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Pd-catalyzed regioselective acylation of α,β-unsaturated ketone derivatives by acylzirconocene chloride as an acyl group donor

Yuji Hanzawa,* Nobuhito Tabuchi, Kensuke Narita, Akito Kakuuchi, Masaya Yabe and Takeo Taguchi*

School of Pharmacy, Tokyo University of Pharmacy and Life Science, 1432-1 Horinouchi, Hachioji, Tokyo 192-0392, Japan

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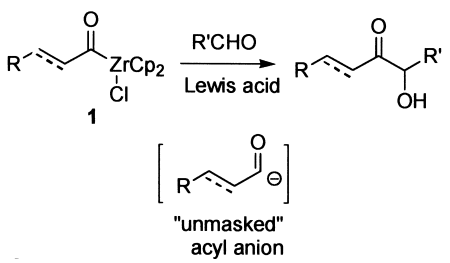
Abstract—Acylzirconocene chlorides reacted with α,β-unsaturated ketones (α,β-enone or -ynone) to give regioselectively 1,2- or 1,4-products under Pd-catalyzed conditions. In the reactions of α,β-enones, excellent regioselectivity was attained by the choice of the Pd(II) catalyst system. Thus, the 1,2- or 1,4-products were selectively prepared by choosing $PdCl_2(PPh_3)_2$ or $Pd(OAc)_2$–$BF_3{\cdot}OEt_2$, respectively. The presence of a monodentate phosphine ligand brought about a 1,2-addition product, selectively. In these Pd-catalyzed reactions, the Pd(0) species was considered to be an active catalyst, which was generated in situ through transmetalation of acyl groups from zirconium to Pd(II) followed by reductive elimination of Pd(0). α,β-Ynones also reacted with acylzirconocene chloride to give regioselectively 1,4-products under the Pd-catalyzed conditions. In contrast to the reactions of α,β-enones, the presence of a triphenylphosphine ligand brought about the selective formation of 1,4-adduct. By virtue of the phosphine ligand-effect in the addition of an acyl anion to α,β-enones, enantioselective 1,2-addition of acylzirconocene chloride to cyclic α,β-enones was carried out in modest optical purity (~66% ee) by the use of 5 mol% $Pd(OAc)_2$-(*R*)-MOP (Pd/P=1:2) catalyst. The origin of the enantioselectivity was deduced by considering an (*R*)-MOP coordinated π-allylic acyl Pd complex.

1. Introduction

The generation and reactions of acyl metals [RC(O)M] as an 'unmasked' acyl anion donor are an intensive research field.[1] In particular, the acyl metal species in which the metal is a main group metal (M=Li, Zn, etc.) has been extensively studied by many research groups.[2] However, their use as an unmasked acyl anion donor for organic synthesis encountered difficulties due to the limited stability and/or the extreme reaction conditions of the acyl metal species. As well as the acyl-main group metal complexes, acyl-transition metal complexes have also long attracted our attention because of their intrinsic usefulness as an acyl anion equivalent.[3] Several stable acyl-transition metal complexes such as nickel,[4] iron,[5] and cobalt[6] complexes have been developed and reported as an unmasked acyl anion donor. These complexes also suffer severe limitations due to the use of highly toxic metal carbonyls as the starting materials. Acylzirconocene chlorides, however, are stable and easily accessible through the hydrozirconation of alkenes or alkynes with the Schwartz reagent (Cp_2ZrHCl) followed by the insertion of carbon monoxide. Although the conversion of acylzirconocene complexes to carboxylic acid derivatives by a hydrolysis–oxidation procedure and the reactivity toward organometallic reagents have been reported,[7] no report as a donor of an unmasked acyl anion had been made until we published the Lewis acid-mediated reactions of acylzirconocene chloride derivatives with aldehydes giving α-ketol derivatives.[8] In these reactions, a salient feature of the acylzirconocene chloride as an unmasked acyl anion donor was revealed for the first time (Scheme 1). During the study of the carbon–carbon bond formation by the use of acylzirconocene chloride with an electrophile, we revealed the regiochemically tunable nucleophilic acylation of α,β-enones under Pd-catalyzed conditions. We describe herein a full account of the Pd-catalyzed reactions of the acylzirconocene chlorides with α,β-unsaturated ketones (enones and ynones) and the enantioselective 1,2-addition of an acyl anion to α,β-enones.[9,10]



Scheme 1.

Keywords: regioselectivity; acylzirconocene; Pd catalyst; acyl anion.

* Corresponding authors. Tel.: +81-426-76-3274; fax: +81-426-76-3257; e-mail: hanzaway@ps.toyaku.ac.jp

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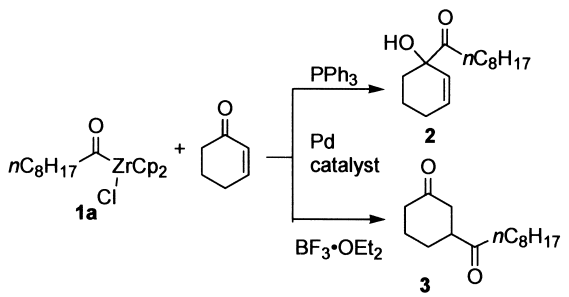


Scheme 2.

Table 1. Pd-catalyzed reaction of 2-cyclohexen-1-one with **1a**

Entry	Pd catalyst[a]	**2** Yield[b] %	**3** Yield[b] %
1	$Pd(PPh_3)_4$	34	–
2	$Pd_2(dba)\cdot CHCl_3-PPh_3$[c]	29	–
3	$PdCl_2(dppe)$	31	17
4	$PdCl_2(PPh_3)_2$	81	–
5	$Pd(OAc)_2-PPh_3$[c]	49	
6	$Pd(OAc)_2$	13	18
7	$Pd(OAc)_2$[d]	20	45
8	$Pd(OAc)_2-BF_3\cdot OEt_2$[d,e]	–	60

Reaction conditions; ambient temperature, toluene, 20 h.
[a] 5 mol% catalyst.
[b] Isolated yield.
[c] Pd/P=1:2.
[d] 10 mol% catalyst.
[e] Solvent; ether/THF=2:1.

2. Results and discussion

2.1. Regioselective acylation of α,β-enones

Michael-type addition of an unmasked acyl anion to α,β-enones by utilizing acyl metals is a practical procedure for the preparation of 1,4-dicarbonyl compounds.[4,11] Acylzirconocene chloride complex **1** is an unreactive species toward α,β-enones even if a Lewis acid or silver salt was employed as an additive.[12] In the presence of a palladium catalyst, however, the reactions of **1** with α,β-enones did proceed efficiently to give acylated products and the regioselectivity could be controlled efficiently by the choice of the catalytic system. Thus, examination of the catalytic system by the reaction of *n*-nonanoylzirconocene chloride (**1a**) with cyclohexenone revealed that the presence of a triphenylphosphine ligand tends to yield selectively 1,2-adducts **2**, and the presence of an equivalent amount of a Lewis acid yields 1,4-adduct **3** (Scheme 2, Table 1).

Among the palladium catalysts examined, $PdCl_2[P(C_6H_5)_3]_2$ and $Pd(OAc)_2-BF_3\cdot OEt_2$ were the catalyst of choice for the regioselective formation of 1,2- and 1,4-adducts, respectively (entries 4 and 8, Table 1). Other Lewis acids, such as $ZnCl_2$ or $MgBr_2\cdot OEt_2$, can be used for $BF_3\cdot OEt_2$ in 1,4-selective addition. It is worth mentioning that $Pd(OAc)_2$ showed an interesting feature because the regioselectivity of the reaction was completely reversed by the additive (entries 5 and 8, Table 1). Nickel catalysts such as, $Ni(acac)_2$ showed a similar efficiency to $Pd(OAc)_2$. Other Ni complexes [$NiCl_2(dppf)$, $NiCl_2(PPh_3)_2$ and $Ni(PPh_3)_4$] were ineffective. Addition of $BF_3\cdot OEt_2$ to the $PdCl_2(PPh_3)_2$-catalyst did not alter the 1,2-regioselectivity. The results of the reactions of **1a** with α,β-enones by the use of

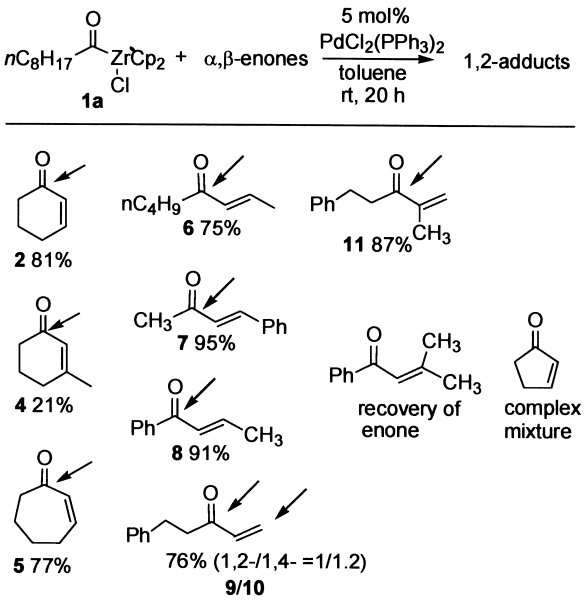


Figure 1. Yields of 1,2-addition products of α,β-enones by **1a** (numbers in bold type indicate 1,2-adducts).

$PdCl_2(PPh_3)_2$ (5 mol%) in toluene and $Pd(OAc)_2$ (10 mol%)–$BF_3\cdot OEt_2$ in Et_2O–THF (2:1) are shown in Figs. 1 and 2, respectively.

Under the respective reaction conditions, the 1,2- or 1,4-products are obtained in mostly good to excellent yields. However, the reaction of cyclopentenone gave a complex mixture under the 1,2-addition conditions (Fig. 1), while the 1,4-product **12** was obtained in good yield under 1,4-addition conditions (Fig. 2).

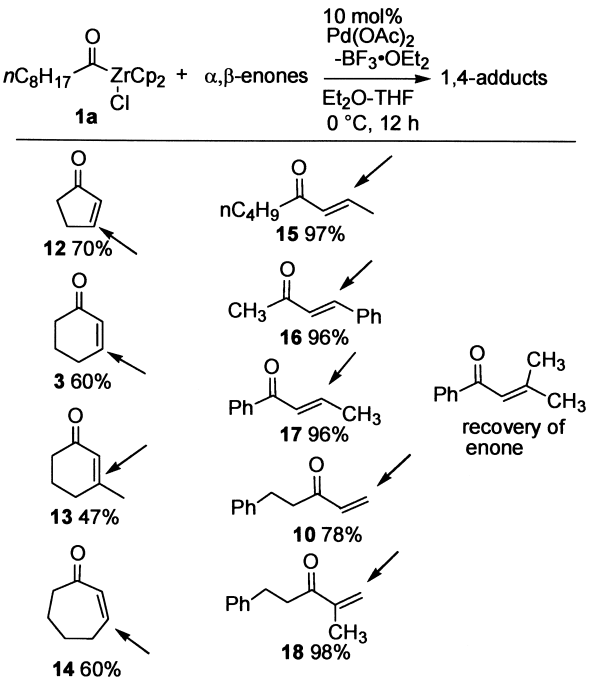


Figure 2. Yields of 1,4-addition products of α,β-enones by **1a** (numbers in bold type indicate 1,4-adducts).

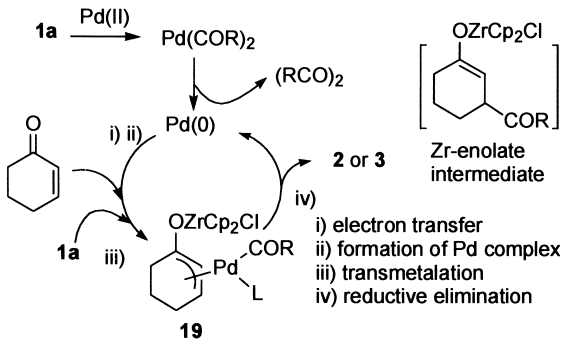


Figure 3. A catalytic cycle for the formation of **2** or **3**.

Bis-substitution at the β-position of acyclic α,β-enone retards not only the formation of the 1,4-adduct but also the formation of the 1,2-adduct. It should be mentioned that concomitant formation (<5%) of a diketone derived from the self-coupling of **1a** under both reaction conditions suggests the participation of the Pd(0) complex as an actual catalyst (Fig. 3), and a similar observation has been made in the Pd-catalyzed coupling reactions of acylzirconocene chloride and organic halide.[13]

Non-reactivity of an α,β-conjugated ester, γ,δ-unsaturated ketone and saturated ketone, and formation of a complex mixture in the reaction of an α,β-enal imply that an α,β-enone skeleton is essential in the present reaction. Based on these observations and the mechanism, which is reported for the Ni or Pd-catalyzed 1,4-addition of alkenylzirconocene chloride to α,β-enones,[10] an electron transfer from Pd(0) to the *α,β*-enone skeleton would take part in the reaction as a crucial process (Fig. 3).[14]

Thus, an electron transfer from Pd(0) to cyclohexenone, for example, formation of acylpalladium π-allylic complex **19** and reductive elimination of Pd(0), would give either a 1,2- or 1,4-acylation product (**2** or **3**). The role of the triphenylphosphine ligand in the regioselective formation of 1,2-acylation product **2** could be explained by the preferred formation of stereochemically less crowded intermediate complex **19A** (L=PPh_3) compared to **19B** (L=PPh_3) and subsequent reductive elimination of Pd(0) from **19A** (L=PPh_3) (Fig. 4).

Although the mechanism involved in the reversal of regioselectivity by changing the palladium catalyst from $PdCl_2(PPh_3)_2$ to $Pd(OAc)_2$–$BF_3{\cdot}OEt_2$ remains to be clarified, an addition of a Lewis acid might exert an electronic or a steric effect by coordinating to the assumed acyl π-allyl complex **19** (L=solvent) intermediate. The described regioselective addition was also carried out by the use of α,β-unsaturated acylzirconocene chloride **1b**, albeit the yield was lower than that of **1a** (Fig. 5). In any event, the

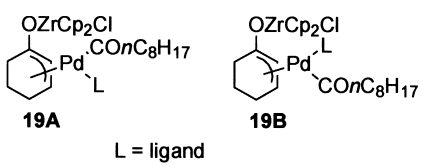


Figure 4. Isomeric complexes **19A** and **B**.

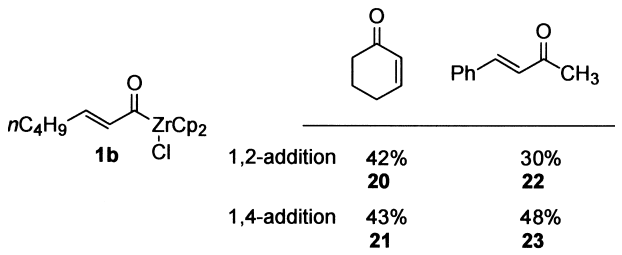


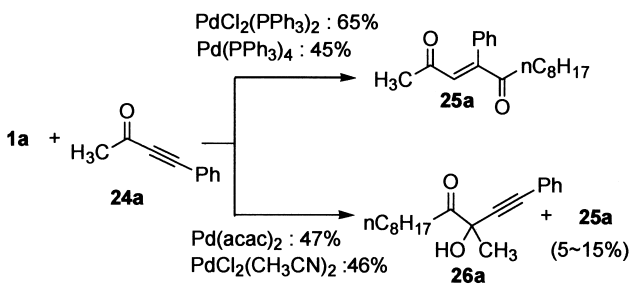
Figure 5. Pd-catalyzed 1,2- or 1,4-selective addition of **1b** (numbers in bold type indicate products).

tunable regioselectivity of **1** toward α,β-enones indicates that the complex **1** is a very useful reagent as a donor of an unmasked acyl anion.

2.2. Regioselective acylation of α,β-ynones

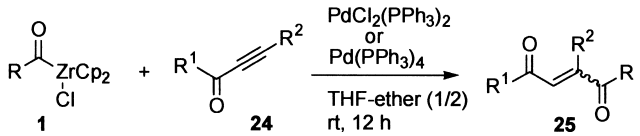
Because α,β-ynone **24** is a good Michael acceptor toward organometallic reagents, we examined the reactions of **1** with **24** on the assumption that the Pd-catalyzed reaction conditions employed for α,β-enones would proceed as well. It turned out that the reactions proceed efficiently to give the acyl addition products as we expected. The regioselectivity of the reaction, however, was contrastive with that of the reactions of α,β-enones; that is, the presence of a phosphine ligand exerted influence on the regioselectivity to afford 1,4-product **25**. Thus, the reaction of **1a** with 4-phenyl-but-3-yn-2-one (**24a**) (Scheme 3) in the presence of $PdCl_2$-$(PPh_3)_2$ or $Pd(PPh_3)_4$-catalyst gave 1,4-acylation product **25a** in a slight preference of *Z*-isomers (*E*/*Z*=1:2.4) in 65 or 45% yield, respectively, together with a trace amount (<5%) of a diketone as in the cases of α,β-enones. On the other hand, use of $Pd(acac)_2$ or $PdCl_2(CH_3CN)_2$ as a catalyst under otherwise identical conditions rendered the reaction slow (by TLC), and a 1,2-adduct **26a** was obtained in 40–47% yield together with a small amount (5–15%) of 1,4-adduct **25a**. Formation of **25** by the $PdCl_2(PPh_3)_2$ or $Pd(PPh_3)_4$-catalyzed 1,4-selective addition of acylzirconocene chlorides **1** to α,β-ynone derivatives **24** is listed in Table 2.

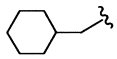
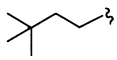
In all cases examined, the reaction proceeds with high 1,4-regioselectivity and efficiency, albeit the stereoselectivity is low. It is notable that the regioselectivity was unaffected even in the reactions of **24** which possesses a bulky substituent at the sp carbon (entries 2, 4 and 5, Table 2). Other catalysts [$PdCl_2$dppe, $(dba)_3Pd_2{\cdot}CHCl_3$, $NiCl_2(PPh_3)_2$, $Ni(PPh_3)_4$, $Ni(acac)_2$ and $Ni(COD)_2$] ended with recovery of the starting material or formation of a



Scheme 3.

Table 2. $PdCl_2(PPh_3)_2$- and/or $Pd(PPh_3)_4$-catalyzed reactions of **24** with saturated acylzirconocene chloride **1**



Entry	**1**, R	**24**		Pd catalyst[a]	**25**		
		R^1	R^2		Yield (%)[b]		(*E*/*Z*)[c]
1	*n*-C_8H_{17} **1a**	Ph	*n*Bu **24b**	A	85	**25b**	(1/2.4)
				B	68		(1/2.4)
2		CH_3	*t*Bu	A	71	**25c**	(1/3)
				B	77		(1/2)
3		Ph	$BnO(CH_2)_2$	A	59	**25d**	(1/2)
				B	83		(1/1)
4		Ph	*t*Bu	A	82	**25e**	(1/1)
				B	95		(1/2.5)
5		*t*Bu	*n*Bu	A	73	**25f**	(1/3.5)
				B	73		(1/3)
6		2-Naphthyl	*n*Bu	A	95	**25g**	(1/2.3)
				B	95		(1/2.5)
7		Ph	*n*Bu	A	70	**25h**	(1/3)
				B	51		(1/3)
8				A	78	**25i**	(1/3.6)
				B	71		(1/3)

[a] Catalyst A: $PdCl_2(PPh_3)_2$, catalyst B: $Pd(PPh_3)_4$.
[b] Isolated yield.
[c] Determined by ^1H NMR.

complex mixture. It is worth noting that ethyl phenylpropiolate and oct-4-yne did not react with **1a** under the same reaction conditions, and the starting materials were recovered unchanged. α,β-Ynone, which possesses alkynyl hydrogen, e.g. 1-phenyl propynone, ended with formation of a complex mixture. Thus, the activation of the triple bond by an electron-withdrawing ketone-carbonyl and the absence of alkynyl-hydrogen are requisite for bringing about the reaction. According to the facts that (i) either $PdCl_2(PPh_3)_2$ or $Pd(PPh_3)_4$ can be used as a catalyst, and (ii) a trace amount of diketone derived from the self-coupling of **1** is formed by the use of $PdCl_2(PPh_3)_2$ catalyst, a mechanism which is analogous to the Pd(0)-catalyzed reactions of α,β-enones with **1** was assumed (Fig. 6). Thus, a catalytic process; (i) an electron transfer from Pd(0) to α,β-ynone **24**, (ii) formation of Pd-allenyl complex **27**, (iii) transmetalation and (iv) reductive elimination of Pd(0) would be involved. Although the quite different effect of the triphenylphosphine ligand on the regioselectivity compared to the reaction of α,β-enones is puzzling, steric or electronic difference between the intermediate Pd-allenyl complexes **27** might exert influence on the regioselectivity. It should be mentioned that the isomerization of α,β-ynone to conjugated dienone via allenyl ketone by Pd(0) or PPh_3 has been reported.[15] In the present reactions, however, this isomerization was scarcely involved since *t*Bu or phenyl-substituted α,β-ynone, which has no isomerizable hydrogen, gave **25**.

$PdCl_2(PPh_3)_2$-catalyzed reactions of α,β-unsaturated acylzirconocene chloride with α,β-ynone turned out to be a one-pot procedure for the preparation of cyclopentenone derivatives **28** (Scheme 4). The reaction of **24a** with **1b** in THF for 12 h at ambient temperature, cyclopentenone derivative **28a** were isolated in 21% yield together with the 1,4-addition products **29a** (27% yield). Formation of **28** was increased by prolonged treatment (48 h) of the reaction mixture. Thus, the reaction of **1b** with **24b** and the reaction of **1c** with **24b** in THF at ambient temperature for 48 h gave **28b** and **28c** in 47 and 63% yields, respectively. The formation of **28** was a result of the secondary process

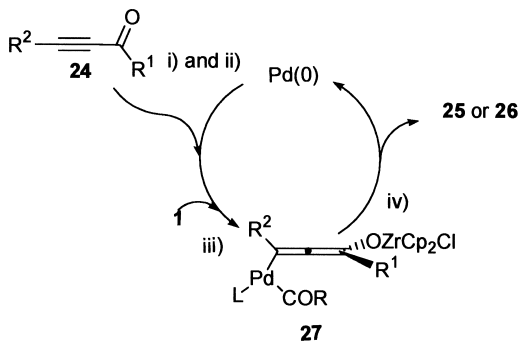
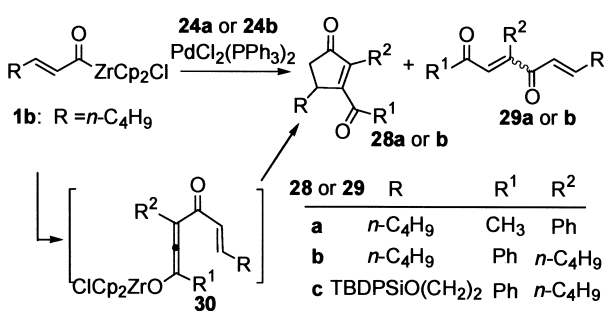
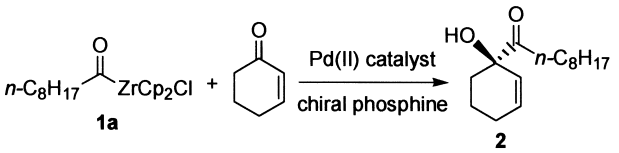


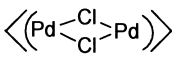
Figure 6. A catalytic cycle for the formation of **25** or **26**.



Scheme 4.

Table 3. Enantioselective formation of **2**



Entry	Pd catalyst[a]	Phosphine[b]	Yield (%)[c]	ee (%)[d]
1	$PdCl_2$[(*R*)-BINAP]	–	19	–
2	$Pd(OAc)_2$	(*R*,*R*)-CHIRAPHOS	14	–
3	$Pd(OAc)_2$	(+)-NMDPP	81	–
4	$PdCl_2(PPh_3)_2$	(*R*)-MOP	90	12
5	$Pd(OAc)_2$	(*R*)-MOP	88	66
6	$PdCl_2(PhCN)_2$	(*R*)-MOP	89	61
7	$Pd(acac)_2$	(*R*)-MOP	92	62
8		(*R*)-MOP	48	56
9	$PdCl_2(CH_3CN)_2$	(*R*)-MOP	86	64
10	$Pd_2(dba)_3{\cdot}CHCl_3$	(*R*)-MOP	70	64

Reaction conditions, see Section 5.
[a] 5 mol% catalyst.
[b] Pd/P=1:2.
[c] Isolated yield.
[d] Determined by chiralcel AD HPLC after being derivatized to benzoyl ester.

of the enolate intermediate **30** through either the Nazarov reaction or by an intramolecular conjugated addition reaction of the enolate **30**.[16] In any event, an access to highly substituted cyclopentenone derivatives **28** in one-pot procedure from ynone **24** under mild conditions would render the present procedure useful.

3. Enantioselective 1,2-addition of acylzirconocene chloride to α,β-enones

The effect of the triphenylphosphine ligand in the π-allyl complex intermediate **19** upon the regioselective formation of the 1,2-adduct (Fig. 3) led us to examine an enantioselective version of the 1,2-acylation by utilizing a chiral phosphine ligand. The Pd(II)-chiral phosphine-catalyzed reactions of **1a** with cyclohexenone in toluene were carried out and the results are listed in Table 3. All reactions were carried out by utilizing 5 mol% palladium catalyst and a chiral phosphine ligand (Pd/P=1:2).

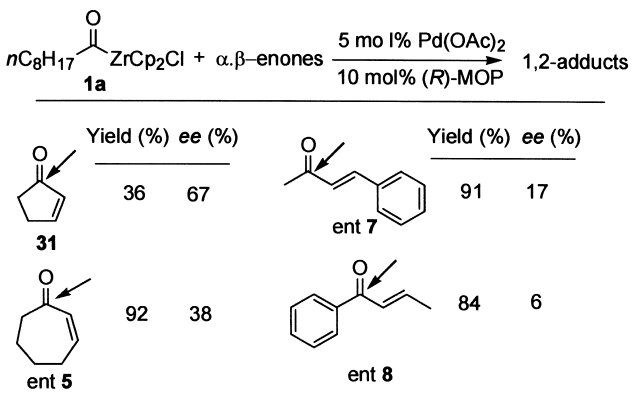


Figure 7. Enantioselective 1,2-addition of **1a** to α,β-enones (numbers in bold type indicate 1,2-adduct).

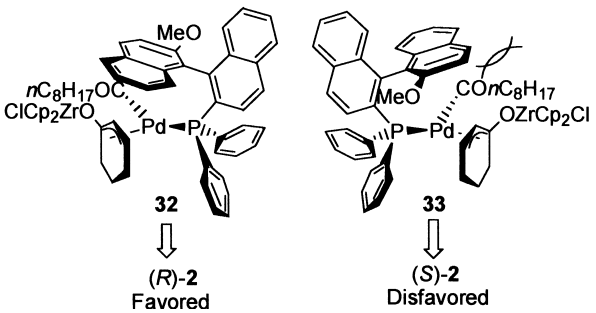
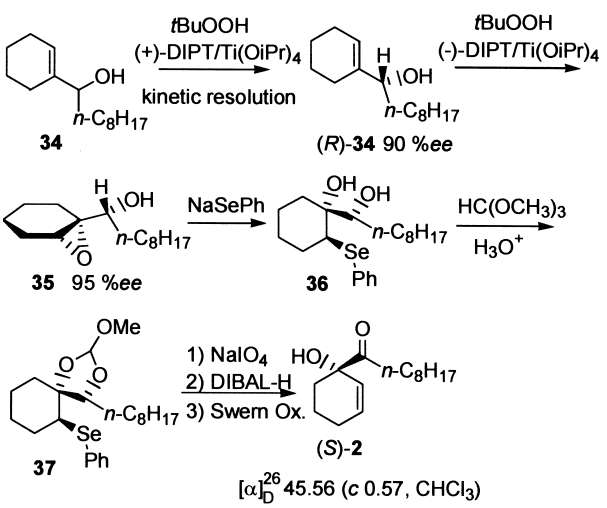


Figure 8. Enantioselective complexation of (*R*)-MOP-Pd.

As can be deduced from the previously discussed results, the use of a chiral bidentate phosphine ligand, (*R*)-BINAP[17] or (*R*,*R*)-CHIRAPHOS[18] was ineffective in the reaction (entries 1 and 2, Table 3). However, a chiral monodentate phosphine ligand, (+)-NMDPP[19] or (*R*)-MOP,[20] enhanced the reaction rate compared to triphenylphosphin ligand, and (*R*)-MOP, which was developed by Hayashi et al.[20] shows considerable efficiency in the chiral induction into the product (*R*)-**2**, $[\alpha]_D^{24}=-42.1$ (c=1.04 in $CHCl_3$), (66% ee, 88% yield) (entry 5). No significant difference between (*R*)-MOP and its derivatives (BnO-, *i*PrO- or TBDMSO-(*R*)-MOP)[20c,d] was observed in the chiral induction. It is worth mentioning that the utilization of the (*R*)-MOP ligand brought about a significant increment of yields and the reaction rate compared to the case of the triphenylphosphine ligand. This ligand effect of (*R*)-MOP enables us to isolate a 1,2-acylation product **31** (67% ee, 36% yield, Fig. 7) from cyclopentenone, which gave a complex mixture under the $Pd(OAc)_2$–PPh_3 conditions (Fig. 1). The present enantioselective reaction is less efficient for acyclic α,β-enones, albeit excellent chemical yields and regioselectivity are attained (Fig. 7).

Based on the discussed acylpalladium π-allylic complex **19A** (L=PPh_3) (Fig. 4) and the reported X-ray structure of the (*R*)-MOP-Pd π-allylic complex,[21] the acylpalladium-(*R*)-MOP π-allylic complex **32** and **33** would be responsible for the formation of (*R*)-**2** and (*S*)-**2**, respectively (Fig. 8).

Complex **33**, which would give (*S*)-**2**, suffers from steric



Scheme 5.

compression between the MeO-naphthyl ring and the acyl group, while there is no such steric interaction in complex **32**. Thus, reductive elimination of Pd(0) from **32** would yield (*R*)-**2**, preferentially. The result of the enantioselective reaction would further support the legitimacy of the proposed complex **19A** in the regioselective 1,2-acylation reactions. The absolute stereochemistry of (*R*)-**2** was confirmed by the following synthesis of (*S*)-**2** from the easily accessible allylic alcohol **34** (Scheme 5). Kinetic resolution[22,23] of **34** with (+)-DIPT, Ti(O-*i*Pr)$_4$ and *t*BuOOH gave optically active (*R*)-allylic alcohol (*R*)-**34** (90% ee, 45% yield).[24] Epoxidation of (*R*)-**34** with Ti(O-*i*Pr)$_4$, *t*BuOOH and (−)-DIPT gave epoxy alcohol **35** (90% yield, >95% ee).[25] Treatment of **35** with sodium phenylselenide gave *vic*-diol **36**, which was protected as cyclic orthoformate **37**. Oxidation of **37** with sodium periodate at 0°C, deprotection of the *vic*-diol protective group (DIBAL-H) followed by oxidation (Swern oxidation) of the secondary alcohol gave (*S*)-**2** (>95% ee), $[\alpha]_D^{26}$=45.5 (c=0.57, $CHCl_3$), which was identical in every respect with the product (*R*)-**2** derived from the enantioselective acylation, except for the sign of specific rotation.

4. Conclusion

Stable and easily accessible acylzirconocene chlorides proved to be an excellent donor of an unmasked acyl anion to α,β-unsaturated ketones under the palladium-catalyzed conditions. The highly tunable regioselectivity of an acylzirconocene chloride complex in the acylation reactions of α,β-enone and α,β-ynone was dependent upon the presence of a monodentate phosphine ligand. However, the effect of the phosphine ligand was quite contrary in α,β-enone and α,β-ynone compounds; that is, 1,2-selectivity in the former and 1,4-selectivity in the latter are observed. In these reactions, an electron transfer from the low-valent Pd-catalyst to α,β-unsaturated ketone is involved at the initial step. A facile access to cyclopentenone derivatives by the Pd-catalyzed reaction of α,β-unsaturated acylzirconocene chlorides with the α,β-ynone system has added a new and simple way for the preparation of cyclopentenone compounds, which constitute an important portion of biologically active molecules. Furthermore, the enantioselective 1,2-addition of an acyl anion to cyclic α,β-enones reveals the new potentiality of the acylzirconocene chloride complex as an unmasked acyl anion donor. The stable acylzirconocene species can be enrolled as a very handy substitute for the reported toxic acyl metal complexes, and we are now continuing our efforts to explore further the reactivity of the acylzirconocene chloride derivatives.

5. Experimental

All reactions were carried out under an argon atmosphere with dry, freshly distilled solvents under anhydrous conditions. Tetrahydrofuran (THF), diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl. Dichloromethane (CH_2Cl_2) was distilled from calcium hydride. Zirconocenehydrochloride (Cp_2ZrHCl) was prepared by the method of Buchwald.[26] Materials were obtained from commercial suppliers and used without further purification unless otherwise noted. NMR spectra were measured at 300 or 400 MHz for ^1H and 75.5 or 100.6 MHz for ^{13}C. Fuji silysia silica gel BW-80S (60–200 mesh) was used for column chromatography and prepacked column CPS-223L-1 was used for medium-pressure liquid chromatography (MPLC). An enantiomeric excess of the optically active product was determined by HPLC-analysis using chiralcel AD or OD column with 254 nm UV detector after being derivatized to benzoate.

5.1. Preparation of a solution of acylzirconocene chloride

To a suspension of $Cp_2Zr(H)Cl$ (2.0 mmol) in CH_2Cl_2 (8 mL) was added alkene or alkyne (4 mmol) at ambient temperature and the mixture was stirred for 0.5 h under Ar atmosphere. After the mixture was stirred for 2 h under CO (1 atm), the solvent was evaporated in vacuo to give a pale yellow solid, and toluene (15 mL) or THF (5 mL) was added to the solid.

5.2. 1,2-Regioselective acylations of α,β-enones: general procedure

To a toluene solution (15 mL) of acylzirconocene chloride (2.0 mmol) were added α,β-unsaturated ketone (1 mmol) and $PdCl_2(PPh_3)_3$ (5 mol%) at ambient temperature. After the reaction mixture was stirred for 20 h at the same temperature, the mixture was treated with aq. $NaHCO_3$ and extracted with ether. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude product was purified by column chromatography (hexane/ethyl acetate=50:1) to give pure 1,2-acylation product.

5.2.1. 1-(Hydroxy-2-cyclohexen-1-yl)-1-nonanone (2). Colorless oil, ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, J=6.8 Hz, 3H), 1.26–1.31 (m, 10H), 1.57–1.66 (m, 3H), 1.77–1.88 (m, 3H), 2.03–2.21 (m, 2H), 2.50 (dt, J=1.3, 8.3 Hz, 2H), 4.03 (s, 1H), 5.47 (qd, J=1.3, 9.9 Hz, 1H), 6.12–6.15 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1, 18.1, 22.6, 24.0, 24.8, 29.1, 29.2, 29.3, 31.8, 33.3, 36.3, 76.0, 126.1, 133.6, 213.8; IR (neat) ν 3467, 1709 cm^{-1}; EIMS m/z 238 (M^+). Anal. calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99. Found: C, 75.28; H, 10.92.

5.2.2. 1-(Hydroxy-3-methyl-2-cyclohexen-1-yl)-1-nonanone (4). Colorless oil, ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, J=6.9 Hz, 3H), 1.26–1.31 (m, 10H), 1.53–1.61 (m, 3H), 1.69–1.90 (m, 6H), 2.02–2.10 (m, 2H), 2.48 (t, J=7.3 Hz, 2H), 4.00 (s, 1H), 5.20 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1, 18.6, 22.6, 24.1, 24.2, 29.1, 29.2, 29.3, 29.9, 31.8, 32.9, 36.3, 76.7, 120.5, 141.9, 214.3; IR (neat) ν 3468, 1708 cm^{-1}; EIMS m/z 252 (M^+). Anal. calcd for $C_{16}H_{28}O_2$: C, 76.14; H, 11.18. Found: C, 76.04; H, 11.01.

5.2.3. 1-(Hydroxy-2-cyclohepten-1-yl)-1-nonanone (5). Colorless oil, ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, J=6.9 Hz, 3H), 1.26–1.31 (m, 10H), 1.53–1.89 (m, 6H), 1.96–2.03 (m, 2H), 2.28 (qd, J=1.3, 5.8 Hz, 2H), 2.56 (m, 2H), 3.86 (s, 1H), 5.36 (qd, J=1.3, 11.5 Hz, 1H), 6.01 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1, 22.6, 23.0,

23.9, 27.1, 27.2, 29.1, 29.2, 29.3, 31.8, 35.4, 36.3, 81.0, 130.4, 135.9, 213.1; IR (neat) ν 3464, 2927, 1711 cm^{-1}; EIMS *m/z* 252 (M^+); HRMS calcd for $C_{16}H_{28}O_2$: 252.2089. Found: 252.2073.

5.2.4. (*E*)-4-*n*-Butyl-2-tridecen-4-ol-5-one (6). Colorless oil, ^1H NMR (400 MHz, $CDCl_3$) δ 0.85–0.92 (m, 6H), 0.95–1.05 (m, 1H), 1.24–1.43 (m, 13H), 1.53–1.60 (m, 2H), 1.66–1.76 (m, 5H), 2.38–2.58 (m, 2H), 4.07 (s, 1H), 5.51 (dq, *J*=1.5, 15.3 Hz, 1H), 5.86 (dq, *J*=6.7, 15.3 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.9, 14.1, 17.8, 22.6, 22.9, 23.8, 25.3, 29.1, 29.2, 29.3, 31.8, 36.1, 37.8, 81.4, 127.5, 131.4, 212.0; IR (neat) ν 3471, 1707 cm^{-1}; EIMS *m/z* 268 (M^+). Anal. calcd for $C_{17}H_{32}O_2$: C, 76.06; H, 12.02. Found: C, 76.05; H, 11.85.

5.2.5. (*E*)-3-Methyl-1-phenyl-1-dodecen-3-ol-4-one (7). Colorless oil, ^1H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, *J*=6.9 Hz, 3H), 1.22–1.25 (m, 10H), 1.54 (s, 3H), 1.59–1.64 (m, 2H), 2.59 (t, *J*=7.3 Hz, 2H), 4.21 (s, 1H), 6.23 (d, *J*=15.9 Hz, 1H), 6.77 (d, *J*=15.9 Hz, 1H), 7.24–7.38 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1, 22.6, 23.9, 25.0, 29.0, 29.1, 29.3, 31.8, 36.1, 79.0, 126.7, 128.0, 128.6, 130.0, 131.1, 136.3, 211.6; IR (neat) ν 3466, 1710 cm^{-1}; EIMS *m/z* 288 (M^+). Anal. calcd for $C_{19}H_{28}O_2$: C, 79.12; H, 9.79. Found: C, 79.13; H, 9.65.

5.2.6. (*E*)-4-Phenyl-2-tridecen-4-ol-5-one (8). Colorless oil, ^1H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, *J*=6.9 Hz, 3H), 1.15–1.28 (m, 10H), 1.40–1.58 (m, 2H), 1.84 (dd, *J*=1.0, 6.2 Hz, 3H), 2.30–2.50 (m, 2H), 4.68 (s, 1H), 6.06 (dq, *J*=6.2, 15.2 Hz, 1H), 6.15 (dd, *J*=1.0, 15.2 Hz, 1H), 7.30–7.41 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.0, 18.0, 22.6, 24.1, 28.9, 29.0, 29.1, 31.7, 36.8, 82.6, 126.8, 128.0, 128.6, 128.8, 129.2, 141.3, 209.9; IR (neat) ν 3456, 1711 cm^{-1}; EIMS *m/z* 288 (M^+); HRMS calcd for $C_{19}H_{28}O_2$: 288.20893. Found: 288.20833.

5.2.7. 3-(2-Phenylethyl)-1-dodecen-3-ol-4-one (9). Colorless oil, ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J*=6.9 Hz, 3H), 1.22–1.31 (m, 10H), 1.55–1.62 (m, 2H), 2.00–2.13 (m, 2H), 2.40–2.61 (m, 3H), 2.71–2.79 (m, 1H), 4.17 (s, 1H), 5.28 (dd, *J*=1.1, 10.6 Hz, 1H), 5.53 (dd, *J*=1.1, 17.0 Hz, 1H), 5.96 (dd, *J*=10.6, 17.0 Hz, 1H), 7.16–7.30 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1, 22.6 23.7, 29.1, 29.2, 29.3, 29.6, 31.8, 36.3, 39.7, 82.0, 116.8, 126.0, 128.4, 128.5, 137.9, 141.5, 211.1; IR (neat) ν 3468, 1709 cm^{-1}; EIMS *m/z* 302 (M^+). Anal. calcd for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00. Found: C, 79.16; H, 10.01.

5.2.8. 1-Phenyl-3,6-tetradecanedione (10). Colorless crystals, mp 31.0–33.5°C; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J*=6.9 Hz, 3H), 1.27–1.32 (m, 10H), 1.50–1.60 (m, 2H), 2.44 (t, *J*=7.5 Hz, 2H), 2.63–2.69 (m, 4H), 2.77–2.81 (m, 2H), 2.87–2.92 (m, 2H), 7.17–7.29 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1, 22.6 23.9, 29.1, 29.2, 29.4, 29.7, 31.8, 36.0, 36.2, 42.9, 44.3, 126.1, 128.3, 128.5, 141.0, 208.5, 209.7; IR (neat) ν 1701 cm^{-1}; EIMS *m/z* 302 (M^+). Anal. calcd for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00. Found: C, 79.23; H, 10.06.

5.2.9. 2-Methyl-3-(2-phenylethyl)-1-dodecen-3-ol-4-one (11). Colorless oil, ^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J*=6.9 Hz, 3H), 1.27–1.32 (m, 10H), 1.53–1.61 (m, 2H), 1.65 (s, 3H), 2.18–2.34 (m, 3H), 2.41 (dt, *J*=7.4, 17.7 Hz, 1H), 2.57 (dt, *J*=7.4, 17.7 Hz, 1H), 2.75–2.82 (m, 1H), 4.28 (s, 1H), 5.15 (s, 1H), 5.22 (s, 1H), 7.17–7.31 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.0, 18.8, 22.6, 23.7, 29.1, 29.2, 29.3, 29.8, 31.8, 35.0, 37.4, 83.3, 114.1, 126.0, 128.4, 128.5, 141.8, 145.3, 212.4; IR (neat) ν 3462, 1706 cm^{-1}; EIMS *m/z* 316 (M^+). Anal. calcd for $C_{21}H_{32}O_2$: C, 79.70; H, 10.19. Found: C, 79.74; H, 10.07.

5.2.10. (*E*)-1-(Hydroxy-2-cyclohexen-1-yl)-2-hepten-1-one (20). Colorless oil, ^1H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, *J*=7.2 Hz, 3H), 1.31–1.47 (m, 4H), 1.57–1.65 (m, 2H), 1.76–1.85 (m, 3H), 2.00–2.10 (m, 1H), 2.19- 2.27 (m, 2H), 4.20 (s, 1H), 5.50 (dq, *J*=1.5, 8.7 Hz, 1H), 6.14–6.18 (m, 1H), 6.34 (td, *J*=1.5, 15.4 Hz, 1H), 7.14 (td, *J*=7.1, 15.4 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.8, 18.0, 22.3, 25.0, 30.1, 32.5, 33.7, 74.9, 123.3, 126.0, 133.7, 151.0, 201.4; IR (neat) ν 3455, 1689 cm^{-1}; EIMS *m/z* 208 (M^+); HRMS calcd for $C_{13}H_{20}O_2$: 208.14633. Found: 208.14641.

5.2.11. (1*E*,5*E*)-3-Methyl-1-phenyl-1,5-decadien-3-ol-4-one (22). Colorless oil, ^1H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, *J*=7.2 Hz, 3H), 1.31–1.51 (m, 4H), 1.58 (s, 3H), 2.26 (dq, *J*=1.4, 7.0 Hz, 2H), 4.43 (s, 1H), 6.27 (d, *J*=15.9 Hz, 1H), 6.46 (td, *J*=1.4, 15.3 Hz, 1H), 6.80 (d, *J*=15.9 Hz, 1H), 7.18 (td, *J*=7.0, 15.3 Hz, 1H), 7.24–7.42 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.7, 22.2, 24.8, 30.0, 32.5, 77.8, 122.7, 126.7, 127.9, 128.5, 129.9, 131.2, 136.4, 151.6, 199.0; IR (neat) ν 3452, 1689 cm^{-1}; EIMS *m/z* 258 (M^+); HRMS calcd for $C_{17}H_{22}O_2$: 258.16198. Found: 258.16122.

5.3. 1,4-Regioselective acylation of α,β-enones: general procedure

To a THF solution (5 mL) of acylzirconocene chloride (2 mmol) were added a solution of α,β-unsaturated ketone (1 mmol) in ether (10 mL), $Pd(OAc)_2$ (10 mol%) and $BF_3{\cdot}OEt_2$ (1 mmol) at 0°C. After the reaction mixture was stirred for 20 h at the same temperature, the mixture was treated with aq. $NaHCO_3$ and extracted with ether. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude product was purified by column chromatography (hexane/ethyl acetate=20:1) to give pure 1,4-acylation product.

5.3.1. 3-*n*-Nonanoylcyclopentanone (12). Colorless oil, ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J*=6.8 Hz, 3H), 1.20–1.30 (m, 10H), 1.57–1.61 (m, 2H), 1.95–2.02 (m, 1H), 2.16–2.57 (m, 7H), 3.20–3.25 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.0, 22.6, 23.6, 26.0, 29.1, 29.2, 29.3, 31.8, 37.5, 40.1, 41.7, 47.7, 210.8, 216.7; IR (neat) ν 1747, 1713 cm^{-1}; EIMS *m/z* 224 (M^+). Anal. calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.82; H, 10.66.

5.3.2. 3-*n*-Nonanoylcyclohexanone (3). Colorless oil, ^1H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, *J*=6.8 Hz, 3H), 1.20–1.29 (m, 10H), 1.54–1.78 (m, 4H), 2.00–2.11 (m, 2H), 2.25–2.53 (m, 6H), 2.82–2.89 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.0, 22.6, 23.6, 25.0, 27.4, 29.1, 29.2, 29.3, 31.8, 41.0, 41.2, 42.6, 50.2, 210.1, 210.8; IR

(neat) ν 1712 cm^{-1}; EIMS *m/z* 238 (M^+). Anal. calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99. Found: C, 75.36; H, 10.88.

5.3.3. 3-Methyl-3-*n*-nonanoylcyclohexanone (13). Colorless oil, ^1H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, *J*=6.9 Hz, 3H), 1.19 (s, 3H), 1.20–1.31 (m, 10H), 1.50–1.57 (m, 2H), 1.67–1.77 (m, 2H), 1.83–1.92 (m, 1H), 1.97–2.04 (m, 1H), 2.09 (d, *J*=14.4 Hz, 1H), 2.19–2.34 (m, 2H), 2.37–2.51 (m, 2H), 2.68 (d, *J*=14.4 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.0, 21.8, 22.6, 23.3, 23.6, 29.1, 29.2, 29.4, 31.8, 33.4, 36.5, 40.2, 49.3, 51.9, 209.7, 213.3; IR (neat) ν 1707 cm^{-1}; EIMS *m/z* 252 (M^+); HRMS calcd for $C_{16}H_{28}O_2$: 252.20893. Found: 252.20745.

5.3.4. 3-*n*-Nonanoylcycloheptanone (14). Colorless oil, ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J*=6.9 Hz, 3H), 1.26 (m, 10H), 1.44–1.68 (m, 5H), 1.83–2.03 (m, 3H), 2.39–2.58 (m, 5H), 2.68–2.78 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1, 22.6, 23.7, 28.2, 29.1, 29.2, 29.3, 31.8, 32.7, 40.9, 43.8, 44.7, 48.2, 211.7, 212.7; IR (neat) ν 1706 cm^{-1}; EIMS *m/z* 252 (M^+); HRMS calcd for $C_{16}H_{28}O_2$: 252.20893. Found: 252.20943.

5.3.5. 7-Methyl-5,8-hexadecanedione (15). Colorless oil, ^1H NMR (400 MHz, $CDCl_3$) δ 0.85–0.90 (m, 6H), 1.06 (m, *J*=7.1 Hz, 3H), 1.26–1.33 (m, 12H), 1.49–1.57 (m, 4H), 2.30–2.45 (m, 3H), 2.52 (t, *J*=7.4 Hz, 2H), 2.93 (dd, *J*=9.1, 17.5 Hz, 1H), 2.99–3.07 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.8, 14.1, 16.8, 22.3, 22.6, 23.6, 25.9, 29.1, 29.3, 29.4, 31.8, 40.9, 41.3, 42.6, 45.6, 209.8, 213.8; IR (neat) ν 1712 cm^{-1}; EIMS *m/z* 268 (M^+). Anal. calcd for $C_{17}H_{32}O_2$: C, 76.06, H, 12.02. Found: C, 75.76, H, 11.92.

5.3.6. 4-Phenyl-2,5-tridecanedione (16). Colorless oil, ^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J*=6.9 Hz, 3H), 1.20–1.34 (m, 10H), 1.47–1.63 (m, 2H), 2.22 (s, 3H), 2.38–2.61 (m, 2H), 2.63 (dd, *J*=3.8, 17.9 Hz, 1H), 3.51 (dd, *J*=10.3, 17.9 Hz, 1H), 4.27 (dd, *J*=3.8, 10.3 Hz, 1H), 7.24–7.40 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.0, 22.6, 23.6, 28.9, 29.0, 29.2, 30.0, 31.4, 41.5, 46.5, 53.3, 127.4, 128.2, 129.0, 138.0, 206.8, 209.4; IR (neat) ν 1715 cm^{-1}; EIMS *m/z* 288 (M^+). Anal. calcd for $C_{19}H_{28}O_2$: C, 79.12, H, 9.79. Found: C, 78.98, H, 9.72.

5.3.7. 3-Methyl-1-phenyl-1,4-dodecanedione (17). Colorless oil, ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J*=6.9 Hz, 3H), 1.18 (d, *J*=7.3 Hz, 3H), 1.27–1.30 (m, 10H), 1.57–1.62 (m, 2H), 2.55–2.70 (m, 2H), 2.91 (dd, *J*=4.5, 17.9 Hz, 1H), 3.18–3.27 (m, 1H), 3.54 (dd, *J*=8.9, 17.9 Hz, 1H), 7.43–7.57 (m, 3H), 7.94–7.96 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1, 17.0, 22.7, 23.6, 29.1, 29.3, 29.4, 31.9, 41.1, 41.5, 41.9, 128.0, 128.6, 133.1, 136.7, 198.7, 213.8; IR (neat) ν 1714, 1686 cm^{-1}; EIMS *m/z* 288 (M^+); HRMS calcd for $C_{19}H_{28}O_2$: 288.20893. Found: 288.20847.

5.3.8. 4-Methyl-1-phenyl-3,6-tetradecanedione (18). Colorless oil, ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J*=6.9 Hz, 3H), 1.04 (d, *J*=7.0 Hz, 3H), 1.20–1.31 (m, 10H), 1.50–1.58 (m, 2H), 2.31–2.45 (m, 2H), 2.84–3.05 (m, 7H), 7.16–7.29 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1, 16.5, 22.6, 23.7, 29.1, 29.2, 29.3, 29.6, 31.8, 41.0, 42.8, 42.9, 45.6, 126.0, 128.3, 128.4, 141.3, 209.7, 212.5; IR (neat) ν 1711 cm^{-1}; EIMS *m/z* 316 (M^+). Anal. calcd for $C_{21}H_{32}O_2$: C, 79.70; H, 10.19. Found: C, 79.63; H, 10.11.

5.3.9. 3-[(*E*)-Heptenoyl]cyclohexanone (21). Colorless oil, ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, *J*=7.3 Hz, 3H), 1.29–1.48 (m, 4H), 1.67–1.77 (m, 2H), 1.99–2.11 (m, 2H), 2.20–2.40 (m, 5H), 2.52–2.59 (m, 1H), 3.06–3.13 (m, 1H), 6.12 (td, *J*=1.4, 15.7 Hz, 1H), 6.91 (td, *J*=7.0, 15.7 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.8, 22.2, 24.9, 27.7, 30.1, 32.2, 41.0, 42.8, 47.8, 128.1, 149.0, 199.8, 210.3; IR (neat) ν 1714, 1666 cm^{-1}; EIMS *m/z* 208 (M^+); HRMS calcd for $C_{13}H_{20}O_2$: 208.14633. Found: 208.14677.

5.3.10. (*E*)-4-Phenyl-6-undecen-2,5-dione (23). Colorless oil, ^1H NMR (400 MHz, $CDCl_3$) δ 0.84 (t, *J*=7.3 Hz, 3H), 1.19–1.39 (m, 4H), 2.10 (dq, *J*=1.4, 7.0 Hz, 2H), 2.16 (s, 3H), 2.59 (dd, *J*=4.2, 17.8 Hz, 1H), 3.44 (dd, *J*=9.8, 17.8 Hz, 1H), 4.40 (dd, *J*=4.2, 9.8 Hz, 1H), 6.06 (td, *J*=1.4, 15.7 Hz, 1H), 6.80 (td, *J*=7.0, 15.7 Hz, 1H), 7.17–7.32 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.7, 22.1, 30.0, 30.1, 32.1, 46.6, 51.6, 127.3, 128.3, 128.5, 129.0, 138.4, 148.5, 197.9, 206.8; IR (neat) ν 1718, 1670 cm^{-1}; EIMS *m/z* 258 (M^+). Anal. calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 79.00; H, 8.54.

5.4. 1,4-Regioselective acylation of α,β-ynones 24: general procedure

To a THF solution (5 mL) of acylzirconocene chloride **1** were added a solution of α,β-ynone **24** (1 mmol) in ether (10 mL) and $PdCl_2(PPh_3)_2$ (10 mol%) at 0°C. After the reaction mixture was stirred for 12 h at ambient temperature, the mixture was treated with aq. $NaHCO_3$ and extracted with ether. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude product was purified by column chromatography (hexane/ethyl acetate=40:1) to give pure 1,4-acylation product **25** as each stereoisomer.

5.4.1. (*E*)-3-Butyl-1-phenyl-2-dodecene-1,4-dione [(*E*)-25b]. ^1H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, *J*=7.1 Hz, 3H), 0.88 (t, *J*=6.9 Hz, 3H), 1.30–1.39 (m,14H), 1.66–1.70 (quint, *J*=7.2 Hz, 2H), 2.58 (t, *J*=7.6 Hz, 2H), 2.75 (t, *J*=7.4 Hz, 2H), 7.32 (s, 1H), 7.47–7.94 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.7, 14.0, 22.6, 22.9, 24.4, 27.6, 29.1, 29.2, 29.4, 31.4, 31.8, 38.6, 128.5, 128.8, 129.8, 133.5, 137.5, 152.5, 193.0, 202.9; IR (neat) ν 2927, 1668, 1607 cm^{-1}; EIMS *m/z* 328 (M^+); HRMS calcd for $C_{22}H_{32}O_2$ 328.24023. Found 328.24006.

5.4.2. (*Z*)-3-Butyl-1-phenyl-2-dodecene-1,4-dione [(*Z*)-25b]. ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J*=6.9 Hz, 3H), 0.95 (t, *J*=7.3 Hz, 3H), 1.26–1.35 (m, 10H), 1.38–1.44 (m, 2H), 1.52–1.59 (m, 2H), 1.68–1.76 (quint, *J*=7.42 Hz, 2H), 2.35–2.40 (m, 2H), 2.55 (t, *J*=7.58 Hz, 2H), 6.77 (t, *J*=1.43 Hz, 1H), 7.44–7.94 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.7, 14.0, 22.3, 22.6, 23.3, 29.0, 29.1, 29.2, 29.4, 31.8, 34.5, 41.5, 120.2, 128.5, 128.6, 133.1, 137.2, 162.5, 189.1, 209.2; IR (neat) ν 2927, 1662, 1605 cm^{-1}; EIMS *m/z* 328 (M^+); HRMS calcd for $C_{22}H_{32}O_2$ 328.24023. Found 328.24195.

5.4.3. (*E*)-4-(1,1-Dimethylethyl)-3-tridecene-2,5-dione [(*E*)-25c]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (dd, J=6.9, 6.0 Hz, 3H), 1.18 (d, J=6.58 Hz, 9H), 1.23–1.25 (m, 10H), 1.54–1.57 (quint, J=6.8 Hz, 2H), 2.24 (d, J=0.5 Hz, 1H), 2.50–2.53 (t, J=7.3 Hz, 2H), 5.85 (s, 1H), 4.40 (s, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.0, 22.5, 23.4, 29.0, 29.3, 29.6, 31.7, 31.8, 35.4, 42.9, 126.3, 160.9, 201.1, 207.3; IR (neat) ν 2930, 1706, 1636 cm^{-1}; EIMS m/z 266 (M^+); HRMS calcd for $C_{17}H_{30}O_2$ 266.22458. Found 266.22514.

5.4.4. (*Z*)-4-(1,1-Dimethylethyl)-3-tridecene-2,5-dione [(*Z*)-25c]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, J=6.9 Hz, 3H), 1.15 (s, 9H), 1.26–1.29 (m, 10H), 1.67–1.75 (quint, J=7.4 Hz, 2H), 2.20 (s, J=6.4 Hz, 3H), 2.42 (t, J=7.6 Hz, 2H), 6.12 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.0, 22.6, 23.2, 29.1, 29.2, 29.3, 29.4, 30.5, 31.8, 35.4, 43.7, 121.1, 169.0, 197.1, 209.0; IR (neat) ν 2925, 1696, 1598 cm^{-1}; EIMS m/z 266 (M^+); HRMS calcd for $C_{17}H_{30}O_2$ 266.22458. Found 266.22511.

5.4.5. (*E*)-4-Phenyl-3-tridecene-2,5-dione [(*E*)-25a]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, J=6.9 Hz, 3H), 1.23–1.29 (m, 10H), 1.56–1.58 (m, 2H), 1.87 (s, 2H), 2.56 (t, J=7.3 Hz, 2H), 6.79 (s, 1H), 7.16–7.41 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1, 22.6, 24.0, 29.0, 29.2, 30.5, 31.7, 40.2, 128.6, 128.9, 129.0, 133.9, 134.5, 147.8, 201.2, 202.2; IR (neat) ν 2925, 2854, 1687 cm^{-1}; EIMS m/z 286 (M^+); HRMS calcd for $C_{19}H_{26}O_2$ 286.19328. Found 286.19249.

5.4.6. (*Z*)-4-Phenyl-3-tridecene-2,5-dione [(*Z*)-25a]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, J=6.9 Hz, 3H), 1.18–1.32 (m, 10H), 1.70 (quint, J=7.4 Hz, 2H), 2.31 (s, 3H), 2.56 (t, J=7.6 Hz, 2H), 6.50 (s, 1H), 7.38–7.41 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1, 22.6, 23.4, 29.0, 29.1, 29.3, 30.5, 31.8, 42.3, 122.2, 126.9, 129.0, 130.5, 133.2, 156.8, 196.6, 207.4; IR (neat) ν 2925, 1686 cm^{-1}; EIMS m/z 286 (M^+); HRMS calcd for $C_{19}H_{26}O_2$ 286.19328. Found 286.19420.

5.4.7. (*E*)-1-Phenyl-3-{2-[(phenylmethyl)oxy]ethyl}-2-dodecene-1,4-dione [(*E*)-25d]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J=6.3 Hz, 3H), 1.27–1.32 (m, 12H), 1.60–1.65 (quint, J=7.2 Hz, 2H), 2.76 (t, J=7.4 Hz, 2H), 2.99 (t, J=6.4 Hz, 2H), 3.60 (t, J=6.4 Hz, 2H), 4.40 (s, 2H), 7.19–7.93 (m, 9H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.4, 23.0, 24.6, 28.5, 29.5, 29.6, 29.8, 32.2, 39.1, 69.6, 73.0, 127.7, 127.8, 128.6, 129.0, 129.1, 131.3, 133.9, 137.8, 138.7, 150.0, 193.1, 203.1; IR (neat) ν 2924, 2854, 1666 cm^{-1}; EIMS m/z 406 (M^+); HRMS calcd for $C_{27}H_{34}O_3$ 406.25079. Found 406.25227.

5.4.8. (*Z*)-1-Phenyl-3-{2-[(phenylmethyl)oxy]ethyl}-2-dodecene-1,4-dione [(*Z*)-25d]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, J=6.9 Hz, 3H), 1.19–1.26 (m, 10H), 1.64–1.69 (quint, J=7.2 Hz, 2H), 2.54 (t, J=7.6 Hz, 2H), 2.67–2.70 (dt, J=1.2, 6.2 Hz, 2H), 3.69 (t, J=6.2 Hz, 2H), 4.54 (s, 2H), 6.88 (t, J=1.2 Hz, 1H), 7.27–7.92 (m, 10H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.1, 21.6, 22.3, 28.1, 28.4, 28.6, 30.8, 34.1, 40.6, 66.3, 72.2, 121.7, 126.8, 127.4, 127.5, 127.6, 132.2, 136.1, 136.8, 157.1, 188.3, 207.7; IR (neat) ν 2917, 2850, 1698 cm^{-1}; EIMS m/z 406 (M^+); HRMS calcd for $C_{27}H_{34}O_3$ 406.25079. Found 406.24908.

5.4.9. (*E*)-3-(1,1-Dimethylethyl)-1-phenyl-2-dodecene-1,4-dione [(*E*)-25e]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, J=6.8 Hz, 3H), 1.14 (s, 9H), 1.21–1.31 (m, 10H), 1.62–1.77 (quint, J=7.2 Hz, 2H), 2.70 (t, J=7.3 Hz, 2H), 6.33 (s, 1H), 7.44 (t, J=7.4 Hz, 2H), 7.57–7.96 (m, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1, 22.6, 23.8, 29.1, 29.2, 29.4, 30.1, 31.8, 36.2, 43.1, 126.3, 128.7, 129.0, 133.7, 136.9, 159.3, 195.7, 207.2; IR (neat) ν 2926, 1670 cm^{-1}; EIMS m/z 328 (M^+). Anal. calcd for $C_{22}H_{32}O_2$: C, 80.44; H, 9.82. Found: C, 80.17; H, 9.80.

5.4.10. (*Z*)-3-(1,1-Dimethylethyl)-1-phenyl-2-dodecene-1,4-dione [(*Z*)-25e]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, J=7.0 Hz, 3H), 1.25–1.36 (m, 19H), 1.73–1.81 (quint, J=7.4 Hz, 2H), 2.52 (t, J=7.6 Hz, 2H), 6.90 (s, 1H), 7.45–7.94 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.0, 22.6, 23.3, 29.1, 29.2, 29.4, 31.8, 36.1, 43.8, 118.0, 128.4, 128.6, 133.3, 137.7, 170.9, 189.4, 209.1; IR (neat) ν 2926, 1698, 1662, 1599 cm^{-1}; EIMS m/z 328 (M^+). Anal. calcd for $C_{22}H_{32}O_2$: C, 80.44; H, 9.82. Found: C, 80.35; H, 9.78.

5.4.11. (*E*)-5-Butyl-2,2-dimethyl-4-tetradecene-3,6-dione [(*E*)-25f]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, J=7.1 Hz, 3H), 0.89 (t, J=7.1 Hz, 3H), 1.18 (s, 9H), 1.27–1.36 (m, 14H), 1.58–1.64 (m, 2H), 2.57 (t, J=7.3 Hz, 2H), 2.66 (t, J=7.4 Hz, 2H), 7.00 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.8, 14.0, 22.6, 22.9, 24.4, 26.2, 27.2, 29.1, 29.2, 29.3, 31.5, 31.8, 38.7, 44.3, 127.4, 152.8, 203.3, 207.4; IR (neat) ν 3000, 1685, 1608 cm^{-1}; EIMS m/z 308 (M^+); HRMS calcd for $C_{20}H_{36}O_2$ 308.27153. Found 308.26984.

5.4.12. (*Z*)-5-Butyl-2,2-dimethyl-4-tetradecene-3,6-dione [(*Z*)-25f]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, J=6.9 Hz, 3H), 0.92 (t, J=7.3 Hz, 3H), 1.15 (s, 9H), 1.27–1.40 (m, 12H), 1.47 (quint, J=7.4 Hz, 2H), 1.66 (m, 2H), 2.23–2.27 (m, 2H), 2.45 (t, J=7.6 Hz, 2H), 6.26 (t, J=1.3 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.7, 14.0, 22.2, 22.6, 23.3, 26.1, 29.11, 29.17, 29.2, 29.4, 31.8, 34.2, 41.3, 42.9, 119.2, 161.2, 203.9, 209.6; IR (neat) ν 2928, 1760, 1608 cm^{-1}; EIMS m/z 308 (M^+); HRMS calcd for $C_{20}H_{36}O_2$ 308.27153. Found 308.27088.

5.4.13. (*E*)-3-Butyl-1-(2-naphthalenyl)-2-dodecene-1,4-dione [(*E*)-25g]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, J=7.2 Hz, 3H), 0.89 (t, J=6.8 Hz, 3H), 1.29–1.40 (m, 14H), 1.71 (quint, J=7.3 Hz, 2H), 2.61 (t, J=7.7 Hz, 2H), 2.81 (t, J=7.4 Hz, 2H), 7.46 (s, 1H), 7.56–8.48 (m, 7H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.7, 14.0, 22.6, 22.8, 24.4, 27.7, 29.1, 29.3, 29.4, 31.4, 31.8, 38.7, 123.8, 126.9, 127.8, 128.8, 129.6, 130.0, 130.6, 132.4, 134.8, 135.8, 152.3, 192.9, 203.0; IR (neat) ν 2926, 2856, 1662, 1626 cm^{-1}; EIMS m/z 378 (M^+); HRMS calcd for $C_{26}H_{34}O_2$ 378.25588. Found 378.25516.

5.4.14. (*Z*)-3-Butyl-1-(2-naphthalenyl)-2-dodecene-1,4-dione [(*Z*)-25g]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, J=7.0 Hz, 3H), 0.98 (t, J=7.3 Hz, 3H), 1.25–1.31 (m, 10H), 1.43–1.48 (m, 2H), 1.59–1.62 (m, 2H), 1.75 (quint,

J=7.4 Hz, 2H), 2.40–2.45 (m, 2H), 2.59 (t, J=7.6 Hz, 2H), 6.93 (t, J=1.4 Hz, 1H), 7.55–8.45 (m, 7H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.8, 14.0, 22.4, 22.6, 23.4, 29.1, 29.2, 29.3, 29.4, 31.8, 34.6, 41.6, 120.4, 124.2, 126.8, 127.8, 128.6, 129.6, 130.1, 132.5, 134.6, 135.6, 162.4, 189.0, 209.2; IR (neat) ν 2926, 1658, 1602 cm^{-1}; EIMS m/z 378 (M^+); HRMS calcd for $C_{26}H_{34}O_2$ 378.25588. Found 378.25458.

5.4.15. (*E*)-3-Butyl-5-cyclohexyl-1-phenyl-2-pentene-1,4-dione [(*E*)-25h]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81 (t, J=7.1 Hz, 3H), 1.09–1.72 (m, 12H), 1.80–1.85 (dd, J=1.2, 14.2 Hz, 2H), 1.95–2.05 (m, 1H), 2.34–2.38 (quint, J=8.2 Hz, 2H), 2.48 (d, J=6.5 Hz, 2H), 6.75 (s, 1H), 7.42–7.98 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.8, 22.3, 26.2, 26.4, 29.3, 32.7, 33.3, 34.3, 48.6, 120.5, 128.5, 128.7, 133.1, 137.4, 162.1, 189.2, 208.1; IR (neat) ν 2924, 1668 cm^{-1}; EIMS m/z 312 (M^+); HRMS calcd for $C_{21}H_{28}O_2$ 312.20893. Found: 312.20893.

5.4.16. (*Z*)-3-Butyl-5-cyclohexyl-1-phenyl-2-pentene-1,4-dione [(*Z*)-25h]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, J=7.3 Hz, 3H), 1.09–1.72 (m, 12H), 1.80–1.85 (dd, J=1.2, 14.2 Hz, 2H), 1.95–2.05 (m, 1H), 2.34–2.38 (quint, J=8.2 Hz, 2H), 2.48 (d, J=6.5 Hz, 2H), 6.75 (s, 1H), 7.42 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.8, 22.3, 26.2, 26.4, 29.3, 32.7, 33.3, 34.4, 48.6, 120.5, 128.5, 128.7, 133.1, 137.4, 162.1, 189.2, 208.1; IR (neat) ν 2926, 1690 cm^{-1}; EIMS m/z 312 (M^+); HRMS calcd for $C_{21}H_{28}O_2$ 312.20893. Found: 312.20894.

5.4.17. (*E*)-3-Butyl-7,7-dimethyl-1-phenyl-2-octene-1,4-dione [(*E*)-25i]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J=7.0 Hz, 3H), 0.95 (s, 9H), 1.23–1.56 (m, 6H), 2.57 (t, J=8.0 Hz, 2H), 2.68–2.77 (m, 2H), 7.33 (s, 1H), 7.45–7.97 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.8, 22.9, 27.6, 29.2, 30.2, 31.4, 34.4, 38.1, 128.6, 128.9, 129.8, 133.5, 152.4, 193.1, 203.3; IR (neat) ν 2930, 1690 cm^{-1}; EIMS m/z 300 (M^+); HRMS calcd for $C_{20}H_{28}O_2$ 300.20893. Found: 300.20892.

5.4.18. (*Z*)-3-Butyl-7,7-dimethyl-1-phenyl-2-octene-1,4-dione [(*Z*)-25i]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (s, 9H), 0.94 (t, J=7.0 Hz, 3H), 1.41 (quint, J=7.2 Hz, 2H), 1.54–1.58 (m, 2H), 1.65–1.69 (m, 2H), 2.30–2.41 (dt, J=1.4, 8.3 Hz, 2H), 2.51–2.54 (m, 2H), 6.78 (t, J=1.3 Hz, 1H), 7.44 (t, J=7.8 Hz, 2H), 7.56 (t, J=7.0 Hz, 1H), (d, J=7.1 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.7, 22.3, 29.1, 29.2, 30.0, 34.6, 37.0, 37.2, 120.2, 128.5, 128.6, 133.1, 137.3, 162.5, 189.2, 209.7; IR (neat) ν 2900, 1688 cm^{-1}; EIMS m/z 300 (M^+); HRMS calcd for $C_{20}H_{28}O_2$ 300.20893. Found: 300.20895.

5.4.19. 3-Acetyl-4-butyl-2-phenyl-2-cyclopenten-1-one (28a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, J=6.9 Hz, 3H), 1.17–1.28 (m, 5H), 1.70–1.73 (m, 1H), 2.05 (s, 3H), 2.30–2.35 (dd, J=2.1, 1.9 Hz, 1H), 2.72–2.78 (dd, J=6.7, 19.1 Hz, 1H), 3.28 (s, 1H), 7.23–7.40 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.0, 27.4, 29.0, 29.2, 30.6, 31.6, 39.4, 41.2, 128.6, 128.8, 129.1, 130.2, 142.2, 169.8, 203.4, 206.6; IR (neat) ν 3389, 1700 cm^{-1}; EIMS m/z 256 (M^+); HRMS calcd for $C_{17}H_{20}O_2$ 256.14633. Found: 256.14635.

5.4.20. 2,4-Dibutyl-3-(phenylcarbonyl)-2-cyclopenten-1-one (28b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.72 (t, J=7.3 Hz, 3H), 0.79 (t, J=6.8 Hz, 3H), 1.22–1.30 (m, 9H), 1.58 (m, 1H), 2.01–2.10 (m, 2H), 2.19–2.24 (dd, J=2.2, 18.9 Hz, 1H), 2.68–2.74 (dd, J=6.5, 18.9 Hz, 1H), 3.23 (s, 1H), 7.49 (t, J=7.8 Hz, 2H), 7.63 (t, J=7.4 Hz, 1H), 7.84 (d, J=7.1 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.5, 13.8, 22.4, 22.5, 23.7, 29.8, 30.1, 33.5, 40.9, 41.0, 128.9, 129.0, 134.2, 135.9, 143.7, 168.7, 197.0, 208.0; IR (neat) ν 1709, 1662 cm^{-1}; EIMS m/z 398 (M^+); HRMS calcd for $C_{20}H_{26}O_2$ 298.19328. Found: 298.19327.

5.4.21. 2-Butyl-4-(2-{[(1,1-dimethylethyl)(diphenyl)-silyl-oxy]}ethyl)-3-(phenylcarbonyl)-2-cyclopenten-1-one (28c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.72 (t, J=7.6 Hz, 3H), 0.97 (s, 9H), 1.06–1.43 (m, 5H), 1.85–1.89 (m, 1H), 2.02–2.13 (m, 2H), 2.21–2.27 (dd, J=2.2, 19.0 Hz, 1H), 2.63–2.69 (dd, J=6.5, 19.0 Hz, 1H), 3.45–3.69 (m, 3H), 7.30–7.86 (m, 15H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.9, 19.4, 22.9, 24.2, 27.1, 27.3, 30.6, 36.9, 38.4, 41.5, 62.4, 128.0, 128.1, 129.4, 129.5, 130.0, 133.7, 133.8, 134.6, 135.8, 135.9, 136.2, 144.4, 169.1, 197.2, 208.3; IR (neat) ν 1688 cm^{-1}; EIMS m/z 524 (M^+); HRMS calcd for $C_{34}H_{40}O_3Si$ 524.27467. Found: 524.27468.

5.5. Enantioselective 1,2-acylation: general procedure

To a toluene solution of acylzirconocene chloride, which was generated from alkene or alkyne (2.0 mmol) and $Cp_2Zr(H)Cl$ (1.0 mmol) in CH_2Cl_2 (8 mL) as described before, were added α,β-unsaturated ketone (1 mmol), $Pd(OAc)_2$ (5 mol%) and (*R*)-MeO-MOP (10 mol%) at 0°C. After the reaction mixture was stirred for 20 h at ambient temperature, the mixture was treated with aq. $NaHCO_3$ and extracted with ether. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude product was purified by column chromatography (hexane/ethyl acetate) to give pure 1,2-acylation product.

5.5.1. 1-(1-Hydroxy-2-cyclopenten-1-yl)-1-nonanone (31). Colorless oil, 67% ee, $[\alpha]_D^{25.0}$=+36.32 (c 1.02, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, J=6.8 Hz, 3H), 1.17–1.30 (m, 10H), 1.37–1.44 (m, 1H), 1.52–1.65 (m, 3H), 1.97 (td, J=8.7, 13.7 Hz, 1H), 2.17–2.23 (m, 1H), 2.44–2.48 (m, 2H), 3.65 (s, 1H), 6.03 (td, J=2.0, 10.0 Hz, 1H), 6.90–9.94 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1, 22.6, 23.0, 25.3, 29.2, 29.5, 29.9, 31.8, 33.9, 36.0, 75.4, 126.5, 150.8, 202.9; IR (neat) ν 3496, 1681 cm^{-1}; EIMS m/z 224 (M^+); HRMS calcd for $C_{14}H_{24}O_2$: 224.17763. Found: 224.17808.

5.5.2. 1-[(1*R*)-1-Hydroxy-2-cyclohexen-1-yl]-1-nonanone [(*R*)-2]. Colorless oil, 66% ee, $[\alpha]_D^{24.0}$=−42.11 (c 1.04, $CHCl_3$). ^{1}H NMR spectrum was identical to racemic **2**.

5.5.3. 1-[(1*R*)-1-Hydroxy-2-cyclohepten-1-yl]-1-nonanone (*ent*-5). Colorless oil, 38% ee, $[\alpha]_D^{23.0}$=−35.65 (c 0.92, $CHCl_3$). ^{1}H NMR spectrum was identical to recemic **5**.

5.5.4. (*E*)-3-Methyl-1-phenyl-1-dodecene-3-ol-4-one (*ent*-7). Colorless oil 17% ee, $[\alpha]_D^{24.8}$=−37.96 (c 1.11, $CHCl_3$). ^{1}H NMR spectrum was identical to racemic **7**.

5.5.5. (*E*)-4-Phenyl-2-tridecene-4-ol-5-one (*ent*-8). Colorless oil 6% ee.[27] ^{1}H NMR spectrum was identical to racemic **8**.

5.6. Preparation of (*S*)-2

5.6.1. 1-(1-Cyclohexen-1-yl)-1-nonanol (34). Under an argon atmosphere, to a cold (−78°C) suspension of cyclohexanone-*p*-toluenesulfonylhydrazone (5 g, 18.8 mmol) and TMEDA (50 mL) in hexane (600 mL) was slowly added a *n*-BuLi (1.46 M in hexane, 28.8 mL). The mixture was stirred at the same temperature for 0.5 and 8 h at ambient temperature. After the mixture was chilled at −78°C, a solution of 1-*n*-nonanal (2.9 mL, 17.1 mmol) in TMEDA (10 mL) was added and the mixture was stirred for 2 h at −78°C and 8 h at ambient temperature. The reaction mixture was treated with H_2O and extracted with ether. The combined ether layer was washed with brine, dried over $MgSO_4$ and filtered. Concentration of the filtrate gave a crude residue which was purified by column chromatography (hexane/ethyl acetate=20:1) gave pure oil **34** (1.83 g, 48%). **34**; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J=6.7 Hz, 3H), 1.20–1.37 (m, 14H), 1.49–1.65 (m, 5H), 1.88–2.08 (m, 4H), 3.94 (t, J=6.7 Hz, 1H), 5.64 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1, 22.7, 23.3, 24.0, 25.8, 29.3, 29.6, 29.7, 31.9, 34.8, 76.7, 123.0, 140.1; IR (neat) ν 3346 cm^{-1}; EIMS *m*/*z* 224 (M^+). Anal. calcd for $C_{15}H_{28}O$: C, 80.29; H,12.58. Found: C, 80.32; H, 12.31.

5.6.2. (1*R*)-1-(1-Cyclohexen-1-yl)-1-nonanol [(*R*)-34]. To a solution of *rac*-**34** (1.69 g, 7.5 mmol) in CH_2Cl_2 (100 mL) were added Ti(O-*i*Pr)$_4$ (2.2 mL, 7.5 mmol) and L-(+)-DIPT (2.1 g, 9 mmol). After the mixture was chilled at −20°C, *t*BuOOH was added and the mixture was stood overnight at the same temperature. The mixture was poured into H_2O/acetone (1:10, 30 mL) and stirred for 1 h. After addition of sat. aq. NaCl–30% NaOH solution, the mixture was extracted with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$, filtered and concentrated. Purification of the reaction product by silica gel column chromatography (hexane/ethyl acetate=50:1) gave (*R*)-**34** (90% ee, 756 mg, 45%) and epoxy alcohol (49% ee, 767 mg, 43%). (*R*)-**34**: colorless oil, $[\alpha]_D^{23.0}$=+6.6 (*c* 0.50, $CHCl_3$).

5.6.3. (1*R*)-1-[(6*R*)-7-Oxabicyclo[4.1.0]hept-1-yl]-1-nonanol (35). According to the same procedure described for the kinetic resolution of **34**, The epoxidation of (*R*)-**34** was carried out by utilizing D-(−)-DIPT to give **35** (>95% ee, 692 mg, 90%). **35**; $[\alpha]_D^{26.0}$=+26.12 (*c* 1.38, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J=6.9 Hz, 3H), 1.22–1.61 (m, 18H), 1.70–1.84 (m, 3H), 1.96–2.04 (m, 1H), 2.13 (s, 1H), 3.20 (d, J=2.5 Hz, 1H), 3.54 (d, J=7.0 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1, 19.7, 20.4, 22.7, 24.5, 25.1, 25.8, 29.3, 29.5, 29.8, 31.9, 32.8, 55.4, 62.3, 71.7; IR (neat) ν 3449, 2928, 2856, 1723 cm^{-1}; EIMS *m*/*z* 240 (M^+). Anal. calcd for $C_{15}H_{28}O_2$: C, 74.95; H,11.74. Found: C, 74.77; H, 11.42.

5.6.4. (1*R*,2*S*)-1-[(1*R*)-1-Hydroxynonyl]-2-(phenylselanyl)-cyclohexanol (36). To a solution of PhSeNa, which was prepared from PhSeSePh (346 mg, 1.1 mmol) and $NaBH_4$ (87 mg, 2.3 mmol) in ethanol (10 mL), was added a solution of **35** (400 mg, 1.7 mmol) in ethanol (3 mL) at 0°C and the mixture was stirred at ambient temperature overnight. After addition of aq. $NaHCO_3$, the mixture was extracted with ether and the combined ether layer was washed with brine before drying ($MgSO_4$). Concentration of the filtrate to dryness and purification by silica gel column chromatography (hexane/ethyl acetate=60:1) gave **36** (661 mg, 95%) as colorless crystals. **36**; $[\alpha]_D^{26.0}$=+43.24 (*c* 0.60, $CHCl_3$), mp 91.0–92.5°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J=6.9 Hz, 3H), 1.24–1.36 (m, 11H), 1.46–1.63 (m, 7H), 1.70–1.94 (m, 4H), 2.10 (brs 1H), 2.17–2.24 (m, 1H), 3.32 (d, J=2.1 Hz, 1H), 3.74 (d, J=10.5 Hz, 1H), 7.23–7.26 (m, 3H), 7.51–7.53 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1, 20.9, 21.5, 22.7, 26.0, 28.4, 28.9, 29.3, 29.6, 31.5, 31.9, 50.2, 75.2, 76.6, 127.5, 129.1, 130.2, 133.9; IR (neat) ν 3388 cm^{-1}; EIMS *m*/*z* 398 (M^+). Anal. calcd for $C_{21}H_{34}O_2Se$: C, 63.46; H,8.66. Found: C, 63.48; H, 8.58.

5.6.5. (4*R*,5*R*,6*S*)-2-Methoxy-4-octyl-6-(phenylselanyl)-1,3-dioxaspiro[4,5]decane (37). To a solution of **36** (300 mg, 0.75 mmol) in DMF (3 mL) were added trimethyl orthoformate (3 mL) and a catalytic amount of PPTS, and the mixture was stirred for 4 h at ambient temperature. After pouring the mixture into aq. $NaHCO_3$, the mixture was extracted with ether. The combined ether layer was washed with brine, dried over $MgSO_4$ and filtered. Concentration of the filtrate gave crude oil which was purified by silica gel column chromatography (hexane/ethyl acetate=40:1) to give **37** (330 mg, quant). **37**; $[\alpha]_D^{27.0}$=+41.13 (*c* 0.50, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J=6.9 Hz, 3H), 1.25–1.47 (m, 14H), 1.55–1.98 (m, 9H), 3.36 (s, 3H), 3.81 (dd, J=2.1, 11.2 Hz, 1H), 5.65 (s, 1H), 7.24–7.27, (m, 3H), 7.47–7.50 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1, 20.9, 21.2, 22.7, 25.7, 28.7, 29.2, 29.3, 29.4, 31.9, 31.9, 47.4, 52.6, 83.0, 85.4, 116.0, 127.3, 129.2, 130.6, 132.9; EIMS *m*/*z* 440 (M^+). Anal. calcd for $C_{23}H_{36}O_3Se$: C, 62.86; H, 8.26. Found: C, 62.85; H, 8.21.

5.6.6. 1-[(1*S*)-1-Hydroxy-2-cyclohexen-1-yl]-1-nonanone [(*S*)-2]. (1) *Elimination of PhSe-group and deprotection of **37**.* To an aq. THF (85%) solution (8 mL) of **37** (302 mg, 0.7 mmol) was added $NaIO_4$ (1.5 g, 7 mmol) and the mixture was stirred overnight at ambient temperature. After the addition of aq. $NaHCO_3$, the mixture was extracted with ether. The ether solution was washed with brine, dried and filtered before concentration. Purification of the crude product by silica gel column chromatography (hexane/ethyl acetate=60:1) gave an elimination product (85 mg), whose CH_2Cl_2 solution (85 mg in 5 mL) was treated with DIBAL-H at −78°C and the solution was stirred at 0°C for 10 min. After adding 2 M solution of NaOH, the mixture was extracted with ether. The ether solution was washed with brine, dried over $MgSO_4$ and filtered before concentration. Purification by silica gel column chromatography (hexane/ethyl acetate=7:1) gave (1*S*)-1-[(1*R*)-1-hydroxynonyl]-2-cyclohexen-1-ol (56 mg, 35% yield from 37). (1*S*)-1-[(1*R*)-1-hydroxynonyl]-2-cyclohexen-1-ol: $[\alpha]_D^{24.0}$=+40.15 (*c* 0.50, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J=6.9 Hz, 3H), 1.27–1.36 (m, 12H), 1.43–1.49 (m, 1H), 1.56–1.65 (m, 2H), 1.67–1.76 (m, 3H), 1.91–2.10 (m, 3H), 2.67 (s, 1H), 3.46, (d, J=9.0 Hz, 1H), 5.73 (d, J=10.2 Hz, 1H), 5.93–5.97 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ

14.1, 18.6, 22.7, 25.4, 26.7, 29.3, 29.6 29.7, 31.1, 31.9, 32.0, 72.2, 76.8, 128.3, 132.4; IR (neat) ν 3396, 2924 cm^{-1}; EIMS *m/z* 223 (M^+-OH); HRMS calcd for $C_{15}H_{27}O$ (M^+-OH): 223.20619. Found: 223.20717.

(2) *Swern oxidation*. To a solution of $(COCl)_2$ (0.03 mL, 023 mmol) in CH_2Cl_2 (7 mL) was added DMSO (0.05 mL, 0.69 mmol) at −60°C and the mixture was stirred for 0.5 h at the same temperature. To the reaction mixture was added a solution of (1*S*)-1-[(1*R*)-1-hydroxynonyl]-2-cyclohexen-1-ol (56 mg, 0.23 mmol) in CH_2Cl_2 (2 mL) at −60°C and the mixture was stirred for 15 min at the same temperature. After addition of $(C_2H_5)_3N$ (0.1 mL, 0.74 mmol), the mixture was stirred 5 min at −60°C and 1 h at ambient temperature. After being added H_2O, the mixture was extracted with ether. The combined ether layer was washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude oil was purified by column chromatography (hexane/ethyl acetate=50:1) to give (*S*)-**2** (41 mg, 75% yield). (*S*)-**2**: $[\alpha]_D^{26.6}$=+45.56 (*c* 0.57, $CHCl_3$). ^1H and ^{13}C NMR spectra were identical to those of *rac*-**2**.

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