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FULL PAPER

A Domino Strategy for the Synthesis of 2*H*-Pyrans from Propargyl Vinyl Ethers.

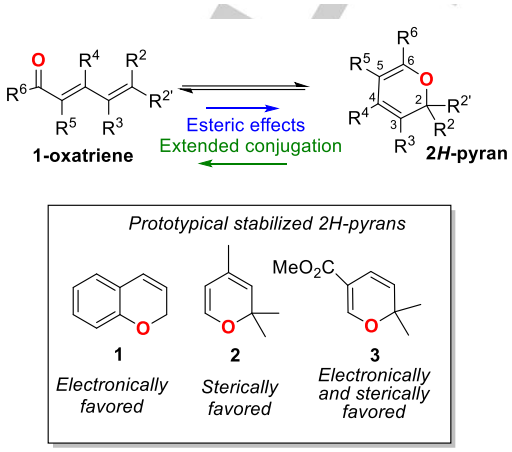
David Tejedor[a], Samuel Delgado-Hernández, [a] [b] Raquel Diana-Rivero, [a] [b] Abián Díaz-Díaz, [a] [b] and Fernando García-Tellado*[a]

Abstract: Stable monocyclic 2*H*-pyrans are synthesized from readily available tertiary propargyl vinyl ethers via a metal-free all-pericyclic domino manifold involving a sequential propargyl Claisen rearrangement / [1,3]H-shift / oxa-6π electrocyclization set of reactions. The wide scope of this protocol is exemplified by the synthesis of 21 different 2*H*-pyrans incorporating a varied substitution pattern at the ring.

Introduction

Stable 2*H*-pyrans are challenging targets in current organic synthesis.[1] In fact, the 2*H*-pyran core constitutes a sub-structural motive present in a wide array of natural products,[2] and also it is a key intermediate in organic synthesis.[3] For these reasons, there is an ongoing interest in the synthesis of this class of oxygenated heterocycles. Strategies designed towards their synthesis need to take into account the known tendency of 2*H*-pyrans to undergo a ring-opening conversion to their 1-oxatriene form (Scheme 1).[4] Typically, this valence isomerization equilibrium is governed by the 1-oxatriene form, except in a few cases where the 2*H*-pyran form is favored. In these cases, significant steric interactions disfavor planarity, and consequently, the π-delocalization through the conjugated system. Studies on these equilibria[5] have shown that the 2*H*-pyran form is stabilized by the presence of electron-withdrawing groups at the C-5 position (R^5 in Scheme 1; electronic factors), disubstitution at the C-2 position ($R^2/R^{2'}\neq H$)(steric factors) or annulation (entropic trap). Prototypical examples of stable 2*H*-pyrans are 2*H*-chromenes (**1**),[6] 2,2,4-trimethyl-2*H*-pyran[7] (**2**) (favored by steric factors) and methyl 2,2-dimethyl-2*H*-pyran-5-carboxylate[8] (**3**) (favored by a combination of steric and electronic factors) (Scheme 1).

From a synthetic point of view, these heterocycles are commonly synthesized by the so-called "1-oxatriene pathway", which entails a tandem Knoevenagel/6π-electrocyclization reaction of 1,3-dicarbonyl compounds and 2-alkenals (a formal [3+3] cycloaddition) (Scheme 2a).[2b],[9] Alternatives to this tandem strategy have merged from the well-studied Claisen



Scheme 1. 1-Oxatriene/2*H*-pyran valence isomerization. Prototypical examples of stable 2*H*-pyrans.

rearrangement of propargyl vinyl ethers (PVEs).[10] Kirsch and col. showed that PVEs bearing a methine carbon atom at the propargylic position (**4**, Scheme 2b), rearranged to trisubstituted 2*H*-pyran-5-carboxylates (2HPCs) **5** through a two-step, one pot reaction entailing a silver-catalyzed propargyl Claisen rearrangement and a tandem base-catalyzed allene-diene isomerization/oxa 6π-electrocyclization reaction.[10e] Among other requirements, substitution at the C-6 position ($R^6\neq$ H) was essential for the stability of the 2*H*-pyran ring. We report herein an efficient, general, metal-free domino alternative to this strategy, which is amenable to be used with PVEs featuring a quaternary carbon center at the propargylic position and a varied functional substitution at the terminal alkyne position.

Results and Discussion

Over the last years, our group has been focused on the development of metal-free domino processes as sustainable alternatives to metal catalyzed synthetic methodologies.[11] In this line of thought, we have reported the implementation of a robust, highly efficient and predictable protocol for the synthesis of PVEs **6** (Scheme 2c), which bear a quaternary carbon atom at the propargylic position (the so-called tertiary PVEs).[12] These PVEs are easily accessible from ketones, through a two-step procedure entailing: 1) generation of the tertiary propargylic alcohol, and 2) transformation of the alcohol into the corresponding β-alkoxy-acrylate derivative **6**. We have also shown that the microwave irradiation of these tertiary PVEs **6** in the presence of catalytic amounts of imidazole generates salicylaldehyde derivatives **8** through an all-pericyclic domino process (Scheme 2c).[13] During these studies, we discovered that this process could be funneled

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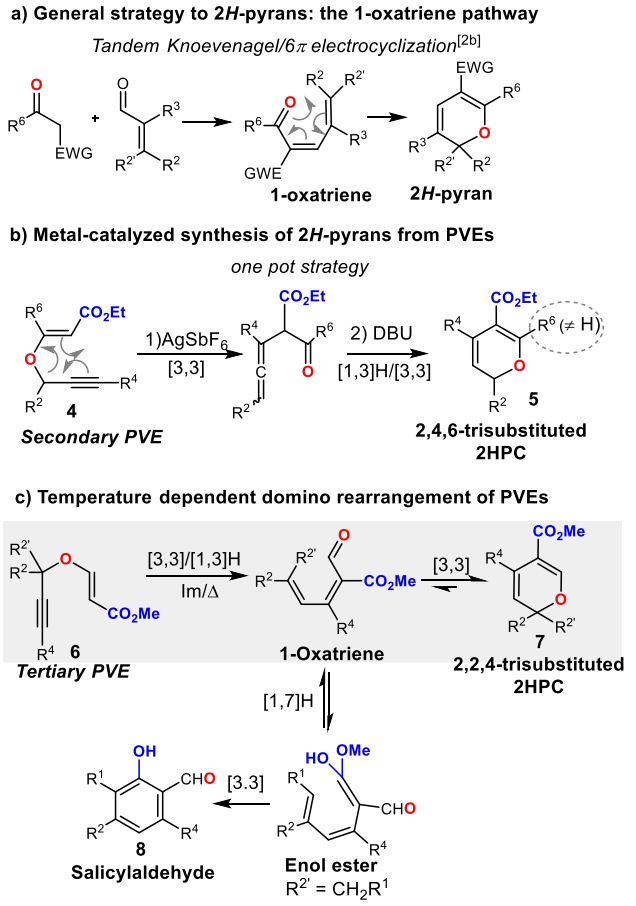
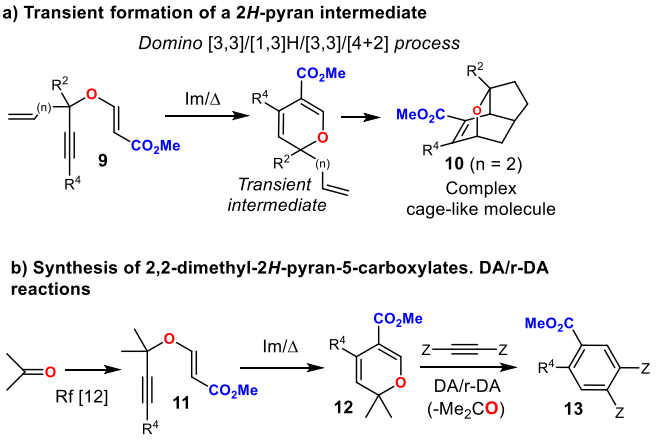


Scheme 2. Synthetic approaches to substituted 2*H*-pyrans from propargyl vinyl ethers (PVEs). 2HPC = 2*H*-pyran-5-carboxylate

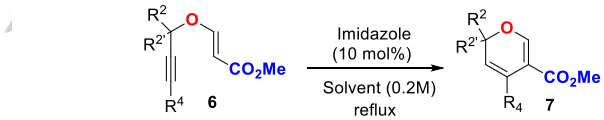
toward the formation of trisubstituted 2HPCs **7** by a careful control of the temperature. This discovery opened us an unexplored 3-step organocatalytic route to these heterocycles using ketones as highly versatile starting materials and tertiary PVEs **6** as the active intermediates. Using this domino manifold, we have synthesized complex cage-like molecules such as **10**, through the generation of a transient and conveniently functionalized 2*H*-pyran intermediate (Scheme 3a).[14] More recently, we have described the use of this manifold to generate 2,2-dimethyl-2*H*-pyran-5-carboxylate derivatives **12**, a family of rigid monocyclic dienes with use in Diels-Alder/retro–Diels-Alder reactions (Scheme 3b).[8] The particular functional pattern exhibited by derivatives **12**, and in general by the 2,2,4-trisubstituted 2HPCs **7**, is not easily accessible through the 1-oxatriene pathway using standard methodologies (it requires the synthesis and coupling of trisubstituted enones or the use of noble metal catalysis).[2b] This prompted us to tackle a deeper study of this synthetic strategy to establish the structural and/or functional limits for its practical (preparative) use (Table 1).

The manifold resulted to be efficient and tolerant with regard to the electronic character of the ketone precursor. Thus, dialkyl, diaryl and aryl alkyl ketones were cleanly transformed into the



Scheme 3. a) Synthetic manifold based on a transient 2*H*-pyran species. b) Synthetic manifold based on discrete 2,2-dimethyl2H-pyran-5-carboxylates **12**.

Table 1. Synthesis of 2,2,4-trisubstituted 2HPCs **7** from PVEs **6**. Yields refer to isolated product.



7a, $R^2 = R^{2'}$ = Me
(92%, toluene, 48 h)
7b, $R^2 = R^{2'}$ = Et
(95%, toluene, 48 h)
7c, R^2 = Ph; $R^{2'}$ = Me
(≥ 95%, toluene, 1 h)
7d, R^2 = Ph; $R^{2'}$ = *n*-Bu
(95%, toluene, 1 h)
7e R^2 = Ph; $R^{2'}$ = *i*-Pr
(≥ 95%, toluene, 1 h)
7f $R^2 = R^{2'}$ = Ph
(80%, toluene, 1h)[a]
7g R^2 = Ph; $R^{2'}$ = H
(23%, toluene, 2 h)[b]

7h
(83%, benzene, 32 h)

7i, $R^4 = SiMe_3$
(83%, toluene, 72 h)
7j, R^4 = Ph
(62%, toluene, 4 h)[c] or
(75%, benzene, 120 h)[d]
7k, R^4 = Me
(77%, toluene, 24 h)
7l, R^4 = *t*-Bu
(4%, toluene, 72 h)[e]
7m, R^4 = H
(68%, toluene, 5 h)

7n, R^4 = Me
(86%, toluene, 1 h)

7o, R^4 = Me
(87%, benzene, 1 h)
7p, R^4 = *t*-Bu
(87%, benzene, 38 h)
7q, R^4 = H
(> 95%, benzene, 3 h)[f]

7r, R^4 = Ph
(83%, toluene, 1 h)[a]
7s, R^4 = Me
(86%, benzene, 2 h)
7t, R^4 = *t*-Bu
(93%, benzene, 48 h)
7u, $R^4 = CO_2Me$
(86%, benzene, 3 h)

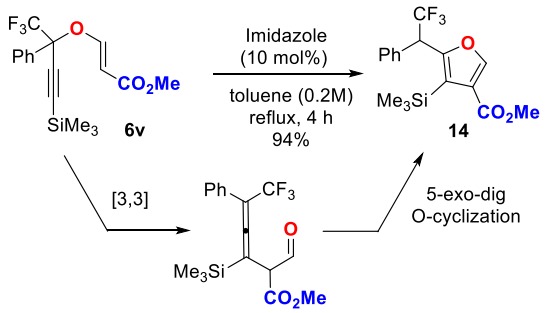
[a]PVE is not isolated. Yield for two steps directly from the propargyl alcohol. [b]Although isolated, it is quite unstable and it quickly decomposes on standing. [c]9% unreacted PVE and 27% corresponding salicylaldehyde. [d]16% unreacted PVE and 9% corresponding salicylaldehyde. [e]NMR yield determined using an internal standard. 26% unreacted PVE and 60% corresponding salicylaldehyde. [f]1-oxatriene derivative. Mixture of the corresponding E/Z isomers as seen in the ^{1}HNMR spectrum of the crude material

corresponding tertiary PVEs **6**, which smoothly rearranged into the 2HPCs **7** in good to excellent yields (Table 1). A dependency of the reaction time with the substrate forced us to monitor each

reaction (TLC) to establish the best reaction time. It spanned from 1 h for the most reactive PVEs (**7c-f**, **7n**, **7o**, **7r**) to 72 h for the most reluctant case (toluene, reflux; **7i**). With regard to the substituent R^4, the reaction accepted a convenient functional diversity, including linear (**7k**, **7n**, **7o**, **7s)** or branched alkyl chains (**7e**, **7l**, **7p**, **7t**), aromatic (**7h**, **7j**), esters (**7u**) and silicon-containing groups (trimethylsilyl, **7a-g**, **7i**). These last two groups of substituents constitute valuable chemical handles amenable for using in later transformations.

The protocol failed with the secondary 2*H*-pyran **7g** (23% after isolation; it decomposes on standing) and the unsubstituted derivative **7q**, which was not obtained, delivering in its place the corresponding 1-oxatriene derivative in almost quantitative yield. In the case of **7j**, endowed with a phenyl group at C-4 and a spiro center at C-2, the reaction manifold also delivered the corresponding salicylaldehyde derivative **8** (27% yield; see Scheme 2c for the general structure). The change of toluene by benzene as solvent allowed to increase the yield of **7j** to 75%, reducing the amount of salicylaldehyde below 10%, but at the expense of increasing the amount of recovered PVE **6j** from 9% to 16%. The lowering of the reaction temperature increased the reaction time from hours to days, because the expected decelerating effect on both the initial propargyl Claisen rearrangement and the enolization step ([1,7]H shift; Scheme 2c). Therefore, while a slower enolization directly benefits the formation of 2*H*-pyran ring, the deceleration of the Claisen rearrangement affects the whole process and, consequently, also the formation of 2*H*-pyran. In the case of the **7l**, the *t*-butyl substituent favors the salicylaldehyde route in detriment of the 1-oxatriene pathway, and funnels the reaction outcome toward the salicylaldehyde formation (60% yield; 26% of r.s.m.).

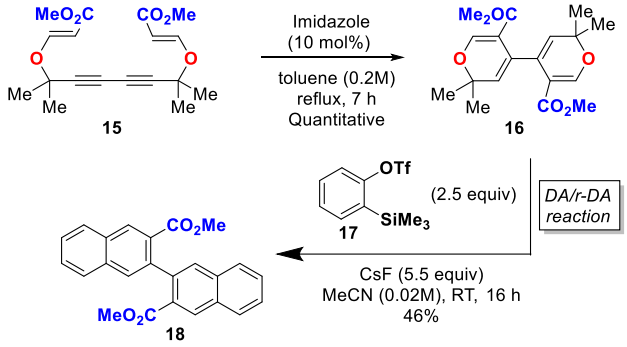
The main limitation of this protocol seems to be associated with a high electrophilicity of the propargylic quaternary carbon center of PVEs **6**. This is the case of PVE **6v**, which features an aromatic and a highly electron withdrawing CF_3 group at the propargylic position (Scheme 4). The high electrophilicity of the quaternary propargyl center translates to the quaternary allene central carbon atom, which ultimately translates into a favored 5-*exo*-dig O-cyclization on the allenal intermediate to generate the furan derivative **14**. The same reactivity profile was also found in the propargyl Claisen rearrangement of tertiary PVEs endowed



Scheme 4. Limitations of the protocol: a high electrophilicity of the quaternary center of the PVE funnels the reaction toward furan formation.

with an ester or an amide at the quaternary propargylic position.[15]

An interesting extension of the protocol is depicted in Scheme 5. Dimeric PVE **15**, when submitted at the standard reaction conditions, delivered the dimer **16** in quantitative yield. Dimer **16** is attractive because it incorporates two units of the 2,2-dimethyl-2*H*-pyran core, an excellent reactive *cisoide* diene for tandem Diels-Alder/retro-Diels-Alder reactions.[8] With dimer **16** in hand, we assayed the tandem reaction using 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**17**) as the dienophile precursor (benzyne) and **16** as a double diene. The reaction needed stirring at room temperature for 16 h to deliver the expected dimethyl [2,2'-binaphthalene]-3,3'-dicarboxylate (**18**)[16] in moderate yield (46%). This result, which is susceptible to optimization, allows laying the foundations of a practical and metal-free strategy for the synthesis of highly conjugated polyaromatic molecules, which constitute highly appreciated platforms in materials science.[17]



Scheme 5. Extension of the domino strategy to dimeric 2*H*-pyran **16** and its applications to the synthesis of dimethyl [2,2'-binaphthalene]-3,3'-dicarboxylate (**18**).

Conclusions

In summary, we have established and implemented a strategy for the practical synthesis of methyl 2,2,4-trisubsituted-2*H*-pyran-5-carboxylates **7** from tertiary propargyl vinyl ethers **6**. The strategy avoids the use of metals and it is highly tolerant with the structure and electronic properties of the propargyl vinyl ether. Although the protocol is quite general, there are some limitations, mainly related to the electrophilicity of the propargylic carbon atom of the tertiary PVE (strong electron withdrawing groups at this position are not allowed) and the nature of the substituent at C-4, which determines the weight of the 2*H*-pyran form in the valence isomerization equilibrium with the corresponding 1-oxatriene. An interesting application was advanced for the synthesis of the dimeric platform **16** (incorporating two unis of 2,2-dimethyl-2*H*-pyran-5-carboxylate), which was reacted with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**17**) to generate the expected dimethyl [2,2'-binaphthalene]-3,3'-dicarboxylate (**18**), a convenient building block for accessing highly conjugated polyaromatic molecules.

Experimental Section

General remarks. ^{1}H NMR and ^{13}C NMR spectra of $CDCl_3$ solutions were recorded either at 400 and 100 MHz or at 500 and 125 MHz, respectively. Mass spectra (low resolution) (EI/CI) and HRMS (EI/TOF) were obtained with a gas chromatograph/mass spectrometer. Analytical thin-layer chromatography plates used UV-active silica gel on aluminum. Flash column chromatography was carried out with silica gel 60 (particle size less than 0.020 mm) using appropriate mixtures of ethyl acetate and hexanes as eluents. All reactions were performed in oven-dried glassware. All materials were obtained from commercial suppliers and used as received. All melting points are uncorrected. The propargyl alcohols were prepared by addition of the lithium or magnesium bromide acetylides onto the appropriate ketones following the standard procedures (see below for a general procedure). The propargyl vinyl ethers were prepared according to our previous experimental procedure[¡Error! Marcador no definido.] (see below for a general procedure). Products **6a**,[8] **6e**,[18a] **6h**,[13] **6i**[13] **6j**[13] **6k**,[18b] **6l**,[18b] **6m**,[12] **6q**[18b], **6r**,[18a] **6t**,[18a] **6u**,[18a] **7a**,[8] **7r**,[18a] and **18**[16] have been previously described.

General procedure for the synthesis of tertiary propargyl alcohols: The terminal alkyne (13 mmol) was dissolved in 25 mL of dry THF in a round-bottom flask. After the mixture was cooled to -78 ºC, a solution of 1,6M BuLi in hexanes (20.8 mL, 13 mmol) was added dropwise. The temperature was maintained between -78 ºC and -40 ºC for 1 h with stirring of the solution. Ketone (10 mmol) was then added slowly (if solid, dissolved in THF), and the stirring was continued overnight allowing the reaction mixture to warm up to room temperature slowly without additional cooling. After completion, the reaction was quenched with saturated NH_4Cl solution and extracted with CH_2Cl_2. This was followed by isolation of the corresponding product by flash column chromatography (silica gel, appropriate mixtures of *n*-hexane/EtOAc) for high boiling alkynes. If the alkyne used had a relatively low boiling point (< 120 ºC), evaporation of the solvent and excess reaction led to a crude alcohol which did not need chromatographic purification.

General procedure for the synthesis of propargyl vinyl ethers 6 from the corresponding tertiary propargyl alcohols. Methyl propiolate (2.0 mmol) was added dropwise (time of addition 10 min) to a solution of the propargyl alcohol (1.0 mmol) and DABCO (0.10 mmol) in a 1:9 mixture of dry CH_2Cl_2 and hexane (5 mL). The reaction mixture was stirred until completion (TLC control). The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (silica gel; n-hexane/EtOAc, 90:10).

(*E*)-Methyl 3-(3-ethyl-1-(trimethylsilyl)pent-1-yn-3-yloxy)acrylate (6b). Colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 0.19$ (s, 9H), 0.95 (t, 6H, ^3J(H,H) = 7.3 Hz), 1.73 (q, 4H, ^3J(H,H) = 1.3 Hz), 3.67 (s, 3H), 5.32 (d, 1H, ^3J(H,H) = 12.1 Hz), 7.96 (d, 1H, ^3J(H,H) = 12.1 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = -0.3 (3C), 8.2 (2C), 32.4 (2C), 50.8, 83.3, 95.3, 98.1, 102.8, 159.5, 168.4 ppm. HRMS (ESI$^+$): m/z [M+Na]$^+$ calculated for $C_{14}H_{24}O_3Si$ 91.1392, found 291.1392.

(*E*)-Methyl 3-(2-phenyl-4-(trimethylsilyl)but-3-yn-2-yloxy)acrylate (6c). Colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 0.25$ (s, 9H), 1.83 (s, 3H), 3.63 (s, 3H), 5.43 (d, 1H, ^3J(H,H) = 12.1 Hz), 7.31-7.38 (m, 3H), 7.52-7.53 (m, 2H), 7.67 (d, 1H, ^3J(H,H) = 12.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = -0.3 (3C), 32.2, 50.8, 80.0, 94.8, 100.0, 103.6, 125.8 (2C), 128.4, 128.5 (2C), 141.6, 159.0, 167.9 ppm. HRMS (ESI$^+$): m/z [M+Na]$^+$ calculated for $C_{17}H_{22}O_3Si$ 325.1236, found 325.1239.

(*E*)-Methyl 3-(3-phenyl-1-(trimethylsilyl)hept-1-yn-3-yloxy)acrylate (6d). Colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 0.25$ (s, 9H), 0.85 (t, 3H, ^3J(H,H) = 7.2 Hz), 1.18-1.33 (m, 3H), 1.39-1.46 (m, 1H), 1.87-1.93 (m, 1H), 2.04-2.09 (m, 1H), 3.62 (s, 3H), 5.40 (d, 1H, ^3J(H,H) = 12.1 Hz), 7.29-7.37 (m, 3H), 7.46-7.48 (m, 2H), 7.65 (d, 1H, ^3J(H,H) = 12.1 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = -0.3 (3C), 13.8, 22.4, 26.5, 44.2, 50.9, 83.8, 96.0, 99.8, 102.9, 126.3 (2C), 128.3, 128.4 (2C), 140.8, 159.4, 168.0 ppm. HRMS (ESI$^+$): m/z [M+Na]$^+$ calculated for $C_{20}H_{28}O_3Si$ 367.1705, found 367.1708.

(*E*)-Methyl 3-(1-phenyl-3-(trimethylsilyl)prop-2-ynyloxy)acrylate (6g). Colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 0.21$ (s, 9H), 3.69 (s, 3H), 5.46 (d, 1H, ^3J(H,H) = 12.4 Hz), 5.62 (s, 1H), 7.37-7.41 (m, 3H), 7.48-7.52 (m, 2H), 7.69 (d, 1H, ^3J(H,H) = 12.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = -0.4 (3C), 51.1, 73.6, 95.8, 99.3, 100.0, 127.5 (2C), 128.7 (2C), 129.2, 136.1, 159.9, 167.9 ppm. HRMS (ESI$^+$): m/z [M+Na]$^+$ calculated for $C_{16}H_{20}O_3Si$ 311.1079, found 311.1082.

(*E*)-Methyl 3-(4-phenyloct-2-yn-4-yloxy)acrylate (6n). Colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 0.84$ (t, 3H, ^3J(H,H) = 7.2 Hz), 1.15-1.31 (m, 3H), 1.38-1.46 (m, 1H), 1.86-1.92 (m, 1H), 2.00 (s, 3H), 2.02-2.09 (m, 1H), 3.62 (s, 3H), 5.40 (d, 1H, ^3J(H,H) = 12.1 Hz), 7.27-7.30 (m, 1H), 7.32-7.35 (m, 2H), 7.46-7.48 (m, 2H), 7.63 (d, 1H, ^3J(H,H) = 12.1 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 3.8, 13.9, 22.5, 26.6, 44.5, 50.9, 76.9, 83.9, 86.7, 99.4, 126.4 (2C), 128.2, 128.3 (2C), 141.5, 159.7, 168.2 ppm. HRMS (ESI$^+$): m/z [M+Na]$^+$ calculated for $C_{18}H_{22}O_3$ 309.1467, found 309.1469.

(*E*)-Methyl 3-(2-phenylpent-3-yn-2-yloxy)acrylate (6o). Colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 1.81$ (s, 3H), 1.98 (s, 3H), 3.63 (s, 3H), 5.41 (d, 1H, ^3J(H,H) = 12.1 Hz), 7.30-7.37 (m, 3H), 7.51-7.53 (m, 2H), 7.65 (d, 1H, ^3J(H,H) = 12.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 3.7, 32.4, 50.9, 78.2, 80.1, 85.9, 99.7, 125.9 (2C), 128.3, 128.5 (2C), 142.3, 159.3, 168.1 ppm.

(*E*)-Methyl 3-(5,5-dimethyl-2-phenylhex-3-yn-2-yloxy)acrylate (6p). Colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 1.30$ (s, 9H), 1.80 (s, 3H), 3.63 (s, 3H), 5.39 (d, 1H, ^3J(H,H) = 12.1 Hz), 7.28-7.37 (m, 3H), 7.49-7.52 (m, 2H), 7.68 (d, 1H, ^3J(H,H) = 12.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 27.7, 30.8 (3C), 32.6, 50.9, 77.6, 80.2, 98.9, 99.5, 125.8 (2C), 128.3, 128.5 (2C), 142.5, 159.4, 168.1 ppm. HRMS (ESI$^+$): m/z [M+Na]$^+$ calculated for $C_{18}H_{22}O_3$ 309.1467, found 309.1464.

(*E*)-Methyl 3-(2-methyl-3-phenylhex-4-yn-3-yloxy)acrylate (6s). Colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 0.71$ (d, 3H, ^3J(H,H) = 6.7 Hz), 1.10 (d, 3H, ^3J(H,H) = 6.7 Hz), 2.01 (s, 3H), 2.15-2.21 (m, 1H), 3.61 (s, 3H), 5.39 (d, 1H, ^3J(H,H) = 12.1 Hz), 7.28-7.34 (m, 3H), 7.43-7.45 (m, 2H), 7.59 (d, 1H, ^3J(H,H) = 12.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 3.7, 17.7, 17.8, 42.3, 50.9, 75.6, 87.4, 88.0, 99.2, 127.1 (2C), 128.1 (2C), 128.2, 140.6, 160.0, 168.2 ppm. HRMS (ESI$^+$): m/z [M+Na]$^+$ calculated for $C_{17}H_{20}O_3$ 295.1310, found 295.1313.

(*E*)-Methyl 3-(1,1,1-trifluoro-2-phenyl-4-(trimethylsilyl)but-3-yn-2-yloxy)acrylate (6v). Colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 0.28$ (s, 9H), 3.66 (s, 3H), 5.60 (d, 1H, ^3J(H,H) = 12.1 Hz), 7.39-7.45 (m, 3H), 7.61-7.63 (m, 2H), 7.65 (d, 1H, ^3J(H,H) = 12.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = -0.7 (3C), 51.2, 81.3 (q, J(C,F) = 32 Hz), 95.3, 100.2, 102.5, 122.0 (q, J(C,F) = 285 Hz), 128.1 (2C), 128.6 (2C), 130.3, 132.6, 156.4, 167.2 ppm. HRMS (ESI$^+$): m/z [M+Na]$^+$ calculated for $C_{17}H_{19}F_3O_3Si$ 379.0953, found 379.0951.

Representative procedure for the synthesis of methyl 2,2,4-trisubstituted-2*H*-pyran-5-carboxylates (7). A solution of propargyl vinyl ether **6** (1.0 mmol) and imidazole (0.1 mmol) in dry toluene (5 mL) was stirred under reflux for 72 hours (TLC control). After removing the solvent

at reduced pressure, the products were purified by flash column chromatography (silica gel, n-hexane/EtOAc 95/5).

Methyl 2,2-diethyl-4-(trimethylsilyl)-2*H*-pyran-5-carboxylate (7b). Yield: 426.1 mg, 95%. Colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.15 (s, 9H), 0.88 (t, 6H, ^3J(H,H) = 7.4 Hz), 1.50-1.59 (m, 2H), 1.57-1.70 (m, 2H), 3.69 (s, 3H), 5.30 (d, 1H, ^3J(H,H) = 1.2 Hz), 7.52 (d, 1H, ^3J(H,H) = 1.2 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = -0.02 (3C), 7.8 (2C), 31.8 (2C), 50.8, 83.3, 108.5, 130.9, 131.1, 155.4, 167.3 ppm. HRMS (ESI$^+$): m/z [M+Na]$^+$ calculated for $C_{14}H_{24}O_3Si$ 91.1392, found 291.1393.

Methyl 2-methyl-2-phenyl-4-(trimethylsilyl)-2*H*-pyran-5-carboxylate (7c). Yield: 332.0 mg, 100%. Colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.20 (s, 9H), 1.70 (s, 3H), 3.69 (s, 3H), 5.76 (d, 1H, ^3J(H,H) = 1.3 Hz), 7.28 (tt, 1H, ^3J(H,H) = 6.2 and 1.3 Hz), 7.32-7.37 (m, 2H), 7.41-7.44 (m, 2H), 7.57 (d, 1H, ^3J(H,H) = 1.3 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = -0.1 (3C), 28.2, 50.9, 79.5, 110.4, 125.2 (2C), 127.6, 128.2 (2C), 130.6, 132.3, 144.6, 154.2, 166.9 ppm. HRMS (ESI$^+$): m/z [M+Na]$^+$ calculated for $C_{17}H_{22}O_3Si$ 325.1236, found 325.1231.

Methyl 2-butyl-2-phenyl-4-(trimethylsilyl)-2*H*-pyran-5-carboxylate (7d). Yield: 135.5 mg, 95%. Colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.19 (s, 9H), 0.87 (t, 3H, ^3J(H,H) = 7.1 Hz), 1.24-1.32 (m, 4H), 1.92-1.95 (m, 2H), 3.67 (s, 3H), 5.81 (s, 1H), 7.24-7.28 (m, 1H), 7.31-7.38 (m, 4H), 7.61 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = -0.1 (3C), 13.9, 22.8, 26.1, 41.6, 50.9, 82.2, 110.5, 125.2 (2C), 127.4, 128.1 (2C), 131.1, 131.6, 144.3, 154.5, 167.0 ppm. HRMS (ESI$^+$): m/z [M+Na]$^+$ calculated for $C_{20}H_{28}O_3Si$ 367.1705, found 367.1707.

Methyl 2-isopropyl-2-phenyl-4-(trimethylsilyl)-2*H*-pyran-5-carboxylate (7e). Yield: 175.8 mg, 98%. Colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.20 (s, 9H), 0.87 (d, 3H, ^3J(H,H) = 6.8z), 0.88 (d, 3H, ^3J(H,H) = 6.8z), 2.15-2.25 (m, 1H), 3.66 (s, 3H), 5.90 (s, 1H), 7.23-7.32 (m, 5H), 7.63 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = -0.1 (3C), 17.1, 17.3, 38.4, 50.8, 84.8, 110.4, 125.5 (2C), 127.3, 127.9 (2C), 129.7, 131.5, 143.6, 154.8, 166.9 ppm. HRMS (ESI$^+$): m/z [M+Na]$^+$ calculated for $C_{19}H_{26}O_3Si$ 353.1549, found 353.1548.

Methyl 2,2-diphenyl-4-(trimethylsilyl)-2*H*-pyran-5-carboxylate (7f). Yield: 306.4 mg, 80%. Colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.22 (s, 9H), 3.68 (s, 3H), 5.93 (s, 1H), 7.26-7.33 (m, 10H), 7.61 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 0.2 (3C), 51.2, 83.5, 111.2, 127.2 (4C), 128.0 (2C), 128.4 (4C), 131.7, 131.9, 144.2 (2C), 153.8, 167.0 ppm. HRMS (ESI$^+$): m/z [M+Na]$^+$ calculated for $C_{22}H_{24}O_3Si$ 387.1392, found 387.1389.

Methyl 2-phenyl-4-(trimethylsilyl)-2*H*-pyran-5-carboxylate (7g). Yield: 33.6 mg, 23%. Colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.19 (s, 9H), 3.73 (s, 3H), 5.61 (bs, 1H), 5.70 (bs, 1H), 7.35-7.39 (m, 5H), 7.57 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = -0.2 (3C), 51.0, 77.3, 111.3, 127.2, 127.4 (2C), 128.7 (3C), 133.2, 139.3, 154.7, 166.9 ppm. HRMS (ESI$^+$): m/z [M+Na]$^+$ calculated for $C_{16}H_{20}O_3Si$ 311.1079, found 311.1080.

Methyl 4-phenyl-1-oxaspiro[5.11]heptadeca-2,4-diene-3-carboxylate (7h). Yield: 123.0 mg, 83%. White crystalline solid. Melting point = 116 - 117ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.30-1.40 (m, 16H), 1.51-1.58 (m, 2H), 1.73-1.80 (m, 2H), 1.86-1.94 (m, 2H), 3.55 (s, 3H), 5.22 (s, 1H), 7.15-7.17 (m, 2H), 7.26-7.31 (m, 3H), 7.59 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 19.0 (2C), 22.1 (2C), 22.6 (2C), 26.0, 26.2 (2C), 32.1 (2C), 50.9, 84.2, 109.3, 122.1, 127.07 (2C), 127.11, 127.7 (2C), 132.6, 139.8, 156.1, 165.9 ppm. HRMS (ESI$^+$): m/z [M+Na]$^+$ calculated for $C_{24}H_{32}O_3$ 391.2249, found 391.2251.

Methyl 4-(trimethylsilyl)-1-oxaspiro[5.5]undeca-2,4-diene-3-carboxylate (7i). Yield: 233.9 mg, 83%. Colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.14 (s, 9H), 1.46-1.50 (m, 1H), 1.55-1.65 (m, 7H), 1.85-1.89 (m, 2H), 3.70 (s, 3H), 5.44 (s, 1H), 7.50 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = -0.13 (3C), 21.3 (2C), 25.2, 35.2 (2C), 50.8, 78.1, 110.4, 130.1, 132.8, 154.5, 167.2 ppm. MS (70 eV): m/z (%): 280 (43) [M$^+$], 265 (97), 237 (100), 233 (24), 221 (15), 147 (18), 89 (31), 73 (50). HRMS (ESI$^+$): m/z [M+Na]$^+$ calculated for $C_{15}H_{24}O_3Si$ 280.1495, found 280.1487.

Methyl 4-phenyl-1-oxaspiro[5.5]undeca-2,4-diene-3-carboxylate (7j). Yield: 191.2 mg, 75%. Colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.39-1.46 (m, 1H), 1.51-1.58 (m, 3H), 1.64-1.71 (m, 4H), 1.93-2.01 (m, 2H), 3.56 (s, 3H), 5.22 (s, 1H), 7.17-7.19 (m, 2H), 7.26-7.32 (m, 3H), 7.64 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.5 (2C), 25.2, 35.5 (2C), 50.9, 80.5, 109.2, 122.3, 127.05 (2C), 127.14, 127.7 (2C), 133.1, 139.7, 156.2, 166.0 ppm. HRMS (ESI$^+$): m/z [M+Na]$^+$ calculated for $C_{18}H_{20}O_3$ 307.1310, found 307.1313.

Methyl 4-methyl-1-oxaspiro[5.5]undeca-2,4-diene-3-carboxylate (7k). Yield: 171.1 mg, 77%. Colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz): nearly 1:1 mixture of tautomers δ = 1.30-1.99 (m, 20H), 1.99 (s, 3H), 2.28 (s, 2H), 3.68 (s, 3H), 3.72 (s, 3H), 4.84 (s, 1H), 4.93 (s, 1H), 5.75 (s, 1H), 7.50 (s, 1H), 7.56 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.4, 21.4 (2C), 21.5 (2C), 25.2, 25.4, 34.6 (2C), 36.0 (2C), 41.8, 50.8, 51.0, 79.6, 80.0, 106.7, 108.6, 112.1, 120.0, 127.5, 131.1, 155.6, 155.9, 166.5, 166.7 ppm. HRMS (ESI$^+$): m/z [M+Na]$^+$ calculated for $C_{13}H_{18}O_3$ 245.1154, found 245.1152.

Methyl 1-oxaspiro[5.5]undeca-2,4-diene-3-carboxylate (7m). Yield: 123.9 mg, 68%. Colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.29-1.37 (m, 1H), 1.45-1.54 (m, 5H), 1.59-1.64 (m, 2H), 1.88-1.93 (m, 2H), 3.71 (s, 3H), 5.22 (d, 1H, ^3J(H,H) = 10.3 Hz), 6.24 (d, 1H, ^3J(H,H) = 10.3 Hz), 7.45 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.2 (2C), 25.1, 36.2 (2C), 51.1, 79.8, 106.9, 118.1, 122.2, 155.0, 166.3 ppm. HRMS (ESI$^+$): m/z [M+Na]$^+$ calculated for $C_{12}H_{16}O_3$ 231.0997, found 231.0997.

Methyl 2-butyl-4-methyl-2-phenyl-2*H*-pyran-5-carboxylate (7n). Yield: 98.5 mg, 86%. Colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.86 (t, 3H, ^3J(H,H) = 6.8 Hz), 1.26-1.28 (m, 4H), 1.89-1.93 (m, 2H), 2.08 (s, 3H), 3.66 (s, 3H), 5.27 (s, 1H), 7.33-7.38 (m, 5H), 7.61 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 13.9, 20.5, 22.8, 26.1, 42.2, 50.8, 84.0, 108.8, 118.8, 125.1 (2C), 127.3, 128.1 (2C), 128.5, 144.8, 156.0, 166.2 ppm. HRMS (ESI$^+$): m/z [M+Na]$^+$ calculated for $C_{18}H_{22}O_3$ 309.1467, found 309.1476.

Methyl 2,4-dimethyl-2-phenyl-2*H*-pyran-5-carboxylate (7o). Yield: 184.8 mg, 87%. Colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.70 (s, 3H), 2.08 (s, 3H), 3.67 (s, 3H), 5.24 (s, 1H), 7.26-7.29 (m, 1H), 7.32-7.36 (m, 2H), 7.42-7.44 (m, 2H), 7.58 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.3, 28.8, 50.8, 81.4, 108.7, 119.9, 125.0 (2C), 127.6, 127.8, 128.2 (2C), 145.1, 155.6, 166.1 ppm. HRMS (ESI$^+$): m/z [M+Na]$^+$ calculated for $C_{15}H_{16}O_3$ 267.0997, found 267.0999.

Methyl 4-tert-butyl-2-methyl-2-phenyl-2*H*-pyran-5-carboxylate (7p). Yield: 81.9 mg, 87%. Colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.25 (s, 9H), 1.68 (s, 3H), 3.65 (s, 3H), 5.43 (s, 1H), 7.24-7.27 (m, 1H), 7.30-7.34 (m, 3H), 7.42-7.34 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 28.8, 30.1 (3C), 34.5, 51.3, 80.6, 111.7, 118.7, 125.3 (2C), 127.5, 128.0 (2C), 141.1, 144.8, 154.6, 167.6 ppm. HRMS (ESI$^+$): m/z [M+Na]$^+$ calculated for $C_{18}H_{22}O_3$ 309.1467, found 309.1464.

Methyl 2-isopropyl-4-methyl-2-phenyl-2*H*-pyran-5-carboxylate (7s). Yield: 126.8 mg, 86%. Colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.85 (d, 3H, ^3J(H,H) = 6.8 Hz), 0.86 (d, 3H, ^3J(H,H) = 6.8 Hz), 2.08 (s, 3H), 2.13-2.20 (m, 1H), 3.63 (s, 3H), 5.33 (s, 1H), 7.23-7.35 (m, 5H), 7.62 (s, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 17.1, 17.2, 20.7, 38.5, 50.8, 86.7, 108.8, 116.8, 125.4 (2C), 127.2, 127.8 (2C), 128.9, 144.2, 156.3, 166.2 ppm. HRMS (ESI$^+$): m/z [M+Na]$^+$ calculated for $C_{17}H_{20}O_3$ 295.1310, found 295.1308.

Methyl 4-tert-butyl-2-isopropyl-2-phenyl-2*H*-pyran-5-carboxylate (7t). Yield: 24.0 mg, 93%. Colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.79 (d, 3H, ^3J(H,H) = 6.8 Hz), 0.90 (d, 3H, ^3J(H,H) = 6.8 Hz), 1.26 (s, 9H), 2.16-2.24 (m, 1H), 3.62 (s, 3H), 5.55 (s, 1H), 7.21-7.24 (m, 1H), 7.26-7.29 (m, 2H), 7.32-7.34 (m, 2H), 7.38 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 17.3, 17.6, 30.1 (3C), 34.8, 38.4, 51.2, 85.9, 111.5, 115.4, 125.9 (2C), 127.3, 127.6 (2C), 141.8, 143.5, 155.2, 167.6 ppm. HRMS (ESI$^+$): m/z [M+Na]$^+$ calculated for $C_{20}H_{26}O_3$ 337.1780, found 337.1780.

Dimethyl 2-isopropyl-2-phenyl-2*H*-pyran-4,5-dicarboxylate (7u). Yield: 86.1 mg, 86%. Colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.86 (d, 3H, ^3J(H,H) = 6.8 Hz), 0.90 (d, 3H, ^3J(H,H) = 6.8 Hz), 2.24-2.29 (m, 1H), 3.65 (s, 3H), 3.79 (s, 3H), 6.20 (s, 1H), 7.25-7.33 (m, 5H), 7.53 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 17.2, 17.3, 38.4, 51.4, 52.2, 86.9, 107.5, 125.0, 125.6 (2C), 127.4, 127.9, 128,1 (2C), 141.9, 155.6, 164.9, 166.8 ppm. HRMS (ESI$^+$): m/z [M+Na]$^+$ calculated for $C_{18}H_{20}O_5$ 339.1208, found 339.1208.

Methyl 5-(2,2,2-trifluoro-1-phenylethyl)-4-(trimethylsilyl)furan-3-carboxylate (14). Yield: 189.7 mg, 94%. Colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.35 (s, 9H), 3.80 (s, 3H), 4.95 (q, 1H, ^3J(F,H) = 9.3 Hz), 7.32-7.38 (m, 3H), 7.45-7.47 (m, 2H), 8.09 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 0.4 (3C), 49.0 (q, J(C,F) = 29 Hz), 51.4, 117.8, 124.9 (q, J(C,F) = 281 Hz), 123.6, 128.5, 128.8 (2C), 129.3 (2C), 132.9, 149.0, 153.4, 163.9 ppm. HRMS (ESI$^+$): m/z [M+Na]$^+$ calculated for $C_{17}H_{19}F_3O_3Si$ 379.0953, found 379.0950.

(2*E*,2'*E*)-Dimethyl 3,3'-(2,7-dimethylocta-3,5-diyne-2,7-diyl)bis(oxy)-diacrylate (15). White crystalline solid (it rearranges upon heating). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.60 (s, 12H), 3.70 (s, 6H), 5.40 (d, 2H, ^3J(H,H) = 12.1 Hz), 7.76 (d, 2H, ^3J(H,H) = 12.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 28.9 (4C), 51.1 (2C), 70.0 (2C), 75.1 (2C), 80.2 (2C), 100.3 (2C), 157.8 (2C), 168.0 (2C) ppm. HRMS (ESI$^+$): m/z [M+Na]$^+$ calculated for $C_{18}H_{22}O_6$ 357.1314, found 357.1317.

Dimethyl 2,2,2',2'-tetramethyl-2*H*,2'*H*-4,4'-bipyran-5,5'-dicarboxylate (16). Yield: 334 mg, 100%. White crystalline solid. Melting point = 148-149 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.41 (s, 12H), 3.60 (s, 6H), 4.98 (s, 2H), 7.41 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 27.7 (4C), 50.8 (2C), 78.7 (2C), 108.6 (2C), 121.1 (2C), 131.4 (2C), 154.2 (2C), 165.9 (2C) ppm. HRMS (ESI$^+$): m/z [M+Na]$^+$ calculated for $C_{18}H_{22}O_6$ 357.1314, found 357.1313.

Dimethyl [2,2'-binaphthalene]-3,3'-dicarboxylate (18).[¡Error! Marcador no definido.] A solution of dimer **16** (134.6 mg, 0.40 mmol), CsF (330 mg, 2.2 mmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**17**) (0.244 mL, 300 mg, 1 mmol) in acetonitrile (20 mL) was stirred for16 h at room temperature. The reaction mixture was quenched with water and extracted using CH_2Cl_2. After removing the solvent at reduced pressure, the crude product **18** was purified by flash column chromatography (silica gel, CH_2Cl_2/ EtOAc/ hexanes (30/4/66) (68 mg, 46%).

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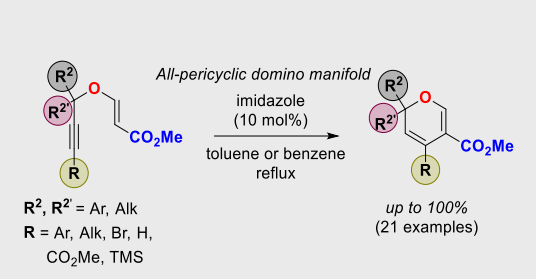

Simple and direct: an all-pericyclic domino manifold transforms propargyl vinyl ethers into 2H-pyrans**.**

Key Topic: Synthesis, heterocycles

David Tejedor, Samuel Delgado-Hernández, Raquel Diana-Rivero, Abián Díaz-Díaz, and Fernando García-Tellado

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A Domino Strategy for the Synthesis of 2H-Pyrans from Propargyl Vinyl Ethers