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Stereochemical Control by an Ester Group or Olefin Ligand in Platinum-Catalyzed Carboalkoxylation of 6-(1-Alkoxyethoxy)-hex-2-ynoates

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Dedicated to Professor Armin de Meijere on the occasion of his 70th birthday.

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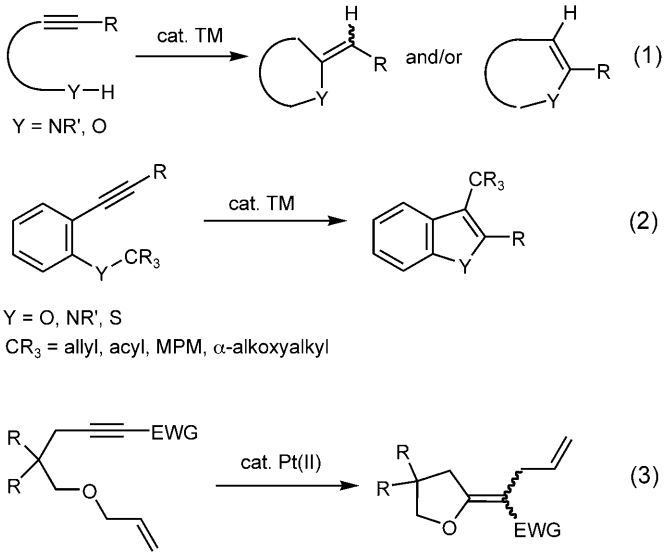
Abstract: The cyclization of 6-(1-alkoxyethoxy)hex-2-ynoantes in the presence of the platinum-olefin catalyst system gave the corresponding multisubstituted 2-[dihydrofuran-2(*3H*)-ylidene]acetates in good to high yields. The *Z/E* selectivity is controlled by the electronic property of the ester group; the 2,2,2-trichloroethyl ester yielded the *Z* isomer, while the phenyl ester gave the *E* isomer. Moreover, we found that the *Z/E* selectivities in the reaction of phenyl esters **1h, 1n**, and **1o** were controlled by the olefin ligand. For example, the platinum-catalyzed reaction of **1h** using 1,5-hexadiene as the olefin ligand gave *E*-**2h** as the major product, while that using 1,5-cyclooctadiene produced mainly the *Z* isomer.

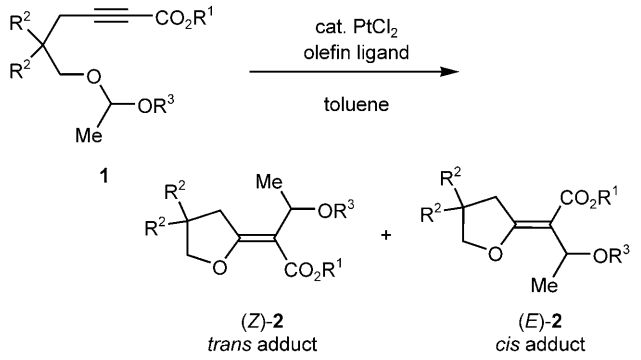
Keywords: alkene ligands; alkynes; cyclization; heterocycles; platinum; stereoselectivity

Introduction

The intramolecular addition reaction involving carbon-carbon triple bonds in the presence of π-acidic transition metal catalysts is one of the most powerful tools to synthesize highly elaborate cyclic compounds in an efficient and atom-economic manner. Particularly, the addition reaction involving hydrogen-heteroatom bonds, such as N–H and O–H bonds, has been extensively investigated and widely utilized in the organic synthesis of heterocycles [Scheme 1, Eq. (1)].[1,2] Recently, the Lewis acidic transition metal-catalyzed cyclization of *ortho*-alkynylanilines,[3,4] *ortho*-alkynylphenyl ethers,[3a,b,5,6] and *ortho*-alkynylphenyl sulfides[7] having a carbon migrating group (CR_3), such as allyl, acyl, *p*-methoxyphenyl (MPM), or α-alkoxylalkyl group, attached to the heteroatom (Y), which proceeds through carbon-heteroatom bond addition, was developed for the synthesis of 2,3-disubstituted indoles, benzofurans, and benzothiophenes [Scheme 1, Eq. (2)]. However, these Lewis acidic transition metal-catalyzed carbon-heteroatom bond addition reactions rarely employed substrates that have an alkyl



Scheme 1. π-Acidic transition metal intramolecular addition to the carbon-carbon triple bond, [Eq. (1)] addition of hydrogen-heteroatom bond, [Eq. (2)] addition of carbon-heteroatom bonds, and [Eq. (3)] allylic carbon-oxygen bonds (Fürstner's work).



Scheme 2. Platinum-catalyzed carboalkoxylation of 6-(1-alkoxyethoxy)hex-2-ynoates **1**.

chain between the alkyne moiety and the heteroatom as the starting material. Fürstner's group reported the platinum-catalyzed cyclization of allyl alkynyl ethers early on [Scheme 1, Eq. (3)].[8] Quite recently, Komeyama and Takaki et al. reported the bismuth-catalyzed carbo-oxycarbonylation of benzylic esters of alkynylcarboxylic acids.[9] We have recently reported that the cyclization of 6-(1-alkoxyethoxy)hex-2-ynoates **1** in the presence of the platinum-olefin catalyst system gave the corresponding multisubstituted 2-[dihydrofuran-2(*3H*)-ylidene]acetates **2** in good to high yields (Scheme 2).[10] The stereoconfiguration of the present reaction was controlled by switching the electronic property of the ester group. In the course of our investigations, we found that the stereochemistry of several substrates could also be controlled by the olefin ligand.[11] Herein we report in detail the platinum-catalyzed carboalkoxylation of 6-(1-alkoxyethoxy)hex-2-yoates **1**, along with our attempt to control the stereoselectivity with the olefin ligand.

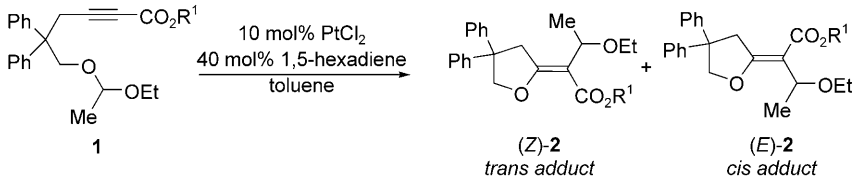
Results and Discussion

E/*Z*-Selective Cyclization Controlled by the Electronic Property of the Ester Group

First, we carried out the reaction of esters **1a–h** of 5,5-diphenyl-6-(1-ethoxyethyl)hex-2-ynoates to examine the electronic effect on the stereoselectivity. The results are summarized in Table 1. The reaction of 2,2,2-trichloroethyl ester **1a** in the presence of 10 mol% $PtCl_2$ and 40 mol% 1,5-hexadiene in toluene at 25 °C gave (*Z*)-**2a**, which was derived from the *trans*-addition of the acetal C–O bond to the alkynyl moiety, in 84% yield with exclusive *Z* stereoselectivity (entry 1). Interestingly, the reaction of substrates **1a**, **1b**, **1c**, and **1d** having an electron-deficient ester group afforded *Z* isomers as the major product (entries 1–4), while the reaction of substrates having a relatively electron-rich ester, such as **1f**, **1g**, and **1h**, proceeded slowly to give the *E* isomers, which were derived from the formal *cis*-addition of the acetal C–O bond (entries 6–8). Particularly, the reaction of phenyl ester **1h** gave (*E*)-**2h** in good yield with exclusive *E* stereoselectivity (entry 8). The stereochemistry of the product was determined by ^{1}H NMR measurement. Furthermore, the structure of (*Z*)-**2e** was unambiguously determined by X-ray crystallographic analysis, as shown in Figure 1.[12]

Then, we explored the substrate scope of the platinum-olefin-catalyzed cyclization of 2,2,2-trichloroeth-

Table 1. Cyclization of **1a–h**.[a]



Entry	**1**	R^1	Time [h]	Yield of **2** [%][b]	Z/E[c]
1	**1a**	Cl_3CCH_2	1.5	**2a**, 84	>99:1
2	**1b**	*p*-O_2N-C_6H_4	3.5	**2b**, 83	96:4
3	**1c**	*p*-Cl-C_6H_4	4	**2c**, 84	95:5
4	**1d**	*p*-Br-C_6H_4	4.5	**2d**, 87	95:5
5[d]	**1e**	Me	4.5	**2e**, 54	31:69
6[d]	**1f**	Et	13	**2f**, 50	<1:99
7[d]	**1g**	*p*-MeO-C_6H_4	24	**2g**, 32	<1:99
8[d]	**1h**	Ph	48	**2h**, 69	<1:99

[a] The reaction of **1** was carried out in the presence of 10 mol% $PtCl_2$ and 40 mol% 1,5-hexadiene in toluene at 25 °C.
[b] ^{1}H NMR yield using 1,3-benzodioxole as the internal standard.
[c] The ratio was determined by ^{1}H NMR.
[d] At 35 °C.

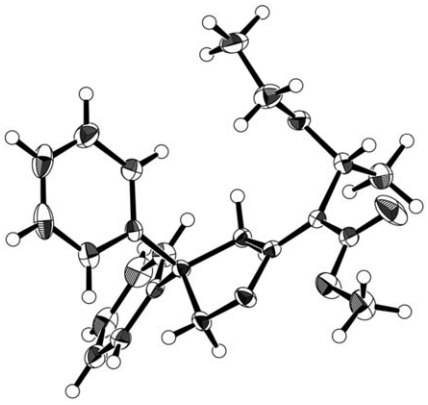
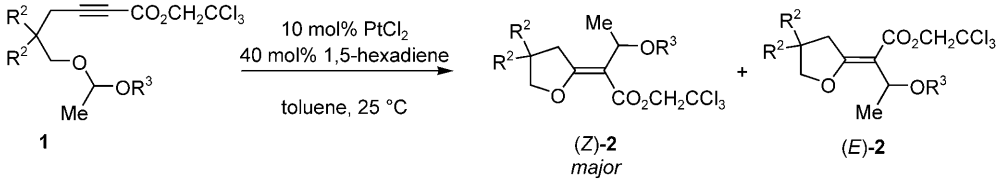


Figure 1. ORTEP drawing of (*Z*)-**2e.**

yl esters (Table 2). Regardless of the bulkiness of the acetal moiety, substrates **1a**, **1i**, and **1j** bearing a *gem*-diphenyl group solely produced *Z* isomers (*Z*)-**2a**, (*Z*)-**2i**, and (*Z*)-**2j**, respectively, in high yields (entries 1–3). The reaction of **1l** having a *gem*-dimethyl group produced **2l** with good stereoselectivity, while that of **1k** having a spirocyclohexyl group proceeded with poor stereoselectivity (entries 4 and 5). Substrate **1m** that did not have a geminal substituent in the tether moiety was converted into **2m** in good yield with acceptable stereoselectivity (entry 6).

Next, we attempted the selective synthesis of *E* isomers using substrates having a phenyl ester (Table 3). The reaction of substrates having a substituent at the tether moiety (R^2) gave the corresponding *E* isomers

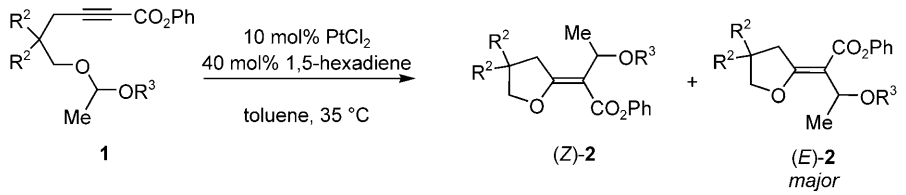
Table 2. Cyclization of 2,2,2-trichloroethyl esters **1a** and **1i–m**.[a]



Entry	**1**	R^2	R^3	Time [h]	Yield of **2** [%][b]	*Z*/*E*[c]
1	**1a**	Ph	Et	1.5	**2a**, 84[d]	>99:1
2	**1i**	Ph	*i*-Pr	1	**2i**, 88	>99:1
3	**1j**	Ph	*i*-Bu	3	**2j**, 78	>99:1
4	**1k**	-$(CH_2)_5$-	Et	4	**2k**, 88	53:47
5	**1l**	Me	Et	2.5	**2l**, 56[d]	71:29
6	**1m**	H	Et	1	**2m**, 75	78:22

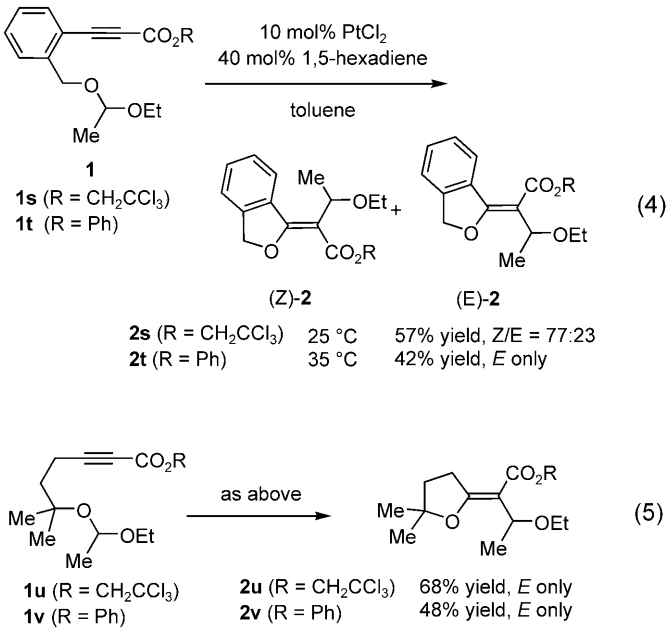
[a] The reaction of **1** was carried out in the presence of 10 mol% $PtCl_2$ and 40 mol% 1,5-hexadiene in toluene at 25 °C.
[b] Isolated yield.
[c] The ratio was determined by ^{1}H NMR.
[d] ^{1}H NMR yield using 1,3-benzodioxole as the internal standard.

Table 3. Cyclization of phenyl esters **1h** and **1n–r**.[a]



Entry	**1**	R^2	R^3	Time [h]	Yield of **2** [%][b]	*Z*/*E*[c]
1	**1h**	Ph	Et	48	**2h**, 69	<1:99
2	**1n**	Ph	*i*-Pr	48	**2n**, 58	12:88
3	**1o**	Ph	*i*-Bu	38	**2o**, 55	18:82
4	**1p**	-$(CH_2)_5$-	Et	43	**2p**, 56	<1:99
5	**1q**	Me	Et	19	**2q**, 58[d]	3:97
6	**1r**	H	Et	1	**2r**, 58	48:52

[a] The reaction of **1** was carried out in the presence of 10 mol% $PtCl_2$ and 40 mol% 1,5-hexadiene in toluene at 35 °C.
[b] Isolated yield.
[c] The ratio was determined by ^{1}H NMR.
[d] ^{1}H NMR yield using 1,3-benzodioxole as the internal standard.

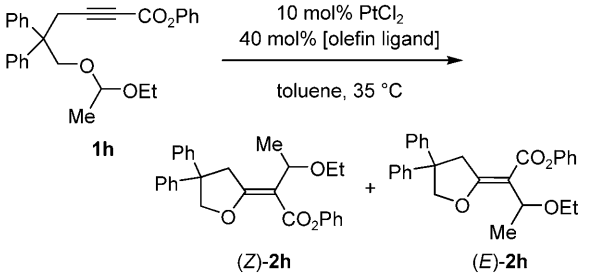


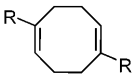
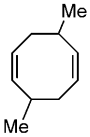
Scheme 3.

as the major product (entries 1–5). In contrast, the reaction of **1r** that did not have any substituents at R^2 afforded a 1:1 mixture of *E*/*Z* isomers (entry 6).

We also examined substrates having substituents at other positions of the tether moiety (Scheme 3). The reaction of the trichloroethyl ester of 3-{*ortho*-[(1-ethoxyethoxy)-methyl]phenyl}-propiolic acid **1s** gave **2s** in 57% yield with moderate *Z* stereoselectivity, while the reaction of phenyl ester **1t** solely afforded *E* isomer (*E*)-**2t** [Scheme 3, Eq. (4)]. In contrast, the reactions of **1u** and **1v**, which had two *gem*-dimethyl groups on the carbon bound to a 1-ethoxyethoxy group, solely produced the corresponding *E* isomers, despite the electronic character of the ester group [Scheme 3, Eq. (5)].

Table 4. Effect of olefin ligand on *Z*/*E* selectivity in the cyclization of **1h**.[a]



Entry	Olefin	Time [h]	Yield [%][b]	*Z*/*E*[c]
1	1,5-hexadiene	48	71	<1:99
2	COT	36	49	<1:99
3	1,3-cyclooctadiene	48	35	<1:99
4	norbornadiene	48	45	27:73
5	COD	37	79	87:13
	 **3**			
6	**3a** (R = CH_3)	48	37	94:6
7	**3b** (R = Ph)	72	63	3:97
8	**3c** (R = CHO)	9	42	<1:99
9	**3d** (R = Br)	48	Nr[d]	–
10	 **3e**	15	86	86:14
11	None	69	–[e]	–

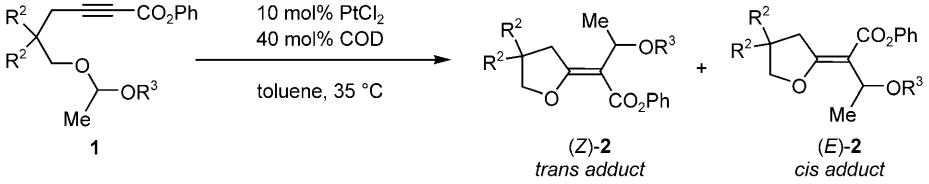
[a] The reaction of **1h** was carried out in the presence of 10 mol% $PtCl_2$ and 40 mol% olefin ligand in toluene at 35 °C.
[b] ^{1}H NMR yield using 1,3-benzodioxole as the internal standard.
[c] The ratio was determined by ^{1}H NMR.
[d] Nr = no reaction.
[e] Decomposition of **1h** was observed.

Attempts to Control Stereoselectivity with the Olefin Ligand

To enhance the synthetic utility of the present methodology, we tried to control the stereoselectivity with the olefin ligand. We studied the effect of the olefin ligand on the stereoselectivity of the reaction of **1h**. The results are summarized in Table 4. When 1,3,5,7-cyclooctatetraene (COT) and 1,3-cyclooctadiene were used as the olefin ligand instead of 1,5-hexadiene, *E* isomer (*E*)-**2h** was predominantly obtained (entries 2 and 3). In contrast, when typical bidentate olefin ligands, such as norbornadiene and 1,5-cyclooctadiene (COD), were used, (*Z*)-**2h** was formed (entries 4 and 5). Notably, the reaction using COD gave the *Z* isomer as a major product (entry 5). Thus, we tested several COD derivatives for *Z*-selective cyclization (entries 6–10). The use of **3a** that had two electron-donating methyl groups at the 1 and 5 positions (olefin moiety) led to higher *Z* selectivity than the use of COD, although the chemical yield was lower (entry 6). In contrast, the use of **3b** and **3c** yielded products with *E* selectivity (entries 7 and 8).[11b,13] 1,5-Dibromo-1,5-cyclooctadiene (**3d**) totally blocked the present reaction (entry 9). Olefin ligand **3e** having two methyl groups at the 3 and 7 positions (methylene moiety) showed a similar *Z* selectivity to COD (entry 10). The reaction in the absence of the olefin ligand did not afford the desired products; **1h** was decomposed (entry 11).[14]

Then, we applied the *Z*-selective synthesis using COD as the olefin ligand to various substrates. The

Table 5. Cyclization of **1h** and **1n–r** using COD as olefin ligand.[a]



Entry	**1**	R^2	R^3	Time [h]	Yield of **2** [%][b]	*Z*/*E*[c]
1	**1h**	Ph	Et	37	**2h**, 79	87:13
2	**1n**	Ph	*i*-Pr	39	**2n**, 58	94:6
3[d]	**1o**	Ph	*i*-Bu	48	**2o**, 66	82:18
4	**1p**	-$(CH_2)_5$-	Et	46	**2p**, 35	37:63
5	**1q**	Me	Et	4.5	**2q**, 76	43:57
6	**1r**	H	Et	15	**2r**, 45	62:38

[a] The reaction of **1** was carried out in the presence of 10 mol% $PtCl_2$ and 40 mol% 1,5-cyclooctadiene in toluene at 35 °C.
[b] ^{1}H NMR yield using 1,3-benzodioxole as the internal standard.
[c] The ratio was determined by ^{1}H NMR.
[d] At 50 °C.

results are summarized in Table 5. The reactions of **1h**, **1n**, and **1o** bearing a *gem*-diphenyl group at the tether moiety showed good *Z* selectivity despite the bulkiness of the migrating group (entries 1–3). However, the reaction of **1p** and **1q** having a spirocyclohexyl group and a *gem*-dimethyl group, respectively, had poor selectivity (entries 4 and 5). Accordingly, the *Z*-selective reaction using COD as ligand is limited to substrates having phenyl groups at R^2 at present.

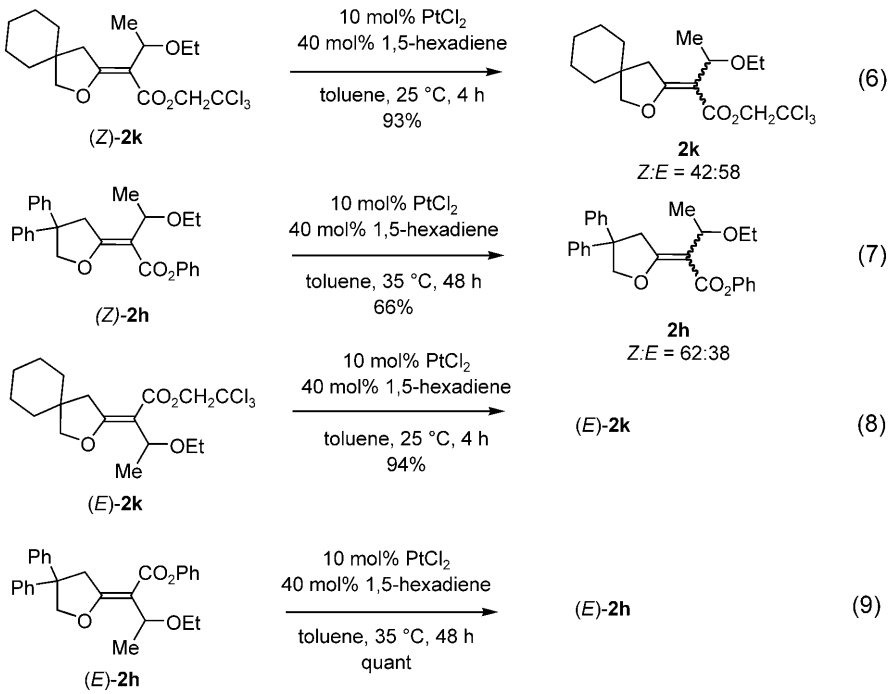
Reaction Mechanism

We observed isomerization from the *Z* product to its corresponding *E* geometrical isomer in the presence of platinum-olefin catalysts.[15] Isolated 2,2,2-trichloroethyl ester (*Z*)-**2k** was rapidly converted into a 42:58 mixture of *Z*/*E* isomers in the presence of the platinum catalyst, indicating that (*E*)-**2k** was formed mainly by the platinum-catalyzed isomerization from (*Z*)-**2k** that was produced in the reaction of **1k** [Scheme 4, Eq. (6) *versus* Table 2, entry 4]. On the other hand, isolated (*Z*)-**2h** was converted into a 62:38 mixture of *Z*/*E* stereoisomers under the reaction conditions, indicating that the *Z*/*E* isomerization occurs on the way of the cyclization process and the interconversion from *Z* isomer to *E* isomer is a minor reaction pathway in the reaction of **1h**, since the interconversion ratio from (*Z*)-**2h** to (*E*)-**2h** was much lower than that in the cyclization reaction of **1h** [Scheme 4, Eq. (7) *versus* Table 1, entry 8]. In contrast, isolated (*E*)-**2k** and (*E*)-**2h** remained unchanged under the reaction conditions, suggesting that the *E* isomers were thermodynamically more stable than the *Z* isomers [Scheme 4, Eqs. (8) and (9)].[16]

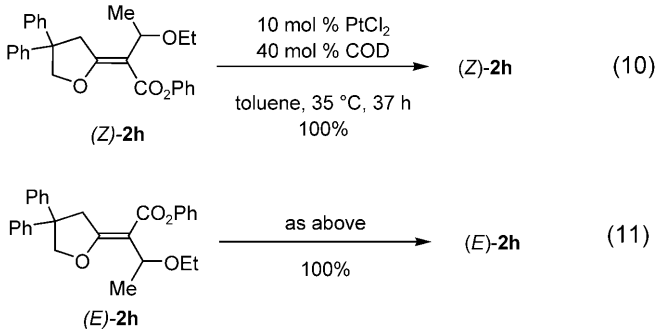
When (*Z*)-**2h** was treated with catalytic amounts of $PtCl_2$ and COD, (*E*)-**2h** was not obtained at all, indicating that the interconversion from (*Z*)-**2h** to (*E*)-**2h** was completely suppressed by COD used as ligand, in contrast to that using 1,5-hexadiene [Scheme 5, Eq. (10) *versus* Scheme 4, Eq. (7)]. Moreover, the isomerization of (*E*)-**2h** to (*Z*)-**2h** did not occur in the presence of $PtCl_2$ and COD, suggesting that (*Z*)-**2h** was directly formed in the cyclization step [Scheme 5, Eq. (11)].

To find out if the migration of the α-alkoxyalkyl group occurs in an intramolecular or intermolecular manner, we performed crossover experiments (Scheme 6). The reaction of a 1:1 mixture of **1b** and **1j** under conventional reaction conditions gave corresponding products (*Z*)-**2b** and (*Z*)-**2j** in 86 and 90% yields, respectively; crossover products, such as (*Z*)-**2a** and (*Z*)-**2w**, were not detected by GC-mass and NMR analysis. This result clearly indicates that the migration of the α-alkoxyalkyl group proceeds in an intramolecular manner.

On the basis of these experiments, we propose the mechanism of this reaction, as shown in Scheme 7. A Lewis acidic platinum catalyst coordinates to the triple bond of substrate **1**, forming π-complex **4**. Nucleophilic attack of the oxygen atom of the acetal moiety on the electron-deficient alkyne moiety leads to cyclized intermediate (*Z*)-**5**. [1,3]Migration of the α-alkoxyalkyl group, followed by elimination of the platinum catalyst, the so-called carbodemetalation, gives the *Z* isomer. In the reaction of phenyl esters (**1h**, **1n–r**, and **1t**) using 1,5-hexadiene, the isomeriza-

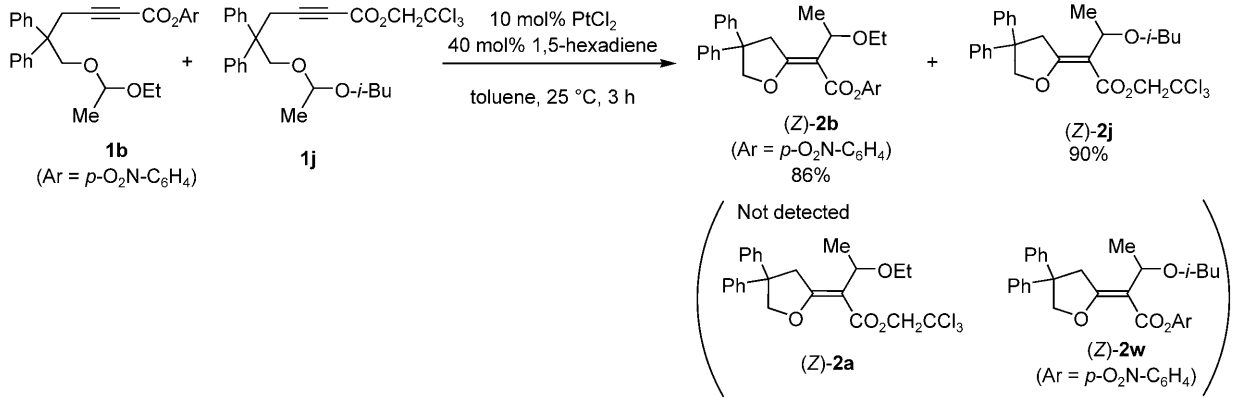


Scheme 4. Isomerization experiments in the presence of $PtCl_2$ and 1,5-hexadiene.

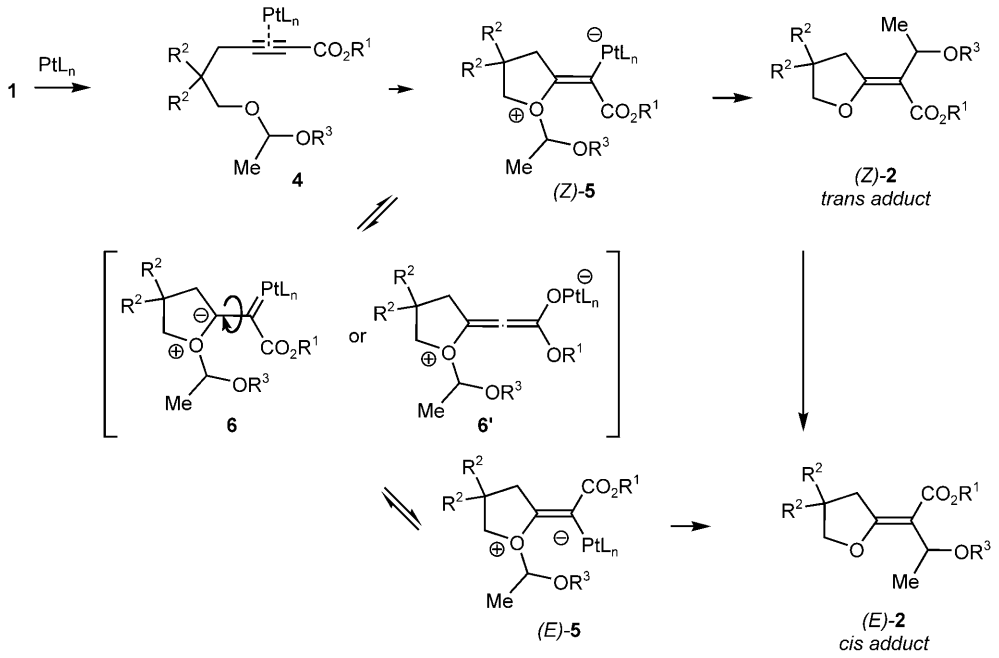


Scheme 5. Isomerization experiments in the presence of $PtCl_2$ and COD.

tion from (*Z*)-**5** to (*E*)-**5** through platinum carbene intermediate **6** or platinum allenoate intermediate takes place.[17,18] Similarly, the following carbodemetalation gives the *E* isomer. In the reaction of 2,2,2-trichloroethyl ester, a strongly electron-withdrawing group facilitates elimination of the α-alkoxyalkyl group, leading to fast carbodemetalation from (*Z*)-**5** to (*Z*)-**2**. The *E* product is also formed *via* isomerization from the *Z* product.[19] The reaction pathway for the formation of the *E* isomer depends on the substrate's structure. The high *Z* selectivity in the reaction of **1h**, **1n**, and **1o** in the presence of COD is presumably due to intramolecular steric repulsion between the alkoxyethyl group and the vinylplatinum coordinated by a strong bidentate COD ligand in intermediate (*E*)-**5**, suppressing the formation of the *E* isomer.[20,21]



Scheme 6. Crossover experiment.



Scheme 7. Plausible mechanism.

Conclusions

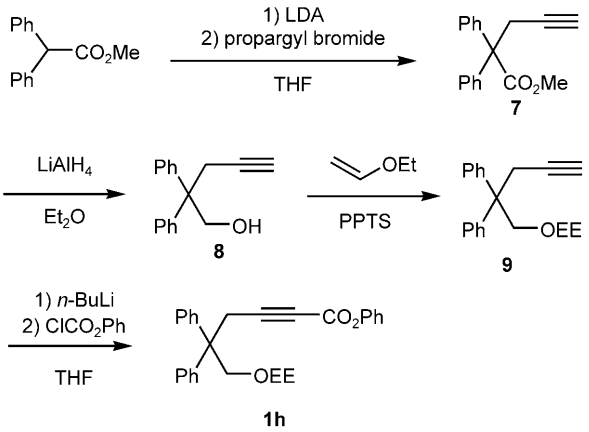
We are now in a position to synthesize multisubstituted 2-[dihydrofuran-2(3*H*)-ylidene]acetates stereoselectively by changing either the ester group or the olefin ligand. The present reaction, that we termed carboalkoxylation and which proceeds with the addition of an acetal C–O bond, is a useful methodology to synthesize [dihydrofuran-2(3*H*)-ylidene]acetates in an efficient and atom-economic manner.

Experimental Section

General Remarks

All reactions were carried out under argon atmosphere. $PtCl_2$ was purchased from Wako Pure Chemical Industries and used as received. Column chromatography was performed with Kanto Chemical silica gel 60N (spherical, neutral, 100–210 μm). Spectroscopic measurements were carried out with the following instruments; JEOL GSX-270 (NMR), JEOL JNM α-500 (NMR), Bruker BioSpin AVANCE 600 (NMR), JEOL ECA-600 (NMR), JASCO FT/IR 4100 (IR), and Bruker Daltonics APEX III (HR-MS). Chemical shifts are reported in ppm relative to tetramethylsilane (for ^1H, $\delta = 0.00$) and $CDCl_3$ (for ^{13}C, $\delta = 77.00$).

Representative Procedure for the Synthesis of 1h (Scheme 8)



Scheme 8. Preparation of **1h**.

Methyl 2,2-diphenylpent-4-ynoate (7): To a stirred solution of diisopropylamine (1.48 mL, 11 mmol) in dry THF (5 mL) at 0 °C was added *n*-BuLi (1.59 M in THF, 6.6 mL, 10.5 mmol), dropwise and stirred for 5 min at 0 °C. After being cooled to −78 °C, methyl diphenylacetate (2.26 g, 10 mmol) in dry THF (15 mL) was added slowly to the reaction mixture and further stirred for 1.5 h at the same temperature before propargyl bromide (0.8 mL, 10.5 mmol) was added. The reaction mixture was then allowed to warm to room temperature and further stirred for 15 h. The reaction was then quenched with aqueous ammonium chloride, extracted with ethyl acetate, and the organic phase was washed with water and brine and dried over anhydrous magnesium sulfate. Solvent was then removed under reduced pressure and the residue was purified by silica gel column chromatography using 6% of ethyl acetate/hexane to provide **7** as a light brown solid; yield: 2.20 g (83%).

2,2-Diphenylpent-4-yn-1-ol (8): To a stirred mixture of lithium aluminum hydride (0.33 g, 8.6 mmol) in ether (15 mL) at 0 °C was added methyl ester **7** (2.20 g, 8.3 mmol)

in ether (5 mL). The reaction mixture was allowed to warm to room temperature and was further stirred at for 1.5 h. To the reaction mixture was then added 5 mL of silica gel and 1 M aqueous NaOH slowly until the precipitate turned white. Water was then added and the mixture was extracted with ether. Nextx, the reaction mixture was filtered through a pad of Celite. Solvent was then removed under reduced pressure and the residue was purified by silica gel column chromatography with using 16% of ethyl acetate/hexane to provide **8** as a yellow oil; yield: 1.83 g (94%).

5-(1-Ethoxyethoxy)-4,4-diphenylpent-1-yne (9): To a stirred solution of alcohol **8** (1.83 g, 8.6 mmol) in dichloromethane (55 mL) at room temperature was added ethyl vinyl ether (1.16 mL, 12.4 mmol), and pyridinium *p*-toluenesulfonate (0.21 g, 0.82 mmol). The reaction mixture was stirred at room temperature and monitored to completion by TLC. After completion, the reaction mixture was washed with water and brine; dried over anhydrous magnesium sulfate and filtered through a pad of Celite. Solvent was then removed under reduced pressure and the residue was purified by silica gel column chromatography using 9% of ethyl acetate/hexane to provide **9** as a white solid; yield: 2.20 g (92%).

Phenyl 6-(1-ethoxyethoxy)-5,5-diphenylhex-2-ynoate (1h): To a stirred solution of alkyne **9** (0.918 g, 3.0 mmol) in THF (20 mL) at −78 °C was added *n*-BuLi (1.63 M in THF, 2.02 mL, 3.3 mmol). After stirring for 30 min at −78 °C, phenyl chloroformate (0.47 mL, 3.69 mmol) was added slowly and further stirred for 50 min. The reaction mixture was quenched with saturated aqueous $NaHCO_3$, washed with water and brine, dried over anhydrous magnesium sulfate and filtered through a pad of Celite. Solvent was then removed under reduced pressure and the residue was purified by silica gel column chromatography using 6% of ethyl acetate/hexane to provide **1h** as a white solid; yield: 1.14 g (88%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.11$ (t, $J = 6.8$ Hz, 3H), 1.27 (d, $J = 5.5$ Hz, 2H), 3.26–3.47 (m, 4H), 4.07 (d, $J = 9.4$ Hz, 1H), 4.27 (d, $J = 9.4$ Hz, 1H), 4.66 (q, $J = 5.5$ Hz, 1H), 7.06 (d, $J = 7.7$ Hz, 2H), 7.21–7.37 (m, 13H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 15.23$, 19.51, 27.89, 50.42, 60.98, 69.94, 75.09, 89.84, 100.10, 121.37, 126.20, 126.67, 127.69, 128.13, 129.46, 144.60, 144.65, 150.09, 151.66; IR (neat): $\nu =$ 3059, 2967, 2887, 2221, 1716, 1241, 1183, 1055 cm^{-1}; HR-MS (ESI): $m/z = 451.1878$, calcd. for $(M+Na)^+$: 451.1880.

Representative Procedure for the Pt(II)-Olefin Catalyzed Synthesis of (*E*)-2h

To a stirred mixture of $PtCl_2$ (26.6 mg, 0.10 mmol) in toluene (2.0 mL) at 35 °C was added 1,5-hexadiene (47.5 μL, 0.40 mmol). After stirring for 5 min at 35 °C, substrate **1h** (428.3 mg, 1.00 mmol) was added. The reaction mixture was monitored to completion by TLC. After completion, the reaction mixture was filtered through a pad of silica gel, and solvent was then removed under reduced pressure. The residue was purified by silica gel column chromatography using 5% of ethyl acetate/hexane to provide (*E*)-**2h** as a white solid; yield: 296.7 mg (69%).

(*Z*)-2,2,2-Trichloroethyl 3-ethoxy-2-[dihydro-4,4-diphenylfuran-2(3*H*)-ylidene]butanoate [(*Z*)-2a]: ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 0.94$ (t, $J = 7.0$ Hz, 3H), 1.31 (d, $J = 6.6$ Hz, 3H), 3.03–3.20 (m, 2H), 3.48 (d, $J = 16.1$ Hz, 1H), 3.79 (d, $J = 16.1$ Hz, 1H), 4.59 (q, $J = 6.6$ Hz, 1H), 4.76–4.94 (m, 4H), 7.18–7.34 (m, 10H); ^{13}C NMR (67 MHz, $CDCl_3$): $\delta = 15.14$, 21.48, 43.40, 53.42, 63.46, 72.09, 73.68, 80.16, 95.65, 102.97, 126.82, 128.64, 143.69, 143.95, 164.26, 171.07; IR (neat): $\nu = 3059$, 2973, 2948, 2892, 1720, 1610, 1133, 1088, 960, 915, 902, 816 cm^{-1}; HR-MS (ESI): $m/z = 505.0710$, calcd. for $(M+Na)^+$: 505.0711.

(*Z*)-4-Nitrophenyl 3-ethoxy-2-[dihydro-4,4-diphenylfuran-2(3*H*)-ylidene]butanoate [(*Z*)-2b]: ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 1.01$ (t, $J = 7.0$ Hz, 3H), 1.38 (d, $J = 6.6$ Hz, 3H), 3.13–3.29 (m, 2H), 3.55 (d, $J = 16.3$ Hz, 1H), 3.86 (d, $J = 16.3$ Hz, 1H), 4.61 (q, $J = 6.6$ Hz, 1H), 4.83 (d, $J = 9.0$ Hz, 1H), 4.95 (d, $J = 9.0$ Hz, 1H), 7.20–7.37 (m, 12H), 8.22–8.28 (m, 2H); ^{13}C NMR (67 MHz, $CDCl_3$): $\delta = 15.24$, 21.46, 43.66, 53.45, 63.70, 72.55, 80.55, 102.75, 122.70, 122.74, 122.77, 124.95, 126.80, 127.15, 128.75, 128.80, 143.65, 143.87, 144.94, 156.16, 163.74, 172.00; IR (neat): $\nu = 3058$, 2973, 2893, 1726, 1697, 1613, 1590, 1519, 1344, 1136, 1089, 966 cm^{-1}; HR-MS (ESI): m/z = 496.1728, calcd. for $(M+Na)^+$: 496.1731.

(*Z*)-4-Chlorophenyl 3-ethoxy-2-[dihydro-4,4-diphenylfuran-2(3*H*)-ylidene]butanoate [(*Z*)-2c]: ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 0.99$ (t, $J = 7.0$ Hz, 3H), 1.37 (d, $J = 6.6$ Hz, 3H), 3.14–3.25 (m, 2H), 3.52 (d, $J = 16.1$ Hz, 1H), 3.83 (d, $J = 16.1$ Hz, 1H), 4.61 (q, $J = 6.6$ Hz, 1H), 4.79 (d, $J = 9.0$ Hz, 1H), 4.91 (d, $J = 9.0$ Hz, 1H), 7.04–7.10 (m, 2H), 7.19–7.34 (m, 12H); ^{13}C NMR (67 MHz, $CDCl_3$): $\delta = 15.23$, 21.46, 43.44, 53.44, 63.59, 72.60, 80.32, 103.27, 123.36, 126.86, 127.06, 128.71, 129.16, 130.53, 143.84, 144.06, 149.62, 164.61, 170.68; IR (neat): $\nu = 3059$, 2973, 2928, 1725, 1694, 1624, 1485, 1201, 1144, 1087, 1013, 970 cm^{-1}; HR-MS (ESI): $m/z =$ 485.1488, calcd. for $(M+Na)^+$: 485.1490.

(*E*)-4-Chlorophenyl 3-ethoxy-2-[dihydro-4,4-diphenylfuran-2(3*H*)-ylidene]butanoate [(*E*)-2c]: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.18$ (t, $J = 6.8$ Hz, 3H), 1.53 (d, $J = 6.8$ Hz, 3H), 3.34–3.46 (m, 2H), 3.82 (d, $J = 17.5$ Hz, 1H), 3.91 (d, $J = 17.5$ Hz, 1H), 4.79–4.88 (m, 3H), 7.02–7.05 (m, 2H), 7.17–7.33 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 15.44$, 20.23, 45.34, 53.55, 63.56, 70.53, 80.50, 104.66, 123.37, 126.74, 126.83, 126.99, 127.03, 128.66, 129.23, 130.69, 144.04, 144.27, 149.39, 166.73, 173.87; IR (neat): $\nu = 3087$, 2972, 2868, 1710, 1617, 1485, 1199, 1078, 1022, 1011, 976 cm^{-1}; HR-MS (ESI): $m/z = 485.1488$, calcd. for $(M+Na)^+$: 485.1490.

(*Z*)-4-Bromophenyl 3-ethoxy-2-[dihydro-4,4-diphenylfuran-2(3*H*)-ylidene]butanoate [(*Z*)-2d]: ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 0.99$ (t, $J = 7.0$ Hz, 3H), 1.37 (d, $J = 6.6$ Hz, 3H), 3.14–3.25 (m, 2H) 3.52 (d, $J = 16.1$ Hz, 1H), 3.83 (d, $J = 16.1$ Hz, 1H), 4.61 (q, $J = 6.6$ Hz, 1H), 4.79 (d, $J = 9.0$ Hz, 1H), 4.91 (d, $J = 9.0$ Hz, 1H), 6.99–7.05 (m, 2H), 7.19–7.34 (m, 10H), 7.42–7.48 (m, 2H); ^{13}C NMR (67 MHz, $CDCl_3$): $\delta = 15.16$, 21.39, 43.36, 53.34, 63.49, 72.50, 80.18, 103.11, 118.13, 123.71, 123.79, 126.76, 126.93, 128.61, 132.01, 132.10, 143.71, 143.94, 150.07, 164.40, 170.67; IR (neat): $\nu = 3059$, 2972, 2893, 1724, 1694, 1625, 1482, 1200, 1144, 1066, 970 cm^{-1}; HR-MS (ESI): $m/z = 529.0982$, calcd. for $(M+Na)^+$: 529.0985.

(*Z*)-Methyl 3-ethoxy-2-[dihydro-4,4-diphenylfuran-2(3*H*)-ylidene]butanoate [(*Z*)-2e]: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.96$ (t, $J = 6.8$ Hz, 3H), 1.29 (d, $J = 6.4$ Hz, 3H), 3.08–3.18 (m, 2H), 3.45 (d, $J = 16.2$ Hz, 1H), 3.73 (d, $J = 16.2$ Hz, 1H), 3.74 (s, 3H), 4.50 (q, $J = 6.4$ Hz, 1H), 4.75 (d, $J = 9.0$ Hz, 1H), 4.86 (d, $J = 9.0$ Hz, 1H), 7.12–7.32 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 15.18$, 21.34, 42.93, 51.22,

53.30, 63.40, 72.59, 79.89, 104.05, 126.82, 126.86, 126.87, 126.95, 128.58, 128.64, 143.98, 144.20, 167.14, 168.11; IR (neat): $\nu = 3022$, 2973, 2893, 1707, 1679, 1634, 1433, 1304, 1164, 1091, 1015 cm^{-1}; HR-MS (ESI): $m/z = 389.1723$, calcd. for $(M+Na)^+$: 389.1723.

(*E*)-Methyl 3-ethoxy-2-[dihydro-4,4-diphenylfuran-2(3*H*)-ylidene]butanoate [(*E*)-2e]: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.13$ (t, $J = 6.8$ Hz, 3H), 1.43 (d, $J = 6.4$ Hz, 3H), 3.26–3.37 (m, 2H), 3.71 (s, 3H), 3.77 (d, $J = 17.1$ Hz, 1H), 3.84 (d, $J = 17.1$ Hz, 1H), 4.69 (q, $J = 6.4$ Hz, 1H), 4.74 (d, $J = 9.0$ Hz, 1H), 4.79 (d, $J = 9.0$ Hz, 1H), 7.17–7.30 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 15.33$, 20.06, 44.92, 50.99, 53.52, 63.40, 70.56, 80.02, 105.42, 126.80, 126.85, 126.89, 128.54, 128.55, 144.27, 144.49, 168.72, 171.22; IR (neat): $\nu = 3060$, 2972, 2893, 1696, 1623, 1281, 1092, 1066, 1027 cm^{-1}; HR-MS (ESI): $m/z = 389.1722$, calcd. for $(M+Na)^+$: 389.1723.

(*E*)-Ethyl 3-ethoxy-2-[dihydro-4,4-diphenylfuran-2(3*H*)-ylidene]butanoate [(*E*)-2f]: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.14$ (t, $J = 6.8$ Hz, 3H), 1.28 (t, $J = 7.3$ Hz, 3H), 1.45 (d, $J = 6.4$ Hz, 3H), 3.26–3.38 (m, 2H), 3.78 (d, $J = 17.1$ Hz, 1H), 3.84 (d, $J = 17.1$ Hz, 1H), 4.13–4.23 (m, 2H), 4.68–4.73 (m, 2H), 4.79 (d, $J = 9.0$ Hz, 1H), 7.17–7.30 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 14.29$, 15.27, 19.97, 44.90, 53.40, 59.57, 63.21, 70.57, 79.90, 105.54, 108.71, 126.71, 126.74, 126.77, 126.80, 128.44, 128.46, 144.22, 144.48, 168.11, 170.85; IR (neat): $\nu = 3084$, 2970, 2882, 1679, 1613, 1264, 1093, 1065 cm^{-1}; HR-MS (ESI): $m/z = 403.1878$, calcd. for $(M+Na)^+$: 403.1880.

(*E*)-4-Methoxyphenyl 3-ethoxy-2-[dihydro-4,4-diphenylfuran-2(3*H*)-ylidene]butanoate [(*E*)-2g]: ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 1.19$ (t, $J = 7.0$ Hz, 3H), 1.54 (d, $J = 6.6$ Hz, 3H), 3.32–3.50 (m, 2H), 3.78–3.95 (m, 5H), 4.77–4.89 (m, 3H), 6.84–6.92 (m, 2H), 6.97–7.03 (m, 2H), 7.16–7.32 (m, 10H); ^{13}C NMR (67 MHz, $CDCl_3$): $\delta = 15.44$, 20.20, 45.29, 53.55, 55.53, 55.62, 63.50, 70.62, 70.72, 80.39, 104.99, 114.32, 122.67, 126.89, 128.62, 144.17, 144.40, 157.00, 167.34, 173.15; IR (neat): $\nu = 3059$, 2971, 2896, 1705, 1620, 1505, 1191, 1079, 1021, 977 cm^{-1}; HR-MS (ESI): $m/z = 481.1983$, calcd. for $(M+Na)^+$ 481.1985.

(*Z*)-Phenyl 3-ethoxy-2-[dihydro-4,4-diphenylfuran-2(3*H*)-ylidene]butanoate [(*Z*)-2h]: ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 0.99$ (t, $J = 7.0$ Hz, 3H), 1.37 (d, $J = 6.7$ Hz, 3H), 3.20 (m, 2H), 3.52 (d, $J = 16.1$ Hz, 1H), 3.83 (d, $J = 16.1$ Hz, 1H), 4.64 (q, $J = 6.7$ Hz, 1H), 4.79 (d, $J = 9.1$ Hz, 1H), 4.92 (d, $J = 9.1$ Hz, 1H), 7.13–7.37 (m, 15H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 15.24$, 21.49, 43.33, 53.41, 63.52, 72.57, 80.14, 103.51, 121.99, 126.83, 126.88, 128.66, 128.71, 129.13, 143.86, 144.12, 151.06, 164.92, 170.24; IR (neat): $\nu = 3059$, 3037, 2972, 2927, 2862, 1718, 1611, 1589, 1488, 1160, 1151, 1132, 965 cm^{-1}; anal. calcd. for $C_{28}H_{28}O_4$: C 78.48, H 6.59, N 0.00; found: C 78.26, H 6.57, N 0.00.

(*E*)-Phenyl 3-ethoxy-2-[dihydro-4,4-diphenylfuran-2(3*H*)-ylidene]butanoate [(*E*)-2h]: ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 1.19$ (t, $J = 7.0$ Hz, 3H), 1.55 (d, $J = 6.9$ Hz, 3H), 3.37–3.46 (m, 2H), 3.85 (d, $J = 17.5$ Hz, 1H), 3.92 (d, $J = 17.5$ Hz, 1H), 4.79–4.88 (m, 3H), 7.08–7.38 (m, 15H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 15.47$, 20.23, 45.36, 53.55, 63.55, 70.70, 80.45, 104.91, 122.00, 126.78, 126.88, 128.65, 128.67, 129.23, 144.13, 144.39, 150.92, 167.04, 173.47; IR (neat): $\nu = 3057$, 2973, 2870, 1698, 1613, 1596, 1492, 1277, 1202, 1024 cm^{-1}; anal. calcd. for $C_{28}H_{28}O_4$: C 78.48, H 6.59, N 0.00; found: C 78.52, H 6.57, N 0.00.

(*Z*)-2,2,2-Trichloroethyl 2-[dihydro-4,4-diphenylfuran-2(3*H*)-ylidene]-3-isopropoxybutanoate [(*Z*)-2i]: ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 0.77$ (d, $J = 6.2$ Hz, 3H), 1.04 (d, $J = 5.8$ Hz, 3H), 1.28 (d, $J = 6.6$ Hz, 3H), 3.31–3.40 (m, 1H), 3.51 (d, $J = 16.1$ Hz, 1H), 3.80 (d, $J = 16.1$ Hz, 1H), 4.69–4.91 (m, 5H), 7.19–7.34 (m, 10H); ^{13}C NMR (67 MHz, $CDCl_3$): $\delta = 21.08$, 21.76, 22.88, 43.60, 53.38, 68.20, 68.59, 73.70, 80.31, 95.62, 103.65, 126.85, 126.98, 128.64, 143.80, 144.04, 164.24, 171.40; IR (neat): $\nu = 3062$, 2965, 2942, 1723, 1613, 1159, 1143, 1085, 1025, 971 cm^{-1}; HR-MS (ESI): $m/z = 519.0863$, calcd. for $(M+Na)^+$: 519.0867.

(*Z*)-2,2,2-Trichloroethyl 2-[dihydro-4,4-diphenylfuran-2(3*H*)-ylidene]-3-isobutoxybutanoate [(*Z*)-2j]: ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 0.72$ (d, $J = 6.6$ Hz, 3H), 0.78 (d, $J = 6.6$ Hz, 3H), 1.30 (d, $J = 6.6$ Hz, 3H), 1.54–1.67 (m, 1H), 2.85 (d, $J = 6.6$ Hz, 2H), 3.50 (d, $J = 16.3$ Hz, 1H), 3.74 (d, $J = 16.3$ Hz, 1H), 4.54 (q, $J = 6.6$ Hz, 1H), 4.75–4.90 (m, 4H), 7.18–7.33 (m, 10H); ^{13}C NMR (67 MHz, $CDCl_3$): $\delta = 19.31$, 19.38, 21.24, 28.26, 43.50, 53.38, 72.61, 73.68, 75.27, 80.29, 95.65, 103.08, 126.85, 128.62, 143.88, 144.01, 164.26, 170.87; IR (neat): $\nu = 3060$, 2956, 2870, 1717, 1614, 1261, 1158, 1088, 1040, 961 cm^{-1}; HR-MS (ESI): $m/z = 533.1026$, calcd. for $(M+Na)^+$: 533.1024.

2,2,2-Trichloroethyl (2*Z*)-3-ethoxy-2-(2-oxaspiro[4.5]dec-3-ylidene)butanoate [(*Z*)-2k]: ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 1.18$ (t, $J = 7.0$ Hz, 3H), 1.39 (d, $J = 6.6$ Hz, 3H), 1.46–1.52 (m, 10H), 2.69 (d, $J = 17.2$ Hz, 1H), 2.91 (d, $J = 17.2$ Hz, 1H), 3.32–3.37 (m, 1H), 3.46–3.51 (m, 1H), 4.08 (d, $J = 8.8$ Hz, 1H), 4.11 (d, $J = 8.8$ Hz, 1H), 4.63 (q, $J = 6.6$ Hz, 1H), 4.74 (d, $J = 12.0$ Hz, 1H), 4.82 (d, $J = 12.0$ Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 15.35$, 21.43, 23.25, 23.33, 25.69, 34.18, 41.34, 42.79, 63.41, 72.16, 73.59, 81.44, 95.68, 101.61, 164.28, 173.23; IR (neat): $\nu = 2972$, 2926, 2854, 1723, 1686, 1616, 1451, 1258, 1158, 1091, 1013 cm^{-1}; HR-MS (ESI): $m/z = 421.0710$, calcd. for $(M+Na)^+$: 421.0711.

2,2,2-Trichloroethyl (2*E*)-3-ethoxy-2-(2-oxaspiro[4.5]dec-3-ylidene)butanoate [(*E*)-2k]: ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 1.17$ (t, $J = 7.0$ Hz, 3H), 1.46–1.48 (m, 13H), 3.01 (d, $J = 18.3$ Hz, 1H), 3.06 (d, $J = 18.3$ Hz, 1H), 3.34–3.45 (m, 2H), 4.01 (d, $J = 8.8$ Hz, 1H), 4.06 (d, $J = 8.8$ Hz, 1H), 4.72 (q, $J = 6.8$ Hz, 1H), 4.77 (d, $J = 12.0$ Hz, 1H), 4.83 (d, $J = 12.0$ Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 15.44$, 19.91, 23.25, 23.36, 25.69, 34.56, 34.60, 41.46, 44.89, 63.44, 70.75, 73.89, 81.68, 95.65, 103.41, 166.33, 175.08; IR (neat): $\nu = 2971$, 2926, 2856, 1703, 1614, 1451, 1371, 1274, 1086, 1009, 911 cm^{-1}; HR-MS (ESI): $m/z = 421.0712$, calcd. for $(M+Na)^+$: 421.0711.

(*Z*)-2,2,2-Trichloroethyl 3-ethoxy-2-[dihydro-4,4-dimethylfuran-2(3*H*)-ylidene]butanoate [(*Z*)-2l]: ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 1.16$–1.20 (m, 9H), 1.39 (d, $J = 6.6$ Hz, 3H), 2.69 (d, $J = 16.9$ Hz, 1H), 2.86 (d, $J = 16.9$ Hz, 1H), 3.29–3.56 (m, 2H), 4.03 (s, 2H), 4.61 (q, $J = 6.6$ Hz, 1H), 4.76 (d, $J = 12.1$ Hz, 1H), 4.84 (d, $J = 12.1$ Hz, 1H); ^{13}C NMR (67 MHz, $CDCl_3$): $\delta = 15.30$, 21.45, 24.79, 37.35, 45.35, 63.40, 72.25, 73.63, 83.07, 95.69, 101.96, 164.26, 173.05; IR (neat): $\nu = 2969$, 2875, 1725, 1687, 1618, 1371, 1303, 1261, 1158, 1088, 1011, 965 cm^{-1}; HRMS (ESI): $m/z = 381.0395$, calcd. for $(M+Na)^+$: 381.0398.

(*E*)-2,2,2-Trichloroethyl 3-ethoxy-2-[dihydro-4,4-dimethylfuran-2(3*H*)-ylidene]butanoate [(*E*)-2l]: ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 1.12$–1.20 (m, 9H), 1.48 (d, $J = 6.6$ Hz, 3H), 2.95 (d, $J = 17.9$ Hz, 1H), 3.03 (d, $J = 17.9$ Hz,

1H), 3.34–3.48 (m, 2H), 3.96 (d, $J=8.5$ Hz, 1H), 4.00 (d, $J=8.5$ Hz, 1H), 4.70–4.86 (m, 3H); ^{13}C NMR (67 MHz, $CDCl_3$): $\delta=15.44$, 19.97, 25.08, 25.18, 37.61, 47.45, 63.44, 70.68, 73.83, 83.05, 95.64, 103.76, 166.40, 175.08; IR (neat): $\nu=2963$, 2933, 2875, 1703, 1615, 1370, 1294, 1254, 1090, 1006, 941 cm^{-1}; HR-MS (ESI): $m/z=381.0396$, calcd. for $(M+Na)^+$: 381.0398.

(*Z*)-2,2,2-Trichloroethyl 3-ethoxy-2-[dihydrofuran-2(3*H*)-ylidene]butanoate [(*Z*)-2m]: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=1.18$ (t, $J=7.0$ Hz, 3H), 1.42 (d, $J=6.8$ Hz, 3H), 2.06–2.12 (m, 2H), 2.88–3.02 (m, 2H), 3.33–3.39 (m, 1H), 3.46–3.52 (m, 1H), 4.33–4.42 (m, 2H), 4.59 (q, $J=6.8$ Hz, 1H), 4.78 (d, $J=12.4$ Hz, 1H), 4.83 (d, $J=12.4$ Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=15.23$, 20.97, 23.39, 30.48, 63.35, 72.39, 72.68, 73.46, 95.53, 100.91, 164.29, 172.28; IR (neat): $\nu=2973$, 2893, 1719, 1686, 1615, 1153, 1090, 1042, 932 cm^{-1}; HR-MS (ESI): $m/z=353.0083$, calcd. for $(M+Na)^+$: 353.0085.

(*E*)-2,2,2-Trichloroethyl 3-ethoxy-2-[dihydrofuran-2(3*H*)-ylidene]butanoate [(*E*)-2m]: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=1.17$ (t, $J=7.0$ Hz, 3H), 1.48 (d, $J=6.8$ Hz, 3H), 2.08–2.14 (m, 2H), 3.13–3.26 (m, 2H), 3.36–3.47 (m, 2H), 4.29–4.39 (m, 2H), 4.73–4.78 (m, 2H), 4.84 (d, $J=12.0$ Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=15.41$, 19.82, 23.60, 32.61, 63.46, 70.88, 72.68, 73.82, 95.59, 102.83, 166.31, 175.00; IR (neat): $\nu=2973$, 2933, 2893, 1702, 1611, 1371, 1274, 1091, 997, 939 cm^{-1}; HR-MS (ESI): $m/z=353.0082$, calcd. for $(M+Na)^+$: 353.0085.

(*Z*)-Phenyl 2-[dihydro-4,4-diphenylfuran-2(3*H*)-ylidene]-3-isopropoxybutanoate [(*Z*)-2n]: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=0.84$, (d, $J=6.4$ Hz, 3H), 1.06 (d, $J=6.0$ Hz, 3H), 1.35 (d, $J=6.4$ Hz, 3H), 3.39–3.47 (m, 1H), 3.53 (d, $J=16.2$ Hz, 1H), 3.81 (d, $J=16.2$ Hz, 1H), 4.74 (q, $J=6.4$ Hz, 1H), 4.81 (d, $J=9.0$ Hz, 1H), 4.88 (d, $J=9.0$ Hz, 1H), 7.08–7.37 (m, 15H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=21.18$, 21.77, 22.96, 43.47, 53.36, 68.21, 69.18, 80.26, 104.20, 121.98, 125.20, 126.86, 126.87, 126.95, 126.99, 128.64, 128.67, 129.10, 143.95, 144.17, 151.04, 164.92, 170.32; IR (neat): $\nu=3060$, 2970, 2930, 2894, 1721, 1691, 1626, 1593, 1492, 1145, 972 cm^{-1}; HR-MS (ESI): $m/z=465.2035$, calcd. for $(M+Na)^+$: 465.2036.

(*E*)-Phenyl 2-[dihydro-4,4-diphenylfuran-2(3*H*)-ylidene]-3-isopropoxybutanoate [(*E*)-2n]: ^{1}H NMR (270 MHz, $CDCl_3$): $\delta=1.11$ (d, $J=6.2$ Hz, 3H), 1.15 (d, $J=6.0$ Hz, 3H), 1.54 (d, $J=6.6$ Hz, 3H), 3.49–3.63 (m, 1H), 3.82 (d, $J=17.5$ Hz, 1H), 3.95 (d, $J=17.5$ Hz, 1H), 4.82 (d, $J=9.1$ Hz, 1H), 4.86 (d, $J=9.1$ Hz, 1H), 4.95 (q, $J=6.6$ Hz, 1H), 7.08–7.40 (m, 15H); ^{13}C NMR (67 MHz, $CDCl_3$): $\delta=20.64$, 21.37, 23.44, 45.15, 53.51, 67.62, 68.20, 80.34, 105.43, 121.97, 125.34, 126.76, 126.82, 126.93, 128.62, 129.20, 144.16, 144.30, 150.90, 167.12, 173.25; IR (neat): $\nu=3064$, 2971, 2931, 2860, 1698, 1611, 1595, 1493, 1203, 1066, 1025 cm^{-1}; HR-MS (ESI): $m/z=465.2037$, calcd. for $(M+Na)^+$: 465.2036.

(*Z*)-Phenyl 2-[dihydro-4,4-diphenylfuran-2(3*H*)-ylidene]-3-isobutoxybutanoate [(*Z*)-2o]: ^{1}H NMR (270 MHz, $CDCl_3$): $\delta=0.76$ (d, $J=6.6$ Hz, 3H), 0.82 (d, $J=6.6$ Hz, 3H), 1.36 (d, $J=6.6$ Hz, 3H), 1.64–1.72 (m, 1H), 2.87–2.97 (m, 2H), 3.53 (d, $J=16.3$ Hz, 1H), 3.77 (d, $J=16.3$ Hz, 1H), 4.58 (q, $J=6.6$ Hz, 1H), 4.83 (d, $J=9.1$ Hz, 1H), 4.88 (q, $J=9.1$ Hz, 1H), 7.13–7.39 (m, 15H); ^{13}C NMR (67 MHz, $CDCl_3$): $\delta=19.44$, 19.48, 21.27, 28.42, 43.47, 53.41, 73.12, 73.19, 75.36, 80.32, 103.72, 122.04, 125.20, 126.92, 128.70, 129.13, 144.11, 144.20, 151.14, 164.88, 169.94; IR (neat): $\nu=3061$, 2960, 2924, 2869, 1717, 1613, 1591, 1490, 1261, 1199, 1146, 1085, 965 cm^{-1}; HR-MS (ESI): $m/z=479.2193$, calcd. for $(M+Na)^+$: 479.2193.

(*E*)-Phenyl 2-[dihydro-4,4-diphenylfuran-2(3*H*)-ylidene]-3-isobutoxybutanoate [(*E*)-2o]: ^{1}H NMR (270 MHz, $CDCl_3$): $\delta=0.86$ (d, $J=6.6$ Hz, 3H), 0.87 (d, $J=6.6$ Hz, 3H), 1.55 (d, $J=6.6$ Hz, 3H), 1.78–1.93 (m, 1H), 3.11 (d, $J=6.8$ Hz, 2H), 3.82 (d, $J=17.5$ Hz, 1H), 3.98 (d, $J=17.5$ Hz, 1H), 4.76–4.85 (m, 3H), 7.08–7.11 (m, 2H), 7.17–7.39 (m, 13H); ^{13}C NMR (67 MHz, $CDCl_3$): $\delta=19.54$, 19.64, 20.14, 28.47, 45.11, 53.55, 70.75, 75.46, 80.38, 104.96, 121.99, 125.33, 126.82, 128.67, 129.20, 144.30, 150.97, 167.05, 173.24; IR (neat): $\nu=3062$, 2963, 2870, 1698, 1613, 1594, 1492, 1275, 1201, 1075, 1024, 976 cm^{-1}; HR-MS (ESI): $m/z=479.2191$, calcd. for $(M+Na)^+$: 479.2193.

Phenyl (2*E*)-3-ethoxy-2-(2-oxaspiro[4.5]dec-3-ylidene)butanoate [(*E*)-2p]: ^{1}H NMR (270 MHz, $CDCl_3$): $\delta=1.22$ (t, $J=7.1$ Hz, 3H), 1.44–1.48 (m, 10H), 1.54 (d, $J=6.6$ Hz, 3H), 2.98 (d, $J=18.1$ Hz, 1H), 3.07 (d, $J=18.1$ Hz, 1H), 3.38–3.58 (m, 2H), 4.02 (d, $J=8.7$ Hz, 1H), 4.08 (d, $J=8.7$ Hz, 1H), 4.81 (q, $J=6.6$ Hz, 1H), 7.07–7.12 (m, 2H), 7.16–7.22 (m, 1H), 7.33–7.40 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=15.53$, 20.18, 23.27, 23.36, 25.67, 34.60, 34.64, 41.43, 44.65, 63.43, 70.58, 81.49, 103.78, 122.06, 125.22, 129.17, 151.04, 167.24, 175.16; IR (neat): $\nu=3066$, 2971, 2925, 2855, 1709, 1614, 1593, 1492, 1194, 1077, 1058, 1015 cm^{-1}; HR-MS (ESI): $m/z=367.1878$, calcd. for $(M+Na)^+$: 367.1880.

(*E*)-Phenyl 3-ethoxy-2-[dihydro-4,4-dimethylfuran-2(3*H*)-ylidene]butanoate [(*E*)-2q]: ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=1.14$ (d, $J=3.8$ Hz, 6H), 1.22 (t, $J=7.1$ Hz, 3H), 1.54 (d, $J=6.7$ Hz, 3H), 2.95 (d, $J=18.1$ Hz, 1H), 3.02 (d, $J=18.1$ Hz, 1H), 3.41–3.46 (m, 1H), 3.50–3.56 (m, 1H), 3.96 (d, $J=8.6$ Hz, 1H), 3.99 (d, $J=8.6$ Hz, 1H), 4.81 (q, $J=6.7$ Hz, 1H), 7.08–7.10 (m, 2H), 7.18–7.21 (m, 1H), 7.35–7.37 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=15.55$, 20.20, 25.14, 25.22, 37.63, 47.17, 63.47, 70.64, 83.01, 104.15, 122.06, 125.27, 129.21, 151.05, 167.17, 175.07; IR (neat): $\nu=3061$, 2966, 2930, 2873, 1710, 1617, 1593, 1492, 1294, 1196, 1078, 1058, 1012, 939 cm^{-1}; HR-MS (ESI): $m/z=327.1566$, calcd. for $(M+Na)^+$: 327.1567.

(*Z*)-Phenyl 3-ethoxy-2-[dihydrofuran-2(3*H*)-ylidene]butanoate [(*Z*)-2r]: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=1.21$ (t, $J=7.0$ Hz, 3H), 1.47 (d, $J=6.8$ Hz, 3H), 2.06–2.11 (m, 2H), 2.89–3.02 (m, 2H), 3.38–3.44 (m, 1H), 3.53–3.59 (m, 1H), 4.32–4.41 (m, 2H), 4.60 (q, $J=6.8$ Hz, 1H), 7.11–7.13 (m, 2H), 7.17–7.20 (m, 1H), 7.34–7.37 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=15.39$, 21.06, 23.56, 30.36, 63.46, 72.64, 73.03, 101.76, 122.00, 125.14, 129.07, 151.05, 165.12, 171.06; IR (neat): $\nu=3096$, 3065, 2972, 2930, 2893, 1726, 1687, 1619, 1592, 1492, 1272, 1203, 1144, 1089, 1023, 936 cm^{-1}; HR-MS (ESI): $m/z=299.1253$, calcd. for $(M+Na)^+$: 299.1254.

(*E*)-Phenyl 3-ethoxy-2-[dihydrofuran-2(3*H*)-ylidene]butanoate [(*E*)-2r]: ^{1}H NMR (270 MHz, $CDCl_3$): $\delta=1.22$ (t, $J=6.9$ Hz, 3H), 1.54 (d, $J=6.6$ Hz, 3H), 2.03–2.15 (m, 2H), 3.08–3.29 (m, 2H), 3.43–3.58 (m, 2H), 4.26–4.40 (m, 2H), 4.82 (q, $J=6.6$ Hz, 1H), 7.06–7.11 (m, 2H), 7.15–7.22 (m, 1H), 7.32–7.39 (m, 2H); ^{13}C NMR (67 MHz, $CDCl_3$): $\delta=15.46$, 20.01, 23.59, 32.22, 63.44, 70.78, 72.51, 103.29, 121.99, 125.17, 129.13, 151.03, 167.06, 174.85; IR (neat): $\nu=3095$,

3064, 2972, 2931, 2895, 1708, 1614, 1592, 1492, 1279, 1194, 1077, 1030, 996 cm^{-1}; HR-MS (ESI): $m/z = 299.1253$, calcd. for $(M+Na)^+$: 299.1254.

(*Z*)-2,2,2-Trichloroethyl 3-ethoxy-2-[isobenzofuran-3(1*H*)-ylidene]butanoate [(*Z*)-2s]: ^1H NMR (270 MHz, $CDCl_3$): $\delta = 1.13$ (t, $J = 7.1$ Hz, 3H), 1.63 (d, $J = 6.8$ Hz, 3H), 3.39–3.67 (m, 2H), 4.83 (d, $J = 12.1$ Hz, 1H), 4.93 (d, $J = 12.1$ Hz, 1H), 5.00 (q, $J = 6.8$ Hz, 1H), 5.46 (d, $J = 16.1$ Hz, 1H), 5.47 (d, $J = 16.1$ Hz, 1H), 7.38–7.52 (m, 3H), 8.41 (d, $J = 7.1$ Hz, 1H); ^{13}C NMR (67 MHz, $CDCl_3$): $\delta = 15.31$, 20.68, 63.70, 71.86, 74.03, 74.49, 95.48, 104.78, 120.97, 127.54, 128.12, 130.68, 131.59, 143.51, 165.36, 165.78; IR (neat): $\nu = 3078$, 2974, 2930, 2873, 1721, 1592, 1465, 1372, 1252, 1196, 1090, 1064, 1027 cm^{-1}; HR-MS (ESI): $m/z = 401.0083$, calcd. for $(M+Na)^+$: 401.0085.

(*E*)-2,2,2-Trichloroethyl 3-ethoxy-2-[isobenzofuran-3(1*H*)-ylidene]butanoate [(*E*)-2s]: ^1H NMR (270 MHz, $CDCl_3$): $\delta = 1.18$ (t, $J = 6.9$ Hz, 3H), 1.59 (d, $J = 6.6$ Hz, 3H), 3.41–3.65 (m, 2H), 4.85 (d, $J = 12.1$ Hz, 1H), 4.92 (q, $J = 6.6$ Hz, 1H), 5.05 (d, $J = 12.1$ Hz, 1H), 5.40 (s, 2H), 7.35–7.49 (m, 3H), 8.24–8.28 (m, 1H); ^{13}C NMR (67 MHz, $CDCl_3$) δ 15.42, 20.55, 63.98, 72.05, 74.02, 74.19, 95.30, 105.82, 120.77, 126.15, 128.21, 130.68, 130.97, 142.93, 164.71, 166.63; IR (neat): $\nu = 3078$, 2969, 2935, 2886, 1724, 1638, 1374, 1251, 1173, 1081, 1050, 1001, 824 cm^{-1}; HR-MS (ESI): $m/z =$ 401.0084, calcd. for $(M+Na)^+$: 401.0085.

(*E*)-Phenyl 3-ethoxy-2-[isobenzofuran-3(1*H*)-ylidene]butanoate [(*E*)-2t]: ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.24$ (t, $J = 6.8$ Hz, 3H), 1.65 (d, $J = 6.4$ Hz, 3H), 3.51–3.57 (m, 1H), 3.66–3.72 (m, 1H), 4.98 (q, $J = 6.4$ Hz, 1H), 5.37 (s, 2H), 7.21–7.24 (m, 3H), 7.32–7.34 (m, 2H), 7.40–7.42 (m, 3H), 8.27 (d, $J = 8.5$ Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 15.44, 20.61, 64.04, 72.08, 73.79, 106.52, 120.68, 121.80, 125.46, 125.91, 128.10, 129.28, 130.45, 130.82, 142.65, 150.97, 163.70, 166.83; IR (neat): $\nu = 3074$, 2973, 2930, 2874, 1715, 1622, 1590, 1491, 1257, 1190, 1159, 1049, 1003 cm^{-1}; HR-MS (ESI); $m/z = 347.1253$, calcd. for $(M+Na)^+$: 347.1254.

(*E*)-2,2,2-Trichloroethyl 2-[5,5-dimethyldihydrofuran-2-(3*H*)-ylidene]-3-ethoxybutanoate [(*E*)-2u]: ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.16$ (t, $J = 7.0$ Hz, 3H), 1.39 (s, 3H), 1.41 (s, 3H), 1.47 (d, $J = 6.6$ Hz, 3H), 1.91 (t, $J = 8.0$ Hz, 2H), 3.23–3.45 (m, 4H), 4.71–4.86 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 15.36$, 19.89, 26.96, 27.08, 33.01, 35.56, 63.00, 70.50, 73.67, 88.32, 95.63, 101.90, 166.35, 174.45; IR (neat): $\nu = 2973$, 2934, 2895, 2873, 1702, 1607, 1455, 1372, 1304, 1251, 1185, 1092, 1055, 989, 955, 928, 844, 809 cm^{-1}; HR-MS (ESI): $m/z = 381.0397$, calcd. for $(M+Na)^+$: 381.0398.

(*E*)-Phenyl 2-[5,5-dimethyldihydrofuran-2(3*H*)-ylidene]-3-ethoxybutanoate [(*E*)-2v]: ^1H NMR (500 MHz, $CDCl_3$): $\delta =$ 1.21 (t, $J = 7.0$ Hz, 3H), 1.39 (s, 3H), 1.41 (s, 3H), 1.53 (d, $J = 6.8$ Hz, 3H), 1.90 (t, $J = 7.9$ Hz, 2H), 3.19–3.38 (m, 2H), 3.42 (dq, $J = 9.0$, 7.0 Hz, 1H), 3.52 (dq, $J = 9.0$, 7.0 Hz, 1H), 4.81 (q, $J = 6.8$ Hz, 1H), 7.08–7.09 (m, 2H), 7.18 (t, $J =$ 7.4 Hz, 1H), 7.26–7.37 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 15.47$, 20.11, 26.98, 27.10, 32.74, 35.60, 63.06, 70.44, 88.18, 102.37, 122.05, 125.09, 129.11, 151.05, 167.24, 174.49; IR (neat): $\nu = 3097$, 3068, 3042, 2972, 2932, 2896, 2871, 1708, 1611, 1592, 1492, 1455, 1386, 1372, 1306, 1254, 1197, 1161, 1077, 1059, 993, 961, 929, 856 cm^{-1}; HR-MS (ESI): $m/z = 327.1565$, calcd. for $(M+Na)^+$: 327.1567.

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