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Tetrahedron: *Asymmetry*

The first asymmetric catalytic halo aldol reaction of β-iodo allenoates with aldehydes by using chiral salen catalyst

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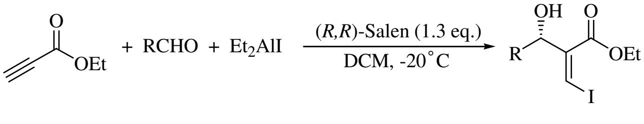
Abstract—The first asymmetric catalytic halo aldol reaction of β-iodo allenoates with aldehydes was established. The reaction was successfully achieved by using (*R*,*R*)-SalenAlCl as the chiral catalyst and LiI as an additive at 0 °C in dichloromethane. Moderate to good yields and up to 62% ee were obtained. The new system showed a good substrate scope in which both aromatic aldehydes and aliphatic aldehydes can be employed. The reaction provided the first catalytic and enantioselective approach to chiral β-iodo Baylis–Hillman ester adducts.

1. Introduction

The asymmetric aldol reaction is amongst the most important carbon–carbon bond formations in organic chemistry.[1–3] Surprisingly, there has been little work reported so far on the asymmetric halo aldol reaction. Over the past few years, we and others have reported various halo aldol reactions and their asymmetric versions.[4–6] Among these reactions, the halo aldol reactions of allenolates/allenoates with aldehydes resulted in β-halo Morita–Baylis–Hillman (MBH) ketone/ester adducts, which are building blocks of chemical and biological importance due to an array of functional groups in their structures.[7,8]

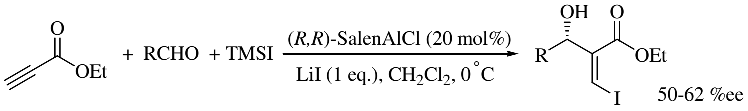


Scheme 1. Ligand-controlled asymmetric synthesis of β-halo MBH ester adducts.

Very recently, we established an enantioselective approach to β-halo MBH ester adducts by reacting β-halo aluminum allenoate with aldehydes.[6] The reaction was successfully conducted with Et_2AlI as the iodine source and Lewis acid promoter (Scheme 1). A stoichiometric amount (1.3 equiv) of (*R*,*R*)-salen was used as the chiral ligand. However, this method suffered from the use of a stoichiometric amount of chiral ligand, which prevented its utility for economic reasons. Thus, to achieve an asymmetric catalytic version of this reaction is both worthwhile and challenging. Herein we report our preliminary results on the asymmetric catalytic synthesis of β-halo MBH ester adducts (Scheme 2).

2. Results and discussion

The present catalytic reaction differs from the stoichiometric process previously reported by us[6] in the following aspects. First, the present system is an asymmetric catalytic process (20 mol % of the chiral complex was used as the catalyst), while the previous one was a chiral



Scheme 2. Asymmetric catalytic synthesis of β-halo MBH ester adducts.

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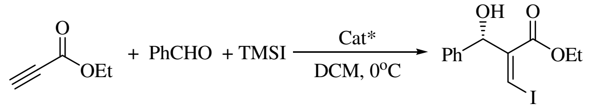
ligand-controlled asymmetric process, in which a stoichiometric amount (1.3 equiv) of chiral ligand was employed. In addition, the chiral Lewis acid catalyst used in the present catalytic system is commercially available and inexpensive. Second, in the present reaction, TMSI was used to generate the allenoates. In contrast, in the previous reaction, Et_2AlI was first combined with chiral salen to generate a chiral reagent, which was then treated with ethyl propiolate in situ to generate the chiral allenoates. Thirdly, lithium iodide was found to be an effective additive to enhance the catalytic effectiveness. Finally, the present catalytic process is easier to perform but gives similar yields and ees compared with the previous process, as shown in Tables 1–3.

Table 1. Results of chiral catalyst selection

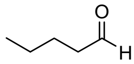
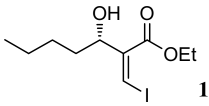
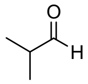
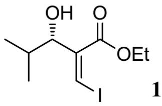
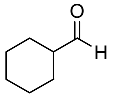
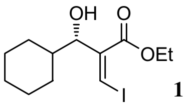
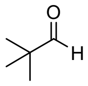
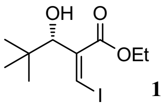


Entry	Cat*	Amount (mol %)	Yield (%)[a]	ee (%)[b]
1	**1a**	20	0	—
2	**1b**	20	0	—
3	**1c**	20	0	—
4	**1d**	20	42	32
5	**1e**	10	54	52
6	**1e**	20	74	62
7	**1e**	40	73	65
8	**1f**	20	70	55
9	**2**	20	0	—
10	**3**	20	21	29
11	**4**	20	74	2

[a] Yields after purification via column chromatography.

[b] Determined by chiral HPLC using chiral OD-H or AD column with isopropyl alcohol and hexane as the mobile phase.

Table 3. Results of the catalytic process with aliphatic aldehydes as the substrates

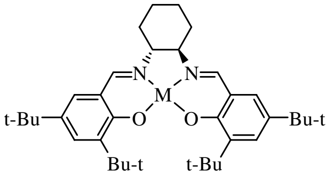
Entry	Substrate	Product	ee (%)[a]	Yield (%)[b]
1		 **13**	62	31
2		 **14**	56	44
3		 **15**	56	42(59)
4		 **16**	50	21

[a] Determined by chiral HPLC using a chiral OD-H or AD column with isopropyl alcohol and hexane as the mobile phase.

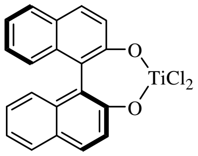
[b] The yields are given after purification via column chromatography. Yields in parentheses are recovered yields.

In the beginning, we tried to reduce the loading of chiral salen ligand[6,9] and perform the reaction using conditions directly based on the conditions of previous halo aldol reactions. Unfortunately, the catalytic reaction of β-halo aluminum allenoate with aldehydes under similar conditions resulted in very limited success. Since a *N*-C_3F_7CO oxazaborolidine catalyst has been successfully used in the asymmetric catalytic synthesis of β-halo MBH *ketone* adducts,[4a] we turned our attention to utilize it as the catalyst to the reaction of aldehydes and silyl allenoates, which were generated by treating ethyl propiolate with iodo trimethylsilane (TMSI). Surprisingly, no enantioselectivity was observed.

Since chiral salen ligands have been successfully used in the previous β-halo aluminum allenoate-based asymmetric system to introduce the chirality,[6] they were next utilized to replace the *N*-C_3F_7CO oxazaborolidine catalyst to activate the addition of silyl allenoates onto aldehydes. A series of chiral salen complexes and other chiral complexes were tested (Fig. 1) using benzaldehyde as the model substrate. We were pleased to find that this effort resulted in encouraging enantioselectivity and chemical yields as listed in Table 1. Meanwhile, the *Z*/*E* selectivity was also controlled very well, essentially, only *Z* isomers were observed for each case.



	M
1a	CrCl
1b	MnCl
1c	CoI
1d	AlI
1e	AlCl
1f	Al-O-Al-salen



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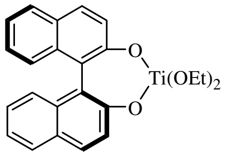

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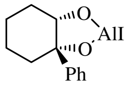
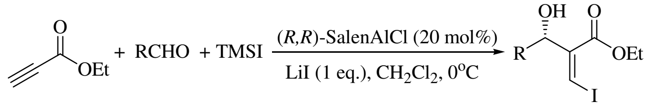


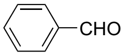
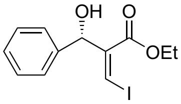
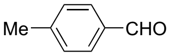
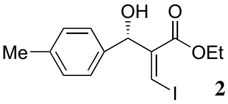
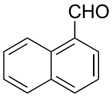
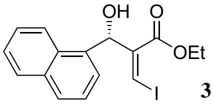
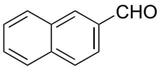
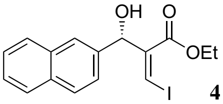
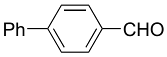
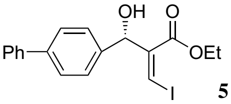
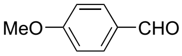
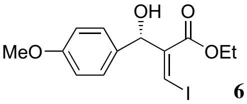
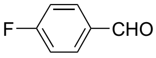
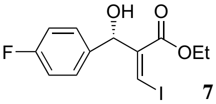
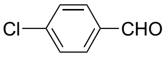
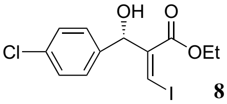
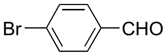
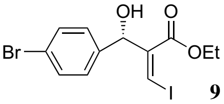
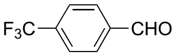
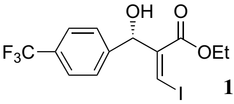
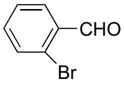
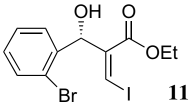
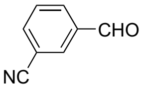
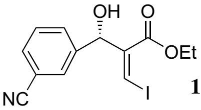
4

Figure 1. Different chiral complexes used as the catalysts.

As shown in Table 1, among the six salen complexes which were examined, (*R*,*R*)-SalenAlCl **1e** was proven to be the best catalyst for this reaction. Interestingly, catalysts **1a**–**c** did not give any desired product under this system while salenAlI **1d** gave only moderate yields and inferior ee. Although complexes **2** and **3** have been successfully utilized in other aldol reactions,[10] catalyst **2** for this reaction afforded no product whereas **3** gave poor chemical yield and ee (21% yield and 29% ee, respectively). Meanwhile, catalyst **4** gave a good yield (74%), but only afforded 3% ee. It should be mentioned that Jacobsen et al. have successfully utilized catalyst **1f** as the catalyst for the highly enantioselective Michael addition of α,β-unsaturated imides with an excellent ee achieved.[11] However, in the current catalytic system the use of **1f** did not result in performance superior to **1e**. Also, there was no obvious improvement in either ee or chemical yields when the loading of **1e** was increased to 40 mol %.

Table 2. Results of the catalytic process with aromatic aldehydes as the substrates



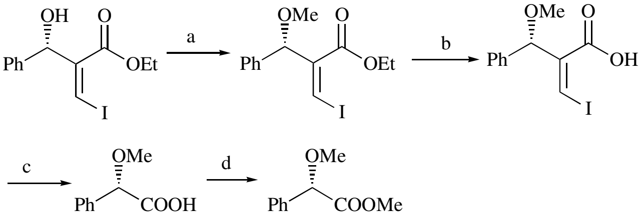
Entry	Substrate	Product	Reaction time (h)	ee (%)[a]	Yield (%)[b]
1		 **1**	30	62	74
2		 **2**	30	54	76(88)
3		 **3**	30	62	82(94)
4		 **4**	48	53	76(89)
5		 **5**	44	58	70(92)
6		 **6**	48	59	40(91)
7		 **7**	28	58	73(85)
8		 **8**	30	57	70(84)
9		 **9**	30	55	75(92)
10		 **10**	36	53[c]	75(82)
11		 **11**	44	50	74(80)
12		 **12**	44	50	54(87)

[a] Determined by chiral HPLC using chiral OD-H or AD column with isopropyl alcohol and hexane as the mobile phase.

[b] Yields after purification via column chromatography. Yields in parentheses are yields after the unreacted aldehydes were recovered.

[c] The compound was first protected by methanesulfonyl group, then the enantiomeric excess was determined by chiral HPLC.

The absolute configuration of the product was determined by chemical correlation, as demonstrated in Scheme 2.[6] The asymmetric induction can be explained based on the similar activation situation of the aldehyde, in which the *si* face of the aldehyde is open to the carbonyl attack by the β-iodo silyl allenoate intermediate (Scheme 3).[12]



Scheme 3. Absolute configuration determination: (a) MeI, Ag_2O, MeCN, reflux for 4 h; (b) NaOH, $MeOH/H_2O$, rt; (c) H_5IO_6, $RuCl_2$, $CCl_4/MeCN/H_2O$ (v/v, 1:1:2); (d) MeOH, TMSCl.

Based on the preliminary results described above, efforts were then made to optimize the catalytic conditions. At first, several solvents were tested and it was found that CH_2Cl_2 was the solvent of choice. The reaction did not proceed at all in THF, CH_3CN, or acetone. In toluene the reaction did proceed, but poor yield and ee (<45% yield and <40% ee, respectively) were obtained. In CH_2Cl_2 the reaction gave similar chemical yields and ee at 0 and at −20 °C, but did not proceed at −78 °C.

Interestingly, LiI was found to be a beneficial additive, which can promote the reaction at a faster rate and improve chemical yields as well, thus making the crude product easier to purify via column chromatography. One molar aqueous HCl was used in the previous system to quench the reaction and cleave the resulting silyl intermediates into the halo aldol products, but it did not result in complete cleavage for the present system. It was then found that the solution of 1 M citric acid in MeOH is superior, which gave higher yields and complete cleavage.

Based on the optimized reaction conditions, the reaction was carried out in CH_2Cl_2 at 0 °C with 20 mol % of (*R*,*R*)-SalenAlCl as the catalyst and LiI (1.0 equiv) as an additive. Various aldehydes were subjected to this reaction to explore the scope of substrates, the results are listed in Tables 2 and 3.

As revealed in Table 2, the reaction worked well for a large scope of aromatic aldehydes. However, when 2- and 4-nitrobenzaldehydes were employed as the substrates, there was only a tiny amount of desired products observed. This phenomenon is difficult to explain at the current stage. A possible hypothesis is that the newly formed $C(sp^3)$–$C(sp^2)$ bonds of the silyl aldol intermediates dissociated back to the starting materials, nitrobenzaldehydes.

The reactions of the aromatic substrates shown in Table 2 generally took 24–48 h to reach the stage at which the starting materials stopped being consumed. The aldehydes with electron-withdrawing groups on their aromatic rings proceeded at faster rates than those with electron-donating groups, which was anticipated.

Similar to our previous Et_2AlI-based stoichiometric asymmetric process, limited success was realized for aliphatic aldehydes. As shown in Table 3, compared with the previous system, lower yields were obtained for the four aliphatic cases, which were examined, though higher enantioselectivities were obtained. Furthermore, α,β-unsaturated aldehydes, such as cinnamaldehyde and crotonaldehyde, which resulted in the desired products with 33–48% ee in the previous system, failed to give any halo aldol product under the current catalytic system. The aldehydes listed in Table 3 generally took 48 h for the reaction to complete.

3. Conclusion

In summary, the first asymmetric catalytic halo aldol reaction of β-iodo allenoate with aldehydes has been established. The reaction provided the first catalytic and enantioselective approach to chiral β-iodo Baylis–Hillman ester adducts. Moderate enantioselectivity and useful yields were obtained for a variety of aromatic aldehydes. Aliphatic aldehydes also showed promising results for this asymmetric reaction.

4. Experimental

4.1. Typical reaction procedure

In a dry vial, trimethylsilyl iodide (TMSI) (0.1 mL, 0.72 mmol) was added dropwise into a 2.5 mL CH_2Cl_2 solution of ethyl propiolate (0.075 mL, 0.75 mmol) under inert gas protection. The resulting solution was stirred at room temperature for 2–3 h. It was then transferred into a 3 mL CH_2Cl_2 solution of Salen aluminum chloride (0.06 g, 0.1 mmol), lithium iodide (0.067 g, 0.5 mmol), and benzaldehyde (0.05 mL, 0.5 mmol) at −78 °C. The reaction mixture was brought to 0 °C bath after 10 min and stirred for 24 h. The reaction was quenched by the addition of 3 mL of 1 M citric acid/MeOH solution. After 10 min, 5 mL of water was added and the two phases were separated. The aqueous phase was extracted with 3 × 15 mL of EtOAc, the combined organic phase then washed with brine and dried with anhydrous sodium sulfate. Purification by flash chromatography (EtOAc/hexane, v/v, 1/5) provided the pure product.

Compound **1**: Isolated as a colorless oil (123 mg, 74% yield). ^1H NMR (500 MHz, $CDCl_3$) $\delta = 7.29$–7.38 (m, 5H), 7.26 (s, 1H), 5.54 (d, $J = 6.0$ Hz, 1H), 4.20 (q, $J = 7.0$ Hz, 2H), 2.85 (d, $J = 6.0$ Hz, 1H), 1.22 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = 166.1$, 145.3, 140.4, 128.9, 128.5, 126.8, 87.1, 76.5, 61.7, 14.2.

Compound **2**: Isolated as a colorless oil (131 mg, 76% yield). ^1H NMR (500 MHz, $CDCl_3$) $\delta = 7.199$–7.24 (m, 3H), 7.13–7.18 (m, 2H), 5.51 (d, $J = 5.5$ Hz, 1H), 4.20 (q, $J = 7.0$ Hz, 2H), 2.78 (d, $J = 5.5$ Hz, 1H), 2.34 (s, 3H), 1.23 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = 165.9$, 145.2, 138.1, 137.1, 129.3, 126.5, 86.4, 76.3, 61.4, 21.1, 13.9.

Compound **3**: Isolated as a colorless oil (157 mg, 82% yield). ^{1}H NMR (500 MHz, CDCl$_3$) $\delta = 7.98$–8.04 (m, 1H), 7.80–7.90 (m, 2H), 7.57–7.62 (m, 1H), 7.44–7.56 (m, 3H), 7.05 (d, $J = 1.5$ Hz, 1H), 6.32 (d, $J = 4.5$ Hz, 1H), 4.23 (q, $J = 7.0$ Hz, 2H), 2.85 (d, $J = 4.5$ Hz, 1H), 1.20 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) $\delta = 166.3$, 145.1, 135.3, 133.8, 130.5, 129.2, 128.8, 126.6, 125.9, 125.3, 124.8, 123.4, 87.4, 72.4, 61.5, 13.9.

Compound **4**: Isolated as a colorless oil (145 mg, 76% yield). ^{1}H NMR (500 MHz, CDCl$_3$) $\delta = 7.80$–7.85 (m, 4H), 7.46–7.51 (m, 2H), 7.39–7.43 (m, 1H), 7.29 (d, $J = 1.0$ Hz, 1H), 5.70 (d, $J = 5.5$ Hz, 1H), 4.18 (q, $J = 7.0$ Hz, 2H), 3.03 (d, $J = 6.0$ Hz, 1H), 1.20 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) $\delta = 165.9$, 145.0, 137.4, 133.13, 133.12, 128.5, 128.1, 127.7, 126.4, 126.3, 125.6, 124.3, 87.2, 76.3, 61.5, 13.9.

Compound **5**: Isolated as a colorless oil (142 mg, 70% yield). ^{1}H NMR (500 MHz, CDCl$_3$) $\delta = 7.56$–7.60 (m, 4H), 7.39–7.46 (m, 4H), 7.33–7.38 (m, 1H), 7.32 (d, $J = 1.5$ Hz, 1H), 5.59 (d, $J = 5.5$ Hz, 1H), 4.22 (q, $J = 7.0$ Hz, 2H), 2.90 (d, $J = 5.5$ Hz, 1H), 1.24 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) $\delta = 165.9$, 144.9, 141.2, 140.5, 139.1, 128.8, 127.5, 127.3, 127.1, 127.0, 87.0, 76.0, 61.5, 14.0.

Compound **6**: Isolated as a colorless oil (72 mg, 40% yield). ^{1}H NMR (500 MHz, CDCl$_3$) $\delta = 7.21$–7.28 (m, 3H), 6.84–6.90 (m, 2H), 5.50 (d, $J = 5.5$ Hz, 1H), 4.20 (q, $J = 7.0$ Hz, 2H), 3.80 (s, 3H), 2.73 (d, $J = 5.0$ Hz, 1H), 1.23 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) $\delta = 165.9$, 159.5, 145.4, 132.2, 127.9, 114.0, 86.0, 75.7, 61.4, 55.3, 14.0.

Compound **7**: Isolated as a colorless oil (128 mg, 73% yield). ^{1}H NMR (500 MHz, CDCl$_3$) $\delta = 7.27$–7.34 (m, 3H), 7.01–7.07 (m, 2H), 5.53 (d, $J = 5.0$ Hz, 1H), 4.20 (q, $J = 7.0$ Hz, 2H), 2.87 (d, $J = 5.5$ Hz, 1H), 1.23 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) $\delta = 165.8$, 163.5, 161.6, 144.9, 135.9, 128.4, 128.3, 115.6, 115.5, 86.9, 75.6, 61.5, 14.0.

Compound **8**: Isolated as a colorless oil (128 mg, 70% yield). ^{1}H NMR (500 MHz, CDCl$_3$) $\delta = 7.25$–7.34 (m, 5H), 5.50 (d, $J = 5.5$ Hz, 1H), 4.20 (q, $J = 7.0$ Hz, 2H), 3.06 (d, $J = 5.5$ Hz, 1H), 1.24 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) $\delta = 165.7$, 144.6, 138.7, 134.0, 128.7, 127.9, 87.3, 75.5, 61.6, 13.9.

Compound **9**: Isolated as a colorless oil (154 mg, 75% yield). ^{1}H NMR (500 MHz, CDCl$_3$) $\delta = 7.45$–7.50 (m, 2H), 7.28–7.32 (m, 1H), 7.18–7.24 (m, 2H), 5.48 (d, $J = 5.5$ Hz, 1H), 4.20 (q, $J = 7.0$ Hz, 2H), 3.06 (d, $J = 6.0$ Hz, 1H), 1.24 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) $\delta = 165.7$, 144.5, 139.2, 131.7, 128.2, 122.2, 87.5, 75.6, 61.6, 13.9.

Compound **10**: Isolated as a colorless oil (149 mg, 75% yield). ^{1}H NMR (500 MHz, CDCl$_3$) $\delta = 7.61$ (d, $J = 8.5$, 2H), 7.47 (d, $J = 8.5$ Hz, 2H), 7.35 (d, $J = 1.0$ Hz, 1H), 5.58 (d, $J = 6.0$ Hz, 1H), 4.21 (q, $J = 7.0$ Hz, 2H), 3.21 (d, $J = 6.0$ Hz, 1H), 1.23 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) $\delta = 165.6$, 144.2, 144.1, 130.3 (q), 126.8, 126.2, 125.5 (q), 125.0, 122.9, 88.1, 75.7, 61.7, 13.9.

Compound **11**: Isolated as a colorless oil (152 mg, 74% yield). ^{1}H NMR (500 MHz, CDCl$_3$) $\delta = 7.53$–7.57 (m, 1H), 7.47–7.51 (m, 1H), 7.32–7.37 (m, 1H), 7.17–7.22 (m, 1H), 7.16 (d, $J = 1.5$ Hz, 1H), 5.91 (d, $J = 3.5$ Hz, 1H), 4.25 (m, 2H), 3.07 (d, $J = 4.5$ Hz, 1H), 1.26 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) $\delta = 165.9$, 143.5, 138.9, 133.0, 129.8, 128.4, 127.9, 123.1, 88.2, 74.5, 61.6, 14.0.

Compound **12**: Isolated as a colorless oil (96 mg, 54% yield). ^{1}H NMR (500 MHz, CDCl$_3$) $\delta = 7.67$–7.70 (m, 1H), 7.58–7.63 (m, 2H), 7.46–7.50 (m, 1H), 7.43 (m, 1H), 5.57 (d, $J = 5.5$ Hz, 1H), 4.23 (q, $J = 7.0$ Hz, 2H), 3.17 (d, $J = 6.0$ Hz, 1H), 1.26 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) $\delta = 165.4$, 143.8, 141.9, 131.8, 130.8, 130.1, 129.4, 118.5, 112.7, 88.4, 75.5, 61.8, 14.0.

Compound **13**: Isolated as a colorless oil (48 mg, 31% yield). ^{1}H NMR (500 MHz, CDCl$_3$) $\delta = 7.09$ (d, $J = 1.0$ Hz, 1H), 4.38 (q, $J = 6.5$ Hz, 1H), 4.33 (q, $J = 7.0$ Hz, 2H), 2.46 (d, $J = 6.5$ Hz, 1H), 1.56–1.68 (m, 2H), 1.24–1.45 (m, 7H), 0.90 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) $\delta = 166.4$, 146.9, 84.2, 75.1, 61.4, 35.8, 27.6, 22.4, 14.1, 13.9.

Compound **14**: Isolated as a colorless oil (66 mg, 44% yield). ^{1}H NMR (500 MHz, CDCl$_3$) $\delta = 7.02$ (d, $J = 1.0$ Hz, 1H), 4.32 (q, $J = 7.0$ Hz, 2H), 4.08 (td, $J = 7.0$, 1.0 Hz, 1H), 2.47 (d, $J = 7.0$ Hz, 1H), 1.84 (o, $J = 6.5$ Hz, 1H), 1.36 (t, $J = 7.0$ Hz, 3H), 0.96 (d, $J = 6.5$ Hz, 3H), 0.90 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) $\delta = 166.7$, 146.2, 84.3, 80.9, 61.5, 32.8, 19.2, 17.5, 14.1.

Compound **15**: Isolated as a colorless oil (71 mg, 42% yield). ^{1}H NMR (500 MHz, CDCl$_3$) $\delta = 6.99$ (d, $J = 1.0$ Hz, 1H), 4.33 (q, $J = 7.0$ Hz, 2H), 4.08 (t, $J = 7.0$ Hz, 1H), 2.49 (d, $J = 7.0$ Hz, 1H), 1.90–1.97 (m, 1H), 1.69–1.80 (m, 2H), 1.64–1.68 (m, 1H), 1.55–1.60 (m, 1H), 1.46–1.54 (m, 1H), 1.38 (t, $J = 7.0$ Hz, 3H), 1.06–1.27 (m, 3H), 0.92–1.01 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) $\delta = 166.6$, 145.9, 84.4, 80.4, 61.5, 42.4, 29.5, 28.2, 26.2, 26.0, 25.8, 14.1.

Compound **16**: Isolated as a colorless oil (33 mg, 21% yield). ^{1}H NMR (500 MHz, CDCl$_3$) $\delta = 7.04$ (d, $J = 1.0$ Hz, 1H), 4.31 (q, $J = 7.0$ Hz, 2H), 4.23 (dd, $J = 5.5$, 1.0 Hz, 1H), 2.66 (d, $J = 6.0$ Hz, 1H), 1.37 (t, $J = 7.0$ Hz, 3H), 0.90 (s, 9H); ^{13}C NMR (125 MHz, CDCl$_3$) $\delta = 167.6$, 145.3, 85.3, 82.8, 61.5, 36.1, 25.6, 14.0.

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