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Palladium-catalyzed regio- and diastereo-selective allylic alkylation using 2-(diphenylphosphino)benzoic acid: construction of vicinal quaternary and tertiary carbon centers

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Abstract—The palladium-catalyzed regio- and diastereo-selective allylic alkylation of allyl acetates with carbon nucleophiles occurred. The stereochemistry was highly controlled by the palladium catalyst with 2-(diphenylphosphino)benzoic acid as the ligand, and vicinal quaternary and tertiary carbon centers were constructed.

1. Introduction

The transition metal-catalyzed allylic substitution reaction is a useful reaction in organic synthesis.[1] Especially, the palladium-catalyzed allylic alkylation is one of the most widely and frequently used carbon–carbon bond forming reactions.[2] On the other hand, the construction of a chiral quaternary carbon center catalyzed by a transition metal catalyst is also one of the most challenging topics in organic synthesis.[3] The carbon nucleophiles successfully used for the asymmetric alkylation have been limited to enolate anions generated from β-dicarbonyl compounds represented by malonate esters, and there have been few investigations into the construction of chiral quaternary carbon centers using this reaction.[4] The use of α-substituted unsymmetrical β-diketones, α-substituted β-ketoesters and α-substituted aminoester derivatives for the reaction with unsymmetrical allylic esters generally gives a mixture of regio- and stereoisomers with poor selectivity. However, if a chiral allylic acetate is employed,[5] the remaining problems for this reaction would be condensed to the control of the regio- and diastereo-selectivities, because the allylic alkylation reaction stereospecifically proceeds with a net retention of the stereochemistry (Fig. 1). Previously, we reported the regio- and diastereo-selective allylic alkylation of (*R*)-2-acetoxy-4-phenyl-3-butene with ethyl 2-methylacetoacetate by a palladium catalyst with 2-(diphenylphosphino)benzoic acid as the ligand,[6] and demonstrated the short synthesis of (−)-acetomycin.[7,8] In this paper, we report several examples of the palladium-catalyzed regio- and diastereo-selective

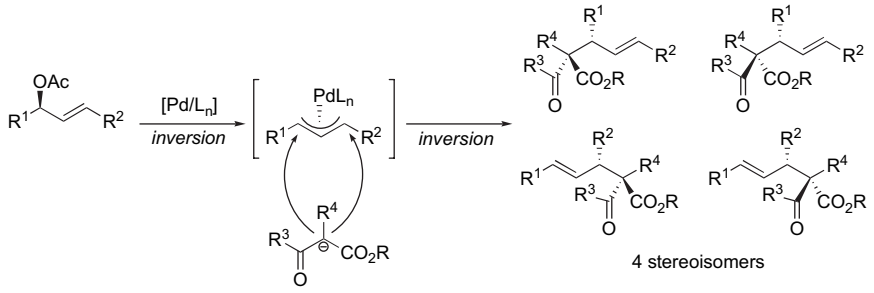

Figure 1. Palladium-catalyzed allylic alkylation of α-substituted β-ketoesters with chiral allyl acetate.

Keywords: Palladium; Catalyst; Diastereoselectivity; Regioselectivity; Quaternary carbon center.
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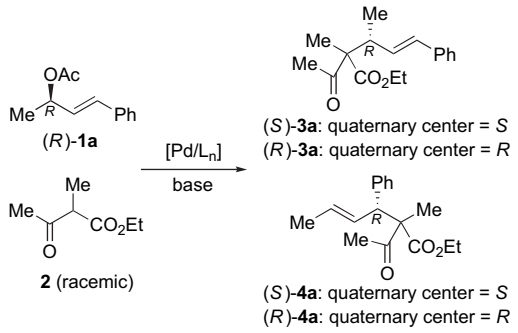
allylic alkylation of allyl acetates with several carbon nucleophiles.



Scheme 1.

2. Results and discussion

2.1. Optimization of palladium catalyst

We chose (*R*)-2-acetoxy-4-phenyl-3-butene ((*R*)-**1a**)[9] as the chiral allyl acetate, and ethyl 2-methylacetoacetate (**2**) was selected as the carbon nucleophile for the standard reaction (Scheme 1). The palladium-catalyzed allylic alkylation easily proceeds using $Pd(PPh_3)_4$, $Pd(OAc)_2/PPh_3$ or $Pd(OAc)_2$/DPPE in good to high yields, and an alkylated product **3a** was obtained as the major product with a high regioselectivity. However, the diastereoselectivity was very low and approximately a 1:1 mixture was obtained (entries 1–3 in Table 1). This poor diastereoselectivity was dramatically improved using a *o*-(diphenylphosphino)arylcarboxylic acid (Fig. 2) as the ligand for palladium. When 2-(diphenylphosphino)benzoic acid (**L1**) was employed as the ligand, the diastereoselectivity was significantly increased to 94:6 with perfect regioselectivity, and (*S*)-**3a** was obtained in a 99% yield (entry 4). As we previously reported, the assignment of the diastereochemistry and absolute stereochemistry was confirmed after converting the predominant (*R*)-diastereomer to (−)-acetomycin.[6] On the other hand, 3- or 4-(diphenylphosphino)benzoic acid (**L2** and **L3**) did not show any diastereoselectivity (entries 5 and 6). These results

Table 1. Palladium-catalyzed allylic alkylation of (*R*)-2-acetoxy-4-phenyl-3-butene ((*R*)-**1a**) with ethyl 2-methylacetoacetate **2**[a]

Entry	[Pd]	Ligand	Conversion[b] (%)	**3a**:**4a**[b]	(*S*)-**3a**:(*R*)-**3a**[b]
1	$Pd(PPh_3)_4$	—	97	99:1	55:45
2	$Pd(OAc)_2$	PPh_3	73	99:1	55:45
3	$Pd(OAc)_2$	DPPE	98	95:5	51:49
4	$Pd(OAc)_2$	**L1**	99[c]	99:1	94:6
5	$Pd(OAc)_2$	**L2**	70	84:16	53:47
6	$Pd(OAc)_2$	**L3**	99	95:5	51:49
7	$Pd(OAc)_2$	**L4**	99	99:1	94:6
8	$Pd(OAc)_2$	**L5**	99	99:1	94:6
9	$Pd(OAc)_2$	**L6**	34	99:1	48:52
10	$[PdCl(C_3H_5)]_2$	**L1**	93	99:1	89:11
11	$Pd_2(dba)_3$	**L1**	95	99:1	90:10

[a] Reaction conditions: (*R*)-**1a** (1.0 mmol), **2** (1.5 mmol), [Pd] (0.05 mmol for $Pd(PPh_3)_4$ and $Pd(OAc)_2$, 0.025 mmol for $[PdCl(C_3H_5)]_2$ and $Pd_2(dba)_3$), ligand (0.1 mmol for DPPE and **L1–6**, entries 3–11, 0.15 mmol for PPh_3), NaHMDS (1.4 mmol), dioxane (7.6 mL), 0 °C to rt, 12 h.
[b] Determined by 400 MHz ^{1}H NMR spectrum of the crude materials.
[c] Isolated yield by silica gel column chromatography was 93%.

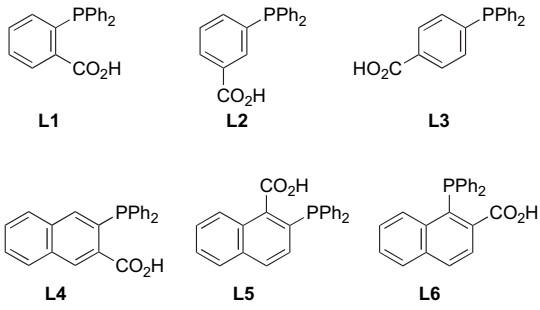


Figure 2. Structure of *o*-(diphenylphosphino)benzoic acid (**L1**) and its analogues (**L2–6**).

indicate that **L1** is the best ligand for this regio- and diastereo-selective allylic alkylation of (*R*)-**1a** with **2**. We also examined this reaction using *o*-(diphenylphosphino)naphthoic acid ligands (**L4–6**),[10] and confirmed that both **L4** and **L5** exhibit an excellent regioselectivity over 99:1 and diastereoselectivity of 94:6 (entries 7 and 8). However, when 1-(diphenylphosphino)-2-naphthoic acid **L6** was used, it only produced a 34% yield of **3a** as a 1:1 mixture of the diastereoisomers (entry 9). Furthermore, we examined the other palladium precursors such as $[PdCl(\pi\text{-allyl})]_2$ and $Pd_2(dba)_3$, but the diastereoselectivity was lower than that of the reaction with $Pd(OAc)_2$ (entries 10 and 11). Overall, we determined in the combination of $Pd(OAc)_2$ with **L1** to be the best catalyst for the regio- and diastereo-selective allylic alkylation of the chiral allyl acetate (*R*)-**1a** with **2**.

2.2. Palladium-catalyzed regio- and diastereo-selective allylic alkylation of several allyl acetates

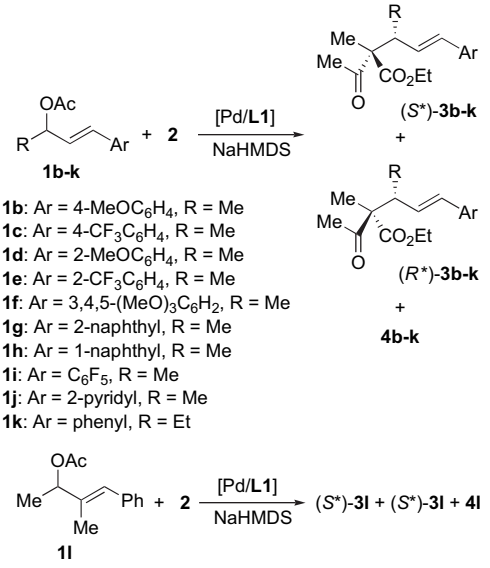
The regio- and diastereo-selectivities were easily checked by the reaction using racemic allyl acetates, if the optically active alkylated product was not needed, and results are summarized in Table 2. Typically, the reaction was carried out as follows: in the presence of 5 mol % of the palladium catalyst generated in situ by mixing 5 mol% $Pd(OAc)_2$ with 10 mol % 2-(diphenylphosphino)benzoic acid (**L1**), the racemic allyl acetates **1a–l** were allowed to react with the sodium salt of ethyl 2-methylacetoacetate (**2**) in dioxane at 0 °C to room temperature for 12 h (Scheme 2). Most of the allyl acetates exhibited a high regioselectivity and

Table 2. Pd/**L1** catalyzed regio- and diastereo-selective allylic alkylation of allyl acetates **1a–l** with ethyl 2-methylacetoacetate (**2**)[a]

Entry	**1**	Yield[b] (%)	**3**:**4**[c]	(*S**)-**3**:(*R**)-**3**[c]
1	**1a**	93 (**3a+4a**)	99:1	94:6
2	**1b**	92 (**3b+4b**)	99:1	95:5
3	**1c**	81 (**3c+4c**)	97:3	96:4
4	**1d**	41 (**3d+4d**)	99:1	95:5
5	**1e**	81 (**3e+4e**)	99:1	62:38
6	**1f**	79 (**3f+4f**)	99:1	97:3
7	**1g**	85 (**3g+4g**)	99:1	93:7
8	**1h**	88 (**3h+4h**)	99:1	92:8
9	**1i**	78 (**3i+4i**)	99:1	95:5
10	**1j**	94 (**3j+4j**)	99:1	93:7
11	**1k**	72 (**3k+4k**)	63:37	86:14
12	**1l**	61 (**3l+4l**)	99:1	91:9

[a] Reaction conditions: allyl acetate **1a–l** (1.0 mmol), **2** (1.5 mmol), $Pd(OAc)_2$ (0.05 mmol), **L1** (0.1 mmol), NaHMDS (1.4 mmol), dioxane (7.6 mL), 0 °C to rt, 12 h. .
[b] Isolated yield by silica gel column chromatography.
[c] Determined by 400 MHz ^{1}H NMR spectrum of the crude materials.

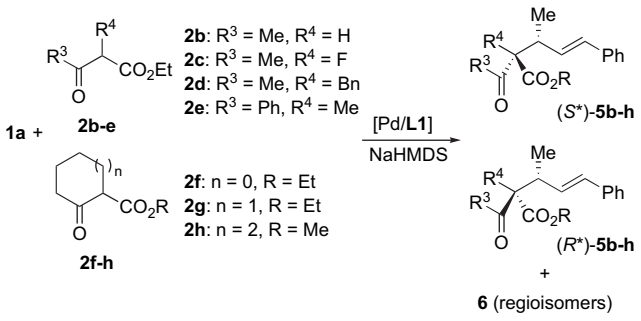
diastereoselectivity. For example, the reaction of the allyl acetate **1b** (Ar=4-$MeOC_6H_4$) proceeded with a 99% regioselectivity and 95% diastereoselectivity (entry 2). Similarly, the allyl acetate **1c** (Ar=4-$CF_3C_6H_4$) gave **3c** with a 96% diastereoselectivity even though the regioselecitivity slightly decreased to 97% (entry 3). On the other hand, the stereoselectivity was affected by an *ortho* substituent on the phenyl group. The reaction of allyl acetate **1d** (Ar=2-$MeOC_6H_4$) resulted in a low yield (entry 4), and a decreased diastereoselectivity (62%) was observed for the reaction of **1e** (Ar=2-$CF_3C_6H_4$) (entry 5). However, the allyl acetate **1f** (Ar=3,4,5-$(MeO)_3C_6H_2$) exhibited the highest diastereoselectivity with a perfect regioselectivity (entry 6). Both the 2- and 1-naphthyl group substituted allyl acetates (**1g** and **1h**) gave alkylated products **3g** and **3h** with a good diastereoselectivity and 99% regioselecitivity (entries 7 and 8). Furthermore, we found that other aromatic groups such as the pentafluorophenyl group or 2-pyridyl group (**1i** or **1j**) also exhibited good stereoselectivities (entries 9 and 10). However, we confirmed that the allyl acetate **1k**, which has an ethyl group on the allyl terminus instead of a methyl group, decreased both the regio- and diastereo-selectivities (entry 11). This result suggests that the steric difference between the methyl or ethyl group and phenyl group is an important factor for the high stereoselectivities. The more substituted allyl acetate **1l** again showed a high regioselectivity and diastereoselectivity even though the isolated yield was slightly decreased (entry 12). Overall, the palladium catalyst, which was generated from $Pd(OAc)_2$ and **L1**, is an efficient catalyst for the regio- and diastereo-selective allylic alkylation of a wide range of allyl acetates with **2**.



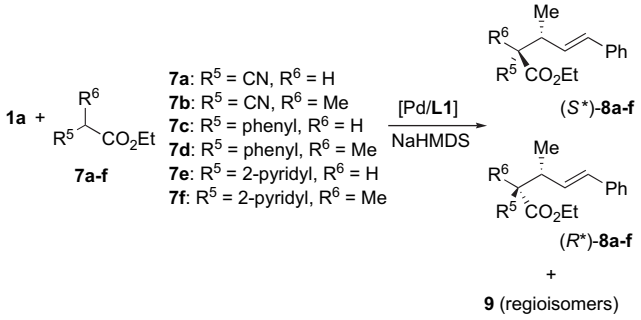
Scheme 2.

2.3. Palladium-catalyzed regio- and diastereo-selective allylic alkylation with several β-ketoesters and other carbon nucleophiles

We next examined the reaction of the racemic 2-acetoxy-4-phenyl-3-butene (**1a**) with several carbon nucleophiles using the Pd/**L1** catalyst (Schemes 3 and 4), and the results are



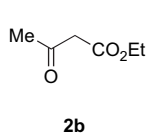
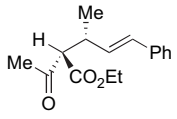
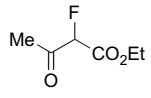
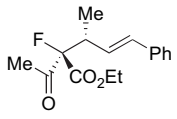
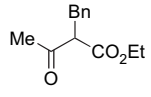
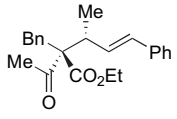
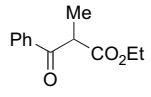
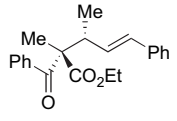
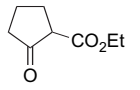
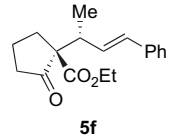
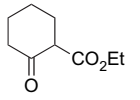
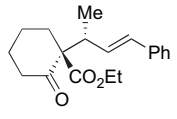
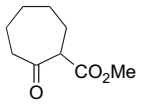
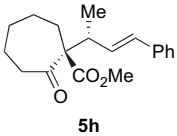
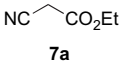
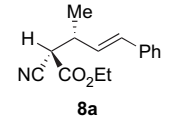
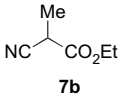
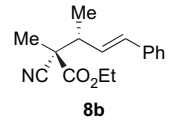
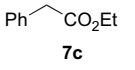
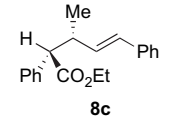
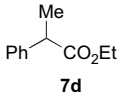
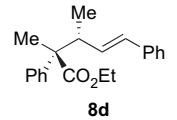
Scheme 3.



Scheme 4.

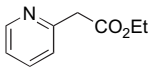
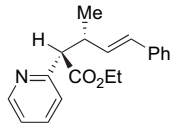
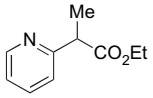
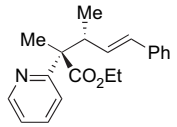
shown in Table 3. Most of the nucleophiles exhibited an excellent regioselectivity (over 94%), but obviously the diastereoselectivity depends upon the nucleophile, which was used. Especially, a substituent at the α position of the β-ketoesters is an important to attain the high diastereoselectivity. For example, the diastereoselectivity for the reaction of **2** was 94% (entry 4 in Table 1), but the reaction of ethyl acetoacetate (**2b**) gave **5b** with only a 58% diastereoselectivity (entry 1 in Table 3). Therefore, a substitution group at the α-position on the β-ketoesters is required for a good diastereoselectivity in this palladium-catalyzed reaction. Actually, the α-fluoro or α-benzyl substituted ethyl acetoacetate (**2c** and **2d**) proceeded with 78% and 81% diastereoselectivities, respectively (entries 2 and 3). Ethyl 2-methyl-3-oxo-3-phenylpropanoate (**2e**) also exhibited a good stereoselectivity (entry 4). Excellent regio- and diastereo-selectivities are observed for the reaction with cyclic β-ketoesters (**2f–h**). The reaction of **1a** with ethyl 2-oxocyclopentanecarboxylate (**2f**) proceeded regio- and diastereoselectively to give **5f** with a 96% diastereoselectivity (entry 5). Similarly, ethyl 2-oxocyclohexanecarboxylate (**2g**) and methyl 2-oxo-1-cycloheptanecarboxylate (**2h**) produced the alkylated products **5g** and **5h** with 96% and 94% diastereoselectivities, respectively (entries 6 and 7). The reaction of cyanoesters was also examined. The reaction of ethyl cyanoacetate (**7a**) produced a product **8a** without any diastereoselectivity (52%), but again the methyl group substituted cyanoester **7b** increased the diastereoselectivity up to 84% (entries 8 and 9). Unfortunately, the reaction of ethyl phenylacetates (**7c**) proceeded without any diastereoselectivity (54%) in a low yield (entry 10), and the methyl group substituted phenyl acetate **7d** did not produce any alkylation product (entry 11). Furthermore, we tried the reaction of two 2-pyridyl acetates (**7e** and **7f**), but both nucleophiles gave **8e** and **8f** with 53% and 60% diastereoselectivities, respectively (entries 12 and 13). These

Table 3. Pd/**L1** catalyzed regio- and diastereo-selective allylic alkylation of (*R*)-2-acetoxy-4-phenyl-3-butene (**1a**) with carbon nucleophiles **2b–h** and **7a–f**[a]

Entry	**2** or **7**	Product[d]	Yield[b] (%)	rs[c] (%)	ds[c] (%)
1	 **2b**	 **5b**	60	99	58
2	 **2c**	 **5c**	75	99	78
3	 **2d**	 **5d**	78	99	81
4	 **2e**	 **5e**	77	99	88
5	 **2f**	 **5f**	83	99	96
6	 **2g**	 **5g**	86	99	96
7	 **2h**	 **5h**	86	99	94
8	 **7a**	 **8a**	92	99	52
9	 **7b**	 **8b**	96	99	84
10	 **7c**	 **8c**	60	94	54
11	 **7d**	 **8d**	0	—	—

(*continued*)

Table 3. (*continued*)

Entry	**2** or **7**	Product[d]	Yield[b] (%)	rs[c] (%)	ds[c] (%)
12	 **7e**	 **8e**	82	98	53
13	 **7f**	 **8f**	86	98	60

[a] Reaction conditions: **1a** (1.0 mmol), **2b–h** and **7a–f** (1.5 mmol), $Pd(OAc)_2$ (0.05 mmol), **L1** (0.1 mmol), NaHMDS (1.4 mmol), dioxane (7.6 mL), 0 °C to rt, 12 h.
[b] Isolated yield by silica gel column chromatography.
[c] Determined by 400 MHz ^{1}H NMR spectrum of the crude materials.
[d] The exact relative stereochemistry of **5b–e** and **8a–f** had not been determined.

results suggest that the palladium catalyst, which was generated from $Pd(OAc)_2$ and **L1**, is highly effective for the regio- and diastereo-selective allylic alkylation of **1a** with α-substituted β-ketoesters and cyanoesters. However, the catalyst is not effective for the reaction with other carbon nucleophiles such as **7c–f**.

3. Conclusion

In conclusion, we demonstrated the palladium-catalyzed regio- and diastereo-selective allylic alkylation of several allyl acetates with several carbon nucleophiles. We developed a palladium catalyst that coordinated with 2-(diphenylphosphino)benzoic acid and highly controlled both the regio- and diastereo-selecitivies for the reaction with α-substituted β-ketoesters, and we succeeded in constructing vicinal quaternary and tertiary carbon centers. Unfortunately, the mechanistic details, especially the role of the carboxylic group in generating the π-allylpalladium intermediate, is still unclear, and will be the subject of a future study.

4. Experimental section

4.1. General methods

All manipulations were carried out under a nitrogen atmosphere. Nitrogen gas was dried by passage through P_2O_5. NMR spectra were recorded on a JEOL JNM MH400 spectrometer (400 MHz for ^{1}H and 125 MHz for ^{13}C). Chemical shifts are reported in δ parts per million referenced to an internal $SiMe_4$ standard for ^{1}H NMR. Residual chloroform (δ 77.0 for ^{13}C) was used as internal reference for ^{13}C NMR. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 25 °C unless otherwise noted. (*R*)-2-Acetoxy-4-phenyl-3-butene (**1a**)[9] was prepared according to the reported procedure, and *o*-(diphenylphosphino)arylcarboxylic acid **L4–6** were prepared according to the reported procedure.[10]

4.2. General procedure for the allylic alkylation of (*R*)-2-acetoxy-4-phenyl-3-butene (1a) with ethyl 2-methylacetoacetate (2)

Typical procedure was given for the reaction by $Pd(OAc)_2$/**L1** (entry 1 in Table 2). To a solution of $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), 2-(diphenylphosphino)benzoic acid (**L1**) (30.6 mg, 0.10 mmol) in dioxane (7.6 mL) was added (*R*)-2-acetoxy-4-phenyl-3-butene (**1a**) (190 mg, 1.0 mmol), ethyl 2-methylacetoacetate (**2**) (216 mg, 1.5 mmol). The solution was cooled to 0 °C, then NaHMDS (1.4 mL, 1.0 M in THF) added slowly. The resultant mixture was allowed to warm to room temperature over 12 h. The reaction mixture was quenched with water, and extracted with ether. The organic phase was washed with brine, dried over anhydrous $MgSO_4$, and evaporated. The regio and diastereo ratios of product were determined by 400 MHz ^{1}H NMR for crude material. The residue was chromatographed on silica gel (EtOAc/hexane=1:9) to give 255 mg (93%) of **3a**.

4.2.1. Major isomer {ethyl (2*S*,3*R*)-2-acetyl-2,3-dimethyl-5-phenyl-4-pentenoate: (2*S*,3*R*)-3a}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35–7.20 (m, 5H), 6.43 (d, J=15.8 Hz, 1H), 6.05 (dd, J=15.8, 8.6 Hz, 1H), 4.22 (q, J=7.1 Hz, 2H), 3.23 (m, 1H), 2.17 (s, 3H), 1.35 (s, 3H), 1.28 (t, J=7.1 Hz, 3H), 1.13 (d, J=6.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 204.9, 172.0, 137.2, 131.4, 130.3, 128.5, 127.4, 126.3, 63.5, 61.3, 41.1, 26.9, 16.4, 16.0, 14.1. EIMS *m*/*z*: 274. EI-HRMS *m*/*z*: 274.1569 (calcd for $C_{17}H_{22}O_3$: 274.1567). Colorless oil. R_f=0.55 (10% EtOAc in hexane). $[\alpha]_D^{25}$ 59.8 (*c* 1.03, $CHCl_3$).

4.2.2. Minor isomer {ethyl (2*R*,3*R*)-2-acetyl-2,3-dimethyl-5-phenyl-4-pentenoate: (2*R*,3*R*)-3a}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43–7.19 (m, 5H), 6.42 (d, J=15.8 Hz, 1H), 6.15 (dd, J=15.8, 8.4 Hz, 1H), 4.15 (q, J=7.1 Hz, 2H), 3.24 (m, 1H), 2.19 (s, 3H), 1.36 (s, 3H), 1.23 (t, J=7.1 Hz, 3H), 1.07 (d, J=7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 205.0, 171.9, 137.3, 131.3, 130.7, 128.5, 127.3, 126.2, 63.7, 61.7, 41.0, 26.8, 15.7, 15.2, 14.1. R_f=0.55 (10% EtOAc in hexane).

4.2.3. Ethyl 2-acetyl-2,3-dimethyl-5-(4-methoxyphenyl)-4-pentenoate (3b).

4.2.3.1. Major isomer {ethyl (2*S,3*R**)-2-acetyl-2,3-dimethyl-5-(4-methoxyphenyl)-4-pentenoate: (2*S**,3*R**)-3b}.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25 (d, J=8.8 Hz, 2H), 6.82 (d, J=8.8 Hz, 2H), 6.37 (d, J=15.6 Hz, 1H), 5.90 (dd, J=15.6, 8.8 Hz, 1H), 4.21 (q, J=7.3 Hz, 2H), 3.79 (s, 3H), 3.21 (m, 1H), 2.16 (s, 3H), 1.34 (s, 3H), 1.28 (t, J=7.3 Hz, 3H), 1.12 (d, J=6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 205.0, 172.0, 159.0, 130.7, 129.9, 127.9, 127.3, 113.9, 63.5, 61.2, 55.2, 41.0, 26.9, 16.5, 15.8, 14.1. Colorless oil. R_f=0.50 (10% EtOAc in hexane). EIMS *m*/*z*: 304, EI-HRMS *m*/*z*: 304.1678 (calcd for $C_{18}H_{24}O_4$: 304.1674).

4.2.3.2. Minor isomer {ethyl (2*R,3*R**)-2-acetyl-2,3-dimethyl-5-(4-methoxyphenyl)-4-pentenoate: (2*R**,3*R**)-3b}.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25 (d, J=8.8 Hz, 1H), 6.82 (d, J=8.8 Hz, 2H), 6.37 (d, J=15.6 Hz, 1H), 6.00 (dd, J=15.6, 8.3 Hz, 1H), 4.13 (q, J=6.8 Hz, 2H), 2.18 (s, 3H), 1.35 (s, 3H), 1.22 (t, J=6.8 Hz, 3H), 1.05 (d, J=6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 208.1, 174.9, 162.5, 130.6, 130.1, 128.4, 127.6, 114.1, 63.7, 61.8, 53.6, 38.6, 26.8, 15.7, 15.1, 12.7. R_f=0.55 (15% EtOAc in hexane).

4.2.4. Ethyl 2-acetyl-2,3-dimethyl-5-(4-trifluoromethylphenyl)-4-pentenoate (3c).

4.2.4.1. Major isomer {ethyl (2*S,3*R**)-2-acetyl-2,3-dimethyl-5-(4-trifluoromethylphenyl)-4-pentenoate: (2*S**,3*R**)-3c}.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (d, J=8.3 Hz, 2H), 7.41 (d, J=8.3 Hz, 2H), 6.46 (d, J=15.6 Hz, 1H), 6.19 (dd, J=15.6, 8.3 Hz, 1H), 4.23 (q, J=7.3 Hz, 2H), 3.25 (m, 1H), 2.17 (s, 3H), 1.35 (s, 3H), 1.28 (t, J=7.3 Hz, 3H), 1.14 (d, J=6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 204.8, 171.8, 140.6, 133.3, 130.1, 126.4, 125.4 (2C), 63.3, 62.7, 61.4, 41.0, 26.9, 16.2, 16.1, 14.1. Colorless oil. EIMS *m*/*z*: 342, EI-HRMS *m*/*z*: 342.1444 (calcd for $C_{18}H_{21}F_3O_3$: 342.1443). R_f=0.48 (10% EtOAc in hexane).

4.2.4.2. Minor isomer {ethyl (2*R,3*R**)-2-acetyl-2,3-dimethyl-5-(4-trifluoromethylphenyl)-4-pentenoate: (2*R**,3*R**)-3c}.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (d, J=8.3 Hz, 2H), 7.41 (d, J=8.3 Hz, 2H), 6.46 (d, J=16.1 Hz, 1H), 6.28 (dd, J=16.1, 8.3 Hz, 1H), 4.16 (q, J=6.8 Hz, 2H), 3.25 (m, 1H), 2.17 (s, 3H), 1.37 (s, 3H), 1.23 (t, J=6.8 Hz, 3H), 1.09 (d, J=6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 204.9, 171.7, 140.5, 133.5, 130.0, 126.5, 125.6 (2C), 63.1, 61.6, 41.2, 27.2, 16.3, 16.0, 14.2. R_f=0.55 (10% EtOAc in hexane).

4.2.5. Ethyl 2-acetyl-2,3-dimethyl-5-(2-methoxyphenyl)-4-pentenoate (3d).

4.2.5.1. Major isomer {ethyl (2*S,3*R**)-2-acetyl-2,3-dimethyl-5-(2-methoxyphenyl)-4-pentenoate: (2*S**,3*R**)-3d}.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38–6.83 (m, 4H), 6.76 (d, J=16.1 Hz, 1H), 6.02 (dd, J=16.1, 8.8 Hz, 1H), 4.22 (q, J=7.3 Hz, 2H), 3.82 (s, 3H), 3.25 (m, 1H), 2.18 (s, 3H), 1.35 (s, 3H), 1.28 (t, J=7.3 Hz, 3H), 1.14 (d, J=6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 205.1, 172.1, 156.5, 130.6, 128.4, 126.6, 126.2, 126.1, 120.6, 110.8, 63.7, 61.3, 55.5, 41.5, 26.9, 16.6, 15.9, 14.1. Colorless oil. EIMS *m*/*z*: 304, EI-HRMS *m*/*z*: 304.1681 (calcd for $C_{18}H_{24}O_4$: 304.1674). R_f=0.50 (10% EtOAc in hexane).

4.2.5.2. Minor isomer {ethyl (2*R,3*R**)-2-acetyl-2,3-dimethyl-5-(2-methoxyphenyl)-4-pentenoate: (2*R**,3*R**)-3d}.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37–6.81 (m, 4H), 6.76 (d, J=16.1 Hz, 1H), 6.02 (dd, J=16.1, 8.8 Hz, 1H), 4.15 (q, J=7.0 Hz, 2H), 3.79 (s, 3H), 3.25 (m, 1H), 2.18 (s, 3H), 1.36 (s, 3H), 1.24 (t, J=7.0 Hz, 3H), 1.08 (d, J=6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 205.2, 172.2, 156.2, 130.5, 128.8, 126.7, 126.1, 126.0, 120.5, 110.6, 63.9, 61.3, 55.4, 41.6, 26.7, 16.7, 15.7, 14.3. R_f=0.50 (10% EtOAc in hexane).

4.2.6. Ethyl 2-acetyl-2,3-dimethyl-5-(2-trifluoromethylphenyl)-4-pentenoate (3e).

4.2.6.1. Major isomer {ethyl (2*S,3*R**)-2-acetyl-5-(2-trifluoromethylphenyl)-2,3-dimethyl-4-pentenoate: (2*S**,3*R**)-3e}.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61–7.28 (m, 4H), 6.81 (d, J=15.7 Hz, 1H), 6.03 (dd, J=15.7, 8.8 Hz, 1H), 4.22 (q, J=7.0 Hz, 2H), 3.29 (m, 1H), 2.18 (s,

3H), 1.35 (s, 3H), 1.29 (t, J=7.0 Hz, 3H), 1.16 (d, J=7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 204.9, 171.8, 136.4, 134.8, 131.9, 127.7, 127.4, 127.1, 125.6, 124.4, 123.0, 63.4, 61.5, 41.1, 26.7, 16.2, 15.3, 14.1. EIMS m/z: 342, EI-HRMS m/z: 304.1447 (calcd for $C_{18}H_{21}F_3O_3$: 304.1443). Colorless oil. R_f=0.49 (10% EtOAc in hexane).

4.2.6.2. Minor isomer {ethyl (2*R,3*R**)-2-acetyl-5-(2-trifluoromethylphenyl)-2,3-dimethyl-4-pentenoate: (2*R**,3*R**)-3e}.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61–7.28 (m, 4H), 6.81 (d, J=15.7 Hz, 1H), 6.15 (dd, J=15.7, 8.8 Hz, 1H), 4.17 (q, J=7.0 Hz, 2H), 3.29 (m, 1H), 2.20 (s, 3H), 1.38 (s, 3H), 1.24 (t, J=7.0 Hz, 3H), 1.10 (d, J=7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 204.9, 171.9, 136.5, 135.3, 131.9, 127.7, 127.6, 127.1, 125.7, 123.0, 63.5, 61.5, 41.1, 26.8, 15.8, 15.5, 14.1. R_f=0.49 (10% EtOAc in hexane).

4.2.7. Ethyl 2-acetyl-2,3-dimethyl-5-(3,4,5-trimethoxyphenyl)-4-pentenoate (3f).

4.2.7.1. Major isomer {ethyl (2*S,3*R**)-2-acetyl-2,3-dimethyl-5-(3,4,5-trimethoxyphenyl)-4-pentenoate: (2*S**,3*R**)-3f}.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (s, 1H), 6.54 (s, 1H), 6.36(d, J=16.1, Hz, 1H), 5.96 (dd, J=16.1, 8.8 Hz, 1H), 4.23 (q, J=7.3 Hz, 2H), 3.87 (s, 6H), 3.83 (s, 3H), 3.22 (dq, J=8.8, 6.8 Hz, 1H), 2.17 (s, 3H), 1.35 (s, 3H), 1.29 (t, J=7.3 Hz, 3H), 1.13 (d J=6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 205.0, 172.0, 153.3, 138.3, 132.8, 131.4, 129.7, 103.4, 63.5, 61.4, 60.9, 56.1, 41.0, 27.0, 16.5, 16.0, 14.1. EIMS m/z: 364, EI-HRMS m/z: 364.1891 (calcd for $C_{20}H_{28}O_6$: 364.1886). Colorless oil. R_f=0.41 (10% EtOAc in hexane).

4.2.7.2. Minor isomer {ethyl (2*R,3*R**)-2-acetyl-2,3-dimethyl-5-(3,4,5-trimethoxyphenyl)-4-pentenoate: (2*R**,3*R**)-3f}.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (s, 1H), 6.54 (s, 1H), 6.36 (d, J=16.1 Hz, 1H), 6.06 (dd, J=16.1, 8.8 Hz, 1H), 4.17 (q, J=6.8 Hz, 2H), 3.87 (s, 6H), 3.85 (s, 3H), 3.22 (m, 1H), 2.17 (s, 3H), 2.17 (s, 3H), 1.35 (s, 3H), 1.25 (t, J=6.8 Hz, 3H), 1.08 (d, J=6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 206.2, 172.1, 153.4, 138.5, 132.9, 131.6, 129.8, 103.5, 63.7, 61.7, 63.9, 61.3, 60.7, 55.9, 41.2, 27.5, 16.6, 15.8, 14.5. R_f=0.41 (10% EtOAc in hexane).

4.2.8. Ethyl 2-acetyl-2,3-dimethyl-5-(2-naphthyl)-4-pentenoate (3g).

4.2.8.1. Major isomer {ethyl (2*S,3*R**)-2-acetyl-2,3-dimethyl-5-(2-naphthyl)-4-pentenoate: (2*S**,3*R**)-3g}.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79–7.25 (m, 7H), 6.59 (d, J=15.7 Hz, 1H), 6.19 (dd, J=15.7, 8.4 Hz, 1H), 4.23 (q, J=7.0 Hz, 2H), 3.29 (m, 1H), 2.18 (s, 3H), 1.38 (s, 3H), 1.28 (t, J=7.0 Hz, 3H), 1.17 (d, J=6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 205.0, 171.9, 134.5, 133.5, 132.8, 131.5, 130.7, 128.1, 127.8, 127.6, 126.2, 125.9, 125.7, 123.5, 63.5, 61.3, 41.2, 26.9, 16.4, 16.0, 14.1. EIMS m/z: 324, EI-HRMS m/z: 324.1719 (calcd for $C_{21}H_{24}O_3$: 324.1725). Colorless oil. R_f=0.56 (10% EtOAc in hexane).

4.2.8.2. Minor isomer {ethyl (2*R,3*R**)-2-acetyl-2,3-dimethyl-5-(2-naphthyl)-4-pentenoate: (2*R**,3*R**)-3g}.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79–7.25 (m, 7H), 6.59 (d, J=15.7, 1H), 6.29 (dd, J=15.7, 8.8 Hz, 1H), 4.15 (q, J=7.0 Hz, 2H), 3.29 (m, 1H), 2.20 (s, 3H), 1.39 (s, 3H), 1.21 (t, J=7.0 Hz, 3H), 1.11 (d, J=7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 204.9, 171.8, 134.6, 133.6, 132.9, 131.5, 130.8, 128.5, 127.9, 127.5, 126.1, 125.8, 125.6, 123.4, 63.4, 61.1, 41.3, 26.7, 16.5, 15.9, 13.9. R_f=0.56 (10% EtOAc in hexane).

4.2.9. Ethyl 2-acetyl-2,3-dimethyl-5-(1-naphthyl)-4-pentenoate (3h).

4.2.9.1. Major isomer {ethyl (2*S,3*R**)-2-acetyl-2,3-dimethyl-5-(1-naphthyl)-4-pentenoate: (2*S**,3*R**)-3h}.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.06–7.23 (m, 7H), 7.18 (d, J=15.7 Hz, 1H), 6.06 (dd, J=15.7, 8.8 Hz, 1H), 4.23 (q, J=7.0 H, 2H), 3.38 (m, 1H), 2.21 (s, 3H), 1.40 (s, 3H), 1.28 (t, J=7.0 Hz, 3H), 1.21 (d, J=6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 204.9, 171.9, 135.0, 133.5, 133.4, 131.1, 128.8, 128.5, 127.7, 126.0, 125.7, 125.6, 123.9, 123.7, 63.5, 61.3, 41.3, 27.0, 16.5, 15.9, 14.1. EIMS m/z: 324, EI-HRMS m/z: 324.1728 (calcd for $C_{21}H_{24}O_3$: 324.1725). Colorless oil. R_f=0.58 (10% EtOAc in hexane).

4.2.9.2. Minor isomer {ethyl (2*R,3*R**)-2-acetyl-2,3-dimethyl-5-(1-naphthyl)-4-pentenoate: (2*R**,3*R**)-3h}.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.06–7.23 (m, 7H), 7.18 (d, J=15.7 Hz, 1H), 6.15 (dd, J=15.7, 8.4 Hz, 1H), 4.15 (q, J=7.0 Hz, 2H), 3.38 (m, 1H), 2.22 (s, 3H), 1.39 (s, 3H), 1.28 (t, J=7.0 Hz, 3H), 1.15 (d, J=7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 204.8, 171.8, 135.1, 134.0, 133.9, 131.5, 128.9, 128.6, 128.1, 126.1, 125.3, 125.2, 123.8, 123.5, 63.7, 61.2, 41.2, 26.8, 16.4, 15.7, 15.1. R_f=0.58 (10% EtOAc in hexane).

4.2.10. Ethyl 2-acetyl-2,3-dimethyl-5-pentafluorophenyl-4-pentenoate (3i).

4.2.10.1. Major isomer {ethyl (2*S,3*R**)-2-acetyl-2,3-dimethyl-5-pentafluorophenyl-4-pentenoate: (2*S**,3*R**)-3i}.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.41 (dd, J=16.6, 8.3 Hz, 1H), 6.32 (d, J=16.6 Hz, 1H), 4.23 (q, J=7.3 Hz, 2H), 3.24 (m, 1H), 2.17 (s, 3H), 1.36 (s, 3H), 1.29 (t, J=7.3 Hz, 3H), 1.13 (d, J=6.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 204.6, 171.6, 145.8, 143.4, 140.9, 140.5, 138.9, 136.4, 115.6, 63.2, 61.6, 42.2, 26.9, 16.3, 16.0, 15.3, 14.1. EIMS m/z: 364, EI-HRMS m/z: 364.1105 (calcd for $C_{17}H_{17}F_5O_3$: 364.1098). Colorless oil. R_f=0.32 (10% EtOAc in hexane).

4.2.10.2. Minor isomer {ethyl (2*R,3*R**)-2-acetyl-2,3-dimethyl-5-pentafluorophenyl-4-pentenoate: (2*R**,3*R**)-3i}.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.49 (dd, J=16.6, 8.3 Hz, 1H), 6.32 (d, J=16.6 Hz, 1H), 4.18 (q, J=7.3 Hz, 2H), 3.24 (m, 1H), 2.19 (s, 3H), 1.36 (s, 3H), 1.26 (t, J=7.3 Hz, 3H), 1.07 (d, J=6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 204.3, 171.6, 145.7, 143.5, 140.7, 140.6, 138.7, 136.5, 115.4, 61.7, 63.0, 61.5, 42.3, 26.8, 16.0, 15.1, 14.0. R_f=0.32 (10% EtOAc in hexane).

4.2.11. Ethyl 2-acetyl-2,3-dimethyl-5-(2-pyridyl)-4-pentenoate (3j).

4.2.11.1. Major isomer {ethyl (2*S,3*R**)-2-acetyl-2,3-dimethyl-5-(2-pyridyl)-4-pentenoate: (2*S**,3*R**)-3j}.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.53–8.51 (m, 1H), 7.64–7.54 (m, 1H), 7.26 (d, J=8.2 Hz, 1H), 7.12–7.09 (m, 1H), 6.69–6.49 (m, 2H), 4.22 (q, J=7.3 Hz, 2H), 3.37–3.26 (m, 1H),

2.18 (s, 3H), 1.35 (s, 3H), 1.28 (t, J=7.3 Hz, 3H), 1.15 (d, J=7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 204.8, 171.8, 155.4, 149.4, 136.4, 134.8, 131.6, 122.0, 121.1, 63.4, 61.4, 40.6, 26.8, 16.1, 15.7, 14.0. EIMS 275, EI-HRMS m/z: 275.1519 (calcd for $C_{16}H_{21}NO_3$: 275.1521). Colorless oil. R_f=0.29 (10% EtOAc in hexane).

4.2.11.2. Minor isomer {ethyl (2*R,3*R**)-2-acetyl-2,3-dimethyl-5-(2-pyridyl)-4-pentenoate: (2*R**,3*R**)-3j}.** ^{1}H NMR (400 MHz, C_6D_6) δ: 8.53–8.51 (m, 1H), 7.64–7.54 (m, 1H), 8.53–8.51 (m, 1H), 7.26 (d, J=8.2 Hz, 1H), 7.12–7.09 (m, 1H), 6.69–6.49 (m, 2H), 4.16 (q, J=7.3 Hz, 2H), 3.37–3.26 (m, 1H), 2.19 (s, 3H), 1.34 (s, 3H), 1.23 (t, J=7.3 Hz, 3H), 1.09 (d, J=7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 204.9, 171.8, 155.4, 149.4, 136.6, 135.3, 131.4, 122.0, 121.1, 62.2, 61.4, 40.6, 26.7, 15.9, 15.4, 15.0. R_f=0.29 (10% EtOAc in hexane).

4.2.12. Ethyl 2-acetyl-2-ethyl-3-methyl-5-phenyl-4-pentenoate (3k).

4.2.12.1. Major isomer {ethyl (2*S,3*R**)-2-acetyl-2-ethyl-3-methyl-5-phenyl-4-pentenoate: (2*S**,3*R**)-3k}.** ^{1}H NMR (400 MHz, C_6D_6) δ: 7.35–6.99 (m, 5H), 6.33 (d, J=16.1 Hz, 1H), 5.92 (dd, J=16.1, 10.2 Hz, 1H), 3.93–3.84 (m, 2H), 2.91 (m, 1H), 1.92 (s, 3H), 1.36 (s, 3H), 1.30–1.19 (m, 2H), 0.92 (t, J=7.3 Hz, 3H), 0.86 (t, J=7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 204.9, 172.1, 137.0, 133.5, 129.5, 128.5, 127.4, 126.3, 61.3, 53.0, 49.5, 26.8, 23.8, 16.3, 14.1, 12.6. EIMS m/z: 288, EI-HRMS m/z: 288.1722 (calcd for $C_{18}H_{24}O_3$: 288.1725). Colorless oil. R_f=0.50 (10% EtOAc in hexane).

4.2.12.2. Minor isomer {ethyl (2*R,3*R**)-2-acetyl-2-ethyl-3-methyl-5-phenyl-4-pentenoate: (2*R**,3*R**)-3k}.** ^{1}H NMR (400 MHz, C_6D_6) δ: 7.35–6.99 (m, 5H), 6.41 (d, J=15.6 Hz, 1H), 6.00 (dd, J=15.6, 9.8 Hz, 1H), 3.93–3.84 (m, 2H), 3.00–2.94 (m, 2H), 1.93 (s, 3H), 1.34 (s, 3H), 1.30–1.19 (m, 2H), 0.92 (t, J=7.3 Hz, 3H), 0.86 (t, J=7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 204.8, 171.8, 137.1, 133.6, 129.6, 128.6, 127.5, 126.5, 61.2, 53.1, 49.5, 27.0, 23.1, 16.3, 14.0, 12.5. R_f=0.50 (10% EtOAc in hexane).

4.2.12.3. Regioisomer {ethyl (2*S,3*R**)-2-acetyl-2-methyl-3-phenyl-4-heptenoate: (2*S**,3*R**)-4k}.** ^{1}H NMR (400 MHz, C_6D_6) δ: 7.34–7.24 (m, 5H), 5.85 (dd, J=15.1, 9.3 Hz, 1H), 5.51 (dt, J=15.1, 6.3 Hz, 1H), 4.47 (d, J=9.1 Hz, 1H), 3.76–3.68 (m, 2H), 1.81 (s, 3H), 1.76–1.61 (m, 2H), 1.45 (s, 3H), 0.83 (t, J=7.3 Hz, 3H), 0.72 (t, J=7.3 Hz, 3H).

4.2.12.4. Regioisomer {ethyl (2*R,3*R**)-2-acetyl-2-methyl-3-phenyl-4-heptenoate: (2*R**,3*R**)-4k}.** ^{1}H NMR (400 MHz, C_6D_6) δ: 7.34–7.24 (m, 5H), 6.10 (dd, J=15.1, 8.1 Hz, 1H), 5.57–5.45 (m, 1H), 4.31 (d, J=8.8 Hz, 1H), 3.76–3.68 (m, 2H), 1.88 (s, 3H), 1.43 (s, 3H), 1.76–1.61 (m, 2H), 0.80 (t, J=7.8 Hz, 3H), 0.80 (t, J=6.8 Hz, 3H).

4.2.13. Ethyl 2-acetyl-2,3,4-trimethyl-5-phenyl-4-pentenoate (3l).

4.2.13.1. Major isomer {ethyl (2*S,3*R**)-2-acetyl-2,3,4-trimethyl-5-phenyl-4-pentenoate: (2*S**,3*R**)-3l}.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33–7.17 (m, 5H), 6.38 (s, 1H), 4.23 (m, 2H), 3.26 (q, J=7.0 Hz, 1H), 2.17 (s, 3H), 1.73 (s, 3H), 1.39 (s, 3H), 1.30 (t, J=7.0 Hz, 3H), 1.23 (d, J=7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 205.1, 172.8, 138.9, 137.7, 129.0, 128.8, 128.0, 126.3, 62.3, 61.3, 47.4, 26.9, 18.1, 15.8, 15.3, 14.0. EIMS m/z: 288, EI-HRMS m/z: 288.1723 (calcd for $C_{18}H_{24}O_3$: 288.1725). Colorless oil. R_f=0.57 (10% EtOAc in hexane).

4.2.13.2. Minor isomer {ethyl (2*R,3*R**)-2-acetyl-2,3,4-trimethyl-5-phenyl-4-pentenoate: (2*R**,3*R**)-3l}.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33–7.17 (m, 5H), 6.38 (s, 1H), 4.17–4.01 (m, 2H), 3.37 (q, J=7.0 Hz, 1H), 2.19 (s, 3H), 1.80 (s, 3H), 1.45 (s, 3H), 1.20 (t, J=7.0 Hz, 3H), 1.14 (d, J=7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 204.9, 172.0, 139.3, 137.8, 128.5, 128.4, 127.9, 126.2, 62.3, 61.2, 45.8, 26.8, 18.0, 16.0, 15.5, 14.1. R_f=0.57 (10% EtOAc in hexane).

4.2.14. Ethyl 2-acetyl-3-methyl-5-phenyl-4-pentenoate (5b).[11]

4.2.14.1. Major isomer {ethyl (2*S,3*R**)-2-acetyl-3-methyl-5-phenyl-4-pentenoate: (2*S**,3*R**)-5b}.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34–7.19 (m, 5H), 6.44 (d, J=15.7 Hz, 1H), 6.10 (dd, J=15.7, 8.4 Hz, 1H), 4.12 (q, J=7.0 Hz, 2H), 3.46 (d, J=9.2 Hz, 1H), 3.20–3.09 (m, 1H), 2.27 (s, 3H), 1.18 (t, J=7.0 Hz, 3H), 1.17 (d, J=6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 202.5, 168.6, 136.9, 131.3, 130.7, 128.5, 127.4, 126.2, 66.1, 61.3, 37.5, 29.5, 18.6, 14.2. EIMS m/z: 260, EI-HRMS m/z: 260.1410 (calcd for $C_{16}H_{20}O_3$: 260.1412). Colorless oil. R_f=0.20 (20% EtOAc in hexane).

4.2.14.2. Minor isomer {ethyl (2*R,3*R**)-2-acetyl-3-methyl-5-phenyl-4-pentenoate (2*R**,3*R**)-5b}.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34–7.19 (m, 5H), 6.44 (d, J=15.7 Hz, 1H), 6.06 (dd, J=15.7, 8.4 Hz, 1H), 4.21 (q, J=7.0 Hz, 2H), 3.44 (d, J=9.2 Hz, 1H), 3.20–3.09 (m, 1H), 2.20 (s, 3H), 1.28 (t, J=7.0 Hz, 3H), 1.13 (d, J=7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 202.4, 168.6, 137.1, 131.2, 130.8, 128.5, 127.5, 126.2, 66.2, 61.4, 37.5, 29.6, 18.6, 14.2. R_f=0.20 (10% EtOAc in hexane).

4.2.15. Ethyl 2-acetyl-2-fluoro-3-methyl-5-phenyl-4-pentenoate (5c).[11]

4.2.15.1. Major isomer {ethyl (2*R,3*R**)-2-acetyl-2-fluoro-3-methyl-5-phenyl-4-pentenoate: (2*R**,3*R**)-5c}.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34–7.21 (m, 5H), 6.47 (d, J=16.0 Hz, 1H), 6.04 (dd, J=16.0, 9.3 Hz, 1H), 4.38–4.24 (m, 2H), 3.51–3.32 (m, 1H), 2.23 (d, J=5.5 Hz, 3H), 1.33 (t, J=7.1 Hz, 3H), 1.19 (d, J=6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 202.3, 201.9, 165.6, 165.3, 136.5, 133.5, 128.5, 126.3, 62.6, 42.6, 42.3, 26.8, 14.7, 14.0. EIMS m/z: 278, EI-HRMS m/z: 278.1316 (calcd for $C_{16}H_{19}FO_3$: 278.1318). Colorless oil. R_f=0.41 (10% EtOAc in hexane).

4.2.15.2. Minor isomer {ethyl (2*S,3*R**)-2-acetyl-2-fluoro-3-methyl-5-phenyl-4-pentenoate (2*S**,3*R**)-5c}.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34–7.21 (m, 5H), 6.50 (d, J=15.8 Hz, 1H), 6.07 (dd, J=15.8, 9.3 Hz, 1H), 4.23–4.12 (m, 2H), 3.51–3.32 (m, 1H), 2.31 (d, J=5.1 Hz, 3H), 1.21 (t, J=7.0 Hz, 3H), 1.12 (d, J=7.0 Hz, 3H). ^{13}C NMR

(75 MHz, $CDCl_3$) δ: 202.3, 201.8, 165.6, 165.3, 136.5, 132.9, 128.3, 126.9, 62.5, 42.5, 42.3, 26.7, 14.4, 14.1. R_f=0.41 (10% EtOAc in hexane).

4.2.16. Ethyl 2-acetyl-2-benzyl-3-methyl-5-phenyl-4-pentenoate (5d).[11]

4.2.16.1. Major isomer {ethyl (2*S,3*R**)-2-acetyl-2-benzyl-3-methyl-5-phenyl-4-pentenoate: (2*S**,3*R**)-5d}.** ^1H NMR (400 MHz, $CDCl_3$) δ: 7.37–7.12 (m, 10H), 6.45 (d, J=15.7 Hz, 1H), 6.17 (dd, J=15.7, 8.9 Hz, 1H), 4.24–4.18 (m, 2H), 3.29–3.10 (m, 1H), 3.28 (d, J=13.8 Hz, 1H), 3.12 (d, J=13.8 Hz, 1H), 1.95 (s, 3H), 1.26 (t, J=7.0 Hz, 3H), 1.11 (d, J=7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 206.1, 171.1, 137.1, 136.8, 131.7, 130.7, 130.1, 128.1, 127.4, 126.7, 126.2, 68.6, 60.9, 42.1, 40.7, 31.2, 16.7, 14.1. EIMS *m*/*z*: 350, EI-HRMS *m*/*z*: 350.1880 (calcd for $C_{23}H_{26}O_3$: 350.1882). Colorless oil. R_f=0.55 (10% EtOAc in hexane).

4.2.16.2. Minor isomer {ethyl (2*R,3*R**)-2-acetyl-2-benzyl-3-methyl-5-phenyl-4-pentenoate: (2*R**,3*R**)-5d}.** ^1H NMR (400 MHz, $CDCl_3$) δ: 7.34–7.21 (m, 5H), 6.39 (d, J=15.4 Hz, 1H), 6.17 (dd, J=15.7, 8.9 Hz, 1H), 4.24–4.18 (m, 2H), 3.29–3.10 (m, 1H), 3.28 (d, J=13.8 Hz, 1H), 3.12 (d, J=13.8 Hz, 1H), 1.95 (s, 3H), 1.26 (t, J=7.0 Hz, 3H), 1.11 (d, J=7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 197.4, 173.0, 137.7, 136.1, 131.2, 130.7, 130.1, 128.5 (2C), 128.0, 126.9, 126.3, 61.1, 60.9, 41.3, 17.4, 15.7, 13.9. R_f=0.55 (10% EtOAc in hexane).

4.2.17. Ethyl 2-benzyl-2,3-dimethyl-5-phenyl-4-pentenoate (5e).[11]

4.2.17.1. Major isomer {ethyl (2*S,3*R**)-2-benzyl-2,3-dimethyl-5-phenyl-4-pentenoate: (2*S**,3*R**)-5e}.** ^1H NMR (400 MHz, $CDCl_3$) δ: 7.84–7.18 (m, 10H), 6.46 (d, J=15.7 Hz, 1H), 6.27 (dd, J=15.7, 8.8 Hz, 1H), 4.18–4.00 (m, 2H), 3.52–3.45 (m, 1H), 1.52 (s, 3H), 1.12 (d, J=7.0 Hz, 3H), 1.05 (t, J=7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 197.4, 173.0, 137.4, 136.5, 131.0, 130.9, 130.5, 128.4 (2C), 128.3, 127.2, 126.2, 61.3, 61.2, 41.4, 17.4, 15.8, 13.8. EIMS *m*/*z*: 336, EI-HRMS *m*/*z*: 336.1720 (calcd for $C_{22}H_{24}O_3$: 336.1725). Colorless oil. R_f=0.60 (10% EtOAc in hexane).

4.2.17.2. Minor isomer {ethyl (2*R,3*R**)-2-benzyl-2,3-dimethyl-5-phenyl-4-pentenoate: (2*R**,3*R**)-5e}.** ^1H NMR (400 MHz, $CDCl_3$) δ: 7.84–7.18 (m, 10H), 6.46 (J=15.7 Hz, 1H), 6.10 (dd, J=15.7 Hz, 1H), 4.18–4.00 (m, 2H), 3.43–3.38 (m, 1H), 1.52 (s, 3H), 1.22 (d, J=6.8 Hz, 3H), 1.09 (t, J=7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 197.5, 172.9, 137.5, 136.3, 131.1, 130.8, 130.3, 128.3 (2C), 128.1, 127.1, 126.3, 61.0, 60.9, 41.4, 17.5, 15.9, 13.6. R_f=0.60 (10% EtOAc in hexane).

4.2.18. Ethyl 2-oxo-1-(1-methyl-3-phenyl-2-propenyl)-cyclopentanecarboxylate (5f).[11]

4.2.18.1. Major isomer {ethyl (2*S,3*R**)-2-oxo-1-(1-methyl-3-phenyl-2-propenyl)cyclopentanecarboxylate: (2*S**,3*R**)-5f}.** ^1H NMR (400 MHz, $CDCl_3$) δ: 7.33–7.19 (m, 5H), 6.41 (d, J=16.1 Hz, 1H), 6.06 (dd, J=16.1, 7.8 Hz, 1H), 4.23–4.17 (m, 2H), 3.28 (dq, J=7.8, 7.0 Hz, 1H), 2.58–1.87 (m, 6H), 1.27 (t, J=7.0 Hz, 3H), 1.11 (d, J=7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 214.0, 169.8, 137.0, 131.9 129.9, 128.5, 127.4, 126.2, 65.2, 61.5, 40.7, 38.8, 28.3, 19.8, 15.7, 14.1. EIMS *m*/*z*: 286, EI-HRMS *m*/*z*: 286.1576 (calcd for $C_{18}H_{22}O_3$: 286.1569). Colorless oil. R_f=0.51 (10% EtOAc in hexane).

4.2.18.2. Minor isomer {ethyl (2*R,3*R**)-2-oxo-1-(1-methyl-3-phenyl-2-propenyl)cyclopentanecarboxylate: (2*R**,3*R**)-5f}.** ^1H NMR (400 MHz, $CDCl_3$) δ: 7.33–7.19 (m, 5H), 6.43 (d, J=15.6 Hz, 1H), 6.02 (dd, J=15.6, 7.8 Hz, 1H), 4.23–4.17 (m, 2H), 3.28 (dq, J=7.8, 7.0 Hz, 1H), 2.58–1.87 (m, 6H), 1.24 (t, J=7.0 Hz, 3H), 1.08 (d, J=7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 213.9, 170.0, 137.1, 131.2, 130.5, 129.4, 127.5, 126.1, 65.1, 61.6, 41.1, 39.1, 28.5, 19.6, 15.6, 14.1. R_f=0.51 (10% EtOAc in hexane).

4.2.19. Ethyl 2-oxo-1-(1-methyl-3-phenyl-2-propenyl)-cyclohexanecarboxylate (5g).[11]

4.2.19.1. Major isomer {ethyl (2*S,3*R**)-2-oxo-1-(1-methyl-3-phenyl-2-propenyl)cyclohexanecarboxylate: (2*S**,3*R**)-5g}.** ^1H NMR (400 MHz, $CDCl_3$) δ: 7.36–7.17 (m, 5H), 6.35 (d, J=15.7 Hz, 1H), 6.25 (dd, J=15.7, 8.4 Hz, 1H), 4.24–4.20 (m, 2H), 2.98 (dq, J=8.4, 7.0 Hz, 1H), 2.55–1.48 (m, 8H), 1.27 (t, J=7.0 Hz, 3H), 1.10 (d, J=7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 207.3, 171.3, 137.3, 131.6 130.7, 128.4, 127.1, 126.1, 64.1, 61.1, 41.7, 41.1, 34.6, 27.3, 22.7, 16.4, 14.2. EIMS *m*/*z*: 300, EI-HRMS *m*/*z*: 300.1719 (calcd for $C_{19}H_{24}O_3$: 300.1725). Colorless oil. R_f=0.55 (10% EtOAc in hexane).

4.2.19.2. Minor isomer {ethyl (2*R,3*R**)-2-oxo-1-(1-methyl-3-phenyl-2-propenyl)cyclohexanecarboxylate: (2*R**,3*R**)-5g}.** ^1H NMR (400 MHz, $CDCl_3$) δ: 7.36–7.17 (m, 5H), 6.35 (d, J=15.7 Hz, 1H), 6.20 (dd, J=15.7, 8.4 Hz, 1H), 4.24–4.20 (m, 2H), 2.98 (dq, J=8.4, 7.0 Hz, 1H), 2.55–1.48 (m, 8H), 1.21 (t, J=7.0 Hz, 3H), 1.14 (d, J=7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 207.2, 170.0, 137.2, 131.5, 130.8, 128.5, 127.0, 126.3, 64.4, 61.2, 41.1, 32.4, 26.9, 22.5, 16.8, 14.4. R_f=0.55 (10% EtOAc in hexane).

4.2.20. Methyl 2-oxo-1-(1-methyl-3-phenyl-2-propenyl)-cycloheptanecarboxylate (5h).[11]

4.2.20.1. Major isomer {methyl (2*S,3*R**)-2-oxo-1-(1-methyl-3-phenyl-2-propenyl)cycloheptanecarboxylate: (2*S**,3*R**)-5h}.** ^1H NMR (400 MHz, $CDCl_3$) δ: 7.36–7.19 (m, 5H), 6.39 (d, J=16.1 Hz, 1H), 6.22 (dd, J=16.1, 8.8 Hz, 1H), 3.74 (s, 3H), 3.05 (dq, J=8.8, 7.0 Hz, 1H), 2.21–1.46 (m, 10H), 1.09 (d, J=7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 209.0, 172.4, 137.4, 131.4 131.0, 128.5, 127.2, 126.2, 66.3, 52.0, 42.8 (2C), 31.7, 30.0, 25.7, 25.5, 16.8. EIMS *m*/*z*: 300, EI-HRMS *m*/*z*: 300.1730 (calcd for $C_{19}H_{24}O_3$: 300.1725). Colorless oil. R_f=0.58 (10% EtOAc in hexane).

4.2.20.2. Minor isomer {methyl (2*R,3*R**)-2-oxo-1-(1-methyl-3-phenyl-2-propenyl)cycloheptanecarboxylate: (2*R**,3*R**)-5h}.** ^1H NMR (400 MHz, $CDCl_3$) δ: 7.36–7.19 (m, 5H), 6.39 (d, J=16.1 Hz, 1H), 6.22 (dd, J=16.1, 8.8 Hz, 1H), 3.71 (s, 3H), 3.05 (dq, J=8.8, 7.0 Hz, 1H), 2.21–1.46 (m, 10H), 1.13 (d, J=7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 209.0, 172.5, 137.5, 131.4, 131.1, 128.6, 127.0, 126.3, 66.3, 52.2, 42.9, 43.1, 31.4, 30.1, 25.8, 25.5, 16.8. R_f=0.58 (10% EtOAc in hexane).

4.2.21. Ethyl 2-cyano-3-methyl-5-phenyl-4-pentenoate (8a).[11]

4.2.21.1. Major isomer {ethyl (2*S,3*R**)-2-cyano-3-methyl-5-phenyl-4-pentenoate: (2*S**,3*R**)-8a}.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41–7.22 (m, 5H), 6.52 (d, J=15.6 Hz, 1H), 6.13 (dd, J=15.6, 8.0 Hz, 1H), 4.23 (q, J=7.0 Hz, 2H), 3.56 (d, J=5.8 Hz, 1H), 3.13 (m, 1H), 1.32 (d, J=7.0 Hz, 3H), 1.25 (t, J=7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 165.3, 136.3, 132.8, 129.2 128.6, 127.9, 126.4, 115.3, 62.7, 44.4, 38.6, 17.6, 14.1. EIMS *m*/*z*: 243, EI-HRMS *m*/*z*: 243.1261 (calcd for $C_{15}H_{17}NO_2$: 243.1259). Colorless oil. R_f=0.83 (20% EtOAc in hexane).

4.2.21.2. Minor isomer {ethyl (2*R,3*R**)-2-cyano-3-methyl-5-phenyl-4-pentenoate: (2*R**,3*R**)-8a}.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41–7.22 (m, 5H), 6.54 (d, J=15.6 Hz, 1H), 6.15 (dd, J=15.6, 8.0 Hz, 1H), 4.25 (q, J=7.0 Hz, 2H), 3.57, (d, J=5.1 Hz, 1H), 3.13 (m, 1H), 1.35 (d, J=7.0 Hz, 3H), 1.30 (t, J=7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 165.4, 136.3, 132.1, 129.2, 128.6, 127.9, 126.5, 115.3, 62.8, 44.8, 38.5, 18.9, 14.1. R_f=0.83 (20% EtOAc in hexane).

4.2.22. Ethyl 2-cyano-2,3-dimethyl-5-phenyl-4-pentenoate (8b).[11]

4.2.22.1. Major isomer {ethyl (2*S,3*R**)-2-cyano-2,3-dimethyl-5-phenyl-4-pentenoate: (2*S**,3*R**)-8b}.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40–7.22 (m, 5H), 6.46 (d, J=15.6 Hz, 1H), 6.14 (dd, J=15.6, 9.3 Hz, 1H), 4.24–4.13 (m, 2H), 2.87–2.76(m, 1H), 1.61 (s, 3H), 1.30 (d, J=6.8 Hz, 3H), 1.21 (t, J=6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.9, 136.3, 132.7, 128.5 128.4, 127.8, 126.4, 119.0, 62.5, 49.0, 44.6, 21.1, 15.7, 14.0. EIMS *m*/*z*: 257, EI-HRMS *m*/*z*: 257.1420 (calcd for $C_{16}H_{19}NO_2$: 257.1416). Colorless oil. R_f=0.20 (20% EtOAc in hexane).

4.2.22.2. Minor isomer {ethyl (2*R,3*R**)-2-cyano-2,3-dimethyl-5-phenyl-4-pentenoate: (2*R**,3*R**)-8b}.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40–7.22 (m, 5H), 6.53 (d, J=15.6 Hz, 1H), 6.09 (dd, J=15.6, 9.3 Hz, 1H), 4.34–4.24 (m, 2H), 2.87–2.76. (m, 1H), 1.56 (s, 3H), 1.35 (t, J=7.3 Hz, 3H), 1.26 (d, J=7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.8, 136.2, 132.9, 128.6, 127.9, 127.6, 126.4, 118.8, 62.6, 48.7, 44.5, 22.1, 17.4, 14.1. R_f=0.20 (20% EtOAc in hexane).

4.2.23. Ethyl 3-methyl-2,5-diphenyl-4-pentenoate (8c).[11]

4.2.23.1. Major isomer {ethyl (2*S,3*R**)-3-methyl-2,5-diphenyl-4-pentenoate: (2*S**,3*R**)-8c}.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27–7.00 (m, 10H), 6.50 (d, J=15.6 Hz, 1H), 6.17 (dd, J=15.6, 8.3 Hz, 1H), 4.09–3.97 (m, 2H), 3.40 (d, J=6.8 Hz, 1H), 3.13–3.00 (m, 1H), 1.12 (t, J=7.3 Hz, 3H), 0.88 (d, J=6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 173.2, 137.4, 133.0, 130.2, 128.6, 128.5, 128.4, 127.4, 127.2, 126.2, 126.0, 65.9, 60.6, 58.6, 41.1, 18.3, 15.3, 14.2. EIMS *m*/*z*: 294, EI-HRMS *m*/*z*: 294.1612 (calcd for $C_{20}H_{22}O_2$: 294.1620). Colorless oil. R_f=0.61 (20% EtOAc in hexane).

4.2.23.2. Minor isomer {ethyl (2*R,3*R**)-3-methyl-2,5-diphenyl-4-pentenoate: (2*R**,3*R**)-8c}.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27–7.00 (m, 10H), 6.15 (d, J=15.6 Hz, 1H), 5.86 (dd, J=15.6, 8.3 Hz, 1H), 4.21–4.14 (m, 2H), 4.06 (d, J=6.8 Hz, 1H), 3.13–3.00 (m, 1H), 1.24 (t, J=6.8 Hz, 3H), 1.23 (d, J=6.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 173.2, 137.4, 133.0, 130.2, 128.6, 128.5, 128.4, 127.4, 127.2, 126.2, 126.0, 65.9, 60.6, 58.6, 41.1, 18.3, 15.3, 14.2. R_f=0.61 (20% EtOAc in hexane).

4.2.24. Ethyl 3-methyl-5-phenyl-2-(2-pyridyl)-4-pentenoate (8e).[11]

4.2.24.1. Major isomer {ethyl (2*S,3*R**)-3-methyl-5-phenyl-2-(2-pyridyl)-4-pentenoate: (2*S**,3*R**)-8e}.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.61–8.52 (m, 1H), 7.70–7.08 (m, 8H), 6.49 (d, J=15.6 Hz, 1H), 6.21 (dd, J=15.6, 6.3 Hz, 1H), 4.09–4.00 (m, 2H), 3.75 (d, J=10.7 Hz, 1H), 3.31–3.17 (m, 1H), 1.25 (d, J=6.8 Hz, 3H), 1.13 (t, J=7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 172.2, 157.2, 149.2, 137.3, 136.4, 132.7, 130.3, 128.3, 127.0, 126.0, 123.1, 122.2, 60.9, 60.6, 40.6, 18.3, 14.2. EIMS *m*/*z*: 295, EI-HRMS *m*/*z*: 295.1579 (calcd for $C_{19}H_{21}NO_2$: 295.1572). Colorless oil. R_f=0.13 (20% EtOAc in hexane).

4.2.24.2. Minor isomer {ethyl (2*R,3*R**)-3-methyl-5-phenyl-2-(2-pyridyl)-4-pentenoate: (2*R**,3*R**)-8e}.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.61–8.52 (m, 1H), 7.70–7.08 (m, 8H), 6.20 (d, J=15.6 Hz, 1H), 5.93 (dd, J=15.6, 7.3 Hz, 1H), 4.26–4.10 (m, 2H), 3.78 (d, J=9.7 Hz, 1H), 3.31–3.17 (m, 1H), 1.24 (t, J=6.8 Hz, 3H), 0.94 (d, J=6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 172.3, 157.4, 149.4, 137.3, 136.6, 132.4, 130.2, 128.4, 127.2, 126.2, 123.1, 122.3, 60.7, 60.4, 40.2, 19.2, 14.2. R_f=0.13 (20% EtOAc in hexane).

4.2.25. Ethyl 2,3-dimethyl-5-phenyl-2-(2-pyridyl)-4-pentenoate (8f).[11]

4.2.25.1. Major isomer {ethyl (2*S,3*R**)-2,3-dimethyl-5-phenyl-2-(2-pyridyl)-4-pentenoate: (2*S**,3*R**)-8f}.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.62–8.60 (m, 1H), 7.67–7.58 (m, 1H), 7.45–7.08 (m, 7H), 6.45 (d, J=15.7 Hz, 1H), 6.27 (dd, J=15.7, 8.1 Hz, 1H), 4.12 (m, 2H), 3.45 (m, 1H), 1.62 (s, 3H), 1.16 (t, J=7.3 Hz, 3H), 0.92 (d, J=7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 174.6, 161.3, 148.7, 137.6, 136.1, 132.2, 130.8, 128.4, 127.0, 126.1, 121.6 (2C), 60.8, 43.1, 17.5, 16.5, 15.3, 14.1. EIMS *m*/*z*: 309, EI-HRMS *m*/*z*: 309.1724 (calcd for $C_{20}H_{23}NO_2$: 309.1729). Colorless oil. R_f=0.20 (20% EtOAc in hexane).

4.2.25.2. Minor isomer {ethyl (2*R,3*R**)-2,3-dimethyl-5-phenyl-2-(2-pyridyl)-4-pentenoate: (2*R**,3*R**)-8f}.** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.58–8.57 (m, 1H), 7.67–7.58 (m, 1H), 7.45–7.08 (m, 7H), 6.23 (d, J=15.7 Hz, 1H), 5.96 (dd, J=15.7, 8.4 Hz, 1H), 4.19 (q, J=7.0 Hz, 2H), 3.42 (m, 1H), 1.62 (s, 3H), 1.21 (t, J=7.0 Hz, 3H), 1.19 (d, J=6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 174.5, 161.8, 148.6, 137.6, 136.0, 131.5, 130.9, 128.3, 126.9, 126.0, 121.7 (2C), 60.8, 43.7, 18.2, 16.5, 15.3, 14.1. R_f=0.20 (20% EtOAc in hexane).

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