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A One-Pot Synthesis of α,β-Unsaturated Esters From Esters

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A convenient method for reductive Horner–Wadsworth–Emmons (HWE) olefination is described. The *E*-selective HWE homologation of various esters to α,β-unsaturated esters was readily achieved and gave the desired products in good-to-moderate yields under mild conditions. The one-pot reaction proceeds through an *in situ* generated aldehyde, formed via the partial reduction of an ester with lithium diisobutyl-*t*-butoxyaluminum hydride. The formation of cyclized metal acetal and subsequent decompose to the aldehyde for the olefination was found to be a crucial step in this C2-carbon homologation protocol.

Keywords: Horner–Wadsworth–Emmons olefination, α,β-Unsaturated esters, Lithium diisobutyl-*t*-butoxyaluminum hydride, Triethyl phosphonoacetate, Ester

Introduction

Horner–Wadsworth–Emmons (HWE) olefination is a variation of the well-known Wittig reaction that employs stabilized phosphonates. Due to its versatility and compatibility, HWE olefination has been widely applied in numerous organic syntheses to conduct C2-carbon homologation and macrocycle ring formation for natural product synthesis. Generally, HWE olefination involves the reaction of phosphonate carbanions with aldehydes or ketones to predominantly give *E*-α,β-unsaturated esters.[1] The advantage of this variation over the classical Wittig reaction is that the phosphonates used are highly reactive, thus generating water soluble by-products. Hence, HWE olefination is applicable to a wide range of aldehydes or ketones and is capable of producing functionalized olefins under relatively mild conditions.[2]

Usually, the HWE olefination of an ester involves a sequential two-step process; specifically, the over-reduction and re-oxidation to corresponding aldehydes, which are both lengthy and time-consuming.[3] There are a few reports of one-pot protocols comprising DIBALH-mediated partial reduction and subsequent olefination, but these take place under cryogenic conditions (−78 °C).[4] For instance, Takacs et al. reported a one-pot reductive HWE reaction of aliphatic esters to produce homologated α,β-unsaturated esters.[5] Additionally, Burton has reported reductive HWE olefinations affording α-fluoro-α,β-unsaturated esters via a one-pot DIBALH reduction at −78 °C.[6] Hoye et al. reported a sequential di-HWE olefination with α,ω-diesters using a DIBALH partial-reduction protocol.[7] In addition to these examples, Dakarapu et al. have recently demonstrated the utility of silyl acetal for reductive HWE olefination.[8]

Of late, our group has reported a new class of reducing agents, including lithium diisobutyl-*t*-butoxyaluminum hydride (LDBBA), sodium diisobutyl-*t*-butoxyaluminum hydride (SDBBA), and potassium diisobutyl-*t*-butoxyaluminum hydride (PDBBA), which showed significant partial-reducing properties for converting various esters to aldehydes in high yields at ambient temperature.[9–11] We also reported the employment of metal acetals (generated *in situ* from an ester and a reducing agent) as synthetic equivalents of aldehydes, as well as their subsequent addition with various alkyl metalates.[12–14]

The challenges associated with one-pot, reductive HWE olefinations of esters at low temperatures, as well as our experience in the utility of metal acetals, prompted us to search for suitable conditions to conduct C2-carbon homologation via HWE olefination at temperatures of 0 °C to room temperature. As a result, the olefination method reported herein was achieved by the partial reduction of an ester with LDBBA, followed by the trapping of the metal-acetal with a phosphonate carbanion, which predominantly provided *E*-α,β-unsaturated esters at ambient temperature (Figure 1).

The preparation of LDBBA comprised lithium *t*-butoxide being treated with DIBALH at 0 °C (Scheme 1).

Results and Discussion

Initially, the effect of base on the formation of phosphonate carbanions (from triethyl phosphonoacetate) during HWE olefination was evaluated under solvent-free conditions (Table 1).

The desired HWE olefination products were formed in low yields of 35%–50% when hydride bases, such as LiH and NaH, were used (entries 1–2). Common *t*-butoxide bases NaO-*t*-Bu and KO-*t*-Bu afforded the olefination product in 64% and 49% yield, respectively (entries 3–4). An increased yield (90%) was achieved when using LDA, LIHMDS, and alkyl lithium bases (entries 5–8). Therefore, the most commonly used and economically favored among

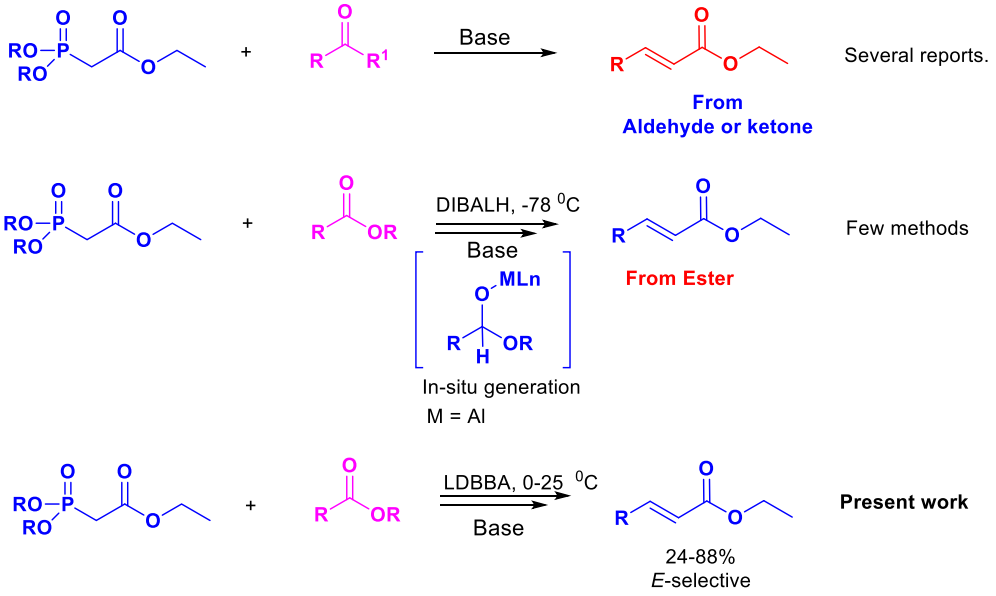
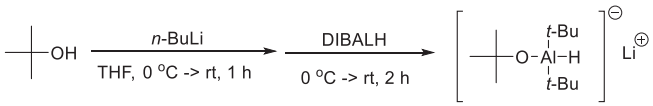


Figure 1. Horner–Wadsworth–Emmons olefination (HWE) of aldehydes/ketones and esters.

these, *n*-BuLi, was chosen as the base for our protocol (Table 1).

After selecting the base, other parameters were evaluated to further improve product formation, including the mol ratio of LDBBA added and the solvent system. First, THF was tested as a solvent and added in different concentrations; however, unreacted starting material was identified upon gas chromatography (GC) analysis (entries 2–4 in Table 2). Upon increasing the LDBBA mol ratio from 1.3 to 1.5 equiv., complete consumption of the starting ester was noted via GC analysis (entry 5). Next, solvents like ether, methylene chloride, and toluene were tested with 1.5 equiv. of LDBBA (entries 6–8). Toluene gave similar results to those of THF, while ether and methylene chloride afforded lower, moderate yields. Since, toluene is carcinogenic and highly nonpolar, THF was ultimately chosen as the solvent. Consequently, the conditions employing 1.5 equiv. of LDBBA in THF (entry 5 in Table 2) were selected as the optimal parameters for the reductive HWE olefinations performed in the present method (Supporting Information).

Using these conditions, the substrate scope was then analyzed. As shown in Table 3, all ester substrates tested, including those that were electron-donating and electron-withdrawing, afforded their corresponding α,β-unsaturated esters in good to moderate yields. Since, the present method proceeds via partial reduction of ester to aldehydes (GC) followed by olefin homologation; as expected, the

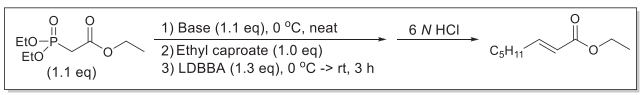


Scheme 1. Preparation of lithium diisobutyl-*t*-butoxy aluminum hydride (LDBBA).

electron-deficient substrates (esters) showed superior reactivities to those of their electron-rich counterparts. For example, substrate **1g** with bromo substitution has given 85% yield compared to **1b** with methyl substitution (62%). Similarly, substrates **1f** having chlorine, **1 k** having nitro substitutions afforded 88% and 72% yields, respectively, when compared to substrate **1d** with methoxy substitution (29%). Further, heteroaromatic esters provided moderate conversion to their corresponding products. In addition, aliphatic esters also afforded the expected C2-homologated α,β-unsaturated esters.

GC analysis of a crude product sample confirmed that there were no impurities (by-products) except aldehyde and over-reduced alcohol. Based on this observation and previous reports, a mechanism was proposed for this protocol (Scheme 2). First, the reaction of triethyl phosphonoacetate

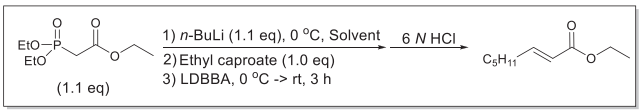
Table 1. Effect of base on HWE olefination.



Entry	Base	Hexanal/hexanol/S.M/product[a]
1	LiH	5/0/60/35
2	NaH	6/2/42/50
3	NaO-*t*-Bu	1/5/30/64
4	KO-*t*-Bu	1/10/40/49
5	LDA	1/3/6/90
6	LiHMDS	7/0/2/91
7	*n*-BuLi	0/0/9/91
8	*t*-BuLi	7/0/3/90

[a] Yields were determined by GC.

Table 2. Optimization of HWE olefination reaction conditions.

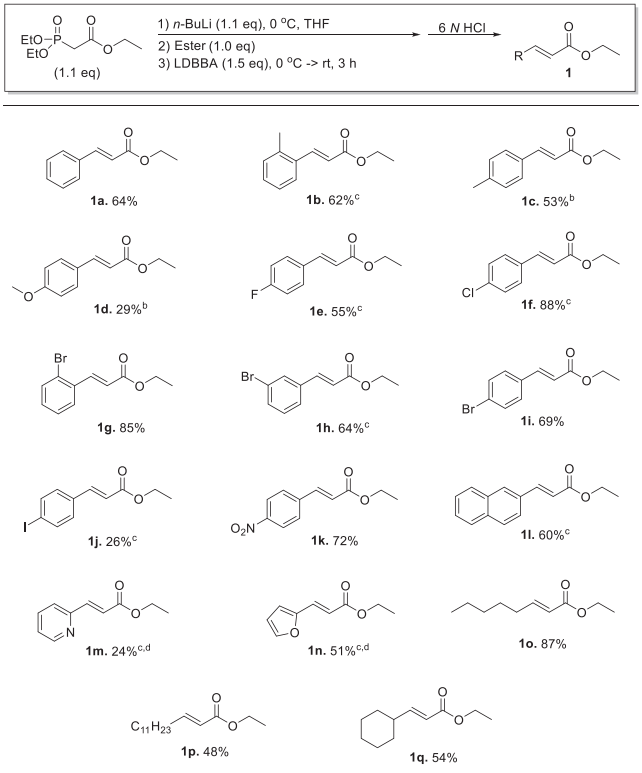


Entry	LDBBA (eq)	Solvent	mL	Hexanal/hexanol/S.M/Product[a]
1	1.3	Neat		0/0/9/91
2		THF	1	2/4/2/92
3			3	2/6/1/91
4			5	2/5/4/88
5	1.5	Neat		3/9/0/88
6		Ether	5	3/2/15/78
7		MC	5	15/0/43/41
8		Toluene	5	5/8/0/87

[a] Yields were determined by GC.

with *n*-BuLi generates the phosphonate carbanion via the deprotonation of the triethyl phosphonoacetate α-proton. Additionally, a cyclized metal acetal is formed by the reaction of LDBBA with the substrate ester. The cyclic metal acetal decomposes (fragments) under the reaction conditions used to give the aldehyde. The addition of the phosphonate anion to the generated aldehyde forms a stable cyclic intermediate, which then undergoes acid hydrolysis to produce the desired two-carbon homologated ester in one pot.

Table 3. Synthesis of α,β-unsaturated esters from representative esters.[a]



[a] Isolated yields after silica column chromatography. [b] Reacted at rt for 72 h. [c] Using LDBBA (1.7 eq). [d] H_2O work up

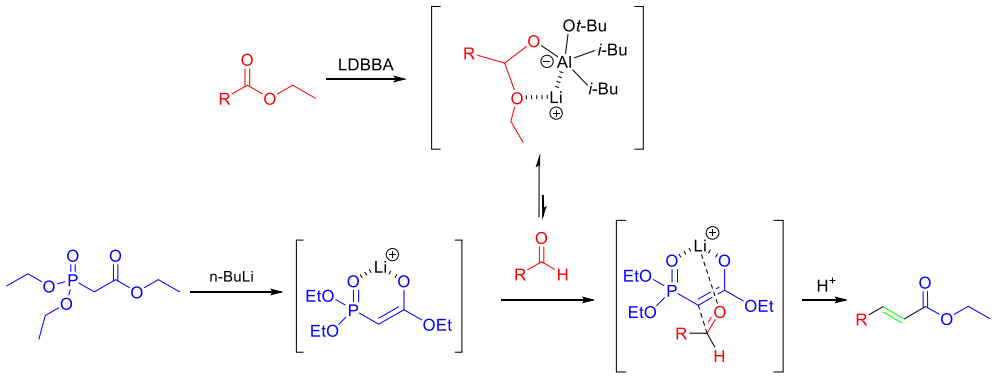
[a] Isolated yields after silica column chromatography.
[b] Reacted at rt for 72 h.
[c] Using LDBBA (1.7 equiv).
[d] H_2O work up.

Conclusion

We have demonstrated a one-pot method for the reductive HWE olefination of esters. The procedure involves the partial reduction of the substrate ester to an aldehyde via treatment with LDBBA at ambient temperature (0 °C). Subsequent one-pot homologation of the aldehyde with a phosphonate carbanion (generated *in situ*) led to the synthetically valuable α,β-unsaturated ester in good-to-moderate yields. Various esters were converted to their corresponding, C2-homologated α,β-unsaturated ester derivatives. This a valuable, alternative approach to the conventional, one-pot, DIBALH-mediated reductive HWE olefination, as the present method allows for the same process to be conducted under ambient conditions rather than at cryogenic temperatures. This makes large-scale applications of this protocol possible. Further developments to produce higher-yielding and chemoselective HWE olefinations are currently in progress and will be reported in due course.

Experimental

General. All glassware used was thoroughly dried in an oven, assembled hot, and cooled under a stream of dry nitrogen prior to use. All reactions and manipulations of air- and moisture-sensitive materials were carried out using standard techniques for the handling of such materials. All chemicals were purchased from the Aldrich Chemical Company, Alfa Aesar, and the Tokyo Chemical Industry Company (TCI). ^{1}H NMR spectra were measured at 400 MHz with $CDCl_3$ as the solvent and at ambient temperature, unless otherwise indicated. The chemical shifts were recorded in parts per million as either downfield from



Scheme 2. Proposed mechanism.

the tetramethylsilane ($\delta = 0$ ppm) reference peak or in reference to the residual $CDCl_3$ ($\delta = 7.26$ ppm) peak. Analytical thin-layer chromatography (TLC) was performed on glass precoated with silica gel (Merck, silica gel 60F254). Column chromatography was carried out using 70–230 mesh silica gel (Merck) at normal pressure. GC analyses were performed on a Younglin Acme 6100 GC and 6500 GC FID chromatography, using an HP-5 capillary column (30 m). All GC yields were determined with the use of naphthalene as the internal standard and the authentic samples.

Preparation of Lithium diisobutyl-t-butoxyaluminum hydride. To a solution of *t*-butyl alcohol (5.16 mL, 55 mmol) in THF (25 mL) was added *n*-BuLi (20 mL, 2.5 M in hexane, 55 mmol) at 0 °C. After being stirred for 1 h at room temperature, DIBALH (50 mL, 1.0 M in hexane, 50 mmol) was added dropwise to the reaction mixture at 0 °C and the mixture was stirred for 2 h at room temperature to give a colorless homogeneous solution. The concentration of the LDBBA solution in THF/hexane was measured gasometrically by the hydrolysis of an aliquot of the solution with a hydrolyzing mixture of *t*-butyl alcohol and THF (1:1) at 0 °C. The LDBBA solution was stable in the refrigerator for 6 months without any appreciable loss of hydride content.

General Procedure for the HWE Olefination of Esters. The following experimental procedure for the synthesis of *α*, *β*-unsaturated esters is representative. A dry and argon-flushed flask, equipped with a magnetic stirring bar and septum, was charged with triethyl phosphonoacetate (0.11 mL, 0.55 mmol) and THF (5 mL). After cooling to 0 °C, 2.5 M *n*-BuLi (in hexane, 0.22 mL, 0.55 mmol), the ester (0.5 mmol), and LDBBA (in THF, 2.0 mL, 0.75 mmol) were added dropwise and the mixture was stirred for 3 h at 0 °C. The reaction was subsequently quenched with 6 *N* HCl (5 mL). The crude mixture was extracted with diethyl ether and the combined organic layers were dried over $MgSO_4$. The product was isolated by column chromatography (hexane:EA = 200:1).

Ethyl Cinnamate (1a). Yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.65 (d, 1H), 7.49 (m, 2H), 7.35 (m, 3H), 6.42 (d, 1H), 4.25 (q, 2H), 1.32 (t, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.1, 144.7, 134.5, 130.0, 129.0, 128.1, 118.3, 60.6, 14.4. NMR data were in accordance with reported literature.[8]

Ethyl (E)-3-(o-tolyl) acrylate (1b). Colorless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96 (d 1H), 7.54 (d, 1H), 7.25 (ddd, 1H), 7.20 (dd, 2H), 6.35 (d, 1H), 4.26 (q, 2H), 2.43 (s, 3H), 1.33 (t, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.2, 142.4, 137.7, 133.5, 130.9, 130.1, 126.5, 125.3, 119.4, 60.6, 19.9, 14.5. NMR data were in accordance with reported literature.[8]

Ethyl (E)-3-(p-tolyl) acrylate (1c). Colorless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.65 (d, 1H), 7.41 (d, 2H), 7.18 (d, 2H), 6.38 (d, 1H), 4.25 (q, 2H), 2.36 (s, 3H), 1.33 (t, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.3, 144.7, 140.7, 131.8, 129.7, 128.1, 117.2, 60.5, 21.6, 14.5. NMR data were in accordance with reported literature.[8]

Ethyl (E)-3-(4-methoxyphenyl) acrylate (1d). Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, 1H), 7.47 (dz, 2H), 6.88 (d, 2H), 6.32 (d, 1H), 4.24 (q, 2H), 3.83 (s, 3H), 1.33 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 161.4, 144.3, 129.8, 127.3, 115.8, 114.4, 60.4, 55.5, 14.5. NMR data were in accordance with reported literature.[15]

Ethyl (E)-3-(4-fluorophenyl) acrylate (1e). Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, 1H), 7.50 (dd, 2H), 7.06 (t, 2H), 6.35 (d, 1H), 4.25 (q, 2H), 1.33 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 165.2162.7,143.4, 130.8, 130.0, 118.0, 116.2, 116.0, 60.7, 14.4. NMR data were in accordance with reported literature.[16]

Ethyl (E)-3-(4-chlorophenyl) acrylate (1f). Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, 1H), 7.43 (d, 1H), 7.35 (d, 1H) 6.41 (d, 1H), 4.25 (q, 2H), 1.33 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 143.2, 136.2, 133.0, 129.3, 129.2, 118.9, 60.7, 14.4. NMR data were in accordance with reported literature.[15]

Ethyl (E)-3-(2-bromophenyl) acrylate (1g). Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, 1H), 7.60 (m, 2H), 7.31 (ddd, 1H), 7.22 (ddd, 1H), 6.38 (d, 1H), 4.27 (q, 2H), 1.34 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 143.0, 134.6, 133.5, 131.3, 127.9, 127.8, 125.4, 121.2, 60.8, 14.4. NMR data were in accordance with reported literature.[17]

Ethyl (E)-3-(3-bromophenyl) acrylate (1h). Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.57 (d,

1H), 7.43 (dd, 2H), 7.23 (t, 1H), 6.42 (d, 1H), 4.25 (q, 2H), 1.33 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 142.9, 136.6, 133.0, 130.8, 130.5, 126.7, 123.1, 119.9, 60.8, 14.4. NMR data were in accordance with reported literature.[16]

Ethyl (E)-3-(4-bromophenyl) acrylate (1i). Colorless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.58 (d, 1H), 7.50 (d, 2H), 7.38 (d, 2H), 6.41 (d, 1H), 4.25 (q, 2H), 1.32 (t, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.9, 143.3, 133.4, 132.2, 129.5, 124.6, 119.0, 60.8, 14.4. NMR data were in accordance with reported literature.[8]

Ethyl (E)-3-(4-iodophenyl) acrylate (1j). Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, 2H), 7.58 (d, 1H), 7.25 (d, 2H), 6.42 (d, 1H), 4.24 (q, 2H), 1.32 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 143.5, 138.2, 134.0, 129.6, 119.1, 96.6, 60.8, 14.4. NMR data were in accordance with reported literature.[18]

Ethyl (E)-3-(4-nitrophenyl) acrylate (1k). Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, 2H), 7.68 (t, 3H), 6.55 (d, 1H), 4.29 (q, 2H), 1.33 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 148.6, 141.7, 140.7, 128.7, 124.3, 122.7, 61.1, 14.4. NMR data were in accordance with reported literature.[16]

Ethyl (E)-3-(naphthalen-2-yl) acrylate (1l). White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.84 (m, 4H), 7.66 (dd, 1H), 7.50 (m, 2H), 6.54 (d, 1H), 4.27 (q, 2H), 1.35 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δz 167.2, 144.8, 134.3, 133.4, 132.0, 130.0, 128.8, 128.7, 127.9, 127.3, 126.8, 123.6, 118.5, 60.7, 14.5. NMR data were in accordance with reported literature.[16]

Ethyl (E)-3-(pyridin-2-yl) acrylate (1m). Colorless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.64 (d, 1H), 7.67 (m, 2H), 7.42 (d, 1H), 7.25 (ddd, 1H), 6.90 (d, 1H), 4.26 (q, 2H), 1.32 (t, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.9, 153.1, 150.3, 143.4, 136.9, 124.3, 124.2, 122.5, 60.8, 14.4. NMR data were in accordance with reported literature.[8]

Ethyl (E)-3-(furan-2-yl) acrylate (1n). Colorless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45 (s, 1H), 7.40 (d, 1H), 6.58 (d, 1H), 6.43 (m, 1H), 6.28 (d, 1H), 4.22 (q, 2H), 1.30 (t, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.1, 151.0, 144.8, 131.0, 116.0, 114.7, 112.3, 60.5, 14.4. NMR data were in accordance with reported literature.[8]

Ethyl (E)-oct-2-enoate (1o). Colorless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.97 (m, 1H), 5.79 (d, 1H), 4.16 (q, 2H), 2.17 (m, 2H), 1.43 (m, 2H), 1.27 (m, 6H), 0.89 (t, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.0, 149.6, 121.3, 60.2, 32.3, 31.4, 27.8, 22.6, 14.4, 14.0. NMR data were in accordance with reported literature.[8]

Ethyl (E)-tetradec-2-enoate (1p). White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (m, 1H), 5.79 (d, 1H), 4.16 (q, 2H), 2.19 (q, 2H), 1.43 (dd, 2H), 1.24 (m, 19H), 0.86 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 149.7, 121.3, 60.2, 32.3, 32.0, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.1, 28.1, 22.8, 14.4, 14.2. NMR data were in accordance with reported literature.[19]

Ethyl (E)-3-cyclohexylacrylate (1q). Colorless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.90 (dd, 1H), 5.74 (d, 1H), 4.16 (q, 2H), 2.11 (m, 1H), 1.72 (m, 5H), 1.26 (m, 5H), 1.13 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.2, 154.3, 118.9, 60.2, 40.5, 31.8, 26.0, 25.8, 14.3. NMR data were in accordance with reported literature.[20]

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Supporting Information. Additional supporting information may be found online in the Supporting Information section at the end of the article.

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