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PAPER

Efficient palladium-catalyzed asymmetric allylic alkylation of ketones and aldehydes†

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Palladium-catalyzed asymmetric allylic alkylation of ketones, *via* enamines generated *in situ* as nucleophiles, were carried out smoothly with chiral metallocene-based P,N-ligands. Under the same conditions, however, reactions of aldehydes could hardly be observed. Subsequently, this obstacle was resolved by using chiral metallocene-based P,P-ligands. Both ketones and aldehydes afforded excellent enantioselectivities with up to 98% ee and 94% ee, respectively.

Introduction

Palladium-catalyzed asymmetric allylic alkylation has become one of the extremely attractive and powerful tools in asymmetric synthesis.[1] However, the use of simple ketones acting as hard nucleophiles has remained a challenge in the palladium-catalyzed asymmetric allylic alkylation.[2] Generally, simple ketones cannot be used directly in palladium-catalyzed asymmetric allylic alkylation because of their weak nucleophilicity. In order to improve their reaction activities, simple ketones were always converted to their reactive intermediates, ketone enolates,[2] sometimes by treating with powerful bases such as LDA[2b] and $ClMgN(i\text{-}Pr)_2$.[2d] Considering that enamines have been widely used as nucleophiles in organic synthesis,[3] we have recently reported the first palladium-catalyzed asymmetric allylic alkylation with enamines as nucleophiles,[4] avoiding using unstable ketone enolates. This procedure contains several advantages, such as inexpensive reagents, simple operation and mild reaction conditions. However, some limitations also exist in enamines: synthesis of the enamines is time-consuming and the stability of enamines is not good enough in the air atmosphere. These obstacles prompted us to pursue a new method to make use of enamines in the reaction system. Herein, we want to report the first palladium-catalyzed asymmetric allylic alkylation of ketones and aldehydes *via* enamines generated *in situ* as nucleophiles with excellent enantioselectivities and yields.

Results and discussion

It was reported that C_2-symmetric chiral metallocene-based P,N-ligands **1**, **2**[3a,5] and P,P-ligands **3**, **4**[6] had been applied in palladium-catalyzed asymmetric allylic substitutions with high reaction activities and excellent enantioselectivities (Fig. 1). These ligands were also selected here for the palladium-catalyzed asymmetric allylic alkylation of ketones and aldehydes.

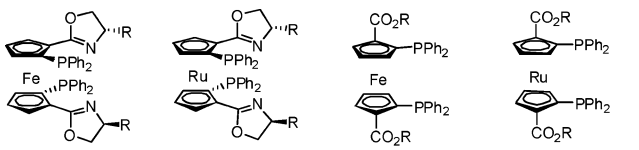

Fig. 1 Chiral ligands.

At first, the palladium-catalyzed asymmetric allylic alkylation of 1,3-diphenyl-2-propenyl acetate with cyclohexanone in the presence of pyrrolidine was examined. Details are summarized in Table 1.

Initially, the influence of solvents on the alkylation was investigated using **1a** as ligand. As shown in Table 1, the reaction hardly occurred using THF, CH_2Cl_2, toluene, Et_2O and 1,4-dioxane as solvents (Table 1, entries 1–5). With the increase of polarity of the solvents, the reactions could be carried out successfully. When DMF and DMSO were used as solvents, excellent enantioselectivities were obtained and a much higher yield was obtained in DMSO (entries 6–7). Encouraged by the experimental results, we envisioned that protonic solvents could also give the same result. As expected, the reactions with CH_3OH, EtOH, *n*-PrOH, *i*-PrOH as solvents also proceeded smoothly in excellent enantioselectivities and high yields (entries 8–11). It was shown that the solvent had a pivotal effect on this reaction and DMSO was found to be more efficient than the others based on the asymmetric catalytic behavior.

This reaction was also carried out with a catalytic amount of pyrrolidine from 10~50% molar ratio. Unfortunately, the reaction process was so slow that not more than 50% conversion was obtained even after a week. This result was not improved by adding tertiary amines such as TEA and DIPEA for avoiding

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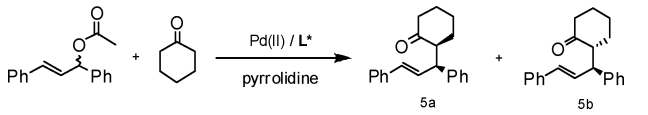
Table 1 Allylic alkylation of cyclohexanone with 1,3-diphenyl-2-propenyl acetate[a]



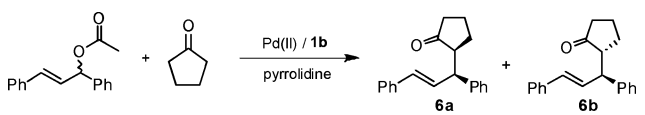
Entry	Solvent	Ligand	Time/h	Yield/%[b]	*anti*/*syn*[c,d]	Ee/%[e]
1	THF	**1a**	48	trace	—	—
2	CH_2Cl_2	**1a**	48	trace	—	—
3	Toluene	**1a**	48	trace	—	—
4	Et_2O	**1a**	48	trace	—	—
5	1,4-dioxane	**1a**	48	trace	—	—
6	DMF	**1a**	20	20	80/20	92/92
7	DMSO	**1a**	20	95	83/17	94/94
8	CH_3OH	**1a**	15	70	80/20	89/92
9	EtOH	**1a**	15	90	79/21	90/92
10	*n*-PrOH	**1a**	18	90	70/30	91/91
11	*i*-PrOH	**1a**	20	90	78/22	90/91
12	DMSO	**2a**	16	95	79/21	90/90
13	DMSO	**3a**[f]	14	82	77/23	77/78
14	DMSO	**4a**[f]	14	85	77/23	81/81
15	DMSO	**1b**	20	95	80/20	98/97

[a] Molecular ratio: $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$/ligand/substrate/pyrrolidine/ketone = 5.0/6.0/200/200/600; reactions were conducted under N_2 atmosphere; the catalysts were prepared by treating $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ with the ligand in suitable solvents at room temperature for 1 h before use. [b] Isolated yield. [c] Determined by ^1H NMR. [d] The absolute configuration of *syn*/*anti*-products was determined according to ref. 2d. [e] Determined by HPLC using chiral AD-H column. [f] 6 mol% ligand was used.

the consumption of pyrrolidine. So, a stoichiometric amount of pyrrolidine was used in the following reaction process.

Then, ligands **2a**, **3a** and **4a** were used with DMSO as solvent in the presence of a stoichiometric amount of pyrrolidine. All ligands gave good to excellent enantioselectivities and yields, albeit a little inferior to **1a** (Table 1, entries 12–14). A bulky group on the oxazolinyl ring had a dramatic effect here, and **1b** having a *tert*-butyl group afforded the best result with up to 98% ee and 95% yield in this asymmetric catalysis (Table 1, entry 15). In addition, a higher diastereomeric ratio (70/30–80/20) was obtained with enamines generated *in situ* as nucleophiles, compared with the corresponding results using enamines directly.[4b]

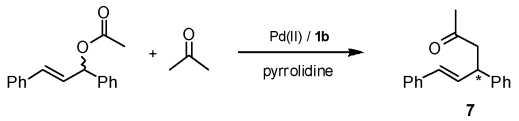
In addition, cyclopentanone and acetone were also used for this reaction under the above reaction conditions using **1b** as ligand. As shown in Scheme 1 and Scheme 2, excellent enantioselectivities were also obtained for both ketones although only 20% yield was obtained for acetone.



[a] Molecular ratio: $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$/ligand/substrate/pyrrolidine/ketone =5.0/6.0/200/200/600, in DMSO in room temperature, completed within 20 h, yield/%: 90, dr: 64/36, ee%: 97/96. The absolute configuration of *syn*/*anti*-products was determined according to **5**.

Scheme 1 Allylic alkylation of cyclopentanone with 1,3-diphenyl-2-propenyl acetate using **1b** as ligand[a].

It can be seen from Table 1 that the palladium-catalyzed asymmetric allylic alkylation of ketones, *via* enamines generated *in situ* as nucleophiles, gave a higher diastereomeric ratio, compared



[a] Molecular ratio: $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$/ligand/substrate/pyrrolidine/ketone =5.0/6.0/200/200/600, in DMSO in room temperature, completed within 20 h, yield /%: 20, ee%: 90.

Scheme 2 Allylic alkylation of acetone with 1,3-diphenyl-2-propenyl acetate using **1b** as ligand[a].

with the reactions using enamines directly as nucleophiles which afforded a diastereomer ratio of about 60 : 40.[4b] This result could be explained with the possible reaction mechanism shown in Fig. 2. If enamine was directly used as nucleophile, the isomerization of **8** to **9** will occur in sufficient time until the reaction was quenched by water. However, when using enamines generated *in situ* as nucleophiles, two competitive reactions coexisted: the isomerization of **8** to **9** and hydrolysis of **8** to give the product **5** by water generated during the formation of enamine. The hydrolysis might be faster than the isomerization, resulting in a higher diastereomeric ratio than for the case with enamines directly as nucleophiles. The existence of enamine generated *in situ* in the above reaction was testified by NMR.[7]

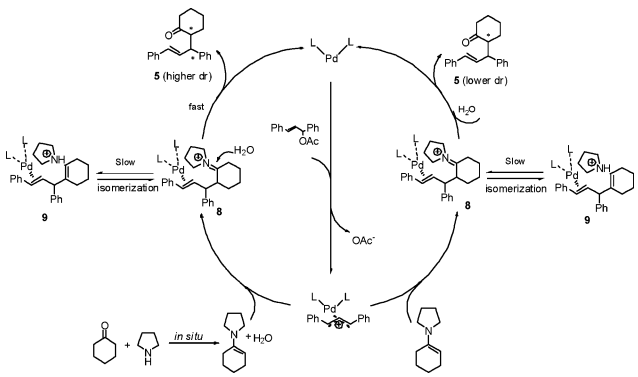


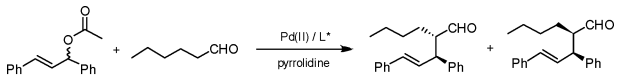
Fig. 2 A plausible reaction mechanism.

Some comparison experiments were performed to further verify that the higher diastereomeric ratio was caused by the presence of water. On the one hand, if 4 Å molecular sieves were added to the reaction mixture, and as a result, the diastereomeric ratio decreased from 80/20 to 63/37. This means that a lower amount of water results in a lower diastereomeric ratio. On the other hand, if 1 equiv. H_2O was added to the reaction directly with enamine rather than enamine generated *in situ* as nucleophile, the diastereomeric ratio was raised from 55/45 to 75/25. These results obviously shown that the water generated *in situ* was related to the higher diastereomeric ratio.

In addition, to explore the scope of the substrates, we have made several attempts on palladium-catalyzed asymmetric allylic alkylation of *n*-hexaldehyde. No reaction occurred for several aldehydes using P,N-ligands **1** and **2** (Table 2, entries 1–4).

Then, attentions were focused on the exploration of more efficient chiral ligands again. To our delight, high catalytic activities and good enantioselectivities were eventually obtained by using P,P-ligands **3** and **4** (Table 2, entries 5–8). The ester group of **3** and **4** with larger steric hindrance gave better enantioselectivity and **4b**

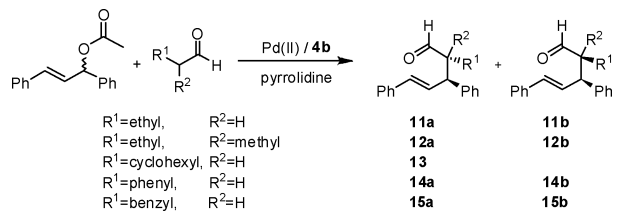
Table 2 Allylic alkylation of *n*-hexaldehyde with 1,3-diphenyl-2-propenyl acetate using **1–4** and (*R*)-**Binap** as ligands[a]



Entry	Ligand	Time/h	Yield/%[b]	*anti*/*syn*[c]	Ee/%[d]
1	**1a**	48	ND	—	—
2	**1b**	48	ND	—	—
3	**2a**	48	ND	—	—
4	**2b**	48	ND	—	—
5	**3a**	16	70	53/47	91/91
6	**3b**	16	72	53/47	94/94
7	**4a**	11	90	54/46	90/90
8	**4b**	11	90	56/44	91/91
9	(*R*)-**Binap**	20	74	52/48	86/86

[a] Molecular ratio: $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$/ligand/substrate/pyrrolidine/aldehyde = 5.0/12.0/200/200/600; reactions were conducted under N_2 atmosphere; the catalysts were prepared by treating $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ with ligand in DMSO at room temperature for 1 h before use. [b] Isolated yield. [c] Determined by ^{1}H NMR. [d] Determined by the HPLC using chiral AD-H column.

Table 3 Allylic alkylation of several aldehydes with 1,3-diphenyl-2-propenyl acetate using **4b** as ligand[a]



Entry	R^1	R^2	Time/h	Yield/%[b]	*anti*/*syn*[c]	Ee/%[d]
1	Et	H	11	86	55/45	92/93
2	Et	Me	11	88	54/46	89/89
3	Cy	H	11	62	—	79
4	Ph	H	15	60	56/44	87/87
5	Bn	H	15	71	53/47	90/90

[a] Molecular ratio: $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$/ligand/substrate/pyrrolidine/aldehyde = 5.0/12.0/200/200/600; reactions were conducted under N_2 atmosphere; the catalysts were prepared by treating $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ with ligands in DMSO at room temperature for 1 h before use. [b] Isolated yield. [c] Determined by ^{1}H NMR. [d] Determined by the HPLC using chiral AD-H, OD-H and OJ-H column.

afforded a much higher yield but a little lower enantioselectivity than **3b** (entries 5–8). Furthermore, (*R*)-Binap was also used in the above reaction but lower enantioselectivities and catalytic activities were obtained compared with **3** and **4** (entry 9).

Thus, ligand **4b** was applied in the palladium-catalyzed asymmetric allylic alkylation reactions for several other aldehydes (Table 3).

As shown in Table 3, the reactions with the linear aldehydes proceeded smoothly in high yields and excellent enantioselectivities (Table 3, entries 1–2). When the linear aldehyde was changed to a cyclic aldehyde, good yield and enantioselectivity was also obtained (entry 3). Then, to further investigate the influences of aldehydes on the reaction, we changed aliphatic aldehyde to aldehyde with aromatic groups in the side chain. As expected, the reactions afforded good yields and excellent enantioselectivities too (entries 4–5). These results showed that both aliphatic and aromatic aldehydes could serve as efficient nucleophiles with good to excellent yields and enantioselectivities here. It was noticed that the diastereomer ratio is not satisfactory mainly due to the faster rate of isomerization of the intermediate than hydrolysis.

Finally, palladium-catalyzed asymmetric allylic alkylation of other allylic acetates, such as cyclohex-2-enyl acetate and (*E*)-4-phenylbut-3-en-2-yl acetate, with cyclohexanone and *n*-hexaldehyde were also examined. Using **1b** and **4b** as chiral ligands respectively, high yields (>80%) were obtained for both cyclohexanone and *n*-hexaldehyde as nucleophiles. However, very low enantioselectivities (<20% ee) were obtained.

Conclusions

In summary, we have developed an efficient palladium-catalyzed asymmetric allylic alkylation of ketones and aldehydes, *via* enamines generated *in situ* as nucleophiles. Firstly, palladium-catalyzed asymmetric allylic alkylations of ketones were carried out smoothly with excellent enantioselectivities by using chiral ferrocene P,N-ligand. Under the same conditions, however, reactions of aldehydes could hardly occur. Subsequently, this obstacle was resolved by using the metallocene-based P,P-ligands with only planar chirality. The reaction could be expanded to a series of both aromatic and aliphatic aldehydes with excellent enantioselectivities. It was obvious that both ketones and aldehydes could achieve excellent results in the palladium-catalyzed asymmetric allylic alkylation.

Experimental

General

All reactions were performed under a nitrogen atmosphere, and the workup was carried out in air. The reaction solvents were distilled prior to use (tetrahydrofuran was distilled from sodium-benzophenone ketyl; dichloromethane, *N*,*N*-dimethylformamide and toluene were distilled from CaH_2). The commercially available reagents were used without further purification. The substrate of asymmetric allylic alkylation was prepared according to literature procedure. TLC was run on 2 cm × 5 cm silica plate. Column chromatography was run on silica gel (100–200 mesh). ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Varian MERCURY plus-400 spectrometer. The ee values were determined by HPLC using Daicel Chiralcel AD-H, OD-H, OJ-H column.

General procedure for palladium-catalyzed asymmetric allylic alkylation

A mixture of ligand (for **1** and **2** 7.5 μmol; for **3** and **4** 15 μmol) and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (2.3 mg, 6.3 μmol) in dry DMSO (1 mL) was stirred at room temperature under N_2 atmosphere for 1 h and 1,3-diphenyl-2-propenyl acetate (126 mg, 0.500 mmol) was added for another 10 min followed by the addition of pyrrolidine (0.50 mmol) and ketone or aldehyde (1.50 mmol). The reaction was monitored by TLC for the disappearance of 1,3-diphenyl-2-propenyl acetate. The reaction mixture was quenched by iced saturated NH_4Cl solution (10 mL) for 2 h and the aqueous layer was extracted with ethyl ether (5 mL × 3). The combined organic extract was

washed with water, brine, dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The ratio of *anti*- and *syn*-configuration[7] was determined by ^{1}H NMR of the mixture and the residue was purified on silica gel column chromatography with petrol ether-ethyl acetate (10 : 1) to afford pure product of *anti*-configuration and *syn*-configuration, respectively. For the determination of ee value by HPLC, a mixture of the products of *anti*- and *syn*-configuration was used.

(*S*)-2-((*S*,*E*)-1,3-Diphenylallyl)cyclohexanone (5a)[4b]

Colorless oil. ^{1}H NMR ($CDCl_3$, 400 Hz): δ 1.33–1.41 (m, 1H), 1.56–1.63 (m, 1H), 1.70–1.81 (m, 3H), 1.90–1.95 (m, 1H), 2.31–2.46 (m, 2H), 2.83–2.89 (m, 1H), 3.87 (t, J = 8.4 Hz, 1H), 6.32 (d, J = 16 Hz, 1H), 6.44 (dd, J = 8.0, 16 Hz, 1H), 7.12–7.32 (m, 10H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 24.2, 28.8, 32.4, 42.5, 48.6, 56.1, 126.5, 126.8, 127.4, 128.6, 128.7, 128.9, 130.7, 132.2, 137.6, 140.1, 212.7.

(*R*)-2-((*S*,*E*)-1,3-Diphenylallyl)cyclohexanone (5b)[4b]

Colorless oil. ^{1}H NMR ($CDCl_3$, 400 Hz): δ 1.57–1.77 (m, 3H), 1.86–2.10 (m, 2H), 2.15–2.37 (m, 3H), 2.85–2.91 (m, 1H), 3.97 (t, J = 8.4 Hz, 1H), 6.25 (dd, J = 9.6, 15.6 Hz, 1H), 6.45 (d, J = 15.6 Hz, 1H), 7.14–7.33 (m, 10H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 24.8, 28.6, 32.1, 42.6, 48.7, 55.9, 126.5, 126.6, 127.5, 128.1, 128.7, 128.8, 131.3, 131.6, 137.5, 143.5, 211.8.

(*S*)-2-((*R*,*E*)-1,3-Diphenylallyl)cyclopentanone (6a)[4b]

Colorless oil. ^{1}H NMR ($CDCl_3$, 400 Hz): δ 1.70–1.78 (m, 1H), 1.93–2.03 (m, 3H), 2.16–2.23 (m, 1H), 2.27–2.34 (m, 1H), 2.55–2.61 (m, 1H), 4.09–4.12 (m, 1H), 6.40 (d, J = 4.4 Hz, 1H), 6.41 (s, 1H), 7.17–7.35 (m, 10H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 20.9, 26.1, 39.1, 48.0, 55.1, 126.5, 126.7, 127.6, 128.1, 128.7, 128.8, 129.3, 132.6, 137.4, 143.0, 219.3.

(*R*)-2-((*R*,*E*)-1,3-Diphenylallyl)cyclopentanone (6b)[4b]

Colorless oil. ^{1}H NMR ($CDCl_3$, 400 Hz): δ 1.70–1.86 (m, 1H), 1.94–2.11 (m, 3H), 2.18–2.28 (m, 1H), 2.29–2.38 (m, 1H), 2.58–2.64 (m, 1H), 4.05–4.10 (m, 1H), 6.44 (d, J = 3.2 Hz, 1H), 6.45 (s, 1H), 7.20–7.41 (m, 10H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 21.0, 26.1, 39.1, 48.0, 55.1, 126.4, 126.6, 128.7, 129.2, 129.3, 132.5, 132.6, 132.7, 137.4, 143.1, 219.3.

(*E*)-4,6-Diphenylhex-5-en-2-one (7)[8]

Colorless oil. ^{1}H NMR ($CDCl_3$, 400 Hz): δ 2.11 (s, 3H), 2.93–2.97 (m, 2H), 4.05–4.12 (dd, J = 6.8, 7.2 Hz, 1H), 6.28–6.41 (m, 2H), 7.17–7.36 (m, 10H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 21.0, 26.1, 39.1, 48.0, 55.1, 126.4, 126.6, 128.7, 129.2, 129.3, 132.5, 132.6, 132.7, 137.4, 143.1, 219.3.

(*E*)-2-(1,3-Diphenylallyl)hexanal (10a and 10b)

Colorless oil. ^{1}H NMR ($CDCl_3$, 400 Hz): δ 0.77–0.81 (t, J = 9.6 Hz, 3H), 0.83–0.88 (t, J = 9.6 Hz, 3H), 1.11–1.38 (m, 8H), 1.47–1.72 (m, 4H), 2.72–2.82 (m, 2H), 3.67–3.77 (m, 2H), 6.25–6.52 (m, 4H), 7.16–7.38 (m, 20H), 9.47–9.50 (d, J = 4.0 Hz, 1H), 9.62–9.66 (d, J = 4.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 14.0, 14.1, 22.8, 22.9, 27.6, 27.7, 29.3, 29.5, 50.2, 50.4, 56.6, 56.8, 126.5, 126.6, 127.1, 127.2, 127.7, 128.1, 128.2, 128.7, 128.8, 129.0, 129.1, 130.4, 130.8, 131.6, 131.9, 137.0, 137.1, 141.5, 141.6, 204.6, 204.9. HRMS (EI$^+$) m/z calculated for $C_{21}H_{24}O$ [M + 1]$^+$: 293.1905; found 293.1911. IR(ν/cm^{-1}): 3086, 3063, 3030, 2957, 2929, 2871, 2860, 1724, 1693, 1638, 1603, 1566, 1493, 1455, 1416, 1379, 966, 749, 699.

(*E*)-2-Ethyl-3,5-diphenylpent-4-enal (11a and 11b)[9]

Colorless oil. ^{1}H NMR ($CDCl_3$, 400 Hz): δ 0.82–0.87 (t, J = 7.2 Hz, 3H), 0.91–0.96 (t, J = 7.2 Hz, 3H), 1.39–1.79 (m, 4H), 2.69–2.77 (m, 2H), 3.71–3.77 (m, 2H), 6.27–6.51 (m, 2H), 7.18–7.40 (m, 20H), 9.49–9.51 (d, J = 4.4 Hz, 1H), 9.65–9.68 (d, J = 4.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 11.7, 11.7, 21.1, 21.2, 49.9, 50.2, 126.5, 126.6, 127.1, 127.2, 127.7, 128.1, 128.3, 128.6, 128.7, 128.8, 129.0, 129.1, 129.2, 130.5, 130.8, 131.6, 131.9.

(*S*)-2-((*S*,*E*)-1,3-Diphenylallyl)cyclohexanone (12a)

Colorless oil. ^{1}H NMR ($CDCl_3$, 400 Hz): δ 0.96–1.02 (t, J = 7.2 Hz, 6H), 1.75–1.79 (m, 1H), 2.67–2.73 (m, 1H), 3.96–4.01 (t, J = 7.2 Hz, 1H), 2.31–2.46 (m, 2H), 2.83–2.89 (m, 1H), 3.87 (t, J = 9.6 Hz, 1H), 6.25–6.31 (dd, J = 8.4, 8.8 Hz, 1H), 6.42–6.47 (d, J = 16.0 Hz, 1H), 7.19–7.37 (m, 10H), 9.79–9.81 (d, J = 5.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 17.6, 21.8, 28.2, 48.0, 61.7, 126.5, 127.1, 127.7, 128.1, 128.7, 129.1, 131.0, 131.6, 137.0, 141.7, 205.9. HRMS (EI$^+$) m/z calculated for $C_{20}H_{22}O$ [M + 1]$^+$: 278.1671; found 278.1668. IR (ν/cm^{-1}): 3088, 3060, 3027, 2960, 2926, 2871, 2855, 1721, 1659, 1599, 1578, 1494, 1464, 1452, 1389, 1371, 965, 799, 745, 697.

(*E*)-1-(1,3-Diphenylallyl)cyclohexanecarbaldehyde (13)

Colorless oil. ^{1}H NMR ($CDCl_3$, 400 Hz): δ 0.09–1.58 (m, 8H), 1.99–2.03 (d, J = 12.4 Hz, 1H), 2.16–2.19 (d, J = 12.4 Hz, 1H), 3.46–3.48 (d, J = 9.6 Hz, 1H), 6.44–6.68 (d, J = 15.6 Hz, 1H), 6.56–6.62 (dd, J = 9.6, 15.6 Hz, 1H), 7.19–7.40 (m, 10H), 9.61 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 23.1, 23.2, 25.7, 30.5, 30.6, 53.2, 57.9, 126.6, 127.1, 127.7, 128.1, 128.6, 128.8, 129.3, 133.1, 137.3, 139.9, 208.5. HRMS (EI$^+$) m/z calculated for $C_{22}H_{24}O$ [M + 1]$^+$: 304.1827; found 304.1833. IR (ν/cm^{-1}): 3086, 3060, 3028, 2931, 2855, 1703, 1600, 1582, 1495, 1451, 1415, 965, 770, 745, 701.

(*E*)-2,3,5-Triphenylpent-4-enal (14a and 14b)

Colorless oil. ^{1}H NMR ($CDCl_3$, 400 Hz): δ 4.09–4.13 (m, 2H), 4.31–4.37 (m, 2H), 6.12–6.24 (m, 2H), 6.43–6.57 (m, 2H), 7.08–7.45 (m, 30H), 9.66–9.68 (d, J = 2.8 Hz, 1H), 9.83–9.85 (d, J = 3.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 49.8, 50.2, 64.1, 64.5, 126.4, 126.6, 126.8, 127.3, 127.5, 127.7, 127.8, 128.1, 128.4, 128.5, 128.6, 128.7, 128.8, 128.9, 129.0, 129.1, 129.2, 129.3, 129.7, 130.0, 130.3, 130.9, 131.9, 132.1, 134.4, 134.5, 137.1, 137.3, 140.7, 141.6, 199.4, 199.8. HRMS (EI$^+$) m/z calculated for $C_{23}H_{20}O$ [M + 1]$^+$: 312.1514; found 312.1512. IR (ν/cm^{-1}): 3082, 3060, 3027, 2924, 2852, 2818, 2716, 1723, 1683, 1664, 1599, 1577, 1493, 1452, 1387, 965, 745, 697.

(2*S*,3*R*,*E*)-2-Benzyl-3,5-diphenylpent-4-enal (15a)

Colorless oil. ^{1}H NMR ($CDCl_3$, 400 Hz): δ 2.68–2.96 (m, 2H), 3.20–3.28 (m, 1H), 3.76–3.83 (t, J = 8.0 Hz, 1H), 6.34–6.49 (m, 2H), 7.05–7.43 (m, 15H), 9.73–9.75 (d, J = 2.8 Hz, 1H). ^{13}C

NMR ($CDCl_3$, 100 Hz): δ 34.3, 50.0, 58.3, 126.6, 126.7, 127.3, 127.9, 128.3, 128.7, 128.8, 129.1, 129.2, 129.8, 132.4, 136.9, 138.8, 141.4, 204.4. HRMS (EI^+) m/z calculated for $C_{24}H_{22}O$ $[M + 1]^+$: 326.1701; found 326.1671. IR (ν/cm^{-1}): 3083, 3060, 3027, 2924, 2851, 2724, 1724, 1681, 1600, 1583, 1494, 1453, 1393, 966, 745, 698.

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