Ruthenium catalyzed dimerization–ring expansion reaction of acetylenylcyclobutanols

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Dedicated to Professor Keiichiro Fukumoto on the occasion of his 70th birthday
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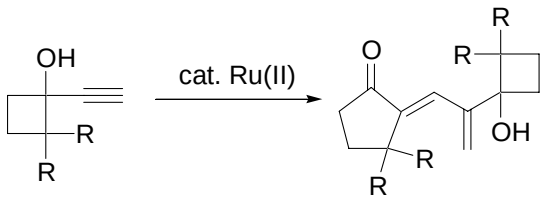
Abstract
A novel type of ring expansion reaction of acetylenylcyclobutanols which involves a dimerization process has been developed. The reaction simply proceeds in the presence of ruthenium catalyst to afford the ring-expanded dimer in moderate yield.

Keywords: Acetylenes, dimerizations, rearrangements, ruthenium catalysts

Introduction

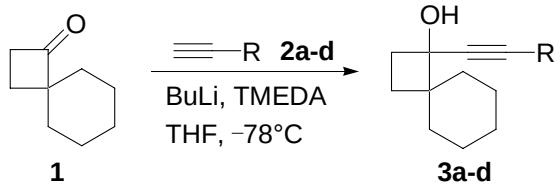
Transition-metal-promoted ring expansion reactions of cyclobutanol derivatives are well investigated reactions that are triggered by release in the strain of the four-membered ring systems.[1,2] Most of these ring expansions are triggered by palladium catalysts,[1] whose methodologies have been successfully applied to the syntheses of natural products.[3] On the other hand, few examples of ring expansion reactions catalyzed by other transition metals have been reported. Recently, we have developed a novel type of ring expansion reaction of allenylcyclobutanols triggered by ruthenium catalysis.[2,4] The reaction enables the one-pot synthesis of α-substituted cyclopentanones from allenylcyclobutanols and α,β-unsaturated carbonyl compounds. During the course of our studies to explore the application of ruthenium catalyzed reactions, we found a novel type of ring expansion reaction of acetylenylcyclobutanols involving a dimerization process[5] (Scheme 1). The results of investigations of this process are presented below.



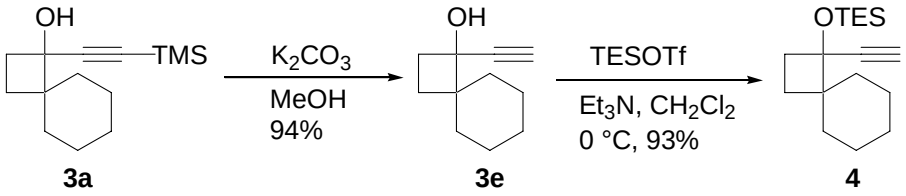
Scheme 1. Ruthenium catalyzed dimerization–ring expansion reaction.

Results and Discussion

The substrates for ruthenium catalyzed ring expansions are synthesized as follows (Scheme 2). Alkynylcyclobutanols **3a–3d**, which have various substituents at terminal position of alkynes are produced by the addition of corresponding alkynes **2a–2d** to spiro[3.5]nonan-1-one **1**[6] in 75% to quantitative yields. Desilylation of **3a** in the presence of K_2CO_3 in MeOH gives the unsubstituted substrate **3e** in 94% yield, and further silylation of the tertiary alcohol moiety by TESOTf affords **4** in 93% yield.



R	product	yield
TMS **2a**	**3a**	quant.
Ph **2b**	**3b**	quant.
Bu **2c**	**3c**	94%
4-pentynyl **2d**	**3d**	75%



Scheme 2. Syntheses of alkynylcyclobutanols.

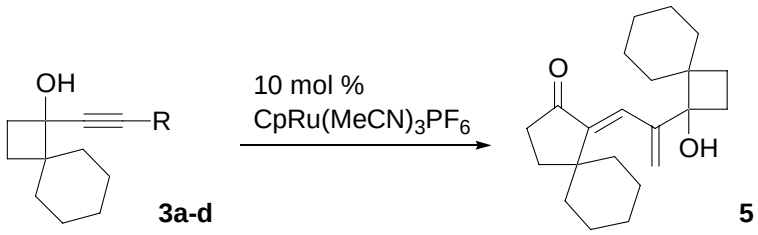
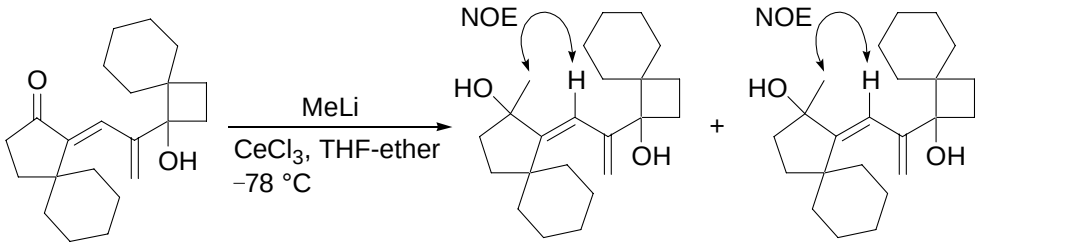


Table 1. Initial attempts at the ruthenium catalyzed dimerization–ring expansion reaction

Entry	Substrate (R)	Solvent	Temp. (°C)	Conc. (M)	Time (h)	Yield (%)[a]
1	TMS **3a**	DMF	60	0.1	24	N.R.
2	Ph **3b**	DMF	60	0.1	24	N.R.
3	Bu **3c**	DMF	60	0.1	24	N.R.
4	4-Pentenyl **3d**	DMF	60	0.1	24	N.R.
5	H **3e**	DMF	60	0.1	2	41
6	**3e**	DMF	80	0.1	4	35
7	**3e**	Dioxane	60	0.1	20	19(22)
8	**3e**	THF	60	0.1	6	23
9	**3e**	Acetone	60	0.1	9	7
10	**3e**	DMF	60	0.05	10	38(56)
11	**3e**	DMF	60	0.3	5	47
12	**3e**	DMF	60	0.5	1	52
13	**3e**	DMF	60	0.75	1	43

[a] The yields in parentheses are based on unrecovered starting material.

Our initial attempts at ruthenium-catalyzed ring expansion began with **3a–3e** in the presence of 10 mol. % $CpRu(MeCN)_3PF_6$ [7] in DMF at 60°C (Table 1). Although no reactions proceed from the substituted alkynes **3a–3d** (entries 1–4), the ring expanded product **5** accompanied by a dimerization process is obtained from the reaction of **3e,** in 41% yield (entry 5). The stereochemistry of **5** is determined unambiguously by NOESY correlation of **6a** and **6b**, which are produced from the reaction of **5** with MeLi (Scheme 3). From the optimization studies in entries 6–13, it is clear that the best result is obtained when the reaction is carried out in 0.5*M* DMF solution at 60°C (52% yield, Entry 12).



5 **6a** 53% **6b** (diastereomer of **6a**) 38%

Scheme 3. Determination of the stereochemistry of **5**.

We next examined the reactions in the presence of various additives (Table 2). Attempts at the reactions using bases such as $^{i}Pr_2NEt$, Et_3N and K_2CO_3 failed completely (entries 1–3). On the other hand, the reactions in the presence of various acids afford **5** in moderate yield (entries 4–9) although the yields are not comparable to those in the absence of any additives.

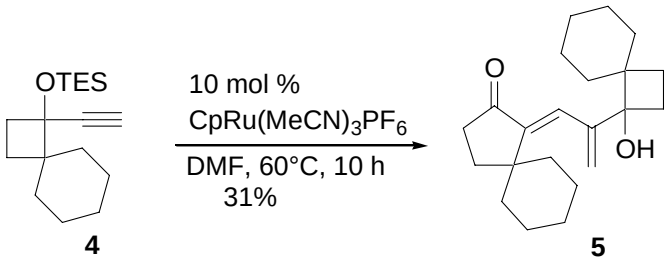
Table 2. Reactions of **3e** in the presence of various additives[a]

Entry	Additive (eq.)	Time (h)	Yield of **5** (%)
1	$^{i}Pr_2NEt$ (1.2)	24	trace
2	Et_3N (1)	24	trace
3	K_2CO_3 (1.5)	48	trace
4	CSA (1)	1.5	37
5	$KHSO_4$ (1)	2	25
6	KH_2PO_4 (1)	6	43
7	Na_2HPO_4 (1)	6	23
8	*p*-Nitrophenol (1)	5	45
9	Amberlyst 15 (1)[b]	4	42

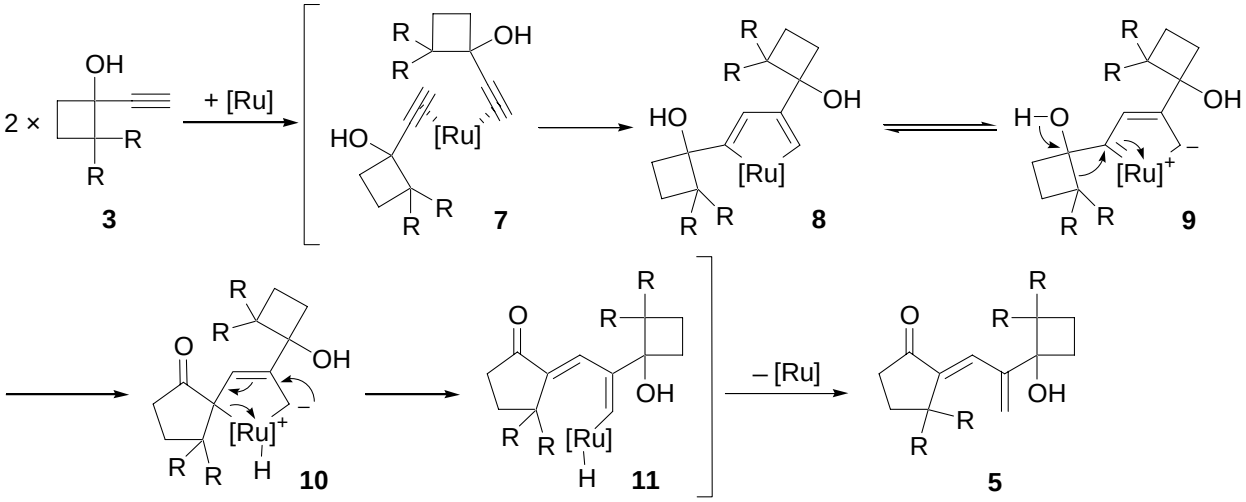
[a] All the reactions were carried out in the presence of 10 mol. % $CpRu(MeCN)_3PF_6$ in DMF at 60°C. [b] One weight equivalent of Amberlyst 15 was added.

The ring expansion reaction also proceeds even for the silylated substrate **4**, which produces the same product **5** in 31% yield (Scheme 4).

Scheme 5 shows the proposed mechanism for this dimerization–ring expansion reaction. It is expected that the key reaction intermediate is a ruthenacycle **8**,[5] which is formed by coordination (**7**) of ruthenium catalyst with two molecules of acetylenylcyclobutanol. There would be an equilibrium between the complex **8** and a zwitterionic intermediate **9**, which causes ring rearrangement followed by ring opening of the ruthenacycle (**10**) to form an alkenyl ruthenium hydride **11**. Finally, reductive elimination of ruthenium from **11** produces a ring-expanded dimer **5** together with regenerated ruthenium catalyst.

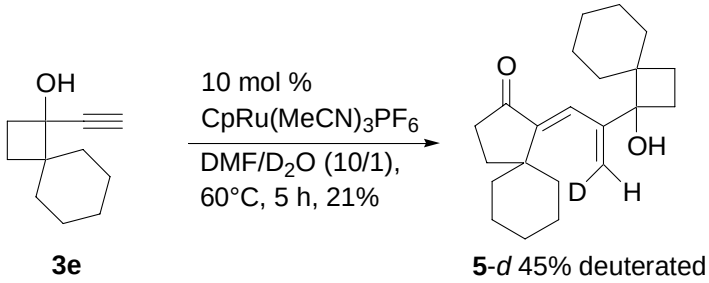


Scheme 4. Reaction of silylated substrate **4**.



Scheme 5. Proposed reaction mechanism.

To support the reaction mechanism described above, a reaction was examined in the presence of D_2O (Scheme 6). When the substrate **3e** is subjected to the reaction in a mixture of DMF and D_2O (10:1), deuterated product **5**-*d* is obtained in 21% yield (45% deuterated). The result is compatible with that the reactions proceed *via* the formation of the ruthenacycle **8**.



Scheme 6. Reaction in the presence of D_2O.

Conclusions

In conclusion, we have developed a novel type of ring expansion reaction of acetylenylcyclobutanols using ruthenium catalysis. The reaction enables the construction of the ring-expanded dimer in a stereoselective manner. Efforts to extend the scope of this reaction are currently in progress.

Experimental Section

General Procedures. All non-aqueous reactions were carried out under a positive atmosphere of argon or nitrogen in dried glassware, unless otherwise indicated. Materials were obtained from commercial suppliers and used without further purification except when otherwise noted. Solvents were dried and distilled according to standard protocols. The phrase "residue upon workup" refers to the residue obtained when the organic layer was separated and dried over anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure. Column chromatography was performed on silica gel 60N (Kanto Chemical Co., 100–210 μm), and flash column chromatography was performed on silica gel 60 (Kanto Chemical Co., 40–50 μm) using the solvent indicated. Reaction and chromatography fractions were analyzed by employing precoated silica gel 60 F_{254} plates (Merck). All melting points were determined on Yanaco micro-melting point apparatus and are uncorrected. IR spectra were measured on a SHIMADZU FTIR-8300 spectrometer. NMR spectra were recorded on Varian Gemini 2000, JEOL AL400 or JEOL JNM-GX 500 spectrometers with tetramethylsilane or chloroform as internal standard. Mass spectra were recorded on JEOL JMS-DX-303 or JMS-AX-500 JMS-AX-700 spectrometers. Elemental analyses were performed by Yanaco CHN CORDER MT-6.

General procedure for the synthesis of alkynylcyclobutanols

Synthesis of 1-[(2-trimethylsilyl)ethynyl]spiro[3.5]nonan-1-ol (3a). To a stirred solution of (trimethylsilyl)acetylene (**2a**) (4.30 g, 43.4 mmol) and TMEDA (5.04 g, 43.4 mmol) in THF (100 mL) was added 1.57 *M* solution of BuLi in hexane (27.6 mL, 43.4 mmol) at –78 °C. After stirring at -78°C for 1 h, a solution of spiro[3,5]nonan-1-one **1**[6] (2.00 g, 14.5 mmol) in THF (10 mL) was added dropwise to this solution, and stirring was continued for 3 h at the same temperature. The reaction mixture was diluted with water and extracted with Et_2O. The combined extracts were washed with aqueous NH_4Cl and saturated aqueous NaCl. The residue from workup was chromatographed on silica gel with hexane–AcOEt (92:8 v/v) as eluent to give the acetylenyl alcohol **3a** (3.43 g, quant.) as a colorless oil: IR (neat) 3364, 2162 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.17 (9H, s), 1.16–1.54 (8H, m), 1.59–1.71 (4H, m), 1.98 (1H, brs), 2.11 (1H, ddd, *J* = 11.7, 10.0 and 8.3 Hz), 2.30 (1H, ddd, *J* = 11.7, 9.0 and 4.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ –0.2, 22.3, 22.7, 25.4, 25.9, 30.7, 33.3, 35.2, 47.5, 72.9, 90.1, 107.6; MS *m/z* 235 (M^+–1); HRMS calcd for $C_{14}H_{23}OSi$ (M^+–1) 235.1519, found 235.1515.

1-(2-Phenylethynyl)spiro[3.5]nonan-1-ol (3b). Quantitative yield; colorless oil; IR (neat) 3369 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.20–1.81 (12H, m), 2.19 (1H, brs), 2.22 (1H, ddd, *J* = 12.0, 9.9 and 8.4 Hz), 2.41 (1H, ddd, *J* = 12.0, 9.0 and 4.8 Hz), 7.27–7.32 (3H, m), 7.41–7.46 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.3, 22.8, 25.6, 25.9, 30.8, 33.5, 35.3, 48.2, 73.2, 85.9, 90.9, 123.0, 128.2, 128.3, 131.7; MS *m/z* 240 (M^+); HRMS calcd for $C_{17}H_{20}O$ (M^+) 240.1514, found 240.1517.

1-(1-Hexynyl)spiro[3.5]nonan-1-ol (3c). Yield 94 %; colorless oil; IR (neat) 3381, 2233 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.92 (3H, t, *J* = 7.5 Hz), 1.18–1.71 (16H, m), 1.93 (1H, brs), 2.11

(1H, ddd, *J* = 11.7, 9.9 and 8.4 Hz), 2.21–2.30 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.4, 18.3, 21.8, 22.4, 22.8, 25.4, 26.0, 30.7, 30.8, 33.7, 35.3, 47.8, 73.0, 81.7, 86.4; MS *m/z* 220 (M^+); HRMS calcd for $C_{15}H_{24}O$ (M^+) 220.1827, found 220.1825.

1-(1,6-Heptadiynyl)spiro[3.5]nonan-1-ol (3d). Yield 75 %; colorless oil: IR (neat) 3418, 3308, 2118, 635 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17–1.78 (14H, m), 1.93 (1H, brs), 1.97 (1H, t, *J* = 2.4 Hz), 2.10 (1H, ddd, *J* = 11.7, 9.8 and 8.1 Hz), 2.26 (1H, ddd, *J* = 11.7, 9.0 and 4.9 Hz), 2.32 (2H, td, *J* = 7.1 and 2.4 Hz), 2.38 (2H, t, *J* = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.4, 17.7, 22.3, 22.8, 25.4, 25.9, 27.5, 30.7, 33.7, 35.3, 47.7, 68.8, 72.9, 82.5, 83.5, 85.0; MS *m/z* 229 (M^+–1); HRMS calcd for $C_{16}H_{21}O$ (M^+–1) 229.1593, found 229.1589.

1-Ethynylspiro[3.5]nonan-1-ol (3e). To a stirred solution of the acetylenyl alcohol **3a** (2.00 g, 8.46 mmol) in MeOH (25 mL) was added K_2CO_3 (1.28 g, 9.23 mmol) at r.t. After stirring for 8 h at the same temperature, the reaction mixture was diluted with water, then concentrated *in vacuo* to remove most of the MeOH. The resulting mixture was extracted with Et_2O and the combined extracts were washed with saturated aqueous NaCl. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (90:10 v/v) as eluent to give the alcohol **3e** (1.31 g, 94 %) as a colorless oil: IR (neat) 3390, 3307, 625 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18–1.76 (12H, m), 2.09 (1H, brs). 2.14 (1H, ddd, *J* = 12.0, 9.6 and 8.1 Hz), 2.33 (1H, ddd, *J* = 12.0, 9.0 and 5.1 Hz), 2.58 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.3, 22.7, 25.4, 25.9, 30.6, 33.3, 35.1, 47.4, 72.8, 73.8, 85.6; MS *m/z* 163 (M^+–1); HRMS calcd for $C_{11}H_{15}O$ (M^+–1) 163.1122, found 163.1098.

1-Ethynyl-1-(triethylsilyloxy)spiro[3.5]nonane (4). To a stirred solution of the acetylenyl alcohol **3e** (299 mg, 1.82 mmol) and Et_3N (442 mg, 4.37 mmol) in CH_2Cl_2 (20 mL) was added TESOTf (577 mg, 2.18 mmol) at 0 °C. After stirring for 3 h at the same temperature, the reaction mixture was diluted with water and extracted with Et_2O. The combined extracts were washed with saturated aqueous $NaHCO_3$ and saturated aqueous NaCl. The residue upon workup was chromatographed on silica gel with hexane as eluent to give the silyl ether **4** (474 mg, 93 %) as a colorless oil: IR (neat) 3308, 621 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.65 (6H, q, *J* = 7.8 Hz), 0.97 (9H, t, *J* = 7.8 Hz), 1.22–1.70 (12H, m), 2.12 (1H, dt, *J* = 11.2 and 9.7 Hz), 2.25 (1H, ddd, *J* = 11.2, 8.8 and 3.4 Hz), 2.51 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 5.8, 6.8, 22.5, 22.9, 25.1, 26.1, 31.0, 35.3, 35.5, 48.5, 73.0, 73.8, 86.8; MS *m/z* 278 (M^+); HRMS calcd for $C_{17}H_{30}OSi$ (M^+) 278.2066, found 278.2052.

Procedure for the ruthenium catalyzed dimerization–ring expansion reaction. (*E*)-1-[2-(1-Hydroxyspiro[3.5]non-1-yl)-2-propenylidene]spiro[4.5]decan-2-one (5)

To a stirred solution of the ethynylcyclobutanol **3e** (147 mg, 0.894 mmol) in DMF (1.8 mL) was added $CpRu(MeCN)_3PF_6$ [7] (38.8 mg, 0.0894 mmol) at r.t. After stirring for 1.5 h at 60 °C, the reaction mixture was diluted with AcOEt, then washed with water and saturated aqueous NaCl. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (85:15 v/v) as eluent to give the cyclopentanone **5** (75.7 mg, 52 %) as a colorless oil: IR (neat) 3347, 1710, 1616 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.12–1.33 (7H, m), 1.36–1.75 (14H, m), 1.78–1.90

(3H, m), 2.08–2.21 (2H, m), 2.31–2.35 (2H, m), 2.38–2.44 (1H, m), 5.27 (1H, s), 5.29 (1H, s), 6.90 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.1, 22.2, 22.4, 25.1, 25.6, 25.8, 28.8, 28.9, 31.5, 33.2, 34.3, 34.6, 35.8, 45.0, 47.7, 81.4, 115.5, 133.8, 146.8, 147.9, 208.5; MS *m/z* 328 (M^+); HRMS calcd for $C_{22}H_{32}O_2$ (M^+) 328.2402, found 328.2388.

(*E*)-1-[2-(1-Hydroxyspiro[3.5]non-1-yl)-2-propenylidene]-2-methylspiro[4.5]decan-2-ols (6a and 6b). To a stirred suspension of anhydrous cerium chloride (183 mg, 0.742 mmol) in THF (1.4 mL) was added a 1.20M solution of MeLi in Et_2O (0.53 mL, 0.636 mmol) at –78 °C. After stirring was continued for 0.5 h at –78 °C, a solution of the cyclopentanone **5** (34.7 mg, 0.106 mmol) in THF (1.2 mL) was added dropwise to this solution and the stirring was continued for 2 h at the same temperature. The reaction mixture was diluted with water and extracted with AcOEt. The combined extracts were washed with saturated aqueous NH_4Cl and saturated aqueous NaCl. The residue from workup was chromatographed on silica gel with hexane–AcOEt (80:20 v/v) as eluent to give the cyclopentanol **6a** (19.3 mg, 53 %) and the diastereomer **6b** (13.7 mg, 38 %). **6a**: colorless prisms; m.p. 152–153 °C (Et_2O–hexane); IR (KBr) 3342, 1640, 1610 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.05–1.38 (12H, m), 1.43–1.60 (10H, m), 1.65–1.90 (7H, m), 1.95–2.01 (1H, m), 2.08 (1H, brs), 2.18 (1H, brs), 2.36 (1H, ddd, *J* = 12.5, 9.0 and 6.5 Hz), 5.12 (1H, s), 5.16 (1H, s), 5.89 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.3, 22.6, 22.9, 23.0, 25.2, 25.6, 26.0, 28.6, 29.0, 31.9, 32.2, 33.3, 35.0, 38.3, 38.6, 46.5, 47.9, 80.3, 81.4, 113.5, 121.7, 147.6, 162.0; MS *m/z* 342 (M^+–2); Anal. Calcd for $C_{23}H_{36}O_2$: C, 80.18; H, 10.52. Found: C, 79.85; H, 10.40. **6b**: colorless prisms; m.p. 124–125 °C (Et_2O–hexane); IR (KBr) 3447, 1628 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10–2.02 (32H, m), 2.39 (1H, ddd, *J* = 12.0, 9.2 and 6.8 Hz), 5.14 (1H, s), 5.16 (1H, s), 5.91 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.3, 22.6, 22.8, 23.0, 25.2, 25.6, 26.0, 28.0, 29.2, 31.9, 32.1, 33.3, 35.8, 38.1, 38.6, 46.7, 47.9, 80.5, 81.3, 113.4, 121.7, 147.3, 163.2; MS *m/z* 344 (M^+); Anal. calcd for $C_{23}H_{36}O_2$: C, 80.18; H, 10.53. Found: C, 79.82; H, 10.52%.

(*E*)-1-[2-(1-Hydroxyspiro[3.5]non-1-yl)-[3-$^2H_1$]-2-propenylidene]spiro[4.5]decan-2-one (5-*d*) and (*E*)-1-[2-(1-Hydroxyspiro[3.5]non-1-yl)-2-propenylidene]spiro[4.5]decan-2-one (5) in the ratio of 45:55. To a stirred solution of the ethynylcyclobutanol **3e** (55.9 mg, 0.340 mmol) in DMF (0.68 mL) and D_2O (0.07 mL) was added $CpRu(MeCN)_3PF_6$ (14.8 mg, 0.0340 mmol) at r.t. After stirring for 5 h at 60°C, the reaction mixture was diluted with AcOEt, then washed with water and saturated aqueous NaCl. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (85:15 v/v) as eluent to give the 45:55 mixture of cyclopentanone **5-*d*** and **5** (11.5 mg, 21 %) as a colorless oil: IR (neat) 3347, 1710, 1616 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.12–1.33 (7H, m), 1.36–1.75 (14H, m), 1.78–1.90 (3H, m), 2.08–2.21 (2H, m), 2.31–2.35 (2H, m), 2.38–2.44 (1H, m), 5.27 (1H, s), 5.29 (0.55H, s), 6.90 (1H, s); MS *m/z* 329 (M^+); HRMS Calcd for $C_{22}H_{31}DO_2$ (M^+) 329.2465, found 329.2469 (**5-*d***), MS *m/z* 328 (M^+); HRMS Calcd for $C_{22}H_{32}O_2$(M^+) 328.2402, found 328.2407 (**5**).

Acknowledgments

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