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Nucleophilic carbene-catalyzed redox-esterification reaction of α-halo-α,β-unsaturated aldehyde

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ABSTRACT

A nucleophilic carbene catalyzed redox esterification between α-halo-α,β-unsaturated aldehydes and various alcohols has been developed. Interestingly, the reaction provided α,β-unsaturated esters instead of the saturated α-halo substituted esters as the only product in good to high yield with excellent trans-selectivity, presumably via the umpolung-halo-elimination pathway.

1. Introduction

Polarity reversal of novel functional group (umpolung) is a versatile strategy in organic chemistry that allows transformations in unconventional way.[1] In the last decade, *N*-heterocyclic carbene (NHC) mediated catalytic umpolung reactions have received considerable attention.[2] Based on this strategy, various reactions, such as benzoin reaction[3] and Stetter reaction,[4] homoenolate transformations and other reactions[5] have been explored extensively. And recently, redox esterification and amination of α,β-unsaturated aldehydes,[6] α-haloaldehydes[7] and other functionalized aldehydes[8] were developed through 'extended umpolung' of carbonyl compounds, giving the corresponding products efficiently. However, in contrast to saturated esters, NHC-mediated redox esterification to unsaturated esters[9] were farless examined. Recently, Zeitler[10] reported that NHC can be used to promote the redox esterification of alkynyl aldehydes to afford *trans*-α,β-unsaturated esters with excellent *E*/*Z* stereoselectivity. As part of our continued efforts on the development of NHC-catalyzed reactions,[11] we found that NHC can catalyze the redox esterification of α-halo-α,β-unsaturated aldehydes[12] efficiently, providing α,β-unsaturated esters in high yield with excellent stereoselectivity. Herein, we would like to disclose our preliminary results about this research.

2. Results and discussion

Our investigation commenced with the reaction of α-bromocinnamaldehyde and ethanol in the presence of catalytic amount of 1, 3-dimesitylimidazol-2-ylidene that generated from NHC precursor **1** and diisopropylethylamine in dry THF (Table 1, entry 1). To our surprise, ethyl cinnamate **6** was obtained in very low yield after 40 h. We reasoned that HBr generated in the redox reaction may neutralize the active NHC, thus, the reaction was stopped and gave **6** in low yield. In view of this, we then kept the catalyst loading and increased base amount to 1.2 equiv, to our delight, **6** was isolated in 75% yield as the only product (Table 1, entry 2). Encouraged by this result, several different types of NHCs generated from the corresponding azolium salts and base were screened (Table 1, entries3–7). It was found that all the NHCs screened for the reaction can catalyze the redox reaction, but only in low efficiency. After evaluation of other reaction parameters, such as base, solvents and catalyst loading (Table 1, entries 8–18). optimal reaction conditions were obtained: room temperature, 0.25 M in THF, 5 mol % IMes, 1.2 equiv DBU (Table 1, entry 16).

Under standard reaction conditions, a variety of alcohols were tested for the reaction and the results were summarized in Table 2. Primary alcohols proceed smoothly to give the desired esters in high yield with excellent stereoselectivity (entries 1–4). While secondary alcohols need more time and afforded the corresponding products in good yield (entries 5, 6). As anticipated, due to sterical hindrance, no desired product was obtained with *tert*-butyl alcohol

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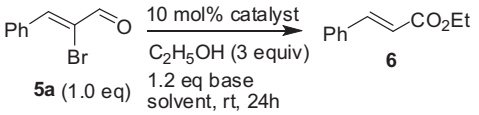
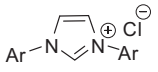
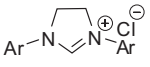
Table 1
Evaluation of NHCs and conditions for redox esterification[a]

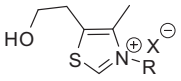






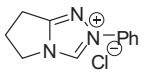
1a: Ar = 1, 3, 5-$Me_3C_6H_2$
1b: Ar = 2, 6-$(i\text{-}Pr)_2C_6H_3$

Ar = 2, 6-$(i\text{-}Pr)_2C_6H_3$



3a: R = Bn, X = Cl

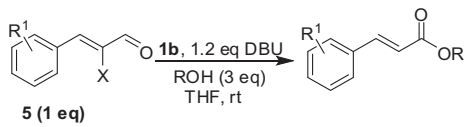
3b: R = Me, X = I

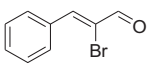
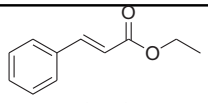
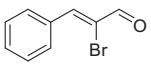
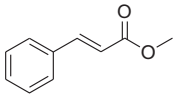
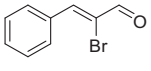
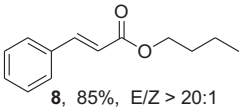


Entry	NHC	Solvent	Time (h)	Yield (%)[b]	Ratio *E*/*Z*[c]
1[d]	**1a**, DIPEA	THF	40	<10	/
2	**1a**, DIPEA	THF	24	75	>20:1
3	**1b**, DIPEA	THF	24	28	>20:1
4	**2**, DIPEA	THF	24	6	/
5	**3a**, DIPEA	THF	24	31	>20:1
6	**3b**, DIPEA	THF	24	40	5:1
7	**4**, DIPEA	THF	24	8	/
8	**1a**, DBU	THF	17	86	>20:1
9	**1a**, Et_3N	THF	40	78	>20:1
10	**1a**, Pyridine	THF	40	<5	/
11	**1a**, DMAP	THF	40	68	>20:1
12	**1a**, *t*-BuOK	THF	18	18	>20:1
13	**1a**, DBU	Et_2O	24	75	>20:1
14	**1a**, DBU	Toluene	18	75	>20:1
15	**1a**, DBU	CH_2Cl_2	24	45	>20:1
16[e]	**1a**, **DBU**	**THF**	**17**	**84**	**>20:1**
17[f]	**1a**, DBU	THF	17	24	>20:1
18[g]	**1a**, DBU	THF	18	61	>20:1

The bold values highlight the standard reaction conditions for the reaction.
[a] All reactions were conducted on a 0.5 mmol scale at 0.25 M in THF, with 1.2 equiv of diisopropylethylamine (DIPEA) as base.
[b] Isolated yields after chromatography.
[c] Determined by ^1H NMR analysis of crude reaction mixtures.
[d] Using 10 mol % base.
[e] Using 5 mol % **1a**.
[f] Using 1 mol % **1a**.
[g] Using 1.5 equiv ethanol.

Table 2
Survey of nucleophiles in redox esterification[a]



Entry	Aldehydes	Alcohols	Product[b]
1		CH_3CH_2OH	 **6**, 87%, E/Z > 20:1
2		CH_3OH	 **7**, 88%, E/Z > 20:1
3		$CH_3(CH_2)_2CH_2OH$	 **8**, 85%, E/Z > 20:1

(*continued on next page*)

Table 2 (*continued*)

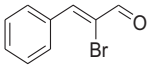
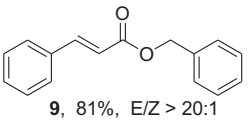
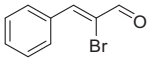
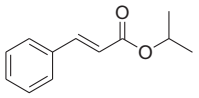
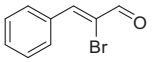
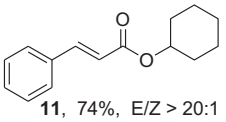
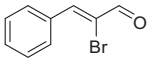
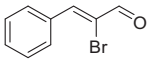
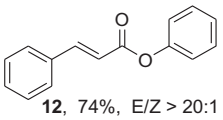
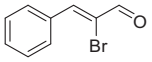
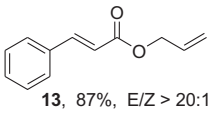
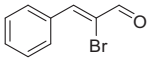
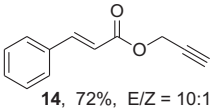
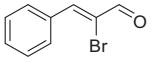
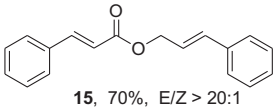
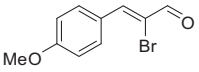
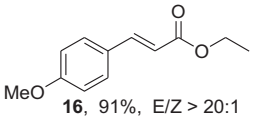
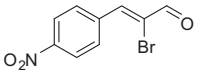
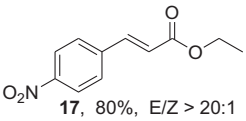
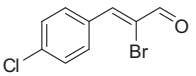
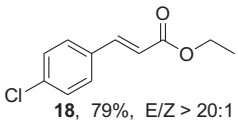
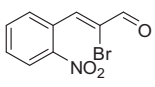
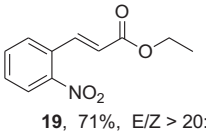
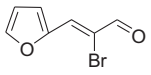
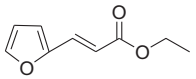
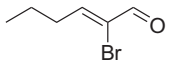
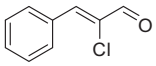
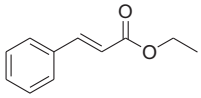
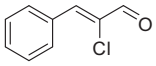
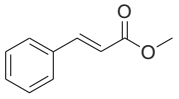
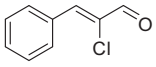
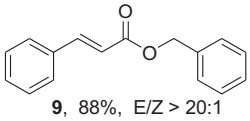
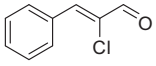
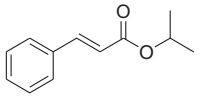
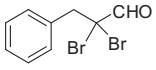
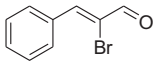
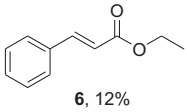
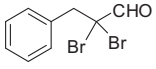
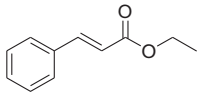
Entry	Aldehydes	Alcohols	Product[b]
4		BnOH	 **9**, 81%, E/Z > 20:1
5		$(CH_3)_2CHOH$	 **10**, 61%, E/Z > 20:1
6		Cyclohexanol	 **11**, 74%, E/Z > 20:1
7[c]		$(CH_3)_3COH$	/
8		PhOH	 **12**, 74%, E/Z > 20:1
9		Allyl alcohol	 **13**, 87%, E/Z > 20:1
10		Propargyl alcohol	 **14**, 72%, E/Z = 10:1
11		Cinnamyl alcohol	 **15**, 70%, E/Z > 20:1
12		C_2H_5OH	 **16**, 91%, E/Z > 20:1
13[d, e]		C_2H_5OH	 **17**, 80%, E/Z > 20:1
14[d]		C_2H_5OH	 **18**, 79%, E/Z > 20:1
15[d, e]		C_2H_5OH	 **19**, 71%, E/Z > 20:1

Table 2 (*continued*)

Entry	Aldehydes	Alcohols	Product[b]
16		C_2H_5OH	 **20**, 78%, E/Z > 20:1
17		C_2H_5OH	ND[f]
18		C_2H_5OH	 **6**, 85%, E/Z > 20:1
19		CH_3OH	 **7**, 80%, E/Z > 20:1
20		BnOH	 **9**, 88%, E/Z > 20:1
21		$(CH_3)_2CHOH$	 **10**, 58%, E/Z > 20:1
22[g]		C_2H_5OH	 **5a**, 80%
			 **6**, 12%
23[h]		C_2H_5OH	 **6**, 76%, E/Z > 20:1

[a] All reactions were performed on a 0.5 mmol scale, the ratio of *E*/*Z* >20:1 for all the reactions based on the ^1H NMR analysis of crude reaction mixtures.
[b] Isolated yield.
[c] Performed at 40 °C.
[d] Using 1.2 equiv Et_3N instead of DBU.
[e] Performed at 60 °C.
[f] No desired product was detected.
[g] Using 1.2 equiv DBU.
[h] Using 2.2 equiv DBU.

as nucleophile (entry 7). Interestingly, phenol was also proved to be good substrate, gave phenyl ester in 76% yield (entry 8). It is worthwhile noting that alkene and alkyne groups were also well tolerated in the reaction and provided the desired esters in high yield (entries 9–11). On the other hand, we were pleased to find that the redox reaction to be general for a range of α-halo-α,β-unsaturated aldehydes.[13] Both electron-donating and withdrawing α-bromocinnamaldehydes were suitable candidates for the esterification and higher yields were obtained for the former (entries 12–15). β-Heteroaryl substituted α-halocinnamaldehyde also exhibit good conversion with high stereoselectivity in the reaction (entry 16). However, when β-Alkyl substituted α-haloenal was applied in the redox esterification, no desired product was obtained (entry 17). Chlorine substituted cinnamaldehyde were also found to be very good electrophile for the reaction, which can react with alcohols efficiently and afford the corresponding products in good to high yield (entries 16–19). α,α-Dibromoaldehyde[14] was also tested for the reaction and the elimination product **5a** (80%), instead of ester **6** (12%), was isolated as the major product (entry 20). But when the base amount was increased to 2.2 equiv, ester **6** was

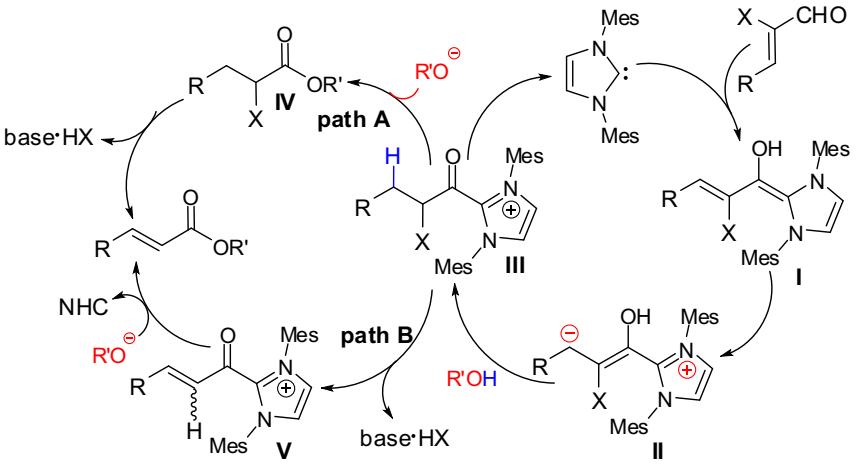
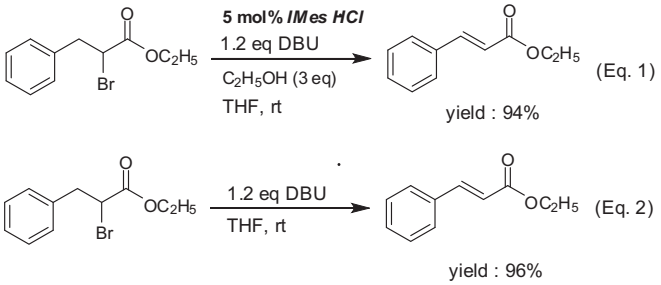


Fig. 1. Possible catalytic cycle.

obtained in good yield as the only product, this maybe due to further catalytic redox conversion of **5a** to **6** under excess of base (entry 21).

Based on the pioneering work on NHC catalyzed redox reactions, one plausible mechanism is proposed and depicted in Fig. 1. Initially, the addition of NHC to aldehyde results in the generation of 'Breslow intermediate' **I**,[15] which isomerizes to homoenolate **II** and the activated carboxylate **III** will be formed after β-protonation of **II**, and the subsequent addition of alcohol to give the saturated α-haloester **IV** with release of NHC. Under basic reaction conditions, the elimination of **IV** lead to the formation of the final product (path **A**), this conclusion is confirmed by control experiment. The results indicate that α-haloester **IV** is unstable under the above redox reaction conditions or under simply basic conditions, which undergo elimination reaction to afford α,β-unsaturated ester efficiently (Scheme 1). On the other hand, carboxylate **III** may also undergo elimination directly to intermediate **V**, and after attack of alcohol to afford the desired ester with release of NHC (path **B**).



Scheme 1. Elimination reaction of α-bromoester.

3. Conclusions

In summary, we have demonstrated a NHC-catalyzed redox esterification reaction of α-halo-α,β-unsaturated aldehydes with different alcohols to provide cinnamic esters in high yield with excellent chemo- and stereoselectivity. Further study of the reaction mechanism are currently under way in our laboratory.

4. Experimental section

4.1. General methods

Unless otherwise indicated, all reactions were conducted under nitrogen atmosphere in oven- dried glassware with magnetic stirring bar. Column chromatograph was performed with silica gel (200–300 mesh) and analytical TLC on silica gel 60-F_{254}. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) spectra were recorded on a Varian Inova-400 spectrometer in $CDCl_3$, with tetramethylsilane as an internal standard and reported in parts per million (δ). EI mass spectra were measured on Agilent 7890A/5975C GC–MS and methanol or acetonitrile was used to dissolve the sample. All alcohols were distilled before to use. α-Bromo-α,β-unsaturated aldehydes prepared according to literature.[1] Other starting materials were obtained from commercial supplies and used as received. Anhydrous THF, ether, toluene, Et_3N were distilled from sodium. Petroleum ether (PE), where used, has a boiling range of 60–90 °C.

4.2. General procedure for preparation of α,β-unsaturated esters

To a stirred suspension of IMes·HCl (9 mg, 0.025 mmol) in anhyd THF (2 mL) was added DBU (0.6 mmol, 88 μL) via micro syringe under N_2. After the mixture was stirred at room temperature for 30 min, α-halo-α,β-unsaturated aldehyde (0.5 mmol) and alcohol (1.5 mmol) were loaded, the reaction mixture was then stirred at room temperature until full consume of the starting aldehyde indicated by TLC. After concentration of the mixture under vacuum, the crude product was purified through flash column chromatography (silica gel, PE/EtOAc, 10:1–15:1) to give desired product.

*4.2.1. Ethyl cinnamate (**6**).*[10] Slightly yellow oil, 77.1 mg (87%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J=16.0 Hz, 1H), 7.51–7.46 (m, 2H), 7.37–7.32 (m, 3H), 6.42 (d, J=16.0 Hz, 1H), 4.25 (q, J=7.1 Hz, 2H), 1.32 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 144.5, 134.4, 130.1, 128.8, 128.0, 118.2, 60.4, 14.3; GC–MS (EI): m/z 176 (M^+).

*4.2.2. Methyl cinnamate (**7**).*[10] Colorless oil, 71.2 mg (88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J=16.0 Hz, 1H), 7.55–7.50 (m, 2H), 7.41–7.36 (m, 3H), 6.45 (d, J=16.0 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 144.8, 134.3, 130.2, 128.8, 128.0, 117.8, 51.6; GC–MS (EI): m/z 162 (M^+).

*4.2.3. Butyl cinnamate (**8**).*[16] Slightly yellow oil, 86.7 mg (85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J=16.0 Hz, 1H), 7.56–7.49 (m, 2H), 7.42–7.35 (m, 3H), 6.44 (d, J=16.0 Hz, 1H), 4.21 (t, J=6.7 Hz, 2H), 1.75–1.64 (m, 2H), 1.50–1.38 (m, 2H), 0.97 (t, J=7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 144.5, 134.5, 130.2, 128.9, 128.0, 118.3, 64.4, 30.8, 19.2, 13.8; GC–MS (EI): m/z 204 (M^+).

*4.2.4. Benzyl cinnamate (**9**).*[10] Slightly yellow oil, 96.2 mg (81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J=16.0 Hz, 1H), 7.52–7.47 (m, 2H), 7.43–7.32 (m, 8H), 6.48 (d, J=16.0 Hz, 1H), 5.24 (s, 2H); ^{13}C NMR

(100 MHz, $CDCl_3$) δ 166.8, 145.2, 136.1, 134.4, 130.4, 128.9, 128.6, 128.3, 128.2, 128.1, 117.9, 66.4; GC–MS (EI): m/z 238 (M^+).

*4.2.5. Isopropyl cinnamate (**10**).*[10] Yellowish oil, 58.0 mg (61%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J=16.0 Hz, 1H), 7.53–7.49 (m, 2H), 7.39–7.35 (m, 3H), 6.41 (d, J=16.0 Hz, 1H), 5.20–5.05 (m, 1H), 0.31 (d, J=6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 144.2, 134.5, 130.1, 128.8, 128.0, 118.8, 67.7, 21.9; GC–MS (EI): m/z 190 (M^+).

*4.2.6. Cyclohexyl cinnamate (**11**).*[17] Slightly yellow oil, 72.0 mg (63%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J=16.0 Hz, 1H), 7.54–7.50 (m, 2H), 7.39–7.34 (m, 3H), 6.43 (d, J=16.0 Hz, 1H), 4.94–4.85 (m, 1H), 1.97–1.89 (m, 2H), 1.81–1.73 (m, 2H), 1.57–1.24 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 144.2, 134.5, 130.1, 128.8, 128.0, 118.8, 72.7, 31.7, 25.4, 23.8; GC–MS (EI): m/z 230 (M^+).

*4.2.7. Phenyl cinnamate (**12**).*[17] White solid, 83.1 mg (74%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J=16.0 Hz, 1H), 7.58–7.54 (m, 2H), 7.42–7.36 (m, 5H), 7.26–7.20 (m, 1H), 7.18–7.14 (m, 2H), 6.62 (d, J=16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 150.8, 146.5, 134.2, 130.7, 129.4, 129.0, 128.3, 125.8, 121.6, 117.3; GC–MS (EI): m/z 224.

*4.2.8. Allyl cinnamate (**13**).*[17] Slightly yellow oil, 81.7 mg (87%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J=16.0 Hz, 1H), 7.54–7.49 (m, 2H), 7.40–7.35 (m, 3H), 6.46 (d, J=16.0 Hz, 1H), 5.99 (ddt, J=17.2, 10.4, 5.7 Hz, 1H), 5.37 (ddd, J=17.2, 3.1, 1.5 Hz, 1H), 5.27 (ddd, J=10.4, 2.6, 1.3 Hz, 1H), 4.71 (dt, J=5.7, 1.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 145.0, 134.4, 132.3, 130.3, 128.9, 128.1, 118.2, 117.9, 65.2; GC–MS (EI): m/z 188 (M^+).

*4.2.9. Prop-2-ynyl cinnamate (**14**).*[18] Slightly yellow oil, 67.0 mg (72%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J=16.0 Hz, 1H), 7.55–7.50 (m, 2H), 7.42–7.37 (m, 3H), 6.46 (d, J=16.0 Hz, 1H), 4.81 (d, J=2.5 Hz, 2H), 2.51 (t, J=2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 146.0, 134.2, 130.6, 128.9, 128.2, 117.0, 77.8, 74.9, 52.1; GC–MS (EI): m/z 186 (M^+).

*4.2.10. Cinnamyl cinnamate (**15**).*[19] Slightly yellow oil, 92.4 mg (70%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J=16.0 Hz, 1H), 7.54–7.48 (m, 2H), 7.42–7.37 (m, 3H), 7.37–7.34 (m, 2H), 7.34–7.24 (m, 3H), 6.70 (d, J=15.9 Hz, 1H), 6.48 (d, J=16.0 Hz, 1H), 6.35 (dt, J=15.9, 6.4 Hz, 1H), 4.86 (dd, J=6.4, 1.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 145.1, 136.2, 134.4, 134.2, 130.3, 128.9, 128.6, 128.1, 128.0, 126.6, 123.3, 117.9, 65.1; GC–MS (EI): m/z 264 (M^+).

*4.2.11. (E)-Ethyl-3-(4-methoxyphenyl)acrylate (**16**).*[19] Slightly yellow oil, 94.2 mg (91%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J=16.0 Hz, 1H), 7.48–7.44 (m, 2H), 6.91–6.87 (m, 2H), 6.30 (d, J=16.0 Hz, 1H), 4.25 (q, J=7.1 Hz, 2H), 3.82 (s, 3H), 1.33 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 161.3, 144.2, 129.7, 127.2, 115.7, 114.3, 60.3, 55.3, 14.3; GC–MS (EI): m/z 206 (M^+).

*4.2.12. (E)-Ethyl-3-(4-nitrophenyl)acrylate (**17**).*[10] White solid, 70.3 mg (64%); ^1H NMR (400 MHz, $CDCl_3$) δ 8.22–8.18 (m, 2H), 7.69–7.61 (m, 3H), 6.51 (d, J=16.0 Hz, 1H), 4.25 (q, J=7.1 Hz, 2H), 1.31 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 148.5, 141.6, 140.6, 128.6, 124.2, 122.6, 61.0, 14.3; GC–MS (EI): m/z 221 (M^+).

*4.2.13. (E)-Ethyl-3-(4-chlorophenyl)acrylate (**18**).*[19] Slightly yellow oil, 83.3 mg (79%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J=16.0 Hz, 1H), 7.46–7.42 (m, 2H), 7.37–7.33 (m, 2H), 6.40 (d, J=16.0 Hz, 1H), 4.26 (q, J=7.1 Hz, 2H), 1.33 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 143.1, 136.1, 132.9, 129.2, 129.1, 118.9, 60.6, 14.3; GC–MS (EI): m/z 210 (M^+).

*4.2.14. (E)-Ethyl-3-(2-nitrophenyl)acrylate (**19**).*[20] Slightly yellow oil, 78.3 mg (71%); ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J=15.8 Hz, 1H), 8.06–8.02 (m, 1H), 7.67–7.63 (m, 2H), 7.58–7.53 (m, 1H), 7.37 (d, J=15.8 Hz, 1H), 4.29 (q, J=7.1 Hz, 2H), 1.35 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 148.3, 139.8, 133.5, 130.6, 130.3, 129.1, 124.9, 123.3, 60.9, 14.3; GC–MS (EI): m/z 221 (M^+).

*4.2.15. (E)-Ethyl-3-(furan-2-yl)acrylate (**20**).*[21] Slightly yellow oil, 64.7 mg (78%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.49–7.46 (m, 1H), 7.43 (d, J=15.8 Hz, 1H), 6.61–6.53 (m, 1H), 6.47–6.39 (m, 1H), 6.31 (d, J=15.8 Hz, 1H), 4.24 (q, J=7.1 Hz, 2H), 1.32 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ(100 MHz, $CDCl_3$) δ 167.00, 150.93, 144.63, 130.92, 115.94, 114.56, 112.20, 60.40, 11.29; GC–MS (EI): m/z 166 (M^+).

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