

HETEROCYCLES, Vol. 91, No. 2, 2015, pp. 388 - 397. © 2015 The Japan Institute of Heterocyclic Chemistry
Received, 1st December, 2014, Accepted, 9th January, 2015, Published online, 13th January, 2015
DOI: 10.3987/COM-14-13141

SELECTIVE SYNTHESIS OF 2,3-DIHYDROFURAN OR CYCLOPROPANE DERIVATIVES VIA TANDEM REACTION OF β,γ -UNSATURATED α -KETOESTERS WITH HALIDES

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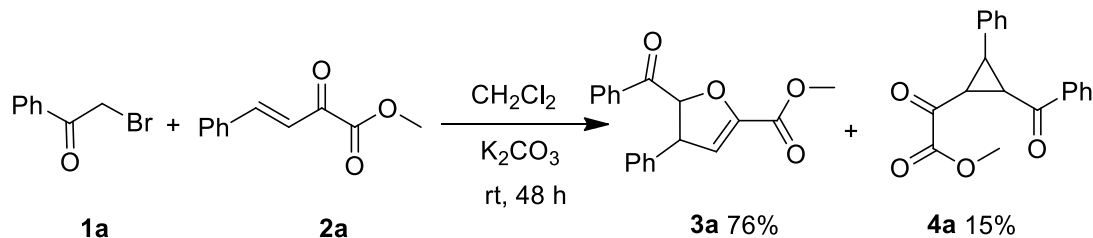
Abstract – 2,3-Dihydrofuran or cyclopropane derivatives were prepared with high selectivity via reaction of β,γ -unsaturated α -ketoesters with α -phenacyl bromide in different conditions.

Dihydrofuran derivatives which are commonly found in the molecular skeleton of natural products and bioactive substances have been studied for many years.¹⁻³ Cyclopropane derivatives are also important in the field of organic synthesis.^{4,5} A number of methods for the synthesis of them have been reported in the literature.⁶⁻⁹ Among them, stereoselective synthesis of 2,3-dihydrofuran or cyclopropane derivatives via the reaction of ylides with different α , β -unsaturated compounds have been reported.¹⁰⁻¹⁴ However, there is no report on selective synthesis of 2,3-dihydrofuran or cyclopropane derivatives via the same starting materials under different conditions.

As a sort of multi-functionalized building blocks, β,γ -unsaturated α -ketoester has recently been found useful utility in organic synthesis.^{15,16} In this work, we report the selective synthesis of 2,3-dihydrofuran or cyclopropane derivatives via reaction of β,γ -unsaturated α -ketoesters with α -phenacyl bromide in different conditions.

We initiated our study by treatment of 2-bromo-1-phenylethanone (**1a**), (*E*)-methyl

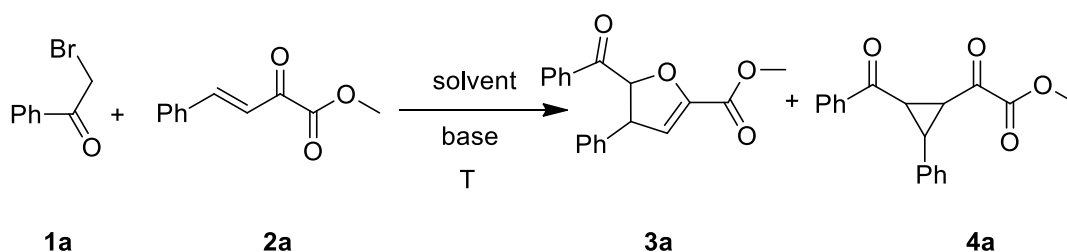
2-oxo-4-phenylbut-3-enoate (**2a**) with K_2CO_3 in CH_2Cl_2 at room temperature for 48 h (Scheme 1), the reaction afforded 2,3-dihydrofuran derivative (**3a**) in 76% yield and a single cyclopropane derivative isomer in 15% yield (**4a**).



Scheme 1. Formation of the 2,3-dihydrofuran and cyclopropane derivatives

Further, we carried out this reaction in different conditions (Table 1). It was found that when NaOH or Et_3N was employed as base, (*E*)-methyl 2-oxo-4-phenylbut-3-enoate (**2a**) was full consumed but neither traces of **3a** nor **4a** was formed (entries 2 and 3). Completely no reaction occurred between **1a** and **2a** in the presence of DABCO in CH_2Cl_2 (entry 4). When the reaction was treated in the presence of DBU (3 eq) at room temperature, **3a** was obtained in 88% and only a few trace of cyclopropanes was detected (entry 5). When the reaction was quenched at 1.5 h, the reaction become complex and the yield of 2,3-dihydrofuran derivative reduced to 24% (entry 6). The combination of DABCO with K_2CO_3 as base did not obtain **3a**, the major product was **4a** (entry 7). CH_2Cl_2 was found to be the best solvent of choice for the synthesis of **3a**, other solvents such as THF, toluene, MeCN and DMF gave **3a** in a moderate yield (entries 8-11).

Table 1. Selective synthesis of **3a** and **4a**^[a]



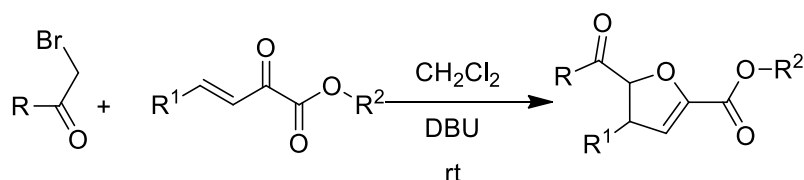
entry	base	solvent	time (h)	Yield 3a (%) ^[b]	dr (3a) ^[c]	yield 4a (%) ^[b]
1	K_2CO_3	CH_2Cl_2	48	76	1:1	15
2	NaOH	CH_2Cl_2	1	--	--	--
3	Et_3N	CH_2Cl_2	48	--	--	--

4	DABCO	CH ₂ Cl ₂	48	--	--	--
5	DBU ^[d]	CH ₂ Cl ₂	0.5	88	1:1	trace
6	DBU ^[d]	CH ₂ Cl ₂	1.5	24	--	--
7	DABCO/K ₂ CO ₃ (1:1)	CH ₂ Cl ₂	48	--	--	60 ^[e]
8	DBU ^[d]	THF	0.2	76	1:1	trace
9	DBU ^[d]	toluene	0.3	70	1:1	trace
10	DBU ^[d]	MeCN	0.2	73	1:1	trace
11	DBU ^[d]	DMF	0.2	78	1:1	trace
12	DABCO/K ₂ CO ₃ (1:1)	THF	48	--	--	56 ^[e]
13	DABCO/K ₂ CO ₃ (1:1)	MeCN	48	--	--	52 ^[e]

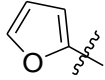

^areaction conditions: 2-bromo-1-phenylethanone (**1a**, 1.5 mmol), (*E*)-methyl 2-oxo-4-phenylbut-3-enoate (**2a**, 1.0 mmol), base (1.5 mmol), and solvent (3 mL). ^bisolated yield. ^cdetermined by ¹H NMR. ^dbase (3.0 equiv). ^emajor isomer of cyclopropane derivatives.

Having established optimal reaction conditions for the synthesis of **3a**, we investigated the scope and limitation of substrates by employing various β,γ -unsaturated α -ketoesters and halides (Table 2). It was observed that aromatic substrates bearing an electron-donating groups (entries 2 and 4), and electron-withdrawing groups (entries 3 and 5) all gave the corresponding 2,3-dihydrofuran derivatives. However, (*E*)-methyl 4-(furan-2-yl)-2-oxobut-3-enoate was not suitable for such transformation and no desired product was observed (entry 6). The ester groups in R² have less effect on the yield (entry 7). 1-Bromopropan-2-one could also react with (*E*)-methyl 2-oxo-4-phenylbut-3-enoate to afford corresponding product (entry 8).

Table 2. Synthesis of 2,3-dihydrofuran derivatives^[a]



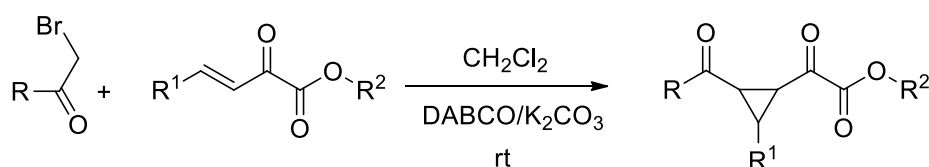
entry	R	R ¹	R ²	time (h)	dr ^[b]	product	yield(%) ^[c]
1	Ph	Ph	Me	0.3	1:1	3a	88
2	<i>p</i> -MeC ₆ H ₄	Ph	Me	0.3	1:0.8	3b	82


3	<i>p</i> -ClC ₆ H ₄	Ph	Me	0.2	1:0.9	3c	83
4	Ph	<i>p</i> -MeC ₆ H ₄	Me	0.2	1:1	3d	80
5	Ph	<i>p</i> -ClC ₆ H ₄	Me	0.2	1:0.5	3e	82
6	Ph		Me	0.4	---	--	--
7	Ph	Ph		0.3	1:0.8	3f	84
8.	Me	Ph	Me	0.2	1:1	3g	86

^areaction conditions: 2-bromo-1-phenylethanone (**1a** 1.5 mmol), β,γ -unsaturated α -ketoester (1.0 mmol), DBU (3.0 mmol), solvent (3.0 mL). ^bdetermined by ¹H NMR. ^cisolated yield.

Further, we synthesized various cyclopropane derivatives by using various β,γ -unsaturated α -ketoesters and halides with the combination of DABCO and K₂CO₃ as base in CH₂Cl₂ at room temperature (Table 3). To our delight, smooth reactions were observed for all substrate and delivered the final products in moderate yields (entries 1-6). However, the reaction of 1-bromopropan-2-one with (*E*)-methyl 2-oxo-4-phenylbut-3-enoate did not give the desired product (entry 7).

Table 3. Synthesis of cyclopropane derivatives^[a]

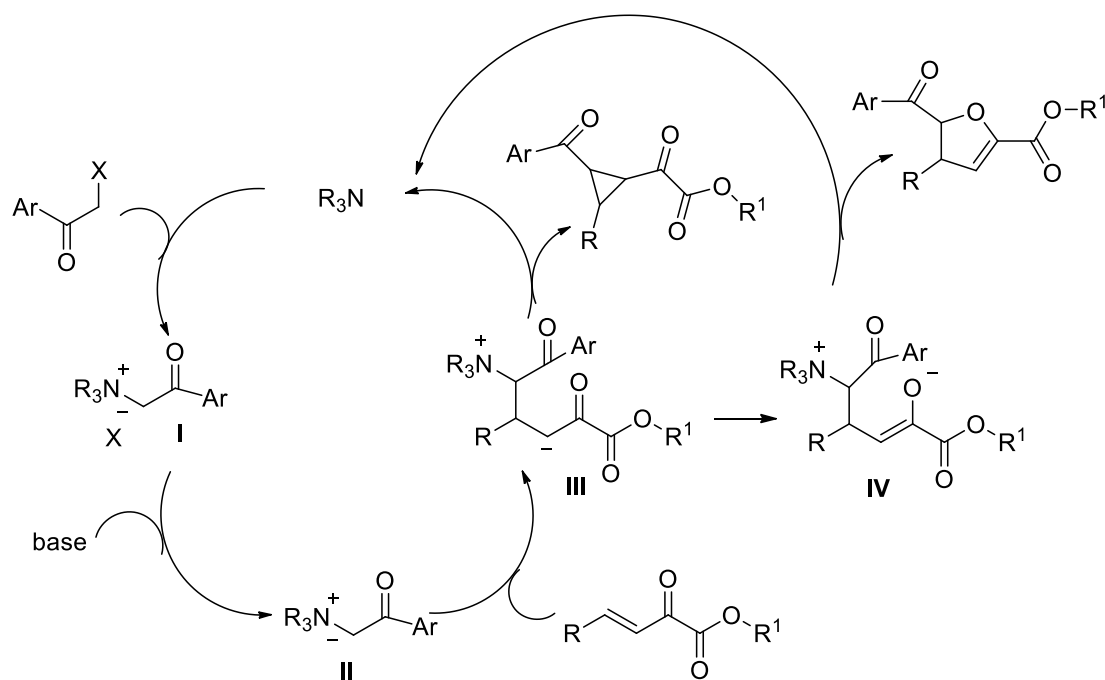


entry	R	R ¹	R ²	time (h)	dr ^[b]	product	yield(%) ^[c]
1	Ph	Ph	Me	48	0.8:1:6	4a	64
2	<i>p</i> -MeC ₆ H ₄	Ph	Me	48	1:1:5	4b	52
3	<i>p</i> -ClC ₆ H ₄	Ph	Me	48	1:1:5	4c	54
4	Ph	<i>p</i> -MeC ₆ H ₄	Me	48	1:1:6	4d	58
5	Ph	<i>p</i> -ClC ₆ H ₄	Me	48	1:1:5	4e	50
6	Ph	Ph		48	0.5:1:6	4f	66

7.	Me	Ph	Me	48	--	--
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^areaction conditions: 2-bromo-1-phenylethanone (**1a** 1.5 mmol), β,γ -unsaturated α -ketoesters (1.0 mmol), DABCO (1.5 mmol), K_2CO_3 (1.5 mmol), solvent (3.0 mL). ^bdetermined by isolated weight. ^cisolated yield of the major isomer of cyclopropane derivatives.

A plausible reaction mechanism is proposed in Scheme 2. First, the quaternary ammonium salt **I** was produced from the addition of α -phenacyl bromide to the tertiary amine. Deprotonation of **I** with base forms the ylide **II**, which undergoes Michael addition with β,γ -unsaturated α -ketoester to afford the intermediate **III**. The intermediate **III** under ring-closing reaction by internal S_N2 reactions forms cyclopropane derivatives, whereas tautomerization of the intermediate **III** leads to generation of **IV**, followed by intramolecular cyclization of **IV** to form 2,3-dihydrofurans.



Scheme 2. Formation of dihydrofurans and cyclopropanes

In summary, we have developed a convenient and efficient method for the synthesis of 2,3-dihydrofuran and cyclopropane derivatives. The reaction takes place via [4+1] or [2+1]-cycloaddition of β,γ -unsaturated α -ketoesters with α -phenacyl bromide. We believe that this method would give a new viable entry to highly functionalized dihydrofurans and cyclopropanes.

EXPERIMENTAL

Column chromatography was carried out on silica gel. The ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. All reagents were used directly as obtained commercially unless otherwise noted.

General procedure for the synthesis of 2,3-dihydrofuran derivatives

DBU (3.0 mmol) was added to a solution of 2-bromo-1-phenylethanone **1a** (1.5 mmol) and (*E*)-methyl 2-oxo-4-phenylbut-3-enoate **2a** (1.0 mmol) in CH_2Cl_2 (3 mL) at room temperature. The reaction was then stirred and followed by TLC. Upon full consumption of 2-oxo-4-phenylbut-3-enoate **2a**. The solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica (EtOAc/petroleum ether = 1:6-1:4) to give 2,3-dihydrofuran derivatives.

General procedure for the synthesis of cyclopropane derivatives

K_2CO_3 (3.0 mmol) was added to a solution of 2-bromo-1-phenylethanone **1a** (1.5 mmol), (*E*)-methyl 2-oxo-4-phenylbut-3-enoate **2a** (1.0 mmol) and DABCO (1.5 mmol) in CH_2Cl_2 (3.0 mL) at room temperature. The reaction was then stirred and followed by TLC. Upon full consumption of 2-oxo-4-phenylbut-3-enoate **2a**. The reaction was quenched with 5 mL of water and extracted with CH_2Cl_2 (3×5 mL). The combined organic extracts were washed with water and brine, and dried (MgSO_4). After evaporating the solvent under reduced pressure, the residue was purified on silica gel (gelusing EtOAc/petroleum ether = 1:6-1:4) to give cyclopropane derivatives.

Methyl 5-benzoyl-4-phenyl-4,5-dihydrofuran-2-carboxylate (**3a**)

^1H NMR (300 MHz, CDCl_3): δ 8.03 (d, $J = 6.9$, 2H), 7.63–7.26 (m, 8H), 7.26 (d, $J = 16.2$, 1H), 6.66 (d, $J = 16.2$, 1H), 4.21 (s, 1H), 3.68 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 190.9, 166.8, 135.2, 135.1, 134.2, 133.8, 128.9, 128.8, 128.5, 126.9, 120.9, 65.7, 63.1, 52.9.

^1H NMR (300 MHz, CDCl_3): δ 7.91 (d, $J = 7.2$, 2H), 7.62–7.57 (m, 3H), 7.49–7.44 (m, 5H), 6.80 (d, $J = 16.2$, 1H), 6.40 (d, $J = 16.2$, 1H), 4.63 (s, 1H), 3.92 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 190.2, 168.3, 135.7, 135.3, 135.2, 134.2, 129.0, 128.5, 128.5, 128.3, 127.0, 115.8, 64.8, 61.5, 53.5.

HRMS EI (m/z): calcd for $\text{C}_{19}\text{H}_{16}\text{O}_4$, 308.1049; found, 308.1047.

Methyl 5-(4-methylbenzoyl)-4-phenyl-4,5-dihydrofuran-2-carboxylate (**3b**)

^1H NMR (300 MHz, CDCl_3): δ 7.82 (d, $J = 6.9$, 2H), 7.28–7.20 (m, 7H), 6.80 (d, $J = 15.9$, 1H), 6.39 (d, $J = 15.9$, 1H), 4.61 (s, 1H), 3.92 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 189.6, 168.4, 145.4, 135.6, 135.4, 132.7, 129.6, 128.7, 128.5, 128.4, 126.9, 116.0, 64.9, 61.4, 53.4, 21.8.

^1H NMR (300 MHz, CDCl_3): δ 7.93–7.86 (m, 2H), 7.43–7.29 (m, 7H), 6.90 (d, $J = 15.9$, 1H), 6.66 (d, $J = 15.9$, 1H), 4.20 (s, 1H), 3.68 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 190.4, 166.9, 145.4, 135.2, 133.7, 132.6, 129.6, 128.8, 128.7, 126.9, 121.0, 65.7, 63.1, 52.9, 21.9.

HRMS EI (m/z): calcd for $\text{C}_{20}\text{H}_{18}\text{O}_4$, 322.1205; found, 322.1204.

Methyl 5-(4-chlorobenzoyl)-4-phenyl-4,5-dihydrofuran-2-carboxylate (3c)

^1H NMR (300 MHz, CDCl_3): δ 7.99–7.97 (d, $J = 8.1$, 2H), 7.50–7.43 (m, 4H), 7.38–7.25 (m, 3H), 6.89 (d, $J = 16.2$, 1H), 6.64 (d, $J = 16.2$, 1H), 4.15 (s, 1H), 3.68 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 190.0, 166.7, 140.8, 135.1, 133.8, 133.4, 130.0, 129.3, 128.9, 128.8, 126.9, 120.6, 65.7, 63.1, 53.0.

^1H NMR (300 MHz, CDCl_3): δ 7.86 (d, $J = 7.5$, 2H), 7.46–7.43 (m, 2H), 7.34–7.25 (m, 5H), 6.76 (d, $J = 15.9$, 1H), 6.37 (d, $J = 15.9$, 1H), 4.58 (s, 1H), 3.92 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 189.2, 166.1, 140.8, 135.7, 135.2, 133.5, 129.7, 129.3, 128.6, 126.9, 115.6, 64.7, 61.4, 53.5.

HRMS EI (m/z): calcd for $\text{C}_{19}\text{H}_{15}\text{ClO}_4$, 342.0659; found, 342.0654.

Methyl 5-benzoyl-4-*p*-tolyl-4,5-dihydrofuran-2-carboxylate (3d)

^1H NMR (300 MHz, CDCl_3): δ 8.02 (d, $J = 7.2$, 2H), 7.63–7.61 (m, 1H), 7.53–7.48 (m, 2H), 7.35–7.33 (m, 2H), 7.17–7.15 (m, 2H), 6.88 (d, $J = 16.2$, 1H), 6.59 (d, $J = 16.2$, 1H), 4.21 (s, 1H), 3.68 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 191.0, 166.9, 138.9, 135.1, 134.2, 133.8, 132.4, 129.5, 128.9, 128.5, 126.9, 119.8, 65.7, 63.3, 52.9, 21.3.

^1H NMR (300 MHz, CDCl_3): δ 7.96–7.79 (m, 2H), 7.60–7.47 (m, 3H), 7.15–7.04 (m, 4H), 6.76 (d, $J = 15.6$, 1H), 6.76 (d, $J = 15.9$, 1H), 4.16 (s, 1H), 3.93 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 190.2, 168.4, 138.5, 135.6, 135.2, 134.2, 132.5, 129.2, 128.9, 128.3, 126.9, 114.7, 64.9, 61.5, 53.4, 21.2.

HRMS EI (m/z): calcd for $\text{C}_{20}\text{H}_{18}\text{O}_4$, 322.1205; found, 322.1203.

Methyl 5-benzoyl-4-(4-chlorophenyl)-4,5-dihydrofuran-2-carboxylate (3e)

^1H NMR (300 MHz, CDCl_3): δ 8.01 (d, $J = 7.2$, 2H), 7.62–7.60 (m, 1H), 7.52–7.47 (m, 2H), 7.37–7.29 (m, 4H), 6.85 (d, $J = 15.9$, 1H), 6.64 (d, $J = 15.9$, 1H), 4.16 (s, 1H), 3.66 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 190.8, 166.7, 135.0, 134.5, 134.3, 133.9, 132.5, 129.0, 128.9, 128.5, 128.2, 121.6, 65.7, 63.0, 53.0.

^1H NMR (300 MHz, CDCl_3): δ 7.89 (d, $J = 7.5$, 2H), 7.80–7.56 (m, 3H), 7.48–7.03 (m, 4H), 6.74 (d, $J = 16.2$, 1H), 6.38 (d, $J = 15.9$, 1H), 4.64 (s, 1H), 3.92 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 190.1, 168.1, 135.1, 134.4, 134.3, 133.8, 129.0, 128.7, 128.3, 128.2, 128.2, 116.5, 64.8, 61.3, 53.5.

HRMS EI (m/z): calcd for $\text{C}_{19}\text{H}_{15}\text{ClO}_4$, 342.0659; found, 342.0658.

Isopropyl 5-benzoyl-4-phenyl-4,5-dihydrofuran-2-carboxylate (3f)

^1H NMR (300 MHz, CDCl_3): δ 8.06–7.90 (m, 2H), 7.63–7.25 (m, 8H), 6.93–6.34 (m, 2H), 5.28–5.22 (m, 1H), 4.58–4.21 (m, 1H), 1.41–1.01 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3): δ 190.6, 190.4, 167.3, 165.7, 135.5, 135.5, 135.3, 135.3, 135.1, 134.2, 134.1, 133.7, 128.9, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 126.9, 121.3, 116.2, 70.7, 70.3, 66.0, 64.8, 62.8, 61.6, 21.7, 21.4, 21.3.

HRMS EI (m/z): calcd for $\text{C}_{21}\text{H}_{20}\text{O}_4$, 336.1362; found, 336.1362.

Methyl 5-acetyl-4-phenyl-4,5-dihydrofuran-2-carboxylate (3g)

^1H NMR (300 MHz, CDCl_3): δ 7.34–7.23 (m, 5H), 6.88–6.82 (m, 1H), 6.46–6.41 (m, 1H), 3.94–3.55 (4H), 2.24–2.06 (3H). ^{13}C NMR (75 MHz, CDCl_3): δ 201.51, 200.58, 167.96, 166.85, 135.52, 135.13, 133.55, 128.72, 126.90, 126.87, 121.15, 116.44, 66.66, 65.31, 63.09, 60.91, 53.26, 53.01, 28.31, 27.57, 23.46, 22.67.

HRMS EI (m/z): calcd for $\text{C}_{16}\text{H}_{18}\text{O}_4$, 274.1205; found, 274.1201.

Methyl 2-(2-benzoyl-3-phenylcyclopropyl)-2-oxoacetate (4a)

^1H NMR (300 MHz, CDCl_3): δ 7.96–7.93 (m, 2H), 7.57–7.23 (m, 7H), 3.87 (s, 3H), 3.46–3.41 (m, 2H), 3.33–3.30 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3): δ 194.2, 188.7, 161.0, 137.4, 136.0, 133.8, 128.9, 128.8, 128.6, 127.6, 126.5, 53.2, 39.5, 34.8, 32.2.

HRMS EI (m/z): calcd for $\text{C}_{19}\text{H}_{16}\text{O}_4$, 308.1049; found, 308.1046.

Methyl 2-(2-(4-methylbenzoyl)-3-phenylcyclopropyl)-2-oxoacetate (4b)

^1H NMR (300 MHz, CDCl_3): δ 7.87–7.84 (m, 2H), 7.35–7.24 (m, 7H), 3.87 (s, 3H), 3.45–3.42 (m, 2H), 3.30–3.27 (m, 1H), 2.39 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 193.8, 188.8, 161.0, 144.8, 137.6, 133.6, 129.5, 128.9, 128.8, 127.5, 126.5, 53.2, 39.6, 34.7, 32.0, 21.8.

HRMS EI (m/z): calcd for $\text{C}_{20}\text{H}_{18}\text{O}_4$, 322.1205; found, 322.1199.

Methyl 2-(2-(4-chlorobenzoyl)-3-phenylcyclopropyl)-2-oxoacetate (4c)

^1H NMR (300 MHz, CDCl_3): δ 7.90–7.87 (m, 2H), 7.43–7.23 (m, 7H), 3.88 (s, 3H), 3.42–3.33 (m, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 193.0, 188.5, 160.9, 140.3, 137.2, 134.4, 130.0, 129.1, 129.0, 127.7, 126.4, 53.3, 39.3, 34.8, 32.3.

HRMS EI (m/z): calcd for $\text{C}_{19}\text{H}_{15}\text{ClO}_4$, 342.0659; found, 342.0657.

Methyl 2-(2-benzoyl-3-*p*-tolylcyclopropyl)-2-oxoacetate (4d)

^1H NMR (300 MHz, CDCl_3): δ 7.96–7.93 (m, 2H), 7.57–7.55 (m, 1H), 7.46–7.41 (m, 2H), 7.25–7.15 (m, 4H), 3.88 (s, 3H), 3.43–3.39 (m, 2H), 3.29–3.27 (m, 1H), 2.45 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ

194.3, 188.8, 161.0, 137.3, 136.1, 134.4, 133.8, 129.6, 128.8, 128.6, 126.4, 53.2, 39.8, 34.8, 32.1, 21.1.

HRMS EI (m/z): calcd for $C_{20}H_{18}O_4$, 322.1205; found, 322.1203.

Methyl 2-(2-benzoyl-3-(4-chlorophenyl)cyclopropyl)-2-oxoacetate (4e)

1H NMR (300 MHz, $CDCl_3$): δ 7.94–7.91 (m, 2H), 7.60–7.55 (m, 1H), 7.47–7.42 (m, 2H), 7.34–7.31 (m, 2H), 7.19–7.17 (m, 2H), 3.87 (s, 3H), 3.42–3.38 (m, 2H), 3.30–3.25 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.9, 188.3, 160.9, 136.0, 135.9, 133.9, 133.3, 129.1, 128.8, 128.6, 127.9, 53.3, 39.3, 34.7, 31.4.

HRMS EI (m/z): calcd for $C_{19}H_{15}ClO_4$, 342.0659; found, 342.0656.

Isopropyl 2-(2-benzoyl-3-phenylcyclopropyl)-2-oxoacetate (4f)

1H NMR (300 MHz, $CDCl_3$): δ 7.98–7.96 (m, 2H), 7.57–7.25 (m, 8H), 5.16–5.12 (m, 1H), 3.45–3.42 (m, 2H), 3.33–3.28 (m, 1H), 1.33–1.31 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.0, 189.1, 160.1, 137.6, 136.2, 133.7, 128.9, 128.7, 128.6, 128.3, 127.5, 126.5, 70.8, 39.0, 35.1, 32.1, 29.7, 21.6.

HRMS EI (m/z): calcd for $C_{21}H_{20}O_4$, 336.1362; found, 336.1360.

ACKNOWLEDGEMENTS

Project was supported by the Natural Science Foundation of Anhui Higher Education Institution (no. KJ2013B166, KJ2013Z232) and Chaohu College Foundation for Doctor in China.

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