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N-heterocyclic carbene-catalysed Peterson olefination reaction

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ABSTRACT

N-heterocyclic carbenes (NHCs) have been utilised as highly efficient organocatalysts to catalyse Peterson olefination reaction of aldehydes with trimethylsilylketene ethyl trimethylsilyl acetal or fluoro(-trimethylsilyl)ketene ethyl trimethylsilyl acetal to produce the corresponding functionalized olefines in 34–93% yields with excellent stereoselectivities.

1. Introduction

Functionalized olefines and their fluorinated analogues are considered to be versatile building blocks in organic synthesis. Fluoroolefines are of particular importance owing to their unique properties and significant applications,[1] i.e., these moieties can serve as amide isostere[2] and utilised widely in the synthesis of peptidomimetics.[3] The olefination reaction of α-silyl carbanion with carbonyl compounds, also known as Peterson olefination,[4] provide facile access to functionalized olefines stereoselectively. More interestingly, compared with phosphorus reagents, the higher reactivity of α-silyl carbanion and simple purification procedure make Peterson olefination to be an attractive alternative to Wittig reaction.[5] However, stoichiometric amount of strong bases, such as *n*-BuLi, LDA and silyl Grignard reagents are generally necessary for the in situ generation of the active α-silyl carbanion species, which makes base sensitive substrates can not be well tolerated. Therefore, the development of more convenient and mild methods for Peterson olefination reaction is highly valuable. Recently, Mukaiyama reported that silyl ketene acetals can be utilised as stable precursors of silyl carbanions to undergo Peterson olefination reaction with aldehydes under mild conditions, which provide a novel protocol for the construction of functionalized olefines.[6]

The past decade has witnessed tremendous progress of *N*-heterocyclic carbene (NHC) catalysis.[7] This important type of nucleophilic organocatalysts can promote a wide range of *Umpolung* reactions[8] and other transformations.[9] In particular, NHCs exhibit high reactivity toward the activation of silicon-based reagents,[10] i.e., only 0.01 mol % NHC can efficiently promote the cyanation reaction of TMSCN and aldehydes.[11] Based on this nucleophilic activation strategy, NHC-catalysed trifluoromethylation reaction,[12a] Mukaiyama aldol reaction,[12b-d] ring-opening reaction,[12e] silyl-Reformatsky reaction,[12f-g] pentafluorophenylation reaction[12h] and polymerisation reaction[13] have been developed in recent years. In line with our continue interest of NHC catalysis, we envisioned that NHCs could be utilised as nucleophilic catalysts to mediate Peterson olefination reaction between silyl ketene acetals and aldehydes.

2. Results and discussion

With this idea in mind, we began our study with the commercially available silyl ketene acetal **1a** and *p*-chlorobenzaldehyde **2a**. To our delight, in the presence of 5 mol % stable NHC **4** (1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene, IPr),[14] the reaction proceeded very smoothly in THF at room temperature to afford the corresponding α,β-unsaturated ester **3a** in 71% yield with excellent *E*/*Z* selectivity (Table 1, entry 1). Encouraged by this result, several other NHCs were subsequently tested for the reaction. NHCs derived from imidazolium can promote the reaction efficiently, whereas NHC generated from the saturated imidazolinium showed very low reactivity (Table 1, entries 2–5). Unfortunately, NHCs derived from both thiazolium and triazolium can not catalyse this reaction (Table 1, entries 6–8). A brief screening of reaction media

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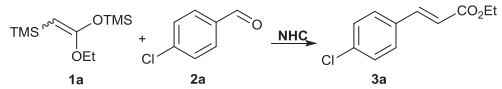
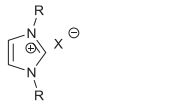
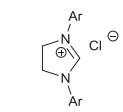
0040-4020/

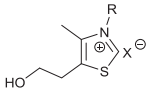
Table 1
Screening of reaction conditions[a]



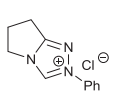


5a: R = 2,4,6-$Me_3C_6H_2$, X = Cl
5b: R = Cy, X = BF_4
5c: R = *t*-Bu, X = BF_4





7a: R = Bn, X = Cl
7b: R = Me, X = I



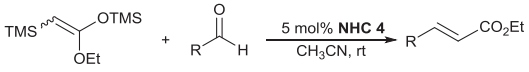
Entry	NHC (mol %)	Solvent	Time (h)	*E*/*Z*[b]	Yield[c]
1	**4**, (5)	THF	4	>25:1	71%
2	**5a**, ^{t}BuOK, (5)	THF	4	>25:1	89%
3	**5b**, ^{t}BuOK, (5)	THF	8	18:1	80%
4	**5c**, ^{t}BuOK, (5)	THF	8	24:1	89%
5	**6**, ^{t}BuOK, (5)	THF	12	/	8%
6	**7a**, ^{t}BuOK, (5)	THF	12	/	Trace
7	**7b**, ^{t}BuOK, (5)	THF	12	/	Trace
8	**8**, ^{t}BuOK, (5)	THF	12	/	Trace
9	**4**, (5)	CH_3CN	12	>25:1	70%
10	**4**, (5)	CH_2Cl_2	12	>25:1	59%
11	**4**, (5)	toluene	12	12:1	69%
12	**4**, (5)	CH_3CN	8	>25:1	85%
13	**4**, (1)	CH_3CN	12	/	Trace

[a] Reaction conditions: NHC precursors (6 mol %), base (5 mol %), 1a (1.5 equiv), 2a (1.0 equiv), room temperature.
[b] Determined by ^{1}H NMR analysis of the crude products.
[c] Isolated total yields of *Z* and *E*-isomers.

revealed that CH_3CN was the best choice in terms of yields and selectivities (Table 1, entries 9–12). Reduction NHC loading to 1 mol % resulted in dramatic decrease of catalytic efficiency (Table 1, entry 13).

With the optimal reaction conditions in hand, the scope of this olefination reaction was next examined. Both aromatic and aliphatic aldehydes are suitable for the olefination reaction (Table 2). For aromatic aldehydes, the electronic properties and varied positions on the aromatic ring had no obvious effects on the reaction yields and selectivities (Table 2, entries 1–10). Interestingly, heteroaromatic aldehydes such as furfural and 2-thenaldehyde

Table 2
Evaluation of aldehydes[a]



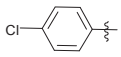
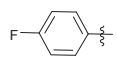
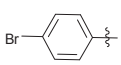
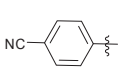
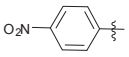
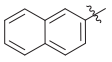
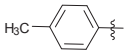
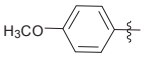
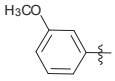
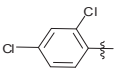
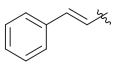
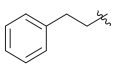
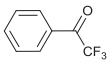
Entry	R	Time (h)	Product	*E*/*Z*[b]	Yield (%)[c]
1		12	**3a**	>25:1	85
2		12	**3b**	>25:1	71
3		12	**3c**	>25:1	88
4		12	**3d**	>25:1	68

Table 2 (*continued*)

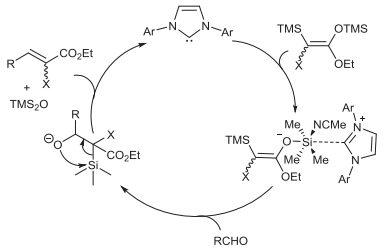
Entry	R	Time (h)	Product	*E*/*Z*[b]	Yield (%)[c]
5		12	**3e**	>25:1	54
6		12	**3f**	>25:1	91
7		12	**3g**	>25:1	82
8		12	**3h**	>25:1	93
9		12	**3i**	>25:1	85
10		12	**3j**	>25:1	82
11		12	**3k**	>25:1	87
12		12	**3l**	>25:1	91
13		12	**3m**	>25:1	91
14		12	**3n**	>25:1	88
15		12	**3o**	>25:1	76
16		12	**3p**	>25:1	88
17		12	**3q**	>25:1	56
18		12	**3r**	>25:1	83
19		12	**3s**	>25:1	78
20		12	**3t**	>25:1	57
21		15	**3u**	14:1	70
22		15	**3v**	>25:1	53
23		15	**3w**	>25:1	70
24		15	**3x**	>25:1	34

[a] 1a (1.5 equiv), 2 (1.0 equiv).
[b] Determined by ^{1}H NMR analysis of the crude products.
[c] Isolated total yields of *Z* and *E*-isomers.

performed very well, producing the desired products in good yields with excellent *E*-selectivity (Table 2, entries 19 and 20). However, when *trans*-cinnamaldehyde was employed for the reaction, the corresponding olefin can be isolated in good yield, but the *E*/*Z* selectivities reduced to 14:1 (Table 2, entry 21). Gratifyingly, when aliphatic aldehydes were introduced to reaction, the final products can be isolated in good yields with excellent selectivities (Table 2, entries 22 and 23). Notably, 2,2,2-trifluoroacetophenone can transform into the desired product stereoselectively, albeit in low yield (Table 2, entry 24).

To extend the utility of this protocol, we further studied the similar Peterson fluoroolefination reaction. Under the optimal reaction conditions, fluoro(trimethylsilyl)ketene ethyl trimethylsilyl acetal **1b** underwent these type of fluoroolefination smoothly. As shown in Table 3, a great variety of aromatic aldehydes and heteroaromatic aldehydes reacted with α-fluoro ketene acetal **1b** very well, affording the corresponding α-fluoroolefines in high yields with excellent *Z*-selectivity. The fluoroolefination of aliphatic aldehyde was also attempted and the final product was isolated in moderate yield with high *Z*-selectivity (Table 3, entry 16).

Based on previous studies on NHC-catalysed Mukaiyama aldol reaction, a possible mechanism was proposed and depicted in Scheme 1. NHC attack silyl ketene acetal to generate the reactive hexavalent silicon intermediate I, which might trigger the following Mukaiyama aldol reaction with aldehyde to produce intermediate II, and after *syn*-elimination, could produce the desired product.



Scheme 1. NHC-catalysed Peterson olefination reaction.

The mechanism was further investigated through NMR experiments. A 1:1 mixture of silyl ketene acetal 1a and NHC 4 was detected by ^{1}H NMR and ^{13}C NMR, respectively. ^{1}H NMR indicated that the characteristic peaks of TMS groups moved from 1.91, 0.38, 0.03, −1.43 ppm to 1.93, 0.40, 0.05, −1.42 ppm, while the characteristic peaks of ^{13}C NMR moved from 0.22, 0.14, 0.08, 0.06 ppm to 0.21, 0.12, 0.07 and 0.05 ppm, respectively. These results indicate that NHC might react with silyl ketene acetal to generate intermediate I and initiate the reaction.

3. Conclusions

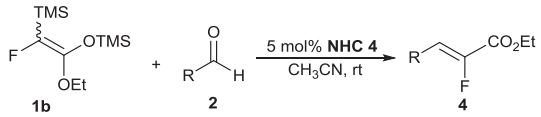
In summary, the first NHC-catalysed Peterson olefination reaction of silyl ketene acetals and carbonyl compounds was developed. The extremely mild conditions, simple procedure and excellent stereoselectivities provide a novel protocol for the synthesis of these important building blocks.

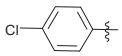
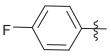
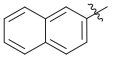
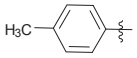
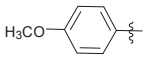
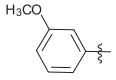
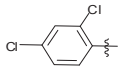
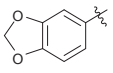
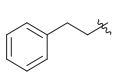
4. Experimental section

4.1. General methods

Unless otherwise indicated, all reactions were conducted under nitrogen atmosphere in oven-dried glassware with magnetic stirring bar. Column chromatography was performed with silica gel (200–300 mesh) and analytical TLC on silica gel 60-F_{254}. ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and spectra were recorded on a Bruker-DMX 400 spectrometer in $CDCl_3$, with tetramethylsilane as an internal standard and reported in ppm (δ). *N*-heterocyclic carbene salts **5b** and **5c** were purchased from Sigma–Aldrich and TCI. Other NHCs were prepared according to

Table 3
NHC-catalysed Peterson fluoroolefination reaction[a]



Entry	R	Time (h)	Product	*Z*/*E*[b]	Yield[c]
1		6	**4a**	>25:1	88
2		6	**4b**	>25:1	84
3		12	**4c**	>25:1	77
4		12	**4d**	>25:1	79
5		12	**4e**	>25:1	82
6		12	**4f**	>25:1	79
7		15	**4g**	>25:1	75
8		12	**4h**	>25:1	79
9		12	**4i**	>25:1	85
10		10	**4j**	>25:1	82
11		8	**4k**	>25:1	83
12		6	**4l**	>25:1	52
13		15	**4m**	>25:1	61
14		12	**4n**	>25:1	55
15		12	**4o**	>25:1	63
16		12	**4p**	15:1	43

[a] **1a** (1.5 equiv), 2 (1.0 equiv).
[b] Determined by ^{1}H NMR analysis of the crude products.
[c] Isolated total yields of *Z* and *E*-isomers.

literature procedure.[14,15a] Silyl ketene acetals **1a** and **1b** were purchased from TCI. All other chemicals were obtained from commercial supplies and used as received. Anhydrous THF and toluene were distilled from sodium and benzophenone. CH_2Cl_2 and CH_3CN were distilled from calcium hydride.

4.2. General procedure for *N*-heterocyclic carbene-catalysed Peterson olefination reaction

NHC **4** (6.0 mg, 0.015 mmol) was added to a solution of aldehyde **2** (0.3 mmol) and silyl ketene acetal (**1a** or **1b**, 0.45 mmol) in anhydrous CH_3CN (1.0 mL) at 0° C. The reaction mixture was then stirred at room temperature until full consume of the starting aldehyde indicated by TLC. The ratio of *E/Z* was determined by ^{1}H NMR analysis of the crude products and the configurations were assigned by ^{1}H NMR comparison with literature.[15b,15c] The crude product was purified by flash column chromatography on silica gel (PE—EtOAc, 50:1) to give the desired product **3** or **4** as a mixture of inseparable *Z* and *E*-isomers.

*4.2.1. Ethyl (E)-3-(4-chlorophenyl)acrylate (**3a**).*[6b] ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.61 (d, *J*=16.0 Hz, 1H), 7.49–7.30 (m, 4H), 6.39 (d, *J*=16.0 Hz, 1H), 4.25 (q, *J*=7.2 Hz, 2H), 1.32 ppm (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=166.7, 143.1, 136.1, 132.9, 129.1, 129.1, 118.8, 60.6, 14.3 ppm.

*4.2.2. Ethyl (E)-3-(4-fluorophenyl)acrylate (**3b**).*[15d] ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.61 (d, *J*=16.0 Hz, 1H), 7.49–7.30 (m, 4H), 6.39 (d, *J*=16.0 Hz, 1H), 4.25 (q, *J*=7.1 Hz, 2H), 1.32 ppm (t, *J*=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) ^{13}C NMR (100 MHz, $CDCl_3$) δ=166.8, 163.8 (d, *J*=251.1 Hz), 143.2, 130.7 (d, *J*=3.0 Hz), 129.8 (d, *J*=8.5 Hz), 118.0 (d, *J*=2.3 Hz), 116.0 (d, *J*=22.1 Hz), 60.5, 14.3 ppm.

*4.2.3. Ethyl (E)-3-(4-bromophenyl)acrylate (**3c**).*[15d] ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.61 (d, *J*=16.0 Hz, 1H), 7.49–7.30 (m, 4H), 6.39 (d, *J*=16.0 Hz, 1H), 4.25 (q, *J*=7.2 Hz, 2H), 1.32 ppm (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=166.6, 143.1, 133.3, 132.1, 129.4, 124.4, 118.9, 60.6, 14.3 ppm.

*4.2.4. Ethyl (E)-3-(4-cyanophenyl)acrylate (**3d**).*[15e] ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.61 (d, *J*=16.0 Hz, 1H), 7.49–7.30 (m, 4H), 6.39 (d, *J*=16.0 Hz, 1H), 4.25 (q, *J*=7.2 Hz, 2H), 1.32 ppm (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=166.1, 142.1, 138.7, 132.6, 128.3, 121.8, 118.3, 113.3, 60.9, 14.2 ppm.

*4.2.5. Ethyl (E)-3-(4-nitrophenyl)acrylate (**3e**).*[15e] ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.61 (d, *J*=16.0 Hz, 1H), 7.49–7.30 (m, 4H), 6.39 (d, *J*=16.0 Hz, 1H), 4.25 (q, *J*=7.2 Hz, 2H), 1.32 ppm (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=166.0, 148.4, 141.6, 140.5, 128.6, 124.1, 122.6, 61.0, 14.2 ppm.

*4.2.6. (E)-Ethyl cinnamate (**3f**).*[6b] ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.71 (d, *J*=16.0 Hz, 1H), 7.59–7.51 (m, 2H), 7.46–7.37 (m, 3H), 6.46 (d, *J*=16.0 Hz, 1H), 4.29 (q, *J*=7.2 Hz, 2H), 1.37 ppm (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=167.0, 144.5, 134.4, 130.2, 128.8, 128.0, 118.2, 60.5, 14.3 ppm.

*4.2.7. Ethyl (E)-3-(naphthalen-1-yl)acrylate (**3g**).*[15d] ^{1}H NMR (400 MHz, $CDCl_3$) δ=8.54 (d, *J*=15.8 Hz, 1H), 8.26–8.16 (m, 1H), 7.95–7.83 (m, 2H), 7.80–7.71 (m, 1H), 7.64–7.44 (m, 3H), 6.54 (d, *J*=15.8 Hz, 1H), 4.33 (q, *J*=7.1 Hz, 2H), 1.39 ppm (t, *J*=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=166.9, 141.6, 133.6, 131.8, 131.4, 130.4, 128.7, 126.8, 126.2, 125.4, 125.0, 123.4, 120.9, 60.6, 14.4 ppm.

*4.2.8. Ethyl (E)-3-(naphthalen-2-yl)acrylate (**3h**).*[15d] ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.97–7.91 (m, 1H), 7.90–7.79 (m, 4H), 7.71–7.62 (m, 1H), 7.57–7.48 (m, 2H), 6.56 (d, *J*=16.0 Hz, 1H), 4.30 (q, *J*=7.2 Hz, 2H), 1.37 ppm (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=167.0, 144.6, 134.2, 133.3, 131.9, 129.8, 128.6, 128.5, 127.7, 127.2, 126.7, 123.5, 118.4, 60.5, 14.3 ppm.

*4.2.9. Ethyl (E)-3-(p-tolyl)acrylate (**3i**).*[15d] ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.61 (d, *J*=16.0 Hz, 1H), 7.49–7.30 (m, 4H), 6.39 (d, *J*=16.0 Hz, 1H), 4.25 (q, *J*=7.2 Hz, 2H), 2.37 (s, 3H), 1.32 ppm (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=167.1, 144.5, 140.6, 131.7, 129.6, 128.0, 117.1, 60.4, 21.4, 14.3 ppm.

*4.2.10. Ethyl (E)-3-(4-methoxyphenyl)acrylate (**3j**).*[6b] ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.61 (d, *J*=16.0 Hz, 1H), 7.49–7.30 (m, 4H), 6.39 (d, *J*=16.0 Hz, 1H), 3.84 (s, 3H), 4.25 (q, *J*=7.2 Hz, 2H), 1.32 ppm (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=167.3, 161.3, 144.2, 129.6, 127.2, 115.7, 114.3, 60.3, 55.3, 14.3 ppm.

*4.2.11. Ethyl (E)-3-(2-methoxyphenyl)acrylate (**3k**).*[15f] ^{1}H NMR (400 MHz, $CDCl_3$) δ=8.01 (d, *J*=16.2 Hz, 1H), 7.55–7.50 (m, 1H), 7.40–7.33 (m, 1H), 7.02–6.92 (m, 2H), 6.55 (d, *J*=16.2 Hz, 1H), 4.29 (q, *J*=7.1 Hz, 2H), 3.91 (s, 3H), 1.36 ppm (t, *J*=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=167.5, 158.3, 140.0, 131.3, 128.9, 123.4, 120.6, 118.8, 111.1, 60.3, 55.4, 14.3 ppm.

*4.2.12. Ethyl (E)-3-(3-methoxyphenyl)acrylate (**3l**).*[15f] ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.61 (d, *J*=16.0 Hz, 1H), 7.49–7.30 (m, 4H), 6.39 (d, *J*=16.0 Hz, 1H), 4.25 (q, *J*=7.2 Hz, 2H), 1.32 ppm (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=166.9, 159.8, 144.4, 135.8, 129.8, 120.7, 118.5, 116.1, 112.8, 60.5, 55.2, 14.3 ppm.

*4.2.13. Ethyl (E)-3-(2-chlorophenyl)acrylate (**3m**).*[6b] ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.61 (d, *J*=16.0 Hz, 1H), 7.49–7.30 (m, 4H), 6.39 (d, *J*=16.0 Hz, 1H), 4.25 (q, *J*=7.1 Hz, 2H), 1.32 ppm (t, *J*=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=166.4, 140.3, 134.9, 132.7, 130.9, 130.1, 127.6, 127.0, 120.9, 60.7, 14.3 ppm.

*4.2.14. Ethyl (E)-3-(3-chlorophenyl)acrylate (**3n**).*[6b] ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.61 (d, *J*=16.0 Hz, 1H), 7.49–7.30 (m, 4H), 6.39 (d, *J*=16.0 Hz, 1H), 4.25 (q, *J*=7.1 Hz, 2H), 1.32 ppm (t, *J*=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=166.5, 142.9, 136.2, 134.9, 130.1, 130.0, 127.7, 126.2, 119.7, 60.6, 14.3 ppm.

*4.2.15. Ethyl (E)-3-(3-bromophenyl)acrylate (**3o**).*[15g] ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.61 (d, *J*=16.0 Hz, 1H), 7.49–7.30 (m, 4H), 6.39 (d, *J*=16.0 Hz, 1H), 4.25 (q, *J*=7.1 Hz, 2H), 1.32 ppm (t, *J*=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=166.5, 142.8, 136.5, 132.9, 130.7, 130.3, 126.6, 123.0, 119.7, 60.6, 14.3 ppm.

*4.2.16. Ethyl (E)-3-(2,5-dichlorophenyl)acrylate (**3p**).*[15h] ^{1}H NMR (400 MHz, $CDCl_3$) δ=8.00 (d, *J*=16.0 Hz, 1H), 7.59–7.51 (m, 1H), 7.46–7.41 (m, 1H), 7.30–7.22 (m, 1H), 6.41 (d, *J*=7.1 Hz, 1H), 4.28 (q, *J*=7.1 Hz, 2H), 1.34 ppm (t, *J*=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=166.2, 139.1, 136.2, 135.4, 131.3, 130.0, 128.3, 127.5, 121.3, 60.8, 14.2 ppm.

*4.2.17. Ethyl (E)-3-(3-nitrophenyl)acrylate (**3q**).*[15d] ^{1}H NMR (400 MHz, $CDCl_3$) δ=8.40–8.35 (m, 1H), 8.25–8.19 (m, 1H), 7.84–7.79 (m, 1H), 7.71 (d, *J*=16.0 Hz, 1H), 7.62–7.54 (m, 1H), 6.56 (d, *J*=16.0 Hz, 1H), 4.29 (q, *J*=7.1 Hz, 2H), 1.35 ppm (t, *J*=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=166.1, 148.7, 141.6, 136.2, 133.6, 129.9, 124.4, 122.4, 121.4, 60.9, 14.2 ppm.

*4.2.18. Ethyl (E)-3-(2-nitrophenyl)acrylate (**3r**).*[15d] ^{1}H NMR (400 MHz, $CDCl_3$) δ=8.09 (d, *J*=15.8 Hz, 1H), 8.05–7.99 (m, 1H), 7.67–7.60 (m, 2H), 7.57–7.49 (m, 1H), 6.35 (d, *J*=15.8 Hz, 1H), 4.27 (q, *J*=7.1 Hz, 2H), 1.33 ppm (t, *J*=7.1 Hz, 3H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ=165.7, 148.3, 139.8, 133.5, 130.6, 130.2, 129.1, 124.8, 123.3, 60.9, 14.2 ppm.

*4.2.19. Ethyl (E)-3-(furan-2-yl)acrylate (**3s**).*[15h] ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.49–7.46 (m, 1H), 7.42 (d, *J*=16.0 Hz, 1H), 6.61–6.58 (m, 1H), 6.48–6.45 (m, 1H), 6.31 (d, *J*=15.7 Hz, 1H), 4.24 (q, *J*=7.1 Hz, 2H), 1.32 ppm (t, *J*=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=167.0, 150.9, 144.6, 130.9, 115.9, 114.5, 112.2, 60.4, 14.3 ppm.

*4.2.20. Ethyl (E)-3-(thiophen-2-yl)acrylate (**3t**).*[15i] ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.80 (d, *J*=15.7 Hz, 1H), 7.43–7.35 (m, 1H), 7.30–7.24 (m, 1H), 7.11–7.02 (m, 1H), 6.26 (d, *J*=15.7 Hz, 1H), 4.27 (q, *J*=7.1 Hz, 2H), 1.35 ppm (t, *J*=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=166.8, 139.6, 137.0, 130.8, 128.3, 128.0, 117.0, 60.4, 14.3 ppm.

*4.2.21. Ethyl (2E,4E)-5-phenylpenta-2,4-dienoate (**3u**).*[15e] ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.51–7.40 (m, 3H), 7.39–7.27 (m, 3H), 6.94–6.82 (m, 2H), 5.99 (d, *J*=15.3 Hz, 1H), 4.23 (q, *J*=7.1 Hz, 2H), 1.32 ppm (t, *J*=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=167.0, 144.5, 140.3, 136.0, 129.0, 128.8, 127.2, 126.2, 121.3, 60.3, 14.3 ppm.

*4.2.22. Ethyl (E)-5-phenylpent-2-enoate (**3v**).*[15j] ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.33–7.27 (m, 2H), 7.24–7.16 (m, 3H), 7.06–6.93 (m, 1H), 5.85 (dt, *J*=15.7, 1.6 Hz, 1H), 4.18 (q, *J*=7.1 Hz, 2H), 2.83–2.73 (m, 2H), 2.59–2.46 (m, 2H), 1.28 ppm (t, *J*=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=166.6, 148.0, 140.8, 128.4, 128.3, 126.1, 121.8, 60.2, 34.3, 33.9, 14.2 ppm.

*4.2.23. Ethyl (E)-3-cyclohexylacrylate (**3w**).*[6b] ^{1}H NMR (400 MHz, $CDCl_3$) δ=6.91 (dd, *J*=15.8, 6.8 Hz, 1H), 5.75 (dd, *J*=15.8, 1.5 Hz, 1H), 4.18 (q, *J*=7.1 Hz, 2H), 2.19–2.06 (m, 1H), 1.82–1.71 (m, 4H), 1.71–1.63 (m, 1H), 1.38–1.06 ppm (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=167.1, 154.3, 118.8, 60.1, 40.4, 31.6, 25.9, 25.7, 14.2 ppm.

*4.2.24. Ethyl (E)-4,4,4-trifluoro-3-phenylbut-2-enoate (**3x**).*[15h] ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.46–7.37 (m, 3H), 7.33–7.27 (m, 2H), 6.61 (q, *J*=1.4 Hz, 1H), 4.04 (q, *J*=7.1 Hz, 2H), 1.06 ppm (t, *J*=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=164.1, 142.3 (q, *J*=30.9 Hz), 131.0, 129.3, 128.6, 128.1, 124.5 (q, *J*=5.4 Hz), 122.5 (q, *J*=274.8 Hz), 61.0, 13.7 ppm.

*4.2.25. Ethyl (Z)-3-(4-chlorophenyl)-2-fluoroacrylate (**4a**).*[15c] ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.63–7.56 (m, 2H), 7.43–7.36 (m, 2H), 6.90 (d, *J*=34.7 Hz, 1H), 4.38 (q, *J*=7.1 Hz, 2H), 1.41 ppm (t, *J*=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=161.1 (d, *J*=34.3 Hz), 147.2 (d, *J*=268.7 Hz), 135.6 (d, *J*=3.9 Hz), 131.4 (d, *J*=8.3 Hz), 129.6 (d, *J*=4.4 Hz), 129.1, 116.2 (d, *J*=4.8 Hz), 62.0, 14.2 ppm.

*4.2.26. Ethyl (Z)-2-fluoro-3-(4-fluorophenyl)acrylate (**4b**).*[15c] ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.69–7.59 (m, 2H), 7.15–7.03 (m, 2H), 6.88 (d, *J*=34.9 Hz, 2H), 4.35 (q, *J*=7.1 Hz, 2H), 1.38 ppm (t, *J*=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=163.2 (dd, *J*=251.5, 4.0 Hz), 161.3 (d, *J*=34.1 Hz), 146.7 (dd, *J*=267.2, 2.7 Hz), 132.2 (t, *J*=8.4 Hz), 127.3 (dd, *J*=4.4, 3.4 Hz), 116.3 (dd, *J*=4.9, 0.9 Hz), 115.9 (d, *J*=21.8 Hz), 61.9, 14.2 ppm.

*4.2.27. Ethyl (Z)-2-fluoro-3-phenylacrylate (**4c**).*[6a] ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.70–7.62 (m, 2H), 7.45–7.33 (m, 3H), 6.92 (d, *J*=35.2 Hz, 1H), 4.36 (q, *J*=7.1 Hz, 2H), 1.39 ppm (t, *J*=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=161.4 (d, *J*=34.2 Hz), 147.0 (d, *J*=267.7 Hz), 131.1 (d, *J*=4.4 Hz), 130.3 (d, *J*=8.1 Hz), 129.6 (d, *J*=2.8 Hz), 128.8, 117.4 (d, *J*=4.7 Hz), 61.9, 14.2 ppm.

*4.2.28. Ethyl (Z)-2-fluoro-3-(naphthalen-1-yl)acrylate (**4d**).*[15c] ^{1}H NMR (400 MHz, $CDCl_3$) δ=8.14–8.05 (m, 1H), 8.03–7.95 (m, 1H), 7.94–7.82 (m, 2H), 7.70 (d, *J*=33.1 Hz, 1H), 7.63–7.48 (m, 3H), ppm 4.42 (q, *J*=7.1 Hz, 2H), 1.44 (t, *J*=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=161.4 (d, *J*=34.5 Hz), 147.8 (d, *J*=268.8 Hz), 133.6, 131.4, 130.0 (d, *J*=1.8 Hz), 128.8, 128.8, 128.7, 127.0 (d, *J*=4.0 Hz), 126.1, 125.4, 123.4, 113.8 (d, *J*=5.5 Hz), 62.0, 14.2 ppm.

*4.2.29. Ethyl (Z)-2-fluoro-3-(naphthalen-2-yl)acrylate (**4e**).*[6a] ^{1}H NMR (400 MHz, $CDCl_3$) δ=8.15–8.07 (m, 1H), 7.92–7.75 (m, 4H), 7.58–7.46 (m, 2H), 7.09 (d, *J*=35.2 Hz, 1H), 4.38 (q, *J*=7.1 Hz, 2H), 1.41 ppm (t, *J*=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=161.4 (d, *J*=34.2 Hz), 147.1 (d, *J*=267.8 Hz), 133.6 (d, *J*=2.1 Hz), 133.1, 130.7 (d, *J*=8.1 Hz), 128.7 (d, *J*=4.7 Hz), 128.6, 128.5, 127.6, 127.2, 126.8 (d, *J*=8.4 Hz), 126.5, 117.6 (d, *J*=4.7 Hz), 61.9, 14.2 ppm.

*4.2.30. Ethyl (Z)-2-fluoro-3-(p-tolyl)acrylate (**4f**).*[15c] ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.64–7.54 (m, 2H), 7.28–7.17 (m, 2H), 6.92 (d, *J*=35.5 Hz, 1H), 4.37 (q, *J*=7.1 Hz, 2H), 2.40 (s, 3H), 1.40 ppm (t, *J*=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=161.5 (d, *J*=34.1 Hz), 146.5 (d, *J*=266.0 Hz), 140.0 (d, *J*=2.9 Hz), 130.2 (d, *J*=8.1 Hz), 129.5, 128.3 (d, *J*=4.4 Hz), 117.5 (d, *J*=4.8 Hz), 61.7, 21.4, 14.2 ppm.

*4.2.31. Ethyl (Z)-2-fluoro-3-(4-methoxyphenyl)acrylate (**4g**).*[15c] ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.78–7.48 (m, 2H), 7.01–6.80 (m, 3H), 4.36 (q, *J*=7.1 Hz, 2H), 3.85 (s, 3H), 1.39 ppm (t, *J*=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=161.6 (d, *J*=33.9 Hz), 160.6, 145.8 (d, *J*=263.8 Hz), 132.0 (d, *J*=8.4 Hz), 123.8, 117.3 (d, *J*=5.0 Hz), 114.2, 61.6, 55.3, 14.2 ppm.

*4.2.32. Ethyl (Z)-2-fluoro-3-(2-methoxyphenyl)acrylate (**4h**).*[15k] ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.95–7.84 (m, 1H), 7.49–7.30 (m, 2H), 7.05–6.86 (m, 2H), 4.42–4.29 (m, 2H), 3.92–3.82 (m, 3H), 1.45–1.31 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=161.6 (d, *J*=34.8 Hz), 157.3 (d, *J*=1.7 Hz), 146.9 (d, *J*=266.0 Hz), 130.9 (d, *J*=14.1 Hz), 120.7, 120.0 (d, *J*=4.8 Hz), 111.2 (d, *J*=3.2 Hz), 110.6, 61.7, 55.6, 14.2 ppm.

*4.2.33. Ethyl (Z)-2-fluoro-3-(3-methoxyphenyl)acrylate (**4i**).*[15l] ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.35–7.28 (m, 1H), 7.25–7.19 (m, 2H), 6.96–6.83 (m, 2H), 4.35 (q, *J*=7.1 Hz, 2H), 3.83 (s, 3H), 1.38 ppm (t, *J*=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=161.38 (d, *J*=34.2 Hz), 159.6, 147.1 (d, *J*=268.1 Hz), 132.3 (d, *J*=4.4 Hz), 129.7, 122.9 (d, *J*=7.7 Hz), 117.4 (d, *J*=4.5 Hz), 115.7 (d, *J*=2.6 Hz), 115.1 (d, *J*=8.8 Hz), 61.9, 55.2, 14.2 ppm.

*4.2.34. Ethyl (Z)-3-(2-chlorophenyl)-2-fluoroacrylate (**4j**).*[6a] ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.94–7.88 (m, 1H), 7.46–7.27 (m, 4H), 4.37 (q, *J*=7.1 Hz, 2H), 1.39 ppm (t, *J*=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=161.0 (d, *J*=34.9 Hz), 147.8 (d, *J*=270.4 Hz), 134.3 (d, *J*=2.0 Hz), 131.3, 131.1, 130.5 (d, *J*=2.1 Hz), 129.2 (d, *J*=4.9 Hz), 127.0, 112.9 (d, *J*=3.3 Hz), 62.1, 14.2 ppm.

*4.2.35. Ethyl (Z)-3-(3-chlorophenyl)-2-fluoroacrylate (**4k**).*[6a] ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.68–7.62 (m, 1H), 7.54–7.48 (m, 1H), 7.39–7.32 (m, 2H), 6.86 (d, *J*=34.3 Hz, 1H), 4.36 (q, *J*=7.1 Hz, 2H), 1.39 ppm (t, *J*=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=161.0 (d, *J*=34.3 Hz), 147.7 (d, *J*=270.3 Hz), 134.7, 132.8 (d, *J*=4.4 Hz), 130.0 (d, *J*=2.3 Hz), 129.9 (d, *J*=5.7 Hz), 129.6 (d, *J*=2.6 Hz), 128.2 (d, *J*=8.1 Hz), 116.0 (d, *J*=4.6 Hz), 62.1, 14.2 ppm.

*4.2.36. Ethyl (Z)-3-(2,4-dichlorophenyl)-2-fluoroacrylate (**4l**).*[15n] ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.85 (t, *J*=6.5 Hz, 1H), 7.48–7.45 (m, 1H), 7.33–7.28 (m, 1H), 7.29 (d, *J*=34.3 Hz, 1H), 4.37 (q, *J*=7.1 Hz, 2H), 1.39 ppm (t, *J*=7.1, 3.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=160.8 (d, *J*=34.7 Hz), 148.1 (d, *J*=271.5 Hz), 135.8 (d, *J*=3.1 Hz), 135.0 (d,

J=2.0 Hz), 131.8 (d, J=14.2 Hz), 129.7, 127.8 (d, J=5.0 Hz), 127.5, 111.9 (d, J=3.3 Hz), 62.2, 14.1 ppm.

*4.2.37. Ethyl (Z)-3-(benzo[d][1,3] dioxol-5-yl)-2-fluoroacrylate (**4m**).*[15m] ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.25–7.21 (m, 1H), 7.10–7.03 (m, 1H), 6.89–6.77 (m, 2H), 6.00 (s, 2H), 4.33 (q, J=7.1 Hz, 2H), 1.37 ppm (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=161.5 (d, J=33.9 Hz), 148.8 (d, J=3.5 Hz), 148.1, 145.9 (d, J=265.1 Hz), 125.7 (d, J=6.8 Hz), 125.2 (d, J=4.5 Hz), 117.4 (d, J=4.6 Hz), 109.7 (d, J=10.7 Hz), 108.5, 101.5, 61.7, 14.2 ppm.

*4.2.38. Ethyl (Z)-2-fluoro-3-(furan-2-yl)acrylate (**4n**).*[15c] ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.56–7.49 (m, 1H), 6.94 (d, J=33.4 Hz, 1H), 6.88–6.84 (m, 1H), 6.55–6.49 (m, 1H), 4.33 (q, J=7.1 Hz, 1H), 1.36 ppm (t, J=7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=161.0 (d, J=32.9 Hz), 146.8 (d, J=4.4 Hz), 145.1 (d, J=266.5 Hz), 144.2 (d, J=3.8 Hz), 115.3 (d, J=11.1 Hz), 112.5, 107.2 (d, J=8.1 Hz), 61.8, 14.2 ppm.

*4.2.39. Ethyl (Z)-2-fluoro-3-(thiophen-2-yl)acrylate (**4o**).*[15c] ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.51 (d, J=5.1 Hz, 1H), 7.35 (d, J=4.1 Hz, 1H), 7.20 (d, J=33.9 Hz, 1H), 7.12–7.07 (m, 1H), 4.34 (q, J=7.1 Hz, 2H), 1.37 ppm (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=161.0 (d, J=32.9 Hz), 145.4 (d, J=265.4 Hz), 133.5 (d, J=5.7 Hz), 131.2 (d, J=4.9 Hz), 130.1 (d, J=9.8 Hz), 127.4, 111.9 (d, J=8.9 Hz), 99.9, 61.8, 14.2 ppm.

*4.2.40. Ethyl (Z)-2-fluoro-5-phenylpent-2-enoate (**4p**).*[15c] ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.34–7.28 (m, 2H), 7.25–7.18 (m, 3H), 6.14 (dt, J=33.1, 7.7 Hz, 1H), 4.27 (q, J=7.1 Hz, 2H), 2.83–2.73 (m, 2H), 2.57 (qd, J=7.7, 2.2 Hz, 2H), 1.32 ppm (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=160.77 (d, J=35.5 Hz), 148.1 (d, J=256.6 Hz), 140.5, 128.5, 128.3, 126.2, 119.5 (d, J=11.6 Hz), 61.5, 34.4 (d, J=2.0 Hz), 25.9 (d, J=2.4 Hz), 14.1 ppm.

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Supplementary data

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