STUDIES ON REDUCTIVE HORNER-WADSWORTH-EMMONS OLEFINATION USING MIXED SILYL ACETALS

by

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Abstract

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Homologation of esters to α,β-unsaturated esters is a useful transformation in organic synthesis. We have developed a new approach for the Ir-catalyzed reductive Horner-Wadsworth-Emmons olefination of esters; a one-pot method for the transformation of esters to α,β-unsaturated esters utilizing silyl acetals as aldehyde equivalents followed by Horner-Wadsworth-Emmons olefination. Lewis based activation of silyl acetals formed by Ir-catalyzed hydrosilylation of esters initially generates putative penta-coordinate silicate acetals which fragment into aldehydes, silanes and alkoxides *in situ*. The alkoxides deprotonate phosphonate esters which subsequently react with the aldehydes to furnish α,β-unsaturated esters. This method is operationally simple compared with aluminium hydride-based reductive Horner-Wadsworth-Emmons olefination. Notably, Horner-Wadsworth-Emmons olefination of traditionally challenging substrates such as aryl, alkenyl and alkynl esters furnishes the corresponding α,β-unsaturated esters at room temperature with excellent stereoselectivities (*E/Z* > 20:1) and moderate to excellent yields (48–91%). This transformation will contribute to enhancing the utility of silyl acetals in synthetic chemistry.

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List of Abbreviations

APCI	atmospheric pressure chemical ionization
Calcd	Calculated
°C	degrees Celsius
CH_2Cl_2	Dichloromethane
coe	cycloocetene
δ	Chemical shift, in NMR spectroscopy
d	Doublet, in NMR spectroscopy
DIBAL-H	Diisobutylaluminum hydride
g	Gram(s)
GC-MS or GCMS	Capillary gas chromatography-mass spectrometry
HRMS	High resolution mass spectrometry
Hz	Hertz (cycles per second)
IR	Infrared
J	Coupling constant (NMR)
KO*t*-Bu	potassium *tert*-butoxide
$KOSiMe_3$	potassium trimethyl silanolate
$LiOSiMe_3$	lithium trimethyl silanolate
m	Multiplet, in NMR spectroscopy
Me	Methyl
mol	Mole(s)
mmol	milliMole
mp	Melting point
MPLC	Medium pressure liquid chromatography
NaOEt	sodium ethoxide

NaO*t*-Bu	sodium *tert*-butoxide
$NaOSiMe_3$	sodium trimethyl silanolate
NMR	Nuclear magnetic resonance
p	pentet (NMR)
Ph	Phenyl
ppm	Parts per million
i-Pr or ^{i}Pr	Isopropyl
q	Quartet, in NMR spectroscopy
R_f	Ratio to front
RT or rt	Room temperature
s	Singlet, in NMR spectroscopy
t	Triplet, in NMR spectroscopy
TBAF	Tetra-*n*-butylammonium flouride
THF	Tetrahydrofuran
TOF	Time of flight
t_R	Retention time

Chapter 1

INTRODUCTION

Olefination reactions are one of the most efficient carbon-carbon bond forming reactions. Among them, the Wittig reaction is one of the most popular methods. The Wittig reaction generally entails reaction of a phosphonium ylide with an aldehyde or ketone to afford the corresponding alkene and phosphine oxide. The Horner-Wadsworth-Emmons reaction is a modification of the Wittig reaction, which involves the reaction of a phosphonate-stabilized carbanion with carbonyl compounds **I-1** to afford α,β-unsaturated esters **I-2** (Figure 1.1). Advantages of the Horner-Wadsworth-Emmons reaction over the Wittig reaction includes 1) the phosphonates used are significantly more reactive species than that of phosphonium ylides, 2) phosphorous byproducts formed are water soluble and hence easily separable from the desired product, and 3) Horner-Wadsworth-Emmons olefination is highly *E*-selective.

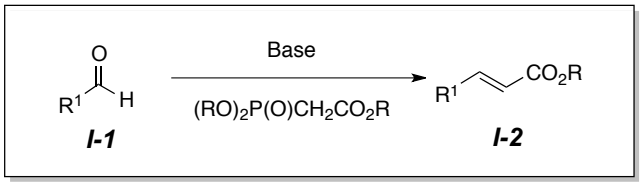
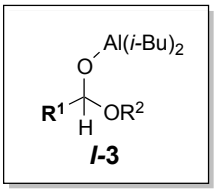


Figure 1.1 Horner-Wadsworth-Emmons olefination

Synthesis of α,β-unsaturated esters or two carbon-homologated esters from esters involves two or three steps: The first step is the controlled reduction of esters to aldehydes or complete reduction of esters to alcohols. If the aldehydes are completely reduced to alcohols, subsequent oxidation converting alcohols to aldehydes is the

second step. The third step is either a Wittig reaction or a Horner-Wadsworth-Emmons reaction for olefination.

The major problem that is encountered in the transformation of the controlled reduction of esters is the high reactivity of the aldehyde intermediates compared to the initial esters towards nucleophilic hydride reducing agents. This high reactivity of aldehydes lead to the formation of a mixture of aldehydes and undesired over-reduced alcohols. Important and major factors that dictating the success of this reduction step is the stability of the intermediate formed (i.e., tetrahedral alanate intermediate **I-3** if diisobutylaluminum hydride DIBAL-H is used) and nature of the R^1 group in the esters (R^1COOR^2) (Figure 1.2). Another problem associated with this reduction of esters is the waste produced in the aldehyde purification step and their associated costs. Moreover, the controlled reduction of esters requires stoichiometric metal reducing agents such as aluminum which is toxic in nature.



***I*-3**

Figure 1.2 Aluminum acetal

Takacs,[1] Burton[2] and Hoye[3] have developed an *in situ* generation of alanate intermediates to impede the inherent inefficiencies. Takacs treated esters with DIBAL-H in the presence of lithio-trialkylphosphonoacetate to furnish homologated α,β-unsaturated esters.[1] Burton has employed DIBAL-H and α-fluoro phosphonacetates to convert esters to α-fluoro-α,β-unsaturated esters.[2] Hoye described the one-pot bidirectional

homologation of 1,n-dioates to corresponding enoates.[3] Takacs, Burton and Hoye used DIBAL-H at –78 °C, which limits the utility of these methods to alkyl substitued esters. Trost[4] and Herzon[5] demonstrated the reductive Horner-Wadsworth-Emmons olefination of enals, where DIBAL-H reduced alkenyl esters to enals at –90 °C and the subsequent HWE reaction yielded corresponding enoates. The An group[6] has reported a new class of reducing agents; for instance, lithium diisobutyl-*t*-butoxyaluminum hydride (LDBBA), sodium diisobutyl-*t*-butoxyaluminum hydride (SDBBA) and potassium diisobutyl-*t*-butoxyaluminum hydride (PDBBA) are capable of reducing esters at 0 °C. Using these reagents, the An group demonstrated reductive HWE reactions of aryl and heterocyclic esters.[6] However, there are no existing studies toward reductive HWE of alkynyl esters so far.

Organosilanes are relatively cheap and a wide variety of organosilanes are commercially available. They are sufficiently stable to acidic or basic conditions. One of the advantages of the use of organosilanes is that organosilanes and their reaction byproducts are generally non-toxic. Organosilanes have a variety of uses in organic chemistry; they are most frequently used as protecting agents in organic synthesis.[7] They are also extensively used as reducing agents.[8] Organosilanes possessing one or more hydrogen atoms attached to silicon have the ability to act as ionic or free radical reducing agents. Organosilanes and the reduction byproducts are generally safer when compared to metal-based reducing agents like lithium aluminum hydride or tributyltin hydride.

Acetals **I-4** are geminal diether derivatives of aldehydes or ketones which are formed when two alcohol molecules react with one molecule of aldehyde (Figure 1.3). Metal acetals **I-5** are the addition products derived from the esters or amides when they react with organometallic reagents like Grignard reagents or alkyl lithium reagents. Silyl acetals **I-6** are the derivatives of esters or amides formed when they react with

organosilanes. Acetals, metal acetals and silyl acetals can be used as aldehyde equivalents.

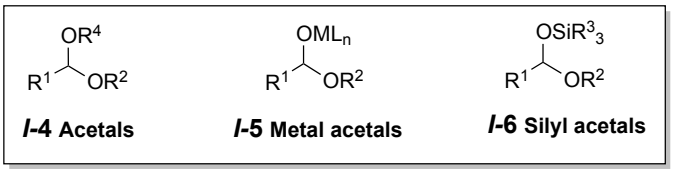


Figure 1.3 Acetals

Stability is the criteria which distinguishes silyl acetals from metal acetals and acetals. Acetals are generally acid labile or base stable at ambient to elevated temperature. Metal acetals are only reasonably stable at low temperature. Silyl acetals are reasonably stable at ambient to elevated temperature, but still acid labile and silaphile labile. However, the application of acetals is quite limited; they are used mostly as protecting groups for aldehydes. Silyl acetal is similar to a metal acetal with the metal being silicon. Silyl acetals also have limited application in synthetic chemistry. Pioneering work on the synthesis and applications of silyl acetals, mainly towards Lewis acid-catalyzed allylsilane addition reactions were demonstrated by Mukaiyama,[9] Tietze[10] and Oshima.[11]

Cheng and Brookhart have developed a method for generating silylacetals intermediates from esters (Figure 1.4).[12] Esters **I-7** undergo hydrosilylation in the presence of $[Ir(coe)_2Cl]_2$ (coe = cyclooctene) and dihydrosilanes in an appropriate solvent at room temperature to furnish silyl acetals **I-6** . Advantages of this method include 1) low catalyst loading and 2) efficient control of the reduction of esters under mild reaction conditions. Subsequent hydrolysis of silyl acetals affords the corresponding aldehydes **I-1**.

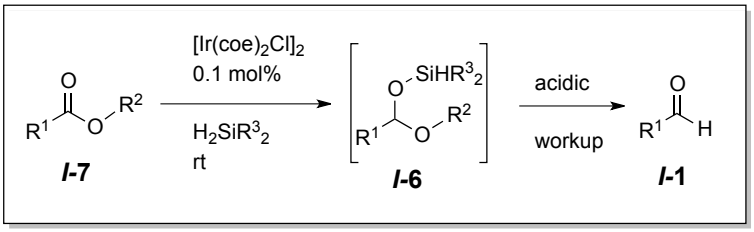


Figure 1.4 Brookhart's hydrosilylation of esters

Chapter 2

REACTION DEVELOPMENT

2.1. Investigation of Reductive Horner-Wadsworth-Emmons Olefination

We aimed to develop a one-pot Iridium-catalyzed hydrosilylation of esters **II-1** to generate silyl acetals followed by the Horner-Wadsworth-Emmons olefination with appropriate silaphiles and phosphonate esters to furnish α,β-unsaturated esters **II-2** (Figure 2.1). We also wanted to 1) perform the reaction under the mild reaction conditions such as at room temperature and 2) deal with the challenging substrates with esters containing aryl, alkenyl, and alkynyl substituents.

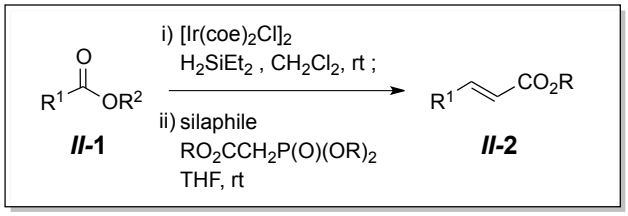


Figure 2.1 Proposed approach of reductive HWE olefination

2.2. Proposed Reaction Design of Lewis-Base Promoted Deprotonative Pronucleophile Addition to Silyl Acetals

To establish the applicability of silyl acetals as aldehyde equivalents Lewis base-promoted deprotonative pronuclephile addition reaction to silyl acetals was envisaged (Figure 2.2).[13] Silyl acetals **II-3** formed by the iridium-catalyzed hydrosilylation of esters[12,14] would serve as aldehyde equivalents. Subsequent nucleophilic addition by Lewis base (silaphile) results in putative penta-coordinate silicate acetals **II-4**,[15] which undergo fragmentation to provide silanes **II-5**, aldehydes **II-6** and alkoxides **II-7**. The

alkoxides **II-7** generated *in situ* deprotonatate pronucleophiles ^{Pro}**Nu** possessing an anion stabilizing group (ASG), which can then trap the aldehydes to furnish alcohols **II-8**. Advantages of our approach are 1) the reactions can be carried out under the mild reaction conditions (i.e., room temperature). 2) premetalation of the nucleophiles which are required in the traditional approaches can be avoided as the fragmentation generates bases *in situ*. 3) this method can be applicable to the functionalization of challenging substrates like aryl, alkenyl and alkynyl esters into their corresponding α,β-unsaturated esters. 4) the use of a substoichiometric amount of the iridium catalyst facilitates the feasibility of the reactions to a wide range of scales from milligram to gram scale of the esters.

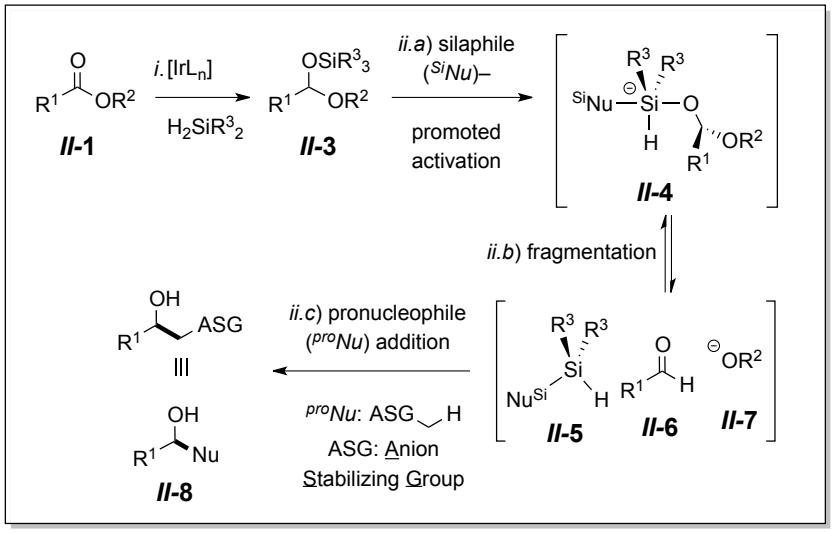


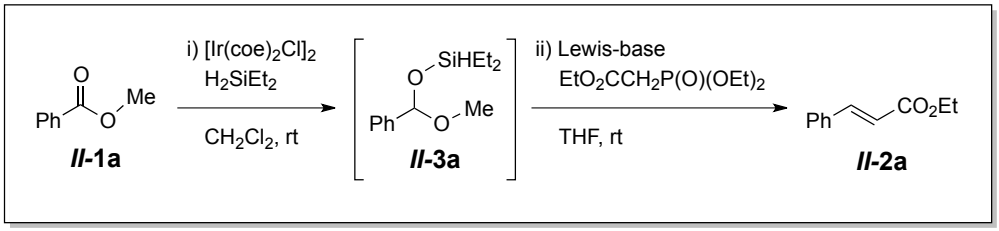
Figure 2.2 Proposed reaction design

2.3. Optimization of the Reaction Conditions for Reductive Horner-Wadsworth-Emmons Olefination

Reaction conditions were screened with different Lewis-base (i.e., silaphiles) for one-pot iridium-catalyzed reductive Horner-Wadsworth-Emmons olefination (Table 2.1). Hydrosilylation of methyl benzoate **II-1a** with chlorobis(cyclooctene)iridium(I)dimer $[Ir(coe)_2Cl]_2$ and diethyl silane generated diethylhydrosilyl acetal intermediate **II-3a**, which was subjected to Horner-Wadsworth-Emmons olefination with various Lewis bases. All reactions were carried out at a 0.2 mmol scale. The percentage yields were determined utilizing dibromomethane as an internal standard with ^{1}H NMR spectroscopy after an hour. TBAF (tetra-*n*-butylammonium fluoride), NaOEt (sodium ethoxide), NaO*t*-Bu (sodium *tert*-butoxide) and KO*t*-Bu (potassium *tert*-butoxide) furnished enoate **II-2a** in low yields. With TBAF as Lewis base (i.e., silaphile) **II-2a** was afforded in 26% yield after one hour with the complete consumption of the silyl acetal **II-3a.** With NaOEt as Lewis base 33% yield of **II-2a** was observed, but there is no complete consumption of the silyl acetal **II-3a** after 48 hours. By the addition of 3 equivalents of NaOEt there was complete consumption of silyl acetal **II-3a** and the reaction resulted in 69% yield of desired product **II-2a** With NaO*t*-Bu as Lewis base 28% yield of the desired product **II-2a** was observed, but there is no complete consumption of silyl acetal **II-3a** after 48 hours . By the addition of 3 equivalents of NaO*t*-Bu there was complete consumption of starting ester and the reaction resulted in 76% yield of desired product **II-2a** . With KO*t*-Bu as Lewis base 66% yield of the desired product **II-2a** was observed in an hour, but there is incomplete consumption of silyl acetal **II-3a** after 48 hours . By the addition of 3 equivalents of KO*t*-Bu there was complete consumption of silyl acetal **II-3a** and the reaction resulted in 80% yield of desired product **II-2a** With $LiOSiMe_3$ (lithium trimethyl silanolate) and $NaOSiMe_3$ (sodium trimethyl silanolate) as Lewis bases within an hour there was complete

consumption of silyl acetal **II-3a** and the desired product **II-2a** was afforded in 84% and 83% yields respectively. With $KOSiMe_3$ (potassium trimethyl silanolate) as Lewis base within an hour there was complete consumption of silyl acetal **II-3a** and the desired product was afforded in 95% yield with high stereoselectivity of *E/Z* > 20:1. The isolated yield of the desired product **II-2a** was 87% . So $KOSiMe_3$ was identified as the best Lewis base for the lewis-base-promoted reductive Horner-Wadsworth-Emmons olefination.

Table 2.1. Lewis-base screening



Entry	Lewis-base	Yield % (**II-2a**)	*E/Z* (**II-2a**)
1	TBAF	26	> 20:1
2	NaOEt	33[a] (69)[b]	> 20:1
3	NaO*t*-Bu	28[a] (76)[b]	> 20:1
4	KO*t*-Bu	66[a] (80)[b]	> 20:1
5	$LiOSiMe_3$	84[c]	> 20:1
6	$NaOSiMe_3$	83[c]	> 20:1
7	$KOSiMe_3$	95[c] (87)[d]	> 20:1

a = ^{1}H NMR yield after 48 h

b = ^{1}H NMR yield after addition of 3 equivalents of Lewis-base

c = ^{1}H NMR yield after 1h

d = Isolated yield.

2.4. Minimizing The Formation Of Major By-Products

Two major byproducts were observed during the reaction, which are 1) *trans*-esterification product **II-2a-OMe** 2) over-reduction product **II-2a-H2** (Figure 2.3). The ethyl cinnamate (**II-2a)** formed underwent *trans*-esterification[16] with the alkoxide generated *in situ* and resulted in the formation of a minor amount of methyl cinnamate (**II-2a-OMe)** (Figure 2.4). Isolation of ethyl cinnamate (**II-2a)** from a mixture of ethyl cinnamate and methyl cinnamte was challenging. Upon investigation it was found that by reducing the reaction time the formation of the *trans*-esterification byproduct **II-2a-OMe** was minimized. We optimized the reaction time within 30 minutes in the second HWE step of our sequential reactions.

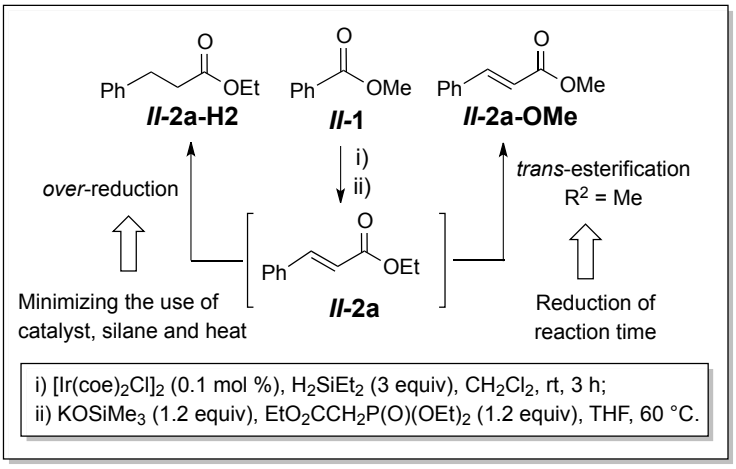


Figure 2.3 Minimizing the formation of major by-products

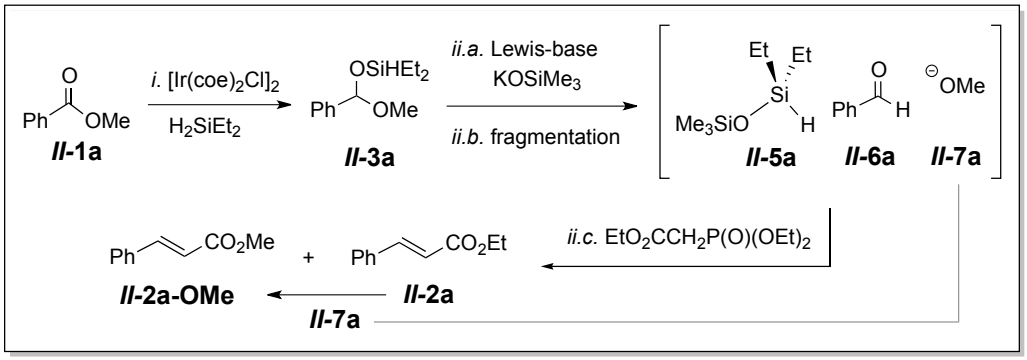


Figure 2.4 *Trans*-esterification

Along with the ethyl cinnamate (**II-2a)** the over-reduced product[16] ethyl 3-phenylpropanoate (**II-2a-H2)** is also observed as a minor byproduct (Figure 2.5). Upon investigation it is found that the presence of excess iridium catalyst and silane are responsible for the over-reduction products. By controlling an amount of catalyst, silane and reaction temperature the over-reduction byproduct **II-2a-H2** was minimized. The equivalents of the potassium trimethyl silanolate and triethylphosphonoacetate were also optimized in the course of reaction.

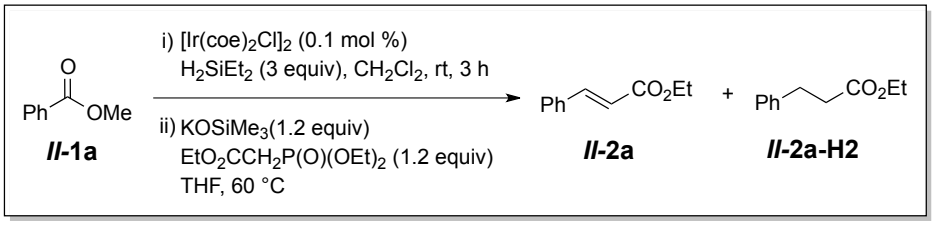


Figure 2.5 Over-reduction

2.5. Stability Of Silyl Acetals

The silyl acetal intermediates formed from initial hydrosilylation of esters were stable at room temperature and at 0 °C for a week or it can be stored by freezing with benzene for a couple of weeks. Upon the complete formation of the silyl acetals the

reaction mixture was subjected to *in vacuo* to remove the volatiles. The reaction solvent was switched from CH_2Cl_2 to THF. The mass recovery of the silyl acetals after subjecting the reaction mixture *in vacuo* was near quantitative, and the yield of the hydrosilylation was determined by ^1H NMR spectroscopy using dibromomethane as an internal standard.

Chapter 3

STUDIES ON REDUCTIVE HORNER-WADSWORTH-EMMONS OLEFINATION REACTION

3.1. Substrate Scope Of Reductive Horner-Wadsworth-Emmons Olefination

Hydrosilylation of esters **III-1** was performed with iridium catalyst $[Ir(coe)_2Cl]_2$ (0.1 mol %) and diethyl silane to furnish silyl acetals. These silyl acetals were then subjected to Horner-Wadsworth-Emmons olefination to furnish enoates **III-2** under optimized conditions (Figure 3.1).

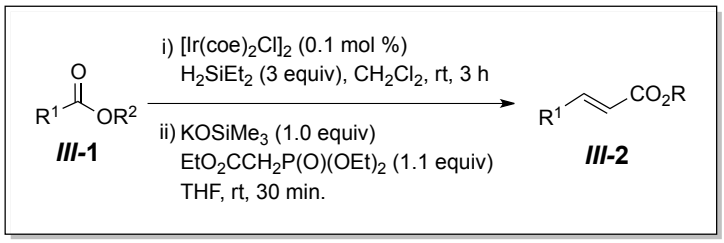


Figure 3.1 Scheme of substrate screening

Aromatic esters with electron-withdrawing and electron-donating groups at the *para* position afforded the corresponding enoates **III-2b** to **III-2h** with good isolation yields as well as high stereoselectivity (*E/Z* > 20:1) (Figure 3.2). Aromatic esters with electron-withdrawing and electron-donating groups at the *meta* position have afforded the corresponding enoates **III-2i** to **III-2k** with moderate to good yields as well as high stereoselectivity (*E/Z* > 20:1). One aromatic ester with an *ortho* methyl group has also afforded the corresponding enoates **III-2l** with good yield as well as high stereoselectivity (*E/Z* > 20:1). These substrates with different electronic and steric properties provided the corresponding enoates in moderate good yields. This result demonstrates the feasibility of our approach to the reductive HWE reaction of aromatic esters at room temperature.

Esters containing heterocyclic moieties like furan, thiophene, pyridine, and indole were subjected to the reductive HWE reaction conditions, which afforded the corresponding enoates **III-2m** to **III-2p** in moderate to good yields and excellent stereoselectivity (*E/Z* > 20:1). These results showed that substrates having some heterocyclic substituents are compatible with the Ir-catalyzed reductive HWE reaction.

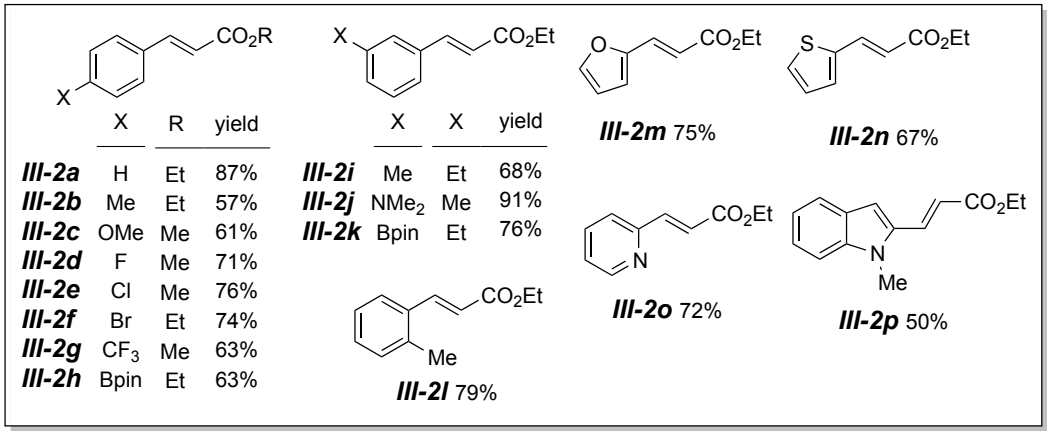


Figure 3.2 Substrate scope of aromatic esters

Acyclic esters having enolizable protons were also tested with the approach and resulted in the corresponding enoates **III-2q** to **III-2s** in diminished yields, yet high stereoselectivity (*E/Z > 20:1*) (Figure 3.3). Methyl tridecanoate, the saturated product of enoate **III-2r** was observed along with the enoate **III-2r** in the ratio **III-2r**:**III-2r**-H2 = 6:1. Alternatively by following the Brookhart's method the silyl acetal of methyl tridecanoate was generated and converted to corresponding aldehyde by acidic workup. Further this aldehyde is subjected to HWE olefination to get the pure **III-2r**. Acyclic ester without containing enolizable protons also yielded the corresponding enoate **III-2t** in improved yield and high stereoselectivity(*E/Z* > 20:1). Presumably, sterically encumbered esters

are less vulnerable to the undesired reduction, where we did not observe any reduction product of **III-2t** during the reductive HWE process.

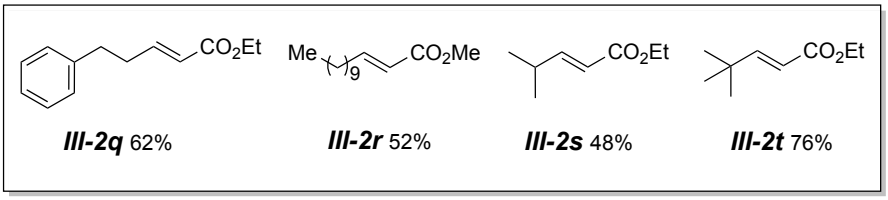


Figure 3.3 Substrate scope of aliphatic esters

Next, the feasibility of bidirectional reductive HWE reactions of diethyl succinate, diethyl isophthalate and diethyl pyridine-2,6-dicarboxylate were examined (Figure 3.4). These reactions afforded corresponding diendioates **III-2u** to **III-2w** in moderate to good yields (48-80%) and high stereoselectivity (*E/Z* > 20:1).

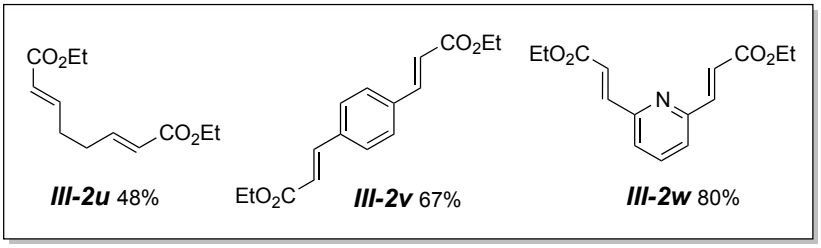


Figure 3.4 Substrate scope of dual reductive HWE olefination

The chemoselective reductive HWE of isopropyl methyl terephthalate was achieved to furnish the enoate **III-2x** in a good yield and high stereoselectivity (*E/Z* > 20:1) (Figure 3.5). Specifically, the chemoselective hydrosilylation was realized by use of sterically hindered diisopropyl silane, which was more selective than diethylsilane in the hydrosilylation.[17] Importantly, the chemoselective reductive HWE has been challenging,

and this Ir-catalyzed reductive HWE reaction has an clear advantage over the traditional reductive HWE olefination.

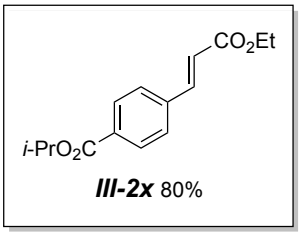


Figure 3.5 Chemoselective reductive HWE olefination

There are limited examples for reductive HWE olefination of alkenyl esters and, to our surprise, no example of an alkynyl ester has been reported so far in literature. Our approach demonstrated that these challenging substrates provided the homologated products in good yields and high stereoselectivity (Figure 3.6). For example, when methyl cinnamates with different para substituents were subjected to the reductive HWE olefination, the dienoates **II-2y** to **III-2aa** were successfully produced in good yields and high stereoselectivity. When alkynyl ester (methyl 3-phenylpropiolate) was examined with our reductive HWE olefination approach, the reaction afforded (*E*)-methyl 5-phenylpent-2-en-4-ynoate **III-2ab** in 79% yield and high stereoselectivity.

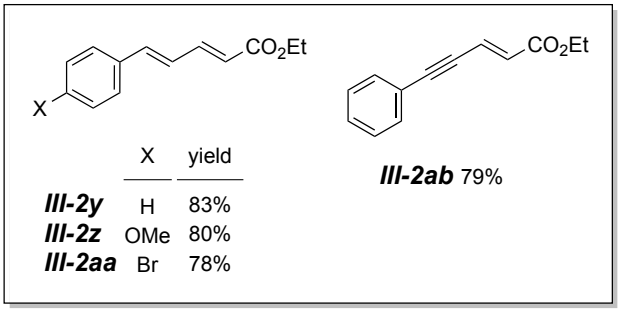


Figure 3.6 Substrate scope alkenyl esters and alkynyl esters

The reductive HWE reactions of lactones were also studied (Figure 3.7). When different ring-size lactones such as γ-butyrolactone, decalactone and ε-caprolactone were subjected to the reductive HWE olefination, hydroxy enoates **III-2ac** to **III-2ae** were produced with good to excellent yields and high stereoselectivity (*E/Z* > 20:1). Along with **III-2ac** (68% yield), cycloetherification product (23% yield) was also observed in case of γ-butyrolactone. As the ring size increases from γ-butyrolactone to ε-caprolactone the cycloetherification product has decreased. The reductive HWE of benzolactone

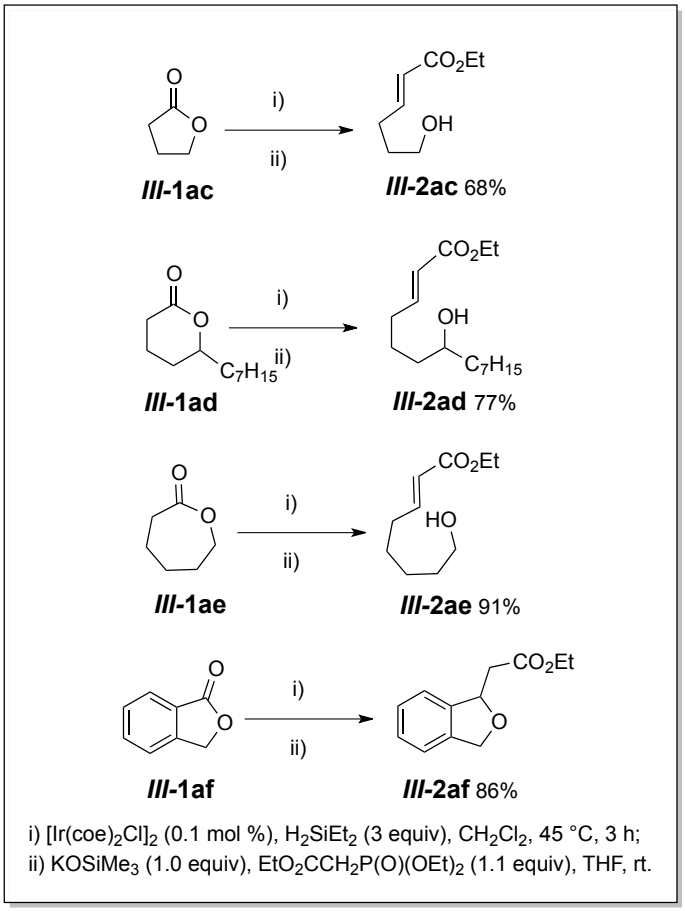


Figure 3.7 Scope of lactones

exclusively furnished entropically favored ethyl 2-(1,3-dihydroisobenzofuran-1-yl)acetate (**III-2af)** via a spontaneous cycloetherification.

3.2. Iterative Reductive Horner-Wadsworth-Emmons Olefination

Feasibility of iterative reductive HWE olefination was examined (Figure 3.8). Synthesis of trienoates through the traditional reductive HWE olefination involves i) reduction of esters, ii) subsequent oxidation of alcohols to form aldehydes and iii) HWE olefination of the aldehydes. For one iteration three steps are associated with it and hence three iterations require a total of 9 steps. We believe that our reductive HWE olefination could reduce the overal synthetic steps compared with the traditional HWE reaction. Therefore, we examined this hypothesis using methyl benzoate. First iteration furnished methyl cinnamate from methyl benzoate. Methyl cinnamate (**III-3**) is isolated in 89% yield, which was subjected to second iteration. Second iteration afforded (2*E*,4*E*)-methyl 5-phenylpenta-2,4-dienoate (**III-4**) from methyl cinnamate, which was isolated in 83% yield and subjected for third iteration. Fortunatley, third iteration of reductive HWE

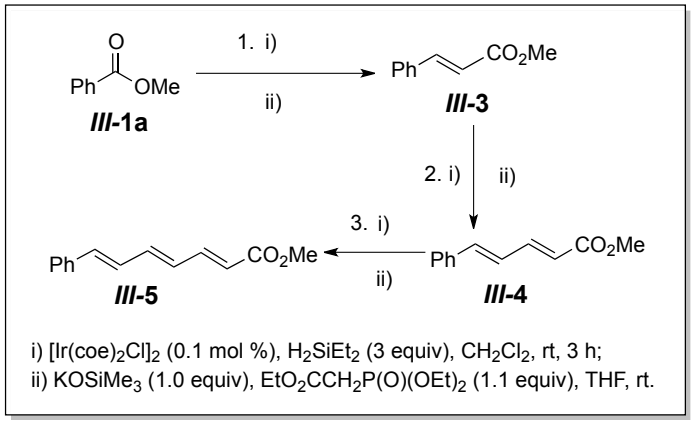
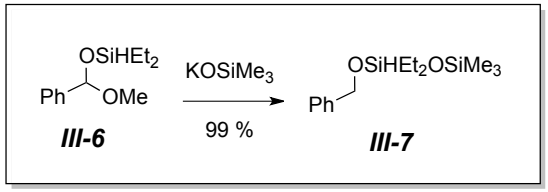


Figure 3.8 Iterative reductive HWE olefination

olefination was compatible and provided (2*E*,4*E*,6*E*)-methyl 7-phenylhepta-2,4,6-trienoate (**III-5**) with 48% yield. Overall, trienoate **III-5** was produced 34% yield in a three-pot reaction sequence. This approach shows the feasibility of the Ir-catalyzed reductive HWE olefination towards iterations, thereby minimizing the steps associated with the traditional HWE olefination.

3.3. Proposed Mechanism

We were curious about the mechanism of the Ir-catalyzed redutive HWE reaction. In order to understand the process of sequential Lewis base activation of silyl acetals and HWE olefination a control experiment was performed (Figure 3.9). When we carried out the reaction with silyl acetal **III-6** and Lewis base in the absence of diethylsilane and trimethylphosphonoacetate, the carbonyl hydrosilylation adduct **III-7** was exclusively produced. This result perhaps explains the observed over-reduced outcomes (Chapter 2, Figure 2.5), where the requisite hydride delievery would be from diethylhydridosilyl acetals, not by external reducing agents such as diethyl silane.



III-6 ***III-7***

Figure 3.9 Control experiment

There are two possible ways of the formation of the carbonyl hydrosilylation adduct **III-7** (Figure 3.10). Aldehyde **III-10** generated *in situ* via dissociation path I can react with disiloxane **III-11** (reduction path I).[18,19] Alternatively, intramolecular hydride delivery within oxonium penta-coordinate silicate **III-9** which can be produced via

dissociation path II can be responsible for the reduction to afford the carbonyl hydrosilylation adduct (reduction path II).[19,20] Therefore, the elucidation for the two possible reduction pathways allows us to think about an alternative HWE mechanism. In detail, the oxonium penta-coordinate silicate **III-9** may react with trimethyl phosphonoacetate anion to afford methyl cinnamate **III-3**.

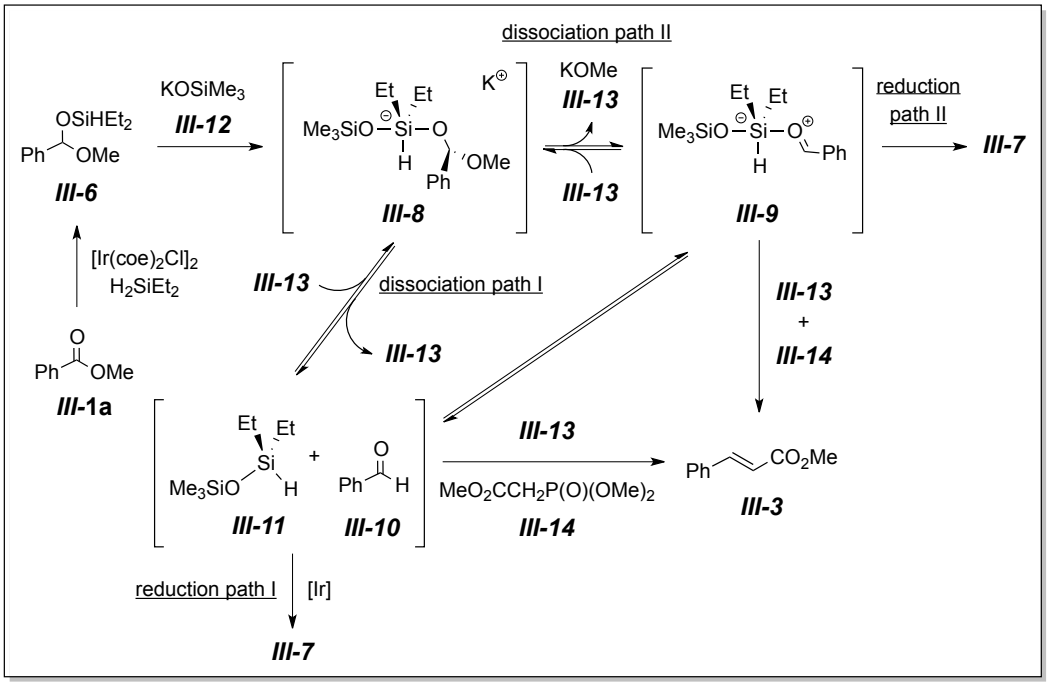


Figure 3.10 Proposed mechanism

In order to understand the reaction mechanism better by identifying the intermediate responsible for the product formation, a competition experiment was performed with an equimolar ratio of silyl acetal **III-6** and deuterobenzaldehyde **III-15** (Figure 3.11). A mixture of **III-3** and **III-3-D** was observed in a ratio of 1:3, which suggests that the fully dissociated aldehyde is likely generated *in situ* and might be responsible in the product formation. We are currently studying on elucidating this mechanism.

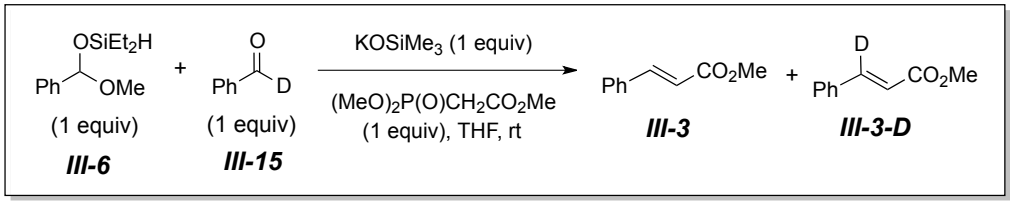


Figure 3.11 Competition experiment

Conclusion

In conclusion, a one-pot reductive Horner-Wadsworth-Emmons olefination has been developed. Lewis base-promoted deprotonative addition of pronucleophiles to silyl acetals is the key strategy of this method. The challenges associated with the traditional reductive HWE olefination have been addressed regarding the croyogenic conditions and limited substrate scope. For instance, the developed Ir-catalyzed reductive Horner-Wadsworth-Emmons olefination proceeds under the mild reaction conditions (i.e., room temperature). Furthermore, a wide range of substrates including traditionally challenging substrates such as alkenyl and alkynyl esters were successfully converted to the corresponding enoates with excellent stereoselctivity and good to excellent yields. Overall, the reductive Horner-Wadsworth-Emmons olefination is operationally convenient and feasible for a wide range of scales from miligram to gram scale. We expect that the reductive Horner-Wadsworth-Emmons olefination will enhance the utility of silyl acetals as aldehyde equivalents in the synthetic chemistry.

Experimental Section

General Experimental Information

Reactions requiring anhydrous conditions were performed under an atmosphere of nitrogen or argon in flame- or oven-dried glassware. Anhydrous toluene and dichloromethane (DCM) were distilled from CaH_2. Anhydrous tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium and benzophenone. Triethylamine and pyridine were distilled from KOH. DMF and DMSO were stored over 4Å molecular sieves. All other solvents and reagents from the commercial sources were used as received. NMR spectra were recorded on a 500 or 300 MHz NMR spectrometer. ^1H NMR chemical shifts are referenced to chloroform (7.26 ppm)and DMSO-d_6 (2.50 ppm). ^{13}C NMR chemical shifts are referenced to $^{13}CDCl_3$ (77.23 ppm), and DMSO-d_6 (39.52 ppm). The following abbreviations are used to describe multiplets: s (singlet), d (doublet), t (triplet), q (quartet), pent (pentet), m (multiplet), nfom (non-first-order multiplet), and br (broad). The following format was used to report peaks: chemical shift in ppm [multiplicity, coupling constant(s) in Hz, integral, and assignment]. ^1H NMR assignments are indicated by structure environment, e.g., CH_aH$_b$. ^1H NMR and ^{13}C NMR were processed with iNMR software program. Infrared (IR) spectra were recorded using neat (for liquid compound) or a thin film from a concentrated DCM solution. Absorptions are reported in cm^{-1}. Only the most intense and/or diagnostic peaks are reported. MPLC refers to medium pressure liquid chromatography (25-200 psi) using hand-packed columns of silica gel (20-45 μm, spherical, 70 Å pore size), an HPLC pump, and a differential refractive index detector. High-resolution mass spectra (HRMS) were recorded in Atmospheric pressure chemical ionization time-of-flight (APCI-TOF) mode. Samples were introduced as solutions in mixed solution of methanol and methylene

chloride (DCM). GC-MS experiments using electron impact ionization (EI) were performed at 70 eV using a mass-selective detector. The method used is noted parenthetically: 5029017 refers to: 2 min @ 50 °C – 20 °C/min – 3 min @ 290 °C. Analytical TLC experiments were performed on F254 plate, 250 μm thickness. Detection was performed by UV light or potassium phosphomolybdic acid, permanganate, *p*-anisaldehyde staining.

General procedure for reductive HWE olefination

$[Ir(coe)_2Cl]_2$ (0.90 mg, 0.1 mol %) and esters (1 mmol) were dissolved with CH_2Cl_2 (0.30 mL, 3.30 M). Diethylsilane (0.30 mL, 3 mmol) was added to the mixture. The septum on the vial was replaced by a screw cap with a Teflon liner [Note: diethylsilane (b.p. 56 °C and density 0.686 g/mL) is volatile]. The reaction mixture was kept at room temperature and stirred for 3 h. The volatiles were removed *in vacuo* to afford the diethylhydrosilyl acetals, which were directly used for subsequent reactions without further purification.

The crude diethylhydrosilyl acetals were dissolved in THF (6.30 ml, 0.16 M) and alkyl phosphonoacetate (1.1 mmol) and potassium trimethylsilanolate (128.30 mg, 1 mmol) dissolved in THF (6.30 ml, 0.16 M) were added at 0 °C in an ice-bath. The reaction mixture is kept at room temperature and stirred for 30 minutes. The reaction mixture was quenched with aqueous ammonium chloride (0.50 ml). The mixture was extracted with diethyl ether (5 mL×4). The combined organic extracts were washed with water (10 mL) and brine (10 mL), and dried over anhydrous sodium sulfate. The volatiles were removed *in vacuo,* and the crude mixture was purified by MPLC to afford the corresponding α,β-unsaturated esters.

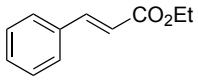
Procedure for a gram-scale reductive HWE olefination reaction

$[Ir(coe)_2Cl]_2$ (9.00 mg, 0.1 mol %) and methyl benzoate (1.36 g, 10 mmol) were dissolved with CH_2Cl_2 (3.30 mL, 3 M). Diethylsilane (3.30 mL, 3 mmol) was added to the mixture. The septum on the vial was replaced by a screw cap with a Teflon liner. The reaction mixture was kept at room temperature and stirred for 4 h. The volatiles were removed *in vacuo* to afford the diethylhydrosilyl acetals, which were directly used for subsequent reactions without further purification.

The crude diethylhydrosilyl acetals were dissolved in THF (10.00 ml, 1 M) and alkyl phosphonoacetate (1.1 mmol) and potassium trimethylsilanolate (128.30 g, 1 mmol) dissolved in THF (15.00 ml, 0.60 M) were added at 0 °C in an ice-bath. The reaction mixture is kept at room temperature and stirred for 30 minutes. The reaction mixture was quenched with aqueous ammonium chloride (2.00 ml). The mixture was extracted with diethyl ether (40 mL×4). The combined organic extracts were washed with water (20 mL) and brine (20 mL), and dried over anhydrous sodium sulfate. The volatiles were removed *in vacuo,* and the crude mixture was purified by MPLC to afford corresponding ethyl cinnamate. (1.49 g, 85%, yellow oily liquid).

Analysis and characterization of synthesized compounds

Ethyl cinnamate (III-2a)



Physical form: Yellow liquid.

Yield: 1 mmol scale, 153 mg, 87% (*E/Z* > 20:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.69 (d, *J* = 16.0 Hz, 1H, ArC*H*=CH), 7.52 (m, 2H, Ar-*H*), 7.39 (m, 3H, Ar-*H*), 6.44 (d, *J* = 16.0 Hz, 1H, ArCH=C*H*), 4.26 (q, *J* = 7.1 Hz, 2H, $CO_2CH_2CH_3$), and 1.34 (t, *J* = 7.1 Hz, 3H, $CO_2CH_2CH_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.2, 144.8, 134.7, 130.4, 129.1, 128.3, 118.5, 60.7 and 14.5.

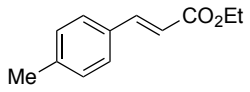
TLC: R_f = 0.60 in 5:1 hexanes: EtOAc.

GC-MS (5032021): t_R = 9.28 min, m/z 176, {[$(M+H)^+$] 177,100} and 131 [$(M–OEt)^+$, 99]

IR (neat): 2980 (m), 1706 (s), 1636 (m), 1308 (m), 1163 (s) and 765 (m) cm^{-1}.

Reference of spectral data: Leung, P.S.; Teng, Y.; Toy, P. H. *Org. Lett.* **2010**, *12*, 4996-4999.

Ethyl (*E*)-3-(*p*-tolyl)acrylate (III-2b)



Physical form: Colorless liquid.

Yield: 0.5 mmol scale, 61 mg, 64% (*E/Z* > 20:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.66 (d, *J* = 16.0 Hz, 1H, ArC*H*=CH), 7.42 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.19 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 6.39 (d, *J* = 16.0 Hz, 1H, ArCH=C*H*), 4.26 (q, *J* = 7.1 Hz, 2H, $CO_2CH_2CH_3$), 2.37 (s, 3H, Ar-CH_3), and 1.34 (t, *J* = 7.1 Hz, 3H, $CO_2CH_2CH_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.4, 144.7, 140.8, 131.9, 129.8, 128.2, 117.3, 60.6, 21.6, and 14.5.

TLC: R_f = 0.60 in 60:1 hexanes: EtOAc.

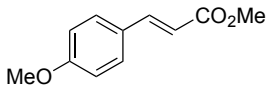
GC-MS (5032021): t_R = 10.01 min, m/z 190, {$[(M+H)^+]$ 191,100} and 145 $[(M–OC_2H_5)^+$, 70]

IR (neat): 2980 (m), 1708 (s), 1634 (m), 1309 (m), 1163 (s) and 811 (m) cm^{-1}.

HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{12}H_{15}O_2)^+$: 191.1067. Found: 191.1063

Reference of spectral data: Peng, Y.; Chen, J.; Ding, J.; Liu, M.; Gao, W.; Wu, H. *Synthesis* **2011**, 213-216

Methyl (*E*)-3-(4-methoxyphenyl)acrylate (III-2c)



Physical form: White solid.

Yield: 0.5 mmol scale, 59 mg, 61% (*E/Z* > 20:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.65 (d, *J* = 16.0 Hz, 1H, ArC*H*=CH), 7.47 (d, *J* = 8.7 Hz, 2H, Ar-*H*), 7.00 (d, *J* = 8.7 Hz, 2H, Ar-*H*), 6.31 (d, *J* = 16.0 Hz, 1H, ArCH=C*H*), 3.83 (s, 3H, Ar-OC*H*$_3$ or CO_2CH_3) and 3.79 (s, 3H, CO_2CH_3 or Ar-OC*H*$_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 168.0, 161.59, 144.7, 129.9, 127.3, 115.4, 114.5, 55.6 and 51.8.

TLC: R_f = 0.40 in 5:1 hexanes: EtOAc.

GC-MS (5032021): t_R = 9.63 min, m/z 192, 193 [$(M+H)^+$, 50], 163[$(M–OC_2H_5)^+$, 50], and 121 (100).

IR (neat): 2955 (m), 1681 (m), 1598 (s), 1511 (s), 1246 (s), 1159 (s), 1004 (s) and 829 (s) cm^{-1}.

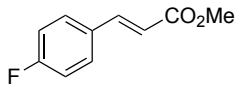
HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{11}H_{13}O_3)^+$: 193.0859. Found: 193.0855

MP: 85-88 °C.

Literature melting point: 85-90 °C.

Reference of spectral data: Peng, Y.; Chen, J.; Ding, J.; Liu, M.; Gao, W.; Wu, H. *Synthesis* **2011**, 213-216

Methyl (*E*)-3-(4-fluorophenyl)acrylate (III-2d)



Physical form: White solid.

Yield: 0.5 mmol scale, 65 mg, 71% (*E/Z* > 20:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.65 (d, *J* = 16.0 Hz, 1H, ArC*H*=CH), 7.50 [dd, *J* = 8.6, 5.3 (J^4_{F-H}) Hz, 2H, Ar-*H*], 7.07 [dd, *J* = 8.6, 8.6 (J^3_{F-H}) Hz, 2H, Ar-*H*], 6.36 (d, *J* = 16.0 Hz, 1H, ArCH=C*H*), and 3.8 (s, 3H, CO_2CH_3).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.4, 163.9 (d, J^1_{F-C} = 251.8 Hz), 143.6, 130.7 (d, J^4_{F-C} = 3.6 Hz), 130 (d, J^3_{F-C} = 8.5 Hz), 117.6 (d, J^5_{F-C} = 2.2 Hz), 116.1 (d, J^2_{F-C} = 22.5 Hz), and 51.8.

TLC: R_f = 0.50 in 5:1 hexanes: EtOAc.

GC-MS (5032021): t_R = 8.73 min, m/z 180, 181[$(M+H)^+$, 100], and 149[$(M–OCH_3)^+$, 99].

IR (neat): 2954 (m), 1716 (m), 1508 (s), 1169 (s), 1006 (m) and 829 (s) cm^{-1}.

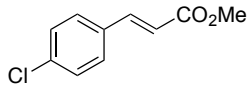
HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{10}H_{10}FO_2)^+$: 181.0659. Found: 181.0647.

MP: 43-45 °C

Literature melting point: 44-46 °C.

Reference of spectral data: Lee, H.; Milner, P. J.; Buchwald, S. L. *Org. Lett*. **2013,** *21*, 5602-5605

Methyl (*E*)-3-(4-chlorophenyl)acrylate (III-2e)



Physical form: White solid.

Yield: 0.5 mmol scale, 75 mg, 76% (*E/Z* > 20:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.62 (d, *J* = 16.0 Hz, 1H, ArC*H*=CH), 7.43 (d, *J* = 8.5 Hz, 2H, Ar-*H*), 7.34 (d, *J* = 8.5 Hz, 2H, Ar-*H*), 6.40 (d, *J* = 16.0 Hz, 1H, ArCH=C*H*), and 3.79 (s, 3H, CO_2CH_3).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.2, 143.4, 136.2, 132.9, 129.3,129.2, 118.4, and 51.8.

TLC: R_f = 0.50 in 5:1 hexanes: EtOAc.

GC-MS (5032021): t_R = 10.00 min, m/z 196, 196[$(M)^+$, 100], 197[$(M+H)^+$, 50], 165[$(M–OCH_3)^+$, 99], and 102 (40).

IR (neat): 2950 (m), 1703 (s), 1633 (m), 1312(s), 1166 (s), 1002 (s) and 817 (s) cm^{-1}.

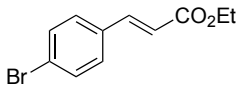
HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{10}H_{10}ClO_2)^+$: 197.0364. Found: 197.0350.

MP: 72-74 °C

Literature melting point: 73-74 °C.

Reference of spectral data: Chintareddy, V. R.; Ellern, A.; Verkade, J. G. *J. Org. Chem*. **2010,** *75*, 7166-7174

Ethyl (*E*)-3-(4-bromophenyl)acrylate (III-2f)



Physical form: Colorless liquid.

Yield: 1 mmol scale, 188 mg, 74% (*E/Z* > 20:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.61 (d, *J* = 16 Hz, 1H, ArC*H*=CH), 7.52 (d, *J* = 8.5 Hz, 2H, Ar-*H*), 7.34 (d, *J* = 8.5 Hz, 2H, Ar-*H*), 6.42 (d, *J* = 16 Hz, 1H, ArCH=C*H*), 4.26 (q, *J* = 7.1 Hz, 2H, $CO_2CH_2CH_3$), and 1.34 (t, *J* = 7.1 Hz, 3H, $CO_2CH_2CH_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.8, 143.2, 133.5, 132.2, 129.5, 124.5, 119.0, 60.7, and 14.4.

TLC: R_f = 0.30 in 60:1 hexanes: EtOAc.

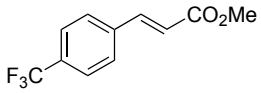
GC-MS (5032021): t_R = 11.04 min, m/z 254, 256[$(M+H)^+$, 100], 209[$(M–OCH_3)^+$, 99], and 102 (40).

IR (neat): 2956 (m), 1709 (s), 1636 (m), 1308(s), 1162 (s), 1008 (s) and 815 (s) cm^{-1}.

HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{11}H_{12}BrO_2)^+$: 255.0015. Found: 255.0005.

Reference of spectral data: Chintareddy, V. R.; Ellern, A.; Verkade, J. G. *J. Org. Chem*. **2010,** *75*, 7166-7174.

Methyl (*E*)-3-[4-(trifluoromethyl)phenyl]acrylate (III-2g)



Physical form: White solid.

Yield: 0.5 mmol, 73 mg, 63% (*E/Z* > 20:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.70 (d, *J* = 16.0 Hz, 1H, ArC*H*=CH), 7.60 (d, *J* = 8.6 Hz, 2H, Ar-*H*), 7.58 (d, *J* = 8.6 Hz, 2H, Ar-*H*), 6.51 (d, *J* = 16.0 Hz, 1H, ArCH=C*H*), and 3.80 (s, 3H, CO_2CH_3).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.9, 143.0, 137.8, 131.8 (q, $J^2_{F\text{-}C}$ = 32.8 Hz), 128.2, 125.9 (q, $J^3_{F\text{-}C}$ = 3.6 Hz), 123.8 (q, $J^1_{F\text{-}C}$ = 272 Hz), 120.41, and 51.9.

TLC: R_f = 0.50 in 5:1 hexanes: EtOAc.

GC-MS (5032021): t_R = 8.54 min, m/z 230, 231 [$(M+H)^+$, 90], 199 [$(M–OCH_3)^+$, 100], and 151 (60).

IR (neat): 2956 (m), 1707 (s), 1637 (m), 1313(s), 1159 (m), 1063 (m) and 831 (s) cm^{-1}.

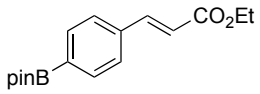
HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{11}H_{10}F_3O_2)^+$: 231.0627. Found: 231.0623.

MP: 70-72 °C

Literature melting point: 72 °C.

Reference of spectral data: Youn, S. W.; Kim, B. S.; Jagdale, A. R. *J. Am. Chem. Soc*. **2012,** *134*, 11308-11311**.**

Ethyl (*E*)-3-[4-(4,4,5,5-tetramethyl-1,3-dioxaborolan-2-yl)phenyl]acrylate (III-2h)



Physical form: Colorless liquid.

Yield: 0.5 mmol, 95 mg, 63% (*E/Z* > 20:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.81 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.69 (d, *J* = 16.0 Hz, 1H, ArC*H*=CH), 7.51 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 6.48 (d, *J* = 16.0 Hz, 1H, ArCH=C*H*), 4.26 (q, *J* = 7.1 Hz, 2H, $CO_2CH_2CH_3$), 1.37-1.33 (s, 12H, Bpin), and 1.33 (t, *J* = 7.1 Hz, 3H, $CO_2CH_2CH_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.0, 144.5, 137.0, 135.3 (2), 127.3, 119.3, 84.1, 60.6, 24.9 and 14.4.

TLC: R_f = 0.50 in 5:1 hexanes: EtOAc.

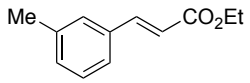
GC-MS (5032021): t_R = 13.01 min, m/z 302, 303 [$(M+H)^+$, 100], 257[$(M–OC_2H_5)^+$, 99], 216 (98) and 157 (50).

IR (neat): 2978 (m), 1711 (s), 1636 (m), 1356 (s), 1165 (s), 1087 (s) and 826 (m) cm^{-1}.

HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{17}H_{24}BO_4)^+$: 303.1762. Found: 303.1753.

Reference of spectral data: Qiu, D.; Jin, L.; Zheng, Z.; Meng, H.; Mo, F.; Wang, X.; Zhang, Y.; Wang, J. *J. Org. Chem*. **2013,** *78*, 1923-1933

Ethyl (*E*)-3-(*m*-tolyl)acrylate (III-2i)



Physical form: Colorless liquid.

Yield: 0.5 mmol, 93 mg, 81% (*E/Z* > 20:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.66 (d, *J* = 16.0 Hz, 1H, ArC*H*=CH), 7.34 (s, 1H, MeCC*H*CCH=CH), 7.33 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 7.27 (dd, *J* = 7.5, 7.5 Hz, 1H, MeCCHC*H*CH), 7.19 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 6.43 (d, *J* = 16.0 Hz, 1H, ArCH=C*H*), 4.26 (q, *J* = 7.1 Hz, 2H, $CO_2CH_2CH_3$), 2.37 (s, 3H, Ar-CH_3), and 1.34 (t, *J* = 7.1 Hz, 3H, $CO_2CH_2CH_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.3, 144.9, 138.7, 134.6, 131.2, 128.93, 128.89, 125.4, 118.2, 60.6, 21.5, and 14.5.

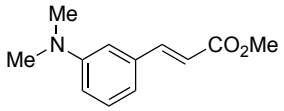
TLC: R_f = 0.60 in 60:1 hexanes: EtOAc.

GC-MS (5032021): t_R = 9.92 min, m/z 190, 191[$(M+H)^+$, 100], and 145[$(M–OC_2H_5)^+$, 90].

IR (neat): 2957 (m), 1708 (s), 1636 (m), 1309 (m), 1157 (s), 1037 (m) and 784 (m) cm^{-1}.

HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{12}H_{15}O_2)^+$: 191.1067. Found: 191.1048.

Methyl (*E*)-3-[3-(dimethylamino)phenyl]acrylate (III-2j)



Physical form: Yellow solid.

Yield: 0.5 mmol, 94 mg, 91% (*E/Z* > 20:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.67 (d, *J* = 16.0 Hz, 1H, ArC*H*=CH), 7.25 (dd, *J* = 8.3, 7.6 Hz, 1H, Me_2NCCHC*H*CH), 6.90 (dd, *J* = 7.6, 1.3 Hz, 1H, Ar-*H*), 6.83 (dd, *J* = 2.6, 1.3 Hz, 1H, Me_2NCC*H*CCH=CH), 6.76 (dd, *J* = 8.3, 2.6, Hz, 1H, Ar-*H*), 6.42 (d, *J* = 16.0 Hz, 1H, ArCH=C*H*), 3.80 (s, 3H, COCH_3), and 2.97 (s, 6H, NMe_2)

^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.8, 150.9, 146.1, 135.2, 129.6, 117.4, 116.4, 114.6, 112.0, 51.8 and 40.6.

TLC: R_f = 0.50 in 5:1 hexanes: EtOAc.

GC-MS (5032021): t_R = 11.46 min, m/z 205, 205 [$(M)^+$, 100], 206 [$(M+H)^+$, 50], 191[$(M–CH_3)^+$, 10], and 144 (10).

IR (neat): 2951 (m), 1716 (s), 1598 (s), 1308 (m), 1167(s) and 840 (m) cm^{-1}.

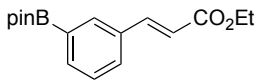
HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{12}H_{16}NO_2)^+$: 206.1176. Found: 206.1159.

MP: 56-58 °C

Literature melting point: 56-58 °C.

Reference of spectral data: Kim, E.; Koh, M.; Lim, B. J.; Park, S. B. *J. Am. Chem. Soc*. **2011**, *133*, 6642-6649

Ethyl (*E*)-3-[3-(4,4,5,5-tetramethyl-1,3-dioxaborolan-2-yl)phenyl]acrylate (III-2k)



Physical form: Colorless liquid.

Yield: 0.5 mmol, 115 mg, 76% (*E/Z* > 20:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.98 (s, 1H, BpinCC*H*CCH=CH), 7.80 (app d, *J* = 7.5 Hz, 1H, Ar-*H*), 7.70 (d, *J* = 16.0 Hz, 1H, ArC*H*=CH), 7.60 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 7.38 (dd, *J* = 7.5, 7.5 Hz, 1H, Ar-*H*), 6.48 (d, *J* = 16.0 Hz, 1H, ArCH=C*H*), 4.26 (q, *J* = 7.1 Hz, 2H, $CO_2CH_2CH_3$), 1.34 (m, 12H, Bpin), and 1.32 (app t, *J* = 7.1 Hz, 3H, $CO_2CH_2CH_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.2, 144.7, 136.7, 134.6 (2), 134.0, 131.0, 128.5, 118.5, 84.2, 60.6, 25.1 and 14.5.

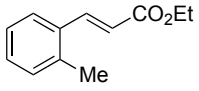
TLC: R_f = 0.40 in 8:1 hexanes: EtOAc.

GC-MS (5032021): t_R = 12.94 min, m/z 302, 303[$(M+H)^+$, 100], 302[$(M)^+$, 20], 257 [$(M–OC_2H_5)^+$, 50], and 170 (60).

IR (neat): 2978 (m), 1711 (s), 1637 (m), 1357 (s), 1141 (s) and 698 (m) cm^{-1}.

HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{17}H_{24}BO_4)^+$: 303.1762. Found: 303.1755.

Ethyl (*E*)-3-(*o*-tolyl)acrylate (III-2l)



Physical form: Colorless liquid.

Yield: 1 mmol, 150.1 mg, 79% (*E/Z* > 20:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.98 (d, *J* = 16.0 Hz, 1H, ArC*H*=CH), 7.55 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 7.26 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H, Ar-*H*), 7.20 (dd, *J* = 7.5, 7.5 Hz, 1H, Ar-*H*), 7.19 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 6.36 (d, *J* = 16.0 Hz, 1H, ArCH=C*H*), 4.27 (q, *J* = 7.1 Hz, 2H, $CO_2CH_2CH_3$), 2.43 (s, 3H, Ar-CH_3), and 1.34 (t, *J* = 7.1 Hz, 3H, $CO_2CH_2CH_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.2, 142.4, 137.8, 133.6, 130.9, 130.1, 126.55, 126.48, 119.4, 60.6, 19.9, and 14.5.

TLC: R_f = 0.60 in 60:1 hexanes: EtOAc.

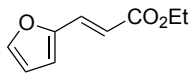
GC-MS (5032021): t_R = 9.75 min, m/z 190, 191 [$(M+H)^+$, 100], and 145[$(M–OC_2H_5)^+$, 50]

IR (neat): 2979 (m), 1708 (s), 1632 (m), 1311 (m), 1164 (s), 1033 (m) and 760 (m) cm^{-1}.

HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{12}H_{15}O_2)^+$: 191.1067. Found: 191.1039.

Reference of spectral data: Khalafi-Nezhad, A.; Panahi, F. *J. Organomet. Chem*. **2013**, *741-742*, 7-14.

Ethyl (*E*)-3-(furan-2-yl)acrylate (III-2m)



Physical form: Colorless liquid.

Yield: 1 mmol, 125 mg, 75% (*E/Z* > 20:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.47 (app d, *J* = 1.5 Hz, 1H, Ar-*H*), 7.42 (d, *J* = 16.0 Hz, 1H, C*H*=CHCO$_2$Et), 6.60 (d, *J* = 3.4 Hz, 1H, Ar-*H*), 6.46 (dd, *J* = 3.4, 1.5 Hz, 1H, Ar-*H*), 6.31 (d, *J* = 16.0 Hz, 1H, CH=C*H*CO$_2$Et), 4.24 (q, *J* = 7.1 Hz, 2H, CO$_2$C*H*$_2$CH$_3$), and 1.31 (t, *J* = 7.1 Hz, 3H, CO$_2$CH$_2$C*H*$_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.3, 151.2, 144.9, 131.2, 116.2, 114.8, 112.4, 60.6 and 14.5.

TLC: R_f = 0.40 in 20:1 hexanes: EtOAc.

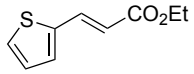
GC-MS (5032021): t_R = 8.00 min, m/z 166, 166 [$(M)^+$, 90] and 121[$(M– OC_2H_5)^+$, 100].

IR (neat): 2981 (m), 1703 (s), 1636 (s), 1208 (s), 1159 (s), 1015 (s) and 748 (m) cm^{-1}.

HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_9H_{11}O_3)^+$: 167.0703. Found: 167.0698.

Reference of spectral data: Chintareddy, V. R.; Ellern, A.; Verkade, J. G. *J. Org. Chem*. **2010,** *75*, 7166-7174

Ethyl (*E*)-3-(thiophen-2-yl)acrylate (III-2n)



Physical form: Colorless liquid.

Yield: 1 mmol, 122 mg, 67% (*E/Z* > 20:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.77 (app d, *J* = 15.7 Hz, 1H, C*H*=CHCO$_2$Et), 7.36 (app d, *J* = 5.0 Hz, 1H, thiophene-*H*), 7.24 (app d, *J* = 3.6 Hz, 1H, thiophene-*H*), 7.04 (q, *J* = 5.0, 3.6 Hz, 1H, thiophene-*H*), 6.23 (d, *J* = 15.7 Hz, 1H, CH=C*H*CO$_2$Et), 4.24 (q, *J* = 7.1 Hz, 2H, CO$_2$C*H*$_2$CH$_3$), and 1.32 (t, *J* = 7.1 Hz, 3H, CO$_2$CH$_2$C*H*$_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.1, 139.8, 137.2, 131.0, 128.5, 128.3, 117.3, 60.7 and 14.5.

TLC: R_f = 0.40 in 20:1 hexanes: EtOAc.

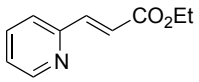
GC-MS (5032021): t_R = 9.34 min, m/z 182, 182[$(M)^+$, 30], 183[$(M+H)^+$, 90], and 137[$(M–OC_2H_5)^+$, 100].

IR (neat): 2979 (m), 1702 (s), 1623 (s), 1156 (s), and 700 (m) cm^{-1}.

HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_9H_{11}SO_2)^+$: 183.0474. Found: 183.0464.

Reference of spectral data: Chintareddy, V. R.; Ellern, A.; Verkade, J. G. *J. Org. Chem*. **2010,** *75*, 7166-7174

Ethyl (*E*)-3-(pyridin-2-yl)acrylate (III-2o)



Physical form: Colorless liquid.

Yield: 1 mmol, 129 mg, 72% (*E/Z* > 20:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.63 (d, *J* = 4.7 Hz, 1H, Ar-*H*), 7.70 (t, *J* = 7.7 Hz, 1H, Ar-*H*), 7.67 (d, *J* = 15.6 Hz, 1H, ArC*H*=CH), 7.40 (d, *J* = 7.7 Hz, 1H, Ar-*H*), 7.25 (ddd, *J* = 7.7, 4.7, 1.1 Hz 1H, Ar-*H*), 6.89 (d, *J* = 15.6 Hz, 1H, ArCH=C*H*), 4.26 (q, *J* = 7.1 Hz, 2H, $CO_2CH_2CH_3$), and 1.32 (t, *J* = 7.1 Hz, 3H, $CO_2CH_2CH_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.8, 153.1, 150.2, 143.3, 136.8, 124.38, 124.25, 122.7, 60.6 and 14.5.

TLC: R_f = 0.50 in 3:1 hexanes: EtOAc.

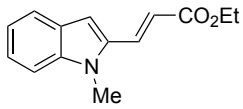
GC-MS (5032021): t_R = 9.57 min, m/z 177, 178 [$(M+H)^+$, 100] and 132 [$(M– OC_2H_5)^+$, 90].

IR (neat): 2981 (m), 1707 (s), 1623 (m), 1329 (m), 1149 (s), 979 (m) and 783 (m) cm^{-1}.

HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{10}H_{12}NO_2)^+$: 178.0863. Found: 178.0860.

Reference of spectral data: Chintareddy, V. R.; Ellern, A.; Verkade, J. G. *J. Org. Chem*. **2010,** *75*, 7166-7174

Ethyl (*E*)-3-(1-methyl-1*H*-indol-2-yl)acrylate (III-2p)



Physical form: Brown solid.

Yield: 0.25 mmol, 29 mg, 50% (*E/Z* > 20:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.80 (d, *J* = 15.8 Hz, 1H, ArC*H*=CH), 7.62 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.31 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.27 (ddd, *J* = 8.0, 6.8, 1.1 Hz, 1H, Ar-*H*), 7.13 (ddd, *J* = 8.0, 6.8, 1.1 Hz, 1H, Ar-*H*), 6.96 (s, 1H, Ar-*H*), 6.50 (d, *J* = 15.6 Hz, 1H, ArCH=C*H*), 4.30 (q, *J* = 7.1 Hz, 2H, $CO_2CH_2CH_3$), 3.81 (s, 3H, ArN-CH_3) and 1.37 (t, *J* = 7.1 Hz, 3H, $CO_2CH_2CH_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.1, 139.2, 135.0, 132.7, 127.6, 123.7, 121.5, 120.5, 118.3, 109.7, 103.8, 60.6, 30.1 and 14.5.

TLC: R_f = 0.40 in 8:1 hexanes: EtOAc.

GC-MS (5032021): t_R = 12.89 min, m/z 229, 230[$(M+H)^+$, 90] and 156 [$(M- CO_2C_2H_5)^+$, 100].

IR (neat): 2987 (m), 1703 (s), 1633 (m), 1275 (m), 1174 (s) and 749 (s) cm^{-1}.

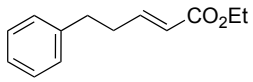
HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{14}H_{16}NO_2)^+$: 230.1176. Found: 230.1172.

MP: 82-85 °C

Literature melting point: 84-87 °C.

Reference of spectral data: Maehara, A.; Tsurugi, H.; Satoh, T.; Miura, M. *Org. Lett*. **2008**, *10*, 1159-1162

Ethyl (*E*)-5-phenylpent-2-enoate (III-2q)



Physical form: Colorless liquid.

Yield: 0.5 mmol, 143 mg, 62% (*E/Z* > 20:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.30 (app t, *J* = 7.3 Hz, 2H, Ar-*H*), 7.21 (app t, *J* = 7.3 Hz, 1H, Ar-*H*), 7.18 (d, *J* = 7.3 Hz, 2H, Ar-*H*), 7.0 (dt, *J* = 15.6, 6.8 Hz, 1H, $ArCH_2CH_2C\mathit{H}$=CH), 5.84 (dt, *J* = 15.6, 1.6 Hz, 1H, $ArCH_2CH_2CH$=C*H*), 4.18 (q, *J* = 7.1 Hz, 2H, $CO_2C\mathit{H}_2CH_3$), 2.78 (t, *J* = 7.4 Hz, 2H, $ArC\mathit{H}_2CH_2CH$=CH), 2.53 (tdd, *J* = 8.3, 6.8, 1.6 Hz, 2H, $ArC\mathit{H}_2CH_2CH$=CH), and 1.28 (t, *J* = 7.1 Hz, 3H, $CO_2CH_2C\mathit{H}_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.8, 148.2, 141.0, 128.7, 128.5, 126.4, 122.0, 60.4, 34.5, 34.1 and 14.5.

TLC: R_f = 0.60 in 20:1 hexanes: EtOAc.

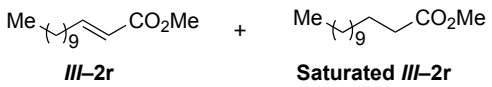
GC-MS (5032021): t_R = 10.10 min, m/z 204, 205 [$(M+H)^+$, 100], 159 [$(M– OC_2H_5)^+$, 30], and 130 (50).

IR (neat): 2935 (m), 1716 (s), 1634 (m), 1265 (m), 1194 (m) and 697 (s) cm^{-1}.

HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{13}H_{17}O_2)^+$: 205.1223. Found: 205.1201.

Reference of spectral data: Webb, D.; Jamison, T. F. *Org. Lett*. **2012,** *14*, 2465-2467

Methyl (*E*)-tridec-2-enoate (III-2r)



***III*–2r** **Saturated *III*–2r**

Physical form: Colorless liquid (*E/Z* > 20:1).

Yield: 1 mmol, 118 mg, 52 % (6:1 of **III-2r**:saturated **III-2r**).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.97 (dt, *J* = 15.8, 7.0 Hz, 1H, CH_2CH=CH), 5.81 (dt, *J* = 15.8, 1.7 Hz, 1H, CH_2CH=C*H*), 3.70 (s, 3H, CO_2CH_3), 2.19 (qd, *J* = 7.3, 1.7 Hz, 2H, CH_2CH_2CH=CH), 1.44 (app p, *J* = 7.3 Hz, 2H, CH_2CH_2CH=CH), 1.32-1.22 (m, 14H, $CH_3(CH_2)_7CH_2CH_2CH$=CH), and 0.87 [t, *J* = 6.9 Hz, 3H, $CH_3(CH_2)_9CH$=CH].

Saturated **III-2r** (methyl tridecanoate): δ 3.65 (s, 3H, CO_2CH_3), 2.29 (q, *J* = 7.5 Hz, 2H, $CH_2CH_2CO_2Me$), 1.60 (app p, *J* = 7.3 Hz, 2H, $CH_2CH_2CO_2Me$), 1.32-1.22 [overlapped with **III-2r** ; 18H, $CH_3(CH_2)_9CH_2CH_2CO_2Me$], and 0.87 [overlapped with **III-2r** ; 3H, $CH_3(CH_2)_9CH$=CH].

^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.4, 150.1, 121, 51.6, 32.4, 32.1, 29.8, 29.7, 29.6, 29.5, 29.3, 28.2, 22.9 and 14.3. Recognizable peaks from saturated **III-2r** (methyl tridecanoate): δ 174.4, 51.5, 34.3, and 25.1.

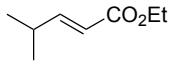
TLC: R_f = 0.40 in 20:1 hexanes: EtOAc.

GC-MS of III-2r (5032021): t_R = 10.30 min, m/z 226, 227 [$(M+H)^+$, 100], and 195 [$(M-OCH_3)^+$, 40],

IR (neat): 2923 (m), 1726 (s), 1634 (m), 1435 (m), 1267 (m) and 980 (m) cm^{-1}.

HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{14}H_{27}O_2)^+$: 227.1973. Found: 227.1959.

Ethyl (*E*)-4-methylpent-2-enoate (III-2s)



Physical form: Colorless liquid.

Yield: 1 mmol, 64 mg, 56% (*E/Z* > 20:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.93 (dd, *J* = 15.7, 6.7 Hz, 1H, *i*PrCH=C*H*), 5.76 (dd, *J* = 15.7, 1.5 Hz, 1H, *i*PrC*H*=CH), 4.18 (q, *J* = 7.1 Hz, 2H, $CO_2CH_2CH_3$), 2.45 [septet of d of d, *J* = 6.7, 6.7, 1.5 Hz, 1H, $(CH_3)_2CHCH$=CH], 1.28 (t, *J* = 7.1 Hz, 3H, $CO_2CH_2CH_3$), and 1.05 [s, *J* = 6.7 Hz, 6H, $(CH_3)_2$CHCH=CH].

^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.3, 155.7, 118.8, 60.4, 31.1, 21.4, and 14.5.

TLC: R_f = 0.30 in 40:1 hexanes: EtOAc.

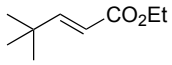
GC-MS (5032021): t_R = 5.49 min, m/z 142, 142 [$(M)^+$, 20], 143[$(M+H)^+$, 100] and 97 [$(M–OC_2H_5)^+$, 40].

IR (neat): 2958 (m), 1720 (s), 1634 (m), 1265 (m), 1054 (s), 841 (m) and 729 (m) cm^{-1}.

HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_8H_{15}O_2)^+$: 143.1067. Found: 143.1055.

Reference of spectral data: Chintareddy, V. R.; Ellern, A.; Verkade, J. G. *J. Org. Chem*. **2010,** *75*, 7166-7174.

Ethyl (*E*)-4,4-dimethylpent-2-enoate (III-2t)



Physical form: Colorless liquid.

Yield: 1 mmol, 82 mg, 76% (*E/Z* > 20:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.97 (d, *J* = 15.8 Hz, 1H, *t*-BuCH=C*H*), 5.72 (d, *J* = 15.7 Hz, 1H, *t*-BuC*H*=CH), 4.18 (q, *J* = 7.1 Hz, 2H, $CO_2CH_2CH_3$), 1.29 (t, *J* = 7.1 Hz, 3H, $CO_2CH_2CH_3$), and 1.07 [s, 9H, $(CH_3)_3CCH=CH$].

^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.6, 159.3, 116.9, 60.4, 34.0, 28.9, and 14.5.

TLC: R_f = 0.30 in 40:1 hexanes: EtOAc.

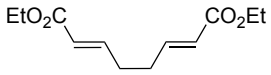
GC-MS (5032021): t_R = 5.90 min, m/z 156, 157 [$(M+H)^+$, 100], 141[$(M-CH_3)^+$, 30], and 111[$(M-OC_2H_5)^+$, 30].

IR (neat): 2958 (m), 1720 (m), 1634 (m), 1251 (m), 1047 (s) and 840 (s) cm^{-1}.

HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_9H_{17}O_2)^+$: 157.1223. Found: 157.1212.

Reference of spectral data: Zeitler, K. *Org. Lett*. **2006,** *8,* 637-640

Diethyl (2*E*,6*E*)-octa-2,6-dienedioate (III-2u)



Physical form: Colorless liquid.

Yield: 1 mmol, 108 mg, 48% (*E/Z* > 20:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.92 (app dt, *J* = 15.7, 6.3 Hz, 2H, C*H*=CHCO$_2$Et), 5.84 (d, *J* = 15.7 Hz, 2H, CH=C*H*CO$_2$Et), 4.18 (q, *J* = 7.1 Hz, 2H, CO$_2$C*H*$_2$CH$_3$), 2.36 (m, 4H, CH=CHC*H*$_2$), and 1.28 (t, *J* = 7.1 Hz, 6H, CO$_2$CH$_2$C*H*$_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.6, 147.1, 122.5, 60.5, 30.6 and 14.4.

TLC: R_f = 0.40 in 20:1 hexanes: EtOAc.

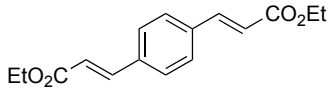
GC-MS (5032021): t_R = 10.43 min, m/z 226, 227 [$(M+H)^+$, 100], 181 [$(M–OC_2H_5)^+$, 20], and 79(80).

IR (neat): 2981 (m), 1713 (s), 1653 (m), 1264 (m), 1149 (m) and 1037 (m) cm^{-1}.

HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{12}H_{19}O_4)^+$: 227.1278. Found: 227.1258.

Reference of spectral data: Carneiro, V. M. T.; Avila, C. M.; Balunas, M. J.; Gerwick, W. H.; Pilli, R. A. *J. Org. Chem*. **2014**, *79*, 630-642

Diethyl (2*E*,2'*E*)-3,3'-(phenyl-2,4-diyl)diacrylate (III-2v)



Physical form: Colorless liquid.

Yield: 1 mmol, 184 mg, 68% (*E/Z* > 20:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.66 (d, *J* = 16.0 Hz, 1H, ArCH=C*H*), 7.53 (s, *J* = 7.9 Hz, 4H, Ar-H), 6.46 (d, *J* = 16.0 Hz, 2H, ArCH=C*H*), 4.27 (q, *J* = 7.1 Hz, 2H, $CO_2CH_2CH_3$) and 1.34 (t, *J* = 7.1 Hz, 6H, $CO_2CH_2CH_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.0, 143.6, 136.4, 128.7, 119.6, 60.9 and 14.5.

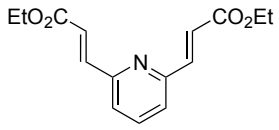
TLC: R_f = 0.45 in 10:1 hexanes: EtOAc.

GC-MS (5032021): t_R = 13.66 min, m/z 274, 275 [$(M+H)^+$, 100], 229 [$(M–OC_2H_5)^+$, 60], and 183 (30).

IR (neat): 2986 (m), 1700 (s), 1630 (s), 1320 (m), 1177 (s), 996 (s) and 773 (m) cm^{-1}.

HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{16}H_{19}O_4)^+$: 275.1278. Found: 275.1270.

Diethyl (2*E*,2'*E*)-3,3'-(pyridine-2,6-diyl)diacrylate (III-2w)



Physical form: Yellow solid.

Yield: 0.25 mmol, 55 mg, 80% (*E/Z* > 20:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.72 (t, *J* = 7.7 Hz, 1H, Ar-*H*), 7.66 (d, *J* = 15.6, 1.6 Hz, 2H, ArCH=C*H*), 7.36 (d, *J* = 7.7 Hz, 2H, Ar-*H*), 7.02 (d, *J* = 15.6 Hz, 2H, ArCH=C*H*), 4.28 (q, *J* = 7.1 Hz, 4H, $CO_2CH_2CH_3$) and 1.34 (t, *J* = 7.1 Hz, 6H, $CO_2CH_2CH_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.9, 153.3, 142.9, 137.8, 124.8, 123.5, 60.9, and 14.5.

TLC: R_f = 0.30 in 5:1 hexanes: EtOAc.

GC-MS (5032021): t_R = 13.52 min, m/z 275, 276 [$(M+H)^+$, 100], 230 [$(M–OC_2H_5)^+$, 40], and 156 (50).

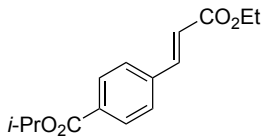
IR (neat): 3076 (m), 2978 (m), 1702 (s), 1643 (m), 1321 (s), 1153 (m) and 810 (m) cm^{-1}.

HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{15}H_{18}NO_4)^+$: 276.1230. Found: 276.1230.

MP: 108-110 °C

Literature melting point: 110-111 °C.

Isopropyl (*E*)-4-(3-ethoxy-3-oxoprop-1-en-1-yl)benzoate (III-2x)



Physical form: White solid.

Yield: 1 mmol, 209 mg, 80% (*E/Z* > 20:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.03 (d, *J* = 7.9 Hz, 2H, Ar-*H*), 7.69 (d, *J* = 16.0 Hz, 1H, ArCH=C*H*), 7.56 (d, *J* = 7.9 Hz, 2H, Ar-H), 6.50 (d, *J* = 16.0 Hz, 1H, ArCH=C*H*), 5.24 (septet, *J* = 6.3 Hz, 1H, CO_2CHiPr), 4.27 (q, *J* = 7.1 Hz, 2H, $CO_2CH_2CH_3$), 1.36 [d, *J* = 6.3 Hz, 6H, $CH(CH_3)_2$], and 1.33 (t, *J* = 7.1 Hz, 3H, $CO_2CH_2CH_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.8, 165.6, 143.5, 138.6, 132.3, 130.2, 128, 120.7, 68.9, 60.9, 22.1, and 14.5.

TLC: R_f = 0.50 in 5:1 hexanes: EtOAc.

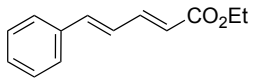
GC-MS (5032021): t_R = 12.20 min, m/z 262, 263 [$(M+H)^+$, 100], 217[$(M–OC_2H_5)^+$, 30], 203 (70) and 151 (60).

IR (neat): 2980 (m), 1707 (s), 1650 (m), 1269 (s), 1096 (s) and 773 (m) cm^{-1}.

HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{15}H_{19}O_4)^+$: 263.1278. Found: 263.1264.

MP: 64-66 °C

Ethyl (2*E*,4*E*)-5-phenylpenta-2,4-dienoate (III-2y)



Physical form: White solid.

Yield: 1 mmol, 166 mg, 83% (*E,E/E,Z* > 20:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.47-7.43 (m, 3H, Ar-*H*, C*H*=CHCO$_2$Et), 7.37-7.29 (m, 3H, Ar-*H*), 6.92-6.83 (m, 2H, C*H*=C*H*CH=CHCO$_2$Et), 5.99 (d, *J* = 15.3 Hz, 1H, CH=CHCH=C*H*CO$_2$Et), 4.23 (q, *J* = 7.1 Hz, 2H, CO$_2$C*H*$_2$CH$_3$), and 1.31 (t, *J* = 7.1 Hz, 3H, CO CH$_2$*CH*$_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.2, 144.7, 140.5, 136.2, 129.2, 129.0, 127.3, 126.4, 121.5, 60.5 and 14.5.

TLC: R_f = 0.50 in 10:1 hexanes: EtOAc.

GC-MS (5032021): t_R = 11.05 min, m/z 202, 203 [$(M+H)^+$, 100] and 157[$(M–OC_2H_5)^+$, 30]

IR (neat): 2980 (m), 1702 (s), 1624 (s), 1234 (s), 1129 (s), 955 (s) and 687 (m) cm^{-1}.

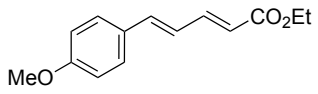
HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{13}H_{15}O_2)^+$: 203.1067. Found: 203.1059.

MP: 38-40 °C

Literature melting point: 39-40 °C.

Reference of spectral data: Chintareddy, V. R.; Ellern, A.; Verkade, J. G. *J. Org. Chem*. **2010,** *75*, 7166-7174

Ethyl (2*E*,4*E*)-5-(4-methoxyphenyl)penta-2,4-dienoate (III-2z)



Physical form: White solid.

Yield: 0.5 mmol, 50 mg, 80% (*E,E/E,Z* > 20:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.43 (dd, *J* = 15.3, 10.9 Hz, 1H, CH=*C*HC*H*=CHCO$_2$Et), 7.41 (d, *J* = 8.7 Hz, 2H, Ar-*H*), 6.88 (d, *J* = 8.7 Hz, 2H, Ar-*H*), 6.85 (d, *J* = 15.5 Hz, 1H, C*H*=*C*HCH=CHCO$_2$Et), 6.74 (dd, *J* = 15.5, 10.9 Hz, 1H, CH=*CH*CH=CHCO$_2$Et), 5.93 (d, *J* = 15.3 Hz, 1H, ArCH=CHCH=C*H*), 4.22 (q, *J* = 7.1 Hz, 2H, CO$_2$C*H*$_2$CH$_3$), 3.83 (s, 3H, Ar-O*Me*), and 1.31 (t, *J* = 7.1 Hz 3H, CO CH$_2$*CH*$_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.5, 160.6, 145.2, 140.3, 129.1, 128.9, 124.4, 120.3, 114.5, 60.5, 55.6, and 14.6.

TLC: R_f = 0.45 in 5:1 hexanes: EtOAc.

GC-MS (5032021): t_R = 12.56 min, m/z 232, 232 [$(M)^+$, 100], 233 [$(M+H)^+$, 70] 187 [$(M–OC_2H_5)^+$, 30], and 159 (50).

IR (neat): 2976 (m), 1697 (s), 1596 (s), 1251 (s), 955 (s) and 838 (m) cm^{-1}.

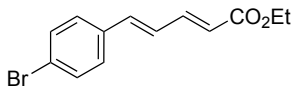
HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{14}H_{17}O_3)^+$: 233.1172. Found: 233.1158.

MP: 52-54 °C

Literature melting point: 52-53 °C.

Reference of spectral data: Hawkins, B.; Paddock, V. L.; Toelle, N.; Zard, S. Z. *Org. Lett*. **2012,** *14*, 1020-1023

Ethyl (2*E*,4*E*)-5-(4-bromophenyl)penta-2,4-dienoate (III-2aa)



Physical form: White solid.

Yield: 0.5 mmol, 114 mg, 78% (*E,E/E,Z* > 20:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.48 (app d, *J* = 8.5 Hz, 2H, Ar-*H*), 7.42 (ddd, *J* = 15.3, 8.9, 1.4 Hz, 1H, CH=*C*HC*H*=CHCO$_2$Et), 7.32 (app d, *J* = 8.5 Hz, 2H, Ar-*H*), 6.89-6.81 (m, 2H, C*H*=C*H*CH=CHCO$_2$Et), 6.01 (d, *J* = 15.3 Hz, 1H, ArCH=*C*HC*H*=CH), 4.23 (q, *J* = 7.1 Hz, 2H, CO$_2$C*H*$_2$CH$_3$), and 1.32 (t, *J* = 7.1 Hz 3H, CO$_2$CH$_2$*CH*$_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 168.4, 144.3, 139.1, 135.2, 132.2, 128.8, 127.1, 123.2, 122.2, 60.6 and 14.5.

TLC: R_f = 0.50 in 5:1 hexanes: EtOAc.

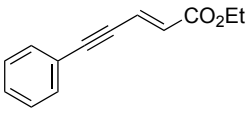
GC-MS (5032021): t_R = 12.71 min, m/z 281, 281 [$(M)^+$, 100], 238 (50), and 156 (50).

IR (neat): 2976 (m), 1694 (s), 1622 (m), 1233 (m), 1131 (m), 1013(s) and 847 (m) cm^{-1}.

HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{13}H_{14}BrO_2)^+$: 281.0172. Found: 281.0157.

MP: 68-71 °C

(*E*)-Ethyl 5-phenylpent-2-en-4-ynoate (III-2ab)



Physical form: Colorless liquid.

Yield: 1 mmol, 158 mg, 79% (*E/Z* > 20:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.48 (m, 2H, Ar-*H*), 7.35 (m, 3H, Ar-*H*), 6.98 (d, *J* = 15.8 Hz, 1H, ArCCCH=C*H*), 6.31 (d, *J* = 15.8 Hz, 1H, ArCH=C*H*), 4.23 (q, *J* = 7.1 Hz, 2H, $CO_2CH_2CH_3$), and 1.31 (t, *J* = 7.1 Hz, 6H, $CO_2CH_2CH_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.0, 132.1, 130.2, 129.4, 128.6, 125.2, 122.3, 98.4, 86.5, 60.9, and 14.4.

TLC: R_f = 0.50 in 10:1 hexanes: EtOAc.

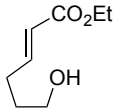
GC-MS (5032021): t_R = 10.64 min, m/z 200, 201 [$(M+H)^+$, 100], 155[$(M–OC_2H_5)^+$, 80], and 144 (30).

IR (neat): 2981 (m), 2199 (m), 1708 (s), 1617 (s), 1311 (m), 1164 (s), 1035 (m) and 754 (m) cm^{-1}.

HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{13}H_{13}O_2)^+$: 201.0910. Found: 201.0907.

Reference of spectral data: Kawamorita, S.; Yamazaki, K.; Ohmiya, H.; Iwai, T.; Sawamura, M. *Adv. Synth. Catal*. **2012,** *354*, 3440-3444.

(*E*)-Ethyl 6-hydroxyhex-2-enoate (III-2ac)



Physical form: Colorless liquid.

Yield: 1 mmol, 107 mg, 68% (*E/Z* > 20:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.95 (dt, *J* = 15.8, 6.9 Hz, 1H, CH_2CH=CH), 5.82 (dt, *J* = 15.8, 1.6 Hz, 1H, CH_2CH=C*H*), 4.16 (q, *J* = 7.1 Hz, 2H, $CO_2CH_2CH_3$), 3.64 (t, *J* = 6.4 Hz, 2H, CH_2OH), 2.28 (q, *J* = 7.1 Hz, 2H, CH_2CH=CH), 1.70 (p, *J* = 14.1, 6.4 Hz, 2H, CH_2CH_2OH), and 1.26 (t, *J* = 7.1 Hz, 3H, $CO_2CH_2CH_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.9, 148.7, 121.9, 62.1, 60.4, 31.0, 28.6 and 14.4.

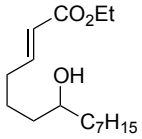
TLC: R_f = 0.40 in 1:1 hexanes: EtOAc.

GC-MS (5032021): t_R = 8.21 min, m/z 158, 159[$(M+H)^+$, 100], and 113 [$(M–OC_2H_5)^+$, 20],

IR (neat): 3399 (broad,m), 2939 (m), 1699 (s), 1651 (m), 1270 (m), 1036 (s) and 979 (m) cm^{-1}.

HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_8H_{15}O_3)^+$: 159.1016. Found: 159.1014.

(*E*)-Ethyl 7-hydroxytetradec-2-enoate (III-2ad)



Physical form: Colorless liquid.

Yield: 1 mmol, 187 mg, 77 % (*E/Z* > 20:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.93 (dt, *J* = 15.6, 6.9 Hz, 1H, CH_2CH=CH), 5.80 (d, *J* = 15.6 Hz, 1H, CH_2CH=C*H)*, 4.16 (q, *J* = 7.1 Hz, 2H, $CO_2CH_2CH_3$), 3.57 (m, 1H, C*H*OH), 2.17 (dq, *J* = 6.8, 1.6 Hz, 2H, CH_2CH=CH), 1.52-1.36 (m, 7H), 1.31-1.21 (m, 10H including $CO_2CH_2CH_3$) and 0.87 (s, 3H).

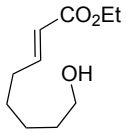
^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.9, 149.2, 121.7, 71.8, 60.3, 37.7, 36.9, 32.3, 32.0, 25.5, 24.3, 22.8, 14.4 and 14.2.

TLC: R_f = 0.40 in 5:1 hexanes: EtOAc.

GC-MS (5032021): t_R = 11.30 min, m/z 270, 271 [$(M+H)^+$, 20], and 225 [$(M–OC_2H_5)^+$, 100].

IR (neat): 3447 (broad,m), 2930 (m), 1703 (s), 1652 (m), 1266 (m), 1041 (m) and 755(s) cm^{-1}.

(*E*)-Ethyl 8-hydroxyoct-2-enoate (III-2ae)



Physical form: Colorless liquid.

Yield: 1 mmol, 170 mg, 91% (*E/Z* > 20:1).

^{1}H NMR δ 6.92 (dt, *J* = 15.6, 6.7 Hz, 1H, CH_2CH=CH), 5.78 (dt, *J* = 15.6, 1.5 Hz, 1H, CH_2CH=C*H*), 4.14 (app q, *J* = 7.1 Hz, 2H, $CO_2CH_2CH_3$), 3.60 (t, *J* = 6.4 Hz, 2H, CH_2OH), 2.18 (q, *J* = 7.1 Hz, 2H, CH_2CH=CH), 1.59–1.31 (m, 6H 3 pentets) and 1.25 (t, *J* = 7.1 Hz, 3H, $CO_2CH_2CH_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.0, 149.3, 121.5, 62.8, 60.3, 32.6, 32.3, 27.9, 25.4 and 14.4

TLC: R_f = 0.50 in 1:1 hexanes: EtOAc.

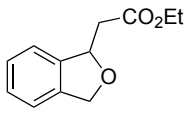
GC-MS (5032021): t_R = 9.55 min, m/z 186, 187 [$(M+H)^+$, 100], and 141 [$(M–OC_2H_5)^+$, 30].

IR (neat): 3362 (broad,m), 2938 (m), 1701 (m), 1651 (m), 1281 (m), 1023 (s) and 615 (m) cm^{-1}.

HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{10}H_{19}O_3)^+$: 187.1329. Found: 187.1323.

Reference of spectral data: Webb, D.; Jamison, T. F. *Org. Lett*. **2012,** *14*, 2465-2467

Ethyl 2-(1,3-dihydroisobenzofuran-1-yl)acetate (III-2af)



Physical form: Colorless liquid.

Yield: 1 mmol, 176.8 mg, 86% (*E/Z* > 20:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.32 – 7.26 (m, *J* = 15.8 Hz, 2H, Ar-*H*), 7.25 – 7.18 (m, 2H, Ar-*H*), 5.67 (dddd, *J* = 7.7, 5.0, 3.0, 1.0 Hz, 1H, C*H*CH_2CO_2Et), 5.08 (dd, *J* = 12.7, 1.0 Hz, 1H, C*H*$_2OCH_2CO_2Et$), 5.15 (dd, *J* = 12.7, 3.0 Hz, 1H, C*H*$_2OCH_2CO_2Et$), 4.2 (q, *J* = 7.1 Hz, 2H, $CO_2CH_2CH_3$), 2.80 (dd, *J* = 15.5, 5.0 Hz, 2H, C*H*$_2CO_2Et$), 2.72 (dd, *J* = 15.5, 7.7 Hz, 2H, C*H*$_2CO_2Et$) and 1.27 (t, *J* = 7.1 Hz, 3H, $CO_2CH_2CH_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 171.1, 140.9, 139.3, 128.0, 127.6, 121.3, 121.2, 80.5, 73.0, 60.9, 41.8 and 14.4.

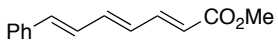
TLC: R_f = 0.40 in 40:1 hexanes: EtOAc.

GC-MS (5032021): t_R = 9.98 min, m/z 206, 206 [$(M)^+$, 50], 205 [$(M-H)^+$, 100], 119 (99) and 91 (20).

IR (neat): 3390 (broad,m), 2986 (m), 1701 (s), 1631 (m), 1320 (m), 1178 (s) and 996 (m) cm^{-1}.

HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{12}H_{15}O_3)^+$: 207.1016. Found: 207.1004.

(2*E*,4*E*,6*E*)-Methyl 7-phenylhepta-2,4,6-trienoate (III-5)



Physical form: White solid.

Yield: 0.2 mmol, 21 mg, 48%.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.43 (d, *J* = 7.2 Hz, 2H, Ar-*H*), 7.37 (dd, *J* = 15.2, 11.2 Hz, 1H, CH=*C*HC*H*=CHCO$_2$Et), 7.32 (t, *J* = 7.2 Hz, 2H, Ar-*H*), 7.27 (dt, *J* = 7.3, 1.3 Hz, 1H, Ar-*H*), 6.86 (d, 1H, CH=C*H*C*H*=CHCH=CHCO$_2$Et), 6.72 (d, *J* = 15.3 Hz, 2H, ArCH=CH*CH*=*CH*CH=CH), 6.44 (dd, *J* = 15.1, 11.3 Hz, 1H, ArCH=C*H*CH=CHCH=CH), 5.92 (d, *J* = 15.2 Hz, 1H, ArCH=CHCH=CHCH=C*H*) and 3.76 (s, 3H, CO$_2$C*H$_3$*).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.6, 144.7, 141.0, 136.8, 136.6, 130.3, 128.8, 128.5, 128.0, 127.0, 120.4, and 51.6

TLC: R_f = 0.50 in 5:1 hexanes: EtOAc.

GC-MS (5032021): t_R = 12.27 min, m/z 214, 214[$(M)^+$, 30], 155 [$(M–CO_2CH_3)^+$, 100], and 128 (20).

IR (neat): 2943 (broad,m), 1712 (s), 1601 (m), 1000 (s), and 752 (m) cm^{-1}.

HRMS (APCI/TOF): Calcd for $(M+H)^+$ $(C_{14}H_{15}O_2)^+$: 215.1067. Found: 215.1063.

MP: 110-112°C

Literature melting point: 111-113 °C.

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Udaya Sree Dakarapu was born and raised in India.She obtained her B.Sc in chemistry from Nagarjuna University, India in 2005. She obtained her M.Sc in Organic chemistry from Andhra University, India in 2007.

She obtained a M.S in organic chemistry from University of Texas at Arlington in 2015. During her graduate studies, she began working with Dr. Jeon Junha in the field of organic chemistry and metal catalysis. She worked on development of new strategies and methodologies to create building blocks for drug synthesis. Her work is mainly focused on developing a new method for Horner-Wadsworth-Emmons olefination. She is intending to continue her graduate studies at University of Texas at Arlington.