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Tandem Sequential Ring-Closing Metathesis/Diels–Alder/Cross-Metathesis: Formation of Polycyclic Compounds by a New Three-Component Reaction

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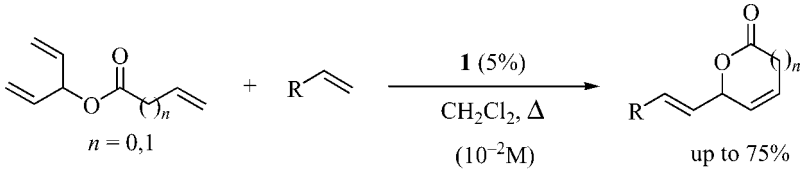
Dedicated to Professor Dieter Enders on the occasion of his 60th birthday

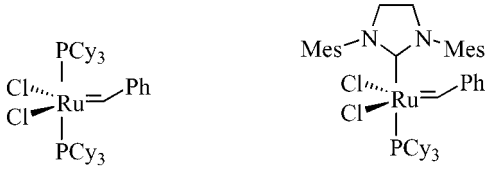
Keywords: Ring-closing metathesis / Cycloaddition / Tandem reaction / Cross-metathesis / Enynes

Polycyclic oxygenated compounds have been generated from penta- or hexadienyl propargyl ethers by a new procedure that combines the selective formation of a 1,3-diene by ring-closing metathesis (RCM), a Diels–Alder (DA) reaction and subsequent cross-metathesis (CM) with a chosen alkene, which allows the functionalization of the vinyl group generated during the first step. All these processes can be performed in a one-pot reaction with a yield of up to 63 %.

Introduction

Since the commercial availability of air-stable catalysts such as **1a** and **1b** that tolerate numerous functionalities, alkene metathesis has been widely used for the formation of complex structures and therefore used in the total synthesis of natural products.[1–6] Reactions of the same ruthenium carbene complexes and other metal catalysts with enynes have also attracted the attention of chemists and usually deliver 1,3-dienes in high yields.[7,8] The usual mild conditions required for these reactions have also favoured the development of tandem or domino procedures.[9–12] For example, enyne ring-closing metathesis provides a direct entry to cyclic 1,3-dienes which could be further used in Diels–Alder reactions.[13–23] In some cases, the thermal cycloaddition reaction has been performed directly without purification to avoid the isolation of sensitive or volatile dienes generated during the first step. In this way, complex polycyclic structures can be obtained in one-pot procedures. In connection with our interest in metathesis reactions, we recently reported the access to functionalized γ- and δ-lactones through a tandem reaction starting from 1,4-pentadien-3-yl acrylates or 3-butenoates.[24,25] After an initial RCM reaction, subsequent cross-coupling with an alkene already present in the reaction medium afforded the target molecules in high yield and with (*E*) stereocontrol of the double bond fixed on the lateral chain (Scheme 1). Despite





1a **1b**

Scheme 1. Tandem RCM/CM of pentadienyl esters.

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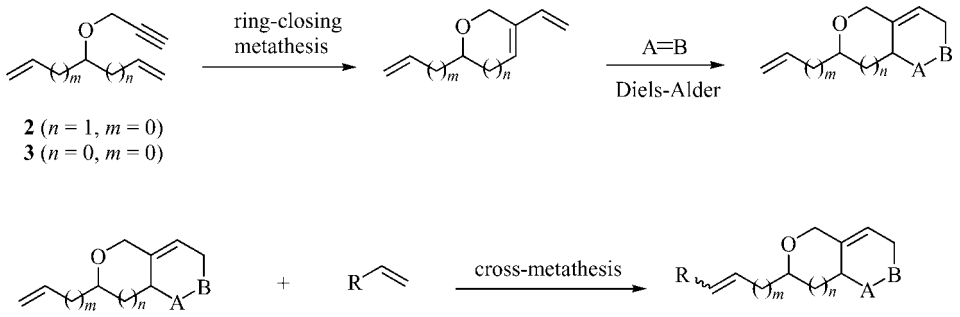


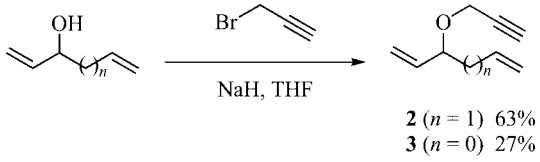
Scheme 2. Sequential ring-closing metathesis, Diels–Alder and cross-metathesis reaction of propargyl ethers **2** and **3**.

their apparent simplicity and great synthetic potential, it should be mentioned that to date, only a few processes combining both RCM and CM have been successfully designed for alkenes[26–30] or enynes.[31–38]

In order to develop new tandem procedures for the synthesis of oxygenated heterocycles that also combine RCM and CM reactions, we have now investigated the reactivity of unsaturated propargyl ethers **2** and **3** (*n*, *m* = 0, 1) in the presence of catalytic amounts of Grubbs reagents **1a** or **1b** (Scheme 2). In our strategy, RCM was expected to deliver first a cyclic 1,3-diene that could be immediately subjected to a Diels–Alder cycloaddition reaction. To avoid intermolecular cross-coupling between the alkynyl group and another alkene moiety and the formation of acyclic 1,3-dienes, we reasoned that the ring-closing metathesis reaction should be carried out first and under highly dilute conditions. Finally, the vinyl group generated during the first cyclization step could later be functionalized by cross-metathesis. For all these processes, it is important to note that the catalyst should tolerate various functionalities such as ketones and carboxylic acid derivatives (esters or amides) often present in dienophiles. According to the overall scheme, three different components could take part in the planned procedure and could give rapid (ideally in a one-pot procedure) access to highly functionalized polycyclic structures.

Results and Discussion

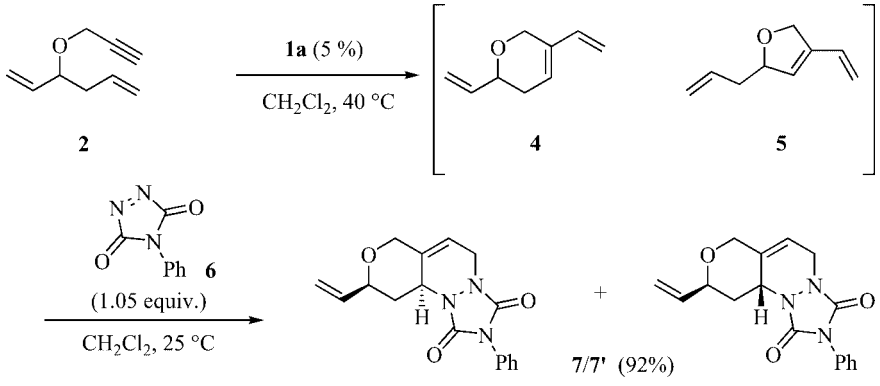
Starting materials **2** and **3** were respectively prepared by alkylation of commercially available 1,5-hexadien-3-ol and 1,4-pentadien-3-ol with propargyl bromide in moderate-to-acceptable yields (Scheme 3).[39,40] Attempts to improve the yields of **3** by using the corresponding propargyl triflate or by varying the nature of the solvent or base were unsuccessful.



Scheme 3. Formation of propargyl ethers **2** and **3** from the corresponding alcohols.

Ether **2** (Scheme 4) was treated with Grubbs type I catalyst **1a** (5%) in dichloromethane (10^{-2} M). After heating for 4 h, TLC control revealed the complete disappearance of the starting material and the formation of a new compound with a similar polarity which was later identified as the vinyl-1,3-diene **4** possessing a six-membered ring. Note that no trace of **5** was detected. Cookson's reagent (4-phenyl-4,5-dihydro-3*H*-1,2,4-triazole-3,5-dione, **6**), which is widely known to undergo Diels–Alder reactions even at room temperature,[41–43] was then added to the reaction mixture. After stirring for only 1 h, polar products were detected by TLC control and were identified as compounds **7**/**7′** which could not be separated by flash chromatography.

The formation of a six-membered cycle was confirmed by ^{1}H NMR spectroscopy and was in agreement with results obtained by Lee with related alkynylsilyloxy-tethered dienynes.[44] Similarly, **4** has also been used in a [4+2] cyclo-



Scheme 4. Sequential RCM/Diels–Alder reaction of ether **2**.

addition reaction with **8**,[45] which required a higher temperature and longer reaction time. After 24 h in refluxing dichloromethane, a mixture of two diastereomers **9/9′** was isolated in 59% yield (Figure 1).

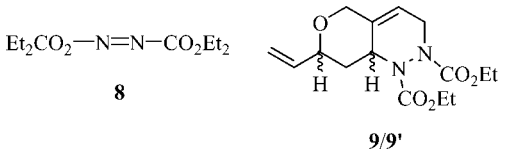
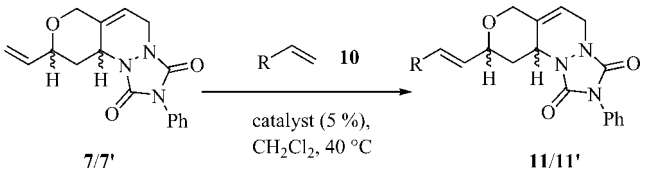


Figure 1. Product obtained in the reaction with diethyl azodicarboxylate (**8**) as dienophile.

Since the regioselectivity of the enyne RCM reaction was high, we decided to functionalize the lateral vinyl group through a cross-metathesis reaction. We considered that RCM and CM could be performed advantageously by using Grubbs type I catalyst **1a** in the same vessel. Therefore, ether **2** dissolved in dichloromethane was directly heated in the presence of catalyst **1a** and alkene **10c** was introduced in large excess in the middle of the reaction (5 equiv.). The reaction was stirred for 4 h under reflux and dienophile **6** was subsequently added at room temperature (Scheme 5, Method A). After purification of the reaction mixture by flash chromatography, compounds **7/7'** were obtained as the major products (62%) with two new compounds also isolated after careful separation by flash chromatography which were identified as the two epimeric compounds **11c/11′c**. At this stage, the poor reactivity of **7/7′** in the cross-metathesis reaction was attributed to the steric hindrance of the vinyl group and the propensity of terminal alkene **10** to react in a competitive self-coupling process.

The reaction conditions were then reconsidered to improve the yield of the last process. The vinyl group of cycloadducts **7/7′** was functionalized by using the ruthenium catalyst **1a** or **1b** in the presence of 2 equiv. of 1-tridecene **10a** chosen as a model (Scheme 6, Table 1). The best results were clearly obtained with catalyst **1b** which is widely known to react in the presence of a variety of functionalities and does not suffer from steric hindrance with the substrates, as already pointed out in the literature.[1,4–5] Furthermore, the ^{1}H NMR spectra allowed the (*E*) conformation to be assigned to the exocyclic double bond in both cases (J = 15.6 Hz), reflecting the reversibility of the final coupling reaction.



Scheme 6. Cross-metathesis of **7/7′** with alkene **10**.

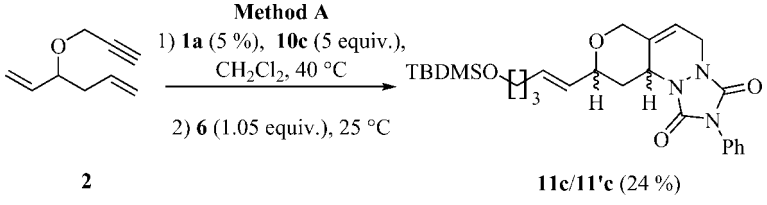
Table 1. Results of the cross-metathesis reaction of **7/7′** with alkene **10**.

	Alkene	Catalyst (%)	Product	% Yield	Ratio[a]
		1a (5)		56	58:42
10a	$C_{11}H_{23}$	**1a** (5)[b]	**11a / 11'a**	49	58:42
		1b (5)		81	63:37
10b	OTBDMS	**1b** (5)	**11b / 11'b**	74	60:40
10c	OBn	**1b** (5)	**11c / 11'c**	66	55:45
10d	Br Br	**1b** (5)	**11d / 11'd**	52	56:44

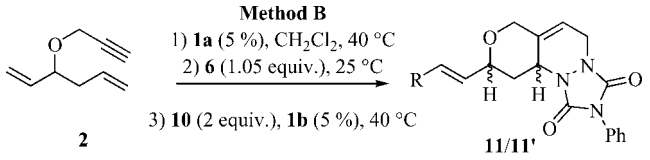
[a] Ratio of diastereoisomers determined for the crude product by ^{1}H NMR spectroscopy. [b] Reaction performed in the presence of Ti(O*i*Pr)$_4$ (0.3 equiv.).

This process was next generalized for alkenes **10b–d** (Table 1). The CM reaction was performed using the conditions defined above. Similar yields were obtained with terminal alkenes **10b**,**c**, whereas the use of 1,4-dibromobut-2-ene led to **11d/11′d** less efficiently. NOE experiments were performed on each diastereomer prepared from **10a–d** in order to assign the *syn* or *anti* configuration of compounds **11/11′**.

In order to develop an efficient one-pot three-component reaction, we then selected the optimal conditions for each process of the RCM/DA/CM sequence. As a consequence, ether **2** was treated with catalyst **1a** to deliver first a 1,3-diene. The cycloaddition reaction then took place following the introduction of Cookson's reagent **6**. Alkene **10** (2 equiv.) was finally added along with Grubbs type II catalyst **1b** to promote the cross-metathesis reaction (Scheme 7, Method B).



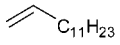
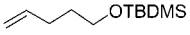
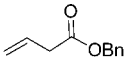
Scheme 5. One-pot RCM/CM/Diels–Alder reaction of ether **2**: Method A.



Scheme 7. One-pot RCM/Diels–Alder/CM reaction of ether **2**: Method B.

Following this method, tricyclic compounds **11/11′** were synthesized in a one-pot procedure with high overall yields (Table 2).

Table 2. Results of the one-pot RCM/Diels–Alder/CM reaction of ether **2** following Method B.

	Alkene	Product	% Yield	Ratio[a]
10a		**11a / 11'a**	61	57:43
10b		**11b / 11'b**	63	61:39
10c		**11c / 11'c**	58	52:48

A similar RCM/DA process was then applied to pentadienyl ether **3** (Scheme 8). As for **2**, the initial ring-closing metathesis took place rapidly within only 4 h leading to the 1,3-diene **12** (TLC control). This compound was trapped directly with **6** to deliver only one cycloadduct **13** in 47% yield. In this case, the formation of a single diastereoisomer was observed probably because the vinyl group is closer to the diene part than in precursor **4**. At this stage, compound **13** was subjected to two new cross-coupling reactions performed in the presence of only 5% catalyst **1b**. The reactions furnished functionalized products **14b**,**c** with (*E*) stereochemistry with the same efficiency.

A one-pot procedure following Method A and in the presence of catalyst **1a** has also been carried out with 5-bromopentene **10e**. In this way, new product **14e** was obtained directly from ether **3** with a modest yield of 32%.

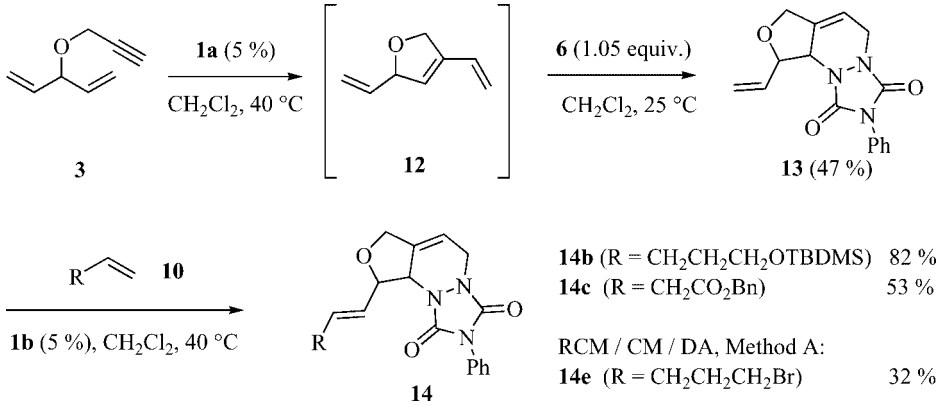
Conclusions

In conclusion, we have described a straightforward one-pot synthesis of new tricyclic compounds by a process based on regioselective ring-closing metathesis of an enyne generating a 1,3-diene. This diene was subsequently involved in a Diels–Alder reaction and the vinyl moiety was functionalized by cross-metathesis to yield a product with (*E*) stereochemistry. Work is now in progress to perform this tandem procedure with other dienophiles and in this way access more complex polycyclic structures.

Experimental Section

General Remarks: NMR spectra were recorded with a Bruker AC 300 or AM 500 spectrometer. ^{1}H and ^{13}C NMR were recorded in $CDCl_3$; chemical shifts are calibrated with reference to the residual proton and carbon resonances of the solvent ($CDCl_3$: δ_H = 7.26, δ_C = 77.36 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintuplet, m = multiplet), coupling constant (Hz), integration and assignment. High-resolution mass spectra were recorded with a Finnigan-MAT 95XL spectrometer. Tetrahydrofuran was distilled from sodium and benzophenone, whereas HPLC grade dichloromethane was used. Grubbs type I and II catalysts are commercially available compounds from Aldrich and were used as received. TLC analysis was conducted using the spray reagent molybdic acid and heating until development of colour.

1,5-Hexadien-3-yl Propargyl Ether (2): Sodium hydride (60% in mineral oil, 300 mg, 7.5 mmol) was added to a stirred suspension of 1,5-hexadien-3-ol (0.49 mL, 4.3 mmol), propargyl bromide (80% in toluene, 0.65 mL, 7.5 mmol) and tetrabutylammonium iodide (185 mg, 0.5 mmol) in dry THF (10 mL). The reaction mixture was stirred at room temperature for 12 h. The reaction was quenched by addition of aqueous saturated solution of NH_4Cl (7 mL). The aqueous phase was extracted with Et_2O (2 × 15 mL) and the combined organic layers were washed with brine (15 mL) and dried with $MgSO_4$. After filtration, the solvent was removed. The residue was purified by flash column chromatography [petroleum ether (PE)/ethyl acetate, 95:5] to afford **2** as a light yellow liquid. Yield 63% (378 mg). R_f = 0.71 (PE/EtOAc, 95:5). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.39 (t, J = 2.3 Hz, 1 H, ≡CH), 2.24–2.47 (m, 2 H, CH_2), 3.97 (q, J = 6.5 Hz, 1 H, CHO), 4.04 (dd, J = 15.7, 2.3 Hz,



Scheme 8. Formation of **14** through a RCM/Diels–Alder reaction and subsequent cross-metathesis from 1,4-pentadien-3-yl ether **3** or by a tandem process.

1 H, CH_2O), 4.21 (dd, J = 15.7, 2.3 Hz, 1 H, CH_2O), 5.08–5.32 (m, 4 H, $=CH_2$), 5.66 (ddd, J = 17.7, 9.8, 7.9 Hz, 1 H, $CH_2=CHCH_2$), 5.81 (ddd, J = 17.1, 10.2, 7.0 Hz, 1 H, $CH_2=CHCHO$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.0 (CH_2), 55.4 (CH_2O), 74.2 (≡CH), 79.7 (CHO), 80.3 (Cq), 117.3–118.7 ($=CH_2$), 134.4–137.5 (=CH) ppm.

1,4-Pentadien-3-yl Propargyl Ether (3): Ether **3** was prepared as a light-yellow liquid following the same procedure as above starting from 1,4-pentadien-3-ol. Yield 27% (167 mg). R_f = 0.75 (PE/EtOAc, 95:5). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.41 (t, J = 2.4 Hz, 1 H, ≡CH), 4.15 (d, J = 2.4 Hz, 2 H, CH_2O), 4.45 (tt, J = 6.6, 1.0 Hz, 1 H, CHO), 5.25 (dt, J = 10.2, 1.1 Hz, 2 H, $=CH_{2cis}$), 5.31 (dt, J = 17.1, 1.2 Hz, 2 H, $=CH_{2trans}$), 5.78 (ddd, J = 17.1, 10.2, 6.6 Hz, 2 H, =CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.2 (CH_2O), 74.5 (≡CH), 80.0 (Cq), 80.6 (CHO), 118.0 ($=CH_2$), 136.9 (=CH) ppm.

General Procedure for Enyne RCM/DA Reaction. Preparation of Compounds 7/7′: Catalyst **1a** (97 mg, 5%) was added to a stirred solution of ether **2** (322 mg, 2.4 mmol) in dichloromethane (240 mL) and the reaction mixture was heated for 4 h at 40 °C. After cooling to room temperature, *N*-phenyltriazole **6** (435 mg, 2.5 mmol) was added and the reaction mixture was stirred for 1 h. The solvent was then removed and the residue purified by flash column chromatography (petroleum ether/ethyl acetate, 60:40) to afford **7** as a brown oil.

Compounds 7/7′: Yield 92% (167 mg). R_f = 0.47 (PE/EtOAc, 50:50), two diastereoisomers: *anti*-**7**/*syn*-**7′** = 57/43. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.70 (dt, J = 12.3, 11.7 Hz, 1 H, CH_2CHN *syn*), 2.08 (td, J = 12.3, 5.7 Hz, 1 H, CH_2CHN *anti*), 2.92 (ddd, J = 12.6, 5.0, 1.9 Hz, 1 H, CH_2CHN *anti*), 3.03 (ddd, J = 12.7, 5.0, 1.9 Hz, 1 H, CH_2CHN *syn*), 4.13 (d, J = 12.9 Hz, 1 H, CH_2N *anti*), 4.14 (d, J = 12.6 Hz, 1 H, CH_2N *syn*), 4.18–4.21 (m, 3 H, CH_2O, CH_2N *anti*, *syn*), 4.34 (d, J = 12.3 Hz, 1 H, CHN *syn*), 4.38 (d, J = 12.3 Hz, 1 H, CHN *anti*), 4.54 (d, J = 11.3 Hz, 1 H, CHO *syn*), 4.64 (d, J = 11.6 Hz, 1 H, CHO *anti*), 4.66–4.70 (m, 1 H, CH_2O), 5.18 (dt, J = 10.7, 1.3 Hz, 1 H, $=CH_{2cis}$ *syn*), 5.32 (dt, J = 17.3, 1.3 Hz, 1 H, $=CH_{2trans}$ *syn*), 5.41 (dd, J = 11.0, 2.2 Hz, 1 H, $=CH_{2cis}$ *anti*), 5.47 (dd, J = 17.6, 1.3 Hz, 1 H, $=CH_{2trans}$ *anti*), 5.82 (s, 1 H, $=CHCH_2N$ *anti*), 5.85 (ddd, J = 17.3, 10.7, 5.0 Hz, 1 H, $CH_2=CH$ *syn*), 5.86 (s, 1 H, $=CHCH_2N$ *syn*), 6.00 (ddd, J = 17.6, 11.0, 3.5 Hz, 1 H, $CH_2=CH$ *anti*), 7.33–7.58 (m, 5 H, arom.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 33.9 (CH_2CHN *anti*), 37.6 (CH_2CHN *syn*), 42.4 (CH_2N), 51.3 (CHN *anti*), 54.4 (CHN *syn*), 64.7 (CH_2O *anti*), 70.0 (CH_2O *syn*), 72.3 (CHO *anti*), 75.8 (CHO *syn*), 114.4 ($=CHCH_2N$ *anti*), 115.3 ($=CHCH_2N$ *syn*), 115.9, 118.2 ($=CH_2$ *anti*, *syn*), 125.3, 128.0, 129.1 (CH arom.), 131.3, 131.8, 132.9 (Cq arom., Cq-CH_2O *anti*, *syn*), 136.3, 136.8 ($CH_2=CH$ *anti*, *syn*), 151.7, 152.3 (C=O) ppm. HRMS: calcd. for $C_{17}H_{17}N_3O_3$ 311.1270; found 311.1271.

Compounds 9/9′: Obtained from ether **2** and **8** as a brown oil. Yield 59% (123 mg). R_f = 0.38 (PE/EtOAc, 70:30). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.17–1.38 (m, 6 H, CH_3), 1.98–2.19 (m, 1 H, CH_2CHN), 2.23–2.43 (m, 1 H, CH_2CHN), 3.63 (d, J = 15.6 Hz, 1 H, CHN), 3.94 (d, J = 12.0 Hz, 1 H, CH_2N), 4.09–4.32 (m, 5 H, CH_2CH_3, CH_2N), 4.47–4.62 (m, 2 H, Cq-CH_2O), 4.66–4.88 (m, 1 H, CHO), 5.39 (d, J = 10.9 Hz, 1 H, $=CH_{2cis}$), 5.44 (d, J = 17.5 Hz, 1 H, $=CH_{2trans}$), 5.70 (s, 1 H, $=CHCH_2N$), 5.98 (ddd, J = 17.5, 10.9, 3.5 Hz, 1 H, $CH=CH_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.7 (CH_3), 34.2 (CH_2CHN), 42.8 (CH_2N), 50.5 (CHN), 62.3, 62.4 (CH_2CH_3), 66.0 (Cq-CH_2O), 73.4 (CHO), 117.6 ($=CHCH_2N$), 118.0 ($=CH_2$), 128.2 (Cq-CH_2O), 136.8 ($CH_2=CH$), 155.2, 155.5 (C=O) ppm. HRMS: calcd. for $C_{15}H_{22}N_2O_5+H^+$ = 310.1519; found 310.1518.

Compound 13: Obtained from ether **3** and **6** as a brown oil. Yield 47% (116 mg). R_f = 0.38 (PE/EtOAc, 50:50). ^1H NMR (300 MHz, $CDCl_3$): δ = 3.97–4.19 (m, 2 H, CH_2N), 4.43–4.64 (m, 4 H, CH_2O, CHO, CHN), 5.29 (dt, J = 10.4, 1.1 Hz, 1 H, $=CH_{2cis}$), 5.51 (dt, J = 17.3, 1.3 Hz, 1 H, $=CH_{2trans}$), 5.83 (s, 1 H, $CHCH_2N$), 6.42 (ddd, J = 17.2, 10.6, 5.3 Hz, 1 H, $CH_2=CH$), 7.30–7.58 (m, 5 H, H arom.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 42.9 (CH_2N), 62.5 (CHN), 68.1 (CH_2O), 81.9 (CHO), 113.2 ($CHCH_2N$), 117.1 ($=CH_2$), 125.7, 128.5, 129.4 (CH arom.), 131.1 (Cq arom.), 136.3 ($CH_2=CH$), 136.9 (Cq-CH_2O), 151.9, 153.9 (C=O) ppm. HRMS: calcd. for $C_{16}H_{15}N_3O_3+H^+$ = 298.1192; found 298.1191.

General Procedure for CM. Preparation of Compounds 11a/11′a: Catalyst **1b** (17 mg, 5%) was added to a dichloromethane solution (5 mL) of compounds **7**/**7′** (130 mg, 0.42 mmol) and alkene **10a** (0.20 mL, 0.84 mmol).The reaction mixture was heated for 6 h at 40 °C. After cooling to room temperature, the solvent was removed and the residue purified by flash column chromatography (petroleum ether/ethyl acetate, 80:20) to afford **11a** and **11′a** in 81% yield and with a 63:37 *anti*/*syn* ratio. ***anti*-11a**: Brown oil. R_f = 0.73 (PE/EtOAc, 50:50). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.5 Hz, 3 H, CH_3), 1.12–1.47 (m, 18 H, CH_2), 2.03 (dd, J = 12.4, 5.6 Hz, 1 H, CH_2CHN), 2.09 (q, J = 7.0 Hz, 2 H, $CH_2CH=CH$), 2.98 (ddd, J = 12.4, 4.9, 1.7 Hz, 1 H, CH_2CHN), 4.07 (d, J = 12.5 Hz, 1 H, CH_2N), 4.16 (s, 2 H, CH_2O), 4.33 (d, J = 12.5 Hz, 1 H, CH_2N), 4.56–4.70 (s, 2 H, CHO, CHN), 5.62 [dd, J = 15.5(*E*), 3.8 Hz, 1 H, $CH=CHCHO$], 5.80 (s, 1 H, $=CHCH_2N$), 5.86 [dt, J = 15.5(*E*), 7.0 Hz, 1 H, $CH=CHCHO$], 7.30–7.58 (m, 5 H, arom.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.4 (CH_3), 23.0, 29.4, 29.5, 29.6, 29.8, 29.9, 30.0, 30.1, 32.2, 32.9, 34.9, 42.8 (CH_2), 42.8 (CHN), 64.9 (CH_2O), 72.6 (CHO), 114.5 ($=CHCH_2N$), 125.7, 127.7, 129.4 (CH arom.), 128.4 (*C*H=CHCHO), 131.4 (Cq arom.), 133.8 (*C*q-CH_2O), 135.5 (CH=*C*HCHO), 152.1, 152.7 (C=O) ppm. ***syn*-11′a**: Brown oil. R_f = 0.67 (PE/EtOAc, 50:50). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.6 Hz, 3 H, CH_3), 1.16–1.44 (m, 18 H, CH_2), 1.70 (dt, J = 12.4, 11.5 Hz, 1 H, CH_2CHN), 2.02 (q, J = 6.8 Hz, 2 H, $CH_2CH=CH$), 2.86 (ddd, J = 12.4, 4.9, 1.7 Hz, 1 H, CH_2CHN), 4.04–4.13 (m, 2 H, CH_2N, CHN), 4.18 (s, 2 H, CH_2O), 4.35 (d, J = 12.4 Hz, 1 H, CH_2N), 4.50 (d, J = 11.5 Hz, 1 H, CHO), 5.46 [dd, J = 15.4(*E*), 6.2 Hz, 1 H, $CH=CHCHO$], 5.76 [dt, J = 15.4(*E*), 6.8 Hz, 1 H, $CH=CHCHO$], 5.84 (s, 1 H, $=CHCH_2N$), 7.30–7.56 (m, 5 H, arom.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.4 (CH_3), 23.0, 29.3, 29.5, 29.7, 29.8, 29.9, 30.0, 30.1, 32.2, 32.6, 38.4, 42.9 (CH_2), 54.9 (CHN), 70.5 (CH_2O), 76.6 (CHO), 115.5 ($=CHCH_2N$), 125.8, 128.7, 129.5 (CH arom.), 128.5 (*C*H=CHCHO), 130.4 (Cq arom.), 132.6 (*C*q-CH_2O), 134.2 (CH=*C*HCHO), 152.2–152.3 (C=O) ppm. HRMS: calcd. for $C_{28}H_{39}N_3O_3$ 465.2991; found 465.2990.

Compounds 11b/11′b: Obtained from compounds **7**/**7′** and alkene **10b**. Yield 74% (140 mg). *anti*/*syn* = 60/40. ***anti*-11b**: Brown oil. R_f = 0.67 (PE/EtOAc, 50:50). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.03 (s, 3 H, CH_3Si), 0.08 (s, 3 H, CH_3Si), 0.90 [s, 9 H, $(CH_3)_3CSi$], 1.50–1.72 (m, 2 H, $CH_2CH_2CH_2$), 2.06 (dt, J = 12.5, 3.8 Hz, 1 H, CH_2CHN), 2.17 (q, J = 7.2 Hz, 2 H, $CH_2CH_2CH=$), 2.98 (ddd, J = 12.5, 4.9, 2.1 Hz, 1 H, CH_2CHN), 3.62 (t, J = 6.4 Hz, 2 H, Si-OCH_2), 4.08 (d, J = 12.4 Hz, 1 H, CH_2N), 4.18 (s, 2 H, CH_2O), 4.34 (d, J = 12.5 Hz, 1 H, CH_2N), 4.56–4.73 (m, 2 H, CHO, CHN), 5.65 [dd, J = 15.9(*E*), 3.9 Hz, 1 H, $CH=CHCHO$], 5.82 (s, 1 H), 5.88 [dt, J = 15.9(*E*), 7.2 Hz, 1 H, $CH=CHCHO$], 7.31–7.60 (m, 5 H arom.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –5.0 (CH_3Si), 18.6 (Cq-Si), 26.2 [$(CH_3)_3CSi$], 29.2, 32.2, 34.8, 42.7 (CH_2), 51.8 (CHN),

62.7 (CH_2Si), 64.9 (CH_2O), 72.5 (CHO), 114.5 (=*C*HCH$_2$N), 125.7, 128.0, 129.4 (CH arom.), 128.4 (*C*H=CHCHO), 131.3 (Cq arom.), 133.6 (*C*q-CH_2O), 134.8 (CH=*C*HCHO), 152.1, 152.7 (C=O) ppm. *syn*-**11′b**: Brown oil. R_f = 0.49 (PE/EtOAc, 50:50). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.03 (s, 3 H, CH_3Si), 0.10 (s, 3 H, CH_3Si), 0.88 [s, 9 H, (C*H*$_3$)$_3$CSi], 1.53–1.64 (m, 2 H, $CH_2CH_2CH_2$), 1.70 (dt, *J* = 12.4, 11.5 Hz, 1 H, C*H*$_2$CHN), 2.10 (q, *J* = 7.0 Hz, 2 H, CH_2CH_2CH=), 2.85 (ddd, *J* = 12.4, 4.9, 1.7 Hz, 1 H, C*H*$_2$CHN), 3.60 (t, *J* = 6.4 Hz, 2 H, $SiOCH_2$), 4.04–4.14 (m, 2 H, CHN, CH_2N), 4.18 (s, 2 H, CH_2O), 4.33 (d, *J* = 12.4 Hz, 1 H, CH_2N), 4.51 (d, *J* = 11.5 Hz, 1 H, CHO), 5.48 [dd, *J* = 15.4(*E*), 6.1 Hz, 1 H, C*H*=CHCHO], 5.77 [dt, *J* = 15.4(*E*), 7.0 Hz, 1 H, CH=C*H*CHO], 5.84 (s, 1 H), 7.30–7.58 (m, 5 H, arom.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –4.9 (CH_3Si), 18.6 (Cq-Si), 26.3 [(*C*H$_3$)$_3$CSi], 28.9, 32.3, 38.4, 42.8 (CH_2), 54.9 (CHN), 62.7 (CH_2Si), 70.5 (CH_2O), 76.4 (CHO), 115.5 (=*C*HCH$_2$N), 125.8, 128.5, 129.4 (CH arom.), 129.0 (*C*H=CHCHO), 131.4 (Cq arom.), 132.6 (*C*q-CH_2O), 133.5 (CH=*C*HCHO), 152.2, 152.6 (C=O) ppm. HRMS: calcd. for $C_{26}H_{37}N_3O_4Si$+H$^+$ 484.2632; found 484.2632.

Compounds 11c/11′c: Obtained from compounds **7**/**7′** and alkene **10c**. Yield 66% (152 mg). *anti*/*syn* = 55/45. *anti*-**11c**: Brown oil. R_f = 0.40 (PE/EtOAc, 50:50). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.05 (dt, *J* = 12.6, 5.8 Hz, 1 H, C*H*$_2$CHN), 2.98 (ddd, *J* = 12.6, 4.9, 2.0 Hz, 1 H, C*H*$_2$CHN), 3.20 (d, *J* = 7.0 Hz, 2 H, C*H*$_2$C=O), 4.05 (d, *J* = 12.6 Hz, 1 H, CH_2N), 4.15 (s, 2 H, C*H*$_2$OCH), 4.28 (d, *J* = 12.6 Hz, 1 H, CH_2N), 4.54 (d, *J* = 11.7 Hz, 1 H, CHO), 4.64 (s, 1 H, CHN), 5.10 (s, 2 H, CH_2–Ph), 5.75 [dd, *J* = 16.1(*E*), 3.6 Hz, 1 H, C*H*=CHCHO], 5.77 (s, 1 H, =C*H*CH$_2$N), 5.98 [dt, *J* = 16.1(*E*), 7.0 Hz, 1 H, CH=C*H*CHO], 7.28–7.40 (m, 5 H, arom.), 7.42–7.58 (m, 5 H, arom.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 34.8, 38.0, 42.6 (CH_2), 51.6 (CHN), 64.9 (CH_2O), 66.8 ($BnOCH_2$) 71.9 (CHO), 114.6 (=*C*HCH$_2$N), 125.6, 126.2, 128.3, 128.5, 128.6, 128.8, 129.3 (CH arom., *C*H=CHCHO), 131.3 (Cq arom.), 132.4 (*C*q-CH_2O), 133.3 (CH=*C*HCHO), 135.9 (Cq arom.), 151.9, 152.7 (C=O), 171.2 (C=O) ppm. *syn*-**11′c**: Brown oil. R_f = 0.35 (PE/EtOAc, 50:50). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.70 (dt, *J* = 12.2, 11.7 Hz, 1 H, C*H*$_2$CHN), 2.89 (ddd, *J* = 12.2, 4.9, 1.7 Hz, 1 H, C*H*$_2$CHN), 3.13 (d, *J* = 7.0 Hz, 2 H, C*H*$_2$C=O), 4.11 (d, *J* = 12.4 Hz, 1 H, CH_2N), 4.07–4.22 (m, 3 H, CHN, C*H*$_2$OCH), 4.37 (d, *J* = 12.4 Hz, 1 H, CH_2N), 4.51 (d, *J* = 11.7 Hz, 1 H, CHO), 5.10 (s, 2 H, CH_2Ph), 5.62 [dd, *J* = 15.6(*E*), 5.6 Hz, 1 H, C*H*=CHCHO], 5.86 (s, 1 H, =C*H*CH$_2$N), 5.91 [dt, *J* = 15.6(*E*), 7.0 Hz, 1 H, CH=C*H*CHO], 7.29–7.42 (m, 5 H, arom.), 7.43–7.57 (m, 5 H, arom.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 37.9, 38.0, 42.8 (CH_2), 54.7 (CHN), 66.8 ($BnOCH_2$), 70.4 (CH_2O), 75.6 (CHO), 115.7 (=*C*HCH$_2$N), 124.6, 125.7, 128.4, 128.5, 128.6, 128.8, 129.4 (CH arom., *C*H=CHCHO), 129.3, 131.3 (Cq arom.), 132.3 (*C*q-CH_2O), 132.8 (CH=*C*HCHO), 152.1, 152.5 (C=O), 171.2 (C=O) ppm. HRMS: calcd. for $C_{26}H_{25}N_3O_5$ 459.1794; found 459.1792.

Compounds 11d/11′d: Obtained from compounds **7**/**7′** and alkene **10d**. Yield 52% (52 mg). *anti*/*syn* = 56:44. *anti*-**11d**: Brown oil. R_f = 0.42 (PE/EtOAc, 50:50). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.10 (dt, *J* = 12.4, 5.6 Hz, 1 H, C*H*$_2$CHN), 2.98 (ddd, *J* = 12.4, 4.9, 1.9 Hz, 1 H, C*H*$_2$CHN), 4.00 (d, *J* = 7.2 Hz, 2 H, CH_2Br), 4.12 (d, *J* = 12.8 Hz, 1 H, CH_2N), 4.17 (s, 2 H, CH_2O), 4.32 (d, *J* = 12.8 Hz, 1 H, CH_2N), 4.56 (d, *J* = 11.9 Hz, 1 H, CHO), 4.68 (s, 1 H, CHN), 5.82 (s, 1 H, =C*H*CH$_2$N), 5.93 [dd, *J* = 15.6(*E*), 3.3 Hz, 1 H, C*H*=CHCHO], 6.10 [dt, *J* = 15.6(*E*), 7.2 Hz, 1 H, CH=C*H*CHO], 7.32–7.59 (m, 5 H, arom.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 31.9, 34.8, 42.7 (CH_2), 51.7 (CHN), 65.3 (CH_2O), 71.6 (CHO), 115.0 (=*C*HCH$_2$N), 125.7 (*C*H=CHCHO), 128.5, 129.5, 130.3 (CH arom.), 131.3 (Cq arom.), 133.1 (*C*q-CH_2O), 133.4 (CH=*C*HCHO), 152.1, 152.8 (C=O) ppm. *syn*-**11′d**: Brown oil. R_f = 0.40 (PE/EtOAc, 50:50). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.67 (dt, *J* = 12.4, 11.5 Hz, 1 H, C*H*$_2$CHN), 2.90 (ddd, *J* = 12.4, 4.9, 1.8 Hz, 1 H, C*H*$_2$CHN), 3.93 (d, *J* = 7.6 Hz, 2 H, CH_2Br), 4.10 (d, *J* = 12.8 Hz, 1 H, CH_2N), 4.18 (s, 2 H, CH_2O), 4.19 (s, 1 H, CHN), 4.38 (d, *J* = 12.8 Hz, 1 H, CH_2N), 4.50 (d, *J* = 11.5 Hz, 1 H, CHO), 5.76 [dd, *J* = 15.3(*E*), 5.1 Hz, 1 H, C*H*=CHCHO], 5.86 (s, 1 H, =C*H*CH$_2$N), 5.98 [dt, *J* = 15.3(*E*), 7.6 Hz, 1 H, CH=C*H*CHO], 7.33–7.62 (m, 5 H, arom.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 31.9, 37.9, 42.8 (CH_2), 54.7 (CHN), 70.5 (CH_2O), 74.9 (CHO), 115.9 (=*C*HCH$_2$N), 125.7 (*C*H=CHCHO), 125.8, 128.1, 129.5 (CH arom.), 128.5 (Cq arom.), 132.1 (*C*q-CH_2O), 133.6 (CH=*C*HCHO), 152.0, 152.1 (C=O) ppm. HRMS: calcd. for $C_{18}H_{18}BrN_3O_3$ – H$^+$ 403.0532; found 403.0533.

Compound 14b: Obtained from compound **13** and alkene **10b** as a brown oil. Yield 82% (75 mg). R_f = 0.71 (PE/EtOAc, 50:50). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.02 (s, 6 H, CH_3Si), 0.87 [s, 9 H, (C*H*$_3$)$_3$CSi], 1.63 (quint, *J* = 7.0 Hz, 2 H, $CH_2CH_2CH_2$), 2.15 (q, *J* = 6.9 Hz, 2 H, C*H*$_2$CH=CH), 3.61 (t, *J* = 6.4 Hz, 2 H, C*H*$_2$OSi), 4.05 (dt, *J* = 16.4, 2.3 Hz, 1 H, CH_2O), 4.14 (d, *J* = 5.0 Hz, 1 H, CHO), 4.43 (dt, *J* = 16.4, 2.8 Hz, 1 H, CH_2O), 4.45–4.51 (m, 2 H, CH_2N, CHN), 4.56 (d, *J* = 12.0 Hz, 1 H, CH_2N), 5.84 (s, 1 H, C*H*CH$_2$N), 5.93 [dt, *J* = 15.4(*E*), 6.3 Hz, 1 H, C*H*=CHCHO], 5.98 [dd, *J* = 15.4(*E*), 5.0 Hz, 1 H, CH=C*H*CHO], 7.30–7.55 (m, 5 H, arom.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –5.0 (CH_3Si), 18.6 (Cq-Si), 26.2 [(*C*H$_3$)$_3$CSi], 28.9, 32.4 (CH_2), 42.9 (CH_2N), 62.7 (CHN), 62.9 (CH_2OSi), 68.0 (CH_2O), 82.1 (CHO), 113.0 (*C*HCH$_2$N), 125.9, 128.6, 129.5 (CH arom.), 128.1 (*C*H=CHCHO), 129.6 (Cq arom.), 134.2 (CH=*C*HCHO), 137.2 (*C*q-CH_2O), 152.1, 153.7 (C=O) ppm. HRMS: calcd. for $C_{25}H_{35}N_3O_4Si$ + H$^+$ = 470.2475; found 470.2472.

Compound 14c: Obtained from compound **13** and alkene **10c** as a brown oil. Yield 53% (51 mg). R_f = 0.44 (PE/EtOAc, 50:50). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.20 (t, *J* = 6.3 Hz, 2 H, C*H*$_2$C=O), 4.05 (dt, *J* = 16.7, 2.2 Hz, 1 H, CH_2O), 4.12 (d, *J* = 5.0 Hz, 1 H, CHO), 4.43 (dt, *J* = 16.7, 2.6 Hz, 1 H, CH_2O), 4.49 (d, *J* = 12.3 Hz, 1 H, CH_2N), 4.50–4.54 (m, 1 H, CHN), 4.57 (d, *J* = 12.3 Hz, 1 H, CH_2N), 5.10 (s, 2 H, CH_2Ph), 5.83 (s, 1 H, =C*H*CH$_2$N), 6.09 [dt, *J* = 15.4(*E*), 7.0 Hz, 1 H, C*H*=CHCHO], 6.24 [dd, *J* = 15.4(*E*), 5.0 Hz, 1 H, CH=C*H*CHO], 7.27–7.40 (m, 5 H, arom.), 7.43–7.55 (m, 5 H, arom.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 37.9, 42.9 (CH_2), 62.6 (CHN), 66.7, 68.2 (CH_2O, $BnOCH_2$), 81.2 (CHO), 113.2 (=*C*HCH$_2$N), 124.7 (*C*H=CHCHO), 125.7, 128.4, 128.5, 128.6–128.8, 129.5 (CH arom.), 131.2 (Cq arom.), 132.1 (CH=*C*HCHO), 136.1, 136.2 (*C*q-CH_2O, Cq arom.), 152.0, 153.9 (C=O), 171.5 (C=O) ppm. HRMS: calcd. for $C_{25}H_{23}N_3O_5$ + H$^+$ = 446.1716; found 446.1714.

General Procedure for RCM/CM/DA, Method A. Preparation of Compound 14e: Catalyst **1a** (21 mg, 5%) was added to a stirred solution of ether **3** (61 mg, 0.5 mmol) and alkene **10e** (0.29 mL, 2.5 mmol) in dichloromethane (50 mL). The reaction mixture was heated for 4 h at 40 °C. After cooling to room temperature, *N*-phenyltriazole **6** (96 mg, 0.55 mmol) was added and the reaction mixture was stirred for 1 h. The solvent was removed and the residue purified by flash column chromatography (petroleum ether/ethyl acetate, 60:40) to afford **14e** as a brown oil in a yield of 32%. R_f = 0.27 (PE/EtOAc, 50:50). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.96 (quint, *J* = 7.0 Hz, 2 H, $CH_2CH_2CH_2$). 2.24 (q, *J* = 6.7 Hz, 2 H, CH_2CH_2CH=), 3.41 (t, *J* = 6.9 Hz, 2 H, CH_2Br), 3.96–4.24 (m, 2 H, CH_2N), 4.32–4.64 (m, 4 H, CH_2O, CHO, CHN), 5.82 (s, 1 H, C*H*CH$_2$N), 5.88 [dt, *J* = 15.4(*E*), 6.6 Hz, 1 H, C*H*=CHCHO], 6.04 [dd, *J* = 15.4(*E*), 5.1 Hz, 1 H, CH=C*H*CHO], 7.30–7.66 (m, 5 H,

arom.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 30.9, 32.1, 33.5 (CH_2), 42.9 (CH_2N), 62.5 (CHN), 68.0 (CH_2O), 81.9 (CHO), 113.1 (*C*HCH_2N), 125.8, 128.5, 128.9 (CH arom.), 129.4 (*C*H=CHCHO), 131.1 (Cq arom.), 132.2 (CH=*C*HCHO), 137.0 (*C*q-CH_2O), 152.0, 153.7 (C=O) ppm. HRMS: calcd. for $C_{19}H_{20}N_3O_3Br + H^+$ = 418.0766; found 418.0766.

General Procedure for RCM/DA/CM, Method B. Preparation of Compound 11a/11′a: Catalyst **1a** (10 mg, 5%) was added to a stirred solution of ether **2** (35 mg, 0.26 mmol) in dichloromethane (26 mL) and the reaction mixture was heated for 4 h at 40 °C. After cooling to room temperature, *N*-phenyltriazole **6** (48 mg, 0.27 mmol) was added and the reaction mixture was stirred for 1 h. Alkene **10a** (0.12 mL, 0.52 mmol) and catalyst **1b** (11 mg, 5%) were both added and the reaction mixture was heated again for 7 h at 40 °C. The solvent was removed and the residue purified by flash column chromatography (petroleum ether/ethyl acetate, 80:20) to afford two brown oils **11a/11′a** in a yield of 61% (*anti*/*syn* = 57:43).

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