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Triaminocyclopentadienyl Ruthenium Complexes – New Catalysts for Cascade Conversions of Propargyl Alcohols

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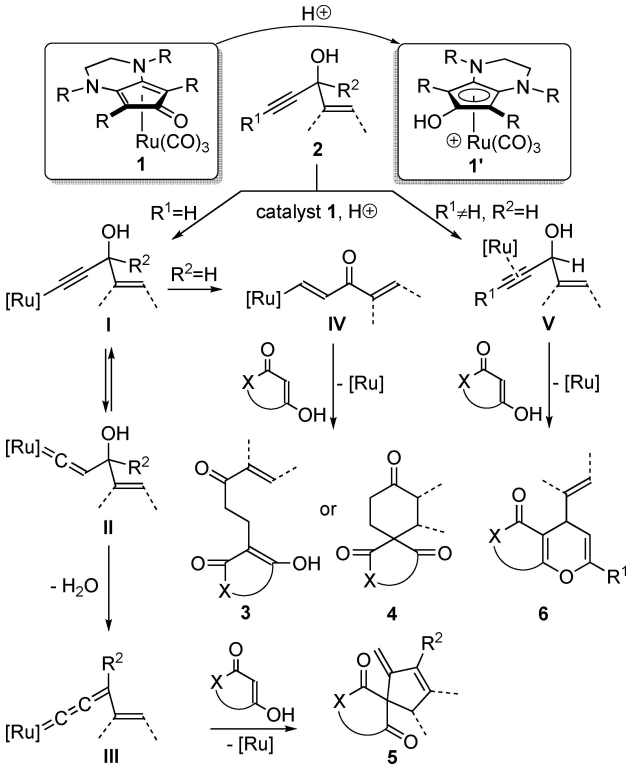
Abstract: Various triaminocyclopentadienyl ruthenium complexes have been synthesized from $Ru_3(CO)_{12}$. The new complexes were tested for their ability to catalyze cascade conversions of propargyl alcohols. Their associated catalytic activities complement the activities of known diaminocyclopentadienone ruthenium complexes. In particular, the substrate scope of catalytic cycloadditions with 3-ketolactones or phloroglucinol derivatives is extended to terpenoid-derived propargyl alcohols containing an internal alkyne moiety. A wide range of cyclic terpenoid and phloroglucinol adducts are obtained by complementary application of both types of catalysts.

Introduction

Transition metal-catalyzed cascade reactions provide an atom-economical approach to the efficient synthesis of complex molecular scaffolds. Such transformations are particularly suitable for the preparation of natural products and analogues as important lead structures in the context of drug discovery.[1,2] With regard to the multiply functionalized precursors required for the desired cascade conversions, 1-alkenylpropargyl alcohols (1-en-4-yn-3-ols) are particularly noteworthy. These enynols are directly accessible from a broad range of readily available α,β-unsaturated aldehydes or ketones by acetylide addition. All carbon atoms of this versatile C_5 subunit are selectively addressable with the aid of various transition-metal catalysts. Due to the presence of three different functional groups, several modes of activation can be applied, giving rise to diverse cascade transformations.[3]

Ruthenium cyclopentadienone complexes of type **1** catalyze diverse cascade conversions of 1-alkenylpropargyl alcohols **2** with various nucleophiles.[4] An acidic promoter is beneficial in most cases. The redox-coupling between the metal and the ligand in complexes of type **1** is crucial for all of these conversions and the activation of the alkyne unit in **2** depends most likely on electrophilic ruthenium(II) species **1'** that is privileged under acidic conditions (Scheme 1). The mode of activation depends on the nature of the substrate. Terminal propargyl alcohols **2** ($R^1 = H$) are converted via alkynyl complex **I**, which is in equilibrium with the corresponding vinylidene compound **II**. Subsequent loss of water generates allenylidene species **III**. Secondary derivatives **2** (R^1, $R^2 = H$) are alternatively transformed in a redox-isomerization process to generate alkenyl species **IV**. Internal substrates **2** ($R^1 \neq H$) are activated via π-complex **V**. Subsequent trapping of the metalated intermediates **I**–**V** with various nucleophiles give rise to diverse carbo- and heterocyclic compounds with release of the catalytically active species.[4] Thus, in presence of cyclic 1,3-dicarbonyl compounds, terminal secondary substrates **2** (R^1, $R^2 = H$) form



Scheme 1. Activation and conversion of propargyl alcohols **2** catalyzed by ruthenium cyclopentadienone complexes **1**.

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Michael-adducts **3** or spirocyclohexanones **4**, whereas terminal tertiary substrates **2** ($R^1 = H$, $R^2 \neq H$) are converted to methylene spirocyclopentenes **5** in an allylation/carbocyclization cascade. Internal secondary substrates **2** ($R^1 \neq H$, $R^2 = H$) form 4*H*-pyrans **6** with cyclic 1,3-dicarbonyl compounds in a formal cycloaddition process (Scheme 1).

Exchange of the ligand's carbonyl oxygen for nitrogen should dramatically affect the redox-coupling with the metal and could thereby alter the catalyst's mode of action. Herein, we present various triaminocyclopentadienyl ruthenium(II) complexes of type **7** and compare some of their catalytic activities with the activity of diamino-cyclopentadienone catalyst **1a** (Scheme 2). Complexes of type **7** can be regarded as aza analogues of the activated species **1'**.

Results and Discussion

The ligands **L7** are generated from cyclopentadienone **L1a** by a modified protocol of the method from Gompper et al.[5] Complexes **7** are formed from iminium precursors **L7** as formal ruthenium(II) species, whereas catalysts of type **1** derived from cyclopentadienone precursors **L1** arise as formal ruthenium(0) complexes (Scheme 2).[4c,6]

Various primary amines are suitable for this conversion including enantiopure derivatives. The range of appropriate secondary amines, however, is rather limited due to strong steric repulsion in the planar iminium compounds **L7**. Further conversion of **L7** with ruthenium carbonyl results in the formation of the desired triaminocyclopentadienyl complexes **7** in almost all cases. The highest yields are obtained from ligand **L7j** and complex **7j** can be easily prepared in racemic or enantiopure (*R*)- or (*S*)-form from inexpensive commercially available amines. Therefore, complex **7j** was used as an exemplary representative of the aza-catalysts **7**. Broadening of the corresponding NMR-signals indicates a significant hindrance to the rotation of the phenyl groups in all complexes of type **7**. Formation of complex **7o** is not successful due to the metal chelating effect of the guanidine unit (Figure 1). We previously reported on the related synthesis of *N*-unsubstituted complex **7a**.[4c]

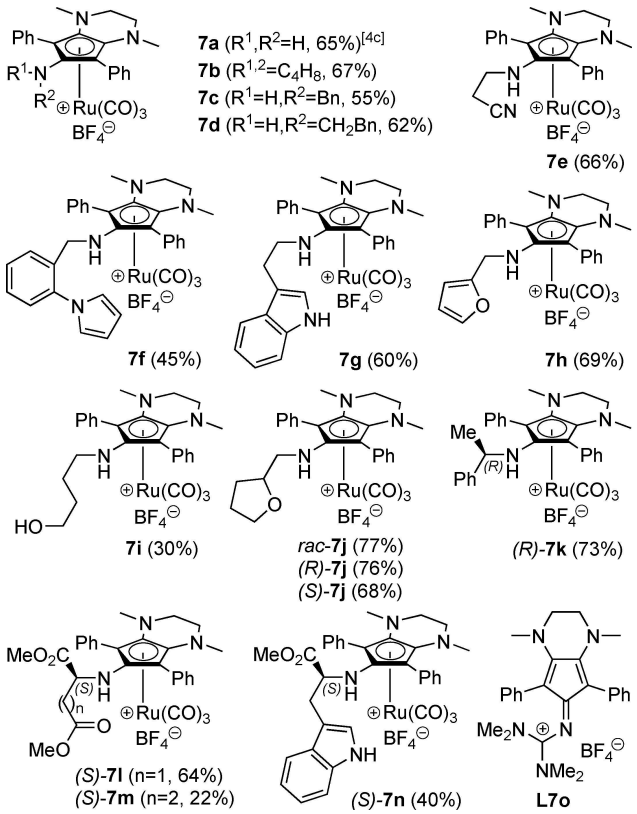
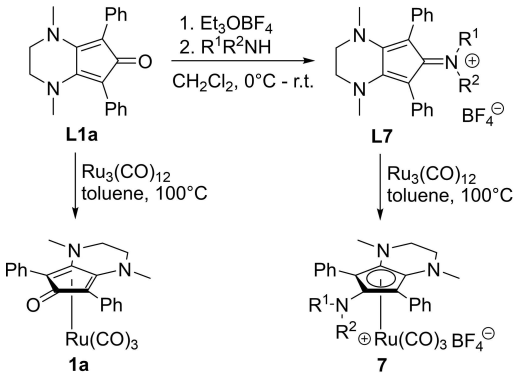
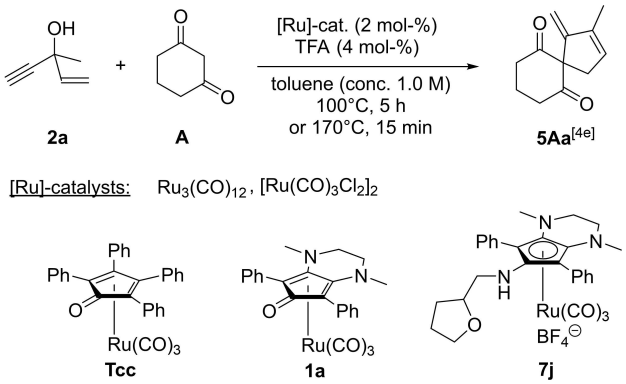


Figure 1. Prepared triaminocyclopentadienyl ruthenium(II) complexes (**7**).

Next, we compared some of the catalytic activities of the new catalysts **7** towards 1-alkenylpropargyl alcohols **2** with those of catalyst **1a**. We based the first systematic comparative study on the allylation/carbocyclization cascade of terminal tertiary 1-alkenylpropargyl alcohols **2** with cyclic carbon nucleophiles. Conversion of alcohol **2a** with 1,3-cyclohexandione (**A**) in toluene (1.0 M) at 100 °C in presence of catalyst **1a** (2 mol %) and trifluoroacetic acid (TFA, 4 mol %) as an acidic promoter, generates compound **5Aa**[4e] in 82 % yield (Scheme 3; Table 1, entry 3). No conversion was observed in absence of the



Scheme 2. Synthesis of complex **1a** and aza-derivatives **7**.



Scheme 3. Conversion of propargyl alcohol **2a** with 1,3-cyclohexanedione (**A**).

Table 1. Formation of compound **5Aa** applying different catalysts.

No	catalyst	promoter	conditions[a]	Yield **5Aa**
1	none	TFA	100 °C, 5 h	n.c.
2	**1a**	none	100 °C, 5 h	31 %[b]
3	**1a**	TFA	100 °C, 5 h	82 %[c]
4	**1a**	TFA	170 °C, 15 min	19 %[b]
5	$Ru_3(CO)_{12}$	TFA	100 °C, 5 h	5 %[b]
6	$Ru_3(CO)_{12}$	TFA	170 °C, 15 min	5 %[b]
7	$[RuCl(CO)_3]_2$	TFA	100 °C, 5 h	3 %[b]
8	$[RuCl(CO)_3]_2$	TFA	170 °C, 15 min	4 %[b]
9	**Tcc**	TFA	100 °C, 5 h	10 %[b]
10	**Tcc**	TFA	170 °C, 15 min	12 %[b]
11	**7j**	TFA	100 °C, 5 h	15 %[b]
12	**7j**	none	100 °C, 5 h	19 %[b]
13	**7j**	none	170 °C, 15 min	8 %[b]

n.c. = no conversion. [a] Substrate concentration 1.0 M. [b] Yield determined by NMR using an internal standard. [c] Isolated yield.

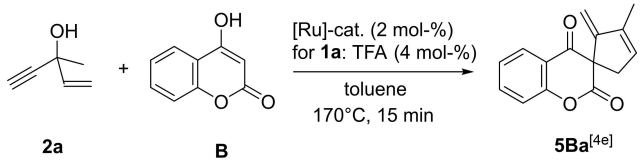
Table 2. Formation of compound **5Ba** applying different catalysts.

No	catalyst	promoter	concentration	conversion[a]	Yield **5Ba**
1[b]	**1a**	TFA	1.0 M	100 %	91 %[d]
2[c]	**1a**	TFA	1.0 M	98 %	87 %[e]
3[c]	**1a**	TFA	0.5 M	79 %	69 %[e]
4[c]	**1a**	TFA	0.25 M	56 %	45 %[e]
5[c]	**1a**	none	0.25 M	58 %	36 %[e]
6[c]	**7a**	none	0.25 M	30 %	25 %[e]
7[c]	**7b**	none	0.25 M	32 %	24 %[e]
8[c]	**7c**	none	0.25 M	50 %	42 %[e]
9[c]	**7d**	none	0.25 M	53 %	41 %[e]
10[c]	**7e**	none	0.25 M	83 %	73 %[e]
11[c]	**7e**	none	1.0 M	95 %	70 %[e]
12[c]	**7f**	none	0.25 M	24 %	17 %[e]
13[c]	**7g**	none	0.25 M	32 %	24 %[e]
14[c]	**7h**	none	0.25 M	59 %	54 %[e]
15[c]	**7i**	none	0.25 M	34 %	19 %[e]
16[c]	**7j**	none	0.25 M	42 %	35 %[e]
17[c]	**7j**	TFA	0.25 M	27 %	22 %[e]
18[c]	**7j**	none	1.0 M	100 %	89 %[d]
19[c]	**7k**	none	0.25 M	37 %	23 %[e]
20[c]	**7l**	none	0.25 M	27 %	15 %[e]
21[c]	**7m**	none	0.25 M	35 %	21 %[e]
22[c]	**7n**	none	0.25 M	23 %	18 %[e]

[a] determined by NMR via remained **B** using an internal standard. [b] 100 °C, 5 h. [c] 170 °C, 15 min. [d] Isolated yield. [e] Yield determined by NMR using an internal standard.

catalyst and a significantly lower yield was obtained in absence of the acidic promoter (Table 1, entries 1, 2). At 170 °C (microwave irradiation) a significant lower yield is obtained (Table 1, entry 4). Complex **1a** shows high long-term stability at higher temperature and no decomposition is observed at 170 °C in toluene about 20 h. However, in presence of the acidic promoter (2 equiv.), decomposition occurs at elevated temperatures. At 170 °C, 49 % of **1a** remained after 5 minutes, 34 % after 10 minutes and 25 % after 15 minutes (determined by NMR using an internal standard). Only small amounts of product **5Aa** are obtained if $Ru_3(CO)_{12}$, $[Ru(CO)_3Cl_2]_2$ or the tetracyclone complex **Tcc** were applied as catalysts under similar reaction conditions (Table 1, entries 5–10). Exemplary aza-catalyst **7j** was applied in absence of an acidic promoter, since a counterproductive effect has been observed (Table 1, entries 11–13). Unfortunately, only low yields of **5Aa** are obtained at 100 °C, as well as at 170 °C, even though complex **7j** shows no remarkable decomposition at 170 °C.

In contrast, if β-ketolactones like 4-hydroxycoumarin (**B**) are used as nuclophiles, catalysts of type **7** exhibit much higher activity. At a concentration of 1.0 M, full conversion of the substrates and comparably high yields of product **5Ba** are obtained with catalyst **1a** in presence of an acidic promoter at 100 °C (5 h) or at 170 °C (μW, 15 min) as well as with catalyst **7j** in absence of an acidic promoter (Scheme 4; Table 2, entries 1, 2, 18). The reaction rate decreases with higher dilution. At a concentration of 0.25 M, 56 % of the nucleophile **B** has been converted in presence of catalyst **1a** (2 mol %) and TFA (4 mol %) after 15 minutes at 170 °C (Table 2, entries 2–4). The latter conditions are applied to compare the activities of all new complexes **7**. Complex **7e** exhibits the highest activity, but no



2a **B** **5Ba**[4e]

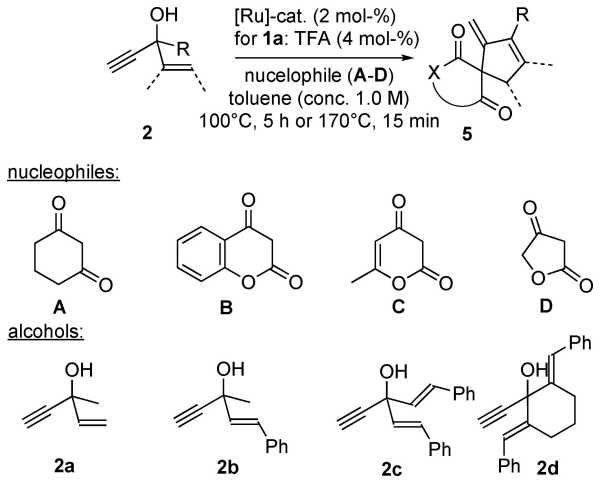
Scheme 4. Conversion of propargyl alcohol **2a** with 4-hydroxycoumarin (**B**).

improvement regarding the yield of **5Ba** is observed at higher concentration. In contrast, full conversion is observed at a concentration of 1.0 M with less active complex **7j** (Table 2, entries 10, 11, 18). Therefore, complex **7j** represents a good compromise in terms of stability, activity, and availability.

Similar results are obtained with other substrates. In general, high yields of products **5** are obtained from alcohols **2a–d** with 2-keto lactones if catalyst **1a** with an acidic promoter or catalyst **7j** are applied at 170 °C (μW, 15 min). With 1,3-diketones, however, high yields are only obtained with catalyst **1a** and an acidic promoter at 100 °C (5 h). The yields and diasteroselectivities of the reactions catalyzed by complex **7j** are generally lower, compared to the same reactions catalyzed by **1a** (Scheme 5; Table 3; Figure 2).

It was previously shown, that catalyst **1a** converts terminal secondary propargyl alcohols with various nucleophiles in a redox-isomerization/Michael addition cascade process (Scheme 1).[4a,e–f] As expected, the conversion of secondary substrates **2e–g** with nucleophiles **A–D** in presence of catalyst **1a** and TFA as an acidic promoter proceeds via redox-isomerization product **8** and leads to the formation of Michael addition products **3** or **4** in most cases. In contrast, catalyst of type **7** do not catalyze conversions of secondary alcohols **2e–g**, neither in the presence nor in the absence of an acidic promoter (Scheme 6; Table 4). This is in accordance with further preliminary examinations regarding the catalytic activity of complexes **7** towards various terminal secondary propargyl alcohols.

The activation of terminal substrates **2** by complexes of type **1** occurs by the initial formation of alkynyl species **I-1** (Scheme 5) as it was shown by labeling experiments.[4f] We assume, that the following 1,2-*H*-shift is initiated by intra-



Scheme 5. Conversion of terminal tertiary substrates with nucleophiles **A**–**D**.

Table 3. Products from alcohols **2a**–**d** with nucleophiles **A**–**D** catalyzed by different catalysts (substrate concentration 1.0 M).

catalyst	nucleophile	products from **2a**	products from **2b**	products from **2c**	products from **2d**
1a	**A**	**5Aa**[a,d] (82%)	**5Ab**[a,d] (49%)	**5Ac**[b,d] (89%)	**5Ad**[a,d] (97%)
1a	**B**	**5Ba**[a,d] (91%)	**5Bb**[a,d] (90%, *dr* 5:4)	**5Bc**[b,d] (54%, *dr* 5:2)	**5Bd**[a,d] (93%, *dr* 5:1)
1a	**C**	**5Ca**[c,e] (86%)	**5Cb**[c,e] (61%, *dr* 15:1)	**5Cc**[c,e] (92%, *dr* 15:1)	**5Cd**[c,e] (98%, *dr* 17:1)
1a	**D**	**5Da**[c,e] (82%)	**5Db**[f] (80%, *dr* 2:1)	**5Dc**[f] (80%, *dr* 2:1)	**5Dd**[c,e] (98%, *dr* 3:1)
7j	**A**	**5Aa**[a,d] (19%)	**5Ab**[a,d] (8%)	**5Ac**[a,d] (15%)	**5Ad**[a,d] (15%)
7j	**B**	**5Ba**[a,f] (89%)	**5Bb**[a,f] (67%, *dr* 2:1)	**5Bc**[b,f] (55%, *dr* 1:1)	**5Bd**[a,f] (85%, *dr* 3:2)
7j	**C**	**5Ca**[c,f] (80%)	**5Cb**[c,f] (62%, *dr* 6:1)	**5Cc**[c,f] (81%, *dr* 4:1)	**5Cd**[c,f] (92%, *dr* 2:1)
7j	**D**	**5Da**[c,f] (39%)			**5Dd**[c,f] (90%, *dr* 5:2)

[a] Compound previously reported in Ref. [4]e. [b] Compound previously reported in Ref. [4]c. [c] Compound previously reported in Ref. [4]b. [d] Prepared by conventional heating (100 °C, 5 h). [e] 180 °C, 5 min. [f] 170 °C, 15 min.

molecular protonation of the alkyne unit via the ligands acidic hydroxyl group. Complexes of type **7** also activate terminal substrates **2** as alkynyl species (**I-7**), but no redox-isomerization takes place, presumably due to the lower acidity of the ligands amino function (Scheme 7).

We previously reported, that complex **1a** catalyze the cycloaddition of 1,3-dicarbonyl compounds with some internal secondary propargyl alcohols. This conversion is especially interesting with substrates containing an additional alkenyl substituent like **2h**, since the diene product (**6Bh**) can be further transformed by a [2+4]-cycloaddition in a one pot

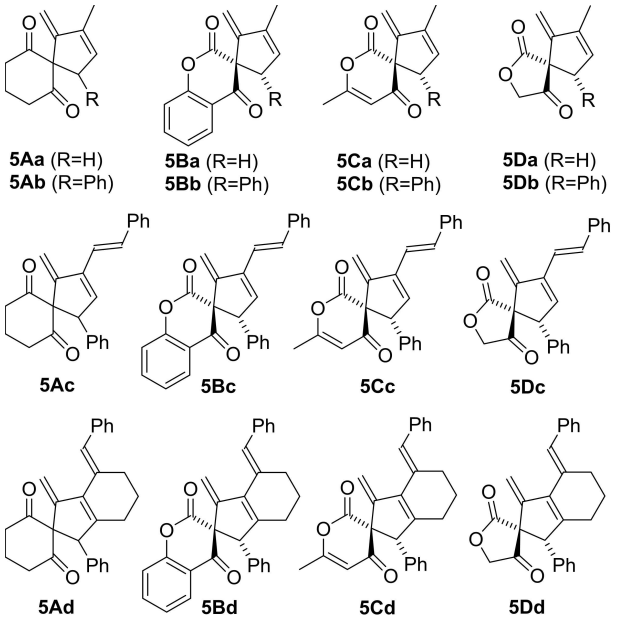
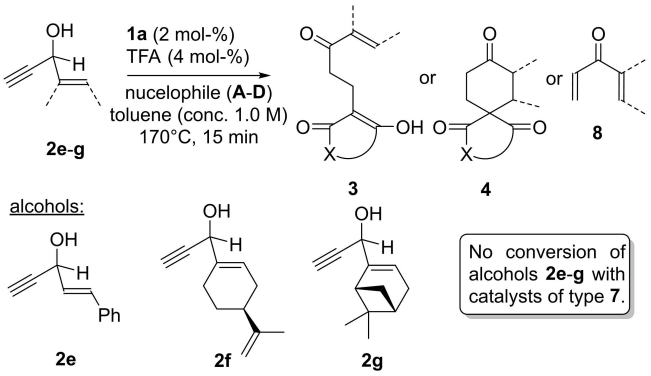


Figure 2. Isolated products from terminal tertiary substrates **2a**–**d** and nucleophiles **A**–**D**.

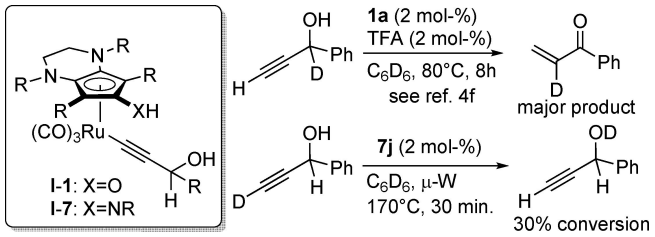


Scheme 6. Conversion of terminal secondary substrates with nucleophiles **A**–**D**.

Table 4. Products of alcohols **2e**–**g** with nucleophiles **A**–**D** catalyzed by catalyst **1a** (substrate concentration 1.0 M; 170 °C, 15 min).

catalyst	nuc.	products from **2e**	products from **2f**	products from **2g**
1a	**A**	**4Ae**[a] (85%) **3Ae**[a] (10%)	**3Af** (68%) **8f**[b] (26%)	**3Ag** (trace) **8g**[b] (96%)
1a	**B**	**3Be**[a] (64%) **8e**[b] (31%)	**8f**[b] (98%)	**8g**[b] (99%)
1a	**C**	**3Ce** (48%) **8e**[b] (46%)	**8f**[b] (95%)	**8g**[b] (97%)
1a	**D**	**4De** (45%, *dr* 2:1) **8e**[b] (28%)		
7a–n	**A–D**	n.c.	n.c.	n.c.

n.c. = no conversion. [a] Compound previously reported in Ref. [4]e. [b] Compound previously reported in Ref. [4]a.

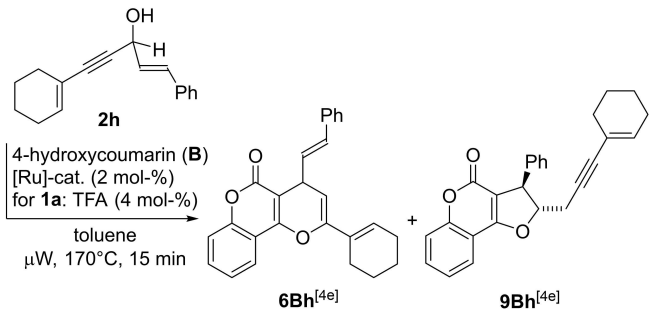


Scheme 7. Activation of terminal propargyl alcohols **2** by complexes **1a** or **7j**.

process (Scheme 8).[4e] Byproduct **9Bh** is formed with low *trans*-selectivity by allylation of the nucleophile and subsequent 5-*exo-trig* cyclization.

Comparable yields and selectivities are obtained at 100 °C (5 h) or at 170 °C (μW, 15 min) if catalyst **1a** (2 mol%) and TFA (4 mol%) are applied. The reaction rate decreases with higher dilution (table 5, entries 1–3). Complexes of type **7** also catalyze this transformation, but with lower activity and chemoselectivity. The complexes of type **7** show hardly any differences in activity among one another (table 5, entries 4–10).

Now, we wanted to apply this transformation to terpenoid-derived propargyl alcohols **2i**–**2l**. With regard to the synthesis of phloroglucinol-terpenoid adducts,[7] ploroglucinol derivative **E** was used as an additional *CH*-acidic nucleophile (Scheme 9).

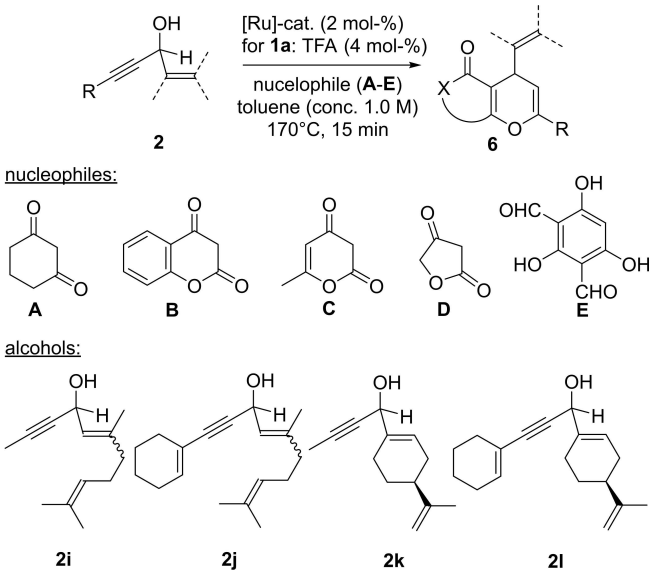


Scheme 8. Conversion of alcohol **2h** with 4-hydroxycoumarin (**B**).

Table 5. Formation of compounds **6Bh** and **9Bh** applying different catalysts

No	catalyst	promoter	conc.	6Bh	9Bh
1[a]	**1a**	TFA	1.0 M	62%[c]	29%[c] (*dr* 3:2)
2[b]	**1a**	TFA	1.0 M	66%[d]	24%[d] (*dr* 3:2)
3[b]	**1a**	TFA	0.5 M	43%[d]	18%[d] (*dr* 3:2)
4[b]	**7c**	none	0.5 M	19%[d]	23%[d] (*dr* 4:3)
5[b]	**7d**	none	0.5 M	20%[d]	23%[d] (*dr* 2:1)
6[b]	**7e**	none	0.5 M	18%[d]	20%[d] (*dr* 2:1)
7[b]	**7h**	none	0.5 M	17%[d]	23%[d] (*dr* 4:3)
8[b]	**7i**	none	0.5 M	22%[d]	15%[d] (*dr* 2:1)
9[b]	**7j**	none	0.5 M	19%[d]	24%[d] (*dr* 2:1)
10[b]	**7j**	none	1.0 M	40%[d]	35%[d] (*dr* 2:1)

[a] 100 °C, 5 h. [b] 170 °C, 15 min. [c] Isolated yield. [d] Yield determined by NMR using an internal standard.



Scheme 9. Conversion of internal secondary substrates with nucleophiles **A**–**E**.

Unfortunately, we found the substrate scope of the original procedure to be very limited. Conversions of terpene derivatives **2i**–**l** with nucleophiles **A**–**E** applying catalyst **1a** (2 mol%) and TFA (4 mol%) lead to extensive decomposition and only small amounts of dihydropyranes **6** are isolated. In contrast, propargyl alcohols **2i**, **2k** and **2l** are converted in moderate to good yields with nucleophiles **B**, **C** or **E** if catalyst **7j** without an acidic promoter is applied. Only small quantities of products **6** are obtained from alcohol **2j**. Conversions of internal secondary propargyl alcohols **2i**–**l** with 1,3-dione **A** are not catalyzed by complex **7j**, whereas nucleophile **D** leads to extensive decomposition. Occasionally, small amounts of the oxidized by-products **10** are isolated. Uncyclized products **11** are formed from nucleophile **E** in some cases (Table 6; Figure 3).

Conclusions

In principle, triaminocyclopentadienyl ruthenium complexes (**7**) are useful catalysts for cascade conversions of propargyl alcohols. Their synthesis is straightforward and enantiopure derivatives for future applications in asymmetric catalysis are easily accessible. However, the simpler diaminocyclopentadienone catalyst **1a** is superior to complexes of type **7** in terms of converting terminal tertiary substrates. Moreover, redox-isomerization processes of terminal secondary derivatives are not catalyzed at all by the new complexes (**7**). In contrast, introducing the third amine-function on the cyclopentadienyl ligand has a significant effect on the conversion of internal substrates. The new catalysts (**7**) extend the scope of cascade conversions of internal 1-alkenylpropargyl alcohols, originally catalyzed by ruthenium catalyst **1a**, to various terpenoid-derived derivatives. In addition, reactions catalyzed by complexes of type **7** are applicable for the conversion of acid-sensitive substrates, since they do not require an acidic

Table 6. Products from internal propargyl alcohols **2h–l** with nucleophiles **A–E** catalyzed by catalysts **1a** or **7j** (substrate concentration 1.0 M).

cat.	nuc.	Products from **2h**	products from **2i**	products from **2j**	products from **2k**	products from **2l**
1a	**A**	**6Ah**[a,b] (59%) **9Ah**[a,b] (16%, *dr* 6:1)	**6Ai**[b] (18%)	dec.	**10k**[b] (24%)	dec.
1a	**B**	**6Bh**[a,c] (66%) **9Bh**[a,c] (24%, *dr* 3:2)	**6Bi** (trace)	dec.	**6Bk** (trace)	**6Bl** (trace)
1a	**C**	**6Ch**[c] (60%) **9Ch**[c] (24%, *dr* 2:1)	**6Ci**[c] (13%)	**6Cj** (trace)	**6Ck**[c] (19%, *dr* 3:2)	**6Cl** (trace) **10l**[c] (5%)
1a	**E**	**6Eh**[c] (30%) **9Eh**[c] (17%, *dr* 2:1)	**6Ei**[c] (10%)	dec.	**6Ek**[c] (12%)	dec.
7j	**A**	**6Ah**[a,b] (28%)	n.c.	n.c.	n.c.	n.c.
7j	**B**	**6Bh**[a,c] (40%) **9Bh**[a,c] (35%, *dr* 2:1)	**6Bi**[c] (50%)	**6Bj**[c] (17%)	**6Bk**[c] (55%, *dr* 2:1) **10k**[c] (9%)	**6Bl**[c] (61%, *dr* 3:1) **10l**[c] (6%)
7j	**C**	**6Ch**[c] (42%) **9Ch**[c] (19%, *dr* 2:1)	**6Ci**[c] (44%)	**6Cj**[c] (15%)	**6Ck**[c] (68%, *dr* 2:1) **10k**[c] (5%)	**6Cl**[c] (75%, *dr* 2:1) **10l**[c] (3%)
7j	**D**	dec.	dec.	dec.	**6Dk**[c] (13%, *dr* 5:2) **10k**[c] (4%)	dec.
7j	**E**	**6Eh**[c] (35%) **9Eh**[c] (43%, *dr* 3:2) **11Eh**[c] (18%)	**6Ei**[c] (33%)	n.c.	**6Ek**[c] (42%, *dr* 5:4)	**11El**[c] (56%, *dr* 1:1)

n.c. = no conversion. dec. = decomposition. [a] Compound previously reported in Ref. [4]e. [b] Prepared by conventional heating (100 °C, 5 h). [c] 170 °C, 15 min.

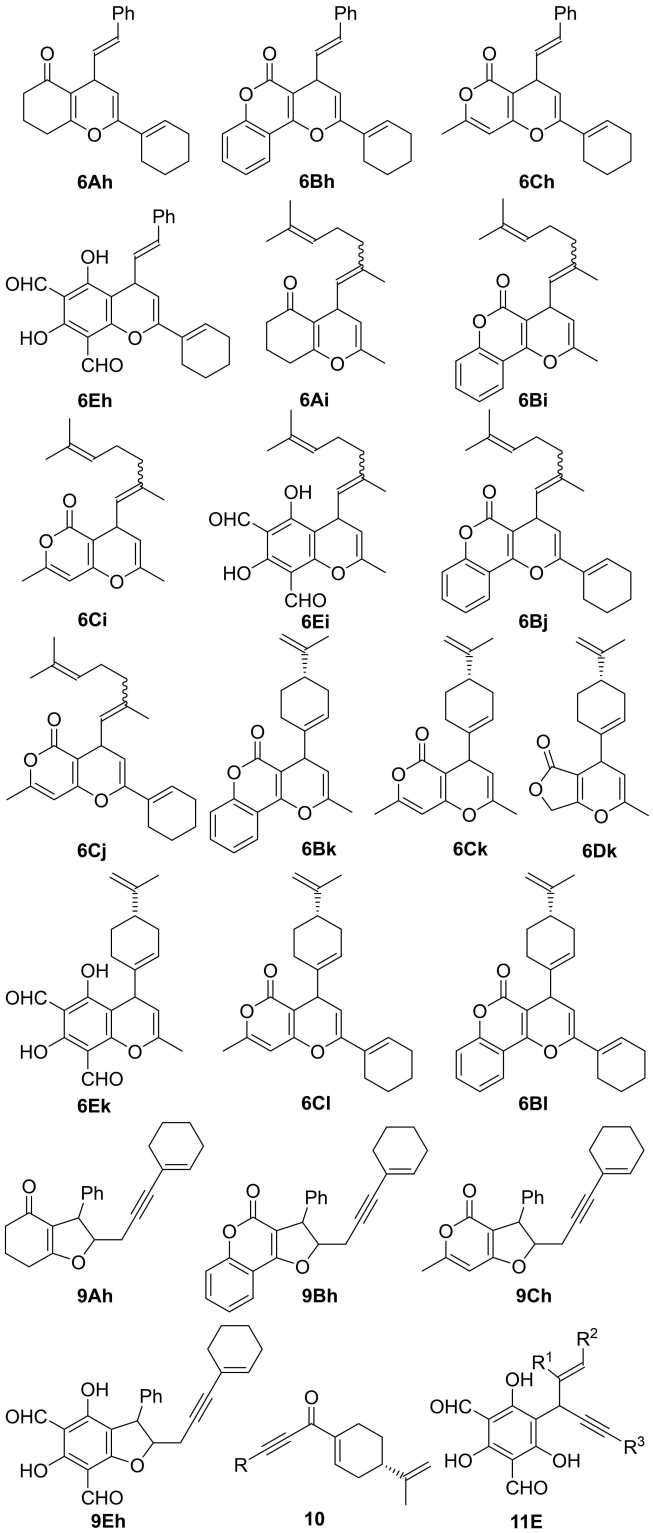


Figure 3. Isolated products from internal secondary substrates **2h–l** and nucleophiles **A–E**.

promoter. A broad range of terpenoid and phloroglucinol adducts are accessible by complementary application of both types of catalysts. The compounds obtained are suitable as structural building blocks for the synthesis of related bioactive natural products and analogues. Further applications of the new catalysts, especially in the context of asymmetric catalysis is the subject of our ongoing research.

Experimental Section

See the Supporting Information for full experimental procedures and characterization data of all products.

General Information

All reactions were carried out in a dry atmosphere under argon. The chemicals used were dried and purified according to common

procedures. Products were identified by spectroscopic analysis (1H NMR, 13 C NMR, IR, MS, HRMS). Multiplicity was determined by DEPT spectra for all compounds. Infrared spectra were obtained with a PERKIN-ELMER FTIR 2000 or a VERTEX 70 V. NMR spectra were recorded on a BRUKER DPX 400 or a BRUKER AVANCE 600 spectrometer. MS data was obtained with a FINNIGAN SSQ 7000 (EI) or a WATERS ACQUITY UPLC-MS H-CLASS (ESI) and HRMS data was obtained on a FINNIGAN MAT 95. Specific optical rotation of chiral compounds was measured on an ANTON PAAR MCP 150 polarimeter. Reactions using microwave irradiation were performed in an ANTON PAAR MONOWAVE 300 reactor.

General procedure for the preparation of catalysts 7: $Ru_3(CO)_{12}$ (0.34 equiv.) and 1 equiv. of the respective ligand **L 7** were dissolved in toluene (0.1 M). The solution was stirred at 100 °C for 5 h. Evaporation of the solvent and rapid flash chromatography on oven dried silica (CH_2Cl_2 /CH_3OH; 100:0, 99.5:0.5, 98:2) furnished the purified products as yellow foams.

7 b ($C_{28}H_{28}N_3O_3RuBF_4$): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.13 (br, d, J = 7.2 Hz, 2H), 7.50–7.45 (m, 4H), 7.42 (br, t, J = 7.4 Hz, 2H), 7.32 (br, d, J = 7.5 Hz, 2H), 3.61 (dd, J = 6.8, 3.7 Hz, 1H), 3.58 (dd, J = 6.6, 3.9 Hz, 1H), 2.65 (dd, J = 6.6, 4.0 Hz, 1H), 2.62 (dd, J = 6.9, 3.6 Hz, 1H), 2.48–2.46 (m, 4H), 2.00 (s, 6H), 1.42–1.40 ppm (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 193.8 (br, 3 C), 141.0 (C), 135.8 (br, 2 CH), 133.7 (br, 2 CH), 130.9 (2 C), 129.8 (2 CH), 129.1 (br, 2 CH), 129.0 (br, 2 CH), 120.1 (2 C), 69.7 (2 C), 53.3 (2 CH_2), 50.3 (2 CH_2), 43.7 (2 CH_3), 25.0 (2 CH_2); IR (KBr) ν = 3058 (w), 2955 (w), 2927 (w), 2875 (w), 2060 (s), 2018 (s), 2000 (s), 1519 (m), 1549 (m), 1455 (m), 1417 (m), 1365 (m), 1348 (m), 1318 (m), 1083 (s), 1057 (s), 726 (m), 705 cm^{-1} (m); MS (EI): m/z (%): 557 (18), 556 [M-BF_4]$^+$ (20), 531 (46), 529 (100), 528 [M–CO,–BF_4]$^+$ (62), 527 (55), 526 (40), 501 (65), 500 (45), 499 (99), 498 (54), 497 (51), 496 (40), 471 (80), 470 (63), 469 (90), 468 (75), 467 (58), 466 (40); HRMS (EI): m/z calcd for $C_{27}H_{28}N_3O_2Ru$: 528.1220 [M–CO,–BF_4]$^+$; found: 528.1224.

7 c ($C_{31}H_{28}N_3O_3RuBF_4$): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.90–7.29 (m, 10H), 7.10–7.09 (m, 3H), 6.75–6.73 (m, 2H), 3.66 (t, J = 5.7 Hz, 1H), 3.54 (dd, J = 6.7, 3.7 Hz, 1H), 3.51 (dd, J = 6.6, 3.8 Hz, 1H), 3.48 (d, J = 5.7 Hz, 2H), 2.68 (dd, J = 6.6, 3.9 Hz, 1H), 2.65 (dd, J = 6.6, 3.8 Hz, 1H), 2.10 ppm (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 192.8 (3 C), 140.2 (C), 135.3 (C), 135.2–133.8 (br, 2 CH), 133.0–131.2 (br, 2 CH), 130.1 (2 CH), 129.6 (br, 4 CH), 128.6 (2 CH), 127.8 (CH), 127.6 (br, 2 C), 126.9 (2 CH), 118.4 (2 C), 65.5 (2 C), 49.8 (2 CH_2), 49.1 (CH_2), 41.4 ppm (2 CH_3); IR (ATR) ν = 3339 (w), 3059 (w), 2950 (w), 2924 (w), 2861 (w), 1728 (m), 1568 (m), 1452 (m), 1275 (m), 1121 (m), 1055 (s), 741 (m), 697 cm^{-1} (m); MS (EI): m/z (%): 592 [M-BF_4]$^+$ (16), 591 (10), 566 (30), 565 (18), 564 [M–CO,–BF_4]$^+$ (57), 563 (33), 562 (25), 561 (21), 408 (23), 407 (32), 406 (100); HRMS (EI): m/z calcd for $C_{30}H_{28}N_3O_2Ru$: 564.1221 [M–CO,–BF_4]$^+$; found: 564.1236.

7 d ($C_{32}H_{30}N_3O_3RuBF_4$): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.88–7.29 (m, 10H), 7.12–7.05 (m, 3H), 6.60 (d, J = 7.0 Hz, 2H), 3.53 (dd, J = 6.6, 3.6 Hz, 1H), 3.50 (dd, J = 6.5, 3.7 Hz, 1H), 3.21 (s, 1H), 2.67 (dd, J = 6.6, 3.8 Hz, 1H), 2.64 (dd, J = 6.5, 3.6 Hz, 1H), 2.48 (t, J = 6.7 Hz, 2H), 2.32 (t, J = 6.7 Hz, 2H), 2.11 ppm (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 192.6 (3 C), 140.8 (C), 136.1 (C), 135.4–133.6 (br, 2 CH), 132.2–131.1 (br, 2 CH), 130.0 (2 CH), 129.7 (br, 4 CH), 128.6 (2 CH), 128.1 (2 CH), 127.6 (br, 2 C), 126.6 (CH), 118.0 (2 C), 68.0 (2 C), 49.7 (2 CH_2), 45.6 (CH_2), 41.3 (2 CH_3), 34.2 ppm (CH_2); IR (ATR) ν = 3362 (w), 3059 (w), 2926 (w), 2859 (w), 1990 (m), 1044 (m), 695 cm^{-1} (m); MS (EI): m/z (%): 579 (28), 578 [M–CO,–BF_4]$^+$ (16), 523 (21), 522 (37), 521 (32), 520 (33), 519 (24), 480 (22), 479 (36), 478 (21), 446 (29), 332 (35), 316 (100); MS (ESI): m/z (%): 598 (25), 580 (33), 579 (60), 578 [M–CO,–BF_4]$^+$ (35), 577 (36), 576 (28), 575 (22), 538 (33), 537 (45), 536 (82), 354 (53), 282 (29), 171 (33); HRMS (EI): m/z calcd for $C_{31}H_{30}N_3O_2Ru$: 578.1377 [M–CO,–BF_4]$^+$; found: 578.1384.

7 e ($C_{27}H_{25}N_4O_3RuBF_4$): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81–7.75 (m, 3H), 7.48–7.38 (m, 7H), 3.76 (t, J = 6.4 Hz, 1H), 3.19 (dd, J = 7.0, 4.2 Hz, 1H), 3.14 (dd, J = 6.8, 4.5 Hz, 1H), 2.95 (q, J = 6.7 Hz, 2H), 2.42 (dd, J = 6.7, 4.6 Hz, 1H), 2.38 (dd, J = 7.0, 4.2 Hz, 1H), 2.04 (s, 6H), 1.96 ppm (t, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.9 (3 C), 136.8 (C), 135.2–131.8 (br, 4 CH), 130.3 (2 C), 129.4 (br, 4 CH), 129.3 (2 CH), 117.5 (C), 111.6 (2 C), 67.9 (2 C), 49.8 (2 CH_2), 43.2 (2 CH_3), 40.2 (CH_2), 19.6 ppm (CH_2); IR (ATR) ν = 3343 (w), 2921 (w), 2861 (w), 2247 (w), 1993 (m), 1932 (m), 1499 (m), 1108 (w), 1063 (w), 1020 (w), 932 (w), 862 (w), 792 (w), 740 (w), 696 cm^{-1} (w); MS (EI): m/z (%): 508 (16), 506 (22), 384 (29), 383 (100), 369 (15), 328 (22), 327 (19); MS (ESI): m/z (%): 527 [M–CO,–BF_4]$^+$ (100), 526 (68), 525 (56), 524 (38), 371 (23), 369 (42), 354 (22); HRMS (EI): m/z calcd for $C_{26}H_{25}N_4O_2Ru$: 527.1016 [M–CO,–BF_4]$^+$; found: 527.1028.

7 f ($C_{35}H_{31}N_4O_3RuBF_4$): ^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90–7.41 (m, 10H), 7.27–7.25 (m, 2H), 7.08–7.05 (m, 1H), 6.88–6.85 (m, 1H), 6.24 (t, J = 2.1 Hz, 2H), 6.12 (t, J = 2.1 Hz, 2H), 3.63 (dd, J = 6.8, 3.6 Hz, 1H), 3.59 (dd, J = 6.5, 3.9 Hz, 1H), 3.45 (d, J = 6.0 Hz, 2H), 3.32 (t, J = 6.0 Hz, 1H), 2.67 (dd, J = 6.7, 4.0 Hz, 1H), 2.64 (dd, J = 6.6, 3.9 Hz, 1H), 2.13 ppm (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.3 (3 C), 140.6 (C), 139.5 (C), 135.5–134.3 (br, 2 CH), 133.1–132.0 (br, 2 CH), 131.2 (C), 130.3 (CH), 129.9 (2 CH), 129.0 (br, 4 CH), 128.5 (br, 2 CH), 127.9 (br, 2 C), 127.7 (CH), 121.5 (2 CH), 119.0 (2 C), 109.9 (2 CH), 68.8 (2 C), 50.1 (2 CH_2), 45.7 (CH_2), 41.5 ppm (2 CH_3); IR (ATR) ν = 3341 (w), 3057 (w), 2923 (w), 2860 (w), 2809 (w), 1986 (m), 1498 (m), 1048 (m), 730 (m), 698 cm^{-1} (w); MS (ESI): m/z (%): 657 [M-BF_4]$^+$ (16), 656 (23), 632 (20), 631 (54), 630 (35), 629 [M–CO,–BF_4]$^+$ (100), 628 (57), 627 (45), 626 (35), 471 (36); HRMS (EI): m/z calcd for $C_{34}H_{31}N_4O_2Ru$: 629.1486 [M–CO,–BF_4]$^+$; found: 629.1505.

7 g ($C_{34}H_{31}N_4O_3RuBF_4$): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.20 (s, 1H), 7.80–7.34 (m, 11H), 7.10 (d, J = 7.8 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 6.91 (t, J = 7.4 Hz, 1H), 6.39 (d, J = 2.1 Hz, 1H), 3.48 (t, J = 5.0 Hz, 1H), 3.46 (dd, J = 6.4, 3.4 Hz, 1H), 3.43 (dd, J = 6.4, 3.8 Hz, 1H), 2.57 (dd, J = 6.9, 4.0 Hz, 1H), 2.55 (dd, J = 6.5, 3.7 Hz, 1H), 2.48–2.42 (m, 4H), 2.07 ppm (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 192.6 (3 C), 141.0 (C), 136.6 (C), 135.0–133.5 (br, 2 CH), 132.2–130.8 (br, 2 CH), 130.4 (2 CH), 129.8 (br, 4 CH), 127.4 (br, 2 C), 126.0 (C), 123.5 (CH), 121.6 (CH), 118.8 (CH), 118.0 (2 C), 117.4 (CH), 112.1 (CH), 107.9 (C), 68.2 (2 C), 49.8 (2 CH_2), 44.2 (CH_2), 41.5 (2 CH_3), 24.0 ppm (CH_2); IR (ATR) ν = 3382 (w), 3318 (w), 3054 (w), 2922 (w), 2859 (w), 2812 (w), 1996 (m), 1569 (m), 1525 (m), 1358 (m), 1049 (s), 738 (m), 697 cm^{-1} (m); MS (ESI): m/z (%): 645 [M-BF_4]$^+$ (20), 619 (20), 617 [M–CO,–BF_4]$^+$ (36), 616 (21), 460 (37), 459 (100); HRMS (EI): m/z calcd for $C_{33}H_{31}N_4O_2Ru$: 617.1486 [M–CO,–BF_4]$^+$; found: 617.1510.

7 h ($C_{29}H_{26}N_3O_4RuBF_4$): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.00–7.44 (m, 10H), 7.19 (dd, J = 1.8, 0.6 Hz, 1H), 6.17 (dd, J = 1.8, 3.2 Hz, 1H), 5.88 (dd, J = 3.2, 0.6 Hz, 1H), 3.70 (t, J = 5.7 Hz, 1H), 3.61 (dd, J = 6.6, 3.5 Hz, 1H), 3.58 (dd, J = 6.5, 3.8 Hz, 1H), 3.49 (d, J = 5.7 Hz, 2H), 2.71 (dd, J = 6.5, 3.8 Hz, 1H), 2.68 (dd, J = 6.6, 3.6 Hz, 1H), 2.16 ppm (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 192.8 (3 C), 147.8 (C), 142.9 (CH), 139.9 (C), 135.2–133.9 (br, 2 CH), 133.2–131.8 (br, 2 CH), 130.4 (2 CH), 130.0 (br, 4 CH), 127.7 (br, 2 C), 118.5 (2 C), 110.6 (CH), 109.0 (CH), 68.6 (2 C), 50.1 (2 CH_2), 41.8 (CH_2), 41.6 ppm (2 CH_3); IR (ATR) ν = 3342 (w), 3057 (w), 2929 (w), 2870 (w), 1597 (m), 1567 (s), 1505 (m), 1444 (m), 1412 (m), 1365 (m), 1336 (m), 1285 (m), 1245 (m), 1051 (s), 1030 (s), 1020 (s), 953 (m), 913 (m), 728 (s), 703 cm^{-1} (s); MS (ESI): m/z (%): 582 [M-BF_4]$^+$ (15), 557 (12), 556 (49), 555 (24), 554 [M–CO,–BF_4]$^+$ (100), 553 (50), 552 (39), 332 (24), 317 (31), 316 (72), 315 (21), 314 (53); HRMS (EI): m/z calcd for $C_{28}H_{26}N_3O_3Ru$: 554.1012 [M–CO,–BF_4]$^+$; found: 554.1021.

7 i ($C_{28}H_{30}N_3O_4RuBF_4$): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00–7.30 (m, 10H), 4.51 (t, J = 5.5 Hz, 1H), 3.54 (dd, J = 6.7, 3.6 Hz, 1H), 3.50 (dd, J = 6.5, 3.9 Hz, 1H), 3.20 (td, J = 5.1, 4.7 Hz, 2H), 2.68 (dd, J = 6.4,

3.8 Hz, 1H), 2.63 (dd, J=6.6, 3.6 Hz, 1H), 2.28 (td, J=6.2, 5.9 Hz, 2H), 2.09 (s, 6H), 2.01 (t, J=4.5 Hz, 1H), 1.14 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=193.1 (3 C), 143.4 (C), 135.7–134.0 (br, 2 CH), 133.3–131.3 (br, 2 CH), 130.1 (2 CH), 129.7 (br, 4 CH), 128.2 (2 C), 118.3 (2 C), 67.7 (2 C), 61.2 (CH_2), 50.0 (2 CH_2), 45.1 (CH_2), 41.7 (2 CH_3), 28.8 (CH_2), 25.2 ppm (CH_2); IR (ATR) ν=3546 (w), 3348 (w), 2930 (w), 2874 (w), 2070 (s), 1991 (s), 1540 (s), 1503 (m),1444 (m), 1416 (m), 1364 (m), 1271 (m), 1199 (w), 1050 (s), 1030 (s), 951 (m), 753 (m), 724 (m), 702 cm^{-1} (m); MS (ESI): m/z (%): 549 (18), 548 (50), 547 (27), 546 [M–CO,–BF_4]$^+$ (100), 545 (53), 544 (42), 543 (30), 540 (18); HRMS (ESI): m/z calcd for $C_{27}H_{30}N_3O_3Ru$: 546.1325 [M–CO,–BF_4]$^+$; found: 546.1349.

7j ($C_{29}H_{30}N_3O_4RuBF_4$): ^{1}H NMR (600 MHz, $CDCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$): δ=8.00–7.35 (m, 10H), 3.82 (t, J=5.4 Hz, 1H), 3.60–3.56 (m, 2H, *H*6), 3.51 (ddd, J=13.8, 6.9, 3.4 Hz, 1H), 3.44 (dt, J=8.3, 7.0 Hz, 1H), 3.37 (dt, J=8.2, 6.5 Hz, 1H), 2.73–2.68 (m, 2H), 2.34 (ddd, J=12.9, 5.6, 3.5 Hz, 1H), 2.17 (s, 3H), 2.16 (s, 3H), 2.13 (ddd, J=12.7, 7.0, 5.3 Hz, 1H), 1.66–1.51 (m, 3H), 1.09–1.03 ppm (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ=192.9 (3 C), 140.9 (C), 135.8–130.8 (br, 4 CH), 130.2 (CH), 130.1 (CH), 129.8 (br, 4 CH), 127.9 (C), 127.8 (C), 118.8 (C), 118.0 (C), 75.3 (CH), 68.5 (C), 68.3 (C), 68.1 (CH_2), 50.0 (CH_2), 49.9 (CH_2), 48.5 (CH_2), 41.6 (CH_3), 41.4 (CH_3), 28.3 (CH_2), 25.5 ppm (CH_2); IR (ATR) ν=3360 (w), 2963 (w), 2874 (w), 2070 (m), 1990 (m), 1529 (m), 1499 (m), 1444 (m), 1417 (m), 1364 (m), 1060 (m), 1048 (s), 1033 (s), 949 (m), 755 (m), 702 cm^{-1} (m); MS (ESI): m/z (%): 586 [M-BF_4]$^+$ (25), 561 (18), 560 (53), 559 (29), 558 [M–CO,–BF_4]$^+$ (100), 557 (58), 556 (44), 400 (40), 385 (20), 328 (45), 316 (51), 315 (31), 314 (100); HRMS (EI): m/z calcd for $C_{28}H_{30}N_3O_3Ru$: 558.1326 [M–CO,–BF_4]$^+$; found: 558.1343; $[\alpha]_D^{20}$ for (*R*)-**7j**=−17.8° (c=0.40, CH_2Cl_2); $[\alpha]_D^{20}$ for (*S*)-**7j**=+21.8° (c=0.40, CH_2Cl_2).

7k ($C_{32}H_{30}N_3O_3RuBF_4$): ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.10–7.35 (m, 10H), 7.15–7.12 (m, 3H), 6.58–6.53 (m, 2H), 3.91 (dq, J=8.3, 6.9 Hz, 1H), 3.65 (d, J=8.6 Hz, 1H), 3.64–3.52 (m, 2H), 2.75–2.62 (m, 2H), 2.19 (s, 3H), 2.03 (s, 3H), 1.00 ppm (d, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=193.0 (3 C), 141.5 (C), 141.0 (C), 135.4–134.2 (br, 2 CH), 132.7–131.6 (br, 2 CH), 130.5 (CH), 130.2 (br, 2 CH), 130.1 (CH), 129.4 (br, 2 CH), 128.7 (2 CH), 127.8 (C), 127.7 (C), 127.5 (CH), 124.9 (2 CH), 120.2 (C), 117.3 (C), 68.1 (C), 67.6 (C), 53.4 (CH), 50.1 (CH_2), 49.8 (CH_2), 41.8 (CH_3), 41.5 (CH_3), 23.9 ppm (CH_3); IR (ATR) ν=3372 (w), 3057 (w), 2958 (w), 2924 (w), 2864 (w), 1532 (m), 1502 (m), 1362 (m), 1044 (s), 695 (m), 648 cm^{-1} (m); MS (ESI): m/z (%): 578 [M–CO,–BF_4]$^+$ (98), 577 (58), 576 (47), 575 (37), 505 (21), 504 (67), 420 (23), 372 (22), 371 (28), 354 (47); HRMS (EI): m/z calcd for $C_{31}H_{30}N_3O_2Ru$: 578.1377 [M–CO,–BF_4]$^+$; found: 578.1404; $[\alpha]_D^{20}$ for (*R*)-**7k**=+64.5° (c=0.33, CH_2Cl_2).

7l ($C_{30}H_{30}N_3O_7RuBF_4$): ^{1}H NMR (600 MHz, $CDCl_3$): δ=8.20–7.40 (m, 10H), 4.66 (d, J=9.4 Hz, 1H), 3.64–3.55 (m, 2H), 3.57 (s, 3H), 3.49 (dt, J=9.3, 4.4 Hz, 1H), 3.45 (s, 3H), 2.72–2.66 (m, 2H), 2.37 (dd, J=17.4, 4.2 Hz, 1H), 2.28 (d, J=17.4, 4.6 Hz, 1H), 2.23 (s, 3H), 2.09 ppm (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ=192.9 (3 C), 170.6 (C), 169.7 (C), 140.3 (C), 135.2–134.6 (br, 2 CH), 132.6–131.9 (br, 2 CH), 130.5 (CH), 130.4 (CH), 129.9 (br, 4 CH), 128.3 (C), 127.1 (C), 120.5 (C), 117.1 (C), 69.6 (C), 67.6 (C), 53.0 (CH), 52.2 (CH_3), 52.1 (CH_3), 50.2 (CH_2), 49.7 (CH_2), 41.8 (CH_3), 41.4 (CH_3), 35.9 ppm (CH_2); IR (ATR) ν=3396 (w), 3056 (w), 2992 (w), 2953 (w), 1742 (m), 1598 (m), 1564 (s), 1514 (m), 1457 (m), 1443 (m), 1412 (m), 1364 (m), 1240 (m), 1208 (m), 1052 (s), 1025 (s), 954 (m), 916 (m), 731 (m), 705 cm^{-1} (m); MS (EI): m/z (%): 618 [M–CO,–BF_4]$^+$ (10), 597 (18), 462 (22), 461 (81), 460 (45), 459 (100), 441 (30), 442 (67), 443 (70); HRMS (EI): m/z calcd for $C_{29}H_{30}N_3O_6Ru$: 618.1173 [M–CO,–BF_4]$^+$; found: 618.1173; $[\alpha]_D^{20}$ for (*S*)-**7l**=−13.0° (c=0.20, CH_2Cl_2).

7m ($C_{31}H_{32}N_3O_7RuBF_4$): ^{1}H NMR (600 MHz, $CDCl_3$): δ=8.14–7.30 (m, 10H), 4.38 (d, J=8.7 Hz, 1H), 3.68–3.61 (m, 2H), 3.54 (s, 3H), 3.53 (s, 3H), 3.40 (dt, J=8.2, 6.5 Hz, 1H), 2.71–2.65 (m, 2H), 2.22 (s, 3H), 2.11 (s, 3H), 1.95 (t, J=7,0 Hz, 2H), 1.56–1.45 ppm (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ=193.2 (3 C), 173.0 (C), 170.8 (C), 140.3 (C), 135.5–134.8 (br, 2 CH), 133.2–132.2 (br, 2 CH), 130.5 (CH), 130.4 (CH), 130.0 (2 CH), 129.9 (br, 2 CH), 128.3 (C), 127.3 (C), 119.7 (C), 118.7 (C), 70.0 (C), 68.0 (C), 55.6 (CH), 52.8 (CH_3), 52.0 (CH_3), 50.2 (CH_2), 49.9 (CH_2), 41.7 (CH_3), 41.6 (CH_3), 29.4 (CH_2), 27.3 ppm (CH_2); IR (ATR) ν=3360 (w), 3018 (w), 2952(w), 2075 (s), 1994 (s), 1735 (s), 1537 (s), 1501 (m), 1442 (m), 1417 (m), 1364 (m), 1268 (w), 1205 (m), 1048 (s), 755 (m), 703 cm^{-1} (m); MS (ESI): m/z (%): 635 (17), 634 (52), 633 (30), 632 [M–CO,–BF_4]$^+$ (100), 631 (55), 630 (47), 629 (40), 626 (15); HRMS (ESI): m/z calcd for $C_{30}H_{32}N_3O_6Ru$: 632.1329 [M–CO,–BF_4]$^+$; found: 632.1339; $[\alpha]_D^{20}$ for (*S*)-**7m**=−12.3° (c=0.30, CH_2Cl_2).

7n ($C_{36}H_{33}N_4O_5RuBF_4$): ^{1}H NMR (600 MHz, $CDCl_3$+CD_3OD): δ=7.54–7.33 (m, 10H), 7.32 (d, J=8.2 Hz, 1H), 7.12 (t, J=7.5 Hz, 1H), 7.01 (d, J=7.9 Hz, 1H), 6.96 (t, J=7.4 Hz, 1H), 6.54 (s, 1H), 3.58 (br t, J=6.0 Hz, 1H), 3.52 (s, 3H), 3.51–3.46 (m, 2H), 2.75 (dd, J=15.2, 5.7 Hz, 1H), 2.73 (dd, J=15.2, 6.4 Hz, 1H), 2.64–2.60 (m, 2H), 2.12 (s, 3H), 2.07 ppm (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$+CD_3OD): δ=192.3 (3 C), 170.8 (C), 140.8 (C), 136.2 (C), 135.0–134.4 (br, 2 CH), 131.4–131.0 (br, 2 CH), 130.5 (CH), 130.4 (CH), 130.0–129.6 (br, 4 CH), 127.3 (C), 127.0 (C), 126.4 (C), 123.6 (CH), 121.8 (CH), 119.9 (br, C), 119.1 (CH), 118.1 (br, C), 117.4 (CH), 111.7 (CH), 106.1 (C), 68.5 (C), 67.9 (C), 55.3 (CH), 52.5 (CH_3), 49.8 (CH_2), 49.7 (CH_2), 41.5 (CH_3), 41.4 (CH_3), 27.9 ppm (CH_2); IR (ATR) ν=3362 (w), 3307 (m), 2974 (w), 2922 (w), 2862 (w), 1569 (m), 1526 (m), 1456 (m), 1443 (m), 1414 (m), 1362 (m), 1277 (m), 1104 (m), 1057 (m), 1007 (s), 911 (m), 743 (m), 732 (m), 703 cm^{-1} (m); MS (EI): m/z (%): 703 [M-BF_4]$^+$ (10), 675 [M–CO,–BF_4]$^+$ (15), 333 (30), 332 (89), 317 (26), 316 (82), 314 (28), 313 (20), 228 (36), 227 (100); HRMS (EI): m/z calcd for $C_{35}H_{33}N_4O_4Ru$: 675.1540 [M–CO,–BF_4]$^+$; found: 675.1539; $[\alpha]_D^{20}$ for (*S*)-**3n**=−20.0° (c=0.25, CH_2Cl_2).

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Conflict of Interest

The authors declare no conflict of interest.

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[1] a) Y. Wang, H. Lu, P. F. Xu, *Acc. Chem. Res.* **2015**, *48*, 1832–1844; b) Y. Wang, L. Zhang, P. Lu, H. Gao, J. Zhang, P.-F. Xu, H. Wei in *Catalytic Cascade Reactions* (Eds.: P.-F. Xu, W. Wang), John Wiley & Sons, Hoboken, **2014**, pp. 145–331; c) E.-I. Negishi, G. Wang, G. Zhu, P. von Zezschwitz, A. De Meijere, N. T. Patil, Y. Yamamoto, G. Balme, D. Bouyssi, N. Monteiro, T. J. J. Müller, J. Pérez-Castells, C. Aubert, L. Fensterbank, V. Gandon, M. Malacria, C. Bruneau, S. Dérien, P. H. Dixneuf in *Metal Catalyzed Cascade Reactions* (Ed.: T. J. J. Müller), Springer, Berlin, **2006**, pp. 1–340; d) L. F. Tietze, B. Brasche, K. Gericke in *Domino Reactions in Organic Synthesis*, Wiley-VCH, Weinheim, **2006**, pp. 359–493.

[2] a) R. Ardkhean, D. F. J. Caputo, S. M. Morrow, H. Shi, Y. Xiong, E. A. Anderson, *Chem. Soc. Rev.* **2016**, *45*, 1557–1569; b) C. I. Stathakis, P. L. Gkizis, A. L. Zografos, *Nat. Prod. Rep.* **2016**, *33*, 1093–1117; c) A. C. Jones, J. A. May, R. Sarpong, B. M. Stoltz, *Angew. Chem.* **2014**, *126*, 2590–2628; *Angew. Chem. Int. Ed.* **2014**, *53*, 2556–2591; d) K. Kumar in *Concepts and Case Studies in Chemical Biology* (Eds.: H. Waldmann, P. Janning), Wiley-

VCH, Weinheim, **2014**, pp. 391–414; e) K. C. Nicolaou, D. J. Edmonds, P. B. Bulger, *Angew. Chem.* **2006**, *118*, 7292–7344; *Angew. Chem. Int. Ed.* **2006**, *45*, 7134–7186; *Angew. Chem. Int. Ed.* **2006**, *43*, 7134–7186.

[3] a) E. Haak, *Eur. J. Org. Chem.* **2017**, *2017*, 940–949; b) Y. Hu, M. Bai, Y. Yang, Q. Zhou, *Org. Chem. Front.* **2017**, *4*, 2256–2275; c) A. L. S. Kumari, A. S. Reddy, K. C. K. Swamy, *Org. Biomol. Chem.* **2016**, *14*, 6651–6671; d) J.-P. Genêt, P. Y. Toullec, V. Michelet in *Modern Alkyne Chemistry* (Eds.: B. M. Trost, C.-J. Li), Wiley-VCH, Weinheim, **2014**, pp. 27–68; e) I. D. G. Watson, F. D. Toste, *Chem. Sci.* **2012**, *3*, 2899–2919; f) P. Pérez-Galán, V. López-Carillo, A. M. Echavarren, *Contrib. Sci.* **2010**, *6*, 143–153; g) E. Jiménez-Núñez, A. M. Echavarren, *Chem. Rev.* **2008**, *108*, 3326–3350; h) V. Michelet, P. Y. Toullec, J.-P. Genêt, *Angew. Chem.* **2008**, *120*, 4338–4386; *Angew. Chem. Int. Ed.* **2008**, *47*, 4268–4315; i) L. Zhang, J. Sun, S. A. Kozmin, *Adv. Synth. Catal.* **2006**, *348*, 2271–2296; j) C. Bruneau, S. Dérien, P. H. Dixneuf, *Top. Organomet. Chem.* **2006**, *19*, 295–326.

[4] a) J. Kaufmann, E. Jäckel, E. Haak, *Angew. Chem.* **2018**, *130*, 6010–6014; *Angew. Chem. Int. Ed.* **2018**, *57*, 5908–5911; b) E. Jäckel, J. Kaufmann, E. Haak, *Synthesis* **2018**, *50*, 742–752; c) N. Thies, E. Haak, *Angew. Chem.* **2015**, *127*, 4170–4174; *Angew. Chem. Int. Ed.* **2015**, *54*, 4097–4101; d) N. Thies, M. Gerlach, E. Haak, *Eur. J. Org. Chem.* **2013**, *2013*, 7354–7365; e) A. Jonek, S. Berger, E. Haak, *Chem. Eur. J.* **2012**, *18*, 15504–15511; f) N. Thies, C. G. Hrib, E. Haak, *Chem. Eur. J.* **2012**, *18*, 6302–6308.

[5] R. Gompper, H. Glöckner, *Angew. Chem.* **1984**, *96*, 48–49; *Angew. Chem. Int. Ed.* **1984**, *23*, 53–54.

[6] a) E. Haak, *Eur. J. Org. Chem.* **2008**, *2008*, 788–792; b) E. Haak, *Eur. J. Org. Chem.* **2007**, *2007*, 2815–2824.

[7] a) X.-W. Yang, R. B. Grossman, G. Xu, *Chem. Rev.* **2018**, *118*, 3508–3558; b) J.-A. Richard, R. H. Puower, D. Y.-K. Chen, *Angew. Chem.* **2012**, *124*, 4612–4638; *Angew. Chem. Int. Ed.* **2012**, *51*, 4536–4561; c) I. P. Singh, J. Sidana, S. B. Bharate, W. J. Foley, *Nat. Prod. Rep.* **2010**, *27*, 393–416; d) I. P. Singh, S. B. Bharate, *Nat. Prod. Rep.* **2006**, *23*, 558–591.

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