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Synthesis of substituted 3-furanoates from MBH-acetates of acetylenic aldehydes *via* tandem isomerization–deacetylation–cycloisomerization: access to Elliott's alcohol†‡

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A new method for the synthesis of 5-substituted furan-3-carboxylates from Morita–Baylis–Hillman acetates of acetylenic aldehydes is reported. The process involves palladium-catalyzed isomerization followed by base-promoted deacetylation and cycloisomerization reactions. The utility of this chemistry is further demonstrated by the synthesis of Elliott's alcohol, a key intermediate of the pyrethroid resmethrins.

Introduction

Furans have received substantial interest as important targets in organic synthesis because of their frequent use in various fields such as pharmaceuticals, agrochemicals, functional materials, cosmetics, *etc*.[1] In particular, 5-substituted furan-3-carboxylate has been recognized as one of the important frameworks due to its occurrence in many bio-active natural products.[2] For example, flufuran (**A**),[2a] tournefolin C (**B**)[2b] and angelone (**C**)[2c] pukalide class of molecules (**D**)[2d] are some of the representative natural products possessing the furan-3-carboxylate skeleton embedded in their structures (Fig. 1). Further, 5-substituted 3-furanoates were also found to be valuable intermediates for the synthesis of bio-active molecules[3] including pesticides such as pyrethroid resmethrin,[4] a synthetic insecticide (**E**, Fig. 1). Although numerous methods have been developed towards diversely functionalized furans,[5] the procedures available for the synthesis of 5-substituted furan-3-carboxylate derivatives are very limited.[6,7] Usually the title compounds are achieved through the functionalization at the C5-position of furan-3-carboxylate.[6] Alternative strategies for their construction from acyclic precursors are (i) the reaction of acrylates with aldehydes in the presence of the Pd-$(OAc)_2$/HPMoV/$CeCl_3$/O_2 system, (ii) Au/Ag-catalyzed annulation of enynyl-aryl ethers, (iii) condensation of the ethylene acetals of 5-substituted levulic esters with ethyl formate followed by acid-mediated cyclization and a few other examples.[7] Nonetheless, the development of novel approaches for the synthesis of 5-substituted 3-furanoates from readily accessible starting materials remains highly desirable.

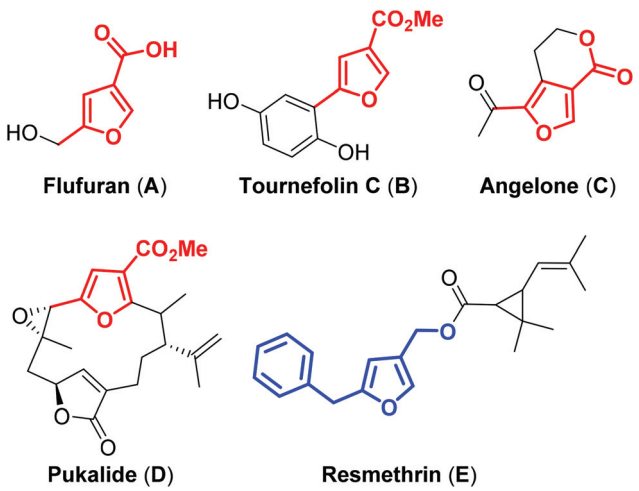

Fig. 1 Structures of selected natural products having substituted 3-furanoate and resmethrin.

Morita–Baylis–Hillman (MBH) adducts and their derivatives have been recognized as handy synthons in the preparation of valuable synthetic products including carbocycles and heterocycles *via* various transformations.[8] These multifunctional adducts were easily accessible through the Morita–Baylis–Hillman reaction,[9] one of the atom-economic carbon–carbon bond forming reactions. Recently, we have explored the utility of MBH-acetates of acetylenic aldehydes in the synthesis of pyrroles, cyclopentenes and thiophenes.[10] In continuation, herein we describe a novel one-pot access to 5-substituted 3-furanoates from MBH-acetates of acetylenic aldehydes *via* a tandem isomerization–deacetylation–cycloisomerization reaction sequence. To the best of our knowledge, to date there

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† Dedicated to Dr. S. Chandrasekhar, CSIR-IICT, on his 50th birthday.

‡ Electronic supplementary information (ESI) available: Copies of ^{1}H NMR and ^{13}C NMR spectra of all the new compounds. See DOI: 10.1039/c3ob42396d

has been no report on the one-pot synthesis of substituted furans starting from MBH adducts.[11]

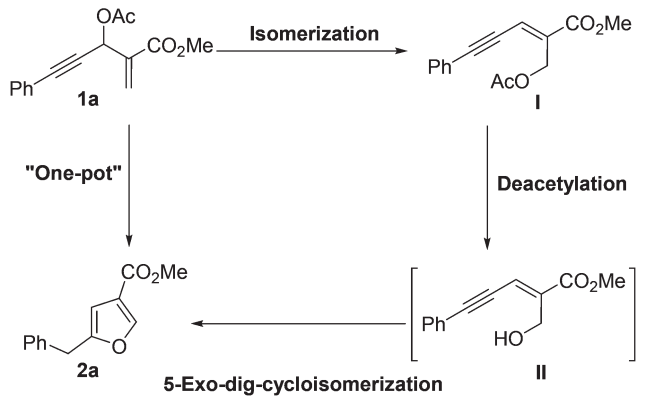
Results and discussion

The optimization of reaction conditions was performed using MBH acetate **1a**, derived from the reaction of 3-phenylpropiolaldehyde with methyl acrylate, as a model substrate (Table 1). Based on our previous study,[10d] we first chose KOAc in acetonitrile as the reaction conditions to get allylic acetate **I** through allylic substitution and to our disappointment the formation of **I** was not observed (entry 1, Table 1). This may be due to the less nucleophilic nature of acetate (OAc), when compared to thioacetate (SAc). Next, we decided to obtain the intermediate **I** through isomerization of **1a**, which was tested using different reaction conditions. We were pleased to find that the allyl acetate **I** was isolated in 98% yield from **1a** after stirring at room temperature in acetonitrile for 12 h in the presence of 10 mol% of $Pd(Ph_3P)_4$ (entry 2, Table 1).[12] The other conditions tested, such as NH_4OAc in methanol, DABCO in tetrahydrofuran and TMSOTf in dichloromethane, were not effective to offer **I** in good yield (entries 3 to 5, Table 1). Having allyl acetate **I** in hand, next we evaluated its conversion to (*Z*)-2-en-4-yn-1-ol **II** through deacetylation using K_2CO_3 in methanol at room temperature. To our delight, directly the formation of 5-benzyl furan-3-carboxylate (**2a**) was observed in 97% yield through deacetylation followed by intramolecular 5-*exo-dig*-oxacycloisomerization and no traces of intermediate **II** were isolated (entry 6, Table 1). This was confirmed by the isolation of **II** from the reaction of **I** with K_2CO_3 at 0 °C for 5 min in 81% yield (entry 7, Table 1) and after characterization of **II**, it was subjected to the same base conditions at room temperature to get **2a**. It is important to mention that previously (*Z*)-2-en-4-yn-1-ols were prepared and used in the synthesis of alkyl/aryl-substituted furans under various reaction conditions.[13] In contrast, the present method offers a direct access to 5-substituted 3-furanoates for the first time, which is an added advance to the *Z*-enynol chemistry. Having defined the reaction conditions for the synthesis of allyl acetate **I** from MBH-acetate **1a** and its conversion to furan **2a**, we were fascinated to develop a one-pot reaction for the conversion of **1a** to **2a**.

Consequently, MBH-acetate **1a** was treated with 10 mol% of $Pd(Ph_3P)_4$ in CH_3CN for 12 h, followed by the addition of K_2CO_3 in MeOH at room temperature, resulting in the clean formation of disubstituted furan **2a** in 94% yield (entry 8, Table 1), which confirmed the success of optimal conditions for one-pot reaction.

To broaden the scope of this method, we carried out the reaction with diverse MBH-acetates of acetylenic aldehydes under optimized conditions (Table 2). Treatment of MBH-acetates **1b** and **1c**, having 4-methylphenyl and 1-naphthyl groups on alkyne, with 10 mol% of $Pd(PPh_3P)_4$ followed by K_2CO_3 in MeOH provided the corresponding 5-substituted 3-furanoates **2b** and **2c** in 85% and 80% yields, respectively (entries 1 and 2,

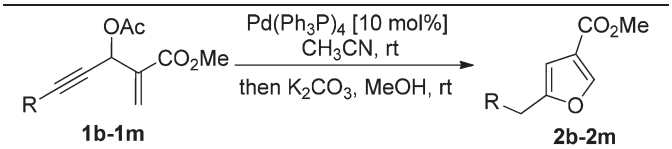
Table 1 Optimization of reaction conditions



Entry	Isomerization (step 1; **1a** to **I**)	Deacetylation/ cyclization (step 2; **I** to **2a** or **II**)	Product	Yield[a]
1	KOAc, CH_3CN, rt, 24 h	—	**I**	—
2	**$Pd(Ph_3P)_4$, CH_3CN, rt, 12 h**	—	**I**	**98**
3	NH_4OAc, MeOH, rt, 6 h	—	**I**	45
4	DABCO, THF, rt, 12 h	—	**I**	63
5	TMSOTf, CH_2Cl_2, 0 °C-rt	—	**I**	27
6[b]	—	**K_2CO_3, MeOH, rt, 4 h**	**2a**	**97**
7[b]	—	K_2CO_3, MeOH, 0 °C, 5 min	**II**	81
8[c]	**$Pd(Ph_3P)_4$, CH_3CN, rt, 12 h**	**K_2CO_3, MeOH, rt, 4 h**	**2a**	**94**

[a] Isolated yields. [b] Starting material for the reaction is **I**. [c] One-pot reaction.

Table 2 Synthesis of 5-substituted 3-furanoates[a]



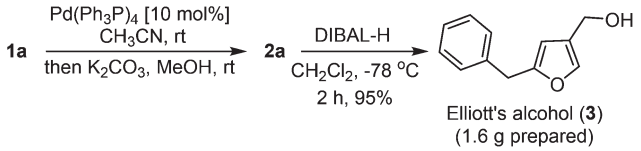
Entry	MBH acetate (**1**)	Time (h)	Furan (**2**)[b]	Yield[c] (%)
1	R = 4-Me-C_6H_4, **1b**	14	**2b**	85
2	R = 1-Napthyl, **1c**	14	**2c**	80
3	R = 4-MeO-C_6H_4, **1d**	14	**2d**	88
4	R = 2-MeO-C_6H_4, **1e**	15	**2e**	81
5	R = 4-Cl-C_6H_4, **1f**	16	**2f**	86
6	R = 4-CN-C_6H_4, **1g**	14	**2g**	84
7	R = 4-$COCH_3$-C_6H_4, **1h**	14	**2h**	88
8	R = 2-Thiophenyl, **1i**	14	**2i**	89
9	R = PhCH=CH, **1j**	15	**2j**	72
10	R = nC_3H_7, **1k**	15	**2k**	64
11	R = nC_5H_{11}, **1l**	14	**2l**	68
12	R = nC_6H_{13}, **1m**	15	**2m**	66

[a] Reaction conditions: MBH acetate 1 (0.38 mmol), $Pd(Ph_3P_4)$ (10 mol%), CH_3CN (3 mL), 12 h, MeOH (3 mL), K_2CO_3 (1.16 mmol), rt. [b] All the products were characterized by ^1H, ^{13}C NMR, IR and MS spectra. [c] Isolated yields.

Table 2). The reaction was found to tolerate the electron-donating groups at various positions around the phenyl group attached to the alkyne of MBH-acetates **1d** and **1e** in affording the 3-furanoates **2d** and **2e** in 88% and 81% yields, respectively (entries 3 and 4, Table 2). Similarly, MBH-acetates bearing aryl substitution with electron-deficient groups such as 4-chloro (**1f**), 4-cyano (**1g**), 4-acetyl (**1h**) were also successfully employed in the tandem reaction to give the 5-substituted 3-furanoates **2f** to **2h** in good yield (entries 5 to 7, Table 2). The reaction of MBH-acetate **1i** containing 2-thiophenyl on alkyne also afforded the furan-3-carboxylate **2i** in 89% yield (entry 8, Table 2). The developed strategy was found to be effective for MBH acetates of acetylenic aldehydes having alkenyl group (phenyl vinyl) **1j** as well as alkyl chain such as *n*-propyl (**1k**), *n*-pentyl (**1l**) and *n*-hexyl (**1m**) substitution, to give the respective substituted 3-furanoates **2j** to **2m**, albeit in moderate yield (entries 9–12, Table 2).

Additionally, MBH acetate **1n**, obtained from the reaction of 3-phenylpropiolaldehyde with *t*-butyl acrylate, was found to be a good substrate in providing 5-benzyl *t*-butyl furan-3-carboxylate in 90% yield. Interestingly, MBH acetate **1o**, derived from methyl vinyl ketone, underwent tandem isomerization–deacetylation–cycloisomerization reactions to give the corresponding aceto-furanone **2o** in 83% yield. Similarly, the present protocol was also extended to MBH acetate **1p**, prepared from cyclohexenone, which successfully furnished the tri-substituted furanone **2p** in 78% yield (Table 3).

Encouraged by the above success, we turned our attention to show the applicability of the obtained 3-furanoates having ester as a handle for further elaboration towards the useful derivatives. In this direction, methyl 5-benzylfuran-3-carboxylate **2a**, achieved from MBH acetate **1a**, was converted to (5-benzylfuran-3-yl)methanol (**3**), Elliott's alcohol,[14] by reduction of the ester using DIBAL-H in dichloromethane (Scheme 1). The resulting Elliott's alcohol (**3**) is a key intermediate for the manufacture of resmethrins, pyrethroid insecticides (Fig. 1). The literature procedures for the preparation of **3** are lengthy and have some drawbacks such as generation of chlorinated by-products and use of expensive starting materials such as isobutene diacetate.[15] In 2008, Righi and co-workers have reported an alternate four-step strategy to Elliott's alcohol starting from triethyl phosphonoacetate involving a tandem olefination/Baylis–Hillman sequence.[16] Herein, we presented a novel approach for the synthesis of **3** using the currently developed methodology in two steps from readily accessible MBH-acetate **1a** (Scheme 1), which was carried out in gram-scale.



Scheme 1 Synthesis of Elliott's alcohol (**3**).

Conclusions

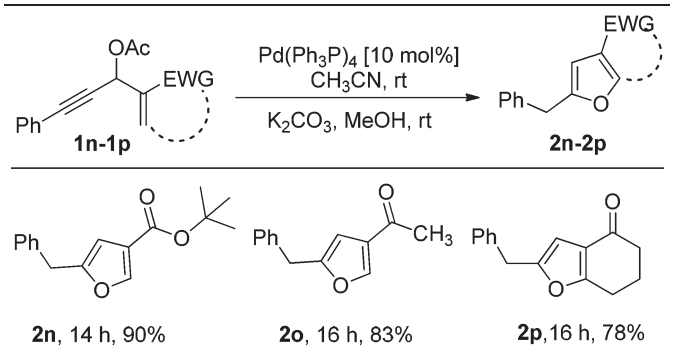
In summary, we have developed a novel approach for the construction of 5-substituted furan-3-carboxylates from readily accessible Morita–Baylis–Hillman acetates of acetylenic aldehydes through tandem Pd-catalyzed isomerization followed by base-promoted deacetylative 5-*exo*-*dig*-cycloisomerization reactions. The method was demonstrated by the synthesis of various 3-furanoates and also extended to furanones. Further, the developed methodology provided an alternative access to Elliott's alcohol, a key subunit of pyrethroid insecticide resmethrin. We believe that the present method may have potential for the synthesis of a wide range of bioactive compounds bearing such furan skeletons.

Experimental

General

Reactions were monitored by thin-layer chromatography carried out on silica plates using UV-light and anisaldehyde or potassium permanganate or β-naphthol for visualization. Column chromatography was performed on silica gel (60–120 mesh) using hexanes and ethyl acetate as eluents. Evaporation of solvents was conducted under reduced pressure at temperatures less than 45 °C. FTIR spectra were recorded on KBr thin film or neat. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ solvent on a 300 MHz and 500 MHz NMR spectrometer. Chemical shifts δ and coupling constants J are given in ppm (parts per million) and Hz (hertz) respectively. Chemical shifts are reported relative to the residual solvent as an internal standard for ^{1}H and ^{13}C ($CDCl_3$: δ 7.26 ppm for ^{1}H and 77.0 ppm for ^{13}C). Mass spectra were obtained on a VG 70–70H or LC/MSD trapSL spectrometer operating at 70 eV using the direct inlet system.

Table 3 Synthesis of substituted furans



Reaction conditions: MBH acetate **1** (0.38 mmol), $Pd(Ph_3P)_4$ (10 mol%), CH_3CN (3 mL), rt, 12 h, MeOH (3 mL), K_2CO_3 (1.16 mmol), rt.

Morita–Baylis–Hillman acetates **1a–1p** have been prepared using the literature procedure[10,17] and known compounds data compared with the reported data. Characterization data for new compounds (**1e**, **g**, **h**, **j**, and **1l**) are given below.

Methyl 3-acetoxy-5-(2-methoxyphenyl)-2-methylenepent-4-ynoate (1e). 0.93 g, 78%; colourless liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42 (dd, J = 7.4, 1.6 Hz, 1H), 7.33–7.29 (m, 1H), 6.92–6.83 (m, 2H), 6.58 (s, 1H), 6.54 (s, 1H), 6.51 (s, 1H), 3.85 (s, 3H), 3.79 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.0, 164.8, 160.3, 136.4, 133.5, 130.2, 130.1, 129.4, 120.1, 110.5, 87.4, 83.7, 62.1, 55.4, 51.9, 20.6; IR (KBr): ν_{max} 2953, 2840, 2232, 1745, 1596, 1493, 1437, 1259, 1148, 1024, 978, 812, 756 cm^{-1}; MS (ESI): m/z 311 $(M + Na)^+$; HRMS (ESI): m/z calcd for $C_{16}H_{16}O_5Na$ $(M + Na)^+$: 311.0895, found: 311.0884.

Methyl 3-acetoxy-5-(4-cyanophenyl)-2-methylenepent-4-ynoate (1g). 0.99 g, 86%; white solid; M.P.: 78–80 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66 (d, J = 6.7 Hz, 2H), 7.60 (d, J = 6.7 Hz, 2H), 7.55 (s, 1H), 7.07 (s, 1H), 6.53 (s, 1H), 3.85 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.4, 165.3, 137.5, 132.3, 132.0, 129.2, 126.4, 118.0, 112.6, 101.1, 87.7, 59.5, 52.4, 20.7; IR (KBr): ν_{max} 2953, 2228, 2194, 1716, 1614, 1442, 1252, 1122, 1030, 839, 760, 554 cm^{-1}; MS (ESI): m/z 306 $(M + Na)^+$; HRMS (ESI): m/z calcd for $C_{16}H_{13}O_4NNa$ $(M + Na)^+$: 306.0742, found: 306.0736.

Methyl 3-acetoxy-5-(4-acetylphenyl)-2-methylenepent-4-ynoate (1h). 1.08 g, 93%; white solid; M.P.: 74–76 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, J = 8.5 Hz, 2H), 7.54 (d, J = 8.5 Hz, 2H), 6.53 (s, 2H), 6.31 (s, 1H), 3.83 (s, 3H), 2.60 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.9, 169.0, 164.4, 136.5, 131.9, 129.0, 127.9, 124.1, 86.7, 85.9, 61.7, 59.5, 52.0, 26.3, 20.6; IR (KBr): ν_{max} 2954, 2193, 1749, 1715, 1681, 1600, 1441, 1369, 1260, 1223, 1149, 1022, 830, 590 cm^{-1}; MS (ESI): m/z 323 $(M + Na)^+$; HRMS (ESI): m/z calcd for $C_{17}H_{16}O_5Na$ $(M + Na)^+$: 323.0895, found: 323.0889.

(*E*)-Methyl 3-acetoxy-2-methylene-7-phenylhept-6-en-4-ynoate (1j). 1.10 g, 94%; brownish liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41–7.25 (m, 5H), 7.01 (d, J = 16.4 Hz, 1H), 6.51 (s, 1H), 6.47 (s, 1H), 6.29 (s, 1H), 6.20 (dd, J = 16.4, 1.8 Hz, 1H), 3.81 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.2, 164.8, 142.8, 136.4, 135.6, 128.9, 128.8, 128.6, 126.2, 106.6, 86.2, 85.5, 62.1, 52.0, 20.7; IR (KBr): ν_{max} 3027, 2950, 1735, 1633, 1442, 1364, 1223, 1144, 956, 763, 694 cm^{-1}; MS (ESI): m/z 307 $(M + Na)^+$; HRMS (ESI): m/z calcd for $C_{17}H_{16}O_4Na$ $(M + Na)^+$: 307.0946, found: 307.0942.

Methyl 3-acetoxy-2-methylenedec-4-ynoate (1l). 0.93 g, 78% yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.45 (s, 1H), 6.28 (s, 1H), 6.25 (s, 1H), 3.79 (s, 3H), 2.24 (t, J = 7.5 Hz, 2H), 2.09 (s, 3H), 1.57–1.47 (m, 3H), 1.41–1.29 (m, 3H), 0.96–0.81 (t, J = 1.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.3, 165.0, 136.9, 128.8, 88.6, 74.7, 62.0, 52.0, 30.9, 27.9, 22.0, 22.0, 18.6, 13.8; IR (KBr): ν_{max} 2956, 2903, 2236, 1747, 1639, 1438, 1368, 1268, 1226, 1132, 1019, 771 cm^{-1}; MS (ESI): m/z 275 $(M + Na)^+$; HRMS-ESI (m/z): calcd for $C_{14}H_{20}O_4Na$ $(M + Na)^+$: 275.1253, found: 275.1255.

General procedure for the preparation of substituted furans (2a–2p)

$Pd(Ph_3P)_4$ (0.038 mmol) was added to a solution of MBH-acetate **1** (0.38 mmol) in 3 mL of CH_3CN and the reaction mixture was stirred at room temperature for 12 h, followed by addition of 3 mL of MeOH and K_2CO_3 (1.14 mmol) stirred for 2 to 4 h at the same temperature. After the completion of the reaction (monitored by TLC), the mixture was evaporated in a vacuum, and the crude residue was purified by column chromatography on silica gel (EtOAc–hexanes) to afford the corresponding furanoates (**2a–2p**).

Methyl 5-benzylfuran-3-carboxylate (2a). 77 mg, 94%; pale yellow solid; M.P.: 92–94 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 (d, J = 7.5 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.17 (t, J = 7.5 Hz, 1H), 7.00 (s, 1H), 5.63 (s, 1H), 5.31 (s, 2H), 3.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.7, 159.6, 146.7, 135.7, 128.6, 128.3, 128.1, 126.3, 104.5, 51.9, 34.3; IR (KBr): ν_{max} 2926, 1727, 1640, 1446, 1271, 1218, 966, 769 cm^{-1}; MS (ESI): m/z 239 $(M + Na)^+$; HRMS-ESI (m/z): calcd for $C_{13}H_{12}O_3Na$ $(M + Na)^+$: 239.0679, found: 239.0682.

Methyl 5-(4-methylbenzyl)furan-3-carboxylate (2b). 67 mg, 85%; pale yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40 (s, 1H), 7.35–7.21 (m, 4H), 6.31 (s, 1H), 4.50 (s, 2H), 3.39 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.7, 147.4, 135.8, 129.2, 129.1, 128.0, 126.4, 107.9, 104.6, 51.9, 29.6, 21.2; IR (KBr): ν_{max} 2925, 1709, 1633, 1367, 1260, 1089, 834, 748 cm^{-1}; MS (ESI): m/z 229 $(M - H)^+$; HRMS-ESI (m/z): calcd for $C_{14}H_{13}O_3$ $(M - H)^+$: 229.0859, found: 229.0856.

Methyl 5-(naphthalen-1-ylmethyl)furan-3-carboxylate (2c). 66 mg, 77%; colourless liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.72 (d, J = 7.3 Hz, 1H), 8.13 (d, J = 8.1 Hz, 1H), 7.86–7.82 (m, 1H), 7.71 (d, J = 7.9 Hz, 1H), 7.55–7.44 (m, 3H), 7.15 (t, J = 2.0 Hz, 1H), 6.37 (s, 1H), 5.33 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.1, 144.8, 135.1, 133.8 133.1, 131.4, 131.2, 128.6, 127.7, 126.8, 126.1, 125.6, 125.4, 125.3, 123.6, 51.5, 33.4; IR (KBr): ν_{max} 2924, 2853, 1627, 1459, 1099, 793, 674 cm^{-1}; MS (ESI): m/z 289 $(M + Na)^+$; HRMS-ESI (m/z): calcd for $C_{17}H_{14}O_3Na$ $(M + Na)^+$: 289.0835, found: 289.0831.

Methyl 5-(4-methoxybenzyl)furan-3-carboxylate (2d). 75 mg, 88%; pale yellow solid; M.P.: 101–103 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 (d, J = 9.0 Hz, 2H), 6.98 (s, 1H), 6.86 (dd, J = 6.7, 9.0 Hz, 2H), 5.59 (s, 1H), 5.27 (s, 2H), 3.81 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.7, 158.4, 156.6, 146.6, 129.6, 129.3, 113.9, 113.6, 105.9, 55.2, 51.4, 33.4; IR (KBr): ν_{max} 2925, 2852, 1724, 1607, 1512, 1441, 1250, 1032, 837, 706 cm^{-1}; MS (ESI): m/z 245 $(M - H)^+$; HRMS-ESI (m/z): calcd for $C_{14}H_{13}O_4$ $(M - H)^+$: 245.0808, found: 245.0807.

Methyl 5-(2-methoxybenzyl)furan-3-carboxylate (2e). 67 mg, 79%; colourless liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.11 (d, J = 7.5, Hz, 1H), 7.31–7.28 (m, 1H), 7.03 (s, 1H), 6.95 (t, J = 7.4, Hz, 1H), 6.85 (d, J = 8.1, Hz, 1H), 6.09 (s, 1H), 5.28 (s, 2H), 3.85 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.8, 159.6, 155.9, 136.2, 133.6, 128.8, 127.5, 124.5, 120.6, 110.2, 97.9, 55.5, 51.9, 29.7; IR (KBr): ν_{max} 2924, 2924, 2854, 1724, 1681, 1607, 1548, 1437, 1250, 1032, 837, 761 cm^{-1}; MS (ESI): m/z 269

$(M + Na)^+$; HRMS-ESI (*m*/*z*): calcd for $C_{14}H_{14}O_4$ $(M + Na)^+$: 269.0790, found: 269.0784.

Methyl 5-(4-chlorobenzyl)furan-3-carboxylate (2f). 73 mg, 86%; pale yellow solid; M.P.: 148–150 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56 (d, J = 8.6 Hz, 2H), 7.27 (d, J = 8.6 Hz, 2H), 6.97 (s, 1H), 5.57 (s, 1H), 5.28 (s, 2H), 3.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.5, 159.9, 135.4, 134.7, 134.0, 131.6, 129.2, 128.4, 103.2, 77.0, 52.0; IR (KBr): ν_{max} 2926, 2854, 1708, 1636, 1440, 1369, 1259, 1086, 833, 741 cm^{-1}; MS (ESI): *m*/*z* 273 $(M + Na)^+$; HRMS-ESI (*m*/*z*): calcd for $C_{13}H_{11}O_3ClNa$ $(M + Na)^+$: 273.0294, found: 273.0296.

Methyl 5-(4-cyanobenzyl)furan-3-carboxylate (2g). 71 mg, 84%; pale yellow solid; M.P.: 85–87 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (s, 1H), 7.61 (d, J = 7.9 Hz, 2H), 7.33 (d, J = 7.9 Hz, 2H), 6.41 (s, 1H), 4.03 (s, 2H), 3.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.4, 137.5, 132.3, 132.0, 131.8, 129.2, 126.4, 123.8, 118.0, 112.6, 59.5, 52.4; IR (KBr): ν_{max} 3029, 2924, 2252, 1755, 1634, 1452, 1250, 1116, 1021, 758, 701 cm^{-1}; MS (ESI): *m*/*z* 264 $(M + Na)^+$; HRMS-ESI (*m*/*z*): calcd for $C_{14}H_{11}NO_3$ $(M + Na)^+$: 264.0637, found: 264.0631.

Methyl 5-(4-acetylbenzyl)furan-3-carboxylate (2h). 75 mg, 88%; white solid; M.P.: 88–90 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.94–7.89 (m, 3H), 7.32 (d, J = 8.3 Hz, 2H), 6.39 (s, 1H), 4.02 (s, 2H), 3.81 (s, 3H), 2.60 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.6, 163.4, 154.8, 146.8, 142.4, 135.7, 128.8, 128.6, 119.7, 106.6, 51.4, 34.1, 26.5; IR (KBr): ν_{max} 2924, 2854, 1722, 1633, 1460, 1375, 1247, 767 cm^{-1}; MS (ESI): *m*/*z* 281 $(M + Na)^+$; HRMS-ESI (*m*/*z*): calcd for $C_{15}H_{14}O_4$ $(M + Na)^+$: 281.0790, found: 281.0784.

Methyl 5-(thiophen-2-ylmethyl)furan-3-carboxylate (2i). 80 mg, 89%; white solid; M.P.: 94–96 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 (d, J = 4.9 Hz, 1H), 7.13 (d, J = 2.9 Hz, 1H), 7.02–6.98 (m, 2H), 5.98 (s, 1H), 5.31 (s, 2H), 3.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.8, 146.1, 138.5, 134.3, 127.1, 125.9, 125.0, 123.6, 98.5, 51.9, 29.7; IR (KBr): ν_{max} 3108, 2950, 2846, 1715, 1544, 1462, 1260, 1234, 770 cm^{-1}; MS (ESI): *m*/*z* 245 $(M + Na)^+$; HRMS-ESI (m/z): calcd for $C_{11}H_{10}O_3SNa$ $(M + Na)^+$: 245.0243, found: 245.0239.

Methyl 5-cinnamylfuran-3-carboxylate (2j). 60 mg, 72%; colourless liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.42–7.25 (m, 5H), 6.50 (d, J = 16.0 Hz, 1H), 6.43 (s, 1H), 6.24–6.29 (m, 1H), 3.81 (s, 3H), 3.54 (d, J = 6.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.7, 155.3, 146.6, 146.5, 136.8, 132.6, 128.5, 127.4, 126.1, 124.3, 105.7, 51.4, 31.4; IR (KBr): ν_{max} 2925, 1723, 1633, 1444, 1206, 1144, 763, 698 cm^{-1}; MS (ESI): *m*/*z* 265 $(M + Na)^+$; HRMS-ESI (*m*/*z*): calcd for $C_{15}H_{14}O_3Na$ $(M + Na)^+$: 265.0841, found: 265.0842.

Methyl 5-butylfuran-3-carboxylate (2k). 52 mg, 64%; pale yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 (s, 1H), 6.33 (s, 1H), 3.82 (s, 3H), 2.62 (t, J = 7.5 Hz, 2H), 1.67–1.52 (m, 2H), 1.42–1.24 (m, 2H), 0.92 (t, J = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.2, 146.9, 146.0, 126.5, 104.6, 51.4, 29.7, 27.4, 22.0, 13.7; IR (KBr): ν_{max} 2959, 2927, 1731, 1634, 1439, 1253, 1087, 760 cm^{-1}; MS (ESI): *m*/*z* 205 $(M + Na)^+$; HRMS-ESI (*m*/*z*): calcd for $C_{10}H_{14}O_3Na$ $(M + Na)^+$: 205.0841, found: 205.0835.

Methyl 5-hexylfuran-3-carboxylate (2l). 56 mg, 68%; pale yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 (s, 1H), 6.32 (s, 1H), 3.81 (s, 3H), 2.61 (t, J = 7.3 Hz, 2H), 1.68–1.54 (m, 2H), 1.41–1.21(m, 6H), 0.88 (t, J = 5.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.0, 146.0, 126.5, 119.4, 104.6, 51.4, 31.4, 28.6, 27.8, 27.6, 22.5, 14.0; IR (KBr): ν_{max} 2927, 2857, 1738, 1727, 1549, 1306, 1202, 1140, 1028, 762, 597 cm^{-1}; MS (ESI): *m*/*z* 233 $(M + Na)^+$; HRMS-ESI (*m*/*z*): calcd for $C_{12}H_{18}O_3Na$ $(M + Na)^+$: 233.1148, found: 233.1157.

Methyl 5-heptylfuran-3-carboxylate (2m). 55 mg, 66%; pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88 (s, 1H), 6.33 (s, 1H), 3.82 (s, 3H), 2.62 (t, J = 7.3 Hz, 2H), 1.66–1.58 (m, 2H), 1.32–1.27 (m, 8H), 0.88 (t, J = 5.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.0, 146.0, 126.5, 119.4, 104.6, 51.4, 31.4, 29.6, 28.6, 27.8, 27.6, 22.5, 14.0; IR (KBr): ν_{max} 2930, 2861, 1734, 1731, 1551, 1310, 1202, 1140, 1028, 762, 597 cm^{-1}; MS (ESI): *m*/*z* 247 $(M + Na)^+$; HRMS-ESI (*m*/*z*): calcd for $C_{13}H_{20}O_3Na$ $(M + Na)^+$: 247.1304, found: 247.1315.

***tert*-Butyl 5-benzylfuran-3-carboxylate (2n).** 77 mg, 90%; colourless liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62 (d, J = 7.5 Hz, 2H), 7.40–7.25 (m, 2H), 7.22–7.11 (m, 1H), 6.89 (s, 1H), 5.58 (s, 1H), 5.24 (s, 2H), 1.53 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.1, 144.5, 139.5, 135.2, 130.2, 128.7, 128.6, 126.7, 125.7, 80.8, 36.2, 28.2; IR (KBr): ν_{max} 2977, 2928, 1715, 1650, 1368, 1271, 1142, 838, 762 cm^{-1}; MS (ESI): *m*/*z* 281 $(M + Na)^+$; HRMS-ESI (*m*/*z*): calcd for $C_{16}H_{18}O_3Na$ $(M + Na)^+$: 281.1148, found: 281.1147.

1-(5-Benzylfuran-3-yl)ethanone (2o). 68 mg, 83%; colourless liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52–7.45 (m, 2H), 7.41–7.33 (m, 4H), 6.91 (s, 1H), 4.45 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.1, 145.3, 142.2, 139.2, 131.4, 128.5, 128.4, 126.6, 120.3, 36.1, 27.1; IR (KBr): ν_{max} 2923, 2854, 2192, 1669, 1601, 1445, 1228, 1106, 757, 690 696 cm^{-1}; MS (ESI): *m*/*z* 223 $(M + Na)^+$; HRMS-ESI (*m*/*z*): calcd for $C_{13}H_{12}O_2Na$ $(M + Na)^+$: 223.0735, found: 223.0731.

2-Benzyl-6,7-dihydrobenzofuran-4(5*H*)-one (2p). 65 mg, 78%; pale yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51–7.48 (m, 2H), 7.39–7.34 (m, 3H), 6.79 (s, 1H), 3.35 (s, 2H), 2.68–2.61 (m, 1H), 2.35–2.28 (m, 1H), 2.25–2.18 (m, 2H), 1.85–1.77 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.1, 150.5, 144.7, 131.7, 129.3, 128.5, 122.3, 119.3, 101.9, 56.2, 39.7, 29.4, 17.7; IR (KBr): ν_{max} 2923, 2854, 2189, 1676, 1429, 1233, 1070, 751, 696 cm^{-1}; MS (ESI): *m*/*z* 249 $(M + Na)^+$; HRMS-ESI (*m*/*z*): calcd for $C_{15}H_{14}O_2Na$ $(M + Na)^+$: 249.0886, found: 249.0888.

(*E*)-Methyl 2-(acetoxymethyl)-5-phenylpent-2-en-4-ynoate (I). $Pd(Ph_3P)_4$ (22 mg, 0.019 mmol) was added to a solution of MBH-acetate **1a** (50 mg, 0.19 mmol) in 4 mL of CH_3CN and the reaction mixture was stirred at room temperature for 12 h, then the reaction mixture was filtered through a pad of celite and the filtrate was evaporated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc–hexanes) to afford the product **I** as a pale yellow solid. 49 mg, 98%; M.P.: 82–84 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.05 (dd, J = 1.5 Hz, 2H), 7.41–7.34 (m, 3H), 7.09 (s, 1H), 5.08 (s, 2H), 3.82 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.5, 165.7, 135.8, 131.9, 129.5, 128.4, 125.1, 121.8, 104.1, 84.4, 59.7, 52.2,

20.7; IR (KBr): ν_{max} 2951, 2924, 1716, 1605, 1439, 1367, 1259, 1147, 1017, 761 cm^{-1}; MS (ESI): *m*/*z* 281 $(M + Na)^+$; HRMS-ESI (*m*/*z*): calcd for $C_{15}H_{14}O_4Na$ $(M + Na)^+$: 281.0790, found: 281.0784.

(*E*)-Methyl 2-(hydroxymethyl)-5-phenylpent-2-en-4-ynoate (II). K_2CO_3 (31 mg, 0.18 mmol) was added to a solution of compound **I** (49 mg, 0.18 mmol) dissolved in 4 mL of MeOH and stirred for 5 min at 0 °C. The mixture was evaporated *in vacuo* and the crude was purified by column chromatography on silica gel (EtOAc–hexanes) to afford the title compound **II** as a yellow solid. 40 mg, 97%; M.P.: 94–96 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 7.05–7.03 (m, 2H), 7.37–7.31 (m, 3H), 6.88 (s, 1H), 4.57 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.8, 139.8, 131.8, 129.4, 128.4, 121.7, 103.3, 84.4, 59.7, 52.2, 29.6; IR (KBr): ν_{max} 3451, 2951, 1742, 1716, 1605, 1439, 1367, 1259, 1147, 1017, 761 cm^{-1}; MS (ESI): *m*/*z* 239 $(M + Na)^+$; HRMS-ESI (*m*/*z*): calcd for $C_{13}H_{12}O_3Na$ $(M + Na)^+$: 239.0679, found: 239.0682

(5-Benzylfuran-3-yl)methanol (Elliott's alcohol, 3). To a stirred solution of furanoate **2a** (2 g, 9.26 mmol) in CH_2Cl_2 (60 mL) was added DIBALH (25% w/v in toluene, 15.8 mL, 27.78 mmol) at −78 °C, and the mixture was stirred at the same temperature for 1 h. The mixture was warmed to 0 °C, quenched with aqueous saturated sodium potassium tartarate (30 mL), and the mixture was stirred for 3 h. The aqueous phase was extracted with ethyl acetate (2 × 20 mL). The combined organic layer was washed with brine (40 mL), dried over Na_2SO_4, and evaporated the organic solvent under reduced pressure. The crude residue was purified by flash column chromatography (silica gel, hexanes–EtOAc = 90 : 10) to give **3** (1.65 g, 95%) as a pale yellow oil; ^1H NMR (300 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.5 Hz, 1H), 7.30–7.21 (m, 3H), 7.18–7.05 (m, 2H), 5.13 (s, 1H), 5.12 (s, 2H), 4.40 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.6, 138.7, 137.7, 131.3, 128.6, 128.4, 126.5, 106.4, 56.7, 34.5; IR (KBr): ν_{max} 3387, 2924, 1755, 1629, 1493, 1451, 1384, 1017, 701, 562 cm^{-1}; MS (ESI): *m*/*z* 211 $(M + Na)^+$; HRMS-ESI (*m*/*z*): calcd for $C_{12}H_{12}O_2Na$ $(M + Na)^+$: 211.0735, found 211.0735.

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