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## SELECTIVE SYNTHESIS OF 2,3-DIHYDROFURAN OR CYCLOPROPANE DERIVATIVES VIA TANDEM REACTION OF $\beta,\gamma$ -UNSATURATED $\alpha$ -KETOESTERS WITH HALIDES

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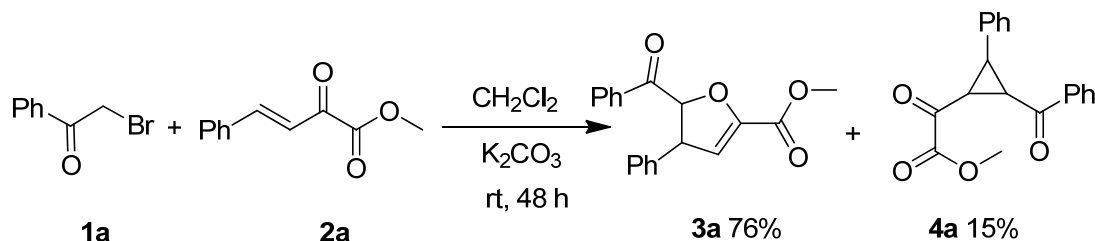
**Abstract** – 2,3-Dihydrofuran or cyclopropane derivatives were prepared with high selectivity via reaction of  $\beta,\gamma$ -unsaturated  $\alpha$ -ketoesters with  $\alpha$ -phenacyl bromide in different conditions.

Dihydrofuran derivatives which are commonly found in the molecular skeleton of natural products and bioactive substances have been studied for many years.<sup>1-3</sup> Cyclopropane derivatives are also important in the field of organic synthesis.<sup>4,5</sup> A number of methods for the synthesis of them have been reported in the literature.<sup>6-9</sup> Among them, stereoselective synthesis of 2,3-dihydrofuran or cyclopropane derivatives via the reaction of ylides with different  $\alpha$ ,  $\beta$ -unsaturated compounds have been reported.<sup>10-14</sup> 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,  $\beta,\gamma$ -unsaturated  $\alpha$ -ketoester has recently been found useful utility in organic synthesis.<sup>15,16</sup> In this work, we report the selective synthesis of 2,3-dihydrofuran or cyclopropane derivatives via reaction of  $\beta,\gamma$ -unsaturated  $\alpha$ -ketoesters with  $\alpha$ -phenacyl bromide in different conditions.

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

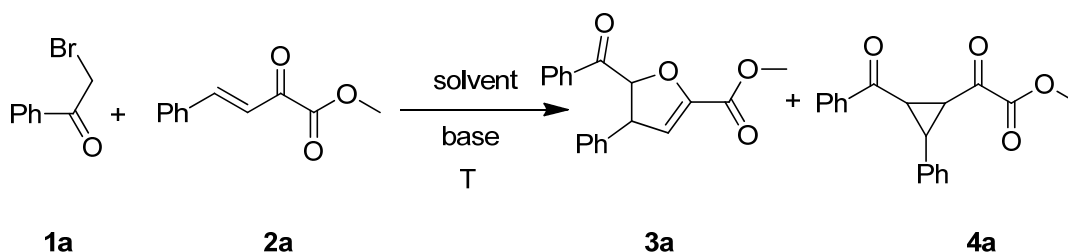
2-oxo-4-phenylbut-3-enoate (**2a**) with  $K_2CO_3$  in  $CH_2Cl_2$  at room temperature for 48 h (Scheme 1), the reaction afforded 2,3-dihydrofuran derivative (**3a**) in 76% yield and a single cyclopropane derivative isomer in 15% yield (**4a**).



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**<sup>[a]</sup>



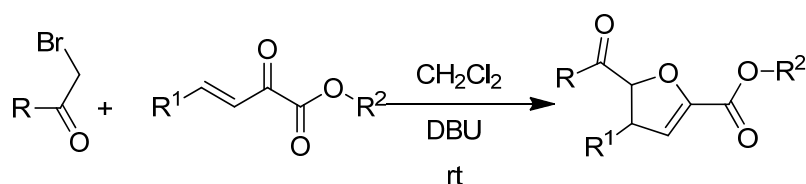
entry	base	solvent	time (h)	Yield 3a (%) <sup>[b]</sup>	dr (3a) <sup>[c]</sup>	yield 4a (%) <sup>[b]</sup>
1	$K_2CO_3$	$CH_2Cl_2$	48	76	1:1	15
2	NaOH	$CH_2Cl_2$	1	--	--	--
3	$Et_3N$	$CH_2Cl_2$	48	--	--	--

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

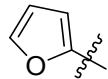

<sup>a</sup>reaction conditions: 2-bromo-1-phenylethanone (**1a** 1.5 mmol), (*E*)-methyl 2-oxo-4-phenylbut-3-enoate (**2a**, 1.0 mmol), base (1.5 mmol), and solvent (3 mL). <sup>b</sup>isolated yield. <sup>c</sup>determined by <sup>1</sup>H NMR. <sup>d</sup>base (3.0 equiv). <sup>e</sup>major isomer of cyclopropane derivatives.

Having established optimal reaction conditions for the synthesis of **3a**, we investigated the scope and limitation of substrates by employing various  $\beta,\gamma$ -unsaturated  $\alpha$ -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 R<sup>2</sup> 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<sup>[a]</sup>



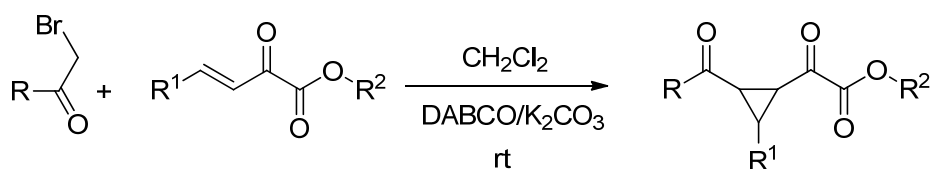
entry	R	R <sup>1</sup>	R <sup>2</sup>	time (h)	dr <sup>[b]</sup>	product	yield(%) <sup>[c]</sup>
1	Ph	Ph	Me	0.3	1:1	3a	88
2	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	Ph	Me	0.3	1:0.8	3b	82


3	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	Ph	Me	0.2	1:0.9	3c	83
4	Ph	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	Me	0.2	1:1	3d	80
5	Ph	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	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

<sup>a</sup>reaction conditions: 2-bromo-1-phenylethanone (**1a** 1.5 mmol),  $\beta,\gamma$ -unsaturated  $\alpha$ -ketoester (1.0 mmol), DBU (3.0 mmol), solvent (3.0 mL). <sup>b</sup>determined by <sup>1</sup>H NMR. <sup>c</sup>isolated yield.

Further, we synthesized various cyclopropane derivatives by using various  $\beta,\gamma$ -unsaturated  $\alpha$ -ketoesters and halides with the combination of DABCO and K<sub>2</sub>CO<sub>3</sub> as base in CH<sub>2</sub>Cl<sub>2</sub> 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<sup>[a]</sup>

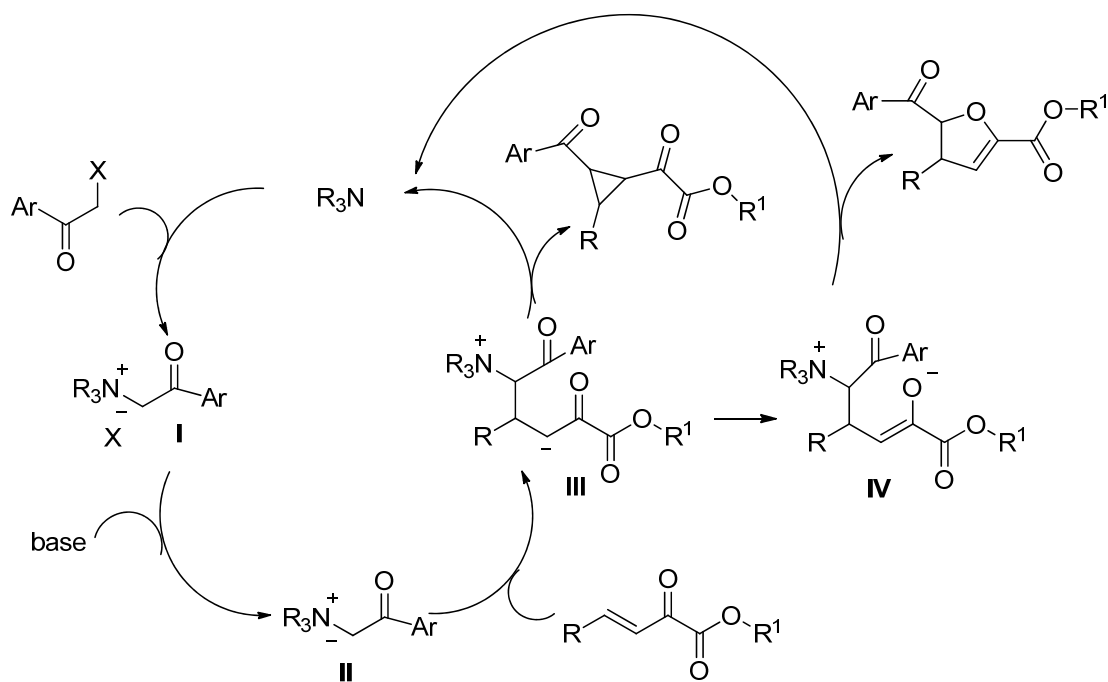


entry	R	R <sup>1</sup>	R <sup>2</sup>	time (h)	dr <sup>[b]</sup>	product	yield(%) <sup>[c]</sup>
1	Ph	Ph	Me	48	0.8:1:6	4a	64
2	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	Ph	Me	48	1:1:5	4b	52
3	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	Ph	Me	48	1:1:5	4c	54
4	Ph	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	Me	48	1:1:6	4d	58
5	Ph	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	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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<sup>a</sup>reaction conditions: 2-bromo-1-phenylethanone (**1a** 1.5 mmol),  $\beta,\gamma$ -unsaturated  $\alpha$ -ketoesters (1.0 mmol), DABCO (1.5 mmol),  $K_2CO_3$  (1.5 mmol), solvent (3.0 mL). <sup>b</sup>determined by isolated weight. <sup>c</sup>isolated 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  $\alpha$ -phenacyl bromide to the tertiary amine. Deprotonation of **I** with base forms the ylide **II**, which undergoes Michael addition with  $\beta,\gamma$ -unsaturated  $\alpha$ -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  $\beta,\gamma$ -unsaturated  $\alpha$ -ketoesters with  $\alpha$ -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  $^1\text{H}$  and  $^{13}\text{C}$  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  $\text{CH}_2\text{Cl}_2$  (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

$\text{K}_2\text{CO}_3$  (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  $\text{CH}_2\text{Cl}_2$  (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  $\text{CH}_2\text{Cl}_2$  (3×5 mL). The combined organic extracts were washed with water and brine, and dried ( $\text{MgSO}_4$ ). 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**)

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  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).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  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.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  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).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  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**)

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  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).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  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.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  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).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  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)**

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  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).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  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.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  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).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  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)**

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  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).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  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.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  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).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  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)**

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  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).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  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.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  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).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  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)**

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  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).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  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)**

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  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).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  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)**

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  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).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  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)**

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  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).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  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)**

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.90–7.87 (m, 2H), 7.43–7.23 (m, 7H), 3.88 (s, 3H), 3.42–3.33 (m, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  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)**

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  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).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$



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,  $CDCl_3$ ):  $\delta$  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,  $CDCl_3$ ):  $\delta$  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,  $CDCl_3$ ):  $\delta$  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,  $CDCl_3$ ):  $\delta$  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.

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