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Visible-Light-Induced Difunctionalization of the C-C Bond of Alkylidenecyclopropanes with Acyl Chlorides

Chuan Ding †, Peng-Fei Huang †, Biquan Xiong, Ke-Wen Tang * and Yu Liu *

Department of Chemistry and Chemical Engineering, Hunan Institute of Science and Technology, Yueyang 414006, China; pengfeihuang@whu.edu.cn (P.-F.H.)
* Correspondence: tangkewen@sina.com (K.-W.T.); 12015015@hnist.edu.cn (Y.L.)
† These authors contributed equally to this work.

Abstract: A new and powerful visible-light-induced difunctionalization of the C-C σ-bond of alkylidenecyclopropanes via a ring-opening process was developed. Importantly, acyl chlorides are used as both acyl and Cl sources. This strategy provides an effective route for the difunctionalization of the C-C bond with an acyl radical and Cl^- to construct a new C-C bond and a C-Cl bond in one pot. In addition, it has a wide range of substrates and can tolerate various functional groups.

Keywords: difunctionalization; photocatalysis; ring opening; acyl chlorides

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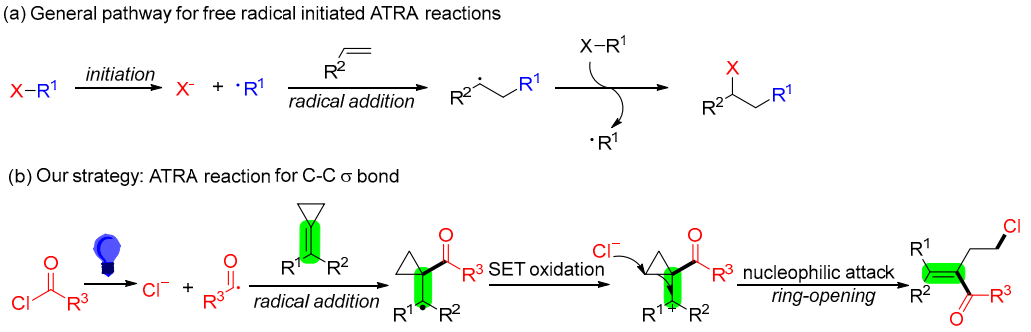
1. Introduction

The ring-opening reactions of cyclopropanes provide a powerful and effective strategy to achieve the functionalization of C–C σ-bonds due to their high strain energy [1–6]. As an exciting class of cyclopropanes, alkylidenecyclopropanes (ACPs) show high reactivities, and they are widely used in fascinating organic transformations to construct cyclic compounds and functional alkenes [7–12]. A typical method for the C-C cleavage of ACPs is the use of transition metals [13–19] and Lewis or Brønsted acids [20–24] as catalysts. Recently, the development of the oxidative ring opening of ACPs has also afforded an alternative option [25–31]. For example, in 2021, Shi and co-workers reported a photochemical ring-opening radical clock reaction using innovative NHPI esters bearing alkylidenecyclopropanes for the facile construction of alkynyl derivatives [31].

As simple and readily available building blocks, acyl chlorides have recently received extensive attention [32–36]. One of the most critical transformations is the acylation reaction. Transition-metal-catalyzed acyl reactions using acyl chlorides as acyl sources provide a classical and valuable method for the construction of functional acyl compounds [37–42]. In addition, the production of acyl compounds via a radical pathway through the reduction of acyl chlorides is attractive [43–49]. Due to the importance of acyl compounds, developing a new method to construct such fascinating chemicals is still appealing.

Over the past few decades, difunctionalization has gained much interest because it allows for the introduction of two functional groups into one molecule in one step [50–54]. Among the most common transformations is the difunctionalization of alkenes, which can form two new bonds with a one-step economy. Except for multicomponent reactions, there is no doubt that using one reagent as two different sources offers an exciting pathway to achieve difunctionalization [55–59]. Atom transfer radical addition (ATRA) reactions afford a high-efficiency path to realize the difunctionalization of alkenes and construct a carbon–halo bond (Scheme 1a) [60–64]. In 2022, Liu's group disclosed a copper-catalyzed asymmetric ATRA reaction and achieved the radical chlorination of acrylamides [64]. Photochemical reactions are regarded as a powerful and green tool in organic synthesis [65–72]. Inspired by our previous work, we herein report a visible-light-induced ATRA reaction for the C-C σ-bond using acyl chlorides as both acyl and Cl sources through a radical addition/SET oxidation/nucleophilic attack and ring-opening process (Scheme 1b).



Scheme 1. ATRA reactions for difunctionalization.

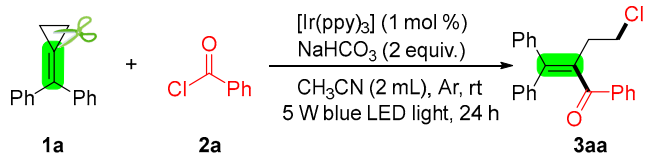
2. Results and Discussion

In our initiated study, we selected (cyclopropylidenemethylene)dibenzene **1a** and benzoyl chloride **2a** as model partners to investigate the influence of the reaction conditions (Table 1). The desired difunctionalization product, **3aa**, could be produced with a 96% yield under irradiation with a 5 W blue LED light at room temperature for 24 h (entry 1). When the photocatalyst [$Ir(ppy)_3$] was replaced with other photocatalysts, such as [$Ru(bpy)_3Cl_2$] and eosin Y, this transformation basically could not occur (entries 2–3). No product was detected in the absence of a photocatalyst or light irradiation, indicating that both were necessary for this reaction (entries 4 and 5). In addition, other light sources showed poorer reactivities (entries 6–8). Both increasing and decreasing the loading of [$Ir(ppy)_3$] led to a slight decrease in the yields (entries 9–10). Next, the effect of the bases was tested, and the results show that $NaHCO_3$ was the most suitable (entries 11–14). In addition, many solvents were explored, and none showed better results than CH_3CN (entries 15–19). Increasing the temperature to 50 °C did not increase the yield of **3aa** (entry 20). Finally, we were satisfied because the yield of the desired product, **3aa**, did not obviously decrease when the reaction expanded to a 1 g scale (entry 21).

After obtaining the optimized reaction conditions, we first tested the reactivities of a series of ACPs in this difunctionalization transformation (Table 2). (Cyclopropylidenemethylene)dibenzene **1a** could smoothly react with benzoyl chloride **2a** and resulted in the arylation/chlorination product **3aa** with a 96% yield. ACPs with electron-donating groups in the para-position of benzene showed greater reactivities than ACPs with electron-withdrawing groups (products **3ba–3ca** compared with products **3da–3fa**). In addition, (cyclopropylidenemethylene)dibenzene with two methyl groups at the para- and ortho-position of two benzene rings, respectively, could also fit for this transformation (product **3ga**). When only one of the benzene rings bore a substitute at the para-position, ACPs were compatible with this difunctionalization reaction and provided a mixture of (Z) and (E)-products **3ha–3ja** with good yields (the ratio of Z: E was 1:1, in which ^1H NMR decided **3ha** and **3ia–3ja** were determined by GC-MS).

Then, many acyl chlorides were tested (Table 3). Benzoyl chlorides containing an electron-donating group (such as methoxy and alkyl group) at the para-position were well tolerated for this transformation, while benzoyl chlorides containing an electron-withdrawing group (such as F, Cl, Br, I, CN, and CF_3) at the para-position led to a slight decrease in yields (products **3ab–3ak**) (X-ray data for **3ad** are shown in Supporting Information 5) [73]. Moreover, benzoyl chlorides containing a substituent at the meta- or ortho-position also caused an inevitable decline in yields due to the steric effect (products **3al–3au**). Disubstituted benzoyl chlorides were compatible with this visible-light-induced arylation/chlorination of the C-C σ bond and provided the corresponding products in moderate yields (products **3av–3aw**). Except for benzoyl chloride derivatives, 2-thiophenecarbonyl chloride also showed great reactivities (product **3ax**). What is more, benzoyl bromide was also tolerated and produced the target product **3ay** with a 79% yield.

Table 1. Screening optimal conditions[1].

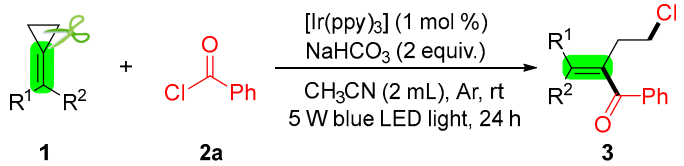


1a **2a** **3aa**

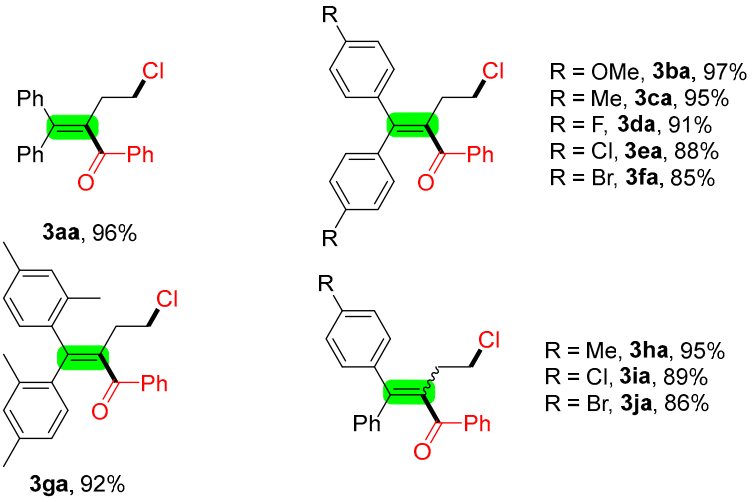
Entry	Variation from the Standard Conditions	Yield (%) [2]
1	None	96
2 [3]	$[Ru(bpy)_3Cl_2]$ instead of $[Ir(ppy)_3]$	9
3 [3]	Eosin Y instead of $[Ir(ppy)_3]$	0
4 [3]	Without $[Ir(ppy)_3]$	0
5 [3]	Without additional light	0
6 [4]	None	68
7 [5]	None	91
8 [6]	None	86
9	$[Ir(ppy)_3]$ (2 mol %)	95
10	$[Ir(ppy)_3]$ (0.5 mol %)	88
11	Na_2CO_3 instead of $NaHCO_3$	75
12	K_2CO_3 instead of $NaHCO_3$	68
13	Et_3N instead of $NaHCO_3$	24
14	2,6-Lutidine instead of $NaHCO_3$	75
15	Toluene instead of CH_3CN	87
16	EtOAc instead of CH_3CN	90
17	THF instead of CH_3CN	85
18 [3]	DMF instead of CH_3CN	<5
19 [3]	DMSO instead of CH_3CN	<5
20	At 50 °C	90
21 [7]	None	86

[1] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol, 2 equiv.), $[Ir(ppy)_3]$ (1 mol %), $NaHCO_3$ (0.4 mmol, 2 equiv.), CH_3CN (2 mL), rt, argon, 5 W blue LED light, and 24 h. [2] Isolated yields. [3] Most of the starting materials were recovered. [4] A 3 W blue LED light instead of a 5 W blue LED light. [5] A 12 W blue LED light instead of a 5 W blue LED light. [6] A 36 W compact fluorescent light instead of a 5 W blue LED light. [7] **1a** (1.0 g, 4.85 mmol), **2a** (9.7 mmol, 2 equiv.), $[Ir(ppy)_3]$ (1 mol %), $NaHCO_3$ (9.7 mmol, 2 equiv.), CH_3CN (5 mL), rt, argon, a 5 W blue LED light, and 72 h.

Table 2. Scope of ACPs (1) [1].

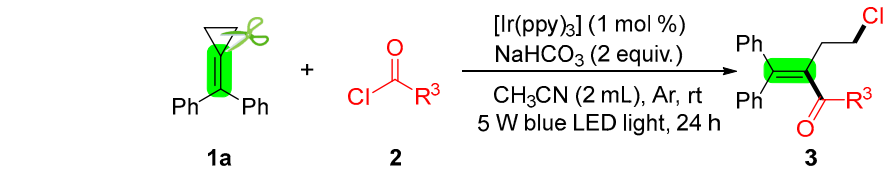


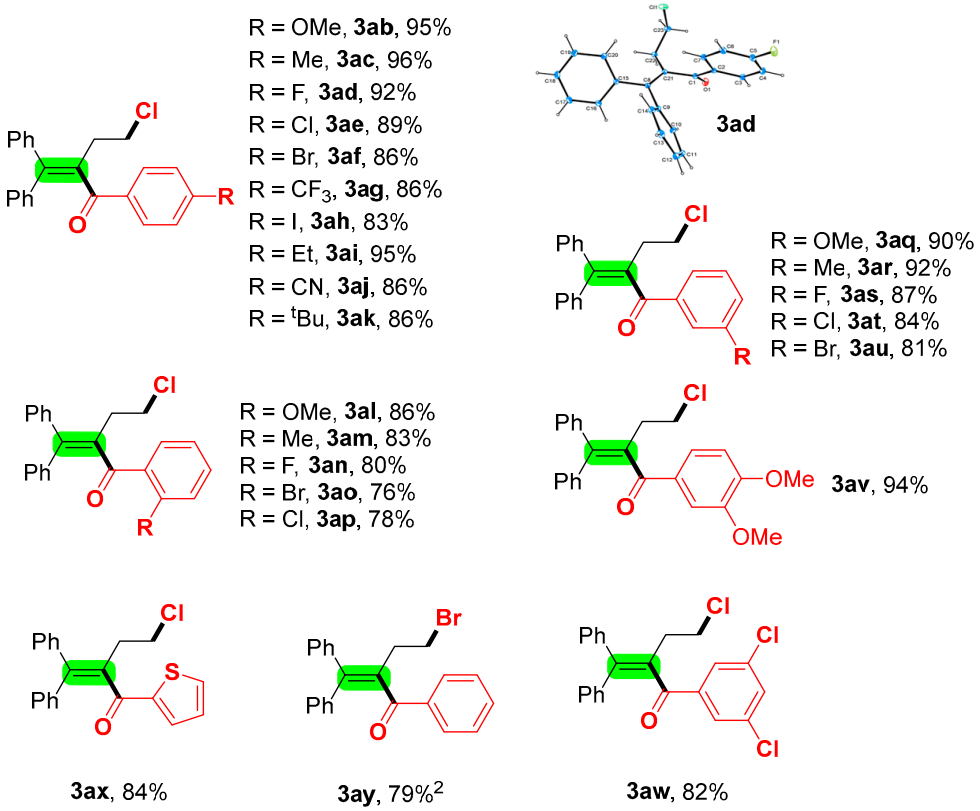
1 **2a** **3**



[1] Reaction conditions: **1** (0.2 mmol), **2a** (0.4 mmol, 2 equiv.), $[Ir(ppy)_3]$ (1 mol %), $NaHCO_3$ (0.4 mmol, 2 equiv.), CH_3CN (2 mL), rt, argon, a 5 W blue LED light and 24 h.

Table 3. Scope of acyl chlorides (2) [1].

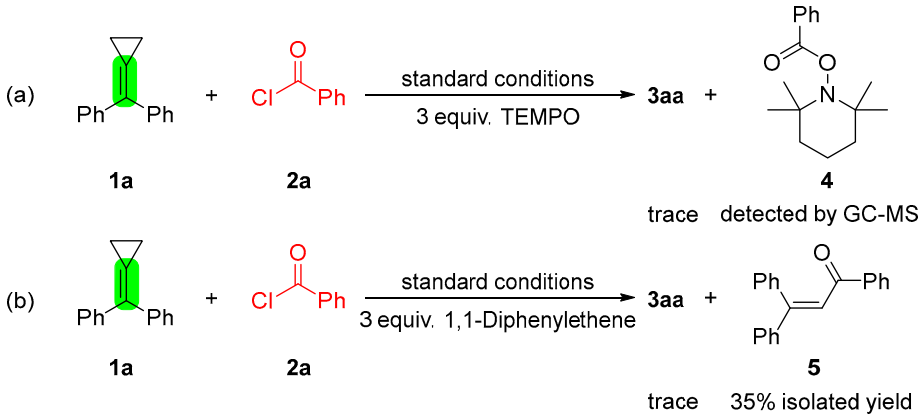




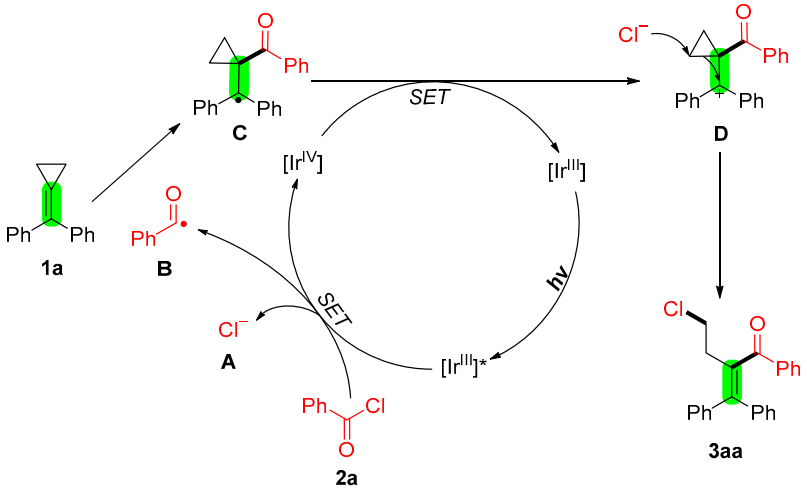
[1] Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol, 2 equiv.), [Ir(ppy)$_3$] (1 mol %), NaHCO$_3$ (0.4 mmol, 2 equiv.), CH$_3$CN (2 mL), rt, argon, a 5 W blue LED light and 24 h. [2] The starting material was benzoyl bromide.

Control experiments were conducted to explore the mechanism of this difunctionalization reaction (Scheme 2). When 3 equiv. radical inhibitor TEMPO or 1,1-diphenylethene was added under the standard conditions, the desired product **3aa** was difficult to detect. In addition, the acyl radical trapping product **4** was detected using GC-MS (Scheme 2a), while **5** could be isolated with a 35% yield (Scheme 2b), which proved that a radical pathway was involved in this transformation.

According to the experimental results and reported literature, a probable mechanism is drawn in Scheme 3. Firstly, benzoyl chloride **2a** underwent a single electron transfer (SET) with an excited photocatalyst [Ir^{III}*] to produce acyl radical **B** and chloride anion **A**. Then, acyl radical **B** added to (cyclopropylidenemethylene)dibenzene **1a** to deliver carbon radical **C,** which was subsequently oxidated by Ir^{IV} to obtain carbon cation **D**. Then, cation **D** was nucleophilically attacked by Cl$^-$ and the subsequent ring opening of cyclopropyl produced the desired product **3aa**.



Scheme 2. Control Experiments.



Scheme 3. Possible mechanisms.

3. Materials and Methods

3.1. General Information

Commercially available reagents were used throughout without purification unless otherwise stated. The starting alkylidenecyclopropanes (**1**) [64] were prepared via methods reported in the literature. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-400 instrument (400 MHz for ^{1}H and 100 MHz for ^{13}C) at 20 °C. Chemical shifts (d) are given in ppm downfield from Me_4Si and are referenced as the internal standard to the residual solvent (unless indicated) $CDCl_3$ (d = 7.26 for ^{1}H and d = 77.00 for ^{13}C). Coupling constants, J, are reported in hertz (Hz). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, td = triplet of doublet, q = quartet, m = multiplet, and br = broad. Melting points were determined in a capillary tube and are uncorrected. TLC was carried out on SiO_2 (silica gel 60 F254), and the spots were located with UV light. Flash chromatography was carried out on SiO_2 (silica gel 60, 230–400 mesh ASTM). Drying of organic extracts during work-up of reactions was performed over anhydrous Na_2SO_4. Evaporation of solvents was accomplished with a Büchi rotatory evaporator. High-resolution mass spectra (HRMS) were obtained on an Agilent mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

3.2. General Procedure for the Synthesis of **3**

To a Schlenk tube were added **1** (0.2 mmol), **2** (0.4 mmol, 2 equiv.), CH_3CN (2 mL), $Ir(ppy)_3$ (1 mol%), and $NaHCO_3$ (2 equiv.). Then, the mixture was stirred at rt (oil bath temperature) in Ar atmosphere for 24 h until complete consumption of the starting material, as monitored by TLC and GC-MS analysis. After the reaction was finished, the

reaction mixture was washed with brine. The aqueous phase was re-extracted with EtOAc (3 × 10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by means of silica gel flash column chromatography (petroleum ether/ethyl acetate = 100:1 to 60:1) to afford the desired product **3**.

3.3. Characterization Data for **3**

4-Chloro-2-(diphenylmethylene)-1-phenylbutan-1-one (**3aa**): The title compound was prepared according to the general procedure and purified by means of column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (80:1) to afford a white solid with a 96% yield (66.6 mg); mp: 183.0–183.5 °C (uncorrected). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80–7.78 (m, 2H), 7.43–7.37 (m, 5H), 7.36–7.28 (m, 1H), 7.21–7.17(d, *J* = 8.0 Hz, 2H), 6.97(s, 5H), 3.65 (t, *J* = 7.2 Hz, 2H), 3.05 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.2, 148.0, 140.9, 140.4, 137.3, 135.1, 132.5, 129.8, 129.3, 129.2, 128.4, 128.0, 127.9, 127.9, 127.7, 42.6, 36.2. HRMS (ESI-TOF) *m*/*z*: $C_{23}H_{20}ClO$ $(M + H)^+$ calcd for 347.1197, found 347.1192.

2-(Bis(4-methoxyphenyl)methylene)-4-chloro-1-phenylbutan-1-one (**3ba**): The title compound was prepared according to the general procedure and purified by means of column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (60:1) to afford a white solid with a 97% yield (78.6 mg); mp: 177.3–178.6 °C (uncorrected). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76 (d, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 3H), 7.17 (s, 2H), 6.91 (t, J = 8.0 Hz, 4H), 6.49 (d, *J* = 8.0 Hz, 2H), 3.83 (s, 3H), 3.66 (t, *J* = 6.8 Hz, 2H), 3.60 (s, 3H), 3.06 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.5, 159.2, 159.3, 148.1, 137.7, 134.0, 133.5, 133.0, 132.2, 131.5, 130.8, 129.1, 127.8, 113.6, 113.1, 55.2, 55.0, 42.8, 36.4; HRMS (ESI-TOF) *m*/*z*: $C_{25}H_{23}ClO_3$ $(M + H)^+$ calcd for 407.1408, found 407.1403.

4-Chloro-2-(di-p-tolylmethylene)-1-phenylbutan-1-one (**3ca**): The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (90:1) to afford a white solid with a 95% yield (72.7mg); mp: 186.6–186.8 °C (uncorrected). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (d, *J* = 8.0 Hz, 2H), 7.28–7.18 (m, 7H), 6.85 (d, *J* = 7.2 Hz, 2H), 6.76 (d, *J* = 7.6 Hz, 2H), 3.63 (t, *J* = 7.2 Hz, 2H), 3.03 (t, *J* = 7.2 Hz, 2H), 2.38 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.4, 148.2, 138.3, 137.7, 137.4, 134.2, 132.2, 129.2, 129.8, 129.2, 129.0, 128.4, 127.8, 42.7, 36.3, 21.2, 20.9; HRMS (ESI-TOF) *m*/*z*: $C_{25}H_{24}ClO$ $(M + H)^+$ calcd for 375.1510, found 375.1514.

2-(Bis(4-fluorophenyl)methylene)-4-chloro-1-phenylbutan-1-one (**3da**): The title compound was prepared according to the general procedure and purified by means of column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (70:1) to afford a yellow solid with a 91% yield (69.7 mg); mp: 176.3–176.9 °C (uncorrected). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (d, *J* = 7.6 Hz, 2H), 7.37–7.31 (m, 3H), 7.21 (t, *J* = 7.6 Hz, 2H), 7.10 (t, *J* = 8.0 Hz, 2H), 6.94 (t, *J* = 6.0 Hz, 2H), 6.67 (t, *J* = 8.4 Hz, 2H), 3.65 (t, *J* = 6.8 Hz, 2H), 3.04 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.8, 163.4, 163.7, 161.2, 145.8, 132.7, 131.6 (d, *J* = 82 Hz, 1C), 131.2(d, *J* = 82 Hz, 1C), 129.1, 128.0, 115.6, 114.9, 114.7, 42.5, 36.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ: 112.9 (d, *J* = 106.0 Hz, 2F); HRMS (ESI-TOF) *m*/*z*: $C_{23}H_{18}ClF_2O$ $(M + H)^+$ calcd for 383.1009, found 383.1003.

2-(Bis(4-chlorophenyl)methylene)-4-chloro-1-phenylbutan-1-one (**3ea**): The title compound was prepared according to the general procedure and purified by means of column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (70:1) to afford a yellow solid with an 88% yield (71.6 mg); mp: 169.2–169.9 °C (uncorrected). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (d, *J* = 7.6 Hz, 2H), 7.40–7.32 (m, 5H), 7.22 (t, *J* = 7.6 Hz, 2H), 6.96 (d, *J* = 7.6 Hz, 2H), 6.90 (d, *J* = 7.6 Hz, 2H), 3.63 (t, *J* = 6.4 Hz, 2H), 3.02 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.5, 145.1, 139.0, 138.3, 136.9, 136.3, 134.2, 134.1, 132.9, 131.0, 130.8, 129.2, 128.7, 128.1, 42.3, 36.1; HRMS (ESI-TOF) *m*/*z*: $C_{23}H_{18}Cl_3O$ $(M + H)^+$ calcd for 415.0418, found 415.0415.

2-(Bis(4-bromophenyl)methylene)-4-chloro-1-phenylbutan-1-one (**3fa**): The title compound was prepared according to the general procedure and purified by means of column

chromatography on silica gel and eluted with petroleum ether/ethyl acetate (70:1) to afford a yellow solid with an 85% yield (85.3 mg); mp: 189.0–189.5 °C (uncorrected). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (d, *J* = 7.6 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.23 (t, *J* = 8.4 Hz, 4H), 7.11 (d, *J* = 7.6 Hz, 2H), 6.83 (d, *J* = 4.0 Hz, 2H), 3.62 (t, *J* = 8.4 Hz, 2H), 3.02 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.6, 145.2, 136.4, 133.0, 131.8, 131.4, 131.1, 129.3, 128.2, 122.5, 42.4, 36.2; HRMS (ESI-TOF) *m*/*z*: $C_{23}H_{18}Br_2ClO$ $(M + H)^+$ calcd for 502.9407, found 502.9404.

2-(Bis(2,4-dimethylphenyl)methylene)-4-chloro-1-phenylbutan-1-one (**3ga**): The title compound was prepared according to the general procedure and purified by means of column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (80:1) to afford a yellow liquid with a 92% yield (74.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80–7.77 (m, 2H), 7.42–7.34 (m, 3H), 7.30–7.28 (m, 1H), 7.22–6.95 (t, *J* = 8.8 Hz, 2H), 6.94 (s, 3H), 3.64 (d, *J* = 7.2 Hz, 2H), 3.01 (d, *J* = 7.2 Hz, 2H), 2.51 (s, 6H), 2.42 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.2, 148.1, 141.0, 140.4, 137.3, 135.1, 132.5, 129.9, 129.4, 129.3, 128.4, 128.1, 128.0, 127.9, 127.8, 42.7, 36.3, 27.9, 24.3; HRMS (ESI-TOF) *m*/*z*: $C_{27}H_{28}ClO$ $(M + H)^+$ calcd for 403.1823, found 403.1821.

4-Chloro-2-((4-fluorophenyl)(4-methoxyphenyl)methylene)-1-phenylbutan-1-one (**3ha**): The title compound was prepared according to the general procedure and purified by means of column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (70:1) to afford a yellow liquid with a 90% yield (71.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74 (t, *J* = 7.2 Hz, 2H), 7.32–7.27 (m, 3H), 7.20 (t, *J* = 8.0 Hz, 2H), 6.95–6.92 (m, 4H), 6.68–6.64 (m, 2H), 3.08 (s, 3H), 3.66 (t, *J* = 7.2 Hz, 2H), 3.09 (t, *J* = 7.2Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.3, 163.4, 161.0, 159.5, 147.0, 137.5, 132.6, 132.5, 131.8 (d, *J*= 8.3 Hz, 1C), 130.8, 129.2, 127.9, 114.8, 114.6, 113.8, 55.2, 42.7, 36.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ: 113.3 (s, 1F); HRMS (ESI-TOF) *m*/*z*: $C_{24}H_{21}FClO_2$ $(M + H)^+$ calcd for 395.1209, found 395.1204.

4-Chloro-1-phenyl-2-(phenyl(p-tolyl)methylene)butan-1-one (**3ia**): The title compound was prepared according to the general procedure and purified by means of column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (80:1) to afford a white solid with a 95% yield (68.5 mg); mp: 166.4–166.9 °C (uncorrected). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (t, *J* = 8.8 Hz, 2H), 7.41–7.35 (m, 3H), 7.30–7.24 (m, 2H), 7.21–7.14 (m, 3H), 6.96–6.94 (m, 2H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 3.2 Hz, 1H), 3.66–3.61 (m, 2H), 3.07–3.01 (m, 2H), 2.37 (s, 1H), 2.08 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.2, 148.2, 148.0, 141.1, 140.5, 137.8, 137.7, 137.5, 137.3, 134.8, 134.4, 132.3, 129.8, 129.8, 129.3, 129.2, 129.0, 128.4, 128.3, 127.8, 127.8, 127.8, 127.6, 42.6, 36.3, 20.9; HRMS (ESI-TOF) *m*/*z*: $C_{24}H_{22}ClO$ $(M + H)^+$ calcd for 361.1354, found 361.1356.

4-Chloro-2-((4-chlorophenyl)(phenyl)methylene)-1-phenylbutan-1-one (**3ja**): The title compound was prepared according to the general procedure and purified by means of column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (70:1) to afford a white solid with an 89% yield (67.8 mg); mp: 184.1–184.8 °C (uncorrected).^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (t, *J* = 8Hz, 2H), 7.43–7.32 (m, 5H), 7.29–7.16 (m, 3H), 6.97–6.90 (m, 4H), 3.66–3.61 (m, 3H), 3.06–3.01 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.8, 146.7, 146.4, 140.5, 139.9, 139.4, 138.7, 137.1, 137.0, 135.7, 135.6, 134.0, 133.9, 132.8, 132.5, 131.0, 130.8, 129.8, 129.3, 129.2, 128.6, 128.5, 128.1, 128.0, 127.9, 127.8, 42.5, 36.1; HRMS (ESI-TOF) *m*/*z*: $C_{23}H_{19}Cl_2O$ $(M + H)^+$ calcd for 381.0807, found 381.0804.

2-((4-Bromophenyl)(phenyl)methylene)-4-chloro-1-phenylbutan-1-one (**3ka**): The title compound was prepared according to the general procedure and purified by means of column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (70:1) to afford a yellow solid with a 86% yield (73.1 mg); mp: 156.1–156.8 °C (uncorrected). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81–7.55 (m, 2H), 7.47 (d, *J* = 4.8 Hz, 1H), 7.39–7.12 (m, 7H), 6.98 (t, *J* = 2.4 Hz, 2H), 6.97–6.84 (m, 1H), 3.66–3.62 (m, 2H), 3.06–3.01 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.9, 146.7, 146.4, 140.4, 139.8, 139.2, 137.1, 137.0, 135.7, 135.6, 132.8, 132.6, 131.6, 131.3, 131.1, 130.9, 129.8, 129.3, 129.3, 129.2, 128.5, 128.2, 128.1, 127.9, 127.8, 122.2, 42.4, 36.2; HRMS (ESI-TOF) *m*/*z*: $C_{23}H_{19}ClBrO$ $(M + H)^+$ calcd for 425.0302, found 425.0301.

4-Chloro-2-(diphenylmethylene)-1-(4-methoxyphenyl)butan-1-one (**3ab**): The title compound was prepared according to the general procedure and purified by means of column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (70:1) to afford a white solid with a 95% yield (71.5 mg); mp: 187.4–187.8 °C (uncorrected). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82 (d, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 4.4 Hz, 5H), 6.99 (t, *J* = 7.2 Hz, 5H), 6.69 (d, *J* = 8.0 Hz, 2H), 3.73 (s, 3H), 3.61 (t, *J* = 6.8 Hz, 2H), 3.00 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.6, 163.1, 146.4, 140.9, 140.5, 135.1, 131.7, 129.9, 129.6, 129.3, 128.3, 127.8, 127.7, 127.7, 113.2, 55.2, 42.5, 36.3; HRMS (ESI-TOF) *m*/*z*: $C_{24}H_{22}ClO_2$ $(M + H)^+$ calcd for 377.1303, found 377.1305.

4-chloro-2-(diphenylmethylene)-1-(p-tolyl)butan-1-one (**3ac**): The title compound was prepared according to the general procedure and purified by means of column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (90:1) to afford a white solid with a 96% yield (69.3 mg); mp: 181.0–182.5 °C (uncorrected). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (d, *J* = 4.0 Hz, 2H), 7.36 (t, *J* = 3.6 Hz, 5H), 7.02–6.96 (m, 7H), 3.61 (t, *J* = 6.8 Hz, 2H), 3.01 (t, *J* = 6.8 Hz, 2H), 2.24 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.7, 143.3, 146.9, 140.9, 140.4, 135.1, 134.5, 129.7, 129.4, 129.3, 128.6, 128.3, 127.8, 127.7, 127.7, 42.5, 36.3, 21.5; HRMS (ESI-TOF) *m*/*z*: $C_{24}H_{22}ClO$ $(M + H)^+$ calcd for 361.1354, found 361.1351.

4-Chloro-2-(diphenylmethylene)-1-(4-fluorophenyl)butan-1-one (**3ad**): The title compound was prepared according to the general procedure and purified by means of column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (80:1) to afford a yellow solid with a 92% yield (67.1 mg); mp: 174.2–174.9 °C (uncorrected). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82 (d, *J* = 7.6 Hz, 2H), 7.42–7.37 (m, 7H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.23 (t, *J* = 8.4 Hz, 4H), 7.11 (d, *J* = 7.6 Hz, 2H), 6.83 (d, *J* = 4.0 Hz, 2H), 3.64 (t, *J* = 8.4 Hz, 2H), 3.05 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.5, 166.3, 163.8, 148.2, 134.9, 131.9, 131.8, 129.8, 129.3, 128.4, 128.0 (d, *J* = 79 Hz, 1C), 127.8, 114.8, 42.6, 36.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ: 105.6 (s, 1F); HRMS (ESI-TOF) *m*/*z*: $C_{23}H_{19}ClFO$ $(M + H)^+$ calcd for 365.1103, found 365.1107.

4-Chloro-1-(4-chlorophenyl)-2-(diphenylmethylene)butan-1-one (**3ae**): The title compound was prepared according to the general procedure and purified by means of column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (80:1) to afford a white solid with a89% yield (67.8 mg); mp: 172.3–172.9 °C (uncorrected). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73 (d, *J* = 8.0 Hz, 2H), 7.74–7.37 (m, 5H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.98 (s, 5H), 3.63 (t, *J* = 6.4 Hz, 2H), 3.05 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.8, 148.5, 140.8, 140.1, 138.6, 135.7, 134.7, 130.5, 129.8, 129.3, 128.4, 128.1, 127.8, 42.6, 36.0; HRMS (ESI-TOF) *m*/*z*: $C_{23}H_{19}Cl_2O$ $(M + H)^+$ calcd for 381.0807, found 381.0805.

1-(4-Bromophenyl)-4-chloro-2-(diphenylmethylene)butan-1-one (**3af**): The title compound was prepared according to the general procedure and purified by means of column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (80:1) to afford a brown solid with a 94% yield (73.1 mg); mp: 175.3–176.5 °C (uncorrected). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65 (d, *J* = 8.4 Hz, 2H), 7.42–7.25 (m, 7H), 7.01–6.95 (m, 5H), 3.63 (t, *J* = 4.0 Hz, 2H), 3.05 (t, *J* = 4.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.1, 148.6, 140.8, 140.1, 136.1, 134.7, 131.1, 130.7, 129.8, 129.3, 128.4, 128.2, 128.1, 127.9, 127.4, 42.6, 36.0; HRMS (ESI-TOF) *m*/*z*: $C_{23}H_{19}ClBrO$ $(M + H)^+$ calcd for 425.0302, found 425.0305.

4-Chloro-2-(diphenylmethylene)-1-(4-(trifluoromethyl)phenyl)butan-1-one (**3ag**): The title compound was prepared according to the general procedure and purified by means of column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (70:1) to afford a yellow liquid with an 86% yield (71.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (d, *J* = 8.0 Hz, 2H), 7.42–7.37 (m, 7H), 6.95 (s, 5H), 3.67 (t, *J* = 6.8 Hz, 2H), 3.09 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.1, 150.0, 140.8, 140.6, 140.0, 134.8, 130.0, 129.3 (d, *J* = 18 Hz, 1C), 128.4 (d, *J* = 22 Hz, 1C), 128.2, 127.9, 124.7 (d, *J* = 3.8 Hz, 1C), 42.7, 35.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ: 63.2 (s, 3F)HRMS (ESI-TOF) *m*/*z*: $C_{24}H_{19}ClF_3O$ $(M + H)^+$ calcd for 415.1071, found 415.1070.

4-Chloro-2-(diphenylmethylene)-1-(4-iodophenyl)butan-1-one (**3ah**): The title compound was prepared according to the general procedure and purified by means of column

chromatography on silica gel and eluted with petroleum ether/ethyl acetate (70:1) to afford a white liquid with an 83% yield (78.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55–7.48 (m, 4H), 7.40–7.35 (m, 5H), 7.01–6.94 (m, 5H), 3.63 (t, *J* = 6.8 Hz, 2H), 3.054 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.4, 148.6, 140.8, 140.1, 137.1, 136.7, 134.7, 130.6, 129.8, 129.3, 128.4, 128.2, 128.1, 127.9, 100.4, 42.6, 36.09; HRMS (ESI-TOF) *m*/*z*: $C_{23}H_{19}ClIO$ $(M + H)^+$ calcd for 473.0164, found 473.0161.

4-Chloro-2-(diphenylmethylene)-1-(4-ethylphenyl)butan-1-one (**3ai**): The title compound was prepared according to the general procedure and purified by means of column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (80:1) to afford a white solid with a 95% yield (71.2 mg); mp: 176.3–176.9 °C (uncorrected)^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74–7.72 (m, 2H), 7.42–7.35 (m, 5H), 7.03–6.96 (m, 7H), 3.62 (t, *J* = 7.2 Hz, 2H), 3.021 (t, *J* = 7.2 Hz, 2H), 2.58–2.52 (m, 2H), 1.14 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.8, 149.5, 147.1, 140.9, 140.5, 135.2, 134.8, 129.7, 129.5, 129.3, 128.4, 127.8, 127.7, 127.4, 42.6, 36.3, 28.82, 14.95; HRMS (ESI-TOF) *m*/*z*: $C_{25}H_{24}ClO$ $(M + H)^+$ calcd for 375.1510, found 375.1513.

4-(4-Chloro-2-(diphenylmethylene)butanoyl)benzonitrile (**3aj**): The title compound was prepared according to the general procedure and purified by means of column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (60:1) to afford a white solid with an 86% yield (63.9 mg); mp: 195.3–195.8 °C (uncorrected). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81–7.94 (m, 2H), 7.44–7.37 (m, 7H), 7.00–6.90 (m, 5H), 3.68 (t, *J* = 6.8 Hz, 2H), 3.11 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.7, 150.9, 141.2, 140.8, 139.9, 134.7, 131.6, 130.1, 129.3, 128.7, 128.5, 128.4, 128.0, 118.1, 114.9, 42.8, 35.8; HRMS (ESI-TOF) *m*/*z*: $C_{24}H_{19}ClNO$ $(M + H)^+$ calcd for 372.1150, found 372.1158.

1-(4-(Tert-butyl)phenyl)-4-chloro-2-(diphenylmethylene)butan-1-one (**3ak**): The title compound was prepared according to the general procedure and purified by means of column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (80:1) to afford a white liquid with an 86% yield (69.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (d, *J* = 8.4 Hz, 2H), 7.42–7.34 (m, 5H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.00–6.93 (m, 5H), 3.63 (t, *J* = 7.2 Hz, 2H), 3.02 (t, *J* = 6.8 Hz, 2H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.8, 156.0, 147.3, 140.9, 140.4, 135.3, 134.5, 129.7, 129.3, 129.3, 128.4, 127.8, 127.7, 124.8, 42.6, 36.2, 34.9, 30.8; HRMS (ESI-TOF) *m*/*z*: $C_{27}H_{28}ClO$ $(M + H)^+$ calcd for 403.1823, found 403.1828.

4-Chloro-2-(diphenylmethylene)-1-(2-methoxyphenyl)butan-1-one (**3al**): The title compound was prepared according to the general procedure and purified by means of column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (70:1) to afford a white solid with an 86% yield (64.8 mg); mp: 177.1–177.9 °C (uncorrected). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39–7.32 (m, 4H), 7.28–7.25 (m, 2H), 7.15 (t, *J* = 4.0 Hz, 1H), 6.96 (t, *J* = 3.6 Hz, 3H), 6.90 (d, *J* = 3.2 Hz, 2H), 6.70 (t, *J* = 7.6 Hz, 1H), 6.62–6.60 (m, 1H), 3.84 (s, 3H), 3.73 (t, *J* = 7.6 Hz, 2H), 3.03 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.3, 157.3, 148.2, 141.1, 140.8, 137.6, 132.6, 130.7, 129.5, 129.3, 129.0, 128.3, 127.8, 127.5, 127.4, 119.9, 110.6, 55.3, 43.0, 36.0; HRMS (ESI-TOF) *m*/*z*: $C_{24}H_{22}ClO_2$ $(M + H)^+$ calcd for 377.1303, found 377.1306.

4-Chloro-2-(diphenylmethylene)-1-(o-tolyl)butan-1-one (**3am**): The title compound was prepared according to the general procedure and purified by means of column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (80:1) to afford a white solid with an 83% yield (59.9 mg); mp: 173.0–173.5 °C (uncorrected). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05 (t, *J* = 7.6Hz, 1H), 7.70 (d, *J* = 1.6 Hz, 1H), 7.50 (t, *J* = 1.6 Hz, 1H), 7.43–7.19 (m, 5H), 7.09–6.87 (m, 4H), 3.73 (t, *J* = 7.0 Hz, 1H), 3.08 (t, *J* = 7.0 Hz, 1H), 2.70 (s, 3H), 2.40 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 201.4, 162.8, 150.2, 142.5, 141.5, 140.5, 138.6, 138.3, 137.0, 133.5, 132.1, 131.3, 131.1, 130.9, 129.9, 129.3, 129.1, 128.3, 128.0, 127.7, 127.6, 127.5, 126.0, 124.8, 42.84, 35.87, 21.98; HRMS (ESI-TOF) *m*/*z*: $C_{24}H_{22}ClO$ $(M + H)^+$ calcd for 361.1354, found 361.1351.

4-Chloro-2-(diphenylmethylene)-1-(2-fluorophenyl)butan-1-one (**3an**): The title compound was prepared according to the general procedure and purified by means of column chromatography on silica gel and eluted with petroleum ether/ethyl acetate 70:1) to afford

a yellow solid with an 80% yield (58.2 mg); mp: 168.2–168.5 °C (uncorrected). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49–7.40 (m, 1H), 7.38–7.30 (m, 3H), 7.29 (d, *J* = 7.2 Hz, 2H), 7.18–7.13 (m, 1H), 6.96 (s, 5H), 6.88 (t, *J* = 7.6 Hz, 1H), 6.75 (t, *J* = 9.2 Hz, 1H), 3.73 (t, *J* = 7.6 Hz, 2H), 3.05 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.8, 161.3, 158.8, 150.0 (d, *J* = 23Hz, 1C), 130.7, 129.7, 129.0, 128.3, 128.1, 128.1, 127.7, 123.6, 123.5, 115.9, 115.6, 42.8, 36.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ: 111.0 (t, *J* = 4.8 Hz, 1F); HRMS (ESI-TOF) *m*/*z*: $C_{23}H_{19}ClFO$ $(M + H)^+$ calcd for 365.1103, found 365.1109.

1-(2-bromophenyl)-4-chloro-2-(diphenylmethylene)butan-1-one (**3ao**): The title compound was prepared according to the general procedure and purified by means of column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (80:1) to afford a white solid with a 76% yield (64.4 mg); mp: 177.2–177.9 °C (uncorrected). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44–7.25 (m, 7H), 7.05–6.89 (m, 7H), 3.79 (t, *J* = 7.2 Hz, 2H), 3.11 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.7, 153.1, 141.2, 140.6, 140.4, 135.6, 133.4, 131.1, 130.9, 129.6, 129.0, 128.3, 128.2, 128.1, 127.8, 126.4, 120.8, 43.0, 35.8; HRMS (ESI-TOF) *m*/*z*: $C_{23}H_{19}BrClO$ $(M + H)^+$ calcd for 425.0302, found 425.0307.

4-Chloro-1-(2-chlorophenyl)-2-(diphenylmethylene)butan-1-one (**3ap**): The title compound was prepared according to the general procedure and purified by means of column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (80:1) to afford a white solid with a 78% yield (59.4 mg); mp: 176.1–176.8 °C (uncorrected). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42–7.35 (m, 4H), 7.32–7.29 (m, 2H), 7.05–6.96 (m, 6H), 6.92–6.89 (m, 2H), 3.78 (t, *J* = 7.2 Hz, 2H), 3.10 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.4, 152.6, 141.1, 140.5, 138.9, 136.0, 131.9, 131.1, 130.7, 130.0, 129.6, 129.0, 128.3, 128.2, 128.1, 127.8, 125.9, 43.0, 35.8; HRMS (ESI-TOF) *m*/*z*: $C_{23}H_{19}Cl_2O$ $(M + H)^+$ calcd for 381.0807, found 381.0808.

4-Chloro-2-(diphenylmethylene)-1-(3-methoxyphenyl)butan-1-one (**3aq**): The title compound was prepared according to the general procedure and purified by means of column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (70:1) to afford a white solid with a 90% yield (67.8 mg); mp: 186.6–186.9 °C (uncorrected). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42–7.33 (m, 7H), 7.09 (t, *J* = 8.0 Hz, 1H), 6.99 (s, 5H), 6.86–6.84 (m, 1H), 3.75 (s, 3H), 3.64 (t, J = 7.2 Hz, 2H), 3.04 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.9, 159.0, 147.9, 140.9, 140.3, 138.6, 135.1, 129.8, 129.3, 128.9, 128.4, 127.9, 127.9, 127.7, 122.2, 119.3, 113.1, 55.2, 42.6, 36.2; HRMS (ESI-TOF) *m*/*z*: $C_{24}H_{22}ClO_2$ $(M + H)^+$ calcd for 377.1303, found 377.1305.

4-Chloro-2-(diphenylmethylene)-1-(m-tolyl)butan-1-one (**3ar**): The title compound was prepared according to the general procedure and purified by means of column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (80:1) to afford a white solid with a 92% yield (66.4 mg); mp: 174.3–174.9 °C (uncorrected). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (d, *J* = 6.0, 2H), 7.42–7.24 (m, 5H), 7.12–7.05 (m, 2H), 6.98 (m, 5H), 3.63 (t, *J* = 6.8 Hz, 2H), 3.02 (t, *J* = 7.2 Hz, 2H), 2.25 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.2, 147.6, 141.0, 140.4, 137.5, 137.1, 135.2, 133.3, 129.8, 129.7, 129.3, 128.4, 127.9, 127.8, 127.8, 127.7, 126.6, 42.6, 36.2, 21.1; HRMS (ESI-TOF) *m*/*z*: $C_{24}H_{22}ClO$ $(M + H)^+$ calcd for 361.1354, found 361.1355.

4-Chloro-2-(diphenylmethylene)-1-(3-fluorophenyl)butan-1-one (**3as**): The title compound was prepared according to the general procedure and purified by means of column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (70:1) to afford a yellow liquid with an 87% yield (63.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57–7.55 (m, 1H), 7.45–7.36 (m, 6H), 7.15 (t, *J* = 5.6 Hz, 1H), 7.14–6.94 (m, 6H), 3.65 (t, *J* = 7.2 Hz, 2H), 3.06 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.9, 163.3, 160.8, 149.2, 140.8, 140.1, 139.7, 139.6, 134.8, 129.9, 129.4 (d, *J*= 7.6 Hz, 1C), 129.3, 128.4 (1C), 127.9, 125.0, 119.3, 119.1, 115.8, 115.6, 42.6, 36.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ: 112.9 (s, 1F); HRMS (ESI-TOF) *m*/*z*: $C_{23}H_{19}ClFO$ $(M + H)^+$ calcd for 365.1103, found 365.1105.

4-Chloro-1-(3-chlorophenyl)-2-(diphenylmethylene)butan-1-one (**3at**): The title compound was prepared according to the general procedure and purified by means of column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (80:1) to afford

a white solid with an 84% yield (64.0 mg); mp: 174.1–174.5 °C (uncorrected). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71 (t, *J* = 1.6 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.41–7.21 (m, 1H), 7.09 (t, *J* = 8.0 Hz, 1H), 7.00-6.95 (m, 5H), 3.65 (t, *J* = 6.8 Hz, 2H), 3.06 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.7, 149.4, 140.9, 140.1, 139.0, 133.9, 134.7, 132.1, 129.9, 129.3, 129.2, 123.1, 128.4, 128.2, 128.1, 127.9, 127.3, 42.6, 36.0; HRMS (ESI-TOF) *m*/*z*: $C_{23}H_{19}Cl_2O$ $(M + H)^+$ calcd for 381.0807, found 381.0802.

1-(3-Bromophenyl)-4-chloro-2-(diphenylmethylene)butan-1-one (**3au**): The title compound was prepared according to the general procedure and purified by means of column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (70:1) to afford a white solid with an 81% yield (68.8 mg); mp: 168.2–168.8 °C (uncorrected). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87 (t, *J* = 1.6 Hz, 1H), 7.69–7.67 (m, 1H), 7.43–7.36 (m, 6H), 7.05–6.94 (m, 6H), 3.65 (t, *J* = 6.8 Hz, 2H), 3.06 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.6, 149.5, 140.8, 140.1, 139.2, 134.9, 134.6, 132.2, 129.8, 129.3, 129.3, 128.4, 128.2, 128.1, 127.9, 127.7, 122.0, 42.6, 36.0; HRMS (ESI-TOF) *m*/*z*: $C_{23}H_{19}BrClO$ $(M + H)^+$ calcd for 425.0302, found 425.0300.

4-Chloro-1-(3,4-dimethoxyphenyl)-2-(diphenylmethylene)butan-1-one (**3av**): The title compound was prepared according to the general procedure and purified by means of column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (60:1) to afford a white solid with a 94% yield (76.5 mg); mp: 198.1–199.4 °C (uncorrected). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53–7.50 (m, 1H), 7.43–7.33 (m, 6H), 7.03–6.98 (m, 5H), 6.66 (m 1H), 3.85 (s, 3H), 3.83 (s, 3H), 3.62 (t, J = 7.0 Hz, 2H), 3.01 (t, J = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.7, 152.9, 148.3, 135.0, 130.0, 129.6, 129.3, 128.4, 127.8, 127.8, 124.7, 111.1, 109.6, 55.8, 55.7, 42.6, 36.3; HRMS (ESI-TOF) *m*/*z*: $C_{25}H_{24}ClO_3$ $(M + H)^+$ calcd for 407.1408, found 407.1405.

4-Chloro-1-(3,5-dichlorophenyl)-2-(diphenylmethylene)butan-1-one (**3aw**): The title compound was prepared according to the general procedure and purified by means of column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (70:1) to afford a white liquid with an 82% yield (68.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56 (d, *J* = 1.6 Hz, 2H), 7.43–7.36 (m, 5H), 7.21 (t, *J* = 2.0 Hz, 1H), 7.04 (t, *J* = 3.6Hz, 3H), 6.96–6.93 (m, 2H), 3.66 (t, *J* = 6.8 Hz, 2H), 3.08 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 197.3, 150.8, 140.8, 140.0, 139.9, 134.5, 134.4, 131.5, 129.9, 129.3, 128.6, 128.5, 128.4, 128.0, 127.5, 42.7, 35.8; HRMS (ESI-TOF) *m*/*z*: $C_{23}H_{18}Cl_3O$ $(M + H)^+$ calcd for 415.0418, found 415.0417.

4-Chloro-2-(diphenylmethylene)-1-(thiophen-2-yl)butan-1-one (**3ax**): The title compound was prepared according to the general procedure and purified by means of column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (70:1) to afford a yellow liquid with an 84% yield (64.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52–7.42 (m, 1H), 7.42–7.39 (m, 3H), 7.37–7.34 (m, 3H), 7.08–7.04 (m 5H), 6.83–6.81 (m, 1H), 3.63 (t, *J* = 7.2 Hz, 2H), 2.99 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.2, 147.1, 144.1, 141.0, 135.4, 140.2, 134.4, 134.2, 129.7, 129.3, 128.4, 127.9, 127.9, 127.5, 42.4, 36.1; HRMS (ESI-TOF) *m*/*z*: $C_{21}H_{18}ClOS$ $(M + H)^+$ calcd for 353.0761, found 353.0763.

4-Bromo-2-(diphenylmethylene)-1-phenylbutan-1-one (**3ay**): The title compound was prepared according to the general procedure and purified by means of column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (80:1) to afford a white solid with a 79% yield (64.1 mg); mp: 188.1–188.6 °C (uncorrected). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80–7.77 (m, 2H), 7.43–7.36 (m, 5H), 7.31–7.25 (m, 1H), 7.21–7.17 (m, 2H), 6.97 (s, 5H), 3.67–3.63 (m, 2H), 3.06–3.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.2, 148.0, 140.9, 140.4, 137.3, 135.1, 132.5, 129.8, 129.3, 129.2, 128.4, 128.0, 127.9, 127.9, 127.7, 42.6, 36.2. HRMS (ESI-TOF) *m*/*z*: $C_{23}H_{20}BrO$ $(M + H)^+$ calcd for 391.0692, found 391.0696.

4. Conclusions

In conclusion, we have developed a new and effective method for the difunctionalization of C-C σ bonds via a visible-light-induced ATRA reaction. Acyl chlorides served as both acyl and Cl sources in this transformation. A lot of fully substituted alkenes were

produced with good yields under room temperature. The preliminary mechanism study indicated that a radical process was involved in this reaction.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal13060919/s1, copies of NMR spectra and X-ray data for **3ad** (CCDC2262739). Crystal structure of **3ad**.

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