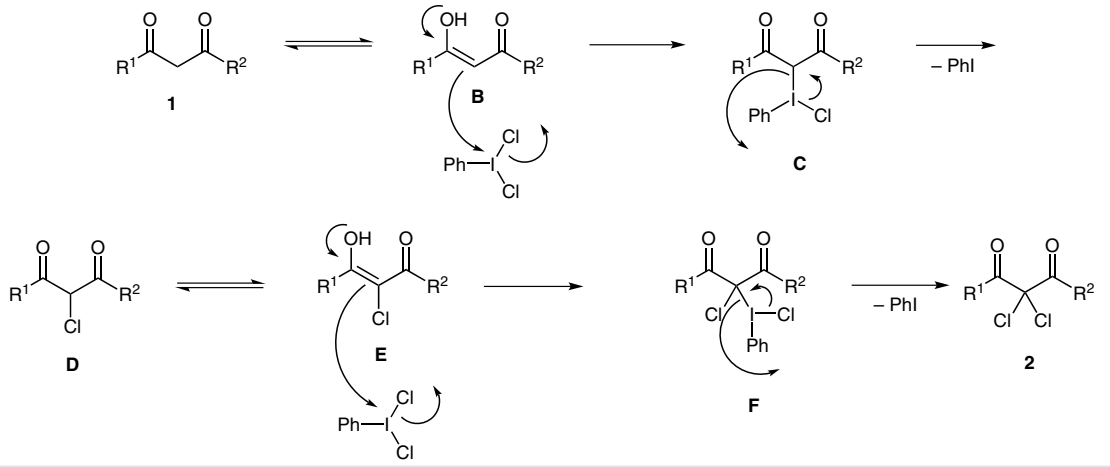
A possible mechanistic pathway is outlined in Scheme 2. Initially, the 1,3-dicarbonyl compound **1** tautomerizes into its enol isomer **B**, which reacts with iodobenzene dichloride to give α-iodo-1,3-dicarbonyl intermediate **C**. The reductive removal of iodobenzene from **C** affords α-chloro-1,3-dicarbonyl intermediate **D**, which tautomerizes into its enol isomer **E**. Further reaction with a second molecule of iodobenzene dichloride and elimination of iodobenzene occurs via the same sequence as described above, to give the dichlorinated products **2**.

In conclusion, we have reported a simple and mild method for the synthesis of α,α-dichloro-β-dicarbonyl compounds via the reactions between various β-dicarbonyl compounds and iodobenzene dichloride in dichloromethane. The advantages of the described method include the ready availability of the starting materials, the mild reaction conditions, and economic application to the synthesis of α,α-dichloro-β-dicarbonyl compounds. Further studies on the application of this method to other more valuable compounds, and detailed investigations of the reaction mechanism are in progress.

Commercially available, analytical grade reagents and solvents were used as received. Solvents were purified and dried according to known procedures. Flash column chromatography was performed over silica gel (200–300 mesh; Qingdao Haiyang Chemical Co., Ltd) using EtOAc–PE as the eluent. Petroleum ether (PE) refers to the fraction boiling in the 60–90 °C range. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise stated. Melting points were determined with a micromelting point apparatus and are not corrected. IR spectra were obtained using a Bio-Rad FTS 6000 Fourier infrared spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 400 MHz spectrometer using $CDCl_3$ as the solvent. The signals were internally referenced to the residual non-deuterated solvent signal at 7.26 ppm (^{1}H NMR), and that at 77.16 ppm (^{13}C NMR). Standard abbreviations are used to define the multiplicities. High-resolution mass spectra (HRMS) were obtained using an FTICR-MS (Ionspec 7.0T) spectrometer.

Dichlorination; General Procedure

To a solution of $PhICl_2$ (2.2 mmol) in anhydrous CH_2Cl_2 (1 mL) was added 4 Å MS (50 mg) and the mixture was stirred at r.t. for ca. 15 min. Next, a solution of 1,3-dicarbonyl compound **1** (1 mmol) in CH_2Cl_2 (1 mL) was added dropwise and the mixture was stirred at r.t. until TLC indicated that consumption of the 1,3-dicarbonyl compound was complete. The reaction mixture was quenched with sat. aq $NaHCO_3$ solution and extracted with CH_2Cl_2 (3 × 10 mL). The combined or-



Scheme 2 Proposed mechanistic pathway

ganic phase was dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the desired product.

2,2-Dichloro-1,3-diphenylpropane-1,3-dione (2a)[11]

Yield: 257 mg (88%); white solid; mp 59–61 °C (Lit.[11] 58–59 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98–7.96 (m, 4 H, ArH), 7.55–7.53 (m, 2 H, ArH), 7.41–7.37 (m, 4 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 185.46, 134.39, 131.55, 130.59, 128.81, 87.67.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{11}Cl_2O_2$: 293.0136; found: 293.0132.

Methyl 2,2-Dichloro-3-oxo-3-phenylpropanoate (2b)[12]

Yield: 257 mg (77%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04–8.02 (m, 2 H, ArH), 7.63–7.61 (m, 1 H, ArH), 7.49–7.45 (m, 2 H, ArH), 3.85 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 183.36, 164.74, 134.41, 130.75, 130.23, 128.82, 81.78, 55.13.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{10}H_9Cl_2O_3$: 246.9929; found: 246.9918.

Ethyl 2,2-Dichloro-3-oxo-3-phenylpropanoate (2c)[13]

Yield: 182 mg (70%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 8.0 Hz, 2 H, ArH), 7.61 (t, *J* = 7.2 Hz, 1 H, ArH), 7.47 (t, *J* = 8.0 Hz, 2H, ArH), 4.31 (q, *J* = 7.2 Hz, 2 H), 1.17 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 183.35, 164.18, 134.34, 131.00, 130.21, 128.79, 82.05, 64.81, 13.69.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{11}Cl_2O_3$: 261.0085; found: 261.0080.

Methyl 2,2-Dichloro-3-(4-methoxyphenyl)-3-oxopropionate (2d)[14]

Yield: 156 mg (60%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 9.2 Hz, 2 H, ArH), 6.94 (d, *J* = 9.2 Hz, 2 H, ArH), 3.88 (s, 3 H), 3.86 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.10, 165.03, 164.49, 132.92, 123.23, 114.13, 82.03, 55.77, 55.13.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{11}Cl_2O_4$: 277.0034; found: 277.0030.

2,2-Dichloro-1-(4-methoxyphenyl)hexane-1,3-dione (2e)

Yield: 138 mg (48%); colorless oil.

IR (neat): 3078, 2968, 2936, 2843, 1746, 1725, 1669, 1599, 1573, 1512, 1259, 1177, 1123, 1028, 854, 609 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 9.2 Hz, 2 H, ArH), 6.93 (d, *J* = 8.8 Hz, 2 H, ArH), 3.87 (s, 3 H), 2.67 (t, *J* = 7.2 Hz, 2 H), 1.74–1.63 (m, 2 H), 0.90 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.09, 184.35, 164.58, 133.26, 123.64, 114.07, 87.30, 55.74, 39.34, 18.11, 13.52.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{15}Cl_2O_3$: 289.0398; found: 289.0388.

2,2-Dichloro-1-phenylhexane-1,3-dione (2f)

Yield: 186 mg (72%); colorless oil.

IR (neat): 3063, 2968, 2935, 2877, 1746, 1708, 1681, 1596, 1580, 1230, 1186, 1126, 689 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.0 Hz, 2 H, ArH), 7.62–7.57 (m, 1 H, ArH), 7.49–7.46 (m, 2 H, ArH), 2.71 (t, *J* = 7.2 Hz, 2 H), 1.70 (m, 2 H), 0.91 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.08, 185.90, 134.50, 131.17, 130.63, 128.76, 86.91, 39.24, 18.02, 13.49.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{12}H_{16}Cl_2O_2N$: 276.0558; found: 276.0553.

2,2-Dichloro-3-oxo-*N*-phenylbutanamide (2g)[5]

Yield: 210 mg (86%); white solid; mp 41–42 °C (Lit.[5] 41–42 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (s, 1 H), 7.55 (d, *J* = 7.6 Hz, 2 H, ArH), 7.38 (t, *J* = 7.6 Hz, 2 H, ArH), 7.22 (t, *J* = 7.2 Hz, 1 H, ArH), 2.54 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.82, 160.98, 136.09, 129.38, 126.09, 120.41, 83.29, 24.59.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{10}H_{10}Cl_2NO_2$: 246.0089; found: 246.0087.

2,2-Dichloro-*N*-(4-ethoxyphenyl)-3-oxobutanamide (2h)[4]

Yield: 202 mg (70%); white solid; mp 52–55 °C..

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.34 (s, 1 H), 7.44 (d, *J* = 8.8 Hz, 2 H, ArH), 6.88 (t, *J* = 8.8 Hz, 2 H, ArH), 4.01 (q, *J* = 7.2, Hz, 2 H), 2.52 (s, 3 H), 1.40 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.83, 160.87, 157.03, 128.89, 122.24, 115.01, 83.35, 63.83, 24.55, 14.87.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{14}Cl_2NO_3$: 290.0351; found: 290.0351.

2,2-Dichloro-*N*-(2-methoxyphenyl)-3-oxobutanamide (2i)[4]

Yield: 203 mg (74%); white solid; mp 45–46 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.17 (s, 1 H), 8.27 (dd, *J* = 8.0, 1.2 Hz, 1 H, ArH), 7.17–7.13 (m, 1 H, ArH), 7.01–6.97 (m, 1 H, ArH), 6.93 (dd, *J* = 8.0, 0.8 Hz, 1 H, ArH), 3.94 (s, 3 H), 2.53 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.56, 160.58, 148.65, 126.04, 125.67, 121.25, 119.72, 110.35, 83.66, 56.11, 24.45.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{12}Cl_2NO_3$: 276.0194; found: 276.0192.

2,2-Dichloro-*N*-(4-methoxyphenyl)-3-oxobutanamide (2j)[5]

Yield: 198 mg (72%); white solid; mp 43–45 °C (Lit.[5] 42–44 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (s, 1 H), 7.44 (d, *J* = 9.2 Hz, 2 H, ArH), 6.88 (d, *J* = 8.8 Hz, 2 H, ArH), 3.79 (s, 3 H), 2.51 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.81, 160.94, 157.65, 129.06, 122.33, 114.42, 83.33, 55.58, 24.48.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{12}Cl_2NO_3$: 276.0194; found: 276.0192.

2,2-Dichloro-3-oxo-*N*-(*o*-tolyl)butanamide (2k)[5]

Yield: 163 mg (63%); white solid; mp 61–63 °C (Lit.[5] 62–65 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (s, 1 H), 7.71 (d, *J* =8.4 Hz, 1 H, ArH), 7.23–7.19 (m, 3 H, ArH), 2.56 (s, 3 H), 2.29 (s, 3 H).

2,2-Dichloro-*N*-(4-chlorophenyl)-3-oxobutanamide (2l)[4]

Yield: 231 mg (83%); white solid; mp 62–64 °C (Lit.[15] 62–63 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (s, 1 H), 7.50 (d, *J* = 8.8 Hz, 2 H, ArH), 7.33 (d, *J* = 8.8 Hz, 2 H, ArH), 2.54 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.98, 161.05, 134.71, 131.30, 129.43, 121.79, 83.10, 24.55.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{10}H_9Cl_3NO_2$: 279.9699; found: 279.9698.

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Supporting Information

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