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Palladium-Catalyzed Intermolecular Oxyvinylcyclization of Alkenes with Alkynes: An Approach to 3-Methylene γ-Lactones and Tetrahydrofurans

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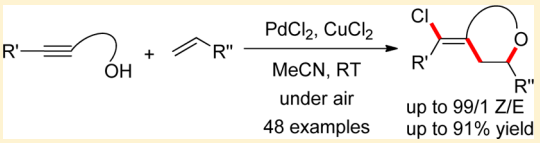
Supporting Information

ABSTRACT: A novel chloropalladation-initiated intermolecular oxyvinylcyclization of alkenes with alkynoic acids or alkynols is developed. This protocol provides a series of 3-methylene γ-lactone and tetrahydrofuran derivatives in moderate to excellent yields with high stereoselectivities in the presence of $PdCl_2$ and $CuCl_2$ or $CuCl_2·2H_2O$. Besides a broad substrate scope, this method has the advantages of mild reaction conditions and easily accessible starting materials. Furthermore, the construction of C−Cl, C(sp^2)−C(sp^3), and C−O bonds in one step was also achieved in this transformation.

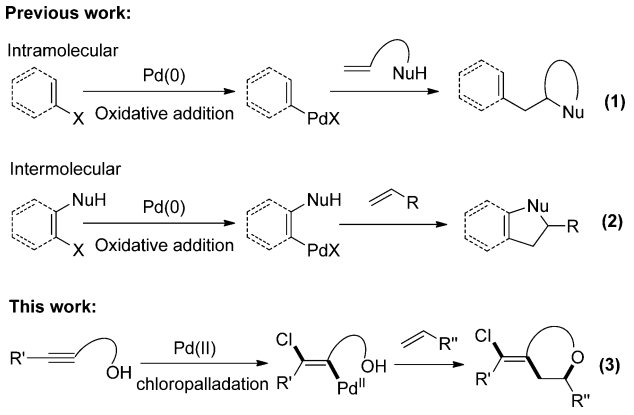


INTRODUCTION

Oxygen-containing five-membered heterocycles, particularly γ-lactones and tetrahydrofurans, are commonly found in many biologically active natural products and pharmaceutical compounds.[1] Accordingly, much effort has been devoted to construct these heterocyclic frameworks,[2] among which, palladium-catalyzed cyclization reaction of alkenes and C(sp^2)-Pd^{II} intermediates is one of the powerful tools.[3] Significant progress has been achieved in palladium-catalyzed intramolecular or intermolecular cyclization reactions of alkenes with aryl or vinyl halides via oxidative addition by Pd^0 (Scheme 1, eqs 1 and 2).[4−10] However, hydrogen halide is always formed during the reaction process with oxidative addition of halides, and a strong base is necessary. Compared to oxidative addition of halides by Pd^0, nucleopalladation by Pd^{II}-initiated cyclization of alkenes showed high reactivity and functional group tolerance under mild conditions.[11−17] On the other hand, nucleopalladation of alkyne-initiated reactions could provide efficient and convenient access to both carbon−carbon and carbon−heteroatom bonds in an atom-economical way.[18]

Our group has continuous interest in developing new transformations based on vinylpalladium species, which can be easily obtained from nucleopalladation of alkynes.[18,19] In 2012, we reported a palladium-catalyzed intermolecular oxyvinylcyclization reaction of alkenes with alkynoates or alkynamides, which provided different substituted α-methylene γ-lactones in good yields.[20] However, either a complex substrate or high temperature was required in this reaction under O_2 atmosphere. Considering that a hydrolysis process of amides or esters and reductive elimination of palladium−oxygen bond would occur during this cyclization reaction of alkenes with alkynoates or alkynamides, we envisioned that the substrates containing a hydroxyl group such as alkynoic acids and alkynols could be employed directly in such reactions. Herein, we report an efficient palladium-catalyzed intermolecular oxyvinylcyclization of alkenes with alkynoic acids or alkynols at room temperature under air to afford diverse α-methylene γ-lactones or 3-methylene tetrahydrofuran derivatives (Scheme 1, eq 3).

Scheme 1. Pd-Catalyzed Oxyvinylcyclization of Alkenes with Halides vs Alkynes



RESULTS AND DISCUSSION

We began our investigation with 3-phenylpropiolic acid (**1a**) and styrene (**2a**) as the model reaction (Table 1). Initial screening found that product **3aa** was obtained in 43% GC yield with high stereoselectivity (Z/E = 85/15) when using $PdCl_2$ (5 mol %) as the catalyst and $CuCl_2$ or $CuCl_2·2H_2O$ (2 equiv) as the additive in DMF at room temperature under air (entry 1). Other solvents such as THF, DCE, and MeCN were also tested (entries 2−4). Notably, MeCN was identified as the

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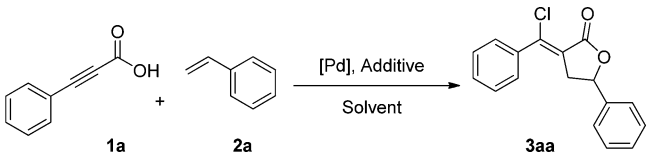
Table 1. Optimization of Reaction Conditions[a]



1a 2a 3aa

entry	[Pd] (mol %)	additive (equiv)	solvent	time (h)	yield[b] (%)	Z/E[c]
1	$PdCl_2$ (5)	$CuCl_2$ (2)	DMF	7	43	85/15
2	$PdCl_2$ (5)	$CuCl_2$ (2)	DCE	5	56	92/8
3	$PdCl_2$ (5)	$CuCl_2$ (2)	THF	5	70	90/10
4	**$PdCl_2$ (5)**	**$CuCl_2$ (2)**	**CH_3CN**	**5**	**93 (89)**	**93/7**
5	$Pd(OAc)_2$ (5)	$CuCl_2$ (2)	CH_3CN	5	88	90/10
6	$Pd(dba)_2$ (5)	$CuCl_2$ (2)	CH_3CN	5	60	91/9
7		$CuCl_2$ (2)	CH_3CN	5	n.d.	nd
8	$PdCl_2$ (5)	LiCl (4)	CH_3CN	12	trace	nd
9	$PdCl_2$ (5)	$CuCl_2$ (1)	CH_3CN	7	45	86/14
10	$PdCl_2$ (2.5)	$CuCl_2$ (2)	CH_3CN	7	89	91/9
11[d]	$PdCl_2$ (5)	$CuCl_2$ (2)	CH_3CN	1	84	65/35

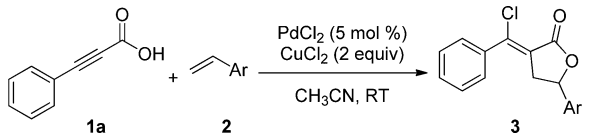
[a]The reaction was carried out with **1** (0.20 mmol), **2** (0.24 mmol), Pd catalyst, and additive in solvent (0.5 mL) at room temperature. nd = not detected. [b]GC yield, isolated yield in parentheses. [c]Determined by GC. [d]The reaction was performed at 80 °C.

optimal solvent for the formation of **3aa** (entry 4). Slightly lower yield was observed with $Pd(OAc)_2$ or $Pd(dba)_2$ as the catalyst (entries 5 and 6). However, no reaction occurred in the absence of palladium catalyst or replacement of $CuCl_2$ by LiCl (entries 7 and 8). These results suggested that both $PdCl_2$ and $CuCl_2$ are crucial for the successful of this transformation. The loading of $PdCl_2$ had a slight effect on the yield and stereoselectivity of the product, but the additive had an obvious one (entries 9 and 10). However, a significant decrease of stereoselectivity was observed when the reaction was performed at reflux (entry 11). Thus, the optimal reaction conditions were $PdCl_2$ (5 mol %) and $CuCl_2$ or $CuCl_2{\cdot}2H_2O$ (2 equiv) in CH_3CN at room temperature under air (Table 1, entry 4).

Under the optimized reaction conditions, we then investigated the substrate scope of this intermolecular Pd-catalyzed oxyvinylcyclization of 3-phenylpropiolic acid (**1a**) and aryl alkenes (**2**) (Table 2). It was found that good to excellent yields and stereoselectivities were achieved regardless of the electronic properties and substitution pattern of the aryl alkenes. Both electron-withdrawing substituents, such as fluoro and bromo groups, and electron-donating substituents such as methoxy group could be tolerated in this reaction system, providing the corresponding products **3ab**−**am** in good yields (80−91%) and stereoselectivities (entries 2−10, 11−13). The structure of product was further confirmed by X-ray crystallography and NOE NMR (see the Supporting Information for details).[21] However, multisubstituted styrenes (**2n** and **2o**) showed slightly lower yields than monosubstituted ones, which was probably caused by the steric effects (entries 14 and 15). Good yield and stereoselectivity could be also obtained when using 2-vinylnaphthalene (**2p**) and 2-vinylthiophene (**2q**) as the substrates (entries 16 and 17). Furthermore, 2-vinylpyridine could transfer to the corresponding product **3ar** in 50% yield with excellent Z/E ratio equaling to 96/4 under the optimized conditions (entry 18). In addition, when α-methylstyrene (**2s**) was employed, better results could be achieved (82% yield and Z/E = 92/8) (entry 19).

After the success of palladium-catalyzed intermolecular oxyvinylcyclization of 3-phenylpropiolic acid with arylalkenes, the reactions of alkylalkenes were also investigated (Table 3). Various alkylalkenes including acrylic esters (entries 1−3),

Table 2. Substrate Scope of Pd-Catalyzed Intermolecular Oxyvinylcyclization of Arylalkenes with 1a[a]



1a 2 3

entry	Ar	product	time (h)	yield (%)	Z/E[b]
1	Ph (**2a**)	**3aa**	5	89	93/7
2	2-ClC_6H_4 (**2b**)	**3ab**	8	78	91/9
3	3-ClC_6H_4 (**2c**)	**3ac**	5	89	96/4
4	4-FC_6H_4 (**2d**)	**3ad**	5	88	97/3
5	4-ClC_6H_4 (**2e**)	**3ae**	5	91	92/8
6	4-BrC_6H_4 (**2f**)	**3af**	6	90	95/5
7	4-CNC_6H_4 (**2g**)	**3ag**	8	84	95/5
8	4-$COOMeC_6H_4$ (**2h**)	**3ah**	8	87	97/3
9	4-$NO_2C_6H_4$ (**2i**)	**3ai**	7	85	92/8
10	4-$CF_3C_6H_4$ (**2j**)	**3aj**	7	79	96/4
11	4-MeC_6H_4 (**2k**)	**3ak**	5	86	98/2
12	4-*t*-BuC_6H_4 (**2l**)	**3al**	7	80	91/9
13	4-$MeOC_6H_4$ (**2m**)	**3am**	6	85	97/3
14	2,4,6-trimethyl-C_6H_2 (**2n**)	**3an**	8	68	94/6
15	perfluorophenyl (**2o**)	**3ao**	8	71	90/10
16	2-naphthyl (**2p**)	**3ap**	5	89	93/7
17	2-thiophene-yl (**2q**)	**3aq**	8	75	92/8
18	2-pyridyl (**2r**)	**3ar**	8	50	96/4
19	α-methylstyrene (**2s**)	**3as**	5	82	92/8

[a]Reaction conditions: unless otherwise noted, all reactions were performed with **1a** (0.5 mmol), **2** (0.6 mmol), $CuCl_2$ (1.0 mmol), and $PdCl_2$ (5 mol %) in 1.0 mL of acetonitrile at room temperature for 5−8 h. [b]Determined by GC.

acrylamide derivatives (entries 4 and 5), and vinyl ketone (entry 6) could be used in the reaction to afford the desired products **5aa**−**af** in good yields and stereoselectivities. Unfortunately, only moderate yield (49%) could be obtained when acrylonitrile (**4g**) was employed in this reaction (entry 7) for 8 h. Notably, linear alkenes **4h** and **4i** were also suitable for this reaction to give the corresponding products in good yields and stereoselectivities (entries 8 and 9).

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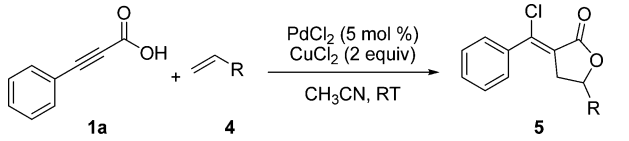
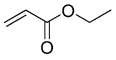
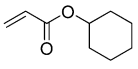
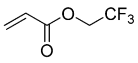
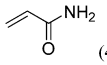
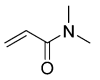
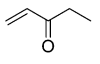
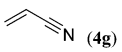
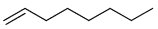
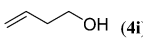
Table 3. Substrate Scope of Pd-Catalyzed Intermolecular Oxyvinylcyclization of Alkenes 4 with 1a[a]



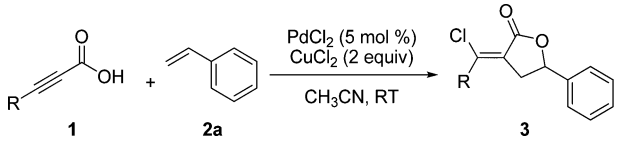
1a 4 5

Entry	Substrate (4)	Product	Time (h)	Yield (%)	Z/E[b]
1	 (4a)	**5aa**	5	89	94/6
2	 (4b)	**5ab**	5	85	91/9
3	 (4c)	**5ac**	5	83	92/8
4	 (4d)	**5ad**	8	65	90/10
5	 (4e)	**5ae**	8	78	91/9
6	 (4f)	**5af**	5	86	91/9
7	 (4g)	**5ag**	8	49	94/6
8	 (4h)	**5ah**	7	81	96/4
9	 (4i)	**5ai**	7	88	96/4

[a]Reaction conditions: unless otherwise noted, all reactions were performed with **1a** (0.5 mmol), **4** (0.6 mmol), $CuCl_2$ (1.0 mmol), and $PdCl_2$ (5 mol %) in 1.0 mL of acetonitrile at room temperature for 5–8 h. [b]Determined by GC.

Next, the reactions of styrene with a variety of alkynoic acids were also examined (Table 4). The alkynoic acids with either electron-withdrawing (**1b-1g**) or electron-donating substituents (**3h** and **3i**) could be transferred to the desired products **3ba–la** in good yields (78–91%) and stereoselectivities (*Z*/*E* up to 98/2) (entries 1–6, 7 and 8). To our delight, this method was successfully applied to 3-alkylpropiolic acids, and these substrates were smoothly converted to the cyclization products (**3ja** and **3ka**) in high yields with excellent stereoselectivities (88% with *Z*/*E* ratio = 98/2 and 90% with *Z*/*E* ratio = 99/1) (entries 9 and 10). Unfortunately, a lower stereoselectivity was observed in the reaction of 3-cyclopropylpropiolic acid (**1l**) and styrene (entry 11).

Table 4. Substrate Scope of Pd-Catalyzed Intermolecular Oxyvinylcyclization of Styrene with Alkynoic Acids 1[a]



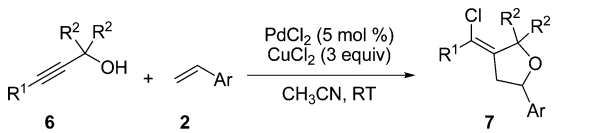
1 2a 3

entry	R	product	time (h)	yield (%)	Z/E[b]
1	2-ClC_6H_4 (**1b**)	**3ba**	7	82	90/10
2	3-ClC_6H_4 (**1c**)	**3ca**	5	85	97/3
3	4-ClC_6H_4 (**1d**)	**3da**	5	91	95/9
4	4-FC_6H_4 (**1e**)	**3ea**	7	88	91/9
5	4-BrC_6H_4 (**1f**)	**3fa**	5	90	95/5
6	4-$NO_2C_6H_4$ (**1g**)	**3ga**	7	78	98/2
7	4-$MeOC_6H_4$ (**1h**)	**3ha**	5	85	90/10
8	4-MeC_6H_4 (**1i**)	**3ia**	5	89	93/7
9	methyl (**1j**)	**3ja**	5	90	98/2
10	pentyl (**1k**)	**3ka**	5	88	99/1
11	cyclopropyl (**1l**)	**3la**	5	90	70/30

[a]Reaction conditions: unless otherwise noted, all reactions were performed with **1** (0.5 mmol), **2a** (0.6 mmol), $CuCl_2$ (1.0 mmol), and $PdCl_2$ (5 mol %) in 1.0 mL of acetonitrile at room temperature for 5–7 h. [b]Determined by GC.

Encouraged by the results of palladium-catalyzed intermolecular oxyvinylcyclization of alkenes and alkynoic acids, we envisioned that alkynols could also undergo a nucleopalladation process to give the corresponding tetrahydrofuran products. To our delight, it was found that under the above optimized conditions, the reaction of 2-methyl-4-phenylbut-3-yn-2-ol (**6a**) and styrene (**2a**) afforded the corresponding product **7aa** in 73% yield with moderate stereoselectivity (*Z*/*E* = 82/18) for 12 h. After simple optimization of the reaction conditions, **7aa** could be obtained in 74% yield with 93/7 *Z*/*E* ratio at room temperature for 12 h when the loading of additive $CuCl_2$ was increased (Table 5, entry 1). Other substituted phenyl alkenes

Table 5. Substrate Scope of Pd-Catalyzed Intermolecular Oxyvinylcyclization of Alkenes with Alkynols[a]



6 2 7

	6							
entry	R^1	R^2		2, Ar	product	time (h)	yield (%)	Z/E[b]
1[c]	Ph	Me	**6a**	**2a**	**7aa**	12	74	93/7
2	Ph	Me	**6a**	**2d**	**7ad**	14	78	94/6
3	Ph	Me	**6a**	**2f**	**7af**	12	71	93/7
4	Ph	Me	**6a**	**2t**	**7at**	12	68	94/6
5	Ph	H	**6b**	**2a**	**7ba**	12	76	95/5
6	2-F-Ph	Me	**6c**	**2a**	**7ca**	16	52	92/8
7	3-Me-Ph	Me	**6d**	**2a**	**7da**	14	72	96/4
8	4-Me-Ph	Me	**6e**	**2a**	**7ea**	12	71	95/5
9	4-Cl-Ph	Me	**6f**	**2a**	**7fa**	12	73	96/4
10	2-pyridyl	Me	**6g**	**2a**	**7ga**	24	nd	

[a]Reaction conditions: all reactions were performed with **1** (0.5 mmol), **2a** (0.6 mmol), $CuCl_2$ (1.5 mmol), and $PdCl_2$ (5 mol %) in 1.0 mL of acetonitrile at room temperature for 12–24 h. nd = not detected. [b]Determined by GC. [c]Under the optimized conditions, the corresponding product was obtained in 73% yield and *Z*/*E* = 85/15.

such as 4-fluorostyrene (**2d**), 4-bromrostyrene (**2f**), and 3-methylstyrene (**2t**) could be also converted to the desired products in good yields with excellent stereoselectivities (entries 2–4). In addition, different substituted alkynols could also be used to construct the 3-methylenetetrahydrofuran derivatives **7ba–fa** in moderate to good yields (52–76%) with excellent stereoselectivities (entries 5–9). Disappointingly, no desired product was observed when pyridine-substituted alkynol was employed in the reaction (entry 10).

On the basis of the above observations and literatures,[11a,19,20] we propose a plausible mechanism as depicted in Scheme 2. First, vinylpalladium intermediate **I** was generated by *trans*-

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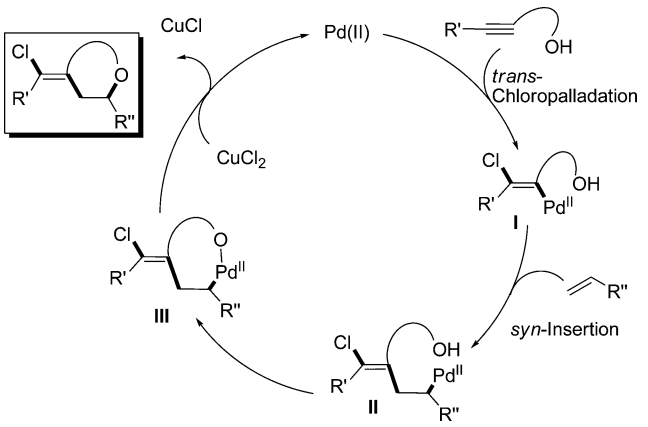
Scheme 2. Plausible Mechanism



chloropalladation of the alkyne moiety. Then, *syn*-insertion of alkene with intermediate **I** occurred to generate alkylpalladium **II**. Simultaneously, the alkylpalladium species **II** coordinated to the oxygen atom of the OH group and generated the intermediate **III**. Subsequently, C−O bond formation by reductive elimination and regeneration of the active Pd(II) species by oxidation took place in the presence of $CuCl_2$, and the catalytic cycle was completed.

CONCLUSION

In summary, we have developed a new palladium-catalyzed intermolecular oxyvinylcyclization of alkenes with alkynoic acids or alkynols under mild conditions. This transformation provides a convenient and efficient method for the synthesis of α-methylene γ-lactones and tetrahydrofuran derivatives in moderate to excellent yields with high regio- and stereoselectivities. Moreover, this oxyvinylcyclization process also provides a new tool for the construction of C−Cl, C(sp^2)−C(sp^3), and C−O bonds in a single step. The readily available starting materials and mild reaction conditions are some of the additional features of this protocol.

EXPERIMENTAL SECTION

General Methods. Unless otherwise noted, all purchased chemicals were used without further purification. ^{1}H and ^{13}C NMR spectra were measured on a 400 MHz NMR spectrometer. IR spectra were measured with an infrared spectrometer on potassium bromide pellets. GC−MS data were obtained using electron ionization. HRMS was obtained with a LCMS−IT-TOF mass spectrometer. TLC was performed using commercially available 100−400 mesh silica gel plates (GF_{254}). The alkynoic acids **1b−l**[22] and alkynols **6a−g**[23] were prepared according to the literature.

General Procedure. A mixture of propiolic acid **1** or alkynol **6** (0.5 mmol), alkene **2** or **4** (0.60 mmol), $PdCl_2$ (5 mol %), $CuCl_2$ or $CuCl_2{\cdot}2H_2O$ (1.0 or 1.5 mmol), and MeCN (1 mL) was placed in a test tube (10 mL) equipped with a magnetic stirring bar. The mixture was stirred at room temperature under air. After the reaction was completed, purification of the mixture on a preparative TLC afforded the desired products.

*(Z)-3-(Chloro(phenyl)methylene)-5-phenyldihydrofuran-2(3H)-one (**3aa**):* yield 89% (126.4 mg); white solid; mp 65−67 °C; TLC R_f = 0.35 (PE/EA = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50−7.49 (m, 2H), 7.43−7.30 (m, 8H), 5.40 (t, J = 8.0 Hz, 1H), 3.43 (dd, J = 16.4 Hz, J = 7.2 Hz, 1H), 3.05 (dd, J = 16.4 Hz, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 140.1, 139.3, 137.7, 130.3, 128.9, 128.7, 128.6, 128.2, 125.3, 122.4, 76.9, 40.0 ppm; IR ν_{max} (KBr)/cm^{-1} 3743, 2922, 2335, 1754, 1644, 1200, 757, 698; MS (EI) m/z 77, 115, 150, 178, 202, 284.

*(Z)-3-(Chloro(phenyl)methylene)-5-(2-chlorophenyl)-dihydrofuran-2(3H)-one (**3ab**):* yield 78% (124.0 mg); white solid; mp 112−114 °C; TLC R_f = 0.48 (PE/EA = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51−7.49 (m, 3H), 7.45−7.44 (m, 3H), 7.37−7.28 (m, 3H), 5.75 (t, J = 7.2 Hz, 1H), 3.65 (dd, J = 16.8 Hz, J = 7.6 Hz, 1H), 3.05 (dd, J = 17.2 Hz, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 140.8, 137.5, 137.4, 131.2, 130.4, 129.7, 129.6, 128.6, 128.2, 127.4, 126.0, 121.6, 74.0, 38.5 ppm; IR ν_{max} (KBr)/cm^{-1} 3745, 3363, 2919, 1699, 1515, 954, 457; MS (EI) m/z 77, 89, 115, 150, 178, 202, 318; HRMS-ESI (m/z) calcd for $C_{17}H_{13}Cl_2O_2$ [M + H]$^+$ 319.0287, found 319.0287.

*(Z)-3-(Chloro(phenyl)methylene)-5-(3-chlorophenyl)-dihydrofuran-2(3H)-one (**3ac**):* yield 89% (141.5 mg); white solid; mp 129−131 °C; TLC R_f = 0.25 (PE/EA = 10:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50−7.47 (m, 2H), 7.44−7.42 (m, 3H), 7.31−7.30 (m, 3H), 7.20−7.18 (m, 1H), 5.46 (t, J = 7.6 Hz, 1H), 3.45 (dd, J = 16.4 Hz, J = 7.2 Hz, 1H), 3.02 (dd, J = 16.4 Hz, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 141.3, 140.7, 137.6, 134.9, 130.4, 130.2, 128.8, 128.6, 128.1, 125.5, 123.4, 121.8, 75.9, 39.7 ppm; IR ν_{max} (KBr)/cm^{-1} 3746, 2362, 1761, 1638, 1200, 1089, 695; MS (EI) m/z 77, 89, 115, 150, 178, 202, 281, 318; HRMS-ESI (m/z) calcd for $C_{17}H_{13}Cl_2O_2$ [M + H]$^+$ 319.0287, found 319.0287.

*(Z)-3-(Chloro(phenyl)methylene)-5-(4-fluorophenyl)-dihydrofuran-2(3H)-one (**3ad**):* yield 88% (132.9 mg); white solid; mp 121−122 °C; TLC R_f = 0.37 (PE/EA = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52−7.50 (m, 2H), 7.45 (d, J = 3.2 Hz, 3H), 7.32−7.29 (m, 2H), 7.07 (t, J = 8.4 Hz, 2H), 5.39 (t, J = 7.2 Hz, 1H), 3.45 (dd, J = 16.4 Hz, J = 7.2 Hz, 1H), 3.04 (dd, J = 16.4 Hz, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 164.0 (J = 246.1 Hz), 140.3, 137.6, 135.0 (J = 3.2 Hz), 130.4, 128.6, 128.2, 127.4 (J = 8.3 Hz), 122.3, 115.9 (J = 21.6 Hz), 76.3, 39.9 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ −112.86 ppm; IR ν_{max} (KBr)/cm^{-1} 3747, 2924, 1756, 1509, 1195, 1091, 833; MS (EI) m/z 75, 95, 115, 150, 178, 202, 221, 302.

*(Z)-3-(Chloro(phenyl)methylene)-5-(4-chlorophenyl)-dihydrofuran-2(3H)-one (**3ae**):* yield 91% (144.7 mg); white solid; mp 95−96 °C; TLC R_f = 0.44 (PE/EA = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51−7.50 (m, 2H), 7.45−7.43 (m, 3H), 7.36 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 5.38 (t, J = 7.2 Hz, 1H), 3.45 (dd, J = 16.4 Hz, J = 7.2 Hz, 1H), 3.02 (dd, J = 16.4 Hz, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 140.4, 137.8, 137.5, 134.5, 130.5, 129.1, 128.6, 128.2, 126.8, 122.1, 76.1, 39.8 ppm; IR ν_{max} (KBr)/cm^{-1} 3491, 2921, 2363, 1760, 1629, 1198, 1089, 756; MS (EI) m/z 75, 89, 115, 150, 178, 202, 318.

*(Z)-5-(4-Bromophenyl)-3-(chloro(phenyl)methylene)-dihydrofuran-2(3H)-one (**3af**):* yield 90% (163.8 mg); white solid; mp 118−119 °C; TLC R_f = 0.51 (PE/EA = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 6.8 Hz, 4H), 7.44 (s, 3H), 7.21 (d, J = 7.6 Hz, 2H), 5.37 (t, J = 7.2 Hz, 1H), 3.46 (dd, J = 16.4 Hz, J = 7.2 Hz, 1H), 3.02 (dd, J = 16.8 Hz, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 140.5, 138.3, 137.5, 132.0, 130.5, 128.6, 128.2, 127.1, 122.6, 122.0, 76.2, 39.8 ppm; IR ν_{max} (KBr)/cm^{-1} 3362, 2921, 2362, 1759, 1628, 1196, 1090, 756; MS (EI) m/z 77, 115, 150, 178, 281, 364.

*(Z)-4-(4-(Chloro(phenyl)methylene)-5-oxotetrahydrofuran-2-yl)-benzonitrile (**3ag**):* yield 84% (129.8 mg); white solid; mp 53−55 °C; TLC R_f = 0.15 (PE/EA = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.0 Hz, 2H), 7.52−7.44 (m, 7H), 5.48 (t, J = 7.6 Hz, 1H), 3.53 (dd, J = 16.8 Hz, J = 7.6 Hz, 1H), 3.02 (dd, J = 16.4 Hz, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.80, 144.5, 141.1, 137.4, 132.7, 130.6, 128.7, 128.1, 126.1, 121.4, 118.4, 112.4, 75.7, 39.5 ppm; IR ν_{max} (KBr)/cm^{-1} 2923, 2228, 1763, 1629, 1198, 1092, 757; MS (EI) m/z 73, 96, 115, 150, 178, 281, 309; HRMS-ESI (m/z) calcd for $C_{18}H_{12}ClNNaO_2$ [M + Na]$^+$ 332.0449, found 332.0452.

*(Z)-Methyl 4-(4-(chloro(phenyl)methylene)-5-oxotetrahydrofuran-2-yl)benzoate (**3ah**):* yield 87% (148.8 mg); white solid; mp 131−132 °C; TLC R_f = 0.33 (PE/EA = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 7.6 Hz, 2H), 7.49 (s, 2H), 7.40−7.39 (m, 5H), 5.47 (t, J = 7.6 Hz, 1H), 3.93 (s, 3H), 3.49 (dd, J = 16.4 Hz, J = 7.6 Hz, 1H), 3.04 (dd, J = 16.4 Hz, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 166.5, 144.2, 140.7, 137.5, 130.5, 130.4, 130.2,

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128.6, 128.1, 125.2, 121.8, 76.1, 52.3, 39.7 ppm; IR ν_{max} (KBr)/cm^{-1} 3061, 2951, 1762, 1750, 1621, 1281, 1195, 1103, 702; MS (EI) *m*/*z* 89, 101, 115, 150, 178, 202, 281, 311, 342; HRMS-ESI (*m*/*z*) calcd for $C_{19}H_{16}ClO_4$ [M + H]$^+$ 343.0732, found 343.0736.

*(Z)-3-(Chloro(phenyl)methylene)-5-(4-nitrophenyl)dihydrofuran-2(3H)-one (**3ai**):* yield 85% (139.8 mg); yellow solid; mp 143−144 °C; TLC R_f = 0.30 (PE/EA = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.4 Hz, 2H), 7.53−7.47 (m, 4H), 7.45−7.43 (m, 3H), 5.53 (t, *J* = 7.2 Hz, 1H), 3.55 (dd, *J* = 16.8 Hz, *J* = 8.0 Hz, 1H), 3.02 (dd, *J* = 16.8 Hz, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 147.9, 146.4, 141.4, 137.4, 130.6, 128.7, 128.1, 126.2, 124.2, 121.2, 75.4, 39.5 ppm; IR ν_{max} (KBr)/cm^{-1} 3061, 2921, 1762, 1627, 1438, 1196, 1087, 1026, 753; HRMS-ESI (*m*/*z*) calcd for $C_{17}H_{12}ClNNaO_4$ [M + H]$^+$ 352.0347, found 352.0346.

*(Z)-3-(Chloro(phenyl)methylene)-5-(4-(trifluoromethyl)phenyl)-dihydrofuran-2(3H)-one (**3aj**):* yield 79% (139.0 mg); white solid; mp 113−114 °C; TLC R_f = 0.45 (PE/EA = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.51−7.46 (m, 9H), 5.49 (t, *J* = 7.2 Hz, 1H), 3.53 (dd, *J* = 16.8 Hz, *J* = 7.6 Hz, 1H), 3.05 (dd, *J* = 16.4 Hz, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 143.3, 140.9, 137.5, 130.8 (*J* = 32.3 Hz), 130.5, 128.7, 128.1, 125.2, 125.9 (q, *J* = 3.7 Hz), 125.6, 121.6, 75.9, 39.7 ppm; ^{19}F NMR (376 MHz, CDCl3) δ −62.85 ppm; IR ν_{max} (KBr)/cm^{-1} 3741, 3062, 2922, 1763, 1626, 1324, 1120, 699; MS (EI) *m*/*z* 89, 115, 150, 178, 202, 333, 318, 352; HRMS-ESI (*m*/*z*) calcd for $C_{18}H_{12}ClF_3NaO_2$ [M + Na]$^+$ 375.0370, found 375.0371.

*(Z)-3-(Chloro(phenyl)methylene)-5-p-tolyldihydrofuran-2(3H)-one (**3ak**):* yield 86% (128.1 mg); white solid; mp 96−97 °C; TLC R_f = 0.60 (PE/EA = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 2H), 7.45 (s, 3H), 7.24−7.20 (m, 4H), 5.39 (t, *J* = 7.2 Hz, 1H), 3.45 (dd, *J* = 16.4 Hz, *J* = 7.2 Hz, 1H), 3.07 (dd, *J* = 16.4 Hz, *J* = 6.8 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 139.9, 138.6, 137.7, 136.2, 130.3, 129.5, 128.6, 128.2, 125.4, 122.6, 77.0, 40.0, 21.2 ppm; IR ν_{max} (KBr)/cm^{-1} 3500, 3027, 2922, 2364, 1758, 1628, 1440, 1198, 1093, 696; MS (EI) *m*/*z* 77, 89, 115, 150, 178, 202, 281, 298.

*(Z)-5-(4-tert-Butylphenyl)-3-(chloro(phenyl)methylene)-dihydrofuran-2(3H)-one (**3al**):* yield 80% (136.0 mg); white solid; mp 96−98 °C; TLC R_f = 0.64 (PE/EA = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54−7.53 (m, 2H), 7.45−7.42 (m, 5H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.41 (t, *J* = 7.2 Hz, 1H), 3.46 (dd, *J* = 16.8 Hz, *J* = 7.6 Hz, 1H), 3.10 (dd, *J* = 16.4 Hz, *J* = 7.2 Hz, 1H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 151.8, 139.8, 137.7, 136.2, 130.3, 128.6, 128.2, 125.8, 125.3, 122.8, 76.9, 39.9, 34.7, 31.3 ppm; IR ν_{max} (KBr)/cm^{-1} 3059, 2961, 1761, 1634, 1199, 1100, 1029, 697; MS (EI) *m*/*z* 91, 115, 150, 163, 178, 325, 340.

*(Z)-3-(Chloro(phenyl)methylene)-5-(4-methoxyphenyl)-dihydrofuran-2(3H)-one (**3am**):* yield 85% (133.5 mg); white solid; mp 110−112 °C; TLC R_f = 0.30 (PE/EA = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53−7.51 (m, 2H), 7.45−7.44 (m, 3H), 7.27 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 5.36 (t, *J* = 7.2 Hz, 1H), 3.82 (s, 3H), 3.41 (dd, *J* = 16.4 Hz, *J* = 7.2 Hz, 1H), 3.08 (dd, *J* = 16.4 Hz, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 159.9, 139.8, 137.7, 131.0, 130.3, 128.6, 128.2, 127.0, 122.8, 114.2, 77.0, 55.4, 40.0 ppm; IR ν_{max} (KBr)/cm^{-1} 3626, 2918, 2370, 1754, 1616, 1512, 1246, 1176, 1029, 696; MS (EI) *m*/*z* 77, 89, 115, 137, 150, 178, 314.

*(Z)-3-(Chloro(phenyl)methylene)-5-mesityldihydrofuran-2(3H)-one (**3an**):* yield 68% (110.8 mg); yellow oil; TLC R_f = 0.68 (PE/EA = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56−7.54 (m, 2H), 7.46−7.44 (m, 3H), 6.88 (s, 2H), 5.79 (t, *J* = 8.0 Hz, 1H), 3.25 (dd, *J* = 7.6 Hz, *J* = 4.8 Hz, 2H), 2.35 (s, 6H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 140.0, 138.2, 137.8, 136.0, 130.9, 130.5, 130.3, 128.6, 128.2, 123.1, 74.7, 37.4, 20.8, 20.6 ppm; IR ν_{max} (KBr)/cm^{-1} 2966, 2362, 1757, 1622, 1448, 1326, 1199, 1101, 758; MS (EI) *m*/*z* 75, 102, 129, 136, 180, 198, 214, 326; HRMS-ESI (*m*/*z*) calcd for $C_{20}H_{20}ClO_2$ [M + H]$^+$ 327.1146, found 327.1149.

*(Z)-3-(Chloro(phenyl)methylene)-5-(perfluorophenyl)-dihydrofuran-2(3H)-one (**3ao**):* yield 71% (132.8 mg); white solid; mp 90−92 °C; TLC R_f = 0.45 (PE/EA = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53−7.52 (m, 2H), 7.47−7.45 (m, 3H), 5.75 (t, *J* = 7.2 Hz, 1H), 3.50 (dd, *J* = 17.2 Hz, *J* = 8.8 Hz, 1H), 3.26 (dd, *J* = 16.8 Hz, *J* = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 145.5 (dm, *J* = 249 Hz), 141.6, 139.8 (dm, *J* = 138 Hz), 137.6, 130.5, 129.1, 128.7, 128.0, 120.7, 112.4, 67.0, 36.5 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ −142.44 (dd, *J* = 21.4 Hz, *J* = 6.4 Hz), −151.66 (t, *J* = 20.7 Hz), −160.61 (td, *J* = 37.6 Hz, *J* = 21.1 Hz, *J* = 7.1 Hz) ppm; IR ν_{max} (KBr)/cm^{-1} 3744, 2919, 2364, 1767, 1628, 1506, 1200, 957; MS (EI) *m*/*z* 77, 89, 115, 150, 178, 274, 374; HRMS-ESI (*m*/*z*) calcd for $C_{17}H_8ClF_5NaO_2$ [M + Na]$^+$ 397.0025, found 397.0028.

*(Z)-3-(Chloro(phenyl)methylene)-5-(naphthalen-2-yl)-dihydrofuran-2(3H)-one (**3ap**):* yield 89% (148.6 mg); white solid; mp 134−135 °C; TLC R_f = 0.53 (PE/EA = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86−7.81 (m, 3H), 7.78 (s, 1H), 7.51−7.48 (m, 4H), 7.41−7.40 (m, 3H), 7.36 (dd, *J* = 8.8 Hz, *J* = 1.6 Hz, 1H), 5.55 (t, *J* = 7.2 Hz, 1H), 3.49 (dd, *J* = 16.8 Hz, *J* = 7.6 Hz, 1H), 3.11 (dd, *J* = 16.4 Hz, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 140.3, 137.7, 136.5, 133.2, 133.1, 130.3, 129.0, 128.6, 128.2, 128.1, 127.8, 126.7, 126.6, 124.6, 122.7, 122.4, 100.0, 76.9, 39.9 ppm; IR ν_{max} (KBr)/cm^{-1} 3057, 2923, 1758, 1628, 1318, 1199, 1059, 754; MS (EI) *m*/*z* 77, 127, 149, 177, 184, 202, 334.

*(Z)-3-(Chloro(phenyl)methylene)-5-(thiophene-2-yl)-dihydrofuran-2(3H)-one (**3aq**):* yield 75% (108.7 mg); brown oil; TLC R_f = 0.35 (PE/EA = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51−7.49 (m, 2H), 7.43−7.42 (m, 3H), 7.31 (d, *J* = 5.2 Hz, 1H), 7.04 (d, *J* = 3.2 Hz, 1H), 6.96 (t, *J* = 3.2 Hz, 1H), 5.61 (t, *J* = 7.2 Hz, 1H), 3.45 (dd, *J* = 16.4 Hz, *J* = 7.2 Hz, 1H), 3.20 (dd, *J* = 16.4 Hz, *J* = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 141.6, 140.5, 137.6, 130.4, 128.7, 128.2, 127.1, 126.5, 126.2, 122.1, 73.1, 39.8 ppm; IR ν_{max} (KBr)/cm^{-1} 3106, 2924, 1760, 1630, 1439, 1204, 1093, 700; MS (EI) *m*/*z* 73, 89, 115, 150, 178, 202, 290; HRMS-ESI (*m*/*z*) calcd for $C_{15}H_{12}ClO_2S$ [M + H]$^+$ 291.0241, found 291.0239.

*(Z)-3-(Chloro(phenyl)methylene)-5-(pyridin-2-yl)dihydrofuran-2(3H)-one (**3ar**):* yield 50% (71.2 mg); brown oil; TLC R_f = 0.63 (PE/EA = 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 4.8 Hz, 1H), 7.76 (t, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 3H), 7.42−7.41 (m, 3H), 7.26 (s, 2H), 5.52 (t, *J* = 7.2 Hz, 1H), 3.55 (dd, *J* = 17.2 Hz, *J* = 8.4 Hz, 1H), 3.31 (dd, *J* = 16.8 Hz, *J* = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 158.1, 149.3, 140.6, 137.7, 137.4, 130.3, 128.6, 128.2, 123.4, 121.7, 120.5, 76.3, 37.4 ppm; IR ν_{max} (KBr)/cm^{-1} 2850, 2362, 1759, 1628, 1401, 1198, 1038, 752; MS (EI) *m*/*z* 78, 115, 150, 194, 206, 222, 250, 268, 285; HRMS-ESI (*m*/*z*) calcd for $C_{16}H_{13}ClNO_2$ [M + H]$^+$ 286.0629, found 286.0627.

*(Z)-3-(Chloro(phenyl)methylene)-5-methyl-5-phenyldihydrofuran-2(3H)-one (**3as**):* yield 82% (122.2 mg); yellow oil; TLC R_f = 0.31 (PE/EA = 6:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.41 (m, 5H), 7.35 (d, *J* = 8.0 Hz, 4H), 7.31−7.27 (m, 1H), 3.25 (q, *J* = 28.0 Hz, *J* = 16.4 Hz, 2H), 1.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 144.2, 140.1, 137.7, 130.3, 128.7, 128.6, 128.2, 127.8, 124.1, 123.1, 82.5, 45.5, 29.8 ppm; IR ν_{max} (KBr)/cm^{-1} 3063, 2927, 2363, 1758, 1629, 1444, 1226, 1054, 938, 698; MS (EI) *m*/*z* 77, 89, 105, 115, 121, 150, 178, 202, 219, 283, 298.

*(Z)-3-(Chloro(2-chlorophenyl)methylene)-5-phenyldihydrofuran-2(3H)-one (**3ba**):* yield 82% (130.4 mg); colorless oil; TLC R_f = 0.52 (PE/EA = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51−7.29 (m, 9H), 5.52−5.44 (m, 1H), 3.28−3.07 (m, 1H), 2.91−2.68 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 139.3, 136.7, 131.6, 131.0, 130.3, 129.3, 129.0, 128.9, 128.7, 127.6, 125.5, 125.3, 77.0, 38.3 ppm; IR ν_{max} (KBr)/cm^{-1} 3064, 2925, 1763, 1653 1433, 1322, 1207, 1103, 756; MS (EI) *m*/*z* 77, 114, 149, 177, 202, 247, 283, 318; HRMS-ESI (*m*/*z*) calcd for $C_{17}H_{13}Cl_2O_2$ [M + H]$^+$ 319.0287, found 319.0290.

*(Z)-3-(Chloro(3-chlorophenyl)methylene)-5-phenyldihydrofuran-2(3H)-one (**3ca**):* yield 85% (135.2 mg); colorless oil; TLC R_f = 0.50 (PE/EA = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.42−7.37 (m, 6H), 4.33 (d, *J* = 7.6 Hz, 1H), 5.44 (t, *J* = 7.2 Hz, 1H), 3.45 (dd, *J* = 16.4 Hz, *J* = 7.2 Hz, 1H), 3.05 (dd, *J* = 16.8 Hz, *J* = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 139.3, 139.0, 138.2, 134.7, 130.4, 129.9, 128.9, 128.8, 128.2, 126.3, 125.4, 123.5, 76.9, 39.8 ppm; IR ν_{max} (KBr)/cm^{-1} 3066, 2925, 2362, 1760, 1633, 1201, 1102, 695; MS (EI) *m*/*z* 77, 149, 177, 184, 202, 212, 318.

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*(Z)-3-(Chloro(4-chlorophenyl)methylene)-5-phenyldihydrofuran-2(3H)-one (**3da**):* yield 91% (144.7 mg); white solid; mp 124−126 °C; TLC R_f = 0.56 (PE/EA = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 7.6 Hz, 2H), 7.42−7.35 (m, 5H), 7.32 (d, J = 7.2 Hz, 2H), 5.43 (t, J = 7.2 Hz, 1H), 3.45 (dd, J = 16.8 Hz, J = 7.6 Hz, 1H), 3.06 (dd, J = 16.4 Hz, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 134.0, 137.7, 130.3, 128.6, 128.1, 122.6, 74.0, 58.8, 38.4, 37.2 ppm; IR ν_{max} (KBr)/cm^{-1} 3035, 2919, 1758, 1628, 1488, 1198, 1092, 828; MS (EI) m/z 63, 77, 105, 114, 149, 177, 184, 212, 318; HRMS-ESI (m/z) calcd for $C_{17}H_{13}Cl_2O_2$ [M + H]$^+$ 319.0287, found 319.0288.

*(Z)-3-(Chloro(4-fluorophenyl)methylene)-5-phenyldihydrofuran-2(3H)-one (**3ea**):* yield 88% (132.9 mg); white solid; mp 96−97 °C; TLC R_f = 0.50 (PE/EA = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (q, J = 8.0 Hz, J = 5.6 Hz, 2H), 7.39−7.29 (m, 5H), 7.10 (t, J = 8.4 Hz, 2H), 5.41 (t, J = 7.2 Hz, 1H), 3.42 (dd, J = 16.4 Hz, J = 7.2 Hz, 1H), 3.03 (dd, J = 16.8 Hz, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 164.7 (J = 250.8 Hz), 139.2, 138.9, 133.7 (J = 3.4 Hz), 130.5 (J = 9.7 Hz), 128.9, 128.7, 125.4, 122.6, 115.9 (J = 21.9 Hz), 76.8, 39.9 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ −108.73 ppm; IR ν_{max} (KBr)/cm^{-1} 3745, 3067, 2922, 1759, 1629, 1504, 1234, 838, 696; MS (EI) m/z 77, 107, 133, 168, 196, 220, 302.

*(Z)-3-((4-Bromophenyl)chloromethylene)-5-phenyldihydrofuran-2(3H)-one (**3fa**):* yield 90% (162.9 mg); white solid; mp 131−132 °C; TLC R_f = 0.55 (PE/EA = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.4 Hz, 2H), 7.42−7.36 (m, 5H), 7.33 (d, J = 8.8 Hz, 2H), 5.43 (t, J = 7.6 Hz, 1H), 3.44 (dd, J = 16.4 Hz, J = 7.2 Hz, 1H), 3.05 (dd, J = 16.8 Hz, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 139.1, 138.8, 136.5, 131.9, 129.8, 128.9, 128.7, 125.3, 124.8, 123.0, 76.8, 39.9 ppm; IR ν_{max} (KBr)/cm^{-1} 3746, 3364, 2919, 1758, 1637, 1199, 1029, 701; MS (EI) m/z 77, 114, 149, 177, 193, 202, 230, 258, 362; HRMS-ESI (m/z) calcd for $C_{17}H_{13}BrClO_2$ [M + H]$^+$ 362.9782, found 362.9784.

*(Z)-3-(Chloro(4-nitrophenyl)methylene)-5-phenyldihydrofuran-2(3H)-one (**3ga**):* yield 78% (128.3 mg); yellow solid, mp 112−116 °C; TLC R_f = 0.52 (PE/EA = 3:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 8.8 Hz, 2H), 7.70 (d, J = 8.8 Hz, 2H), 7.43−7.38 (m, 3H), 7.32 (d, J = 7.2 Hz, 2H), 5.48 (t, J = 7.6 Hz, 1H), 3.44 (dd, J = 16.8 Hz, J = 7.6 Hz, 1H), 3.07 (dd, J = 16.4 Hz, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 148.4, 143.5, 138.8, 137.0, 129.3, 129.0, 128.9, 125.2, 125.0, 123.9, 76.9, 39.7 ppm; IR ν_{max} (KBr)/cm^{-1} 3744, 3360, 2918, 2362, 1754, 1645, 1517, 1346, 699; HRMS-ESI (m/z) calcd for $C_{17}H_{12}ClNNaO_4$ [M + Na]$^+$ 352.0347, found 352.0344.

*(Z)-3-(Chloro(4-methoxyphenyl)methylene)-5-phenyldihydrofuran-2(3H)-one (**3ha**):* yield 85% (133.5 mg); colorless oil; TLC R_f = 0.45 (PE/EA = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 8.0 Hz, 2H), 7.42−7.33 (m, 5H), 6.95 (d, J = 8.0 Hz, 2H), 5.41 (t, J = 7.2 Hz, 1H), 3.86 (s, 3H), 3.49 (dd, J = 16.0 Hz, J = 7.2 Hz, 1H), 3.09 (dd, J = 16.4 Hz, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 161.1, 140.1, 139.4, 130.1, 129.8, 128.9, 128.6, 125.4, 120.9, 113.8, 76.8, 55.5, 40.3 ppm; IR ν_{max} (KBr)/cm^{-1} 2840, 2335, 1757, 1602, 1508, 1401, 1303, 1249, 1178, 698; MS (EI) m/z 73, 91, 105, 145, 180, 207, 281, 314; HRMS-ESI (m/z) calcd for $C_{18}H_{16}ClO_3$ [M + H]$^+$ 315.0782, found 315.0781.

*(Z)-3-(Chloro(p-tolyl)methylene)-5-phenyldihydrofuran-2(3H)-one (**3ia**):* yield 89% (132.6 mg); colorless oil; TLC R_f = 0.49 (PE/EA = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.33 (m, 7H), 7.27 (d, J = 8.0 Hz, 2H), 5.41 (t, J = 7.2 Hz, 1H), 3.48 (dd, J = 16.4 Hz, J = 7.2 Hz, 1H), 3.08 (dd, J = 16.4 Hz, J = 7.2 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 140.9, 140.3, 139.4, 134.8, 129.2, 128.9, 128.6, 128.2, 125.4, 121.8, 76.8, 40.1, 21.4 ppm; IR ν_{max} (KBr)/cm^{-1} 3033, 2922, 2335, 1759, 1627, 1453, 1198, 1032, 697; MS (EI) m/z 77, 105, 129, 164, 192, 298; HRMS-ESI (m/z) calcd for $C_{18}H_{16}ClO_2$ [M + H]$^+$ 299.0833, found 299.0834.

*(Z)-3-(1-Chloroethylidene)-5-phenyldihydrofuran-2(3H)-one (**3ja**):* yield 90% (99.9 mg); white solid; mp 92−93 °C; TLC R_f = 0.40 (PE/EA = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.29 (m, 5H), 5.44 (d, J = 7.6 Hz, 1H), 3.43 (dd, J = 16.8 Hz, J = 8.4 Hz, 1H), 2.89 (dd, J = 16.4 Hz, J = 6.4 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 140.3, 139.8, 128.9, 128.6, 125.3, 120.8, 76.2, 37.5, 26.5 ppm; IR ν_{max} (KBr)/cm^{-1} 3745, 2917, 1753, 1650, 1226, 1142, 1019, 696; MS (EI) m/z 53, 77, 88, 105, 116, 143, 187, 222.

*(Z)-3-(1-Chlorohexylidene)-5-phenyldihydrofuran-2(3H)-one (**3ka**):* yield 88% (122.3 mg); colorless oil; TLC R_f = 0.55 (PE/EA = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41−7.31 (m, 5H), 5.43 (t, J = 7.2 Hz, 1H), 3.44 (dd, J = 16.4 Hz, J = 8.4 Hz, 1H), 2.91 (dd, J = 16.4 Hz, J = 7.2 Hz, 1H), 2.44 (t, J = 7.2 Hz, 2H), 1.69−1.64 (m, 2H), 1.33−1.24 (m, 4H), 0.88 (t J = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 145.3, 139.8, 128.9, 128.6, 125.3, 120.4, 76.3, 39.3, 37.5, 30.9, 26.5, 22.4, 13.9 ppm; IR ν_{max} (KBr)/cm^{-1} 3064, 2930, 2361, 1760, 1646, 1227, 1140, 1033, 697; MS (EI) m/z 77, 88, 116, 137, 172, 202, 278.

*(Z)-3-(chloro(cyclopropyl)methylene)-5-phenyldihydrofuran-2(3H)-one (**3la**):* yield 90% (111.6 mg); yellow oil; TLC R_f = 0.38 (PE/EA = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.35 (m, 5H), 5.51 (t, J = 7.6 Hz, 1H), 3.60 (dd, J = 16.4 Hz, J = 8.4 Hz, 1H), 3.06 (dd, J = 16.4 Hz, J = 6.4 Hz, 1H), 1.80−1.73 (m, 1H), 1.20−1.14 (m, 2H), 1.01−0.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 146.7, 140.1, 128.7, 128.5, 125.4, 118.8, 76.3, 37.4, 18.0, 8.0, 8.0 ppm; IR ν_{max} (KBr)/cm^{-1} 3068, 2925, 1747, 1639, 1236, 1168, 995, 698; MS (EI) m/z 77, 79, 91, 107, 114, 129, 153, 167, 191, 220, 248; HRMS-ESI (m/z) calcd for $C_{14}H_{14}ClO_2$ [M + H]$^+$ 249.0677, found 249.0674.

*(Z)-Ethyl 4-(chloro(phenyl)methylene)-5-oxotetrahydrofuran-2-carboxylate (**5aa**):* yield 89% (124.6 mg); colorless oil; TLC R_f = 0.27 (PE/EA = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50−7.45 (m, 5H), 4.86 (dd, J = 9.6 Hz, J = 5.2 Hz, 1 H), 4.30−4.19 (m, 2H), 3.40 (q, J = 17.2 Hz, J = 9.2 Hz, 1H), 3.10 (q, J = 17.2 Hz, J = 4.8 Hz, 1H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 166.2, 141.4, 137.5, 130.5, 128.7, 128.0, 119.9, 71.8, 62.2, 34.5, 14.0 ppm; IR ν_{max} (KBr)/cm^{-1} 3743, 2984, 2361, 1769, 1760, 1628, 1195, 1068, 696; MS (EI) m/z 77, 89, 115, 144, 171, 179, 217, 245, 280.

*(Z)-Cyclohexyl 4-(chloro(phenyl)methylene)-5-oxotetrahydrofuran-2-carboxylate (**5ab**):* yield 85% (141.9 mg); colorless oil; TLC R_f = 0.50 (PE/EA = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48−7.43 (m, 5H), 4.85−4.79 (m, 2H), 3.39 (dd, J = 16.8 Hz, J = 8.8 Hz, 1H), 3.06 (dd, J = 16.8 Hz, J = 4.4 Hz, 1H), 1.80−1.78 (m, 2H), 1.68−1.66 (m, 2H), 1.51−1.23 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 166.4, 141.4, 137.5, 130.5, 128.7, 128.1, 128.0, 120.1, 74.8, 72.1, 34.6, 31.2, 25.1, 23.3 ppm; IR ν_{max} (KBr)/cm^{-1} 3061, 2937, 1772, 1765, 1631, 1446, 1195, 1067, 696; MS (EI) m/z 55, 83, 115, 144, 179, 217, 252, 281, 334; HRMS-ESI (m/z) calcd for $C_{18}H_{20}ClO_4$ [M + H]$^+$ 335.1045, found 335.1042.

*(Z)-2,2,2-Trifluoroethyl 4-(chloro(phenyl)methylene)-5-oxotetrahydrofuran-2-carboxylate (**5ac**):* yield 83% (138.6 mg); colorless oil; TLC R_f = 0.35 (PE/EA = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 5H), 5.00 (dd, J = 9.2 Hz, J = 4.8 Hz, 1H), 4.58 (q, J = 15.6 Hz, J = 7.6 Hz, 2H), 3.46 (dd, J = 17.2 Hz, J = 9.2 Hz, 1H), 3.13 (dd, J = 17.2 Hz, J = 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 165.6, 142.6, 137.3, 132.5, 130.7, 128.8, 128.5 (q, J = 236 Hz), 118.8, 71.1, 61.1 (q, J = 36.9 Hz), 34.3 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ −77.08 (t, J = 8.6 Hz); IR ν_{max} (KBr)/cm^{-1} 2929, 2363, 1767, 1760, 1628, 1201, 1070, 696; HRMS-ESI (m/z) calcd for $C_{14}H_{11}ClF_3O_4$ [M + H]$^+$ 335.0292, found 335.0285.

*(Z)-4-(Chloro(phenyl)methylene)-5-oxotetrahydrofuran-2-carboxamide (**5ad**):* yield 65% (81.6 mg); white solid; mp 153−155 °C; TLC R_f = 0.45 (PE/EA = 0:1, v/v); ^{1}H NMR (400 MHz, CD_3OD) δ 7.65−7.63 (m, 2H), 7.55−7.52 (m, 3H), 7.23 (br, 1H), 6.87 (br, 1H), 4.90 (dd, J = 8.8 Hz, J = 5.2 Hz, 1H), 3.45 (dd, J = 17.2 Hz, J = 8.8 Hz, 1H), 3.18 (dd, J = 16.8 Hz, J = 5.2 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ 171.1, 165.8, 138.6, 137.8, 130.3, 128.7, 128.2, 122.2, 72.9, 34.4 ppm; IR ν_{max} (KBr)/cm^{-1} 3440, 2924, 2363, 1764, 1682, 1628, 1438, 1203, 1057, 697; MS (EI) m/z 89, 115, 144, 179, 216, 251. **5ad** is known.

*(Z)-4-(Chloro(phenyl)methylene)-N,N-dimethyl-5-oxotetrahydrofuran-2-carboxamide (**5ae**):* yield 78% (108.8 mg); white solid; mp 110−113 °C; TLC R_f = 0.46 (PE/EA = 0:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54−7.53 (m, 2H), 7.44−7.43 (m, 3H), 5.09 (dd, J = 7.6 Hz, J = 6.4 Hz, 1H), 3.58 (dd, J = 16.8 Hz, J = 5.2 Hz, 1H), 3.15 (dd, J = 26.4 Hz, J = 17.2 Hz, 1H), 3.12 (s, 3H), 2.97 (s, 3H); ^{13}C

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NMR (100 MHz, $CDCl_3$) δ 166.8, 166.4, 140.6, 137.7, 130.3, 128.6, 128.2, 121.1, 71.0, 37.0, 36.1, 33.0 ppm; IR ν_{max} (KBr)/cm^{-1} 2935, 1764, 1657, 1496, 1207, 1060, 696; MS (EI) m/z 89, 115, 144, 179, 216, 279.

*(Z)-3-(Chloro(phenyl)methylene)-5-propionyldihydrofuran-2(3H)-one (**5af**):* yield 86% (113.5 mg); yellow oil; TLC R_f = 0.30 (PE/EA = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50−7.46 (m, 5H), 4.74 (q, J = 8.4 Hz, J = 6.0 Hz, 1H), 3.29 (dd, J = 17.2 Hz, J = 8.8 Hz, 1H), 3.14 (dd, J = 17.2 Hz, J = 6.0 Hz, 1H), 2.70 (q, J = 14.4 Hz, J = 7.2 Hz, 2H), 1.10 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.0, 166.3, 141.8, 137.4, 130.6, 128.7, 128.1, 120.1, 77.5, 33.2, 32.5, 6.9 ppm; IR ν_{max} (KBr)/cm^{-1} 3744, 2927, 2360, 1763, 1719, 1626, 1200, 1066, 696; MS (EI) m/z 77, 89, 144, 179, 217, 264.

*(Z)-4-(Chloro(phenyl)methylene)-5-oxotetrahydrofuran-2-carbonitrile (**5ag**):* yield 49% (57.1 mg); yellow oil; TLC R_f = 0.45 (PE/EA = 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 5H), 5.09 (dd, J = 8.8 Hz, J = 4.8 Hz, 1H), 3.49 (dd, J = 16.8 Hz, J = 8.8 Hz, 1H), 3.35 (dd, J = 16.8 Hz, J = 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 144.6, 136.9, 131.1, 128.9, 128.0, 117.0, 116.1, 61.0, 35.5 ppm; IR ν_{max} (KBr)/cm^{-1} 3363, 3062, 2366, 1776, 1628, 1440, 1200, 1044, 699; MS (EI) m/z 77, 89, 115, 127, 158, 177, 216, 233.

*(Z)-3-(Chloro(phenyl)methylene)-5-hexyldihydrofuran-2(3H)-one (**5ah**):* yield 81% (118.3 mg); colorless oil; TLC R_f = 0.54 (PE/EA = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51−7.49 (m, 2H), 7.60−7.32 (m, 3H), 4.38 (t, J = 6.4 Hz, 1H), 3.11 (dd, J = 16.0 Hz, J = 7.2 Hz, 1H), 2.70 (dd, J = 16.8 Hz, J = 6.8 Hz, 1H), 1.74−1.68 (m, 1H), 1.62−1.53 (m, 1H), 1.32−1.28 (m, 8H), 0.94−0.82 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 139.3, 137.8, 130.1, 128.5, 128.1, 123.1, 76.3, 37.1, 35.9, 31.6, 28.9, 24.8, 22.5, 14.0 ppm; IR ν_{max} (KBr)/cm^{-1} 3061, 2929, 2860, 2362, 1758, 1630, 1447, 1204, 1093, 696; MS (EI) m/z 89, 95, 115, 150, 179, 256, 292; HRMS-ESI (m/z) calcd for $C_{17}H_{22}ClO_2$ $[M + H]^+$ 293.1303, found 293.1305.

*(Z)-3-(Chloro(phenyl)methylene)-5-(2-hydroxyethyl)-dihydrofuran-2(3H)-one (**5ai**):* yield 88% (110.9 mg); colorless oil; TLC R_f = 0.28 (PE/EA = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51−7.50 (m, 2H), 7.49−7.45 (m, 3H), 4.67−4.60 (m, 1H), 3.87−3.77 (m, 2H), 3.18 (dd, J = 16.4 Hz, J = 7.2 Hz, 1H), 2.82 (dd, J = 16.4 Hz, J = 6.8 Hz, 1H), 2.06 (br, 1H), 2.00−1.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 140.0, 137.7, 130.3, 128.6, 128.1, 122.6, 74.0, 58.8, 38.4, 37.2 ppm; IR ν_{max} (KBr)/cm^{-1} 3469(br), 3061, 2924, 2363, 1750, 1630, 1206, 1054, 697; MS (EI) m/z 77, 89, 115, 150, 178, 202, 252; HRMS-ESI (m/z) calcd for $C_{13}H_{13}ClNaO_3$ $[M + Na]^+$ 275.0445, found 275.0444.

*(Z)-3-(Chloro(phenyl)methylene)-2,2-dimethyl-5-phenyltetrahydrofuran (**7aa**):* yield 74% (110.3 mg); colorless oil; TLC R_f = 0.65 (PE/DCM = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 7.6 Hz, 2H), 7.43−7.31 (m, 8H), 5.99 (dd, J = 10.8 Hz, J = 2.8 Hz, 1H), 2.81 (dd, J = 16.8 Hz, J = 10.4 Hz, 1H), 2.64 (dd, J = 16.8 Hz, J = 2.8 Hz, 1H), 1.66 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 139.9, 133.5, 131.9, 128.5, 128.2, 128.1, 127.7, 127.4, 126.1, 77.4, 70.3, 40.9, 28.5, 24.3 ppm; IR ν_{max} (KBr)/cm^{-1} 3060, 2930, 2363, 1450, 1369, 1023, 697; MS (EI) m/z 77, 91, 105, 115, 129, 142, 157, 177, 192, 283, 298; HRMS-ESI (m/z) calcd for $C_{19}H_{19}ClNaO$ $[M + Na]^+$ 321.1017, found 321.1013.

*(Z)-3-(Chloro(phenyl)methylene)-5-(4-fluorophenyl)-2,2-dimethyltetrahydrofuran (**7ad**):* yield 78% (123.2 mg); colorless oil; TLC R_f = 0.69 (PE/DCM = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (q, J = 15.6 Hz, J = 8.0 Hz, 4H), 7.37−7.32 (m, 3H), 7.09 (t, J = 8.0 Hz, 2H), 4.96 (dd, J = 10.4 Hz, J = 2.0 Hz, 1H), 2.77 (dd, J = 16.8 Hz, J = 10.8 Hz, 1H), 2.61 (dd, J = 16.8 Hz, J = 2.4 Hz, 1H), 1.64 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5 (J = 244.1 Hz), 139.8, 137.5 (J = 3.1 Hz), 133.5, 131.7, 128.3, 128.1, 127.8 (J = 8.1 Hz), 127.5, 115.4 (J = 21.2 Hz), 77.5, 69.7, 41.0, 28.5, 24.3 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ −114.84 ppm; IR ν_{max} (KBr)/cm^{-1} 3058, 2982, 2363, 1605, 1511, 1226, 1082, 965, 698; MS (EI) m/z 77, 109, 123, 142, 157, 177, 192, 266, 301, 316; HRMS-ESI (m/z) calcd for $C_{19}H_{18}ClFNaO$ $[M + Na]^+$ 339.0922, found 339.0918.

*(Z)-5-(4-Bromophenyl)-3-(chloro(phenyl)methylene)-2,2-dimethyltetrahydrofuran (**7af**):* yield 71% (133.8 mg); white solid; mp 81−83 °C; TLC R_f = 0.61 (PE/DCM = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.0 Hz, 2H), 7.44−7.32 (m, 7H), 4.94 (dd, J = 10.4 Hz, J = 2.4 Hz, 1H), 2.74 (dd, J = 16.8 Hz, J = 10.8 Hz, 1H), 2.62 (dd, J = 16.8 Hz, J = 2.8 Hz, 1H), 1.65 (s, 3H), 1.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 139.7, 133.5, 131.6, 131.6, 128.3, 128.1, 127.8, 127.5, 121.5, 77.5, 69.7, 40.8, 28.5, 24.3 ppm; IR ν_{max} (KBr)/cm^{-1} 3747, 3363, 2923, 2363, 2648, 1487, 1367, 1078, 697; MS (EI) m/z 77, 115, 142, 157, 177, 192, 361, 377; HRMS-ESI (m/z) calcd for $C_{19}H_{18}BrClNaO$ $[M + Na]^+$ 399.0122, found 399.0119.

*(Z)-3-(Chloro(phenyl)methylene)-2,2-dimethyl-5-m-tolyltetrahydrofuran (**7at**):* yield 68% (106.1 mg); colorless oil; TLC R_f = 0.52 (PE/DCM = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.27 (m, 8H), 7.14 (d, J = 6.8 Hz, 1H), 4.96 (dd, J = 14.4 Hz, J = 2.4 Hz, 1H), 2.81 (dd, J = 16.8 Hz, J = 10.8 Hz, 1H), 2.62 (dd, J = 16.8 Hz, J = 2.8 Hz, 1H), 2.41 (s, 3H), 1.66 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 134.0, 138.1, 133.5, 131.9, 128.5, 128.4, 128.2, 128.1, 127.4, 126.7, 123.2, 77.4, 70.4, 40.9, 28.6, 24.3, 21.5 ppm; IR ν_{max} (KBr)/cm^{-1} 3054, 2981, 2361, 1606, 1449, 1369, 1174, 1029, 698; MS (EI) m/z 77, 91, 105, 142, 157, 177, 192, 297, 312; HRMS-ESI (m/z) calcd for $C_{20}H_{22}ClO$ $[M + H]^+$ 313.1354, found 313.1349.

*(Z)-4-(Chloro(phenyl)methylene)-2-phenyltetrahydrofuran (**7ba**):* yield 76% (102.6 mg); colorless oil; TLC R_f = 0.68 (PE/DCM = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.0 Hz, 2H), 7.42−7.32 (m, 8H), 5.03 (dd, J = 9.2 Hz, J = 6.0 Hz, 1H), 4.91 (d, J = 15.2 Hz, 1H), 4.71 (d, J = 14.8 Hz, 1H), 3.08 (dd, J = 16.0 Hz, J = 5.2 Hz, 1H), 2.78 (dd, J = 15.6 Hz, J = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 138.3, 137.8, 128.5, 128.4, 128.2, 128.0, 127.9, 125.8, 121.9, 82.3, 72.4, 41.6 ppm; IR ν_{max} (KBr)/cm^{-1} 3734, 3062, 2924, 2360, 1763, 1686, 1449, 1028, 697; MS (EI) m/z 77, 104, 129, 164, 202, 235, 270; HRMS-ESI (m/z) calcd for $C_{17}H_{15}ClNaO$ $[M + Na]^+$ 293.0704, found 293.0716.

*(Z)-3-(Chloro(2-fluorophenyl)methylene)-2,2-dimethyl-5-phenyltetrahydrofuran (**7ca**):* yield 52% (82.2 mg); white solid; mp 65−67 °C; TLC R_f = 0.45 (PE/DCM = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 7.6 Hz, 2H), 7.38 (t, J = 7.6 Hz, 2H), 7.33−7.28 (m, 3H), 7.20−7.01 (m, 2H), 5.00 (dd, J = 10.4 Hz, J = 1.2 Hz, 1H), 2.77 (dd, J = 16.8 Hz, J = 10.4 Hz, 1H), 2.58 (dd, J = 16.8 Hz, J = 1.6 Hz, 1H), 1.65 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6 (J = 245.3 Hz), 141.5, 135.9, 130.5 (J = 3.8 Hz), 129.4, 129.4, 128.5, 127.7, 127.3, 126.1, 124.0 (J = 3.5 Hz), 115.9 (J = 21.8 Hz), 77.4, 70.2, 40.0, 28.5, 24.3 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ −114.94 ppm; IR ν_{max} (KBr)/cm^{-1} 3745, 2924, 1698, 1540, 1459, 1019, 753; MS (EI) m/z 77, 91, 105, 133, 160, 175, 195, 210, 301, 316; HRMS-ESI (m/z) calcd for $C_{19}H_{18}ClFNaO$ $[M + Na]^+$ 339.0922, found 339.0924.

*(Z)-3-(Chloro(m-tolyl)methylene)-2,2-dimethyl-5-phenyltetrahydrofuran (**7da**):* yield 72% (112.3 mg); colorless oil; TLC R_f = 0.53 (PE/DCM = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 7.6 Hz, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.35−7.29 (m, 2H), 7.17−7.14 (m, 3H), 4.98 (dd, J = 10.4 Hz, J = 1.6 Hz, 1H), 2.80 (dd, J = 16.8 Hz, J = 10.8 Hz, 1H), 2.62 (dd, J = 16.8 Hz, J = 2.0 Hz, 1H), 2.41 (s, 3H), 1.65 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 139.9, 137.8, 133.3, 132.0, 128.7, 128.5, 128.2, 128.1, 127.7, 126.1, 125.2, 77.4, 70.3, 41.0, 28.6, 24.3, 21.5 ppm; IR ν_{max} (KBr)/cm^{-1} 3031, 2981, 2363, 1603, 1490, 1454, 1368, 1169, 1071, 699; MS (EI) m/z 77, 91, 105, 141, 156, 171, 191, 206, 297, 312; HRMS-ESI (m/z) calcd for $C_{20}H_{22}ClO$ $[M + H]^+$ 313.1354, found 313.1350.

*(Z)-3-(Chloro(p-tolyl)methylene)-2,2-dimethyl-5-phenyltetrahydrofuran (**7ea**):* yield 71% (110.7 mg); colorless oil; TLC R_f = 0.55 (PE/DCM = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 7.6 Hz, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.32 (d, J = 8.8 Hz, 1H), 7.23 (q, J = 17.2 Hz, J = 8.0 Hz, 4H), 4.96 (dd, J = 10.8 Hz, J = 2.4 Hz, 1H), 2,77 (dd, J = 16.8 Hz, J = 10.8 Hz, 1H), 2.60 (dd, J = 16.8 Hz, J = 2.8 Hz, 1H), 2.39 (s, 3H), 1.63 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 137.2, 136.9, 133.2, 131.7, 128.9, 128.5, 128.0, 127.6, 126.0, 77.2, 70.3, 40.9, 28.5, 24.2, 21.2 ppm; ν_{max} (KBr)/cm^{-1} 3029, 2928, 2362, 1646, 1510, 1454, 1175, 1023, 698; MS (EI) m/z 77, 91, 105, 141, 156, 171, 191, 206, 297, 312; HRMS-ESI (m/z) calcd for $C_{20}H_{21}ClNaO$ $[M + Na]^+$ 335.1173, found 335.1172.

*(Z)-3-(Chloro(4-chlorophenyl)methylene)-2,2-dimethyl-5-phenyltetrahydrofuran (**7fa**):* yield 73% (121.2 mg); white solid; mp 85−87

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°C; TLC R_f = 0.56 (PE/DCM = 4:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 7.6 Hz, 2H), 7.45−7.29 (m, 7H), 4.99 (d, J = 10.8 Hz, 1H), 2.80 (dd, J = 16.8 Hz, J = 10.4 Hz, 1H), 2.60 (dd, J = 16.4 Hz, J = 2.0 Hz, 1H), 1.67 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 138.2, 134.2, 133.3, 130.8, 129.6, 128.5, 128.5, 127.8, 126.1, 77.4, 70.3, 40.8, 28.5, 24.3 ppm; IR ν_{max} (KBr)/cm^{-1} 3745, 3360, 2923, 2362, 1646, 1488, 1018, 696; MS (EI) m/z 77, 91, 105, 141, 156, 176, 191, 211, 226, 317, 332; HRMS-ESI (m/z) calcd for $C_{19}H_{18}Cl_2NaO$ $[M + Na]^+$ 355.0627, found 355.0626.

■ ASSOCIATED CONTENT

Supporting Information

Spectra data for all products and the crystallographic data of **3ai** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org

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Notes

The authors declare no competing financial interest.

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