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A Gold(I)-Initiated Cycloisomerization/Diels-Alder/Retro-Diels-Alder Cascade Strategy to Biaryls

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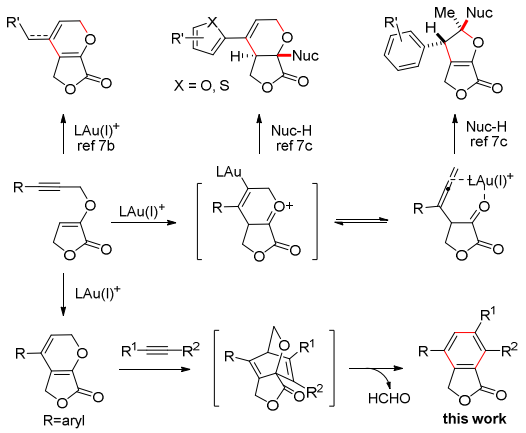
ABSTRACT: **A unique approach to biaryls was developed based on propargyl vinyl ethers and dienophiles substrates via a gold(I)-initiated cycloisomerization/Diels-Alder/retro-Diels-Alder cascade reaction. The scope and mechanism of the reaction were investigated based on a series of synthetic substrates, control experiments and DFT calculations.**

Introduction

Biaryls are important scaffolds in a wide range of natural products, pharmaceutically active molecules,[1] chiral ligands,[2] crown ethers[3] and liquid crystals.[4] Due to the increasing requirement for the efficient strategies to constructing biaryl compounds, a number of methodologies have been developed,[5] in which the transition metal-catalyzed cross-coupling reactions were the predominant methods.[5b,5f-5g5i] Moreover, a strategy to the synthesis of biaryls by the construction of one aryl ring via transition metal-catalyzed [2+2+2] cycloaddition of alkynes or Diels-Alder cycloaddition/aromatization also drew considerable attention.[5a,5c,5e] Also, some gold-catalyzed approaches to biaryls have been reported.[6]

As our continued efforts on constructing structural diverse small molecules by gold-catalyzed pathway-tunable reactions,[7]an angle strain-controlled strategy of propargyl vinyl ether substrates to synthesize furofuran and furopyran derivatives by altering the regioselectivity and disturbing intermediate formation has been developed.[7b] The existence of diene fragments in the furopyran derivatives inspired us to expand the structural diversity of the methodology by introducing dienophiles in the cycloisomerization of the propargyl vinyl ether to promote a cascade Diels-Alder reaction. To our delight, the cycloaddition between the furopyran and dimethyl diacetylenedicarboxylate (DMAD) underwent smoothly to give the bridged-ring as expected by following the gold-catalyzed cycloisomerization. Furthermore, the driving force to collapse into thermodynamically stable aromatic ring from the strained bridged-ring by releasing formaldehyde caused a sequential retro-Diels-Alder reaction to occur, leading to a biaryl product (Scheme 1). Examples describing the aromatization via the release of volatile small molecules such as carbon dioxide,[8] alkene,[9] sulfur dioxide[10] and aldehyde[11] to form phenyl rings have been reported previously. In this study, by releasing formaldehyde via a cycloisomerization/Diels-Alder/retro-Diels-Alder strategy, a novel gold-catalyzed cascade reaction to yield biaryl compounds was developed.

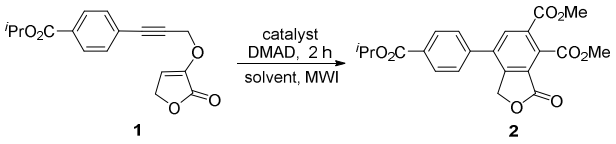
Scheme 1. Strained-controlled Tandem Cyclization of Propargyl Vinyl Ether



Results and Discussion

At the outset, substrate **1** was chosen as the model substrate for condition optimization. A variety of gold catalysts (5 mol %) were first examined using toluene as the solvent and 120 °C as the initial temperature. Among the gold catalysts screened, commercially available [bis-(trifluoromethanesulfonyl) imidate] (triphenylphosphine) gold(I), ($Ph_3PAuNTf_2$)[12] gave the best result. Other catalysts such as Ph_3PAuCl, $Ph_3PAuCl/AgSbF_6$ $Ph_3PAuCl/AgOTf$ and $(IPr)AuCl/AgNTf_2$ were less reactive (Table 1, entries 1-5). $AgNTf_2$ was tested and showed lower activity (Table 1, entry 6). The possibility of the reaction catalyzed by trace amount of acid was excluded by using $HNTf_2$ as the catalyst (Table 1, entry 7). The optimal reaction time was identified to be 2 h by conducting several experiments (Table 1, entries 8-9). The Diels-Alder reaction would not occur at lower reaction temperatures and only corresponding cycloisomerized product was isolated as we reported before[7b] (Table 1, entries 10-11). A control experiment using conventional heating condition was performed to afford the product with lower yields and longer reaction times (Table 1, entry 12). $AuCl_3$ was also examined in the biaryl formation reaction with an unsatisfactory yield (Table 1, entry 13). In the end, the optimal condition was determined as stirring the reaction at 120 °C for 2 h in the solvent of toluene with $Ph_3PAuNTf_2$ as the catalyst under the irradiation of microwave.

Table 1. Screening of Reaction Conditions



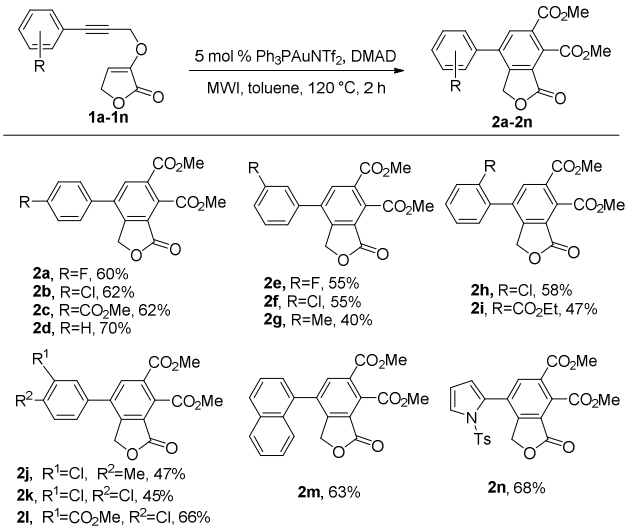
1 2

entry	catalyst	solvent	T (°C)	yield (%)[a, b]
1	$Ph_3PAuNTf_2$	toluene	120	68
2	Ph_3PAuCl	toluene	120	5[c]
3	$Ph_3PAuCl/AgSbF_6$	toluene	120	46
4	$Ph_3PAuCl/AgOTf$	toluene	120	55
5	$(IPr)AuCl/AgNTf_2$	toluene	120	20[c]
6	$AgNTf_2$	toluene	120	30
7	$HNTf_2$	toluene	120	0[c]
8	$Ph_3PAuNTf_2$	toluene	120	50[d]
9	$Ph_3PAuNTf_2$	toluene	120	69[e]
10	$Ph_3PAuNTf_2$	DCE	80	0[f]
11	$Ph_3PAuNTf_2$	toluene	80	0[f]
12	$Ph_3PAuNTf_2$	toluene	120	40[g]
13	$AuCl_3$	toluene	120	38

[a] Isolated yield and the reaction time was 2 h; [b] The reaction was performed under microwave irradiation; [c] IPr=1,3-bis(diisopropylphenyl) imidazol-2-ylidene], starting material 1 remained; [d] Run for 1 h; [e] Run for 3 h; [f] Only the cycloisomerized product was isolated; [g] Reaction was conducted with the conventional heating.

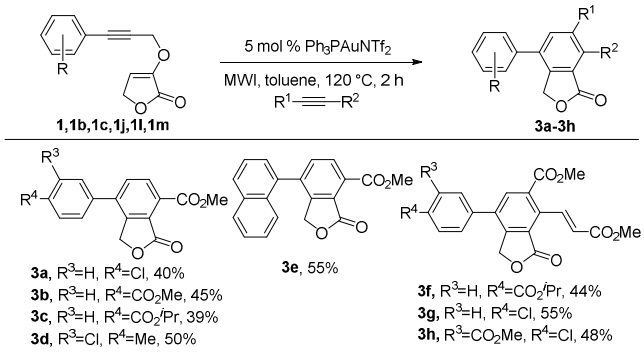
With the optimal condition in hand, we explored the scope of the cascade reaction with a variety of aromatic or heteroaromatic substituted propargyl vinyl ethers using DMAD as the dienophile. The substrates with para electron-withdrawing substituted phenyl ring were first examined and the yields of the products were lower than that of the substrate without substitutions (**2a-2d**). The substrates with ortho or meta-substituents phenyl rings afforded the corresponding biaryls in 40-58% yields, which were also lower that of the substrate with no substitutions (**2e-2i**). The substrates with multi-substituted phenyl rings afforded similar results (**2j-2l**). It was worth mentioning that naphthalene and heterocycle-contained substrates showed good tolerance to the reaction condition and provided acceptable yields (**2m-2n**).

Scheme 2. Substrate Scopes of the Aryl Substitutions



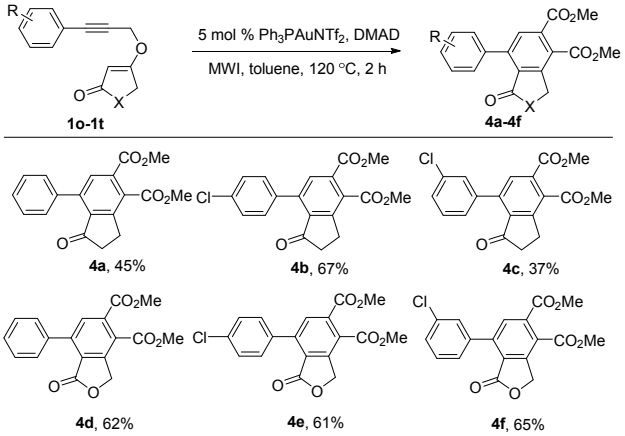
Having successfully achieved the cascade transformation employing DMAD as the dienophile, we shifted our attention to explore the regioselectivity of the cycloaddition by encompassing non-symmetrical dienophiles. We anticipated that enone ether fragment existing in the furopyran intermediate derived from Claisen-rearrangement/*6-endo*-trig cyclization could control the regioselectivity of the Diels-Alder cycloaddition by raising the HOMO coefficient at C4 of the diene moiety to give the "ortho" product. In this light, a methyl propiolate was used as the dienophile and the "ortho" product-derived biaryls as shown in Scheme 3 were isolated as the single regioisomers (**3a-3e**). Next, 2-hexen-4-ynedioic acid dimethyl ester synthesized via the dimerization of methyl propiolate was used as a dienophile in the biaryl synthesis reaction (**3f-3h**). The remote vinyl ester had totally dictated the regioselectivity of the reaction, which was consistent with the results of the precedent research.[13]

Scheme 3. Substrate Scopes of the Dienophiles



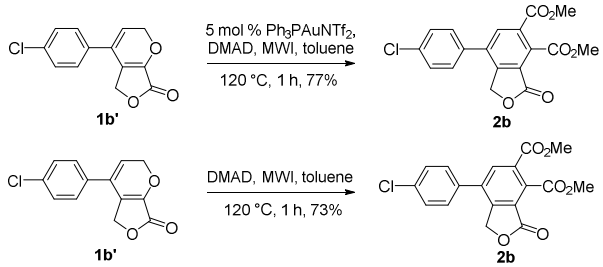
Next, the scopes of the cyclic vinyl ethers in the cascade reaction were examined by several synthetic propargyl vinyl ether substrates with similar angle strains as shown in Scheme 4. The substrates with the ketone moiety afforded the biaryls with relative lower yields attributing to the electron deficient nature of the carbonyl groups (**4a-4c**). The yields of the propargyl β-tetronic acid ether substrates were similar to those of the substrates shown in Scheme 2 (**4d-4f**).

Scheme 4. **Substrate Scopes of the Vinyl Ethers**



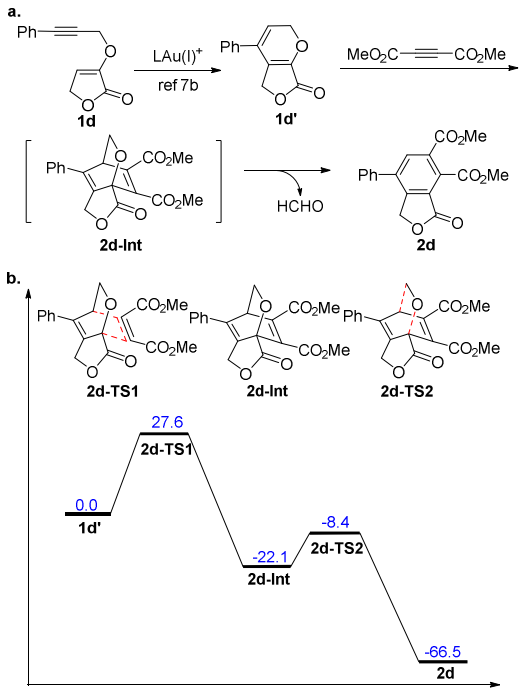
To probe the detailed mechanism of the biaryl formation reaction, the furopyran intermediate 1b' was isolated by following our previous procedure.[7b] Then the isolated intermediate was subjected to the standard condition and the condition with the absence of gold catalyst. Both conditions could provide the biaryl product with similar yields, which suggested that the reaction proceeded through the cycloaddition/fragmentation of furopyran and DMAD leading to the biaryl and the gold catalyst was not essential to the aromatization stage of the reaction (Scheme 5).

Scheme 5. **Control Experiments**



Based on the experimental results and previous work, a proposed mechanism for this gold-initiated cascade sequence is illustrated in Scheme 6a. Initially, under the activation of gold catalyst substrate **1d** went through 3,3-Claisen rearrangement to give allene intermediate followed by a *6-endo*-trig cyclization to give furopyran intermediate **1d'**. In the presence of DMAD, a Diels-Alder reaction happened to deliver a highly congested intermediate **2d-Int** following the cycloisomerization. A tandem retro-Diels-Alder reaction occurred to provide the biaryl product **2d** with the fragmentation of formaldehyde, which to our knowledge was never reported before. Attempts on the isolation of Diels-Alder cycloaddition product **2d** under mild conditions failed owing to the congested nature of the cycloaddition intermediate and the inherent driving force to generate aromatic biaryl product by releasing formaldehyde. This result was also illustrated by density functional theory (DFT) calculations (B3LYP/6-31G)[14] on the free energy of activation for the Diels-Alder cycloaddition (**2d-TS1**) and retro-Diels-Alder reaction (**2d-TS2**) by following our previous protocol.[6d] The results are shown in Scheme 6b. These computed barriers indicate that the Diels-Alder cycloaddition is the rate-determining step and the retro-Diels-Alder reaction will proceed rather easily once the **2d-Int** is formed, which is also consistent with our experimental observations.

Scheme 6. Proposed Mechanism and DFT Calculations (the energy unit: kcal/mol)



Conclusion

In summary, we have demonstrated a facile, one-pot and straightforward approach toward a variety of structurally diverse biaryls via a gold(I)-initiated cycloisomerization/Diels-Alder/retro-Diels-Alder cascade reaction of propargyl vinyl ethers and readily available dienophiles. The detailed mechanism of this transformation was probed by control experiments and DFT calculations. Further studies on the applications of the synthesized biaryls are in progress in our laboratory.

Experimental Section

General Experimental Methods. Unless otherwise noted, reagents were obtained commercially and used without further purification. Tetrahydrofuran was distilled from sodium under a nitrogen atmosphere. Dichloroethane was distilled from calcium chloride under a nitrogen atmosphere. TLC analysis of reaction mixtures was performed on Dynamicadsorbents silica gel F-254 TLC plates. Flash chromatography was carried out on Zeoprep 60 (200-300 mesh) silica gel. Microwave reactions were performed with a Discover SP Microwave Synthesizer in sealed reaction vessels. The temperature was monitored with an internal vertically focused IR temperature sensor. ^{1}H and ^{13}C NMR spectra were recorded with Bruker Avance-III 600 spectrometers and referenced to $CDCl_3$ and DMSO-d_6. HR-ESI-MS was recorded on a Bruker micro-TOFQ-Q instrument. IR spectra were recorded on a Bruker IFS 55 spectrometer. Melting points were tested on Thomas Hoover capillary melting point apparatus.

General Procedures for the Preparation of Propargylic Alcohols (A1-A15). To a stirring solution of alkyne (5 mmol) in THF (5 mL) was added dropwise *n*-BuLi (1.0 M in THF, 5.5 mL) at −78 °C. Paraformaldehyde (6 mmol, 180 mg) was added portionwise after 0.5 h. The solution was warmed to room temperature after 1.0 h. The reaction was monitored by TLC till the consumption of the starting material; the reaction mixture was quenched by addition of saturated aqueous ammonium chloride (20 mL) and extracted with ethyl acetate three times (20 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude material was purified by a flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to obtain the propargylic alcohols **A2-A8**, **A15**.[7b]

To a solution of aryl iodide (7.6 mmol), propargyl alcohol (555 mg, 10 mmol) and triethylamine (2 mL) in THF (20 mL) was added dichlorobis(triphenylphosphine) palladium(II) (155 mg, 0.2 mmol), followed by CuI (0.24 mmol, 45.4 mg). The reaction mixture was stirred at room temperature for 24 h. Water was added and the aqueous solution was washed with EtOAc. The organic solutions were combined, dried over anhydrous $MgSO_4$, filtered and concentrated. The crude material was purified by a flash column chromatography on silica gel using

petroleum ether/ethyl acetate as eluent to obtain the propargylic alcohols **A1**, **A9-A14**. **A9-A12** and **A14** were reported in previous work.[15]

*Isopropyl 4-(3-hydroxyprop-1-yn-1-yl)benzoate (**A1**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) as an eluent to give the product **A1** (1.7 g) with a yield of 80%; colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08–7.87 (m, 2H), 7.51–7.41 (m, 2H), 5.24 (dt, *J* = 12.5, 6.2 Hz, 1H), 4.52 (d, *J* = 6.1 Hz, 2H), 2.20–1.87 (m, 1H), 1.36 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.7, 131.6, 130.7, 129.5, 127.1, 90.2, 85.1, 68.8, 51.7, 22.1; IR (thin film, cm^{-1}) 3399, 2985, 1711, 1605, 1405, 1376, 1346, 1289, 1177, 1019, 857, 767; HRMS (ESI): *m/z* calcd. for $C_{13}H_{14}O_3Na$ $[M+Na]^+$ 241.0835, found 241.0843.

*Methyl 2-chloro-5-(3-hydroxyprop-1-yn-1-yl)benzoate (**A13**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (7:1) as an eluent to give the product **A13** (1.5 g) with a yield of 69%; colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 2.0 Hz, 1H), 7.42 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.38 (d, *J* = 8.3 Hz, 1H), 4.48 (d, *J* = 6.1 Hz, 2H), 3.92 (s, 3H), 2.08 (t, *J* = 6.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.5, 135.3, 134.7, 134.0, 131.3, 130.2, 121.6, 89.4, 83.6, 52.7, 51.6; IR (thin film, cm^{-1}) 3490, 1705, 1475, 1440, 1309, 1254, 1232, 1052, 1033, 835, 784; HRMS (ESI): *m/z* calcd. for $C_{11}H_9O_3ClNa$ $[M+Na]^+$ 247.0132, found 247.0129.

General Procedures for the Preparation of Propargyl γ-Butyrolactone-2-enol Ether (1, 1a-1n). A solution of diisopropyl azodiformate (3 mmol, 606 mg) in dry THF was added dropwise to a solution of propargylic alcohol **A1-A15** (2 mmol), 3-hydroxy-2,5-dihydrofuran-2-one **B** (2 mmol, 200 mg) and triphenylphosphine (3 mmol, 787 mg) in THF at 0 °C for 15 min under a nitrogen atmosphere. The reaction was stirred at room temperature overnight. The crude mixture was evaporated to dryness and purified by a flash column chromatography to afford the products **1**, **1a-1n**. **1a**, **1b**, **1e**, **1g** were reported in our previous work.[7b]

*Isopropyl 4-(3-((2-oxo-2,5-dihydrofuran-3-yl)oxy)prop-1-yn-1-yl)benzoate (**1**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (8:1) as an eluent to give the product **1** (239 mg) with a yield of 38%; white solid; Mp 100.7–102.1 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 6.40 (t, *J* = 2.1 Hz, 1H), 5.30–5.17 (m, 1H), 4.91 (s, 2H), 4.83 (d, *J* = 2.1 Hz, 2H), 1.36 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.9, 165.4, 144.9, 131.8, 131.3, 129.6, 126.1, 115.3, 88.0, 84.3, 68.9, 67.7, 59.2, 22.0; IR (thin film, cm^{-1}) 3425, 2920, 1765, 1707, 1650, 1454, 1274, 1134, 1104, 804, 762; HRMS (ESI): *m/z* calcd. for $C_{17}H_{16}O_5Na$ $[M+Na]^+$ 323.0890, found 323.0883.

*Methyl-4-(3-((2-oxo-2,5-dihydrofuran-3-yl)oxy)prop-1-yn-1-yl)benzoate (**1c**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (8:1) as an eluent to give the product **1c** (180 mg) with a yield of 33%; white solid; Mp 160.5–161.2 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 6.40 (t, *J* = 2.0 Hz, 1H), 4.91 (s, 2H), 4.83 (d, *J* = 2.0 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.9, 166.4, 144.9, 131.8, 130.5, 129.7, 126.3, 115.3, 87.9, 84.5, 67.7, 59.1, 52.5; IR (thin film, cm^{-1}) 3431, 1783, 1763, 1715, 1650, 1431, 1136, 1045, 794; HRMS (ESI): *m/z* calcd. for $C_{15}H_{12}O_5Na$ $[M+Na]^+$ 295.0577, found 295.0585.

*3-((3-Phenylprop-2-yn-1-yl)oxy)furan-2(5H)-one (**1d**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (8:1) as an eluent to give the product **1d** (193 mg) with a yield of 45%; white solid; Mp 98.2–99.6 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.38–7.29 (m, 3H), 6.41 (t, *J* = 2.1 Hz, 1H), 4.89 (s, 2H), 4.81 (d, *J* = 2.1 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.1, 144.8, 131.9, 129.2, 128.5, 121.7, 115.3, 88.7, 81.6, 67.7, 59.3; IR (thin film, cm^{-1}) 3429, 3091, 1766, 1649, 1491, 1445, 1396, 1332, 1256, 1127, 1053, 818, 760, 691; HRMS (ESI): *m/z* calcd. for $C_{13}H_{10}O_3Na$ $[M+Na]^+$ 237.0522, found 237.0525.

*3-((3-(3-Chlorophenyl)prop-2-yn-1-yl)oxy)furan-2(5H)-one (**1f**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (8:1) as an eluent to give the product **1f** (199 mg) with a yield of 40%; white solid; Mp 92.0–93.9 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (t, *J* = 1.6 Hz, 1H), 7.36–7.29 (m, 1H), 7.25 (dd, *J* = 10.3, 5.3 Hz, 1H), 6.40 (t, *J* = 2.1 Hz, 1H), 4.88 (s, 2H), 4.82 (d, *J* = 2.1 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.9, 144.8, 134.4, 131.7, 130.1, 129.8, 129.5, 123.4, 115.4, 87.2, 82.8, 67.7, 59.1; IR (thin film, cm^{-1}) 3432, 3115, 1762, 1653, 1474, 1455, 1384, 1319, 1247, 1130, 1045, 801, 780, 678; HRMS (ESI): *m/z* calcd. for $C_{13}H_9O_3ClNa$ $[M+Na]^+$ 271.0132, found 271.0148.

*3-((3-(2-Chlorophenyl)prop-2-yn-1-yl)oxy)furan-2(5H)-one (**1h**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (7:1) as an eluent to give the product **1h** (194 mg) with a yield of 39%; white solid; Mp 69.3–93.9 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.38 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.31–7.24 (m, 1H), 7.22 (td, *J* = 7.6, 1.2 Hz, 1H), 6.50 (t, *J* = 2.1 Hz, 1H), 4.94 (s, 2H), 4.81 (d, *J* = 2.1 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.1, 144.6, 136.2, 133.7, 130.3, 129.4, 126.7, 121.7, 115.9, 86.7, 85.5, 67.7, 59.1; IR (thin film, cm^{-1}) 3425, 1772, 1654, 1473, 1364, 1267, 1116, 1047, 999, 950, 801, 755; HRMS (ESI): *m/z* calcd. for $C_{13}H_9O_3ClNa$ $[M+Na]^+$ 271.0132, found 271.0124.

*Ethyl-2-(3-((2-oxo-2,5-dihydrofuran-3-yl)oxy)prop-1-yn-1-yl)benzoate (**1i**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (8:1) as an eluent to give the product **1i** (200 mg) with a yield of 35%; yellow solid; Mp 65.5–66.7 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.61–7.34 (m, 3H), 6.59 (t, *J* = 2.1 Hz, 1H), 4.95 (s, 2H), 4.83 (d, *J* = 2.1 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz,

3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.2, 165.8, 144.7, 134.6, 132.5, 131.9, 130.5, 128.9, 122.3, 116.2, 87.4, 86.6, 67.8, 61.4, 59.4, 14.4; IR (thin film, cm^{-1}) 3428, 2920, 1770, 1721, 1653, 1253, 1118, 1049, 759; HRMS (ESI): *m/z* calcd. for $C_{16}H_{14}O_5Na$ $[M+Na]^+$ 309.0733, found 309.0736.

*3-((3-(2-Chloro-4-methylphenyl)prop-2-yn-1-yl)oxy)furan-2(5H)-one (**1j**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (8:1) as an eluent to give the product **1j** (210 mg) with a yield of 40%; yellow solid; Mp 65.1–66.3 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 1.4 Hz, 1H), 7.21 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.17 (d, *J* = 7.9 Hz, 1H), 6.39 (t, *J* = 2.1 Hz, 1H), 4.87 (s, 2H), 4.82 (d, *J* = 2.1 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.0, 144.8, 137.7, 134.4, 132.1, 131.0, 130.1, 120.7, 115.3, 87.4, 82.1, 67.7, 59.2, 20.2; IR (thin film, cm^{-1}) 3426, 1765, 1649, 1365, 1121, 1108, 1047, 955, 813; HRMS (ESI): *m/z* calcd. for $C_{14}H_{11}O_3ClNa$ $[M+Na]^+$ 285.0289, found 285.0283.

*3-((3-(3,4-Dichlorophenyl)prop-2-yn-1-yl)oxy)furan-2(5H)-one (**1k**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) as an eluent to give the product **1k** (238 mg) with a yield of 42%; white solid; Mp 106.1–107.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 1.8 Hz, 1H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.27 (dd, *J* = 7.7, 2.3 Hz, 1H), 6.38 (t, *J* = 2.0 Hz, 1H), 4.89 (s, 2H), 4.84 (d, *J* = 2.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.8, 145.0, 133.9, 133.6, 132.9, 131.1, 130.7, 121.7, 115.3, 86.4, 83.6, 67.7, 59.1; IR (thin film, cm^{-1}) 3431, 2925, 1775, 1748, 1654, 1461, 1367, 1328, 1264, 1141, 1044, 1008, 959, 884, 804; HRMS (ESI): *m/z* calcd. for $C_{13}H_7O_3Cl_2$ $[M-H]^-$ 280.9777, found 280.9778.

*Methyl-2-chloro-5-(3-((2-oxo-2,5-dihydrofuran-3-yl)oxy)prop-1-yn-1-yl)benzoate (**1l**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) as an eluent to give the product **1l** (184 mg) with a yield of 30%; white solid; Mp 109.3–110.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 2.0 Hz, 1H), 7.43 (dd, *J* = 17.8, 5.2 Hz, 2H), 6.38 (t, *J* = 2.1 Hz, 1H), 4.88 (s, 2H), 4.83 (d, *J* = 2.1 Hz, 2H), 3.93 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.9, 165.3, 144.9, 135.4, 134.8, 134.7, 131.5, 130.5, 120.6, 115.3, 86.6, 83.6, 67.7, 59.1, 52.8; IR (thin film, cm^{-1}) 3426, 2922, 1766, 1724, 1650, 1471, 1427, 1392, 1303, 1231, 1117, 1049, 826; HRMS (ESI): *m/z* calcd. for $C_{15}H_{10}O_5Cl$ $[M-H]^-$ 305.0222, found 305.0223.

*3-((3-(Naphthalen-1-yl)prop-2-yn-1-yl)oxy)furan-2(5H)-one (**1m**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) as an eluent to give the product **1m** (236 mg) with a yield of 45%; yellow solid; Mp 102.3–103.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.3 Hz, 1H), 7.86 (dd, *J* = 8.0, 3.3 Hz, 2H), 7.71–7.63 (m, 1H), 7.61–7.50 (m, 2H), 7.43 (dd, *J* = 8.1, 7.3 Hz, 1H), 6.47 (t, *J* = 2.1 Hz, 1H), 5.04 (s, 2H), 4.82 (d, *J* = 2.1 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.1, 144.9, 133.3, 133.2, 131.1, 129.7, 128.5, 127.2, 126.7, 125.8, 125.2, 119.4, 115.5, 87.0, 86.4, 67.7, 59.5; IR (thin film, cm^{-1}) 3396, 2920, 1768, 1652, 1397, 1326, 1250, 1118, 1049, 979, 801, 775; HRMS (ESI): *m/z* calcd. for $C_{17}H_{12}O_3Na$ $[M+Na]^+$ 287.0679, found 287.0682.

General Procedures for the Preparation of Propargyl Vinyl Ether (1o-1t). A solution of diisopropyl azodiformate (3 mmol, 606 mg) in dry THF was added dropwise to a solution of propargylic alcohol **A5-A7** (2 mmol), **C** (2 mmol) and triphenylphosphine (3 mmol, 787 mg) in THF at 0 °C for 15 min under a nitrogen atmosphere. The reaction was stirred at room temperature overnight. The crude mixture was evaporated to dryness and purified by a flash column chromatography to afford the products **1o-1t**.

*3-(3-Phenylprop-2-ynyloxy)cyclopent-2-enone (**1o**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (8:1) as an eluent to give the product **1o** (191 mg) with a yield of 45%; white solid; Mp 71.7–73.2 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.48 (d, *J* = 6.4 Hz, 2H), 7.43 (dd, *J* = 11.6, 7.1 Hz, 2H), 5.51 (s, 1H), 5.09 (s, 2H), 2.65–2.61 (m, 2H), 2.36–2.32 (m, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 179.2, 172.9, 156.2, 131.7, 129.5, 128.9, 121.0, 89.8, 88.1, 82.5, 67.9, 67.5, 60.7, 22.0; IR (thin film, cm^{-1}) 3426, 2979, 2922, 1677, 1589, 1436, 1339, 1240, 1113, 1008, 955, 696, 543; HRMS (ESI): *m/z*: calcd. for $C_{14}H_{13}O_2$ $[M+H]^+$ 213.0916, found 213.0915.

*3-(3-(4-Chlorophenyl)prop-2-ynyloxy)cyclopent-2-enone (**1p**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (8:1) as an eluent to give the product **1p** (444 mg) with a yield of 90%; white solid; Mp 84.4–85.7 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.51 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H), 5.51 (s, 1H), 5.08 (s, 2H), 2.64–2.60 (m, 2H), 2.36–2.32 (m, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 204.4, 188.8, 134.2, 133.4, 129.0, 120.0, 105.6 , 86.3, 84.2, 59.7, 34.1, 27.8; IR (thin film, cm^{-1}) 3429, 2980, 2924, 1739, 1711,1593, 1467, 1339, 1237, 832, 723, 544; HRMS (ESI): *m/z* calcd. for $C_{14}H_{12}O_2Cl$ $[M+H]^+$ 247.0526, found 247.0531.

*3-(3-(3-Chlorophenyl)prop-2-ynyloxy)cyclopent-2-enone (**1q**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (8:1) as an eluent to give the product **1q** (439 mg) with a yield of 89%; white solid; Mp 82.9–84.5 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.56 (s, 1H), 7.52 (dt, *J* = 7.4, 1.9 Hz, 1H), 7.47–7.42 (m, 2H), 5.52 (s, 1H), 5.09 (s, 2H), 2.64–2.61 (m, 2H), 2.37–2.33 (m, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 204.4, 188.8, 133.4, 131.0, 130.7, 130.4, 129.6, 123.1, 105.7, 85.9, 84.5, 59.6, 34.1, 27.8; IR (thin film, cm^{-1}) 3425, 2924, 2853, 1590, 1384, 1111, 961, 791, 618; HRMS (ESI): *m/z* calcd. for $C_{14}H_{12}ClO_2$ $[M+H]^+$ 247.0526, found 247.0529.

*4-(3-Phenylprop-2-ynyloxy)furan-2(5H)-one (**1r**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (8:1) as an eluent to give the product **1e** (343 mg) with a yield of 80%; white solid; Mp 96.9–97.6 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.50 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.43 (dt, *J* = 14.1, 6.1 Hz, 2H), 5.51 (s, 1H), 5.17 (s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 179.2, 172.9, 131.7, 129.5, 128.9, 121.0, 89.8, 88.1, 82.5, 67.5, 60.7; IR (thin film, cm^{-1}) 3424, 2926, 2854, 1775, 1744, 1628, 1489, 1443, 1362, 1313, 1234, 1151, 1044.8, 954, 884, 768, 695; HRMS (ESI): *m/z* calcd. for $C_{13}H_{11}O_3$ $[M+H]^+$ 215.0708, found 215.0711.

*4-(3-(4-Chlorophenyl)prop-2-ynyloxy)furan-2(5H)-one (**1s**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (8:1) as an eluent to give the product **1s** (448 mg) with a yield of 90%; white solid; Mp 91.7–93.5 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.53 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 5.51 (s, 1H), 5.17 (s, 2H), 4.82 (s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 179.1, 172.9, 134.3, 133.5, 129.1, 119.9, 89.9, 86.9, 83.6, 67.4, 60.6; IR (thin film, cm^{-1}) 3286, 3250, 2980, 2944, 1745, 1689, 1526, 1456, 1385, 1361, 1259, 1110, 1050, 953, 799, 638; HRMS (ESI): *m/z* calcd. for $C_{13}H_{10}ClO_3$ $[M+H]^+$ 249.0318, found 249.0323.

*4-(3-(3-Chlorophenyl)prop-2-ynyloxy)furan-2(5H)-one (**1t**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (8:1) as an eluent to give the product **1t** (249 mg) with a yield of 50%; white solid; Mp 70.1–72.0 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.58 (s, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.45 (dt, *J* = 15.4, 7.6 Hz, 2H), 5.53 (s, 1H), 5.18 (s, 2H), 4.82 (s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 179.1, 172.8, 133.4, 131.1, 130.7, 130.4, 129.6, 122.9, 90.0, 86.5, 83.8, 67.4, 60.5; IR (thin film, cm^{-1}) 3426, 3100, 2923, 1780, 1746, 1626, 1472, 1444, 1357, 1318, 1244, 1156, 1044, 958, 885, 828, 787, 714, 682; HRMS (ESI): *m/z* calcd. for $C_{13}H_{10}ClO_3$ $[M+H]^+$ 249.0318, found 249.0322.

General Procedures for the Preparation of Biaryl Derivatives (2, 2a-2n). To a solution of the substrates **1**, 1**a-1n** (0.05 mmol) and $Ph_3PAuNTf_2$ (0.0025 mmol, 2 mg) in dry toluene was added dimethyl diacetylenedicarboxylate (0.015 mmol, 2 mg) under a nitrogen atmosphere. The reaction mixture was reacted under the irradiation of microwave at 120 °C for 2 h. The solvent was removed *in vacuo* and the residue was purified by a flash column chromatography to afford the products **2**, **2a-2n**.

*Dimethyl-7-(4-(isopropoxycarbonyl)phenyl)-3-oxo-1,3-dihydroisobenzofuran-4,5-dicarboxylate (**2**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (7:1) as an eluent to give the product **2** (14 mg) with a yield of 68%; white solid; Mp 162.3–163.5 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.38 (s, 1H), 8.09 (d, *J* = 8.3 Hz, 2H), 7.83 (d, *J* = 8.3 Hz, 2H), 5.70 (s, 2H), 5.25–5.10 (m, 1H), 3.92 (d, *J* = 5.6 Hz, 6H), 1.35 (d, *J* = 6.2 Hz, 7H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 167.8, 165.5, 164.7, 164.1, 149.8, 134.0, 136.4, 134.5, 132.2, 130.6, 129.9, 128.4, 128.1, 123.6, 69.9, 68.5, 53.2, 52.9, 21.6; IR (thin film, cm^{-1}) 3434, 2923, 1775, 1742, 1383, 1275, 1133, 1101, 1017, 798, 710; HRMS (ESI): *m/z* calcd. for $C_{22}H_{21}O_8$ $[M+H]^+$ 413.1230, found 413.1248.

*Dimethyl-7-(4-fluorophenyl)-3-oxo-1,3-dihydroisobenzofuran-4,5-dicarboxylate (**2a**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (7:1) as an eluent to give the product **2a** (10 mg) with a yield of 60%; white solid; Mp 185.0–186.3 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.31 (s, 1H), 7.74 (dd, *J* = 8.8, 5.3 Hz, 2H), 7.40 (t, *J* = 8.8 Hz, 2H), 5.69 (s, 2H), 3.91 (d, *J* = 4.9 Hz, 6H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 167.9, 165.6, 164.2, 162.6 (d, *J* = 247.1 Hz), 149.5, 136.5, 134.4, 132.1 (d, *J* = 3.1 Hz), 131.7, 130.3 (d, *J* = 8.5 Hz), 128.0, 123.4, 116.3 (d, *J* = 21.7 Hz), 69.9, 53.1, 52.8; IR (thin film, cm^{-1}) 3446, 1767, 1738, 1783, 1286, 1258, 1134, 978, 846, 795, 620; HRMS (ESI): *m/z* calcd. for $C_{18}H_{12}O_6F$ $[M-H]^-$ 343.0623, found 343.0630.

*Dimethyl-7-(4-chlorophenyl)-3-oxo-1,3-dihydroisobenzofuran-4,5-dicarboxylate (**2b**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (7:1) as an eluent to give the product **2b** (11 mg) with a yield of 62%; white solid; Mp 191.2–193.0 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.33 (s, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 5.69 (s, 2H), 3.91 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 167.9, 165.6, 164.1, 149.6, 136.2, 134.5, 134.4, 134.1, 131.9, 129.9, 129.3, 128.1, 123.4, 69.9, 53.1, 52.8; IR (thin film, cm^{-1}) 3427, 1772, 1743, 1723, 1256, 1220, 1135, 1092, 1012, 979, 797; HRMS (ESI): *m/z* calcd. for $C_{18}H_{12}O_6Cl$ $[M-H]^-$ 359.0327, found 359.0329.

*Dimethyl-7-(4-(methoxycarbonyl)phenyl)-3-oxo-1,3-dihydroisobenzofuran-4,5-dicarboxylate (**2c**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (8:1) as an eluent to give the product **2c** (12 mg) with a yield of 62%; white solid; Mp 159.9–161.1 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.38 (s, 1H), 8.11 (d, *J* = 8.3 Hz, 2H), 7.84 (d, *J* = 8.3 Hz, 2H), 5.71 (s, 2H), 4.00–3.79 (m, 9H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 167.8, 165.8, 165.5, 164.1, 149.8, 140.1, 136.3, 134.6, 132.2, 130.0, 128.5, 128.1, 123.6, 69.9, 53.1, 52.9, 52.4; IR (thin film, cm^{-1}) 3447, 2922, 1771, 1734, 1437, 1288, 1220, 1138, 801, 769, 709; HRMS (ESI): *m/z* calcd. for $C_{20}H_{15}O_8$ $[M-H]^-$ 383.0772, found 383.0773.

*Dimethyl-3-oxo-7-phenyl-1,3-dihydroisobenzofuran-4,5-dicarboxylate (**2d**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (8:1) as an eluent to give the product **2d** (11 mg) with a yield of 70%; white solid; Mp 177.6–178.9 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.32 (s, 1H), 7.67 (d, *J* = 7.4 Hz, 2H), 7.59–7.41 (m, 3H), 5.70 (s, 2H), 3.91 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 168.0, 165.7, 164.2, 149.5, 137.5, 135.6, 134.4, 131.6, 129.3, 129.2, 128.0, 127.9, 123.4, 70.0, 53.1, 52.8; IR (thin film, cm^{-1})

3425, 1768, 1745, 1384, 1282, 1255, 1217, 1129, 1004, 706; HRMS (ESI): *m/z* calcd. for $C_{18}H_{13}O_6$ $[M-H]^-$ 325.0717, found 325.0719.

*Dimethyl-7-(3-fluorophenyl)-3-oxo-1,3-dihydroisobenzofuran-4,5-dicarboxylate (**2e**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (7:1) as an eluent to give the product **2e** (10 mg) with a yield of 55%; white solid; Mp 189.2–190.7 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.35 (s, 1H), 7.67–7.55 (m, 2H), 7.54–7.43 (m, 1H), 7.36 (td, *J* = 8.3, 2.0 Hz, 1H), 5.72 (s, 2H), 3.91 (d, *J* = 5.5 Hz, 6H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 167.9, 165.5, 164.1, 162.5 (d, *J* = 244.9 Hz), 149.7, 137.9 (d, *J* = 8.0 Hz), 136.2 (d, *J* = 2.2 Hz), 134.7, 132.1, 131.4 (d, *J* = 8.5 Hz), 128.1, 124.3 (d, *J* = 2.7 Hz), 123.4, 116.0 (d, *J* = 21.0 Hz), 115.0 (d, *J* = 22.6 Hz), 69.9, 53.1, 52.9; IR (thin film, cm^{-1}) 3432, 1768, 1720, 1432, 1383, 1294, 1258, 1206, 1013, 792; HRMS (ESI): *m/z* calcd. for $C_{18}H_{14}O_6F$ $[M+H]^+$ 345.0768, found 345.0777.

*Dimethyl-7-(3-chlorophenyl)-3-oxo-1,3-dihydroisobenzofuran-4,5-dicarboxylate (**2f**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (7:1) as an eluent to give the product **2f** (10 mg) with a yield of 55%; white solid; Mp 192.9–194.3 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.34 (s, 1H), 7.78 (s, 1H), 7.69–7.54 (m, 3H), 5.71 (s, 2H), 3.91 (d, *J* = 6.1 Hz, 6H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 167.9, 165.5, 164.1, 149.7, 137.7, 136.0, 134.7, 134.0, 132.1, 131.1, 129.1, 128.1, 127.8, 126.8, 123.4, 69.8, 53.1, 52.9; IR (thin film, cm^{-1}) 3432, 1771, 1744, 1724, 1429, 1286, 1253, 1218, 1154, 1086, 975, 796; HRMS (ESI): *m/z* calcd. for $C_{18}H_{12}O_6Cl$ $[M-H]^-$ 359.0327, found 359.0330.

*Dimethyl-3-oxo-7-(m-tolyl)-1,3-dihydroisobenzofuran-4,5-dicarboxylate (**2g**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (7:1) as an eluent to give the product **2g** (7 mg) with a yield of 40%; white solid; Mp 169.3–170.7 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.31 (s, 1H), 7.54–7.39 (m, 3H), 7.33 (d, *J* = 6.9 Hz, 1H), 5.70 (s, 2H), 3.91 (d, *J* = 4.2 Hz, 6H), 2.41 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 168.0, 165.7, 164.2, 149.5, 138.8, 137.6, 135.6, 134.3, 131.5, 129.8, 129.2, 128.5, 128.0, 125.0, 123.4, 70.0, 53.1, 52.8; IR (thin film, cm^{-1}) 3433, 1769, 1751, 1429, 1384, 1263, 1205, 1084, 1017, 798, 713; HRMS (ESI): *m/z* calcd. for $C_{19}H_{15}O_6$ $[M-H]^-$ 339.0874, found 339.0875.

*Dimethyl-7-(2-chlorophenyl)-3-oxo-1,3-dihydroisobenzofuran-4,5-dicarboxylate (**2h**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (7:1) as an eluent to give the product **2h** (10 mg) with a yield of 58%; white solid; Mp 186.2–187.1 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.24 (s, 1H), 7.68 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.59 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.54 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.52 (dd, *J* = 7.4, 1.3 Hz, 1H), 5.42 (s, 2H), 3.93 (s, 3H), 3.89 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 167.8, 165.5, 164.0, 150.7, 136.2, 135.0, 134.0, 132.4, 131.4, 131.1, 130.9, 130.1, 127.9, 127.5, 123.2, 69.5, 53.2, 52.9; IR (thin film, cm^{-1}) 3429, 1769, 1752, 1723, 1278, 1262, 1214, 1157, 1133, 1055, 974; HRMS (ESI): *m/z* calcd. for $C_{18}H_{12}O_6Cl$ $[M-H]^-$ 359.0327, found 359.0329.

*Dimethyl-7-(2-(ethoxycarbonyl)phenyl)-3-oxo-1,3-dihydroisobenzofuran-4,5-dicarboxylate (**2i**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (6:1) as an eluent to give the product **2i** (9 mg) with a yield of 47%; white solid; Mp 129.2–130.1 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 5.30 (s, 2H), 4.05 (q, *J* = 7.1 Hz, 2H), 3.92 (s, 3H), 3.87 (s, 3H), 0.96 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 167.9, 165.9, 165.6, 164.1, 150.2, 138.0, 136.1, 134.8, 132.7, 131.8, 130.6, 130.4, 129.4, 127.6, 122.4, 69.3, 60.9, 53.1, 52.9; IR (thin film, cm^{-1}) 3440, 1772, 1722, 1435, 1333, 1284, 1152, 1133, 1071, 800; HRMS (ESI): *m/z* calcd. for $C_{21}H_{17}O_8$ $[M-H]^-$ 397.0928, found 397.0931.

*Dimethyl-7-(3-chloro-4-methylphenyl)-3-oxo-1,3-dihydroisobenzofuran-4,5-dicarboxylate (**2j**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (7:1) as an eluent to give the product **2j** (9 mg) with a yield of 47%; white solid; Mp 132.3–133.9 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.32 (s, 1H), 7.75 (d, *J* = 1.5 Hz, 1H), 7.64–7.41 (m, 2H), 5.70 (s, 2H), 3.91 (d, *J* = 4.1 Hz, 6H), 2.41 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 167.9, 165.6, 164.2, 149.6, 136.6, 136.0, 135.1, 134.5, 134.2, 132.0, 131.9, 128.1, 126.7, 123.4, 69.9, 53.1, 52.9, 19.4; IR (thin film, cm^{-1}) 3434, 2922, 1768, 1725, 1432, 1253, 1218, 1134, 981, 796; HRMS (ESI): *m/z* calcd. for $C_{19}H_{14}O_6Cl$ $[M-H]^-$ 373.0484, found 373.0485.

*Dimethyl-7-(3,4-dichlorophenyl)-3-oxo-1,3-dihydroisobenzofuran-4,5-dicarboxylate (**2k**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (8:1) as an eluent to give the product **2k** (9 mg) with a yield of 45%; white solid; Mp 167.4–169.1 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.36 (s, 1H), 7.99 (d, *J* = 2.1 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.67 (dd, *J* = 8.3, 2.2 Hz, 1H), 5.70 (s, 2H), 3.91 (d, *J* = 4.9 Hz, 6H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 167.8, 165.5, 164.1, 149.8, 136.2, 135.1, 134.8, 132.3, 132.1, 132.1, 131.3, 130.0, 128.4, 128.1, 123.4, 69.8, 53.1, 52.9; IR (thin film, cm^{-1}) 3433, 1780, 1739, 1432, 1282, 1267, 1128, 1082, 1011; HRMS (ESI): *m/z* calcd. for $C_{18}H_{11}O_6Cl_2$ $[M-H]^-$ 392.9938, found 392.9939.

*Dimethyl-7-(4-chloro-3-(methoxycarbonyl)phenyl)-3-oxo-1,3-dihydroiso-benzofuran-4,5-dicarboxylate (**2l**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (7:1) as an eluent to give the product **2l** (14 mg) with a yield of 66%; white solid; Mp 184.6–186.1 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.36 (s, 1H), 8.05 (d, *J* = 2.3 Hz, 1H), 7.87 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.76 (d, *J* = 8.3 Hz, 1H), 5.69 (s, 2H), 3.99–3.84 (m, 9H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 167.8, 165.5, 165.2, 164.1, 149.8, 135.3, 134.8, 134.6, 132.4, 132.24,

132.21, 131.5, 131.2, 130.3, 128.1, 123.4, 69.8, 53.1, 52.9, 52.8; IR (thin film, cm^{-1}) 3446, 1779, 1733, 1630, 1383, 1292, 1244, 1216, 1089, 1014; HRMS (ESI): *m/z* calcd. for $C_{20}H_{14}O_8Cl$ $[M-H]^-$ 417.0382, found 417.0384.

*Dimethyl-7-(naphthalen-1-yl)-3-oxo-1,3-dihydroisobenzofuran-4,5-dicarboxylate (**2m**)*. Purified by a column chromatography on silica gel with petroleum ether/ethyl acetate (8:1) as an eluent to give the product **2m** (12 mg) with a yield of 63%; white solid; Mp 177.8–179.2 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.26 (s, 1H), 8.16–7.97 (m, 2H), 7.75–7.56 (m, 4H), 7.52 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 5.43 (d, *J* = 13.8 Hz, 1H), 5.14 (d, *J* = 14.2 Hz, 1H), 3.96 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 168.1, 165.7, 164.2, 151.2, 136.3, 136.3, 133.4, 133.00, 132.03, 130.1, 129.4, 128.6, 127.6, 127.2, 127.2, 126.5, 125.6, 124.7, 123.5, 69.6, 53.1, 52.9; IR (thin film, cm^{-1}) 3431, 1779, 1745, 1582, 1442, 1262, 1154, 971, 802, 777; HRMS (ESI): *m/z* calcd. for $C_{22}H_{15}O_6$ $[M-H]^+$ 375.0874, found 375.0874.

*Dimethyl-3-oxo-7-(1-tosyl-1H-pyrrol-2-yl)-1,3-dihydroisobenzofuran-4,5-dicarboxylate (**2n**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (6:1) as an eluent to give the product **2n** (16 mg) with a yield of 68%; white solid; Mp 188.2–189.7 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.00 (s, 1H), 7.68 (dd, *J* = 3.3, 1.6 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 6.66 (dd, *J* = 3.3, 1.6 Hz, 1H), 6.54 (t, *J* = 3.4 Hz, 1H), 5.11 (s, 2H), 3.94 (s, 3H), 3.90 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 167.6, 165.4, 163.9, 151.3, 145.9, 137.3, 134.2, 132.5, 130.2, 127.9, 127.7, 126.7, 126.7, 126.4, 122.8, 118.6, 113.8, 69.4, 53.2, 52.9, 21.0; IR (thin film, cm^{-1}) 3446, 2954, 2922, 1778, 1731, 1594, 1434, 1369, 1282, 1150, 669, 590, 541; HRMS (ESI): *m/z* calcd. for $C_{23}H_{18}NO_8S$ $[M-H]^-$ 468.0758, found 468.0762.

General Procedures for the Preparation of Biaryls (3a-3h). To a solution of the substrates **1**,**1b**,**1c**,**1j**,**1l**,**1m** (0.05 mmol) in anhydrous toluene $Ph_3PAuNTf_2$ (0. 0025 mmol, 2 mg) was added under a nitrogen atmosphere. Then the dienophiles (0.015 mmol) were added. The reaction mixture was irradiated under microwave at 120 °C for 2 h. The solvent was removed *in vacuo* and the residue was purified by a flash column chromatography to afford the products **3a-3h**.

*Methyl-7-(4-chlorophenyl)-3-oxo-1,3-dihydroisobenzofuran-4-carboxylate (**3a**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (7:1) as an eluent to give the product **3a** (6 mg) with a yield of 40%; white solid; Mp 165.0–166.2 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.94 (d, *J* = 7.7 Hz, 1H), 7.85 (s, 1H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 2H), 5.60 (s, 2H), 3.90 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 168.0, 166.2, 145.9, 137.2, 135.3, 133.8, 133.6, 130.2, 129.9, 129.2, 129.0, 122.9, 69.4, 52.7; IR (thin film, cm^{-1}) 3495, 2921, 1767, 1725, 1432, 1283, 1199, 1055, 1002, 833, 758; HRMS (ESI): *m/z* calcd. for $C_{16}H_{10}O_4Cl$ $[M-H]^-$ 301.0273, found 301.0273.

*Methyl-7-(4-(methoxycarbonyl)phenyl)-3-oxo-1,3-dihydroisobenzofuran-4-carboxylate (**3b**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (8:1) as an eluent to give the product **3b** (7 mg) with a yield of 45%; white solid; Mp 150.3–151.6 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.21–8.05 (m, 2H), 8.01 (d, *J* = 7.7 Hz, 1H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.84–7.71 (m, 2H), 5.63 (s, 2H), 3.90 (d, *J* = 4.4 Hz, 6H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 168.0, 166.1, 165.8, 146.1, 141.0, 137.2, 133.8, 130.6, 129.9, 129.7, 129.0, 128.4, 122.9, 69.4, 52.7, 52.4; IR (thin film, cm^{-1}) 3436, 2923, 1767, 1741, 1713, 1292, 1116, 1052, 756; HRMS (ESI): *m/z* calcd. for $C_{18}H_{13}O_6$ $[M-H]^-$ 325.0717, found 325.0720.

*Methyl-7-(4-(isopropoxycarbonyl)phenyl)-3-oxo-1,3-dihydroisobenzofuran-4-carboxylate (**3c**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (7:1) as an eluent to give the product **3c** (7 mg) with a yield of 39%; white solid; Mp 142.7–143.5 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.08 (d, *J* = 8.3 Hz, 2H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 2H), 5.62 (s, 2H), 5.24–5.09 (m, 1H), 3.91 (s, 3H), 1.35 (d, *J* = 6.2 Hz, 6H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 168.0, 166.1, 164.8, 146.1, 140.9, 137.3, 133.8, 130.5, 130.3, 129.8, 129.0, 128.4, 122.9, 69.4, 68.4, 52.7, 21.6; IR (thin film, cm^{-1}) 3434, 1772, 1713, 1628, 1384, 1278, 1116, 757; HRMS (ESI): *m/z* calcd. for $C_{20}H_{17}O_6$ $[M-H]^-$ 353.1030, found 353.1032.

*Methyl-7-(3-chloro-4-methylphenyl)-3-oxo-1,3-dihydroisobenzofuran-4-carboxylate (**3d**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (7:1) as an eluent to give the product **3d** (8 mg) with a yield of 50%; white solid; Mp 186.8–187.9 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.95 (d, *J* = 7.7 Hz, 1H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.71 (s, 1H), 7.52 (s, 2H), 5.62 (s, 2H), 3.90 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 168.1, 166.1, 146.0, 137.0, 136.3, 135.9, 134.1, 133.7, 131.9, 130.1, 129.0, 128.1, 126.7, 122.8, 69.4, 52.7, 19.4; IR (thin film, cm^{-1}) 3426, 2922, 1765, 1726, 1638, 1383, 1297, 1135, 1019; HRMS (ESI): *m/z* calcd. for $C_{17}H_{12}O_4Cl$ $[M-H]^-$ 315.0429, found 315.0431.

*Methyl-7-(naphthalen-1-yl)-3-oxo-1,3-dihydroisobenzofuran-4-carboxylate (**3e**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (7:1) as an eluent to give the product **3e** (9 mg) with a yield of 55%; white solid; Mp 150.9–152.5 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.06 (dd, *J* = 11.7, 4.3 Hz, 2H), 7.88 (dd, *J* = 29.0, 7.6 Hz, 2H), 7.66–7.62 (m, 1H), 7.62–7.57 (m, 3H), 7.52 (dd, *J* = 6.9, 1.5 Hz, 1H), 5.34 (d, *J* = 13.0 Hz, 1H), 5.03 (d, *J* = 11.6 Hz, 1H), 3.94 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 168.2, 166.2, 147.5, 137.4, 135.5, 133.9, 133.4, 130.2, 129.1, 128.7, 128.6, 127.1, 126.9, 126.4, 125.6, 124.8, 122.8, 69.0, 52.7; IR (thin film,

cm^{-1}) 3437, 1754, 1721, 1638, 1384, 1295, 1141, 1078, 1035, 778; HRMS (ESI): *m/z* calcd. for $C_{20}H_{13}O_4$ [M-H]$^-$ 317.0819, found 317.0820.

*Methyl-(E)-7-(4-(isopropoxycarbonyl)phenyl)-4-(3-methoxy-3-oxoprop-1-en-1-yl)-3-oxo-1,3-dihydroisobenzofuran-5-carboxylate (**3f**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) as an eluent to give the product **3f** (10 mg) with a yield of 44%; white solid; Mp 167.3–168.9 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.25 (d, *J* = 16.3 Hz, 1H), 8.22 (s, 1H), 8.08 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 2H), 6.25 (d, *J* = 16.3 Hz, 1H), 5.61 (s, 2H), 5.28–5.08 (m, 1H), 3.87 (s, 3H), 3.77 (s, 3H), 1.35 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 168.8, 166.5, 165.6, 164.7, 148.7, 140.2, 137.3, 135.3, 134.14, 134.11, 132.2, 130.4, 129.8, 128.4, 125.4, 124.1, 68.7, 68.5, 52.9, 51.9, 21.6; IR (thin film, cm^{-1}) 3423, 1772, 1715, 1647, 1434, 1277, 1144, 1103, 976, 809, 707; HRMS (ESI): *m/z* calcd. for $C_{24}H_{21}O_8$ [M-H]$^-$ 437.1241, found 437.1243.

*Methyl-(E)-7-(3-chlorophenyl)-4-(3-methoxy-3-oxoprop-1-en-1-yl)-3-oxo-1,3-dihydroisobenzofuran-5-carboxylate (**3g**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (9:1) as an eluent to give the product **3g** (11 mg) with a yield of 55%; white solid; Mp 161.6–163.3 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.25 (d, *J* = 16.3 Hz, 1H), 8.19 (s, 1H), 7.75 (d, *J* = 0.8 Hz, 1H), 7.62 (dd, *J* = 3.8, 2.1 Hz, 1H), 7.57 (dd, *J* = 3.8, 1.4 Hz, 2H), 6.25 (d, *J* = 16.3 Hz, 1H), 5.62 (s, 2H), 3.87 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 168.8, 166.5, 165.6, 148.7, 137.9, 137.3, 135.0, 134.3, 134.0, 133.9, 132.2, 131.1, 128.9, 127.7, 126.7, 125.4, 124.0, 68.6, 52.9, 51.9; IR (thin film, cm^{-1}) 3438, 1770, 1723, 1632, 1384, 1276, 1115, 1034, 618; HRMS (ESI): *m/z* calcd. for $C_{20}H_{14}O_6Cl$ [M-H]$^-$ 385.0484, found 385.0486.

*Methyl-(E)-7-(4-chloro-3-(methoxycarbonyl)phenyl)-4-(3-methoxy-3-oxoprop-1-en-1-yl)-3-oxo-1,3-dihydroisobenzofuran-5-carboxylate (**3h**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (7:1) as an eluent to give the product **3h** (11 mg) with a yield of 48%; white solid; Mp 129.3–130.5 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.25 (d, *J* = 16.3 Hz, 1H), 8.21 (s, 1H), 8.03 (d, *J* = 2.3 Hz, 1H), 7.90–7.82 (m, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 6.25 (d, *J* = 16.3 Hz, 1H), 5.61 (s, 2H), 3.90 (s, 3H), 3.87 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 168.8, 166.5, 165.6, 165.2, 148.8, 137.2, 135.0, 134.2, 134.2, 134.1, 132.3, 132.2, 131.5, 131.2, 130.3, 125.4, 124.0, 109.5, 68.6, 52.9, 52.8, 51.9; IR (thin film, cm^{-1}) 3435, 2922, 1761, 1734, 1431, 1383, 1245, 1140, 1045; HRMS (ESI): *m/z* calcd. for $C_{22}H_{16}O_8Cl$ [M-H]$^-$ 443.0539, found 443.0541.

General Procedures for the Preparation of Biaryl Derivatives (4a-4f). To a solution of the substrates **1o-1t** (0.05 mmol) in dry toluene, $Ph_3PAuNTf_2$ (0. 0025 mmol, 2 mg) was added under a nitrogen atmosphere. Then DMAD (0.015 mmol, 2 mg) were added into the mixture. The reaction mixture was reacted under the irradiation of microwave at 120 °C for 2 h. The solvent was removed *in vacuo* and the residue was purified by a flash column chromatography to afford the products **4a-4f**.

*Dimethyl 1-oxo-7-phenyl-2,3-dihydro-1H-indene-4,5-dicarboxylate (**4a**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) as an eluent to give the product **4a** (7 mg) with a yield of 45%; yellow solid; Mp 146.3–147.8 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.64 (s, 1H), 7.47 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.45–7.42 (m, 3H), 3.89 (s, 3H), 3.87 (s, 3H), 3.18–3.15 (m, 2H), 2.72–2.68 (m, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 204.0, 166.5, 166.2, 154.9, 142.3, 136.3, 135.6, 134.1, 129.8, 129.6, 129.3, 128.5, 127.9, 53.1, 52.9, 36.5, 24.3; IR (thin film, cm^{-1}) 3426, 2923, 2853, 1773, 1715, 1441, 1383, 1331, 1289, 1160, 1066, 986, 781, 618; HRMS (ESI): *m/z* calcd. for $C_{19}H_{17}O_5$ [M+H]$^+$ 325.1076, found 325.1083.

*Dimethyl 7-(4-chlorophenyl)-1-oxo-2,3-dihydro-1H-indene-4,5-dicarboxylate (**4b**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) as an eluent to give the product **4b** (12 mg) with a yield of 67%; yellow solid; Mp 89.1–90.1 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.65 (s, 1H), 7.50 (s, 4H), 3.89 (s, 3H), 3.87 (s, 3H), 3.18–3.14 (m, 2H), 2.72–2.68 (m, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 204.1, 166.5, 166.1, 154.9, 140.8, 135.7, 135.0, 134.2, 133.4, 131.2, 129.9, 129.7, 127.9, 53.1, 52.8, 36.5, 24.3; IR (thin film, cm^{-1}) 3425, 2953, 2854, 1722, 1436, 1384, 1293, 1225, 1126, 1110, 1069, 979, 840, 798, 726; HRMS (ESI): *m/z* calcd. for $C_{19}H_{16}ClO_5$ [M+H]$^+$ 359.0686, found 359.0697.

*Dimethyl 7-(3-chlorophenyl)-1-oxo-2,3-dihydro-1H-indene-4,5-dicarboxylate (**4c**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) as an eluent to give the product **4c** (7 mg) with a yield of 37%; yellow solid; Mp 90.3–91.7 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.67 (s, 1H), 7.55 (t, *J* = 1.7 Hz, 1H), 7.51–7.49 (m, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.42 (dt, *J* = 7.5, 1.4 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 3.19–3.13 (m, 2H), 2.74–2.67 (m, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 204.0, 166.4, 166.0, 154.8, 140.4, 138.2, 135.7, 134.1, 132.4, 130.1, 129.8, 129.1, 128.3, 128.0, 53.1, 52.8, 36.5, 24.3; IR (thin film, cm^{-1}) 3422, 2924, 2853, 1718, 1591, 1562, 1465, 1442, 1312, 1123, 1048, 961, 849, 783; HRMS (ESI): *m/z* calcd. for $C_{19}H_{16}ClO_5$ [M+H]$^+$ 359.0686, found 359.0689.

*Dimethyl 1-oxo-7-phenyl-1,3-dihydroisobenzofuran-4,5-dicarboxylate (**4d**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) as an eluent to give the product **4d** (10 mg) with a yield of 62%; light yellow solid; Mp 102.8–104.2 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.74 (s, 1H), 7.59 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.50–7.47 (m, 3H), 5.57 (s, 2H), 3.90 (s, 3H), 3.88 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 168.1, 167.3, 164.3, 149.7, 145.2, 138.4, 134.7, 130.2, 129.7, 129.1, 128.1, 123.9, 122.2, 69.4, 53.2, 53.1; IR (thin

film, cm^{-1}) 3286, 3251, 2981, 2854, 1737, 1689, 1526, 1459, 1384, 1259, 1179, 1110, 1051, 927, 794, 593; HRMS (ESI): *m/z* calcd. for $C_{18}H_{15}O_6$ $[M+H]^+$ 327.0869, found 327.0874.

*Dimethyl 7-(4-chlorophenyl)-1-oxo-1,3-dihydroisobenzofuran-4,5-dicarboxylate (**4e**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) as an eluent to give the product **4e** (11 mg) with a yield of 61%; white solid; Mp 134.5–135.8 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.76 (s, 1H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 5.57 (s, 2H), 3.90 (s, 3H), 3.88 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 168.1, 167.2, 164.3, 149.7, 143.7, 138.4, 134.2, 133.4, 131.6, 130.1, 128.1, 124.0, 122.5, 69.5, 53.16, 53.12; IR (thin film, cm^{-1}) 3425, 2954, 2854, 1722, 1436, 1384, 1293, 1225, 1110, 1069, 979, 840, 798, 726, 692; HRMS (ESI): *m/z*: calcd for $C_{18}H_{14}ClO_6$ $[M+H]^+$ 361.0479, found 361.0485.

*Dimethyl 7-(3-chlorophenyl)-1-oxo-1,3-dihydroisobenzofuran-4,5-dicarboxylate (**4f**)*. Purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) as an eluent to give the product **4f** (12 mg) with a yield of 65%; white solid; Mp 169.9–171.6 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.80 (s, 1H), 7.70 (t, *J* = 1.7 Hz, 1H), 7.57–7.54 (m, 2H), 7.52 (d, *J* = 7.6 Hz, 1H), 5.57 (s, 2H), 3.90 (s, 3H), 3.88 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 168.0, 167.1, 164.2, 149.5, 143.2, 138.4, 136.6, 132.6, 130.2, 129.9, 129.4, 128.9, 128.3, 124.2, 122.8, 69.4, 53.1; IR (thin film, cm^{-1}) 3426, 2923, 2853, 1773, 1715, 1441, 1383, 1331, 1289, 1150, 1066, 986, 780, 618; HRMS (ESI): *m/z* calcd. for $C_{18}H_{14}ClO_6$ $[M+H]^+$ 361.0479, found 361.0459.

Associate Content

The Supporting Information is available free of charge on the ACS Publications website. ^{1}H and ^{13}C NMR spectra for all compounds and computational details for proposed mechanism (PDF)

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Notes

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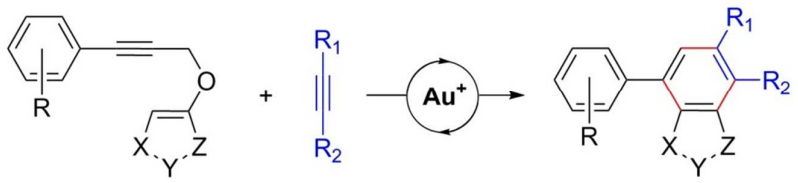
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