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Syntheses of *Z*-Iodovinylfurans and 2-Acyl Furans *via* Controllable Cyclization of Ynenones

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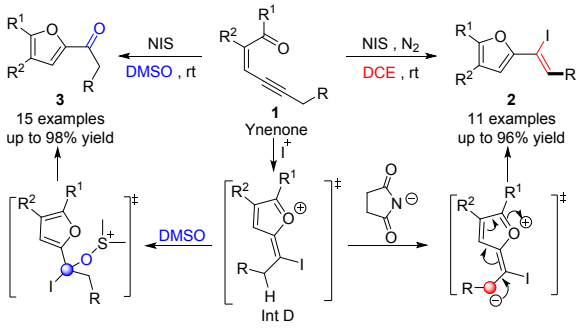


ABSTRACT: A divergent synthesis of *Z*-iodovinylfurans and 2-acyl furans promoted by NIS *via* controllable cyclization of ynenones is reported. The reaction proceeded by sequential *5-exo-dig* electrophilic cyclization to intermediate 2-(iodomethylene)-2*H*-furanium cation **D**, providing a range of synthetically valuable and useful *tri*-substituted furan derivatives **2** and **3** in moderate to excellent yields. This approach is metal-free, mild and atom-economic, with good selectivity and high stereoselectivity.

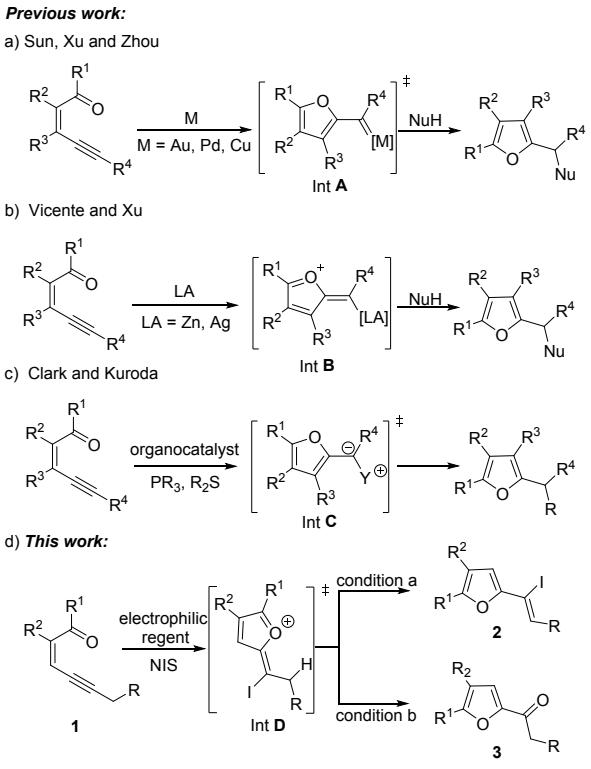
INTRODUCTION

Furan motif is a common structure pattern found in natural products,[1] pharmaceuticals[2] and functional materials,[3] which is also served as a building block in organic synthesis.[4] Driven by this prevalence, much attention has been paid to the synthesis of substituted furans to increase their structural diversity and which are valuable in medicinal chemistry and drug discovery.[5] In spite of several well-established general approaches for furan synthesis, [6] metal-catalyzed reactions[7-11] and organocatalyst-promoted ractions[12-13] were reported successively in recent years.[14] However, these

methods have been used less frequently in medicinal chemistry and drug discovery.[5] So, the development of new and more efficient methods, especially non-metal participated, for the synthesis of furans is a general interest to organic chemists.

Ynenones, serving as the carbene precursors, were reported for the synthesis of furan derivatives in the presence of gold, palladium and copper catalysts, respectively[15-17](Scheme 1a). Moreover, Lewis acids, such as zinc and silver complexes, were also reported to catalyze ynenones to construct furan derivatives *via* the intermediate furanium cation **B**[8b,18,19] as shown in Scheme **1b**. In contrast, the number of non-metal participated examples is limited.[12,13] Only phosphine and sulfur were reported as organocatalysts to synthesize highly substituted furan derivatives[12, 13](Scheme 1c). We envisioned that electrophilic regent, such as *N*-iodosuccinimide, could react with ynenone to form the 2-(iodomethylene)-*2H*-furanium intermediate **D**, followed by nucleophile trapping (Scheme 1d).

Scheme 1. Strategies for the Synthesis of Furans from Ynenones

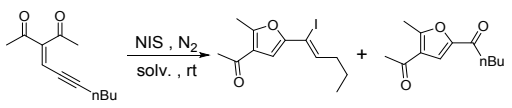


Herein, we report the first *NIS*-promoted tandem cyclization of ynenones to synthesize *Z*-iodovinylfuran and 2-acyl furan derivatives selectively. This approach is metal-free, mild, efficient and atom-economic, with good selectivity and high stereoselectivity (Scheme 1d).

RESULTS AND DISCUSSION

At the beginning, we employed ynenone **1a** for the reaction discovery and condition optimization, and some results are shown in Table 1. The reaction was initially carried out in chlorobenzene (PhCl) at room temperature under nitrogen for 20 minutes with *N*-iodosuccinimide (NIS, 1.1 equiv.) as the initiator. To our delight, the product (*Z*)-1-(5-(1-iodopent-1-en-1-yl)-2-methylfuran-3-yl)ethan-1-one **2a** was obtained in 64% yield, along with 72% yield of succinimide and less than 2% of 1-(4-acetyl-5-methylfuran-2-yl)pentan-1-one **3a** was observed from crude ^{1}H NMR (entry 1). Screening of various other solvents, revealed that aprotic solvent DCE (entry 2) was the most effective (entries 2-7). To our surprise, no desired product **2a** was observed by employing dimethylsulfoxide (DMSO) as the solvent, but **3a** was obtained in 94% yield, which revealed that the solvent (DMSO) may be served as one of oxidants during the reaction (entry 8). Furthermore, neither decreasing nor increasing the loading of NIS (entries 9-11) improved the yield of **2a**. Excessive NIS causes a messy reaction, indicating that **2a** is unstable in the presence of excess NIS. Other electrophilic regents I_2 and NBS (*N*-bromosuccinimide)[22] were also investigated with no better results. Meanwhile, no reaction was observed with iodide-anion (KI) instead of NIS.

Table 1. Optimization of the Reaction Conditions[a]



1a **2a** **3a**

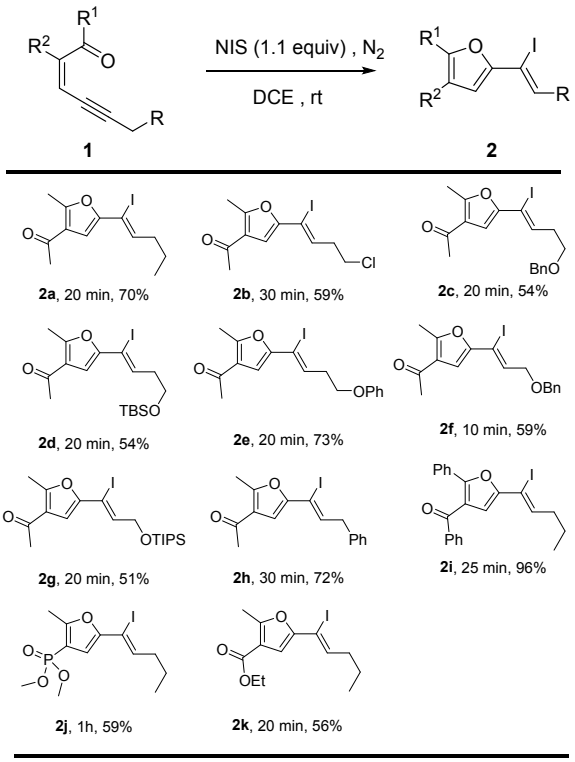
entry	NIS[b] (equiv)	solvent	time (min)	yield (%) **2a**	yield (%) **3a**

1	1.1	PhCl	20	64	< 2
2	***1.1***	***DCE***	***20***	***70***	***< 2***
3	1.1	DCM	60	62	< 2
4	1.1	THF	60	42	< 2
5	1.1	Toluene	60	52	< 2
6	1.1	PhF	20	69	< 2
7	1.1	$CHCl_3$	20	47	< 2
8	1.1	DMSO	50	0	94
9	1.0	DCE	30	65	< 2
10	1.2	DCE	20	55	< 2
11	1.5	DCE	20	33	< 2
12[c]	1.1	DCE	70	31	< 2
13[d]	1.1	DCE	24 h	0	0

[a]The reactions were conducted in the capped vial with a septum under a nitrogen atmosphere. Initially, [1a] = 0.1 M. [b]The loading of NIS. [c]Replaced NIS with I_2. [d]Replaced NIS with KI.

With the optimal conditions (Table 1, entry 2) in hand, the reaction scope was examined. As shown in Scheme 2. Ynenones **1a−1e** possessing aliphatic R groups reacted as expected, despite of exhibiting moderate yields. Different functional groups at the end of the alkyl chain, such as Cl, OBn, OTBS and OPh, were readily tolerated. Other substrates like **1f-1h**, with OTIPS, OBn and Ph installed at the *β*-carbon position of ynenones, reacted smoothly to afford *Z*-iodovinylfurans **2f-2h** in good yields. The relative configuration of the product **2h** was unambiguously assigned by X-ray crystallography (CCDC 1906176) (see the Supporting Information). Ynenone **1i** with a phenyl group at the end of carbonyl group provided excellent yield of the product. The reaction tolerated phosphate and ester R^2 groups as well, the desired products **2j-2k** were obtained in 59% and 56% yields respectively.

Scheme 2. Reaction Scope[a,b]

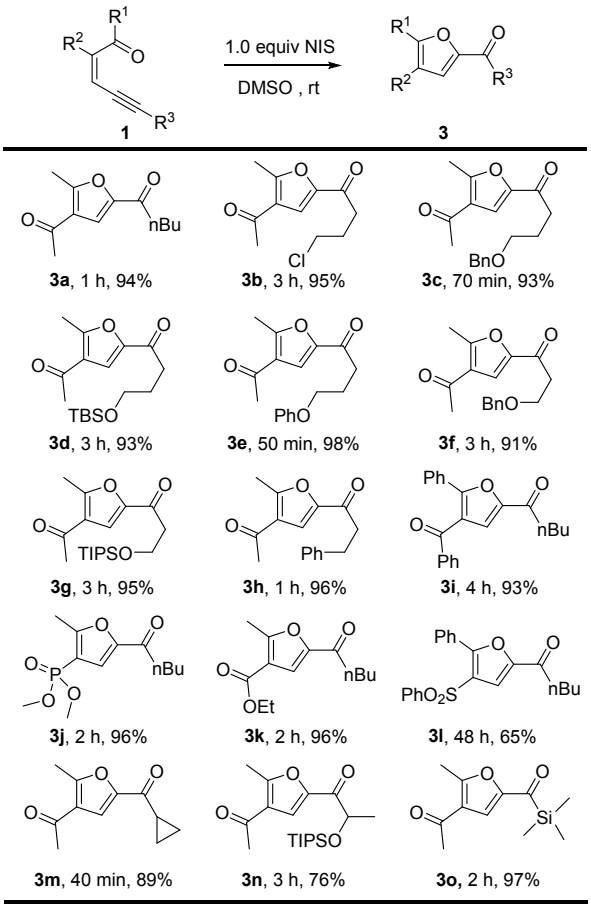


[a]All reactions were performed with **1** (0.2 mmol, 1.0 equiv) and NIS (0.22 mmol, 1.1 equiv) in DCE 2 mL at rt under a static nitrogen atmosphere.
[b]The products were isolated as single isomer.

Furthermore, more useful reactions of ynenone was investigated, namely the synthesis of 2-acyl furans. The optional condition was that the reaction was carried out in DMSO at room temperature with 1.0 equivalent of NIS in the air (see the Supporting Information). Thus, a tandem predictably cyclization of ynenones **1a−1o** proceeded smoothly to provide various 2-acyl furans **3a−3o** in good to excellent yields. The reaction works well with aliphatic R groups. Different functional groups at the end of the alkyl chain, such as Cl, OBn, OTBS, OPh and Ph groups, were readily tolerated and the corresponding products **3b-3i** were obtained in excellent yields (up to 98% yield). The reaction also tolerated phosphate and ester R^2 groups, like **1j-k**, and provided the **3j-k** in excellent yields. Ynenone bearing a sulfonyl R^2 group provided a moderate yield of **3l** because of the poor solubility of **1l**. To our delight, different substituted 2-acyl furans, like **3m-n**, were also formed efficiently through this process. Additionally, transformation of ynenone **1o** with trimethylsilyl group at the end of alkyne to useful furan-2-yl(trimethylsilyl)methanone **3o** was also

realized in a 97% yield.

Scheme 3. Reaction scope[a]

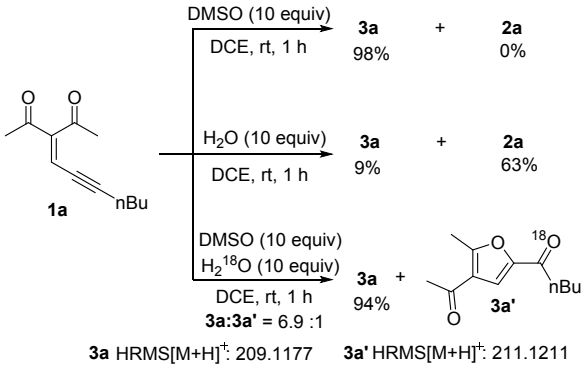


[a]Reaction conditions: 1a (0.2 mmol, 1.0 equiv) and NIS as initiator in DMSO (2 mL) in the air.

In order to gather experimental evidence for the mechanism, the ynenone **1a** was tested in DCE, with NIS (1.0 equiv) and DMSO (10 equiv) at room temperature, as shown in Scheme 4. To our delight, a 98% yield of desired product **3a** was isolated in 1 h, as well as no *Z*-iodovinylfuran **2a** was observed, which indicated that DMSO acted as a source of oxygen. Moreover, we also carried out the reaction in the presence of H_2O (10 equiv) in DCE without DMSO; however, less than 10% yield of **3a** was observed in 1 h. The reaction was also attempted in the presence of H_2O^{18} (10 equiv) and DMSO (10 equiv) in DCE at room temperature, and minor O^{18} labeled product **3a′** was detected from HRMS, indicating that the new oxygen of **3a** was major from the DMSO and

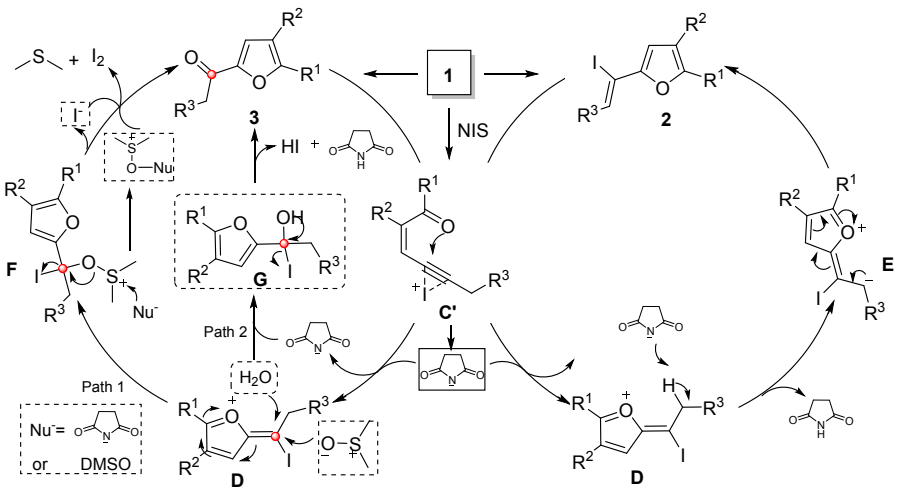
H_2O existed in the reaction system can not only serve as a less efficient oxygen donor but also a consequence of NIS inactivation with arising hydroiodic acid leading to molecular iodine.

Scheme 4. Control Experiments.



On the basis of the above observations, we propose the following plausible mechanisms for this transformation (Scheme 5). (i) Electrophile I^+ generated from NIS first coordinates selectively with C−C triple bonds of ynenone **1** to give iodirenium intermediate **C'**, subsequently the oxygen from carbonyl group attacks iodirenium intermediate **C'** *via 5-exo-dig* cyclization to generate oxonium intermediate **D**. (ii) Succinimide anion generated from NIS eliminates the *α*-H of oxonium intermediate **D** to form *Z*-iodovinylfurans **2**. (iii) If the reaction is carried out in DMSO, DMSO serves as a nucleophile to attack iodirenium intermediate **D** and gives sulfonium salt intermediate **F**, where one molecular of DMSO or succinimide anion as nucleophile attacks the sulfonium salt intermediate **F** and drives the iodine anion away to give the 2-acyl furan **3** and

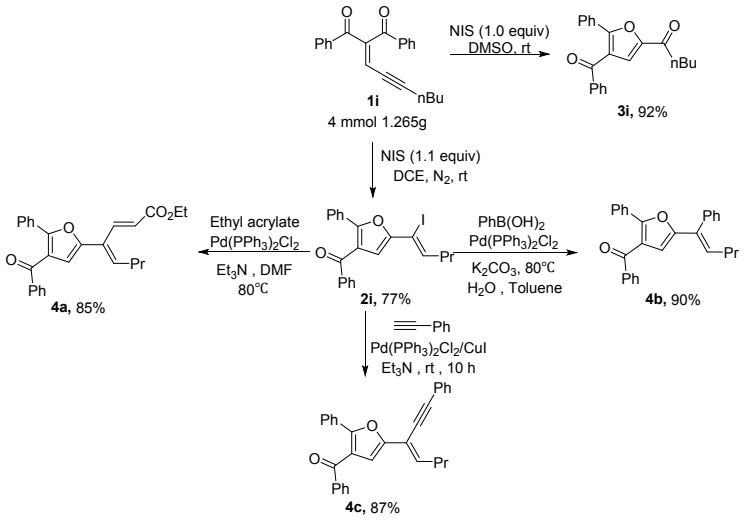
Scheme 5. Proposed mechanisms



sulfonium salt **H**, which is reduced by iodine anion to iodine and dimethyl sulfide[23]. (iv) Moreover, H_2O existed in the reaction system can also serve as a less efficient nucleophile to attack iodirenium intermediate **D** and gives intermediate **G**, which is unstable and quickly transfers to 2-acyl furan **3**.

We also carried out **1i** at a gram scale (1.265g, 4 mmol) with NIS as the initiator， where the desired *Z*-iodovinylfuran **2i** and 2-acyl furan **3i** were isolated in 77% and 92% yields respectively. The synthetic utility of the *Z*-iodovinylfuran products were also examined by using **2i** as an illustrative example, as shown in Scheme 6. Several palladium-catalyzed processes performed well, including Heck reaction, Suzuki coupling and Sonogashira coupling, and the desired products **4a-4c** were synthesized in excellent yields.

Scheme 6. Transformations of 2i



We have reported an efficient strategy starting from ynenones to construct substituted *Z*-iodovinylfurans **2** and 2-acyl furan derivatives **3** selectively *via* a *N*-iodosuccinimide promoted tandem cyclization. This approach is metal-free, mild and efficient. And the *Z*-iodovinylfuran product **2i** readily undergo further transformations, substantially broaden the scope of accessible multi-substituted furan products and notably enhance the synthetic utility of these cascade reactions. Meanwhile, a useful transformation product furan-2-yl(trimethylsilyl)methanone **3o** can be synthesized in the yield of 97% from simple ynenone. Control experiments suggest that DMSO is an efficient oxygen donor in the synthesis of 2-acyl furans **3**.

EXPERIMENTAL SECTION

General Information. Ethyl acetate (ACS grade), hexanes (ACS grade), diethyl ether (ACS grade) and anhydrous 1,2-dichloroethane (anhydride, 99.8%) were purchased from Fisher Scientific and used without further purification. Methylene chloride and tetrahydrofuran were purified using MBraun Solvent Purifier. Commercially available reagents were used without further purification. Reactions were monitored by thin layer chromatography (TLC) using Sorbent Technologies' pre-coated silica gel plates. Flash column chromatography was performed over Sorbent Technologies' silica gel (230-400 mesh). $^{1}H\{^{13}C\}$ NMR and $^{13}C\{^{1}H\}$NMR spectra were recorded on Bruker 500 MHz spectrometers using residue solvent peaks as internal standards. Mass spectra were recorded with Micromass Thermo Scientific LTQ Orbitrap XL and AB SCIEX Triple TOF5600^{+} using electron spray ionization or Waters GCT Premier time-of-flight mass spectrometer with a field ionization (FI) ion source. $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker AV-500 spectrometer and a Bruker AV-500 spectrometer in chloroform-d3. Chemical shifts are reported in ppm with the internal chloroform signal at 7.26 and 77.0 ppm as a standard

and CD_3OD signal at 3.31 and 49.0 ppm as a standard.

General Procedure for the Synthesis of 1. *Example for the Synthesis of **1b**.* Piperidine (75.0 mg, 0.8 mmol, 0.1 equiv), acetic acid (317.0 mg, 5.3 mmol, 0.6 equiv) and magnesium sulfate (1.10 g, 8.8 mmol, 1.0 equiv) were added to a stirred solution of 6-chlorohex-2-ynal (1.15 g, 8.8 mmol, 1.0 equiv) and acetylacetone (889.9 mg, 8.8 mmol, 1.01 equiv) in toluene (25 mL) at ambient temperature. The reaction mixture was stirred at 35°C for overnight with oil bath and the reaction was quenched by the addition of water (30 cm^3). The aqueous layer was extracted with ethyl acetate (3 × 100 cm^3) and the combined organic layers were dried (magnesium sulfate) and concentrated in vacuo. The residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 20:1) and **1b** was isolated in 729.9 mg, 3.4 mmol, 39%, yellow liquid.

3-(hept-2-yn-1-ylidene)pentane-2,4-dione **(1a).**[20] Isolated by column chromatography (hexanes/ethyl acetate = 30:1) in 299.9 mg, 1.56 mmol, 82%, yellow liquid. $^1H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 6.69 (1H, td, J = 2.5, 1.0 Hz), 2.46 (3H, d, J = 1.0 Hz), 2.43 (2H, tdd, J = 7.5, 2.5, 1.0 Hz), 2.30 (3H, d, J = 1.0 Hz), 1.57 - 1.52 (2H, m), 1.45 - 1.37 (2H, m), 0.92 (3H, td, J = 7.5, 1.0 Hz).

3-(6-chlorohex-2-yn-1-ylidene)pentane-2,4-dione **(1b)**. 729.9 mg, 3.4 mmol, 39%, yellow liquid. $^1H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 6.65 - 6.64 (1H, t, J = 2.5 Hz), 3.64 - 3.61 (2H, t, J = 6.0 Hz), 2.65 - 2.62 (2H, td, J = 2.5, 7.0 Hz), 2.44 (3H, s), 2.30 (3H, s), 2.03 - 1.98 (2H, m). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 201.1, 195.6, 150.1, 122.4, 107.4, 77.4, 43.3, 30.8, 30.6, 27.0, 17.5. HRMS (ESI) m/z calcd for $C_{11}H_{14}ClO_2^+$ $(M+H)^+$ 213.0677, found 213.0676.

3-(6-(benzyloxy)hex-2-yn-1-ylidene)pentane-2,4-dione **(1c)**. Isolated by column chromatography (hexanes/ethyl acetate = 25:2) in 341.2 mg, 1.2 mmol, 13%, yellow liquid. $^1H\{^{13}C\}$ NMR (500

MHz, $CDCl_3$) δ: 7.36 - 7.31 (4H, m), 7.30 - 7.27 (1H, m), 6.66 - 6.65 (1H, t, J = 2.5 Hz), 4.51 (2H, s), 3.56 - 3.53 (2H, t, J = 6.3 Hz), 2.59 - 2.56 (2H, td, J = 7.1, 2.2 Hz), 2.44 (3H, s), 2.31 (3H, s), 1.89 - 1.83 (2H, m). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 201.0, 195.5, 149.5, 138.1, 128.2, 127.4, 122.7, 122.7, 109.3, 76.8, 72.8, 68.2, 30.7, 28.1, 26.9, 16.9. HRMS (ESI) m/z calcd for $C_{18}H_{21}O_3^+$ $(M+H)^+$ 285.1485, found 285.1488.

3-(6-((tert-butyldimethylsilyl)oxy)hex-2-yn-1-ylidene)pentane-2,4-dione **(1d)**. Isolated by column chromatography (hexanes/ethyl acetate = 20:1) in 431.9 mg, 1.4 mmol, 16%, yellow liquid. $^1H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 6.68 - 6.67 (1H, t, J = 2.5 Hz), 3.68 - 3.65 (2H, t, J = 5.8 Hz), 2.54 - 2.51 (2H, td, J = 7.1, 2.5 Hz), 2.46 (3H, s), 2.30 (3H, s), 1.77 - 1.72 (2H, m), 0.88 (9H, s), 0.04 (6H, s) . $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 201.2, 195.7, 149.6, 123.1, 110.0, 76.9, 61.2, 31.1, 30.9, 27.2, 25.8, 18.2, 16.7, -5.4. HRMS (ESI) m/z calcd for $C_{17}H_{29}O_3Si^+$ $(M+H)^+$ 309.1881, found 309.1881.

3-(6-phenoxyhex-2-yn-1-ylidene)pentane-2,4-dione **(1e)**. Isolated by column chromatography (hexanes/ethyl acetate = 20:1) in 621.8 mg, 2.3 mmol, 21%, yellow liquid. $^1H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 7.30 - 7.25 (2H, m), 6.96 - 6.93 (1H, t, J = 6.8 Hz), 6.90 - 6.89 (2H, d, J = 8.0 Hz), 6.66 (1H, s), 4.05 - 4.03 (2H, t, J = 6.0 Hz), 2.68 - 2.66 (2H, t, J = 7.0 Hz), 2.42 (3H, s), 2.30 (3H, s), 2.06 - 2.01 (2H, m). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 201.2, 195.7, 158.7, 149.9, 129.5, 122.8, 120.8, 114.4, 108.7, 77.2, 65.8, 30.9, 27.9, 27.1, 17.0. HRMS (ESI) m/z calcd for $C_{17}H_{19}O_3^+$ $(M+H)^+$ 271.1329, found 271.1330.

3-(5-(benzyloxy)pent-2-yn-1-ylidene)pentane-2,4-dione **(1f)**. Isolated by column chromatography (hexanes/ethyl acetate = 10:1) in 973.2 mg, 3.6 mmol, 23%, yellow liquid. $^1H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 7.37 - 7.28 (5H, m), 6.68 – 6.67 (1H, t, J = 2.3 Hz), 4.54 (2H, s), 3.64 – 3.61 (2H,

t, J = 6.8 Hz), 2.76 – 2.73 (2H, td, J = 6.5, 2.0 Hz), 2.45 (3H, s), 2.30 (3H, s). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ : 201.1, 195.7, 149.8, 137.7, 128.4, 127.8, 127.7, 122.6, 106.6, 77.5, 73.1, 67.5, 30.9, 27.2, 21.7. HRMS (ESI) m/z calcd for $C_{17}H_{18}O_3Na^+$ $(M+Na)^+$ 293.1148, found 293.1143; HRMS (ESI) m/z calcd for $C_{17}H_{19}O_3^+$ $(M+H)^+$ 271.1329, found 271.1329.

3-(5-((triisopropylsilyl)oxy)pent-2-yn-1-ylidene)pentane-2,4-dione **(1g)**. Isolated by column chromatography (hexanes/ethyl acetate = 30:1) in 605.8 mg, 1.8 mmol, 25%, yellow liquid. $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 6.69 - 6.68 (1H, t, J = 2.5 Hz), 3.85 - 3.83 (2H, t, J = 6.8 Hz), 2.69 - 2.66 (2H, td, J = 2.3, 6.8 Hz), 2.48 (3H, s), 2.30 (3H, s), 1.10 - 1.07 (3H, m), 1.06 - 1.05 (18H, d, J = 5.5 Hz). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 201.1, 195.7, 149.6, 122.9, 107.3, 77.7, 61.4, 31.0, 27.3, 24.7, 17.9, 11.9. HRMS (ESI) m/z calcd for $C_{19}H_{33}O_3Si^+$ $(M+H)^+$ 337.2194, found 337.2195.

3-(5-phenylpent-2-yn-1-ylidene)pentane-2,4-dione **(1h)**.[21] Isolated by column chromatography (hexanes/ethyl acetate = 15:1) in 192.2 mg, 0.8 mmol, 50%, yellow liquid. $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 7.32 - 7.29 (2H, m), 7.24 - 7.19 (3H, m), 6.65 (1H, t, J = 2.5 Hz), 2.87 (2H, t, J = 7.3 Hz), 2.75 (2H, td, J = 7.4, 2.7 Hz), 2.34 (3H, s), 2.29 (3H, s). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 201.2, 195.7, 149.6, 139.7, 128.5, 128.3, 126.5, 122.7, 108.9, 77.4, 34.2, 30.8, 27.1, 22.1.

2-(hept-2-yn-1-ylidene)-1,3-diphenylpropane-1,3-dione **(1i)**.[12] Isolated by column chromatography (hexanes/ethyl acetate = 100:1) in 348.0 mg, 1.1 mmol, 23%, yellow liquid. $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 7.96 - 7.94 (2H, m), 7.79 - 7.77 (2H, m), 7.58 - 7.51 (2H, m), 7.47 - 7.41 (4H, m), 6.72 (1H, t, J = 1.1 Hz), 2.19 (2H, td, J = 7.0, 2.2 Hz), 1.26 - 1.21 (2H, m), 1.17 - 1.10 (2H, m), 0.76 (3H, t, J = 7.3 Hz). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 194.4, 193.1, 147.8, 136.9, 136.3,

133.6, 132.7, 129.5, 129.2, 128.6, 128.5, 125.5, 109.7, 76.8, 29.8, 21.6, 19.6, 13.4.

dimethyl (E)-(2-oxodec-3-en-5-yn-3-yl)phosphonate **(1j)**.[12] Isolated by column chromatography (hexanes/ethyl acetate = 5:2) in 309.9 mg, 1.2 mmol, 15%, orange liquid. $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 6.95 - 6.90 (1H, dt, J = 21.8, 2.4 Hz), 3.78 - 3.75 (6H, d, J = 11 Hz), 2.50 (3H, s), 2.46 - 2.42 (2H, td, J = 7.0, 3.0 Hz), 1.58 - 1.52 (2H, m), 1.45 - 1.39 (2H, m), 0.92 - 0.89 (3H, t, J = 7.3 Hz).

ethyl (E)-2-acetylnon-2-en-4-ynoate **(1k)**.[12] Isolated by column chromatography (hexanes/ethyl acetate = 50:1) in 367.8 mg, 1.6 mmol, 38%, yellow liquid. $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 6.78 - 6.77 (1H, t, J = 2.8 Hz), 4.25 - 4.21 (2H, q, J = 7.0 Hz), 2.42 (3H, s), 2.41 - 2.38 (2H, td, J = 7.2, 2.8 Hz), 1.54 - 1.49 (2H, m), 1.43 - 1.35 (2H, m), 1.29 - 1.26 (3H, t, J = 7.3 Hz), 0.91 - 0.88 (3H, t, J = 7.3 Hz).

(E)-1-phenyl-2-(phenylsulfonyl)non-2-en-4-yn-1-one **(1l)**. Isolated by column chromatography (hexanes/ethyl acetate = 20:1) in 761.3 mg, 2.2 mmol, 36%, white solid. $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 7.90 - 7.88 (4H, d, J = 7.5 Hz), 7.66 - 7.58 (2H, m), 7.56 - 7.53 (2H, t, J = 7.5 Hz), 7.47 - 7.44 (2H, t, J = 7.5 Hz), 7.16 - 7.15 (1H, t, J = 2.5 Hz), 2.10 - 2.07 (2H, td, J = 6.9, 2.8 Hz), 1.11 - 1.06 (2H, m), 1.02 - 0.97 (2H, m), 0.70 - 0.67 (3H, t, J = 7.3 Hz). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 190.1, 148.6, 139.7, 135.8, 134.2, 133.8, 129.9, 129.1, 128.6, 128.6, 124.9, 110.8, 74.9, 29.6, 21.5, 19.4, 13.3. HRMS (ESI) m/z calcd for $C_{21}H_{20}O_3SNa^+$ $(M+Na)^+$ 375.1025, found 375.1028.

3-(3-cyclopropylprop-2-yn-1-ylidene)pentane-2,4-dione **(1m)**.[10d] Isolated by column chromatography (hexanes/ethyl acetate = 20:1) in 405.3 mg, 2.3 mmol, 31%, yellow solid. $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 6.65 - 6.64 (1H, t, J = 2.5 Hz), 2.41 (3H, s), 2.26 (3H, s),

1.45 - 1.43 (1H, m), 0.96 - 0.93 (2H, m), 0.81 - 0.79 (2H, m). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 201.0, 195.7, 148.8, 123.6, 114.5, 72.7, 30.8, 27.2, 9.8, 1.1. HRMS (ESI) m/z calcd for $C_{11}H_{13}O_2^+$ $(M+H)^+$ 177.0910, found 177.0913.

3-(4-((triisopropylsilyl)oxy)pent-2-yn-1-ylidene)pentane-2,4-dione **(1n)**. Isolated by column chromatography (hexanes/ethyl acetate = 30:1) in 1.15 g, 3.4 mmol, 41%, white solid. $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 6.71 (1H, s), 4.81 - 4.77 (1H, q, J = 6.5 Hz), 2.47 (3H, s), 2.31 (3H, s), 1.49 - 1.48 (3H, d, J = 6.5 Hz), 1.11 - 1.05 (21H, m). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 200.8, 195.5, 149.9, 121.7, 110.2, 78.8, 59.6, 30.9, 27.3, 25.0, 17.9, 12.1. HRMS (ESI) m/z calcd for $C_{19}H_{33}O_3Si^+$ $(M+H)^+$ 337.2194, found 337.2196.

3-(3-(trimethylsilyl)prop-2-yn-1-ylidene)pentane-2,4-dione **(1o)**.[12] Isolated by column chromatography (hexanes/ethyl acetate = 50:1) in 748.8 mg, 3.6 mmol, 80%, yellow solid. $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 6.65 (1H, s), 2.48 (3H, s), 2.29 (3H, s), 0.20 (9H, s). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 200.8, 195.4, 150.6, 121.4, 114.7, 99.7, 30.8, 27.4, -0.7. HRMS (ESI) m/z calcd for $C_{11}H_{17}O_2Si^+$ $(M+H)^+$ 209.0992, found 209.0994.

General Procedure for the Synthesis of 2. *Example for the Synthesis of* ***2a****.* Under nitrogen atmosphere, 0.2 mmol **1a** (38.5 mg, 1.0 equiv), 0.22 mmol *N*-iodosuccinimide (NIS) (49 mg, 1.1 equiv) and 2 mL dry DCE were added to a flamed dried Schlenk flask. The resulting mixture was stirred at room temperature for about 20 minutes and the progress of the reaction was monitored by TLC. Upon completion, the reaction mixture was concentrated under vacuum. The residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 50:1) to afford the desired product **2a** (44.3 mg) in 70% yield as a light yellow liquid.

(Z)-1-(5-(1-iodopent-1-en-1-yl)-2-methylfuran-3-yl)ethan-1-one **(2a)**. 44.3 mg, light yellow liquid,

70%. $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 6.68 (1H, s), 6.33 (1H, t, J = 7.0 Hz), 2.57 (3H, s), 2.40 (3H, s), 2.29 (2H, q, 7.2 Hz), 1.57 - 1.50 (2H, m), 0.99 (3H, t, J = 7.5 Hz). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 194.0, 158.6, 151.3, 136.3, 122.6, 111.1, 88.4, 38.5, 29.1, 21.7, 14.6, 13.8. HRMS (ESI) m/z calcd for $C_{12}H_{16}IO_2^+$ $(M+H)^+$ 319.0190, found 319.0188.

(Z)-1-(5-(4-chloro-1-iodobut-1-en-1-yl)-2-methylfuran-3-yl)ethan-1-one **(2b)**. Isolated by short column chromatography (hexanes/ethyl acetate = 30:1) in 40.0 mg, yellow solid, 59%. $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 6.74 (1H, s), 6.44 - 6.41 (1H, t, J = 6.8 Hz), 3.66 - 3.63 (2H, t, J = 6.8 Hz), 2.82 - 2.78 (2H, q, J = 6.7 Hz), 2.58 (3H, s), 2.41 (3H, s). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 193.8, 159.1, 150.7, 131.3, 122.7, 112.2, 90.9, 42.6, 39.6, 29.1, 14.7. HRMS (ESI) m/z calcd for $C_{11}H_{13}ClIO_2^+$ $(M+H)^+$ 338.9643, found 338.9645.

(Z)-1-(5-(4-(benzyloxy)-1-iodobut-1-en-1-yl)-2-methylfuran-3-yl)ethan-1-one **(2c)**. Isolated by short column chromatography (hexanes/ethyl acetate = 15:1) in 42.8 mg, yellow liquid, 54%. $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 7.36 - 7.33 (4H, m), 7.31 - 7.28 (1H, m), 6.71 (1H, s), 6.45 - 6.42 (1H, t, J = 7.0 Hz), 4.56 (2H, s), 3.63 - 3.61 (2H, t, J = 6.5 Hz), 2.65 - 2.61 (2H, q, J = 6.7 Hz), 2.57 (3H, s), 2.41 (3H, s). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 193.9, 158.8, 151.0, 138.1, 132.8, 128.4, 127.6, 127.6, 122.6, 111.4, 89.8, 72.9, 68.2, 37.2, 29.1, 14.6. HRMS (ESI) m/z calcd for $C_{18}H_{20}IO_3^+$ $(M+H)^+$ 411.0452, found 411.0453.

(Z)-1-(5-(4-((tert-butyldimethylsilyl)oxy)-1-iodobut-1-en-1-yl)-2-methylfuran-3-yl)ethan-1-one **(2d)**. Isolated by short column chromatography (hexanes/ethyl acetate = 50:1) in 48.1 mg, light yellow liquid, 54%. $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 6.69 (1H, s), 6.43 - 6.40 (1H, t, J = 7.0 Hz), 3.76 - 3.73 (2H, t, J = 6.8 Hz), 2.56 (3H, s), 2.55 - 2.51 (2H, q, J = 6.7 Hz), 2.40 (3H, s), 0.90 (9H, s), 0.07 (6H, s). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 193.9, 158.8, 151.1, 133.1, 122.6, 111.3,

89.5, 61.4, 40.1, 29.1, 25.9, 18.3, 14.6, -5.3. HRMS (ESI) m/z calcd for $C_{17}H_{28}IO_3Si^+$ $(M+H)^+$ 435.0847, found 435.0849.

(Z)-1-(5-(1-iodo-4-phenoxybut-1-en-1-yl)-2-methylfuran-3-yl)ethan-1-one **(2e)**. Isolated by short column chromatography (hexanes/ethyl acetate = 50:1) in 57.7 mg, white solid, 73%. $^1H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 7.31 - 7.28 (2H, t, J = 7.8 Hz), 6.98 - 6.92 (3H, m), 6.74 (1H, s), 6.53 - 6.50 (1H, t, J = 6.8 Hz), 4.11 - 4.09 (2H, t, J = 6.3 Hz), 2.83 - 2.79 (2H, q, J = 6.7 Hz), 2.58 (3H, s), 2.41 (3H, s). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 193.8, 158.9, 158.7, 151.0, 131.9, 129.5, 122.7, 120.9, 114.5, 111.7, 90.4, 65.9, 36.8, 29.1, 14.6. HRMS (ESI) m/z calcd for $C_{17}H_{18}IO_3^+$ $(M+H)^+$ 397.0295, found 397.0297.

(Z)-1-(5-(3-(benzyloxy)-1-iodoprop-1-en-1-yl)-2-methylfuran-3-yl)ethan-1-one **(2f)**. Isolated by short column chromatography (hexanes/ethyl acetate = 20:1) in 46.7 mg, light yellow liquid, 59%. $^1H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 7.37 – 7.29 (5H, m), 6.67 (1H, s), 6.64 - 6.62 (1H, t, J = 5.8 Hz), 4.58 (2H, s), 4.30 – 4.28 (2H, d, J = 5.5 Hz), 2.57 (3H, s), 2.41 (3H, s). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 193.7, 159.3, 150.5, 137.8, 132.2, 128.4, 127.8, 127.8, 122.8, 112.4, 88.3, 74.2, 72.7, 29.1, 14.6. HRMS (ESI) m/z calcd for $C_{17}H_{17}IO_3Na^+$ $(M+Na)^+$ 419.0115, found 419.0122.

(Z)-1-(5-(1-iodo-3-((triisopropylsilyl)oxy)prop-1-en-1-yl)-2-methylfuran-3-yl)ethan-1-one **(2g)**. Isolated by short column chromatography (hexanes/ethyl acetate = 50:1) in 46.7 mg, yellow liquid, 51%. $^1H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 6.74 (1H, s), 6.58 - 6.56 (1H, t, J = 5.5 Hz), 4.47 - 4.46 (2H, d, J = 5.0 Hz), 2.58 (3H, s), 2.41 (3H, s), 1.17 - 1.12 (3H, m), 1.10 - 1.08 (18H, d, J = 6.5 Hz). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 193.8, 159.2, 150.6, 135.8, 122.8, 111.8, 85.0, 68.7, 29.1, 18.0, 14.7, 12.0. HRMS (ESI) m/z calcd for $C_{19}H_{32}IO_3Si^+$ $(M+H)^+$ 463.1160, found

463.1155.

(Z)-1-(5-(1-iodo-3-phenylprop-1-en-1-yl)-2-methylfuran-3-yl)ethan-1-one **(2h)**. Isolated by short column chromatography (hexanes/ethyl acetate = 100:3) in 52.5 mg, yellow solid, 72%. $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 7.37 - 7.34 (2H, m), 7.30 - 7.27 (3H, m), 6.78 (1H, s), 6.53 (1H, t, J = 7.3 Hz), 3.71 (2H, d, J = 7.0 Hz), 2.58 (3H, s), 2.44 (3H, s). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 193.9, 158.9, 151.0, 138.5, 134.6, 128.7, 128.6, 126.6, 122.7, 111.9, 89.2, 42.4, 29.1, 14.6. HRMS (ESI) m/z calcd for $C_{16}H_{16}IO_2^+$ $(M+H)^+$ 367.0190, found 367.0185.

(Z)-(5-(1-iodopent-1-en-1-yl)-2-phenylfuran-3-yl)(phenyl)methanone **(2i)**. Isolated by short column chromatography (hexanes/ethyl acetate = 150:1) in 84.9 mg, light yellow solid, 96%. $^{1}H\{^{13}C\}$ NMR (500 MHz, CD_3OD) δ: 8.60 - 8.59 (2H, m), 8.45 - 8.39 (3H, m), 8.29 - 8.25 (2H, m), 8.18 - 8.15 (3H, m), 7.61 (1H, s), 7.44 (1H, t, J = 7.0 Hz), 3.11 - 3.07 (2H, m), 2.36 - 2.28 (2H, m), 1.75 (3H, t, J = 7.3 Hz). $^{13}C\{^{1}H\}$ NMR (125 MHz, CD_3OD) δ: 200.1, 163.5, 161.3, 147.2, 146.6, 142.8, 138.8, 138.7, 138.4, 138.1, 138.0, 136. 5, 131.5, 122.6, 98.2, 47.6, 30.6, 23.2. HRMS (ESI) m/z calcd for $C_{22}H_{20}IO_2^+$ $(M+H)^+$ 443.0503, found 443.0508.

dimethyl (Z)-(5-(1-iodopent-1-en-1-yl)-2-methylfuran-3-yl)phosphonate **(2j)**. Isolated by short column chromatography (hexanes/ethyl acetate = 3:1) in 45.4 mg, orange liquid, 59%. $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 6.51 (1H, d, J = 3.5 Hz), 6.33 - 6.30 (1H, t, J = 7.0 Hz), 3.74 (3H, s), 3.72 (3H, s), 2.50 (3H, d, J = 1.5 Hz), 2.30 - 2.25 (2H, q, J = 7.3 Hz), 1.56 - 1.48 (2H, m), 0.99 - 0.96 (3H, t, J = 7.3 Hz). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 160.9 - 160.7 (d, J = 26.1 Hz), 152.7 - 152.6 (d, J = 15.8 Hz), 136.5, 112.8 - 112.7 (d, J = 11.8 Hz), 108.2, 106.5, 88.1, 52.4 (d, J = 5.4 Hz), 38.5, 21.7, 13.8. HRMS (ESI) m/z calcd for $C_{12}H_{19}IO_4P^+$ $(M+H)^+$ 385.0060, found 385.0063.

ethyl (Z)-5-(1-iodopent-1-en-1-yl)-2-methylfuran-3-carboxylate **(2k)**. Isolated by short column

chromatography (hexanes/ethyl acetate = 100:1) in 36.2 mg, yellow solid, 56%. $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 6.71 (1H, s), 6.32 - 6.29 (1H, t, J = 7.0 Hz), 4.30 - 4.26 (2H, q, J = 7.0 Hz), 2.56 (3H, s), 2.30 - 2.26 (2H, q, J = 7.3 Hz), 1.57 - 1.49 (2H, m), 1.36 - 1.33 (3H, t, J = 7.3 Hz), 1.00 - 0.97 (3H, t, J = 7.3 Hz). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 163.8, 159.2, 151.3, 136.0, 115.0, 111.3, 88.6, 60.2, 38.5, 21.7, 14.4, 14.0, 13.8. HRMS (ESI) m/z calcd for $C_{13}H_{18}IO_3^+$ $(M+H)^+$ 349.0295, found 349.0294.

General Procedure for the Synthesis of Products 3. *Example for the Synthesis of **3a**.* To a 3 dram vial containing 2 mL of DMSO were added sequentially the ynenone **1a** (0.20 mmol) and *N*-iodosuccinimide (NIS) (0.20 mmol, 45.0 mg, 1.0 equiv). The resulting mixture was stirred at room temperature for about 3.5 hours, and the progress of the reaction was monitored by TLC. Upon completion, the reaction mixture was quenched by H_2O (8 mL), extracted by diethyl ether and dried by Na_2SO_4 and then concentrated under vacuum. The residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 20:1) to afford the desired product **3a** (38.5 mg) in 94% yield as a yellow solid.

1-(4-acetyl-5-methylfuran-2-yl)pentan-1-one **(3a)**.[13a] 38.5 mg, yellow solid, 94%. $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 7.35 (1H, s), 2.76 (2H, t, J = 7.5 Hz), 2.65 (3H, s), 2.43 (3H, s), 1.70 - 1.64 (2H, m), 1.41 - 1.33 (2H, m), 0.92 (3H, t, J = 7.3 Hz). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 193.3, 189.3, 162.1, 150.1, 123.1, 116.9, 38.0, 28.9, 26.3, 22.3, 14.8, 13.8. HRMS (ESI) m/z calcd for **3a** $C_{12}H_{17}O_3^+$ $(M+H)^+$ 209.1172, found 209.1169.

1-(4-acetyl-5-methylfuran-2-yl)-4-chlorobutan-1-one **(3b)**. Isolated by short column chromatography (hexanes/ethyl acetate = 15:1) in 44.2 mg, yellow liquid, 95%. $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 7.41 (1H, s), 3.65 - 3.63 (2H, t, J = 6.3 Hz), 3.02 - 2.99 (2H, t, J = 7.0 Hz),

2.67 (3H, s), 2.45 (3H, s), 2.22 - 2.17 (2H, m). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 193.2, 187.7, 162.4, 149.8, 123.2, 117.3, 44.3, 35.0, 29.0, 26.4, 14.8. HRMS (ESI) m/z calcd for $C_{11}H_{14}ClO_3^+$ $(M+H)^+$ 229.0626, found 229.0626.

1-(4-acetyl-5-methylfuran-2-yl)-4-(benzyloxy)butan-1-one **(3c)**. Isolated by short column chromatography (hexanes/ethyl acetate = 8:1) in 55.4 mg, light yellow solid, 93%. $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 7.36 (1H, s), 7.33 - 7.29 (4H, m), 7.28 - 7.25 (1H, m), 4.48 (2H, s), 3.56 - 3.64 (2H, t, J = 6.0 Hz), 2.93 - 2.90 (2H, t, J = 7.3 Hz), 2.66 (3H, s), 2.42 (3H, s), 2.06 - 2.01 (2H, m). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 193.3, 188.7, 162.2, 145.0, 138.3, 128.3, 127.5, 123.0, 117.2, 72.8, 69.1, 34.9, 28.9, 24.2, 14.8. HRMS (ESI) m/z calcd for $C_{18}H_{21}O_4^+$ $(M+H)^+$ 301.1434, found 301.1439.

1-(4-acetyl-5-methylfuran-2-yl)-4-((tert-butyldimethylsilyl)oxy)butan-1-one **(3d)**. Isolated by short column chromatography (hexanes/ethyl acetate = 12:1) in 59.0 mg, colorless liquid, 91%. $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 7.38 (1H, s), 3.69 - 3.67 (2H, t, J = 6.0 Hz), 2.90 - 2.87 (2H, t, J = 7.5 Hz), 2.67 (3H, s), 2.45 (3H, s), 1.96 - 1.90 (2H, m), 0.88 (9H, s), 0.04 (6H, s). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 193.4, 189.1, 162.2, 150.1, 123.1, 117.1, 62.0, 34.7, 29.0, 27.3, 25.9, 18.3, 14.8, -5.4. HRMS (ESI) m/z calcd for $C_{17}H_{29}O_4Si^+$ $(M+H)^+$ 325.1830, found 325.1831.

1-(4-acetyl-5-methylfuran-2-yl)-4-phenoxybutan-1-one **(3e)**. Isolated by short column chromatography (hexanes/ethyl acetate = 20:1) in 56.1 mg, white solid, 98%. $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 7.39 (1H, s), 7.28 - 7.24 (2H, t, J = 8.0 Hz), 6.94 - 6.91 (1H, t, J = 7.8 Hz), 6.88 - 6.87 (2H, d, J = 7.5 Hz), 4.05 - 4.02 (2H, t, J = 5.3 Hz), 3.08 - 3.01 (2H, t, J = 7.5 Hz), 2.65 (3H, s), 2.41 (3H, s), 2.23 - 2.19 (2H, m). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 193.3, 188.4, 162.3, 158.7, 149.9, 129.4, 123.0, 120.7, 117.2, 114.3, 66.4, 34.7, 28.9, 23.7, 14.8. HRMS (ESI)

m/z calcd for $C_{17}H_{19}O_4^+$ $(M+H)^+$ 287.1278, found 287.1280.

1-(4-acetyl-5-methylfuran-2-yl)-3-(benzyloxy)propan-1-one **(3f)**. Isolated by short column chromatography (hexanes/ethyl acetate = 8:1) in 52.1 mg, light yellow solid, 91%. $^1H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 7.37 – 7.29 (5H, m), 6.67 (1H, s), 6.64 - 6.62 (1H, t, J = 5.8 Hz), 4.58 (2H, s), 4.30 – 4.28 (2H, d, J = 5.5 Hz), 2.57 (3H, s), 2.41 (3H, s). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 193.7, 159.3, 150.5, 137.8, 132.2, 128.4, 127.8, 127.8, 122.8, 112.4, 88.3, 74.2, 72.7, 29.1, 14.6. HRMS (ESI) m/z calcd for $C_{17}H_{18}O_4Na^+$ $(M+Na)^+$ 309.1097, found 309.1108.

1-(4-acetyl-5-methylfuran-2-yl)-3-((triisopropylsilyl)oxy)propan-1-one **(3g)**. Isolated by short column chromatography (hexanes/ethyl acetate = 15:1) in 67.1 mg, yellow solid, 95%. $^1H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 7.40 (1H, s), 4.10 - 4.08 (2H, t, J = 6.3 Hz), 3.01 - 2.99 (2H, t, J = 6.5 Hz), 2.66 (3H, s), 2.44 (3H, s), 1.08 - 1.03 (3H, m), 1.01 - 1.00 (18H, d, J = 6.0 Hz). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 193.3, 187.8, 162.5, 150.5, 123.1, 117.7, 59.5, 41.8, 29.0, 17.9, 14.8, 11.9. HRMS (ESI) m/z calcd for $C_{19}H_{33}O_4Si^+$ $(M+H)^+$ 353.2143, found 353.2146.

1-(4-acetyl-5-methylfuran-2-yl)-3-phenylpropan-1-one **(3h)**. Isolated by short column chromatography (hexanes/ethyl acetate = 12:1) in 48.8 mg, yellow solid, 96%. $^1H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 7.34 (1H, s), 7.30 - 7.27 (2H, m), 7.24 - 7.18 (3H, m), 3.12 (2H, t, J = 7.8 Hz), 3.04 (2H, t, J = 7.8 Hz), 2.65 (3H, s), 2.43 (3H, s). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 193.3, 188.0, 162.3, 149.9, 140.7, 128.5, 128.4, 126.2, 123.1, 117.2, 40.0, 29.9, 29.0, 14.8. HRMS (ESI) m/z calcd for $C_{16}H_{17}O_3^+$ $(M+H)^+$ 257.1172, found 257.1177.

1-(4-benzoyl-5-phenylfuran-2-yl)pentan-1-one **(3i)**. Isolated by short column chromatography (hexanes/ethyl acetate = 80:1) in 62.0 mg, yellow liquid, 93%. $^1H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 7.84 - 7.83 (2H, m), 7.80 - 7.78 (2H, m), 7.55 (1H, t, J = 7.3 Hz), 7.43 - 7.33 (6H, m), 2.89 (2H,

t, J = 7.3 Hz), 1.79 - 1.73 (2H, m), 1.47 - 1.40 (2H, m), 0.97 (3H, t, J = 7.3 Hz). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 190.8, 189. 6, 158.1, 150.4, 137.3, 133.4, 130.3, 129.7, 128.6, 128.6, 128.5, 128.0, 122.5, 119.6, 38.4, 26.4, 22.4, 13.9. HRMS (ESI) m/z calcd for $C_{22}H_{21}O_3^+$ $(M+H)^+$ 333.1485, found 333.1489.

dimethyl (2-methyl-5-pentanoylfuran-3-yl)phosphonate **(3j)**. Isolated by short column chromatography (hexanes/ethyl acetate = 1:1) in 52.9 mg, yellow liquid, 96%. $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 7.21 (1H, d, J = 3.5 Hz), 3.77 (3H, s), 3.75 (3H, s), 2.77 - 2.74 (2H, t, J = 7.8 Hz), 2.60 - 2.59 (3H, d, J = 2.0 Hz), 1.71 - 1.65 (2H, m), 1.41 - 1.34 (2H, m), 0.94 - 0.91 (3H, t, J = 7.5 Hz). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 189.0, 164.3 - 164.1 (d, J = 26.1 Hz), 151.3, 119.8 - 119.7 (d, J = 11.1 Hz), 109.9, 108.2, 52.7 - 52.6 (d, J = 5.5 Hz), 38.1, 26.4, 22.4, 14.0 - 13.8 (d, J = 25.0 Hz). HRMS (ESI) m/z calcd for $C_{12}H_{20}O_5P^+$ $(M+H)^+$ 275.1043, found 275.1044.

ethyl 2-methyl-5-pentanoylfuran-3-carboxylate **(3k)**.[13a] Isolated by short column chromatography (hexanes/ethyl acetate = 30:1) in 48.3 mg, yellow liquid, 96%. $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 7.38 (1H, s), 4.32 - 4.28 (2H, q, J = 7.0 Hz), 2.77 - 2.74 (2H, t, J = 7.5 Hz), 2.65 (3H, s), 1.71 - 1.65 (2H, m), 1.41 - 1.34 (5H, m), 0.94 - 0.91 (3H, t, J = 7.3 Hz); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 189.1, 162.9, 150.0, 118.0, 115.8, 60.6, 38.0, 26.5, 22.4, 14.3, 14.2, 13.8.

1-(5-phenyl-4-(phenylsulfonyl)furan-2-yl)pentan-1-one **(3l)**. Isolated by short column chromatography (hexanes/ethyl acetate = 15:1) in 47.9 mg, light yellow solid, 65%. $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 7.94 - 7.93 (2H, d, J = 7.5 Hz), 7.79 - 7.78 (2H, d, J = 7.5 Hz), 7.55 - 7.40 (7H, m), 2.85 - 2.81 (2H, t, J = 7.3 Hz), 1.74 - 1.68 (2H, m), 1.44 - 1.36 (2H, m), 0.96 - 0.93 (3H, t, J = 7.5 Hz). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 189.0, 157.2, 150.0, 141.0, 133.7, 131.2, 129.2, 129.1, 128.5, 127.2, 126.2, 118.3, 38.3, 26.1, 22.3, 13.8. HRMS (ESI) m/z calcd for

$C_{21}H_{21}O_4S^+$ $(M+H)^+$ 369.1155, found 369.1158.

1-(5-(cyclopropanecarbonyl)-2-methylfuran-3-yl)ethan-1-one **(3m)**. Isolated by short column chromatography (hexanes/ethyl acetate = 20:1) in 34.3 mg, white solid, 89%. $^1H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 7.42 (1H, s), 2.68 (3H, s), 2.55 - 2.51 (1H, m), 2.45 (3H, s), 1.24 - 1.22 (2H, m), 1.04 - 1.02 (2H, m). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 193.4, 188.9, 162.1, 150.6, 123.1, 116.6, 29.0, 17.2, 14.8, 11.5. HRMS (ESI) m/z calcd for $C_{11}H_{13}O_3^+$ $(M+H)^+$ 193.0859, found 193.0857.

1-(4-acetyl-5-methylfuran-2-yl)-2-((triisopropylsilyl)oxy)propan-1-one **(3n)**. Isolated by short column chromatography (hexanes/ethyl acetate = 20:1) in 53.5 mg, yellow solid, 76%. $^1H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 7.75 (1H, s), 4.72 - 4.68 (1H, q, J = 6.7 Hz), 2.68 (3H, s), 2.43 (3H, s), 1.51 - 1.50 (3H, d, J = 6.5 Hz), 1.14 - 1.08 (3H, m), 1.06 - 1.03 (18H, t, J = 6.7 Hz). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 193.3, 190.5, 162.9, 147.0, 122.8, 120.6, 74.5, 28.9, 22.9, 17.9, 14.8, 12.1. HRMS (ESI) m/z calcd for $C_{19}H_{33}O_4Si^+$ $(M+H)^+$ 353.2143, found 353.2145.

1-(2-methyl-5-((trimethylsilyl)carbonyl)furan-3-yl)ethan-1-one **(3o)**. Isolated by short column chromatography (hexanes/ethyl acetate = 40:1) in 43.3 mg, yellow solid, 97%. $^1H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 7.24 (1H, s), 2.67 (3H, s), 2.45 (3H, s), 0.34 (9H, s). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 221.1, 193.5, 161.8, 155.3, 123.0, 115.0, 29.0, 14.8, -2.4. HRMS (ESI) m/z calcd for $C_{11}H_{17}O_3Si^+$ $(M+H)^+$ 225.0942, found 225.0940.

The data of diphenyl sulfide **(6a).** Isolated by short column chromatography (hexanes/ethyl acetate = 80:1) in 8.0 mg, light yellow liquid, 21%. $^1H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ: 7.36 – 7.34 (4H, m), 7.32 – 7.29 (4H, m), 7.27 – 7.23 (2H, m).

The ynenone 1i was carried out on a larger scale to desire the product *Z*-iodovinylfuran 2i.

Under nitrogen atmosphere, 4.4 mmol *N*-iodosuccinimide (NIS) (990 mg, 1.1 equiv) and 20 mL dry DCE was added to a flamed dried Round-bottomed flask (50 mL), then 4.0 mmol **1i** (1.265 g, 1.0 equiv) was added into the reaction. The resulting mixture was stirred at room temperature for about 20 minutes and the progress of the reaction was monitored by TLC. Upon completion, the reaction mixture was concentrated under vacuum. The residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 50:1) to afford the desired product *Z*-iodovinylfuran **2i** (1.37 g) in 77% yield as a light yellow solid.

The ynenone 1i was carried out on a larger scale to desire the product 2-acyl furan 3i.

The ynenone **1i** (4.0 mmol, 1.265 g, 1.0 equiv) and *N*-iodosuccinimide (NIS) (4.0 mmol, 900 mg, 1.0 equiv) were added to a 50 mL Round-bottomed flask with 20 mL of DMSO was added. The resulting mixture was stirred at room temperature open to the air overnight, and the progress of the reaction was monitored by TLC. Upon completion, the reaction mixture was quenched by H_2O (80 mL), extracted by diethyl ether and dried by Na_2SO_4 and then concentrated under vacuum. The residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 20:1) to afford the desired product 2-acyl furan **3i** (1.22 g) in 92% yield as a yellow liquid.

Preparation of products 4

ethyl (2E,4E)-4-(4-benzoyl-5-phenylfuran-2-yl)octa-2,4-dienoate **(4a).** To a solution of **2i** (119.4 mg, 0.27 mmol, 1.0 equiv) , $Pd(PPh_3)_2Cl_2$ (5.6 mg, 0.0081 mmol, 3 mol %), Et_3N (32.8 mg, 0.32 mmol, 1.2 equiv) and ethyl acrylate (75.7 mg, 0.76 mmol, 2.8 equiv) in DMF (5 mL). The reaction mixture was heated at 80℃ for 2 h with oil bath. After the completion of reaction quenched by aqueous NH_4Cl (10 mL) and reaction mixture was stirred for 30 min. The mixture was extracted with EtOAc (2 x 5 mL) organic layer was washed with H_2O (5 mL), brine (5 mL), dried over

Na_2SO_4 and concentrated in vacuo. The crude was purified by column chromatography on silica gel (hexanes/ethyl acetate = 80:1) and the product was isolated in 70.4 mg, yellow liquid, yield = 85%. $^1H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ : 7.86 - 7.84 (2H, d, J = 8.0 Hz), 7.70 - 7.68 (3H, m), 7.53 - 7.49 (1H, t, J = 7.5 Hz), 7.40 - 7.37 (2H, t, J = 7.3 Hz), 7.31 - 7.29 (3H, m), 6.62 (1H, s), 6.48 - 6.45 (1H, t, J = 7.8 Hz), 6.29 - 6.26 (1H, d, J = 16 Hz), 4.27 - 4.21 (2H, m), 2.45 - 2.40 (2H, q, J = 7.7 Hz), 1.60 - 1.54 (2H, m), 1.33 - 1.30 (3H, t, J = 7.3 Hz), 1.02 - 0.99 (3H, t, J = 7.0 Hz). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ : 191.6, 167.0, 154.7, 151.3, 139.4, 137.9, 137.8, 132.9, 129.7, 129.6, 129.0, 128.4, 128.3, 128.3, 127.5, 126.4, 122.2, 110.8, 60.6, 30.7, 22.6, 14.3, 13.8. HRMS (ESI) m/z calcd for $C_{27}H_{27}O_4^+$ $(M+H)^+$ 415.1904, found 415.1907.

(E)-phenyl(2-phenyl-5-(1-phenylpent-1-en-1-yl)furan-3-yl)methanone **(4b)**. To a solution of **2i** (119.4 mg, 0.2 mmol, 1.0 equiv), K_2CO_4 (69.1 mg, 0.5 mmol 2.5 equiv), $Pd(PPh_3)_2Cl_2$ (1.4 mg, 0.002 mmol, 1 mol %) and phenylboronic acid (25.6 mg, 0.21 mmol, 1.05 equiv) in toluene (5 mL) and water (1 mL) was degassed with N_2 for 20 min. The reaction mixture was heated at 80℃ for 6 h with oil bath. After the completion of reaction, DMF was removed under vacuum, and the residue was dissolved in EtOAc (5 mL), filtered through celite and concentrated in vacuo. The crude was purified by column chromatography on silica gel (hexanes/ethyl acetate = 100:1) and the product was isolated in 70.6 mg, yellow liquid, yield = 90%. $^1H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ : 7.81 - 7.79 (2H, d, J = 7.5 Hz), 7.72 - 7.71 (2H, d, J = 7.0 Hz), 7.48 - 7.45 (1H, t, J = 7.3 Hz), 7.42 - 7.30 (10H, m), 6.53 – 6.50 (1H, t, J = 7.5 Hz), 6.05 (1H, s), 2.12 – 2.08 (2H, q, J = 7.3 Hz), 1.54 – 1.46 (2H, m), 0.94 – 0.91 (3H, t, J = 7.3 Hz). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ : 191.8, 154.5, 154.1, 137.9, 136.8, 132.7, 131.1, 129.8, 129.7, 129.1, 128.8, 128.3, 128.3, 128.2, 127.5, 127.4, 127.2, 122.5, 110.7, 31.0, 22.9, 13.9. HRMS (ESI) m/z calcd for $C_{28}H_{25}O_2^+$ $(M+H)^+$ 393.1849,

found 393.1852. *Z* : *E* = 7:1.

(E)-phenyl(2-phenyl-5-(1-phenylhept-3-en-1-yn-3-yl)furan-3-yl)methanone **(4c).** To a solution of **2i** (119.4 mg, 0.27 mmol, 1.0 equiv) in trethylamine (3 mL) was added to a mixture of $Pd(PPh_3)_2Cl_2$ (1.9 mg, 0.0027 mmol, 1 mol %) and copper(I)iodide (1.0 mg, 0.0054 mmol, 2 mol %) in a flame dried flask. The mixture was degassed with N_2 for 15 min. Phenylacetylene (27.5 mg, 0.27 mmol, 1.0 equiv) was added, and the mixture was stirred at room temperature overnight. After the completion of reaction, the mixture was diluted with Water (3 mL) and then the mixture was extracted with EtOAc (10 mL x 2). The combined organic layers were dried with anhydrous Na_2SO_4, filtered through celite, and concentrated in vacuo. The crude was purified by column chromatography on silica gel (hexanes/ethyl acetate = 30:1) and the product was isolated in 72.4 mg, red liquid, yield = 87%. $^1H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ : 7.90 - 7.88 (2H, d, J = 7.5 Hz), 7.74 - 7.72 (2H, d, J = 6.0 Hz), 7.52 - 7.51 (3H, d, J = 5.0 Hz), 7.41 - 7.38 (2H, t, J = 7.3 Hz), 7.35 - 7.31 (6H, m), 6.77 (1H, s), 6.74 - 6.71 (1H, t, J = 7.8 Hz), 2.60 - 2.56 (2H, q, J = 7.2 Hz), 1.65 - 1.61 (2H, m), 1.07 - 1.04 (3H, t, J = 7.3 Hz). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ : 191.7, 154.8, 151.1, 137.9, 137.3, 132.9, 131.6, 129.8, 129.7, 129.0, 128.5, 128.4, 128.3, 128.3, 127.4, 122.9, 122.5, 113.8, 110.4, 94.1, 83.7, 32.8, 22.4, 13.9. HRMS (ESI) m/z calcd for $C_{30}H_{25}O_2^+$ $(M+H)^+$ 417.1849, found 417.1854.

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Notes

The authors declare no competing financial interest.

■ ASSOCIATED CONTENT

Supporting Information: concise list of types of data or files found in the SI.

Reaction conditions optimization, the data of X-ray structure of **2h**, the spectra of HRMS (ESI) m/z calcd for **3a** and **3a'** and copies of characterization data ($^{1}H\{^{13}C\}$, $^{13}C\{^{1}H\}$ NMR) (PDF)

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(22) We have carried out **1a** with NBS (1.1 equiv) as electrophilic source, the desired product **5a**

was obtained in 70% yield after 15 minutes. However, the desired product was unstable in the reaction system.

(23) Because the dimethyl sulfide is difficult to detect, diphenyl sulfoxide (2.0 equiv) instead of DMSO served as oxidant was used in the reaction, and 21% yield of diphenyl sulfide was obtained after 1 h. So, we think that there is the formation of dimethylsulphide during the reaction