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A Robust and General Protocol for the Lewis-Base-Catalysed Reaction of Alcohols and Alkyl Propiolates

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A general and practical protocol for the tertiary-amine-catalysed synthesis of β-alkoxyacrylates from primary, secondary, and tertiary alcohols is described. Of the currently used catalysts, DABCO proved to be the best one for this process. Three factors seem to influence the outcome of the reaction: (1) the nucleophilic strength of the catalyst, (2) the electrophilicity of the intermediate ammonium acrylate, and (3) the pK_a/nucleophilicity of the alcohol/alkoxide nucleophile. Reactivity tuning enables the transformation of a range of tertiary alcohols into the corresponding β-alkoxyacrylate derivatives. Differences in the reactivity of different types of alcohol allow the selective transformation of diols containing two different hydroxy groups into the corresponding monoprotected derivatives. This protocol will aid other synthetic organic chemists to easily prepare such vinyl ethers under atom-economic, efficient, and bench-friendly reaction conditions.

Introduction

The Lewis-base-catalysed conjugate addition of alcohols to the activated triple bond of alkyl propynoates is a known reaction that leads to valuable β-alkoxyacrylates (Figure 1).[1] These derivatives have been widely used in modern organic chemistry, because they have an excellent reactivity profile for C–C bond-forming reactions by using carbon-centered radicals[2] (radical ring-closing reactions), or, in the case of propargyl or allyl derivatives, they are excellent substrates for [3,3]-sigmatropic rearrangements (useful, for example, in the synthesis of functionalized allenes).[3] During the last few years, our research group has frequently prepared such vinyl ethers, but we have almost exclusively started from secondary propargylic alcohols.[4] With this type of substrate, we, and others,[5] have sometimes used Et_3N as a catalyst to trigger the reaction and to obtain the desired products in high yields. Interestingly, we have observed in the laboratory and also found in a literature search that other types of alcohols are not efficiently transformed into the corresponding vinyl ethers by using Et_3N as the catalyst.[6] *N*-Methylmorpholine (NMM),[7] 1,4-diazabicyclo[2.2.2]octane (DABCO),[8] 4-(dimethylamino)-pyridine (DMAP),[9] quinuclidine,[10] Ph_3P,[11] Bu_3P,[12] and Me_3P[13] are other typical Lewis bases that appear in the literature. But we have not found a standard set of reaction conditions (nature and amount of the catalyst, solvent, concentration, and reaction time) with which the reaction outcome with a given alcohol would be predictable. In fact, the literature is full of inconsistencies in the reaction conditions, and this prevents the Lewis-base-catalysed conjugate addition of alcohols to the activated triple bond of alkyl propynoates from being a reliable and predictable methodology.[14] Probably the most common problem is that each

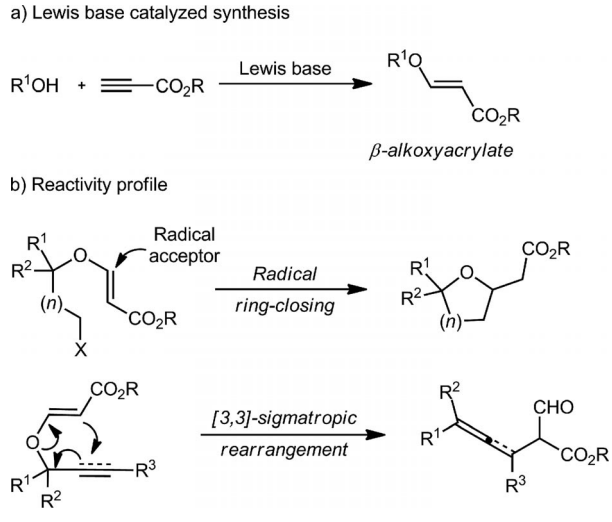

Figure 1. Lewis-base-catalysed synthesis of β-alkoxyacrylates, and their most common transformations.

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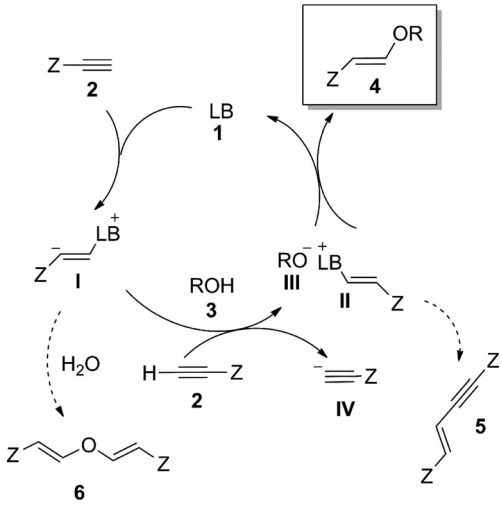
catalyst only works for a limited range of substrates,[15] and in particular, there are almost no examples in which tertiary alcohols participate in this reaction.[16] Thus, we decided to carry out a detailed study with the aim of finding standard reaction conditions for different types of alcohols.

Results and Discussion

Full understanding of a chemical process begins with a comprehensive knowledge of its reaction mechanism. Fortunately, experience gained over the years has helped to identify the most accepted mechanistic proposal for the Lewis-base-catalysed synthesis of β-alkoxyacrylates **4** and the two major by-products, **5** and **6** (Scheme 1). In this mechanism, the catalyst adds to the triple bond to form a zwitterion **I**, which is far more basic than the initial catalyst (i.e., the tertiary amine or phosphine). At this stage, trace amounts of water from the solvent or from the reactants will routinely produce trace amounts of compound **6**, so anhydrous reaction conditions are essential. In the presence of an alcohol **3**, an alkoxide **III** or an acetylide **IV** will form, depending on the relative acidities of the alcohol and the starting alkynoate. The outcome of the reaction will be determined by the amounts of alkoxide **III** or acetylide **IV** formed and by the relative reaction rates of their nucleophilic addition to cationic intermediate **II** (typically a β-ammonioacrylate derivative). This explains why it is very rare for tertiary alcohols to undergo this reaction. It should also be pointed out that the stereochemistry of the double bonds formed is predominantly or exclusively (*E*).

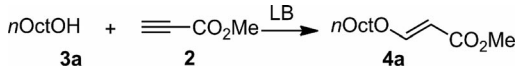


Scheme 1. Accepted mechanistic proposal for the synthesis of β-alkoxyacrylates **4**. Dashed arrows represent the established routes to the observed by-products. LB = Lewis base; Z = electron-withdrawing group.

Based on this information, we began our search to find the best set of reaction conditions for each general type of alcohols (primary, secondary, and tertiary).[17] To make a fair comparative study, three alcohols without any additional functionalities were chosen: 1-octanol, cyclohexanol, and 1-adamantanol. Additionally, five representative Lewis bases with somewhat different nucleophilic and basic characteristics were studied: DABCO, DMAP, Et_3N, NMM, and Bu_3P. The reactions were carried out in dichloromethane (0.4 M) at room temperature.

Considering 1-octanol, the model for primary alcohols (Table 1), we first compared each catalyst under similar reaction conditions (Table 1, Entries 1–5). After a standardized time of 2 h, and by using 20 mol-% of each catalyst, the reactions with DABCO, Bu_3P, and Et_3N had reached completion, although with Et_3N, poor yields of the desired product were observed due to undesired side-reactions (mainly transesterification).[6a] With DABCO, the excess methyl propiolate completely dimerized (to give **5**), while in the case of Bu_3P, the excess apparently polymerized into a dark material. DMAP was the least efficient nucleophile. In the case of NMM, when larger amounts of the catalyst (50 mol-%) and/or longer reaction times were used, nearly quantitative yields of **4a** were observed (Table 1, Entries 9 and 10). The most convenient results were obtained with DABCO (10 mol-%) in less than 1 h, and with only a small excess of methyl propiolate (1.1 equiv.; Table 1, Entry 7). The validity of the proposed protocol was confirmed with a wide range of primary alcohols (Figure 2). Different vinyl ethers **4a**–**4k** were synthesized in excellent yields, and no by-products were detected other than trace amounts of compounds **5** and **6**. The high tolerance for functional groups in the alcohol substrate should be highlighted (i.e., alkynes, alkenes, aromatic rings, halogens, esters or ketones). The double bond was formed as the (*E*) isomer exclusively in all cases except for **4d**, **4h**, and **4i**, where small amounts of the (*Z*) isomers were observed.

Table 1. Reaction of 1-octanol and methyl propiolate.



Entry	Lewis base	[mol-%]	*t* [h]	**2** [equiv.]	Yield of **4a** [%][a]
1	DABCO	20	2	1.5	(100)
2	DMAP	20	2	1.5	(26)[b]
3	Et_3N	20	2	1.5	(38)
4	NMM	20	2	1.5	(85)[b]
5	Bu_3P	20	2	1.5	(100)
6	DABCO	10	1	1.3	99 (100)
7	DABCO	10	1	1.1	98 (100)
8	NMM	10	4	1.1	(91)[b]
9	NMM	10	16	1.1	(96)
10	NMM	50	4	1.3	(97)

[a] Isolated yields without parentheses. NMR yields by using $Me_3SiSiMe_3$ as internal standard in parentheses. [b] Incomplete reaction (unreacted alcohol remained).

Similarly, considering cyclohexanol as the model for secondary alcohols (Table 2), we again compared each catalyst under similar reaction conditions (Table 2, Entries 1–5). It soon became evident that the reduced acidity of the alcohol or the reduced nucleophilicity of the corresponding alkoxide had an important effect on the reaction outcome. Only DABCO was capable of producing the desired product in high yield after 2 h with a 20 mol-% catalyst loading.

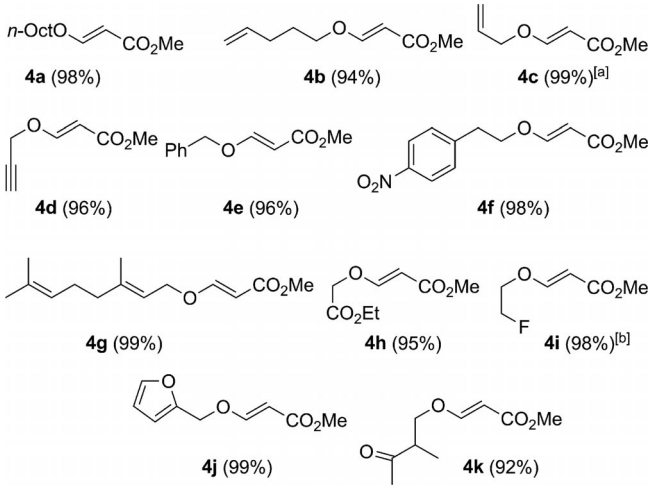
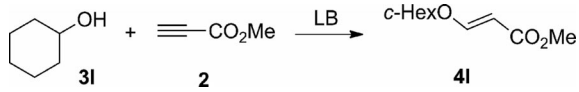


Figure 2. Synthesis of β-alkoxyacrylates **4** from primary alcohols. Yields of isolated products. [a] NMR yield (relatively low boiling point). [b] Includes 7% yield of the (*Z*) isomer.

As previously reported by Inanaga et al. for a secondary alcohol,[12a] Bu_3P was no longer an efficient catalyst. NMM gave good yields of **4l** only when it was used in larger amounts (50 mol-%) and with longer reaction times (Table 2, Entries 9 and 10), which is consistent with typical reaction protocols found in the literature. Once again, the most convenient results in our opinion were obtained with DABCO (10 mol-%), which gave the product (i.e., **4l**) in less than 1 h, with only a small excess of methyl propiolate (Table 2, Entry 6). The slightly lower yields obtained with cyclohexanol can be explained by the formation of a higher amount of dimer **5** (acetylide **IV** vs. alkoxide **III**).

Table 2. Reaction of cyclohexanol and methyl propiolate.



3l 2 4l

Entry	Lewis base	[mol-%]	*t* [h]	**2** [equiv.]	Yield of **4l** [%][a]
1	DABCO	20	2	1.5	(90)
2	DMAP	20	2	1.5	(< 5)[b]
3	Et_3N	20	2	1.5	(20)
4	NMM	20	2	1.5	(49)[b]
5	Bu_3P	20	2	1.5	(27)[b]
6	DABCO	10	1	1.3	94 (95)
7	DABCO	10	1	1.1	(92)
8	NMM	10	16	1.1	(78)[b]
9	NMM	25	16	1.1	(91)
10	NMM	50	4	1.3	(94)

[a] Isolated yields without parentheses. NMR yields by using $Me_3SiSiMe_3$ as internal standard in parentheses. [b] Incomplete reaction (unreacted alcohol remained).

Again, the validity of the protocol was confirmed with a diverse set of secondary alcohols (Figure 3). Thirteen different vinyl ethers **4l**–**4x** were synthesized in good to excellent yields ranging from 80 to 98%. As expected, the main by-product was compound **5**, but the fact that the yields of the desired products sometimes dropped below a desirable value (<80% for **4m**, **4o**, **4w**, and **4x**) urged us to devise a small change in the reaction protocol to increase these yields. The slow dropwise addition (over a 25 min period) of the methyl propiolate to a solution containing both the alcohol and the catalyst was sufficient to significantly increase the yields (Method B).

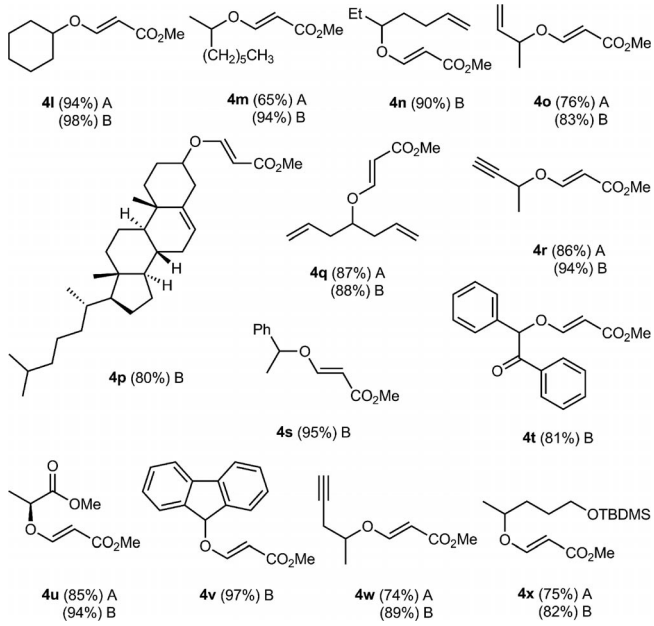
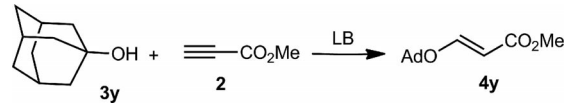


Figure 3. Synthesis of β-alkoxyacrylates **4** from secondary alcohols. Yields of isolated products from Methods A and B.

We decided to test whether a tertiary alcohol such as 1-adamantanol would be able to provide the desired vinyl ether. As expected, we could not find a set of reaction conditions that resulted in the formation of the desired product. Neither the previously screened reaction conditions (Table 3) nor other solvents, different reaction times, or different catalyst loadings were successful. It appears that the acidity of 1-adamantanol and/or the nucleophilicity of the corresponding tertiary alkoxide are not sufficient that vinyl ether formation can compete with the formation of dimer **5** (Scheme 1). Methyl propiolate dimerizes to give **5** at a rate that depends on the catalyst (it polymerizes in the presence of Bu_3P).

Table 3. Reaction of 1-adamantanol and methyl propiolate.



3y 2 4y

Entry	Lewis base	[mol-%]	*t* [h]	**2** [equiv.]	Yield of **4y** [%]
1	DABCO	20	2	1.5	n.o.r.[a]
2	DMAP	20	2	1.5	n.o.r.
3	Et_3N	20	2	1.5	n.o.r.
4	NMM	20	2	1.5	n.o.r.
5	Bu_3P	20	2	1.5	n.o.r.

[a] n.o.r. = no observed reaction.

Based on the experience gained with primary and secondary alcohols, and on our previous report,[16b] our next goal was to find out which functionalities, when appended

to a tertiary alcohol, would allow it to participate in the reaction to form the corresponding vinyl ethers. Since an alkynyl substituent is known to increase the acidity of an alcohol by about 2 pK_a units,[18] propargylic alcohol **3z** was chosen to test whether significantly lowering the pK_a would enable the reaction. Gratifyingly, when the reaction was carried out under the reaction conditions shown in Table 3 by using DABCO (10 mol-%), the desired propargyl vinyl ether (i.e., **4z**) was formed in 48% yield (52% unreacted starting alcohol, and quantitative formation of dimer **5** from the remaining methyl propiolate). Again, to increase the effective concentration of alkoxide **III**, while maintaining a lower concentration of acetylide **IV** (and thus decrease the competitive formation of **5**), a change in the protocol was devised so that methyl propiolate could be introduced last by slow dropwise addition (over 25 min). This simple change in the reaction protocol allowed us to obtain **4z** in an excellent 93% yield. All the propargylic alcohols studied followed the same pattern to deliver the corresponding propargyl vinyl ethers in excellent yields (Figure 4). The slow-addition protocol was needed to synthesize **4z** and **4aa** in 93% isolated yield in each case, but propargyl vinyl ethers **4ab** and **4ac** were formed in quantitative yields without changing to the slow-addition protocol. This proves that an additional functionality that is capable of increasing the acidity of the tertiary alcohol aids the formation of the desired products (i.e., **4**) over formation of dimer **5**.

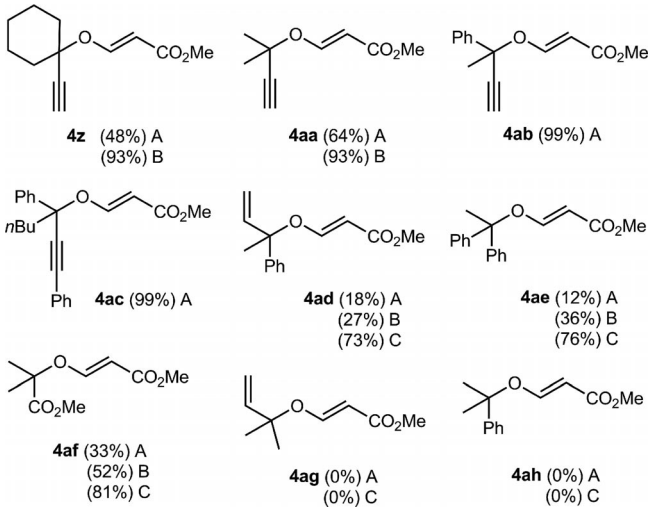
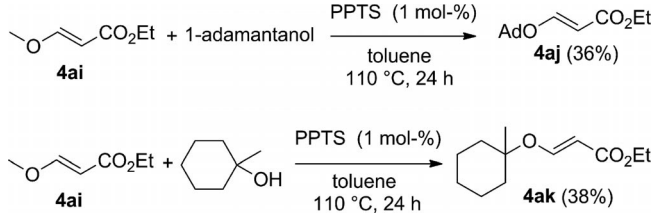


Figure 4. Synthesis of β-alkoxyacrylates **4** from tertiary alcohols. Yields of isolated products from Methods A, B, and C.

Next, we studied other common functionalities that are known to increase the acidity of an alcohol, albeit to a lesser extent (i.e., alkenyl, phenyl, and ester groups). 2-Methylbut-3-en-2-ol (**3ag**) and 2-phenylpropan-2-ol (**3ah**) did not give the desired vinyl ethers under any of the reaction conditions tested, due to their relatively low acidity. On the other hand, 2-phenylbut-3-en-2-ol (**3ad**), 1,1-diphenylethanol (**3ae**) and methyl 2-hydroxy-2-methylpropanoate (**3af**) gave the corresponding products with modest yields, even when the revised protocol (Method B) was used. Importantly, the yield based on alcohol consumed was 100%, since the only other by-product detected was **5**, and this compound was formed from methyl propiolate and not the alcohol.

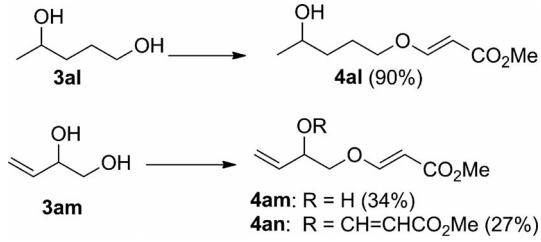
Because acidity and nucleophilicity are solvent-dependent properties, we reasoned that the relative acidities and nucleophilicities of methyl propiolate and the alcohols (and the corresponding alkoxides) studied would vary in different solvents. After a screening of a diverse set of solvents (see Supporting Information, Table S1), we arrived at the conclusion that solvents with a low dielectric constant favoured the formation of the desired products. Thus, we were able to increase the yields of products **4ad**, **4ae**, and **4af** by using a new revised protocol in which methyl propiolate (2 equiv.) was added slowly to a solution of the selected alcohol and DABCO in hexane (Method C). It should be noted that the positive effect resulting from the use of hexane as solvent did not extend to allow effective formation of products **4ag** and **4ah** from less acidic alcohols.

In view of the fact that we were not able to prepare the enol ether from 1-adamantanol and methyl propiolate, we attempted the acid-catalysed transetherification conditions reported by Kozmin et al.[19] from a secondary alcohol and ethyl (*E*)-3-methoxyacrylate (**4ai**; Scheme 2). Under these conditions, products **4aj** and **4ak** could be synthesized from the corresponding alcohols, albeit in modest yields (the reactions were not optimized). In both cases, the reaction products were isolated along with the unreacted tertiary alcohols.



Scheme 2. Acid-catalysed transetherification of tertiary alcohols with ethyl (*E*)-3-methoxyacrylate (**4ai**).[19]

Finally, we were interested in finding out what kind of selectivity we could obtain from the reaction of diols containing two different hydroxy groups (Scheme 3). Not surprisingly, diol **3al**, bearing a primary and a secondary hydroxy group and without any additional functionalities, was converted almost exclusively into monovinyl ether **4al** in 90% yield. On the other hand, diol **3am**, which contains



Scheme 3. Selective protection of diols. Reaction conditions: diol (2.0 mmol), methyl propiolate (2.2 mmol), DABCO (0.2 mmol), CH_2Cl_2, room temp., 1 h.

a primary hydroxy group and a secondary allylic hydroxy group, gave a mixture of the monoprotected **4am** (34%) and diprotected **4an** (27%).

Conclusions

We have identified efficient, atom-economical, and practical reaction conditions for the synthesis of β-alkoxyacrylates **4** from primary, secondary, and tertiary alcohols. In all cases, DABCO (10 mol-%) is the best catalyst for the process; other nucleophiles do not offer significant advantages over the reaction conditions reported in this manuscript. Additionally, despite being reported in some cases in the literature, aqueous quenching of the reactions or time-consuming workup procedures are not necessary (see Experimental Section). Finally, we have identified the three factors that seem to influence the outcome of the reaction: (1) nucleophilic strength of the catalyst, (2) electrophilicity of the ammonioacrylate **II**, and (3) pK_a or nucleophilicity of the alcohol or alkoxide. Our understanding of the process has allowed us to identify tertiary alcohols that react to form the desired β-alkoxyacrylate products, and to explain the outcome of the reaction of diols containing two different hydroxy groups. We hope that our results will aid other synthetic organic chemists to easily prepare such vinyl ethers under economic and bench-friendly reaction conditions.[20]

Experimental Section

Compounds **4a**,[21] **4c**,[22] **4d**,[23] **4e**,[21] **4l**,[24] **4p**,[12a] **4q**,[19] **4r**,[4a] and **4s**[21] have been reported previously, and all data were consistent with those published in the literature.

Representative Procedure for the Synthesis of Vinyl Ethers 4a–4k from Primary Alcohols: See Figure 2. DABCO (0.20 mmol) was added to a solution of 1-octanol (**3a**; 2.0 mmol) and methyl propiolate (**2**; 2.2 mmol) in dry CH_2Cl_2 (5 mL). The reaction mixture was stirred for 1 h or less (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) to give **4a** (98%).

Methyl (*E*)-3-(Pent-4-en-1-yloxy)acrylate (4b): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.79 (m, 2 H), 2.15 (m, 2 H), 3.68 (s, 3 H), 3.84 (m, 2 H), 5.02 (m, 2 H), 5.19 (d, $^3J_{H,H}$ = 12.6 Hz, 1 H), 5.79 (m, 1 H), 7.58 (d, $^3J_{H,H}$ = 12.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.9, 29.7, 50.9, 70.3, 96.1, 115.6, 137.1, 162.6, 168.2 ppm. MS (70 eV): *m*/*z* (%) = 170 (7) $[M]^+$, 139 (38), 84 (100), 69 (81), 68 (52). HRMS: calcd. for $C_9H_{14}O_3$ 170.0943; found 170.0942.

Methyl (*E*)-3-[2-(4-Nitrophenyl)ethoxy]acrylate (4f): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.11 (t, $^3J_{H,H}$ = 6.4 Hz, 2 H), 3.68 (s, 3 H), 4.08 (t, $^3J_{H,H}$ = 6.4 Hz, 2 H), 5.20 (d, $^3J_{H,H}$ = 12.6 Hz, 1 H), 7.38 (d, $^3J_{H,H}$ = 8.6 Hz, 2 H), 7.54 (d, $^3J_{H,H}$ = 12.6 Hz, 1 H), 8.11 (d, $^3J_{H,H}$ = 8.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.1, 51.1, 70.3, 96.9, 123.8 (2 C), 129.8 (2 C), 145.1, 161.7, 167.8 ppm. MS (70 eV): *m*/*z* (%) = 251 (2) $[M]^+$, 150 (100), 104 (39), 92 (22). HRMS: calcd. for $C_{12}H_{13}NO_5$ 251.0794; found 251.0789.

Methyl (*E*)-3-{[(E)-3,7-Dimethylocta-2,6-dien-1-yl]oxy}acrylate (4g): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.58 (s, 3 H), 1.66 (s, 3 H), 1.68 (s, 3 H), 2.09 (m, 4 H), 3.68 (s, 3 H), 4.38 (m, 2 H), 5.05 (m, 1 H), 5.20 (d, $^3J_{H,H}$ = 12.6 Hz, 1 H), 5.36 (m, 1 H), 7.59 (d, $^3J_{H,H}$ = 12.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.6, 17.7, 25.6, 26.2, 39.5, 51.0, 67.7, 96.4, 117.9, 123.6, 131.9, 143.1, 162.4, 168.3 ppm. MS (70 eV): *m*/*z* (%) = 238 (1) $[M]^+$, 137 (45), 81 (35), 69 (100), 68 (11). HRMS: calcd. for $C_{14}H_{22}O_3$ 238.1569; found 238.1566.

Methyl (*E*)-3-(2-Ethoxy-2-oxoethoxy)acrylate (4h): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.29 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H), 3.69 (s, 3 H), 4.25 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H), 4.42 (s, 2 H), 5.24 (d, $^3J_{H,H}$ = 12.6 Hz, 1 H), 7.54 (d, $^3J_{H,H}$ = 12.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 51.2, 61.7, 67.2, 98.1, 161.2, 167.2, 167.4 ppm. MS (70 eV): *m*/*z* (%) = 188 (8) $[M]^+$, 157 (100), 115 (77), 84 (52), 71 (53), 59 (82), 55 (52). HRMS: calcd. for $C_8H_{12}O_5$ 188.0657; found 188.0681.

Methyl (*E*)-3-(2-Fluoroethoxy)acrylate (4i): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.69 (d, $^3J_{H,H}$ = 14 Hz, 3 H), 4.03 (m, 1 H), 4.1 (m, 1 H), 4.88 (m, 1 H), 4.72 (m, 1 H) 5.25 (d, $^3J_{H,H}$ = 12.6 Hz, 1 H), 7.59 (d, $^3J_{H,H}$ = 12.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.1, 69.8 (d, $^2J_{F,C}$ = 20 Hz), 81.2, (d, $^1J_{F,C}$ = 171 Hz), 97.2, 161.9, 167.7 ppm. MS (70 eV): *m*/*z* (%) = 148 (18) $[M]^+$, 117 (100), 71 (96), 58 (17). HRMS: calcd. for $C_6H_9O_3F$ 148.0536; found 148.0540.

Methyl (*E*)-3-(Furan-2-ylmethoxy)acrylate (4j): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.69 (s, 3 H), 4.83 (s, 2 H), 5.33 (d, $^3J_{H,H}$ = 12.6 Hz, 1 H), 6.37 (m, 1 H), 6.43 (m, 1 H), 7.44 (m, 1 H), 7.62 (d, $^3J_{H,H}$ = 12.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.1, 64.9, 97.5, 110.6, 110.9, 143.7, 148.7, 161.6, 167.9 ppm. MS (70 eV): *m*/*z* (%) = 182 (2) $[M]^+$, 161 (24), 81 (100), 53 (79). HRMS: calcd. for $C_9H_{10}O_4$ 182.0579; found 182.0583.

Methyl (*E*)-3-(2-Methyl-3-oxobutoxy)acrylate (4k): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16 (d, $^3J_{H,H}$ = 7.2 Hz, 3 H), 2.19 (s, 3 H), 2.93 (m, 1 H), 3.69 (s, 3 H), 3.81 (m, 1 H), 4.03 (m, 1 H), 5.21 (d, $^3J_{H,H}$ = 12.6 Hz, 1 H), 7.54 (d, $^3J_{H,H}$ = 12.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.3, 28.8, 46.1, 51.1, 71.9, 96.8, 162.0, 167.9, 208.9 ppm. MS (70 eV): *m*/*z* (%) = 186 (2) $[M]^+$, 155 (20), 102 (63), 85 (100), 71 (62). HRMS: calcd. for $C_9H_{14}O_4$ 186.0919; found 186.0917.

Representative Procedure for the Synthesis of Vinyl Ethers 4l–4x from Secondary Alcohols: See Figure 3, Method B. Methyl propiolate (**2**; 2.6 mmol) was added portionwise (in six portions, one portion every 5 min) to a solution of cyclohexanol (**3l**; 2.0 mmol) and DABCO (0.20 mmol) in dry CH_2Cl_2 (5 mL). The reaction mixture was stirred for 1 h or less (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) to give **4l** (94%).

Methyl (*E*)-3-(Oct-2-yloxy)acrylate (4m): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H), 1.20–1.42 (m, 11 H), 1.45–1.69 (m, 2 H), 3.68 (s, 3 H), 3.98–4.07 (m, 1 H), 5.22 (d, $^3J_{H,H}$ = 12.4 Hz, 1 H), 7.52 (d, $^3J_{H,H}$ = 12.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 20.0, 22.5, 25.2, 29.1, 31.7, 36.2, 50.9, 79.9, 96.6, 162.2, 168.6 ppm. MS (70 eV): *m*/*z* (%) = 214 (1.4) $[M]^+$, 183 (4.0), 112 (24), 103 (84), 83 (17), 71 (76), 70 (27), 57 (100). HRMS: calcd. for $C_{12}H_{22}O_3$ 214.1569; found 214.1575.

Methyl (*E*)-3-(Hept-6-en-3-yloxy)acrylate (4n): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H), 1.55–1.75 (m, 4 H), 1.99–2.18 (m, 4 H), 3.66 (s, 3 H), 3.77–3.87 (m, 1 H), 4.93–5.04 (m, 2 H), 5.22 (d, $^3J_{H,H}$ = 12.4 Hz, 1 H), 5.68–5.81 (m,

1 H), 7.50 (d, $^3J_{H,H}$ = 12.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.3, 27.2, 29.3, 32.9, 50.9, 84.8, 96.5, 115.4, 137.4, 162.9, 168.6 ppm. MS (70 eV): *m/z* (%) = 198 (0.1) $[M]^+$, 121 (2.5), 97 (11), 81 (12), 71 (15), 55 (100). HRMS: calcd. for $C_{11}H_{18}O_3$ 198.1256; found 198.1247.

Methyl (*E*)-3-(But-3-en-2-yloxy)acrylate (4o): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.37 (d, $^3J_{H,H}$ = 6.4 Hz, 3 H), 3.67 (s, 3 H), 4.43–4.51 (m, 1 H), 5.20–5.28 (m, 3 H), 5.75–5.85 (m, 1 H), 7.50 (d, $^3J_{H,H}$ = 12.5 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.6, 50.9, 79.6, 97.6, 117.1, 137.5, 161.3, 168.3 ppm. MS (70 eV): *m/z* (%) = 156 (5.6) $[M]^+$, 127 (5.9), 102 (14), 84 (9.3), 71 (21), 55 (100). HRMS: calcd. for $C_8H_{12}O_3$ 156.0786; found 156.0786.

Methyl (*E*)-3-({(8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-[(*R*)-6-methylhept-2-yl]-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl}oxy)acrylate (4p): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.67 (s, 3 H), 0.85 (d, $^3J_{H,H}$ = 6.6 Hz, 6 H), 0.91 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H), 0.92–2.06 (m, 29 H), 2.31–2.42 (m, 2 H), 3.68 (s, 3 H), 3.73–3.83 (m, 1 H), 5.25 (d, $^3J_{H,H}$ = 12.4 Hz, 1 H), 5.36–5.40 (m, 1 H), 7.54 (d, $^3J_{H,H}$ = 12.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.9, 18.7, 19.3, 21.1, 22.6, 22.8, 23.8, 24.3, 28.0, 28.15, 28.21, 31.8, 31.9, 35.8, 36.2, 36.6, 36.9, 38.5, 39.5, 39.7, 42.3, 50.1, 51.0, 56.2, 56.7, 82.3, 97.0, 123.0, 139.3, 161.6, 168.5 ppm.

Methyl (*E*)-3-(2-Oxo-1,2-diphenylethoxy)acrylate (4t): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.63 (s, 3 H), 5.33 (d, $^3J_{H,H}$ = 12.6 Hz, 1 H), 6.21 (s, 1 H), 7.29–7.55 (m, 8 H), 7.63 (d, $^3J_{H,H}$ = 12.6 Hz, 1 H), 7.92 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.2, 84.5, 99.0, 127.8 (2 C), 128.8 (2 C), 129.0 (2 C), 129.2 (2 C), 129.5, 133.7, 133.9, 134.1, 160.4, 167.6, 193.5 ppm. MS (70 eV): *m/z* (%) = 380 (1.4) $[M]^+$, 195 (19), 191 (52), 167 (30), 165 (56), 131 (19), 105 (100), 77 (25). HRMS: calcd. for $C_{18}H_{16}O_4$ 296.1049; found 296.1053.

Methyl (*S*,*E*)-3-[(1-Methoxy-1-oxoprop-2-yl)oxy]acrylate (4u): $[\alpha]_D^{25}$ = –77.3 (*c* = 1.0, acetone). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.52 (d, $^3J_{H,H}$ = 6.8 Hz, 3 H), 3.65 (s, 3 H), 3.75 (s, 3 H), 4.44–4.53 (m, 1 H), 5.22 (d, $^3J_{H,H}$ = 12.6 Hz, 1 H), 7.46 (d, $^3J_{H,H}$ = 12.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.8, 51.1, 52.5, 75.4, 98.2, 160.7, 167.6, 170.7 ppm. MS (70 eV): *m/z* (%) = 188 (17) $[M]^+$, 157 (41), 156 (40), 129 (80), 87 (54), 85 (43), 71 (52), 69 (29), 59 (100). HRMS: calcd. for $C_8H_{12}O_5$ 188.0685; found 188.0685.

Methyl (*E*)-3-[(9*H*-Fluoren-9-yl)oxy]acrylate (4v): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.64 (s, 3 H), 5.47 (d, $^3J_{H,H}$ = 12.3 Hz, 1 H), 5.94 (s, 1 H), 7.28–7.35 (m, 2 H), 7.40–7.47 (m, 3 H), 7.55 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H),7.67 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.1, 82.7, 99.4, 120.3 (2 C), 125.5 (2 C), 128.1 (2 C), 130.0 (2 C), 140.9 (2 C), 141.1 (2 C), 160.8, 168.0 ppm. MS (70 eV): *m/z* (%) = 266 (1.2) $[M]^+$, 166 (30), 165 (100), 163 (11), 139 (5.1), 115 (2.9). HRMS: calcd. for $C_{17}H_{14}O_3$ 266.0943; found 266.0942.

Methyl (*E*)-3-(Pent-4-yn-2-yloxy)acrylate (4w): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.38 (d, $^3J_{H,H}$ = 6.2 Hz, 3 H), 2.04 (s, 1 H), 2.39–2.57 (m, 2 H), 3.68 (s, 3 H), 4.14–4.23 (m, 1 H), 5.26 (d, $^3J_{H,H}$ = 12.5 Hz, 1 H), 7.51 (d, $^3J_{H,H}$ = 12.5 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.3, 26.0, 51.1, 71.1, 77.2, 79.2, 97.6, 161.3, 168.2 ppm. MS (70 eV): *m/z* (%) = 167 (19) $[M – 1]^+$, 139 (24), 137 (40), 129 (24), 124 (22), 109 (37), 103 (28), 102 (35), 71 (100), 67 (89), 66 (57), 65 (50). HRMS: calcd. for $C_9H_{11}O_3$ 167.0708; found 167.0705.

Methyl (*E*)-3-({5-[(*tert*-Butyldimethylsilyl)oxy]pent-2-yl}oxy)-acrylate (4x): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.02 (s, 6 H), 0.87 (s, 9 H), 1.25 (d, $^3J_{H,H}$ = 6.2 Hz, 3 H), 1.45–1.71 (m, 4 H), 3.59 (t, $^3J_{H,H}$ = 5.8 Hz, 3 H), 3.66 (s, 3 H), 4.02–4.11 (m, 1 H), 5.21 (d, $^3J_{H,H}$ = 12.5 Hz, 1 H), 7.51 (d, $^3J_{H,H}$ = 12.5 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = –5.4, 18.3, 20.0, 25.9, 28.4, 32.7, 50.9, 62.6, 79.6, 96.8, 162.1, 168.5 ppm. MS (70 eV): *m/z* (%) = 245 (5.8) $[M – 57]^+$, 201 (5.9), 160 (12), 159 (100), 143 (10), 89 (27), 75 (33), 69 (53). HRMS: calcd. for $C_{11}H_{21}O_4Si$ 245.1209; found 245.1204.

Representative Procedure for the Synthesis of Vinyl Ethers 4z–4af from Tertiary Alcohols: See Figure 4, Method C. Methyl propiolate (**2**; 4.0 mmol) was added portionwise (in six portions, one portion every 5 min) to a solution of 2-phenylbut-3-en-2-ol (**3ad**; 2.0 mmol) and DABCO (0.20 mmol) in dry hexanes (5 mL). The reaction mixture was stirred for 1 h or less (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) to give **4ad** (73%).

Methyl (*E*)-3-(1-Ethynylcyclohexyloxy)acrylate (4z): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28–1.35 (m, 1 H), 1.48–1.59 (m, 3 H), 1.62–1.74 (m, 4 H), 1.90–1.95 (m, 2 H), 2.65 (s, 1 H), 3.67 (s, 3 H), 5.38 (d, $^3J_{H,H}$ = 12.1 Hz, 1 H), 7.88 (d, $^3J_{H,H}$ = 12.1 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.3 (2 C), 24.7, 37.5 (2 C), 50.9, 76.4, 78.2, 82.9, 99.5, 158.1, 168.2 ppm. MS (70 eV): *m/z* (%) = 208 (1.3) $[M]^+$, 179 (2.8), 149 (7.4), 107 (56), 106 (35), 91 (61), 79 (100), 67 (44). HRMS: calcd. for $C_{12}H_{16}O_3$ 208.1099; found 208.1102.

Methyl (*E*)-3-(2-Methylbut-3-yn-2-yloxy)acrylate (4aa): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.55 (s, 6 H), 2.61 (s, 1 H), 3.66 (s, 3 H), 5.35 (d, $^3J_{H,H}$ = 12.1 Hz, 1 H), 7.83 (d, $^3J_{H,H}$ = 12.1 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.1 (2 C), 50.9, 74.8, 75.0, 83.6, 99.7, 158.2, 168.0 ppm. MS (70 eV): *m/z* (%) = 168 (2.0) $[M]^+$, 109 (23), 71 (35), 67 (100), 65 (27). HRMS: calcd. for $C_9H_{12}O_3$ 168.0786; found 168.0783.

Methyl (*E*)-3-(2-Phenylbut-3-yn-2-yloxy)acrylate (4ab): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.86 (s, 3 H), 2.87 (s, 1 H), 3.63 (s, 3 H), 5.43 (d, $^3J_{H,H}$ = 12.2 Hz, 1 H), 7.30–7.40 (m, 3 H), 7.52–7.55 (m, 2 H), 7.60 (d, $^3J_{H,H}$ = 12.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 32.2, 51.0, 77.4, 79.5, 82.4, 100.4, 125.8 (2 C), 128.6, 128.7 (2 C), 141.1, 158.8, 167.9 ppm. MS (70 eV): *m/z* (%) = 230 (1.3) $[M]^+$, 129 (100), 128 (45), 127 (18), 51 (13). HRMS: calcd. for $C_9H_{12}O_3$ 230.0943; found 230.0953.

Methyl (*E*)-3-(1,3-Diphenylhept-1-yn-3-yloxy)acrylate (4ac): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H), 1.28–1.35 (m, 3 H), 1.50–1.62 (m, 1 H), 1.99–2.06 (m, 1 H), 2.17–2.23 (m, 1 H), 3.62 (s, 3 H), 5.47 (d, $^3J_{H,H}$ = 12.1 Hz, 1 H), 7.33–7.41 (m, 6 H), 7.53–7.57 (m, 4 H), 7.72 (d, $^3J_{H,H}$ = 12.1 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 22.5, 26.7, 44.5, 50.9, 84.1, 86.9, 90.2, 100.0, 121.8, 126.4 (2 C), 128.40 (2 C), 128.43, 128.52 (2 C), 129.1, 132.0 (2 C), 141.1, 159.4, 168.0 ppm. MS (70 eV): *m/z* (%) = 348 (2.6) $[M]^+$, 291 (100), 273 (25), 247 (53), 231 (17), 217 (29), 202 (34), 191 (35), 115 (25), 91 (34). HRMS: calcd. for $C_{23}H_{24}O_3$ 348.1725; found 348.1713.

Methyl (*E*)-3-(2-Phenylbut-3-en-2-yloxy)acrylate (4ad): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.74 (s, 3 H), 3.64 (s, 3 H), 5.33–5.38 (m, 2 H), 5.46 (d, $^3J_{H,H}$ = 12.1 Hz, 1 H), 6.08 (dd, $^3J_{H,H}$ = 17.2 and 10.9 Hz, 1 H), 7.27–7.32 (m, 1 H), 7.33–7.39 (m, 4 H), 7.50 (d, $^3J_{H,H}$ = 12.1 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.1, 50.9, 84.6, 99.3, 116.6, 126.0 (2 C), 127.9, 128.5 (2 C), 140.6, 142.4, 158.7, 168.2 ppm. MS (70 eV): *m/z* (%) = 232 (7.1) $[M]^+$, 131 (100), 129 (56), 118 (53), 115 (48), 105 (59), 91 (42), 77 (46). HRMS: calcd. for $C_{14}H_{16}O_3$ 232.1099; found 232.1105.

Methyl (*E*)-3-(1,1-Diphenylethoxy)acrylate (4ae): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.02 (s, 3 H), 3.62 (s, 3 H), 5.53 (d, $^3J_{H,H}$

= 12.1 Hz, 1 H), 7.26–7.36 (m, 10 H), 7.42 (d, $^3J_{H,H}$ = 12.1 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.7, 50.9, 86.1, 99.9, 126.6 (4 C), 127.9 (2 C), 128.3, 128.4 (4 C), 144.2, 158.5, 168.1 ppm. MS (70 eV): *m/z* (%) = 282 (0.04) $[M]^+$, 182 (20), 181 (100), 166 (18), 165 (31), 103 (33), 77 (16). HRMS: calcd. for $C_{18}H_{18}O_3$ 282.1256; found 282.1262.

Methyl (*E*)-3-(1-Methoxy-2-methyl-1-oxoprop-2-yloxy)acrylate (4af): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.55 (s, 6 H), 3.66 (s, 3 H), 3.75 (s, 3 H), 5.37 (d, $^3J_{H,H}$ = 12.1 Hz, 1 H), 7.49 (d, $^3J_{H,H}$ = 12.1 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.0 (2 C), 51.0, 52.7, 81.1, 99.8, 158.1, 168.0, 172.8 ppm. MS (70 eV): *m/z* (%) = 202 (14) $[M]^+$, 171 (9.1), 143 (41), 101 (100), 73 (36), 69 (18). HRMS: calcd. for $C_9H_{14}O_5$ 202.0841; found 202.0846.

Ethyl (*E*)-3-(1-Adamantyloxy)acrylate (4aj): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.24 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H), 1.59–1.69 (m, 6 H), 1.85 (s, 6 H), 2.20 (s, 3 H), 4.12 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H), 5.30 (d, $^3J_{H,H}$ = 12.1 Hz, 1 H), 7.78 (d, $^3J_{H,H}$ = 12.1 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.4, 30.7, 35.9, 41.8, 59.5, 79.0, 98.5, 156.9, 168.4 ppm. MS (70 eV): *m/z* (%) = 250 (1.3) $[M]^+$, 135 (100), 95 (32), 93 (18).

Ethyl (*E*)-3-(1-Methylcyclohexyloxy)acrylate (4ak): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.24 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H), 1.26 (s, 3 H), 1.21–1.29 (m, 1 H), 1.38–1.57 (m, 7 H), 1.77–1.82 (m, 2 H), 4.12 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H), 5.30 (d, $^3J_{H,H}$ = 12.1 Hz, 1 H), 7.64 (d, $^3J_{H,H}$ = 12.1 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.4, 21.7 (2 C), 25.1, 25.9, 36.8 (2 C), 59.4, 80.6, 98.7, 157.6, 165.4 ppm. MS (70 eV): *m/z* (%) = 212 (0.5) $[M]^+$, 167 (4.5), 117 (14), 97 (100), 81 (10), 55 (75). HRMS: calcd. for $C_{12}H_{20}O_3$ 212.1412; found 212.1418.

Representative Procedure for the Synthesis of Vinyl Ethers 4al–4an from Diols: See Scheme 3. DABCO (0.20 mmol) was added to a solution of pentane-1,4-diol (**3al**; 2.0 mmol) and methyl propiolate (**2**; 2.2 mmol) in dry CH_2Cl_2 (5 mL). The reaction mixture was stirred for 1 h or less (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) to give **4al** (90%).

Methyl (*E*)-3-(4-Hydroxypentyloxy)acrylate (4al): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.19 (d, $^3J_{H,H}$ = 6.1 Hz, 3 H), 1.45–1.58 (m, 2 H), 1.65–1.87 (m, 3 H), 3.67 (s, 3 H), 3.78–3.86 (m, 3 H), 5.18 (d, $^3J_{H,H}$ = 12.6 Hz, 1 H), 7.57 (d, $^3J_{H,H}$ = 12.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.6, 25.2, 35.2, 51.0, 67.5, 71.1, 96.2, 162.5, 168.3 ppm. MS (70 eV): *m/z* (%) = 188 (0.1) $[M]^+$, 103 (12), 102 (14), 87 (51), 71 (35), 69 (100). HRMS: calcd. for $C_9H_{16}O_4$ 188.1049; found 188.1042.

Methyl (*E*)-3-(2-Hydroxybut-3-enyloxy)acrylate (4am): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.63 (br. s, 1 H), 3.65 (s, 3 H), 3.72–3.77 (m, 1 H), 3.83–3.87 (m, 1 H), 4.39–4.43 (m, 1 H), 5.19–5.24 (m, 2 H), 5.38 (d, $^3J_{H,H}$ = 12.6 Hz, 1 H), 5.79–5.87 (m, 1 H), 7.57 (d, $^3J_{H,H}$ = 12.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.1, 70.7, 74.4, 96.9, 117.4, 135.6, 162.3, 168.0 ppm. MS (70 eV): *m/z* (%) = 172 (0.5) $[M]^+$, 116 (13), 102 (35), 87 (100), 71 (82), 57 (60). HRMS: calcd. for $C_8H_{12}O_4$ 172.0736; found 172.0738.

Methyl (*E*)-3-{2-[(*E*)-3-methoxy-3-oxo-prop-1-enoxy]but-3-enoxy}-acrylate (4an): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.66 (s, 3 H), 3.67 (s, 3 H), 4.60 (d, $^3J_{H,H}$ = 5.0 Hz, 2 H), 4.58–4.62 (m, 1 H), 5.21 (d, $^3J_{H,H}$ = 12.6 Hz, 1 H), 5.30 (d, $^3J_{H,H}$ = 12.6 Hz, 1 H), 5.38–5.43 (m, 2 H), 5.71–5.80 (m, 1 H), 7.47 (d, $^3J_{H,H}$ = 12.6 Hz, 1 H), 7.53 (d, $^3J_{H,H}$ = 12.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.11 (2 C), 72.2, 81.0, 97.4, 98.8, 120.6, 131.5, 160.8, 161.7, 167.6, 167.8 ppm.

Supporting Information (see footnote on the first page of this article): Copies of the ^{1}H and ^{13}C NMR spectra of all new compounds, a comparative study of the effect of the solvent on the DABCO-catalysed reaction of 1-ethynylcylohexanol and methyl propiolate (Table S1).

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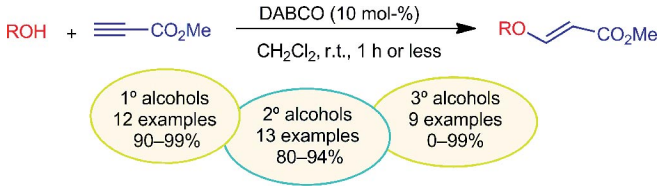

A practical protocol for the DABCO-catalysed synthesis of β-alkoxyacrylates is described. The protocol is efficient and economical, and it allows the transformation of a range of alcohols (including tertiary alcohols) into the corresponding β-alkoxyacrylate derivatives and the selective monoprotection of different diols (primary vs. secondary and tertiary).

Keywords: Alkynes / Organocatalysis / Amines / Alcohols / Vinyl ethers

