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Tetrahedron
Tetrahedron 61 (2005) 10811–10817

A new method for the synthesis of 2-cyclopenten-1-one-5-carboxylic ester derivatives via $Rh_2(OAc)_4$-mediated intramolecular C–H insertion reaction of 4*Z*-β-vinyl-α-diazo β-ketoesters

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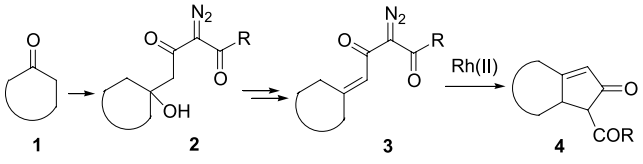
Received 14 March 2005; revised 23 May 2005; accepted 25 May 2005

Available online 23 September 2005

Abstract—2-Cyclopenten-1-one-5-carboxylic ester derivatives **14** are synthesized in a four-step-reaction sequence starting from alkynyl aldehydes **9** via 4*Z*-β-vinyl-α-diazo β-ketoesters intermediate **8**. The synthetic method for **8** is described. When the δ substituent is an alkyl group, Rh(II)-mediated decomposition of the diazo compounds **8** led to an intramolecular C–H insertion to afford 2-cyclopenten-1-one-5-carboxylic ester derivatives **14** in high yields. When the δ substituent is an aryl group, 2-hydroxynaphthoate **15** is obtained exclusively. In both cases, no Wolff rearrangement product was observed.

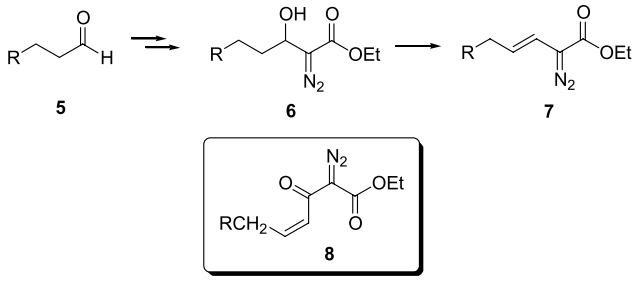
1. Introduction

2-Cyclopenten-1-one-5-carboxylic ester derivatives are useful intermediates in organic chemistry. The synthesis of these derivatives has been an attractive subject over the decades, and various methodologies have been developed for this purpose.[1] Intramolecular C–H insertion of Rh(II)-mediated α-diazo compounds has been an efficient approach to the formation of five-member ring structure.[2] However, this powerful approach has been so far limited to the synthesis of saturated cyclopentanone derivatives. We have recently reported a four-step sequence leading to bicyclic fused cyclopentanone derivatives **4** starting from cyclic ketones **1** via intermediates **2** and **3** (Scheme 1).[3] This study demonstrates the possibility of applying Rh(II)-carbene intramolecular C–H insertion in the synthesis of α,β-unsaturated cyclopentenone derivatives. Based on our interest in the synthetic application of α-diazo compounds and in connection with earlier research,[4] we conceived to develop a new method for the synthesis of 2-cyclopenten-1-one-5-carboxylic ester derivatives with intramolecular C–H insertion of Rh(II)-carbene as the key step.



Scheme 1.

Similar aldol condensation of a α-diazo-β-ketoester with aldehydes **5**, followed by a dehydration of the resulting δ-hydroxy-α-diazo-β-ketoester **6**, only gave the *E*-isomer **7** (Scheme 2).[5] Obviously, intramolecular C–H insertion will not occur from **7**. It has been reported that Wolff rearrangement occurred to generate vinylketenes when similar diazo compounds as **7** were decomposed with



Scheme 2.

Keywords: Synthesis; Insertion; 2-Cyclopenten-1-one-5-carboxylic ester derivatives; 4*Z*-β-vinyl-α-diazo β-ketoesters.
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doi:10.1016/j.tet.2005.05.106

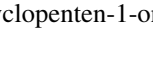
$Rh_2(OAc)_4$.[6] Therefore, the above reaction sequence is not suitable for the synthesis of 2-cyclopenten-1-one-5-carboxylic ester derivatives in general. In order to do that, the preparation of *Z*-isomer diazo compound **8** is crucial. We solved this problem by a three-step-reaction sequence starting from alkynyl aldehydes. Here we report our results concerning the preparation of intermediates **8** and the subsequent transformation to 2-cyclopenten-1-one-5-carboxylic ester derivatives.

2. Results and discussion

Initially, the requisite diazo compounds **8** were synthesized in four-steps starting from alkynyl aldehydes **9** (Scheme 3, (a)→(b)→(c)→(d)). Although the nucleophilic addition to aromatic aldehydes, aliphatic aldehydes, and α,β-unsaturated aldehydes by ethyl diazoacetate has been well developed,[7] the corresponding reaction with alkynyl aldehydes has not been reported. As anticipated, the compounds **10** were generated by aldol condensation of alkynyl aldehydes **9** with ethyl diazoacetate by treatment with a catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). We found that 20% molar ratio of DBU to the substrates was the best suitable for the condensation reaction. Otherwise, the reaction of alkynyl aldehydes **9** with ethyl diazo acetate afforded the compounds **10a–e** in poorer yield. The aldol-type condensation was also carried out with NaH as base. The results are summarized in Table 1. As we can see the reaction with NaH as base gave better yields of the products **10a–e**.

Next, we studied the transformation of the diazo compounds **10** to the corresponding β-ketoesters **11**. Although the Rh(II)-mediated reactions of β-vinyl-β-hydroxy-α-diazo esters,[8] β-aryl-β-hydroxy-α-diazo esters,[9] and β-alkyl-β-hydroxy-α-diazo esters[10] have been reported, the corresponding reaction of β-alkynyl-β-hydroxy-α-diazo esters **10** has not been investigated. As expected, the diazo compounds **10a**, **10b**, and **10e** were converted to compounds **11a**, **11b**, and **11e**, respectively, in good yields upon exposure to rhodium(II) acetate in methylene chloride at room temperature (Table 2). The results are similar to the previously reported Rh(II)-mediated decomposition of β-vinyl-β-hydroxy-α-diazo esters.[8,11]

Table 1. The condensation of alkynyl aldehydes **9a–e** with ethyl diazoacetate

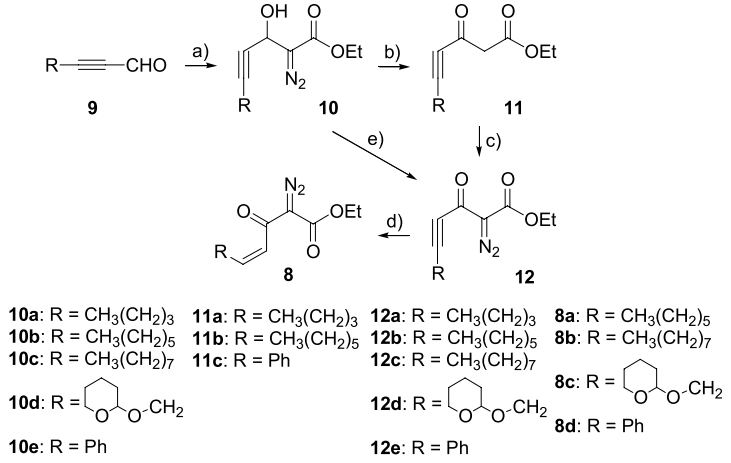
Entry	Aldehydes **9** R=	Product	Reaction time (h) (method A/method B)	Yield (%) (method A/method B)[a]
1	**a**, $CH_3(CH_2)_3$	**10a**	24/24	26/59
2	**b**, $CH_3(CH_2)_5$	**10b**	24/20	20/60
3	**c**, $CH_3(CH_2)_7$	**10c**	24/24	24/65
4	**d**, 	**10d**	—/22	—[b]/38
5	**e**, Ph	**10e**	18/24	55/62

[a] Isolated yield after column chromatography. Method A: the reaction carried in CH_3CN in the presence of 20% DBU at room temperature. Method B: the reaction carried in THF in the presence of NaH at 0 °C to room temperature.
[b] The reaction was not performed.

β-Keto esters **11a–c** were then transformed to the corresponding diazo compounds **12a–c** by treatment with TsN_3 in the presence of Et_3N in CH_3CN at room temperature in high yields (Table 3).

Although the above four-step transformation of **9** to **12** is efficient, we conceived that the diazo compounds **10a–e** may be directly oxidized to give the corresponding compounds **12a–e**, thereby the four-step sequence of the transformation can be shortened to a three-step synthetic sequence (Scheme 3, (a)→(e)→(d)). Therefore, we examined the oxidation of the β-hydroxy diazo compounds **10a–e** using MnO_2 as oxidant, because MnO_2 is a mild oxidant and has been used for the oxidation of a variety of compounds.[12] We were delighted to find that the hydroxy group of the compounds **10a–e** were efficiently oxidized to carbonyl group, while the diazo group kept intact (Table 4). Considering the fact that the diazo group can be easily oxidized,[13] it is rather astonishing to note the diazo group has tolerated the MnO_2 oxidation. This result may further broaden the scope of the chemical transformation of diazo carbonyl compounds.

Triple bond in compounds **12a–e** could be efficiently hydrogenated in the presence of Lindlar catalyst, giving



Scheme 3. (a) N_2CHCO_2Et, NaH, THF; (b) $Rh_2(OAc)_4$, CH_2Cl_2; (c) TsN_3, Et_3N, CH_3CN; (d) Lindlar catalyst, H_2, *n*-hexane; (e) MnO_2, CH_2Cl_2.

Table 2. The transformation of β-hydroxy-α-diazo esters **10a**, **10b**, **10e** to the compounds **11a–c**

Entry	β-Hydroxy diazo esters **10**	Product	Reaction time (h)	Yields (%)[a]
1	**a**, $CH_3(CH_2)_3$	**11a**	4	70
2	**b**, $CH_3(CH_2)_5$	**11b**	6	73
3	**e**, Ph	**11c**	6	78

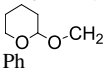
[a] Isolated yield after column chromatography.

Table 3. Reaction of β-keto esters **11b,c** with TsN_3

Entry	β-Keto ester **11** R=	Product	Reaction time (h)	Yields (%)[a]
1	**b**, $CH_3(CH_2)_5$	**12b**	14	90
2	**c**, Ph	**12e**	14	93

[a] Isolated yield after column chromatography.

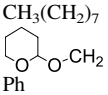
Table 4. The oxidation of **10a–e** with MnO_2

Entry	Diazo compounds **10**	Product	Reaction time (h)	Yield (%)[a]
1	**a**, $CH_3(CH_2)_3$	**12a**	6	88
2	**b**, $CH_3(CH_2)_5$	**12b**	15	90
3	**c**, $CH_3(CH_2)_7$	**12c**	10	89
4	**d**, 	**12d**	12	90
5	**e**, Ph	**12e**	10	92

[a] Isolated yield after column chromatography.

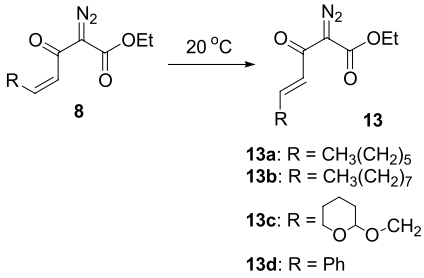
the corresponding 4*Z*-β-vinyl-α-diazo β-ketoesters **8a–d** in almost quantitative yields (Table 5). It is worth to note that the diazo group can be hydrogenated to methylene group with 10% Pd/C as the catalyst,[14] but in our study the diazo group remains intact in the hydrogenation reaction with Lindlar catalyst.

Table 5. The hydrogenation of **12b–e** with Lindlar catalyst

Entry	Diazo compound **9**	Product	Reaction time (h)	Yields (%)[a]
1	**b**, $CH_3(CH_2)_5$	**8a**	1	97
2	**c**, $CH_3(CH_2)_7$	**8b**	1	95
3	**d**, 	**8c**	1.5	94
4	**e**, Ph	**8d**	1.5	92

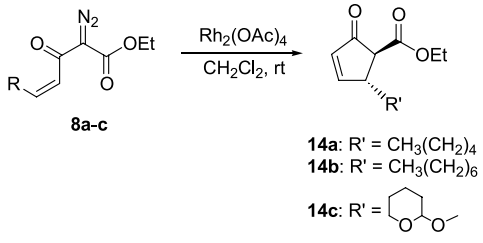
[a] Isolated yield after column chromatography.

It was noted that 4*Z*-β-vinyl-α-diazo β-ketoesters **8a–d** were unstable, and could be slowly isomerized into 4*E*-β-vinyl-α-diazo β-ketoesters **13a–d** at 20 °C (Scheme 4). Nevertheless, they could be stored for a month at −20 °C. This isomerisation could be monitored with ^1H NMR spectra (Table 6).

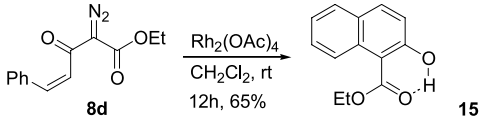


Scheme 4.

The $Rh_2(OAc)_4$-catalyzed decomposition of 4*Z*-β-vinyl-α-diazo β-ketoesters **8a–c**, in which the R is alkyl group, gave the corresponding 2-cyclopenten-1-one-5-carboxylic ester derivatives **14a–c** in excellent yields (Scheme 5, Table 7). In all the cases only one diastereoisomer was formed. When the R is aryl group, however, the corresponding $Rh_2(OAc)_4$-catalyzed decomposition resulted in 2-hydroxynaphthoate **15** (Scheme 6). This latter result is in accordance with the reported findings.[15] In all cases, no Wolff rearrangement product was detected.

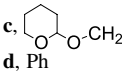


Scheme 5.



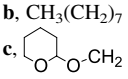
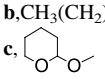
Scheme 6.

Table 6. The isomerisation of **8a–d** to **13a–d** monitored by ^1H NMR

Entry	R	^1H NMR of *Z*-isomer **8**	^1H NMR of *E*-isomer **13**	The molecular ratio[a] of *Z*-isomer **8** to *E*-isomer **13** (3/10/25 days)[b]
1	**a**, $CH_3(CH_2)_5$	γ-H: 6.18 (dt, *J*=11.4, 7.2 Hz); δ-H: 6.94 (dt, *J*=11.4, 1.5 Hz)	γ-H: 7.02 (dt, *J*=15.6, 6.6 Hz); δ-H: 7.14 (d, *J*=15.6 Hz)	70:30/25:75/10:90
2	**b**, $CH_3(CH_2)_7$	γ-H: 6.17 (dt, *J*=11.4, 7.5 Hz); δ-H: 6.93 (dt, *J*=11.4, 1.8 Hz)	γ-H: 7.06 (dt, *J*=15.6, 6.6 Hz); δ-H: 7.19 (d, *J*=15.6 Hz)	100:0/90:10/45:55
3	**c**, 	γ-H: 6.39 (dt, *J*=11.7, 4.8 Hz); δ-H: 7.06 (dt, *J*=11.7, 2.4 Hz)	γ-H: 7.08 (dt, *J*=15.3, 7.5 Hz); δ-H: 7.44 (dt, *J*=15.3, 2.1 Hz)	100:0/85:15/35:65
4	**d**, Ph	γ-H: 6.86 (d, *J*=12.6 Hz); δ-H: 6.91 (d, *J*=12.6 Hz)	γ-H: 7.76 (d, *J*=15.9 Hz); δ-H: 7.91 (d, *J*=15.9 Hz)	100:0/82:18/15:85

[a] The ratio was determined by ^1H NMR.
[b] The ^1H NMR spectra were measured when the diazo compounds **8a–d** were stored at 20 °C for 3, 10, and 25 days, respectively.

Table 7. The $Rh_2(OAc)_4$-catalyzed decomposition of 4*Z*-β-vinyl-β-keto-α-diazo esters **8a–c**

Entry	Diazo compound **8** R=	Product **14** R′=	Reaction time (h)	Yield (%)[a]
1	**a**, $CH_3(CH_2)_5$	**a**, $CH_3(CH_2)_4$	12	88
2	**b**, $CH_3(CH_2)_7$	**b**,$CH_3(CH_2)_6$	10	86
3	**c**, 	**c**, 	12	82

[a] Isolated yield after column chromatography.

In summary, we have found the diazo group has tolerated the MnO_2 oxidation and the hydrogenation with Lindlar catalyst. This remarkable observation leads to the development of a new approach to cyclopentenone ester derivatives, based on $Rh_2(OAc)_4$-mediated intramolecular C–H insertion of 4*Z*-β-vinyl-α-diazo β-ketoesters.

3. Experimental

3.1. General procedures

IR spectra were recorded on a WQF-200 spectraphotometer. NMR spectra were measured on Varian YH 300 apparatus in $CDCl_3$ solution using tetramethylsilane as an internal standard. MS spectra were recorded on ZAB-HS or +Q1 MCA spectrometer. Hexane, CH_3CN, and CH_2Cl_2 were dried on CaH_2, THF was distilled from sodium, and other solvents were distilled prior to use. Organic extracts were concentrated using a rotary evaporator at below 50 °C. Melting points were uncorrected. Column chromatography was performed using ZCX-α (200–300 mesh). Ethyl diazoacetate was prepared according to the known procedure.[16]

3.2. Typical procedure for the formation of 10a–e by aldol-type condensation

3.2.1. Ethyl 2-diazo-3-hydroxy-5-phenylpent-4-ynoate (10e). *Method A*. To a solution of ethyl diazo acetate (274 mg, 2.4 mmol) in anhydrous CH_3CN (10 mL) was added 1, 8-diazabicyclo[5.4.0]undec-7-ene (DBU) (60 mg, 0.4 mmol) in anhydrous CH_3CN (2 mL) and 3-phenylpropioaldehyde (260 mg, 2 mmol) in anhydrous CH_3CN (3 mL). The reaction mixture was stirred for 18 h at room temperature and then concentrated in vacuo. The residue was chromatographed on silica (petroleum ether/Et_2O 4:1) to give **10e** (268 mg, 55%) as brown yellow oil. *Method B*. To a suspension of NaH (58 mg, 2.4 mmol) in anhydrous THF (9 mL) at 0 °C was added dropwise ethyl diazo acetate (274 mg, 2.4 mmol) in anhydrous THF (3 mL). The reaction mixture was stirred for 30 min at 0 °C and then warmed to room temperature. The stirring was continued for another 30 min. 3-Phenylpropioaldehyde (260 mg, 2 mmol) in anhydrous THF (3 mL) was then added dropwise to this mixture. The reaction mixture was stirred for another 24 h at room temperature and then filtrated quickly. The filtrate was concentrated in vacuo and chromatographed on silica (petroleum ether/Et_2O 4:1) to give **10e** (302 mg, 62%) as brown yellow oil. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.45–7.26 (m, 5H), 5.74 (s, 1H), 4.26 (q, *J*=7.1 Hz, 2H), 3.20 (br s, 1H), 1.28 (t, *J*=7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.8, 131.8, 129.0, 128.3, 121.4, 87.2, 83.6, 77.2, 61.3, 58.8, 14.4; IR (KBr, cm^{-1}) 3419, 2983, 2235, 2102, 1693, 1672, 1491, 1400, 1373, 1342, 1292, 1111, 1018; EIMS (*m/z*) 216 [$(M-N_2)^+$], 197, 188, 170, 160, 142, 129, 126, 114 (100), 103, 89, 77, 63, 52, 29. Anal. Calcd for $C_{13}H_{12}N_2O_3$: C, 63.93; H, 4.95; N, 11.47. Found: C, 63.87; H, 5.03; N, 11.59.

3.2.2. Ethyl 2-diazo-3-hydroxynon-4-ynoate (10a). A yellow oil was obtained in 26 and 59% yields with method A and method B, respectively. ^1H NMR ($CDCl_3$, 300 MHz) δ 5.52 (t, *J*=1.8 Hz, 1H), 4.26 (q, *J*=7.2 Hz, 2H), 3.33 (br s, 1H), 2.25 (dt, *J*=7.1, 1.8 Hz, 2H), 1.54–1.34 (m, 4H), 1.29 (t, *J*=7.2 Hz, 3H), 0.91 (t, *J*=7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 165.5, 88.5, 77.2, 75.1, 61.2, 58.5, 30.4, 21.8, 18.2, 14.4, 13.4; IR (KBr, cm^{-1}) 3425, 2960, 2935, 2875, 2227, 2102, 1701, 1672, 1466, 1375, 1344, 1290, 1109, 1016; EIMS (*m/z*) 224 [M^+], 207, 196, 182, 179, 167, 151, 139, 136, 121, 107, 97, 93, 79, 69, 55, 52, 41, 27 (100). Anal. Calcd for $C_{11}H_{16}N_2O_3$: C, 58.91; H, 7.19; N, 12.49. Found: C, 58.73; H, 7.29; N, 12.40.

3.2.3. Ethyl 2-diazo-3-hydroxyundec-4-ynoate (10b). A yellow oil was obtained in 20 and 60% yields with method A and method B, respectively. ^1H NMR ($CDCl_3$, 300 MHz) δ 5.52 (t, *J*=2.0 Hz, 1H), 4.26 (q, *J*=7.2 Hz, 2H), 2.24 (dt, *J*=7.1, 2.0 Hz, 2H), 1.53–1.46 (m, 2H), 1.42–1.26 (m, 6H), 1.29 (t, *J*=7.2 Hz, 3H), 0.89 (t, *J*=6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 165.5, 88.5, 77.2, 75.2, 61.2, 58.5, 31.2, 28.4, 28.3, 22.4, 18.5, 14.4, 13.9; IR (KBr, cm^{-1}) 3433, 2956, 2931, 2860, 2227, 2100, 1697, 1676, 1466, 1373, 1342, 1290, 1105, 1016; EIMS (*m/z*) 252 [M^+], 207, 195, 182, 179, 163, 149, 135, 121, 109, 97, 93, 79, 67, 55, 52, 41, 29 (100). Anal. Calcd for $C_{13}H_{20}N_2O_3$: C, 61.88; H, 7.99; N, 11.10. Found: C, 61.81; H, 7.87; N, 11.19.

3.2.4. Ethyl 2-diazo-3-hydroxytridec-4-ynoate (10c). A yellow oil was obtained in 24 and 65% yields with method A and method B, respectively. ^1H NMR ($CDCl_3$, 300 MHz) δ 5.52 (t, *J*=2.1 Hz, 1H), 4.26 (q, *J*=7.2 Hz, 2H), 2.24 (dt, *J*=6.9, 2.1 Hz, 2H), 1.53–1.46 (m, 2H), 1.42–1.26 (m, 10H), 1.27 (t, *J*=7.2 Hz, 3H), 0.88 (t, *J*=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 165.5, 88.8, 77.2, 75.1, 61.2, 58.7, 31.8, 29.7, 29.0, 28.8, 28.4, 22.6, 18.5, 14.4, 14.0; IR (KBr, cm^{-1}) 3406, 2956, 2931, 2858, 2229, 2104, 1697, 1678, 1466, 1373, 1344, 1290, 1107, 1018; EIMS (*m/z*) 252 [$(M-N_2)^+$], 207, 195, 182, 177, 165, 153, 149, 135, 121, 109, 95, 81, 67, 55, 41, 29 (100). Anal. Calcd for $C_{15}H_{24}N_2O_3$: C, 64.26; H, 8.63; N, 9.99. Found: C, 64.37; H, 8.56; N, 9.85.

3.2.5. Ethyl 2-diazo-3-hydroxy-6-(tetrahydro-2*H*-pyran-2-yloxy)hex-4-ynoate (10d). A yellow oil was obtained in 38% yield (method B). ^1H NMR ($CDCl_3$, 300 MHz) δ 5.56 (s, 1H), 4.80 (t, *J*=3.2 Hz, 1H), 4.33 (dd, *J*=3.2, 1.8 Hz, 2H), 4.26 (q, *J*=7.2 Hz, 2H), 3.87–3.79 (m, 1H), 3.56–3.53 (m, 1H), 1.83–1.71 (m, 2H), 1.63–1.57 (m, 4H), 1.30 (t, *J*=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 165.2, 96.9, 83.4, 81.0, 77.2, 62.0, 61.3, 58.4, 53.9, 30.2, 25.3, 18.9, 14.4; IR (KBr, cm^{-1}) 3396, 2943, 2871, 2360, 2343, 2102, 1697, 1442, 1373, 1342, 1288, 1105, 1026, 903; EIMS (*m/z*) 282 [M^+], 253, 226, 198, 181, 167, 153, 135, 125, 107, 85

(100), 67, 43, 29. Anal. Calcd for $C_{13}H_{18}N_2O_5$: C, 55.31; H, 6.43; N, 9.92. Found: C, 55.34; H, 6.55; N, 9.99.

3.3. Typical procedure for the formation of 11a–c by $Rh_2(OAc)_4$-mediated 1,2-hydrogen shift reaction

3.3.1. Ethyl 3-oxo-5-phenylpent-4-ynoate (11c). To a suspension of $Rh_2(OAc)_4$ (6.3 mg, 0.0143 mmol) in anhydrous CH_2Cl_2 (10 mL) at room temperature was added **10e** (348 mg, 1.43 mmol) in anhydrous CH_2Cl_2 (5 mL) over 5 min. The reaction mixture was stirred for another 6 h and then concentrated in vacuo. The residue was chromatographed on silica (petroleum ether/Et_2O 10:1) to give **11c** (240 mg, 78%) as yellow oil. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.57–7.30 (m, 5H), 4.21 (q, $J=7.2$ Hz, 2H), 3.66 (s, 2H), 1.26 (t, $J=7.2$ Hz, 3H); IR (KBr, cm^{-1}) 2981, 2927, 2854, 2206, 1741, 1674, 1616, 1410, 1281, 1211, 1122, 1082, 1034.

3.3.2. Ethyl 3-oxonon-4-ynoate (11a). A colorless oil was obtained in 70% yield. ^1H NMR ($CDCl_3$, 300 MHz) δ 4.17 (q, $J=7.2$ Hz, 2H), 3.51 (s, 2H), 2.34 (t, $J=6.9$ Hz, 2H), 1.57–1.47 (m, 2H), 1.44–1.32 (m, 2H), 1.24 (t, $J=7.2$ Hz, 3H), 0.88 (t, $J=7.2$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 178.8, 166.1, 96.8, 80.3, 61.4, 51.4, 29.5, 21.8, 18.6, 14.0, 13.3; IR (KBr, cm^{-1}) 2962, 2935, 2875, 2216, 1745, 1680, 1614, 1466, 1414, 1321, 1248, 1176, 1034; EIMS (*m/z*) 197 [$(M+H)^+$], 179 (100), 123, 109, 95, 81, 67. Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.54; H, 8.13.

3.3.3. Ethyl 3-oxoundec-4-ynoate (11b). A colorless oil was obtained in 73% yield. ^1H NMR ($CDCl_3$, 300 MHz) δ 4.14 (q, $J=7.2$ Hz, 2H), 3.49 (s, 2H), 2.31 (t, $J=7.1$ Hz, 2H), 1.55–1.43 (m, 2H), 1.38–1.08 (m, 6H), 1.22 (t, $J=7.2$ Hz, 3H), 0.80 (t, $J=6.9$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 178.7, 166.0, 96.7, 80.3, 61.3, 51.3, 31.1, 28.4, 27.4, 22.3, 18.9, 13.9, 13.8; IR (KBr, cm^{-1}) 2958, 2933, 2860, 2216, 1745, 1680, 1614, 1466, 1415, 1321, 1250, 1176, 1034; EIMS (*m/z*) 225 [$(M+H)^+$], 197, 179, 137, 109, 95 (100), 81, 67, 55. Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.70; H, 8.81.

3.4. Typical procedure for the formation of 12a, 12b, 12e from 11a–c by diazo transfer reaction

3.4.1. Ethyl 2-diazo-3-oxo-5-phenylpent-4-ynoate (12e). Et_3N (0.28 mL, 2 mmol) and *p*-toluene sulfonyl azide (237 mg, 1.2 mmol) in anhydrous CH_3CN (4 mL) were added dropwise to a solution of **8c** (216 mg, 1 mmol) in anhydrous CH_3CN (16 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 15 h at this temperature. Then, the solution was concentrated in vacuo and the residue was chromatographed on silica (petroleum ether/Et_2O 10:1) to give **9e** (225 mg, 93%) as yellow crystals: mp 78–80 °C. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.62–7.59 (m, 2H), 7.44–7.34 (m, 3H), 4.33 (q, $J=7.2$ Hz, 2H), 1.32 (t, $J=7.2$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.4, 160.0, 133.0, 130.9, 128.6, 120.0, 96.1, 85.5, 77.2, 61.7, 14.3; IR (KBr, cm^{-1}) 2983, 2935, 2210, 2152, 1718, 1589, 1466, 1442, 1371, 1331, 1215, 1171, 1130, 1039; EIMS (*m/z*) 242 [M^+], 214, 142, 129 (100), 114, 101, 87, 75, 63, 52, 29. Anal. Calcd for $C_{13}H_{10}N_2O_3$: C, 64.46; H, 4.16; N, 11.56. Found: C, 64.59; H, 4.30; N, 11.50.

3.4.2. Ethyl 2-diazo-3-oxoundec-4-ynoate (12b). A yellow oil was obtained in 90% yield. ^1H NMR ($CDCl_3$, 300 MHz) δ 4.33 (q, $J=7.2$ Hz, 2H), 2.44 (t, $J=7.2$ Hz, 2H), 1.67–1.57 (m, 2H), 1.47–1.21 (m, 6H), 1.34 (t, $J=7.2$ Hz, 3H), 0.89 (t, $J=6.9$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.5, 160.1, 99.8, 78.1, 77.2, 61.6, 31.2, 28.5, 27.5, 22.4, 19.3, 14.3, 13.9; IR (KBr, cm^{-1}) 2956, 2933, 2860, 2222, 2139, 1734, 1697, 1610, 1466, 1371, 1315, 1259, 1105; EIMS (*m/z*) 251 [$(M+H)^+$], 222, 205, 193, 180, 165, 152, 147, 137, 125, 107, 97, 79, 67, 55, 43, 41, 29 (100). Anal. Calcd for $C_{13}H_{18}N_2O_3$: C, 62.38; H, 7.25; N, 11.19. Found: C, 62.30; H, 7.36; N, 11.28.

3.5. Typical procedure for the formation of 12b–e from 10b–e by MnO_2 oxidation reaction

3.5.1. Ethyl 2-diazo-3-oxo-5-phenylpent-4-ynoate (12e). Activated MnO_2 (2.175 g, 25 mmol, Aldrich) was added in 2 portions over 4 h to a solution of **10e** (610 mg, 2.5 mmol) in CH_2Cl_2 (15 mL). After stirring for 10 h at room temperature, the manganese dioxide was removed by filtration. The filtrate was concentrated in vacuo and chromatographed on silica (petroleum ether/Et_2O 6:1) to give **12e** (555 mg, 92%).

3.5.2. Ethyl 2-diazo-3-oxonon-4-ynoate (12a). A yellow oil was obtained in 88% yield. ^1H NMR ($CDCl_3$, 300 MHz) δ 4.29 (q, $J=7.2$ Hz, 2H), 2.41 (t, $J=7.2$ Hz, 2H), 1.61–1.52 (m, 2H), 1.47–1.35 (m, 2H), 1.30 (t, $J=7.2$ Hz, 3H), 0.89 (t, $J=7.2$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.4, 160.1, 99.8, 78.1, 77.2, 61.6, 31.5, 22.5, 19.3, 14.3, 14.0; IR (KBr, cm^{-1}) 2960, 2935, 2873, 2222, 2137, 1734, 1697, 1608, 1466, 1371, 1317, 1259, 1109; EIMS (*m/z*) 223 [$(M+H)^+$], 194, 165, 152, 147, 123, 107, 95, 79, 69, 55, 43, 41, 29 (100). Anal. Calcd for $C_{11}H_{14}N_2O_3$: C, 59.45; H, 6.35; N, 12.60. Found: C, 59.50; H, 6.41; N, 12.53.

3.5.3. Ethyl 2-diazo-3-oxoundec-4-ynoate (12b). A yellow oil was obtained in 90% yield.

3.5.4. Ethyl 2-diazo-3-oxotridec-4-ynoate (12c). A yellow oil was obtained in 89% yield. ^1H NMR ($CDCl_3$, 300 MHz) δ 4.33 (q, $J=7.2$ Hz, 2H), 2.44 (t, $J=7.2$ Hz, 2H), 1.66–1.57 (m, 2H), 1.46–1.21 (m, 10H), 1.34 (t, $J=7.2$ Hz, 3H), 0.88 (t, $J=6.6$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.5, 160.1, 99.8, 78.1, 77.2, 61.6, 31.7, 29.0, 28.9, 28.8, 27.5, 22.6, 19.3, 14.3, 14.0; IR (KBr, cm^{-1}) 2954, 2924, 2854, 2224, 2135, 1736, 1701, 1614, 1464, 1371, 1313, 1259, 1103; EIMS (*m/z*) 279 [$(M+H)^+$], 203, 193, 180, 165, 153, 147, 123, 107, 95, 79, 69, 55, 43 (100), 41, 29. Anal. Calcd for $C_{15}H_{22}N_2O_3$: C, 64.73; H, 7.97; N, 10.06. Found: C, 64.87; H, 7.90; N, 10.21.

3.5.5. Ethyl 2-diazo-3-oxo-6-(tetrahydro-2*H*-pyran-2-yloxy)hex-4-ynoate (12d). A yellow oil was obtained in 90% yield. ^1H NMR ($CDCl_3$, 300 MHz) δ 4.82 (br s, 1H), 4.41 (s, 2H), 4.25 (q, $J=7.1$ Hz, 2H), 3.79–3.71 (m, 1H), 3.51–3.46 (m, 1H), 1.76–1.64 (m, 2H), 1.58–1.46 (m, 4H), 1.26 (t, $J=7.1$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.8, 159.6, 96.9, 93.3, 81.9, 78.0, 61.9, 61.7, 53.7, 29.9, 25.1, 18.7, 14.1; IR (KBr, cm^{-1}) 2945, 2873, 2225, 2141, 1736, 1697, 1610, 1442, 1371, 1321, 1261, 1101, 1032, 903; EIMS (*m/z*) 262 [$(M-N_2)^+$], 179, 151 (100), 123, 101, 96,

85, 67, 55, 43, 41, 29. Anal. Calcd for $C_{13}H_{16}N_2O_5$: C, 55.71; H, 5.75; N, 9.99. Found: C, 55.69; H, 5.81; N, 10.10.

3.6. Typical procedure for the catalytic hydrogenation of 12b–e

3.6.1. Ethyl 2-diazo-3-oxoundec-4-enoate (8a). To a solution of **12b** (250 mg, 1 mmol) in hexane (10 mL) was added Lindlar catalyst (30 mg), and the reaction mixture was stirred vigorously for 1 h at room temperature under hydrogen gas balloon. The precipitate was filtrated and then the solvent was removed in vacuo. The residue was purified by chromatography (petroleum ether/Et_2O 8:1) to give **8a** (244 mg, 97%) as yellow oil. ^1H NMR ($CDCl_3$, 300 MHz) δ 6.93 (dt, $J=11.4$, 1.5 Hz, 1H), 6.18 (dt, $J=11.4$, 7.2 Hz, 1H), 4.25 (q, $J=7.1$ Hz, 2H), 2.66–2.58 (m, 2H), 1.61–1.53 (m, 2H), 1.32–1.22 (m, 6H), 1.30 (t, $J=7.1$ Hz, 3H), 0.83 (t, $J=6.6$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 182.5, 161.3, 150.2, 123.4, 77.2, 31.6, 30.0, 29.1, 29.0, 28.0, 22.5, 14.3, 14.0; IR (KBr, cm^{-1}) 2954, 2924, 2854, 2131, 1720, 1647, 1614, 1464, 1369, 1302, 1221, 1134, 1043; EIMS (*m/z*) 252 [M^+], 226, 224, 205, 195, 178, 167, 150, 139, 121 (100), 108, 94, 81, 69, 55, 43, 41, 28. Anal. Calcd for $C_{13}H_{20}N_2O_3$: C, 61.88; H, 7.99; N, 11.10. Found: C, 61.93; H, 7.89; N, 11.16.

3.6.2. Ethyl 2-diazo-3-oxotridec-4-enoate (8b). A yellow oil was obtained in 95% yield. ^1H NMR ($CDCl_3$, 300 MHz) δ 6.93 (dt, $J=11.4$, 1.8 Hz, 1H), 6.17 (dt, $J=11.4$, 7.5 Hz, 1H), 4.25 (q, $J=7.1$ Hz, 2H), 2.65–2.57 (m, 2H), 1.43–1.36 (m, 2H), 1.21–1.32 (m, 10H), 1.28 (t, $J=7.1$ Hz, 3H), 0.83 (t, $J=6.6$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 182.5, 161.3, 150.1, 123.4, 77.2, 61.3, 31.8, 30.0, 29.6, 29.3, 29.2, 28.1, 22.6, 14.3, 14.0; IR (KBr, cm^{-1}) 2958, 2927, 2856, 2133, 1718, 1647, 1612, 1464, 1369, 1304, 1219, 1134, 1041; EIMS (*m/z*) 280 [M^+], 254, 252, 223, 206, 195, 178, 167, 156, 149, 135, 121, 108, 94, 81, 67, 55, 43, 41, 29 (100). Anal. Calcd for $C_{15}H_{24}N_2O_3$: C, 64.26; H, 8.63; N, 9.99. Found: C, 64.31; H, 8.70; N, 9.90.

3.6.3. Ethyl 2-diazo-3-oxo-6-(tetrahydro-2*H*-pyran-2-yloxy)hex-4-enoate (8c). A yellow oil was obtained in 94% yield. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.06 (dt, $J=11.7$, 2.4 Hz, 1H), 6.39 (dt, $J=11.7$, 4.8 Hz, 1H), 4.76–4.74 (m, 1H), 4.65–4.63 (m, 1H), 4.59–4.57 (m, 1H), 4.25 (q, $J=7.2$ Hz, 2H), 3.84–3.78 (m, 1H), 3.49–3.42 (m, 1H), 1.85–1.67 (m, 2H), 1.57–1.49 (m, 4H), 1.28 (t, $J=7.2$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 182.0, 161.1, 148.2, 122.4, 98.8, 77.2, 66.9, 62.4, 61.5, 30.6, 25.4, 19.6, 14.3; IR (KBr, cm^{-1}) 2943, 2871, 2360, 2133, 1718, 1647, 1606, 1419, 1371, 1306, 1211, 1122, 1030, 968, 910 cm^{-1}; EIMS (*m/z*) 264 [$(M-N_2)^+$], 198, 181, 155, 141, 124, 109, 97, 85 (100), 67, 57, 43, 41, 29. Anal. Calcd for $C_{13}H_{18}N_2O_5$: C, 55.31; H, 6.43; N, 9.92. Found: C, 55.40; H, 6.49; N, 9.83.

3.6.4. Ethyl 2-diazo-3-oxo-5-phenylpent-4-enoate (8d). A yellow oil was obtained in 92% yield. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.62–7.59 (m, 2H), 7.32–7.30 (m, 3H), 6.91 (d, $J=12.6$ Hz, 1H), 6.86 (d, $J=12.7$ Hz, 1H), 4.27 (q, $J=7.2$ Hz, 2H), 1.30 (t, $J=7.2$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 182.5, 161.0, 141.6, 135.0, 129.8, 129.2, 128.0, 124.1, 77.2, 61.4, 14.2; IR (KBr) 2958, 2925, 2854, 2360, 2343, 2131, 1712, 1637, 1603, 1369, 1302, 1217, 1130, 1034 cm^{-1}; EIMS (*m/z*) 216 [$(M-N_2)^+$], 170 (100), 143, 131, 127, 115, 103, 89, 77, 65, 63, 52, 29. Anal. Calcd for $C_{13}H_{12}N_2O_3$: C, 63.93; H, 4.95; N, 11.47. Found: C, 63.88; H, 4.87; N, 11.49.

3.7. Typical procedure for the $Rh_2(OAc)_4$-catalyzed reaction of 8a–d

3.7.1. Ethyl 2-cyclopente-1-one-4-pentyl-5-carboxylate (14a). To a suspension of $Rh_2(OAc)_4$ (5.1 mg, 0.0115 mmol) in anhydrous CH_2Cl_2 (10 mL) at room temperature was added **8a** (290 mg, 1.15 mmol) in anhydrous CH_2Cl_2 (5 mL) over 5 min. After stirring for another 12 h, the reaction mixture was concentrated in vacuo. The residue was chromatographed on silica (petroleum ether/Et_2O 6:1) to give **14a** (228 mg, 88%) as colorless oil. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.64 (dd, $J=5.7$, 2.4 Hz, 1H), 6.07 (dd, $J=5.7$, 2.1 Hz, 1H), 4.17 (q, $J=7.2$ Hz, 2H), 3.26–3.22 (m, 1H), 2.96 (d, $J=3.0$ Hz, 1H), 1.63–1.54 (m, 2H), 1.49–1.22 (m, 6H), 1.24 (t, $J=7.2$ Hz, 3H), 0.84 (t, $J=7.1$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 202.5, 169.0, 168.0, 131.5, 61.4, 58.0, 46.0, 33.8, 31.5, 27.0, 22.3, 14.1, 13.8; IR (KBr, cm^{-1}) 2958, 2929, 2858, 1739, 1712, 1589, 1466, 1369, 1255, 1146, 1024; EIMS (*m/z*) 225 [$(M+H)^+$], 179 (100), 151, 123, 109, 95, 81, 67. Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.55; H, 9.01.

3.7.2. Ethyl 2-cyclopente-4-heptyl-1-one-5-carboxylate (14b). A colorless oil was obtained in 86% yield. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.63 (dd, $J=5.7$, 2.7 Hz, 1H), 6.06 (dd, $J=5.7$, 2.3 Hz, 1H), 4.16 (q, $J=7.1$ Hz, 2H), 3.25–3.21 (m, 1H), 2.95 (d, $J=2.7$ Hz, 1H), 1.62–1.53 (m, 2H), 1.47–1.21 (m, 10H), 1.23 (t, $J=7.1$ Hz, 3H), 0.82 (t, $J=7.1$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 202.5, 168.9, 167.9, 131.5, 61.4, 58.0, 46.0, 33.9, 31.6, 29.3, 29.0, 27.3, 22.5, 14.1, 13.9; IR (KBr, cm^{-1}) 2958, 2929, 2856, 1739, 1709, 1591, 1466, 1369, 1252, 1146, 1032; EIMS (*m/z*) 253 [$(M+H)^+$], 225, 207, 179 (100), 151, 123, 109, 95, 81, 67. Anal. Calcd for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59. Found: C, 71.35; H, 9.64.

3.7.3. Ethyl 2-cyclopente-1-one-4-(tetrahydro-2*H*-pyran-2-yloxy)-5-carboxylate (14c). A colorless oil was obtained in 82% yield. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.58 (dd, $J=6.0$, 2.4 Hz, 1H), 6.19 (dd, $J=6.0$, 2.7 Hz, 1H), 5.21 (m, 1H), 4.75–4.73 (m, 1H), 4.22 (q, $J=7.1$ Hz, 2H), 3.89–3.74 (m, 1H), 3.54–3.46 (m, 1H), 3.43 (d, $J=3.0$ Hz, 1H), 1.77–1.71 (m, 2H), 1.52–1.51 (m, 4H), 1.27 (t, $J=7.1$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 199.0, 168.1, 162.4, 133.4, 100.3, 79.5, 63.2, 61.5, 59.2, 30.6, 25.2, 19.7, 14.2; IR (KBr, cm^{-1}) 2945, 2873, 1741, 1716, 1595, 1444, 1369, 1346, 1261, 1146, 1024, 906 cm^{-1}; EIMS (*m/z*) 254 [M^+], 225, 207, 179 (100), 151, 123, 107, 95, 81, 67, 55. Anal. Calcd for $C_{13}H_{18}O_5$: C, 61.40; H, 7.14. Found: C, 61.32; H, 7.25.

3.7.4. Ethyl 2-hydroxy-1-naphthoate (15). A colorless oil was obtained in 65% yield. ^1H NMR ($CDCl_3$, 300 MHz) δ 12.08 (s, 1H), 8.40 (d, $J=8.4$ Hz, 1H), 7.77 (d, $J=8.7$ Hz, 1H), 7.74–7.33 (m, 3H), 7.26 (d, $J=8.7$ Hz, 1H), 4.45 (q, $J=7.2$ Hz, 2H), 1.44 (t, $J=7.2$ Hz, 3H); IR (KBr, cm^{-1}) 2954, 2925, 2854, 1649, 1579, 1466, 1398, 1375, 1381, 1255, 1207, 1161, 1092, 829, 796, 773.

Acknowledgements

The project is supported by Education Department of Hunan Province, P. R. China (Grant 03C247). One of the authors (J. W.) thanks the financial support from NSFC (20225205, 20390050).

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