Rh-catalyzed highly enantioselective formation of functionalized cyclopentanes and cyclopentanones†

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A catalyst system, $[Rh(COD)Cl]_2$–BINAP–$AgSbF_6$, has been developed as a second-generation catalyst for the cycloisomerization of 1,6-enynes tethered by carbon chains. Cyclopentanes and cyclopentanones, which can contain functional groups, such as the 1,4-dienes, vinyl ether, aldehyde *etc.*, were obtained from readily available starting materials in high yields and selectivities. Both regioselectivities and enantioselectivities are excellent: only 1,4-dienes were observed and in over 99% ee.

Introduction

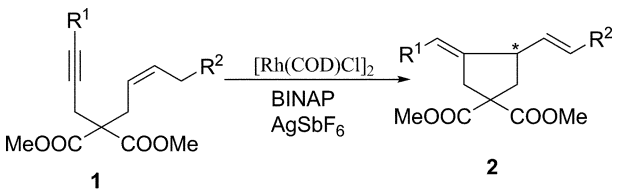
Cyclopentanes and cyclopentanones are amongst the most basic skeletons of organic molecules. Because numerous natural products and biologically active molecules contain these motifs, functionalized cyclopentanes and cyclopentanones are obviously valuable building blocks for the construction of complex molecules. The syntheses of natural products such as prostaglandins and jasmonates illustrate the significance of developing a highly efficient methodology for the formation of cyclopentanes and cyclopentanones.[1]

Without doubt, the transition metal-catalyzed Alder-ene type cycloisomerization of enynes is an elegant method to form these skeletons.[2–8] Since pioneering work was done with Pd-catalysts, which lead to 1,3- and 1,4-dienes,[9,10] highly regioselective cycloisomerization of enynes forming 1,4-dienes, has been carried out using Ti-,[11] Ru-,[12] and Rh-catalysts.[13–15] The asymmetric version of this transformation has remained relatively unexplored and the development of efficient catalysts for this purpose still remains a challenge.[7,16–20] Efforts by the Trost lab in 1989[9] and 1994[10] were carried-out using a Pd-catalyst, chiral ligands, and chiral auxiliary groups. Recently, Mikami *et al.* reported the Pd-mediated cycloisomerization of enynes in excellent enantioselectivities.[21–26] However, its application in forming cyclopentanes and cyclopentanones in high enantioselectivities is still not satisfactory.[9,10] Fürstner *et al.* developed a beautiful cycloisomerization of enynes promoted by an Fe-catalyst to form carbobicyclic compounds,[27] while producing the enantiomerically pure carbobicyclic compounds remains a challenge. Very recently, Nicolaou *et al.* showed the potential of the Rh-catalyzed enyne cycloisomerization in the total syntheses of platensimycin, which includes racemic and asymmetric versions.[28,29]

Previously, the $[Rh(diphos)Cl]_2$–$AgSbF_6$ system for the intramolecular Alder-ene reaction of 1,6-enynes was reported.[15,30] Two years later, the second-generation catalyst, $[Rh(COD)Cl]_2$–BINAP–$AgSbF_6$ was proven to be more efficient and convenient for the cycloisomerization to form lactones, lactams, and tetrahydrofurans.[31–35] Herein, we communicate our results on the highly enantioselective formation of functionalized cyclopentanes and cyclopentanones by employing a second-generation catalyst in the cycloisomerization of 1,6-enynes with a carbon tether.

Results and discussion

The reaction of enyne **1a** in the presence of the second-generation catalyst was examined first. It was carried out in the presence of 5 mol% $[Rh(COD)Cl]_2$, 11 mol% (*S*)-BINAP, and 20 mol% $AgSbF_6$. Although the corresponding desired product can be identified *via* NMR and GC, a complicated mixture was produced, from which it was difficult to isolate the product. However, the rapid consumption of the starting material **1a** (100% conversion after 2 min reaction time) shows the high reactivity with this catalyst. We were then pleased to find that when substrate **1b** was employed in the cycloisomerization with the second-generation catalyst using (*S*)-BINAP as the ligand, the desired product **2b** was obtained exclusively in over 99% ee (Scheme 1). No 1,3-diene regioisomer was detected in this reaction.



Scheme 1 Rh(I)-catalyzed intramolecular Alder-ene reaction of 1,6-enynes.

Encouraged by the excellent regioselectivity and enantioselectivity with the reaction of **1b** shown in Scheme 1, we examined the reaction with the substrate, allylic ether **3** (Scheme 2). A versatile alkenyl ether will be the product if this reaction remains regiospecific. Our result is shown in Scheme 2. The corresponding alkenyl ether **4** was obtained in high yield and excellent ee value.

Our success in constructing cyclopentanes encouraged us to explore the formation of cyclopentanones using a similar strategy.

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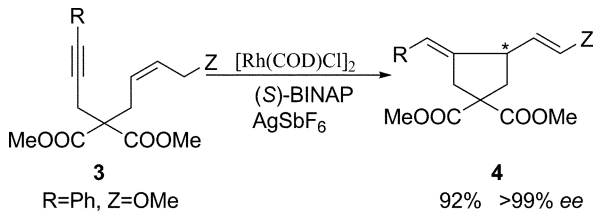
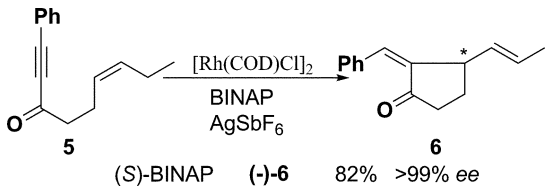


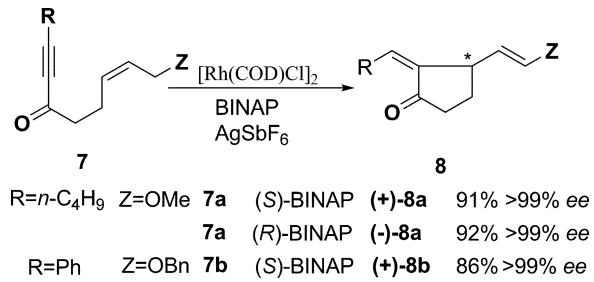
Scheme 2 Formation of functionalized cyclopentanes.

First, enyne **5** was examined as a substrate, and the results are shown in Scheme 3. The desired product, cyclopentanone **6**, was obtained in high yield with excellent enantioselectivity in the presence of (*S*)-BINAP(Scheme 3).



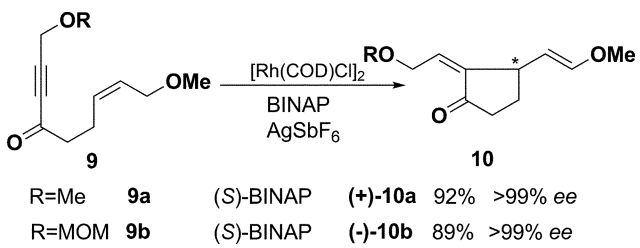
Scheme 3 Formation of functionalized cyclopentanones.

The results detailed above promoted us to further explore the formation of functionalized cyclopentanones. The cycloisomerization of **7a** and **7b** yielded the corresponding vinyl methyl ethers and benzyl ether substituted cyclopentanones **9a** and **9b** in high yields with over 99% ee (Scheme 4).



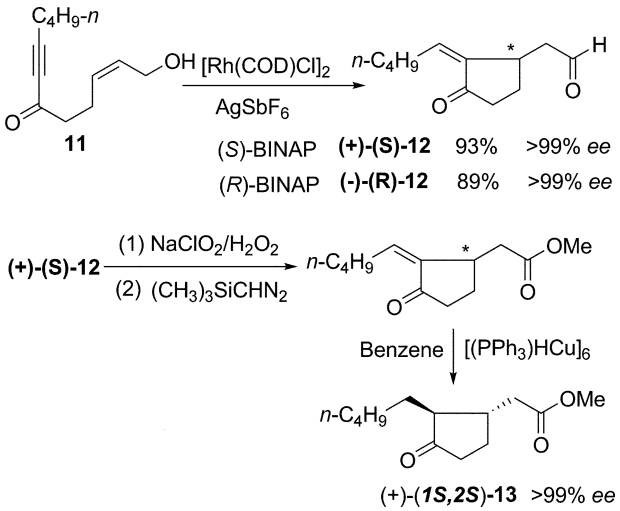
Scheme 4 Formation of polyfunctionalized cyclopentanones.

The results shown in Scheme 5 demonstrate our efforts in introducing more functional groups at the alkyne site in order to obtain a more flexible synthetic motif. The cyclopentanones, **10a** and **10b**, in which both side chains are functionalized, were formed in high yields and over 99% ee (Scheme 5).



Scheme 5 Formation of polyfunctionalized cyclopentanones.

The results of further experimentation are shown in Scheme 6. The unprotected allylic alcohol, **11**, also served as a good substrate in the Rh-catalyzed intramolecular Alder-ene reaction. The aldehyde-substituted cyclopentanone **12** was formed in high yield and over 99% ee.



Scheme 6 Synthesis of dihydrojasmonate (+)-(1*S*,2*S*)-**13**.

To demonstrate the synthetic utility of the cycloisomerization of enynes and identify the absolute configuration of the products, methyl dihydrojasmonate **13** was chosen as one of our target molecules. The synthesis started from (+)-**12**. After mild oxidation, methylation with $(CH_3)_3SiCHN_2$ [(trimethylsilyl)diazomethane, 2.0 M in hexane)] and reduction using $[(PPh_3)HCu]_6$ in benzene, *trans*-(+)-(1*S*,2*S*)-**13** was obtained in over 99% ee and high diastereoselectivity (*trans* : *cis* >97 : 3) from (+)-**12** in 62% overall yield. The results also revealed the absolute configuration of (+)-**12**: the (*S*)-configuration.[36]

Conclusion

In summary, a highly efficient Rh(I)-catalyzed intramolecular Alder-ene type cycloisomerization reaction of 1,6-enynes tethered by carbon chains was developed. Polyfunctionalized cyclopentanes and cyclopentanones were obtained in good yields. The regioselectivity is specific, and only 1,4-dienes were observed as the products. Excellent enantioselectivities were obtained in employing the commercially available BINAP as the ligand. Syntheses of more complex biologically active molecules and mechanistic details are currently under investigation in our laboratory and the results will be published in due course.

Experimental

General methods

All reactions were carried out in an inert atmosphere using standard Schlenk techniques. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker DPX-300, DRX-400 and AMX-360 spectrophotometers. 1,2-Dichloroethane was purchased from commercial sources (Aldrich) and used without further purification. All the substrates were synthesized according to the literature.[37]

General procedure for the asymmetric Alder-ene reaction catalyzed by rhodium complexes

In a dried Schlenk tube, $[Rh(COD)Cl]_2$ (2.5 mg, 0.005 mmol) and *S*-BINAP (6.9 mg, 0.011 mmol) were dissolved in freshly distilled 1,2-dichloroethane (1 mL), then freshly prepared substrate (0.1 mmol) was added into the solution at room temperature under nitrogen. After stirring for 1 min, $AgSbF_6$ (0.02 mmol) was added into the mixture. The reaction was run at room temperature and followed by GC or TLC. After the reaction was complete, the reaction mixture was directly subjected to column chromatography.

(*E*)-Dimethyl 3-benzylidene-4-vinylcyclopentane-1, 1-dicarboxylate (2b)

>99.0% ee, HPLC, OJ, Hex (hexane) : Iso (isopropyl alcohol) = 97 : 3, 0.5 ml min^{-1}, $t1 = 25.2$, $t2 = 28.3$; *S*-BINAP, $[\alpha]_D^{25} = +33.53$, $c = 0.5$, $CHCl_3$.

^1H NMR (360 MHz, $CDCl_3$) δ 7.38–7.23 (m, 5H), 6.24 (s, 1H), 5.73–5.68 (m, 1H), 5.21–5.17 (m, 2H), 3.77 (s, 6H), 3.46–3.21 (m, 3H), 2.68–2.62 (m, 1H), 2.04 (dd, $J = 6.7$, 13.3 Hz, 1H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 172.46, 172.36, 143.60, 139.65, 138.08, 128.68, 126.82, 124.45, 117.25, 59.78, 53.33, 50.14, 40.14, 39.22; MS *m/z*: 301.1 [M^+ + 1]; HRMS (APCI) Calcd for $C_{18}H_{21}O_4$ (M^+ + 1): 301.1440; found: 301.1434.

(*E*)-Dimethyl 3-benzylidene-4-((*E*)-2-methoxyvinyl)-cyclopentane-1,1-dicarboxylate (4)

>99% ee, HPLC, OJ-H, Hex : Iso = 90 : 10, 254 nm, 1 ml min^{-1}, $t1 = 11.47$, $t2 = 13.58$; *S*-BINAP, $[\alpha]_D^{25} = -15.13$, $c = 1$, $CHCl_3$.

^1H NMR (400 MHz, $CDCl_3$) δ 7.28–7.12 (m, 5H), 6.34 (d, $J =$ 12.6 Hz, 1H), 6.17–6.15 (m, 1H), 4.54 (dd, $J = 12.6$, 9.0 Hz, 1H), 3.67 (s, 6H), 3.51 (s, 3H), 3.33 (d, $J = 18.6$ Hz, 1H), 3.18–3.12 (m, 2H), 2.54–2.49 (m, 1H), 1.87 (t, $J = 6.3$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.57, 172.47, 149.52, 144.99, 138.15, 128.71, 128.64, 126.73, 123.93, 104.53, 59.43, 56.57, 53.31, 44.95, 41.60, 39.14; MS *m/z*: 331.2 [M^+ + 1]; HRMS (APCI) Calcd for $C_{19}H_{23}O_5$ (M^+ + 1): 331.1546; found: 331.1546.

(*Z*)-2-Benzylidene-3-((*E*)-prop-1-enyl)cyclopentanone (6)

>99.9% ee, GC with Chiralselect 1000, 150 °C, 1.5 ml min^{-1}, $t1 =$ 98.83, $t2 = 101.16$; *S*-BINAP, $[\alpha]_D^{25} = -15.4$, $c = 0.5$, $CHCl_3$.

^1H NMR (400 MHz, $CDCl_3$) δ 7.84–7.80 (m, 2H), 7.37–7.29 (m, 3H), 6.56 (s, 1H), 5.65–5.61 (m, 1H), 5.43–5.37 (m, 1H), 3.44–3.40 (m, 1H), 2.42–2.16 (m, 3H), 1.77–1.71 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.96, 142.43, 140.86, 137.92, 136.23, 134.03, 133.82, 132.54, 131.16, 51.62, 42.22, 31.13, 21.20.

(*Z*)-3-((*E*)-2-Methoxyvinyl)-2-pentylidenecyclopentanone (8a)

>99% ee, GC, Chiralselect 1000, 150 °C, 1.5 ml min^{-1}, $t1 = 28.646$, $t2 = 29.549$; *S*-BINAP, $[\alpha]_D^{25} = +47.60$, $c = 1$, $CHCl_3$, *R*-BINAP, $[\alpha]_D^{25} = -46.70$, $c = 1$, $CHCl_3$

^1H NMR (400 MHz, $CDCl_3$) δ 6.33 (d, $J = 12.6$ Hz, 1H), 5.84 (dt, $J = 1.3$, 6.2 Hz, 1H), 4.57–4.51 (m, 1H), 3.52 (s, 3H), 3.16–3.10 (m, 1H), 2.70–2.60 (m, 2H), 2.34–2.06 (m, 3H), 1.59–1.48 (m, 1H), 1.44–1.22 (m, 4H), 0.86 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.41, 149.13, 142.74, 139.29, 105.66, 56.58, 42.73, 39.20, 31.87, 29.80, 27.81, 22.82, 14.33; MS *m/z*: 209.2 [M^+ + 1]; HRMS (APCI) Calcd for $C_{13}H_{21}O_2$ (M^+ + 1): 209.1542; found: 209.1545.

(*Z*)-3-((*E*)-2-(Benzyloxy)vinyl)-2-pentylidenecyclopentanone (8b)

>99.5% ee, HPLC, OJ-H, Hex : Iso = 90 : 10, 254 nm, 1 ml min^{-1}, $t1 = 7.48$, $t2 = 9.69$; *S*-BINAP, $[\alpha]_D^{25} = +55.3$, $c = 1$, $CHCl_3$.

^1H NMR (300 MHz, $CDCl_3$) δ 7.36–7.24 (m, 5H), 6.38 (d, $J =$ 12.6 Hz, 1H), 5.78 (dt, $J = 7.6$, 2.5 Hz, 1H), 4.76 (s, 2H), 4.69 (dd, $J = 8.8$, 12.6 Hz, 1H), 3.16–3.13 (m, 1H), 2.67–2.63 (m, 2H), 2.31–2.01 (m, 3H), 1.59–1.51 (m, 1H), 1.35–1.28 (m, 4H), 0.86 (t, $J =$ 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.37, 147.80, 142.87, 139.15, 137.30, 128.92, 128.37, 127.93, 107.79, 71.75, 42.83, 39.22, 31.87, 29.67, 27.82, 22.82, 14.36; MS *m/z*: 285.2 [M^+ + 1]; HRMS (APCI) Calcd for $C_{19}H_{25}O_2$ (M^+ + 1): 285.1855; found: 285.1857.

(*Z*)-2-(2-(Methoxymethoxy)ethylidene)-3-((*E*)-2-methoxyvinyl)cyclopentanone (10b)

>99% ee, GC, Chiralselect 1000, 180 °C, 1.5 mL min^{-1}, $t1 =$ 28.402, $t2 = 28.949$; *S*-BINAP, $[\alpha]_D^{25} = +45.60$, $c = 1$, $CHCl_3$.

^1H NMR (300 MHz, $CDCl_3$) δ 6.38 (d, $J = 12.6$ Hz, 1H), 5.98–5.94 (m, 1H), 4.75–4.53 (m, 5H), 3.54 (s, 3H), 3.46 (s, 3H), 3.23–3.11 (m, 1H), 2.33–2.18 (m, 3H), 1.65–1.58 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.03, 149.59, 140.26, 138.14, 104.57, 96.80, 65.73, 56.51, 55.74, 42.32, 38.65, 30.03; MS *m/z*: 195.1 [M^+ − OCH_3]; HRMS (APCI) Calcd for $C_{11}H_{15}O_3$ (M^+ + 1): 195.1021; found: 195.1022.

(*Z*)-2-(2-Methoxyethylidene)-3-((*E*)-2-methoxyvinyl)cyclopentanone (10a)

>99% ee, GC, Chiralselect 1000, 150 °C, 1.5 mL min^{-1}, $t1 =$ 16.728, $t2 = 17.495$; *S*-BINAP, $[\alpha]_D^{25} = +36.39$, $c = 1$, $CHCl_3$.

^1H NMR (300 MHz, $CDCl_3$) δ 6.38 (d, $J = 12.7$ Hz, 1H), 5.97–5.93 (m, 1H), 4.58–4.47 (m, 3H), 3.53 (s, 3H), 3.35 (s, 3H), 3.21–3.14 (m, 1H), 2.33–2.14 (m, 3H), 1.64–1.57 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.98, 149.36, 139.92, 138.38, 104.28, 70.23, 58.74, 56.24, 42.07, 38.46, 29.82; MS *m/z*: 197.1 [M^+ + 1]; HRMS (APCI) Calcd for $C_{11}H_{17}O_3$ (M^+ + 1): 197.1178; found: 197.1184.

(*Z*)-2-(3-Oxo-2-pentylidenecyclopentyl)acetaldehyde (12)

>99% ee, GC, gama 225, 1.5 ml min^{-1}, 170 °C, $t1 = 12.916$, $t2 =$ 13.226; *S*-BINAP, $[\alpha]_D^{25} = +4.20$, $c = 1$, $CHCl_3$, *R*-BINAP, $[\alpha]_D^{25} =$ -4.19, $c = 1$, $CHCl_3$.

^1H NMR (360 MHz, $CDCl_3$) δ 9.83 (s, 1H), 5.54 (dt, $J = 2.3$, 7.4 Hz, 1H), 3.22–3.20 (m, 1H), 2.70–2.49 (m, 4H), 2.34–2.16 (m, 3H), 1.57–1.47 (m, 1H), 1.39–1.20 (m, 4H), 0.87 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 207.61, 138.05, 49.28, 38.74, 36.85, 31.85, 27.83,27.31, 22.76, 14.27; MS *m/z*: 195.1 [M^+ + 1]; HRMS (APCI) Calcd for $C_{12}H_{19}O_2$ (M^+ + 1): 195.1385; found: 195.1395.

(*Z*)-Methyl 2-(3-oxo-2-pentylidenecyclopentyl)acetate

A solution of KH_2PO_4 (20 mg, 0.15 mmol) and H_2O_2 (30%; 0.01 mL, 0.1 mmol) in 0.5 mL of water was added to a solution of (3-oxo-2-pentylidenecyclopentyl)acetaldehyde (10 mg, 0.05 mmol) in 1 mL of acetonitrile. A solution of $NaClO_2$ (80%;

17 mg, 0.15 mmol) in 1 mL of water was then added dropwise with ice water cooling, and the mixture was stirred at room temperature for 24 h. After addition of a small amount of sodium sulfite, the mixture was subject to standard work-up to provide crude acid. The subsequent esterification of the crude acid with (trimethylsilyl)diazomethane (2 M; 0.1 mL, 0.2 mmol) in THF–MeOH (1 : 1, 4 mL) was allowed to stir for 1 h at room temperature. Purification of the crude product by flash column yielded (4.5 mg, 40%) of product as a colorless residue.

^{1}H NMR (360 MHz, $CDCl_3$) δ 5.90 (dt, J = 7.5, 2.2 Hz, 1H), 3.71 (s, 3H), 3.08–3.18 (m, 1H), 2.67–2.73 (m, 1H), 2.61 (dd, J = 15.4, 5.9 Hz, 1H), 2.24–2.42 (m, 2H), 2.17–2.23 (m, 1H), 1.26–1.40 (m, 6H), 0.90 (t, J = 7.2 Hz, 3H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 207.77, 172.76, 138.05, 51.86, 39.63, 38.94, 38.46, 31.70, 27.67, 26.88, 22.58, 14.13.

Methyl 2-((1*S*,2*S*)-3-oxo-2-pentylcyclopentyl)acetate (13)

$[\alpha]_D^{25}$ = +38.20, c = 0.25, $CHCl_3$ >99.6% ee (detected by GC, Chiralselect 1000, 190 °C, 2 ml min^{-1}).

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.68 (s, 3H), 2.66–2.58 (m, 1H), 2.37–2.11 (m, 4H), 1.84–1.75 (m, 1H), 1.60–1.19 (m, 10H), 0.90 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 218.70, 171.65, 53.21, 50.63, 37.93, 37.06, 36.68, 31.07, 26.81, 26.21, 25.32, 21.46, 13.02.

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