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Application of ring closing metathesis in efficient synthesis of macrocyclic crown compounds

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Abstract

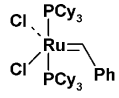
RCM of suitable α,ω-dienes led to efficient atom economic synthetic approaches towards azacrown ether derivatives with 8–40 membered ring sizes.

Keywords: Ring closing metathesis; α,ω-Dienes; Azacrown ethers; Crown-amides; Crown-formazans

1. Introduction

Crown compounds and azacrown compounds constitute important macrocyclic groups in supramolecular chemistry. They have been shown to exhibit important applications including selective ion separation and detection, molecular recognition, catalysis, biological applications as well as many other interesting applications in diverse fields of supramolecular chemistry [1,2]. Synthetic approaches towards such macrocycles usually suffer from low yields, loss of considerable amount of the starting precursors during the macrocyclization step due to polymer formation in addition to the need for high dilution conditions and template effect [1]. We have been investigating several synthetic approaches towards macrocyclic azacrown compounds where some of them showed useful application in ion selective electrodes and as spectrophotometric reagents [2].

Recently, ring closing metathesis (RCM) [3] has found increasing application in the synthesis of macrocyclic compounds [4–16]. The application of RCM as the key macrocyclization step in the synthesis of crown compounds has opened efficient routes towards macrocyclic crown compounds of important applications in supramolecular chemistry [10,17–19]. The present review describes our recent contribution to the utility of RCM technique as an efficient route to a large number of highly functionalized macrocyclic compounds utilizing mainly Grubbs' catalyst **I**:



Grubbs' catalyst (I)

2. Azacrown sulfonamides

Scheme 1 illustrates our synthetic routes starting from the appropriate readily available bistosylamides or tosylamide which were, converted via their potassium salts into the corresponding α,ω-dienes (**1**)–(**12**). RCM of these dienes proceeded under mild condition using 2.5 mol% of **I** in CH_2Cl_2 to give excellent yield of the corresponding macrocyclic products (**13**)–(**24**) (Table 1) [20]. Table 1 shows also, that the photo catalyst {[(*p*-cymene)$RuCl_2$]$_2$ and PCy_3 in the presence of normal laboratory neon tubes} gave only moderate yield of RCM products in two cases (Run 1, 3, condition c). Moreover, attempts to convert **3** into **15** (Run 5) using photo RCM conditions [21] gave less than 10% conversion, yielding a mixture of products including **15**. Therefore, we applied in all other cases catalyst (**I**) which showed excellent conversion yields (Table 1).

All yields (Tables 1–12) were calculated by ^{1}H NMR in the reaction mixture as described in details in a previous publication [22]. The isolated yields of the pure product after column chromatography were almost identical to those calculated by ^{1}H NMR. Dashed lines at the olefinic double bonds indicate either *E* or *Z* cyclic olefins and the actual ratio of these two isomers

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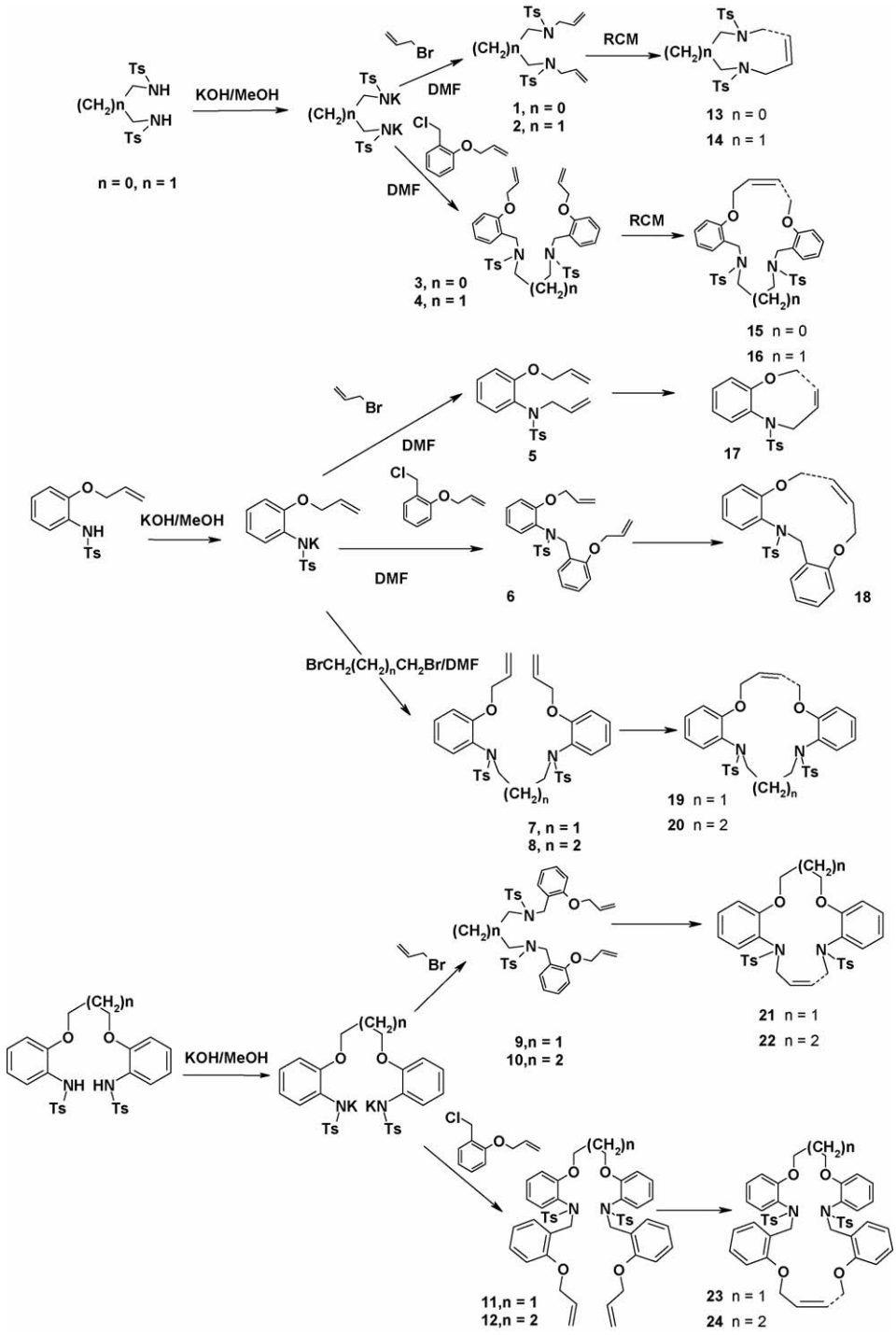


Scheme 1.

have been calculated easily in most cases from the ^{1}H NMR as shown in Tables 1–12.

3. Azacrown polyoxa-monoamides, diamides and tetraamides

RCM of the suitable α,ω-dienes led to an efficient synthesis of many crown amides shown in Tables 2–11.

3.1. From bis-(o-hydroxyphenyl)amides

Scheme 2 illustrates the synthetic routes starting from the appropriate readily available bis-(*o*-hydroxyphenyl)amides which were, converted *via* their potassium salts into the corresponding α,ω-dienes (**25**)–(**32**), (**41**)–(**44**). Some α,ω-dienes derivatives were also readily obtained by reacting the appropriate diamine with *o*-allyloxybenzoyl chloride. RCM of these dienes (Tables 2 and 3) proceeded under mild conditions using

Table 1
Reaction conditions, yields and *E*:*Z* ratios of macrocycles (**49**)–(**54**)

Entry	Conditions/yield (%)	Product	*E*:*Z* ratio[a]
1	92[b], 60[c]	**13**	0:1
2	85[b]	**14**	1:2
3	90[b], 60[c]	**15**	1:2
4	95[b]	**16**	1:7
5	88[b], 10[c]	**17**	1:3
6	95[b]	**18**	[d]
7	76[b]	**19**	1:1
8	100[b]	**20**	2:1
9	100[b]	**21**	0:1
10	100[b]	**22**	1:2
11	85[b]	**23**	2.5:1
12	95[b]	**24**	[d]

[a] *E*:*Z* ratios are the same under all conditions.
[b] Substrate (0.01 M), **I** (2.5 mol%); CH_2Cl_2 (10 mL), reflux 2 h.
[c] Substrate (0.01 M), [(*p*-cymene)$RuCl_2$]$_2$ (2.5 mol%), PCy_3 (5.5 mol%), CH_2Cl_2 (10 mL), Neon light, Ar atmosphere, reflux 16 h.
[d] *E*/*Z* ratios could not be determined.

Table 2
Reaction conditions, yields and *E*:*Z* ratios of macrocycles (**33**)–(**40**)

Entry	Conditions/yield (%)	Product	*E*:*Z* ratio[a]
1	60[b], 100[c]	**33**	6:1
2	40[b], 60[c]	**34**	2:1
3	100[d]	**35**	1.1:1
4	5[b], 60[c]	**36**	1:1
5	10[b], 70[c]	**37**	2:1
6	100[b]	**38**	7:1
7	80[b]	**39**	3:1
8	80[b]	**40**	2.5:1

[a] *E*:*Z* ratios are the same under all conditions.
[b] Substrate (0.01 M), **I** (2.5 mol%); CH_2Cl_2 (10 mL), reflux 2 h.
[c] Substrate (0.01 M), **I** (5 mol%); CH_2Cl_2 (10 mL), reflux 2 h.
[d] Substrate (0.01 M), **I** (1.25 mol%); CH_2Cl_2 (10 mL), reflux 2 h.

Table 3
Reaction conditions, yields and *E*:*Z* ratios of macrocycles (**45**)–(**48**)

Entry	Conditions/yield (%)	Product	*E*:*Z* ratio
1	100[a], 60[b]	**45**	[c]
2	100[b]	**46**	1:1
3	100[a]	**47**	1:1
4	70[a]	**48**	1:1

[a] Substrate (0.01 M), **I** (2.5 mol%); CH_2Cl_2 (10 mL), reflux 2 h.
[b] Substrate (0.01 M), **I** (1 mol%); CH_2Cl_2 (10 mL), reflux 2 h.
[c] *E*:*Z* ratio could not be determined.

Table 4
Reaction conditions, yields and *E*:*Z* ratios of macrocycles (**49**)–(**54**)

Entry	Conditions/yield (%)	Product	*E*:*Z* ratio[a]
1	5[b], 10[c], 40[d]	**49**	[e]
2	5[b], 15[c], 47[d]	**50**	[e]
3	5[b], 25[c], 50[d]	**51**	[e]
4	12[b], 25[c], 50[d]	**52**	[e]
5	10[b], 25[c], 50[d]	**53**	5:1
6	13[b], 26[c], 60[d]	**54**	3:1

[a] *E*:*Z* ratios are the same under all conditions.
[b] Substrate (0.2 mM), **I** (2.5 mol%); CH_2Cl_2 (5 mL), reflux 3 h.
[c] Substrate (0.2 mM), **I** (5 mol%); CH_2Cl_2 (5 mL), reflux 3 h.
[d] Substrate (0.2 mM), **I** (10 mol%); CH_2Cl_2 (5 mL), reflux 3 h.
[e] *E*:*Z* ratios have not be determined.

Table 5
Reaction conditions, yields and *E*:*Z* ratios of macrocycles (**55**)–(**60**)

Entry	Conditions/yield (%)	Product	*E*:*Z* ratio[a]
1	78[b], 100[c]	**55**	5:1
2	81[b], 100[c]	**56**	5:1
3	80[b], 100[c]	**57**	5:1
4	90[c], 100[d]	**58**	3:1
5	80[b], 100[d]	**59**	3:1
6	100[b]	**60**	3:1

[a] *E*:*Z* ratios are the same under all conditions.
[b] Substrate (0.2 mM), **I** (1 mol%); CH_2Cl_2 (5 mL), reflux 3 h.
[c] Substrate (0.2 mM), **I** (2 mol%); CH_2Cl_2 (5 mL), reflux 3 h.
[d] Substrate (0.2 mM), **I** (5 mol%); CH_2Cl_2 (5 mL), reflux 3 h.

Table 6
Reaction conditions, yields and *E*:*Z* ratios of macrocycles (**61**)–(**66**)

Entry	Conditions/yield (%)	Product	*E*:*Z* ratio[a]
1	67[b], 90[c]	**61**	4:1
2	60[b], 80[c]	**62**	3:1
3	82[b], 82[c]	**63**	4:1
4	60[c], 100[d]	**64**	5:1
5	65[b], 100[d]	**65**	3:1
6	100[d]	**66**	2:1

[a] *E*:*Z* ratios are the same under all conditions.
[b] Substrate (0 2 mM), **I** (2 mol%), CH_2Cl_2 (5 mL), reflux 3 h.
[c] Substrate (0 2 mM), **I** (5 mol%), CH_2Cl_2 (5 mL), reflux 3 h.
[d] Substrate (0 2 mM), **I** (1 mol%), CH_2Cl_2 (5 mL), reflux 3 h.

Table 7
Reaction conditions, yields and *E*:*Z* ratios of macrocycles (**67**)–(**71**)

Entry	Conditions/yield (%)	Product	*E*:*Z* ratio
1	62[a]	**67**	1:1
2	93[b]	**68**	19:1
3	70[a]	**69**	1:1
4	80[a]	**70**	1:1
5	89[b]	**71**	1.3:1

[a] Substrate (0.2 mM), **I** (2 mol%); CH_2Cl_2 (25 mL), reflux 3 h.
[b] Substrate (0.2 mM), **I** (2.5 mol%); CH_2Cl_2 (25 mL), reflux 3 h.

Table 8
Reaction conditions, yields and *E*:*Z* ratios of macrocycles (**72**)–(**76**)

Entry	Conditions/yield (%)	Product	E:Z ratio
1	91[a]	**72**	4:1
2	92[b]	**73**	3:1
3	86[a]	**74**	3:1
4	95[b]	**75**	2:1
5	94[a]	**76**	2:1

[a] Substrate (0.2 mM), **I** (1.5 mol%); CH_2Cl_2 (25 mL), reflux 3 h.
[b] Substrate (0.2 mM), **I** (2 mol%); CH_2Cl_2 (25 mL), reflux 3 h.

Table 9
Reaction conditions, yields and E:Z ratios of macrocycles (**77**)–(**83**)

Entry	Conditions/yield (%)	Product	*E*:*Z* ratio
1	97[a]	**77**	5:1
2	91[b]	**78**	7:1
3	52[a]	**79**	5:1
4	78[a]	**80**	5:1
5	88[a]	**81**	13:1
6	70[b]	**82**	2.5:1
7	60[b]	**83**	3.5:1

[a] Substrate (0.2 mM), **I** (2.5 mol%); CH_2Cl_2 (25 mL), reflux 24 h.
[b] Substrate (0.2 mM), **I** (5 mol%); CH_2Cl_2 (25 mL), reflux 24 h.

Table 10
Reaction conditions, yields and *E*:*Z* ratios of macrocycles (**84**)–(**89**)

Entry	Conditions/yield (%)	Product	*E*:*Z* ratio
1	99[a]	**84**	3:1
2	85[b]	**85**	1.7:1
3	99[a]	**86**	2:1
4	98[a]	**87**	3:1
5	96[c]	**88**	2.5:1
6	60[b]	**89**	1.4:1

[a] Substrate (0.2 mM), **I** (2.5 mol%); CH_2Cl_2 (25 mL), reflux 24 h.
[b] Substrate (0.2 mM), **I** (5 mol%); CH_2Cl_2 (25 mL), reflux 24 h.
[c] Substrate (0.2 mM), **I** (2.5 mol%); CH_2Cl_2 (25 mL), reflux 4 h.

1–5 mol% of **I** in refluxing CH_2Cl_2 to give excellent yield of the corresponding macrocyclic products [22].

Table 2 shows that the RCM reactions proceeded in high yield in most cases by heating the substrate in dichloromethane with 2.5–5 mol% of **I**. It is also remarkable that the formation of the 16 membered ring (entries 1 and 3) led to 100% macrocyclization by this technique. Moreover, only 1.25% molar ratio of the catalyst was needed for the full RCM macrocyclization of **27**, however, using 1% molar ratio of **I** led to only 75% macrocyclization where 25% of the starting compound (**27**) recovered unreacted (entry 3). On increasing the ring size to 17 (entries 2, 4 and 5) the RCM reaction could only be accomplished in reasonably good yields by increasing the catalyst to 5% molar ratio. However, by increasing the ring size even more to 24 and 25 (entries 6–8) macrocyclization yields of 80–100% were achieved with only 2.5% molar ratio of the catalyst (**I**).

Table 11
Reaction conditions, yields and *E*:*Z* ratios of macrocycles (**90**)–(**97**)

Entry	Conditions/yield (%)	Product	*E*:*Z* ratio
1	92[a]	**90**	3.6:1
2	73[b]	**91**	2:1
3	91[a]	**92**	3:1
4	97[b]	**93**	3:1
5	100[c]	**94**	2:1
6	80[d]	**95**	2.6:1
7	75[e]	**96**	1:1
8	82[f]	**97**	2.5:1

[a] Substrate (0.2 mM), **I** (2.5 mol%); CH_2Cl_2 (25 mL), reflux 24 h.
[b] Substrate (0.2 mM), **I** (5 mol%); CH_2Cl_2 (25 mL), reflux 24 h.
[c] Substrate (0.2 mM), **I** (7.5 mol%); CH_2Cl_2 (25 mL), reflux 3 h.
[d] Substrate (0.2 mM), **I** (5 mol%); CH_2Cl_2 (25 mL), reflux 3 h.
[e] Substrate (0.2 mM), **I** (2.5 mol%); CH_2Cl_2 (25 mL), reflux 4 h.
[f] Substrate (0.2 mM), **I** (2.5 mol%); CH_2Cl_2 (25 mL), reflux 2 h.

Table 12
Reaction conditions, yields and *E*:*Z* ratios of macrocycles (**98**)–(**104**)

Entry	Conditions/yield (%)	Product	*E*:*Z* ratio[a]
1	20[b], 40[c], 60[d]	**98**	13:1
2	40[b], 65[c]	**99**	24:1
3	60[b], 95[c]	**100**	24:1
4	20[b], 60[c]	**101**	32:1
5	20[b], 60[c]	**102**	32:1
6	5[b], 8[c], 10[d]	**103**	19:1
7	40[b], 90[b]	**104**	9:1

[a] *E*:*Z* ratios are the same under all conditions.
[b] Substrate (0.1 mM), **I** (2.5 mol%); CH_2Cl_2 (10 mL), reflux 12 h.
[c] Substrate (0.1 mM), **I** (5 mol%); CH_2Cl_2 (10 mL), reflux 12 h.
[d] Substrate (0.1 mM), **I** (7.5 mol%); CH_2Cl_2 (10 mL), reflux 12 h.

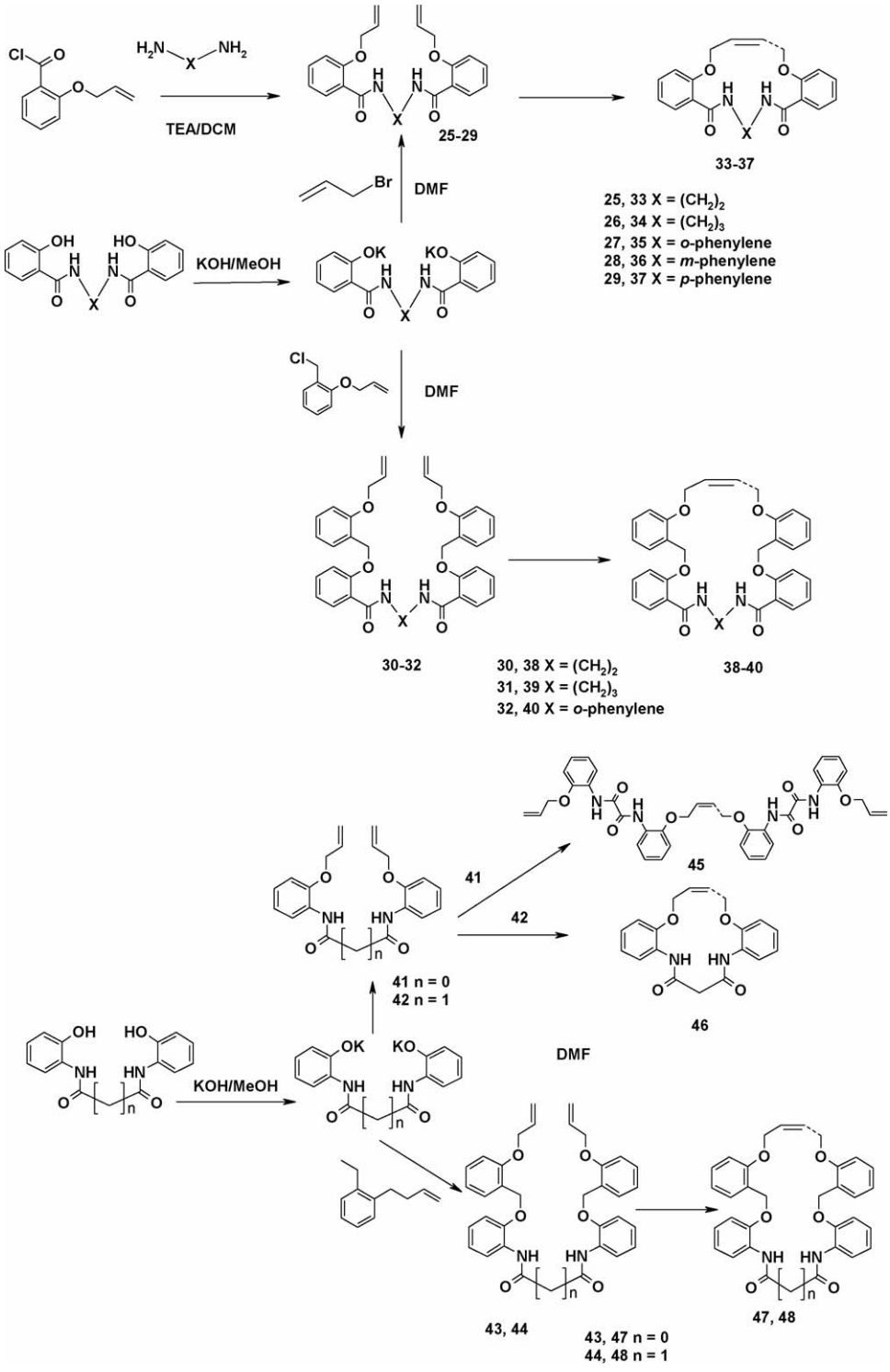
Application of RCM techniques using catalyst **I** to the oxalic diamides (**41**), (**43**) and bis-malonamides (**42**), (**44**) was also, investigated (Table 3). All attempts to metathesize compound (**41**) led only to the precipitation of the dimeric ring open structure (**45**). On other hand the application of RCM techniques to the malonic diamide (**42**) led to 100% formation of the macrocyle (**46**). Likewise compounds (**43**), (**44**) undergo RCM reactions with **I** to give the corresponding macrocycles (**47**), (**48**), respectively [22].

3.2. From N-allylsalicylamide and N-(o-allyloxyphenyl)salicylamide

Extension of the RCM to different α,ω-dienes readily obtained from *N*-allylsalicylamide and *N*-(*o*-allyloxyphenyl)-salicylamide gave the macrocyclic crown diamides shown in Fig. 1. Experimental results of the RCM reactions are summarized in Tables 4–6 [23].

RCM syntheses of **49**–**54** were investigated using different ratios of the catalyst (**I**) (2.5–10 mol%) and the best yields (40–60%) were obtained using 10 mol% of **I** in refluxing CH_2Cl_2 for 3 h (Table 4). On the other hand RCM of syntheses of **55**–**60** and **61**–**66** (Tables 5 and 6) proceeded well with 1–5 mol% of **I** in refluxing CH_2Cl_2 for 3 h to give excellent yield of the corresponding macrocyclic products. The larger amount of catalyst required in the RCM synthesis of **49**–**54** might be due to the proximity effect of the C=O group which would chelate with ruthenium carbene, the catalyst thus being sequestered in the form of unproductive complex [14].

From Table 6 it is clear that larger amount of the catalyst (**I**) was needed in comparable entries to accomplish the systems of macrocycles of similar ring sizes to those in Table 5. Exception occurred in one case where olefin metathesis occurred with only 1% catalyst (entry 6, Tables 5 and 6) in which the two isomeric pentabenzo-24-crowndiamides (**60**) and (**66**) were obtained in almost quantitative yields.



Scheme 2.

3.3. From bis(o-allyloxyacetanilides) and bis(o-allyloxyphenoxyacetanilides)

We have also, been able to obtain from readily available starting materials the bis(*o*-allyloxyacetanilides) and bis(*o*-allyloxyphenoxyacetanilides) which are the precursor dienes needed for the RCM synthesis of the macrocycles (**67**)–(**76**) shown in Figs. 2 and 3. The results of RCM synthesis of compounds (**67**)–(**76**) using Grubbs' catalyst (**I**) are shown in Tables 7 and 8 [24]. Thus, RCM synthesis of the macrocycles (**67**)–(**71**) proceeded smoothly to give 62–93% yields with Grubbs' catalyst (**I**) (2–2.5 mol%) in refluxing CH_2Cl_2 for 3 h. The results are presented in Table 7 [24].

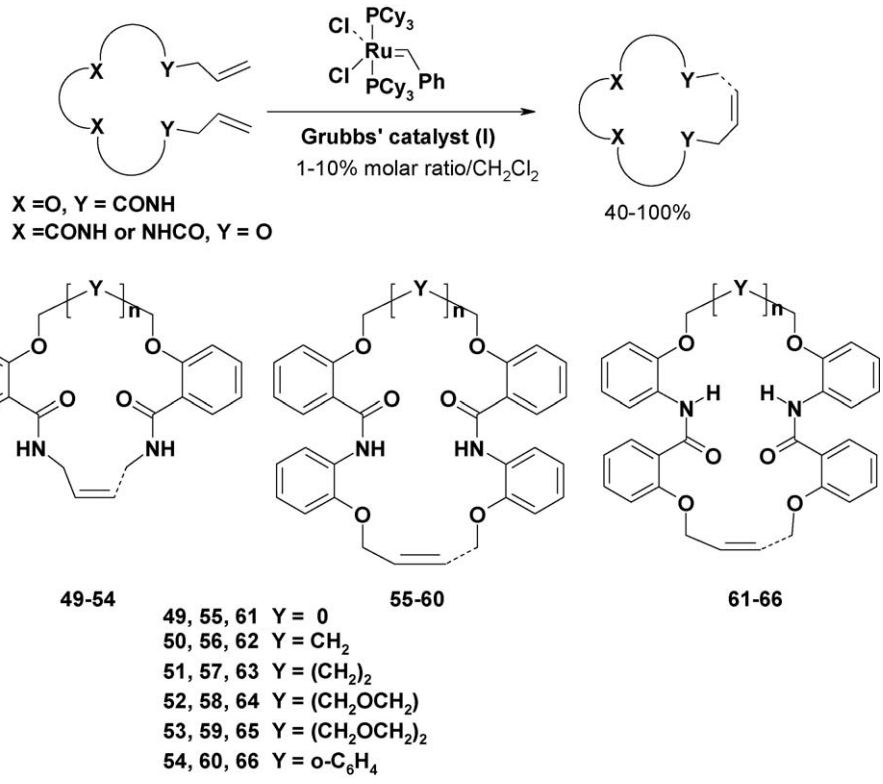
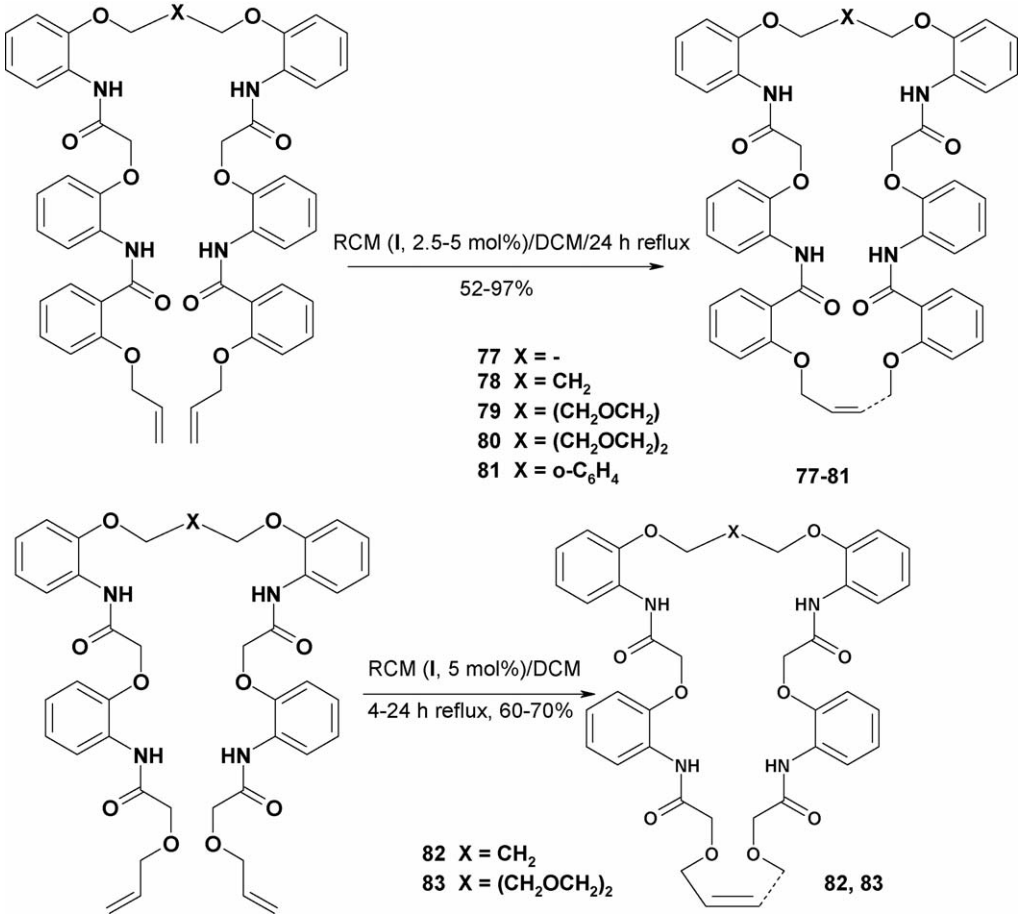
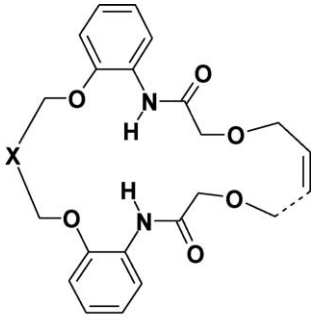


Fig. 1. Macrocyclic crown diamides **49–66** prepared by RCM from bis(*N*-allylsalicylamides), bis[*N*-(*o*-allyloxyphenyl)salicylamides] and [bis(*o*-allyloxybenzamides)].

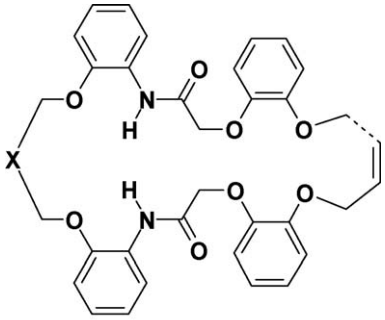


Scheme 3.



67 X = 0
68 X = CH_2
69 X = (CH_2OCH_2)
70 X = $(CH_2OCH_2)_2$
71 X = o-C_6H_4

Fig. 2. Macrocyclic crown diamides **67–71** prepared by RCM from bis(*o*-allyloxyacetanilides).

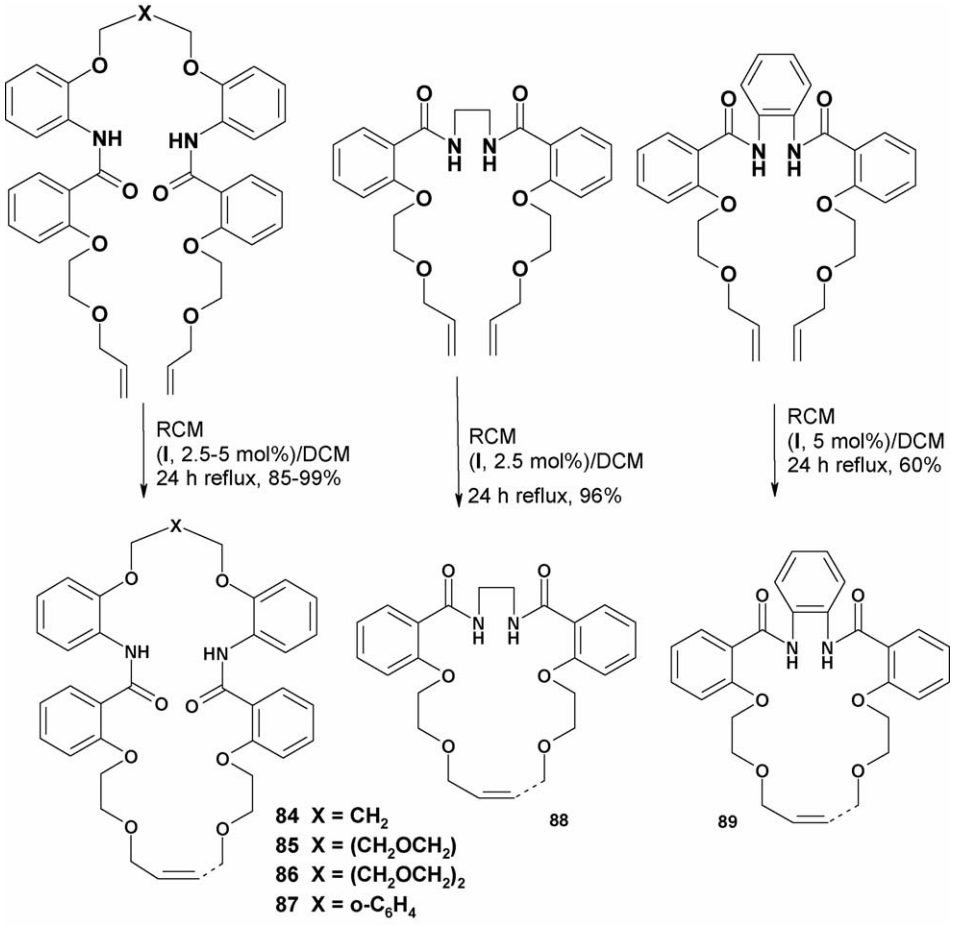


72 X = 0
73 X = CH_2
74 X = (CH_2OCH_2)
75 X = $(CH_2OCH_2)_2$
76 X = o-C_6H_4

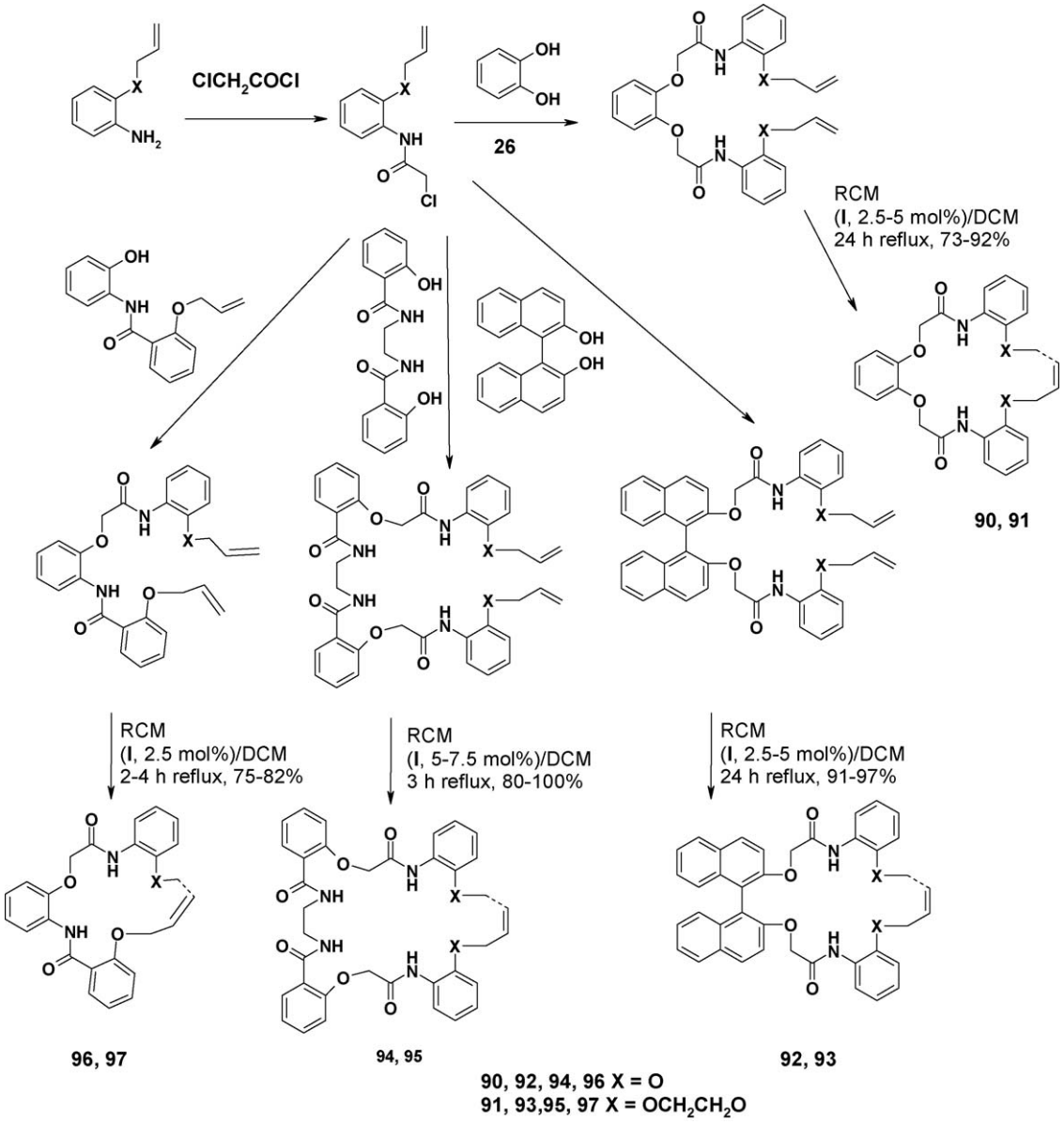
Fig. 3. Macrocyclic crown diamides **67–71** prepared by RCM from bis(*o*-allyloxyphenoxyacetanilides).

On the other hand, RCM of the appropriate α,ω-dienes proceeded smoothly to give the corresponding macrocycles (**72**)–(**76**) in 86–95% yields upon heating with Grubbs' catalyst (**I**) (1.5–2 mol%) in refluxing CH_2Cl_2 for 3 h. The results are presented in Table 8 [24].

RCM of the appropriate α,ω-dienes precursors (Scheme 3) proceeded smoothly to give the corresponding macrocycles (**77**)–(**81**) in 52–97% yields with Grubbs' catalyst (**I**) (2.5–5 mol%) in refluxing CH_2Cl_2 for 24 h. The results are presented in Table 8. Also, RCM synthesis of (**82**), (**83**) proceeded smoothly to give 70% and 60% yields respectively upon heating



Scheme 4.



Scheme 5.

with Grubbs' catalyst (**I**) (5 mol%) in refluxing CH_2Cl_2 for 24 h. The results are presented in Table 9 [25].

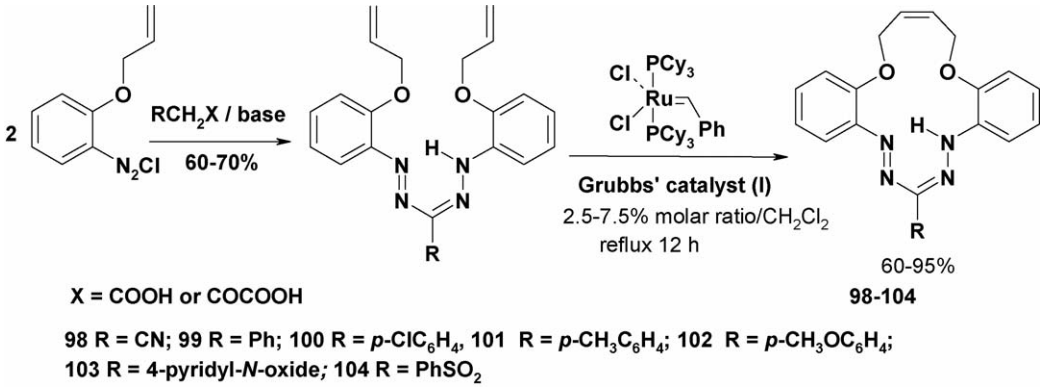
Scheme 4 outlines the RCM synthesis of macrocycles (**84**)–(**88**). RCM of the starting readily available α,ω-dienes afforded corresponding macrocycles in 60–99% yields upon heating with Grubbs' catalyst (**I**) (2.5–5 mol%) in refluxing CH_2Cl_2 for 4–24 h. The results are presented in Table 10 [25].

On the other hand, RCM of the starting readily available α,ω-dienes shown in Scheme 5 afforded the corresponding macrocycles (**90**)–(**97**) in 73–100% yields upon heating with Grubbs' catalyst (**I**) (2.5–7.5 mol%) in refluxing CH_2Cl_2 for 2–24 h. The results are presented in Table 11 [25].

4. Macrocyclic polyoxaformazans (crown-formazans)

We also, investigated the application of RCM technique with catalyst (**I**) as the key macrocyclization step in the synthesis of macrocyclic crown-formazans. Results obtained in this work (Table 12) provide efficient atom economic synthetic approaches towards macrocyclic crown-formazans incorporating an olefinic double bond inside the macrocyclic ring with potential applications in supramolecular chemistry [26].

Scheme 6 illustrates our synthetic route starting from the readily available *o*-allyloxybenzenediazonium chloride obtained from *o*-allyloxyaniline hydrochloride which is then coupled with the appropriate active methylene compound to give 60–70% yields of the corresponding 1,5-bis-*o*-allyloxyphenyl-3-substituted formazans. RCM of the latter dienes proceeded under mild conditions using 2–7.5 mol% of (**I**) in refluxing CH_2Cl_2 to give high yields of the corresponding crown-formazans (Table 12). In contrast to other synthetic procedures where the by-products are waste polymeric materials, the present RCM methodology yields only the desired crown-formazans in



Scheme 6.

addition to recyclable starting materials in almost quantitative molar ratios.

The major product in all the RCM synthesis of compounds (**98**)–(**104**) was shown to be the *Z* isomer with the characteristic ^{13}C signal of the OCH_2 (of the $OCH_2CH{=}CHCH_2O$) at ca. $\delta = 63$. On the other hand the ^{13}C signal of the OCH_2 of *E* isomers appears more upfield at around $\delta = 70$. The highly stereoselective *cis* double-bond formation was readily determined by the OCH_2 ^{13}C NMR chemical shift, which appears more downfield in the ^1H NMR and more upfield in the ^{13}C NMR than for the *trans* isomer. It is interesting to note that the presence of the formazan moiety inside the ring enhanced considerably the stereoselectivty of the newly formed double bond in favour of the *cis* geometry. This is in contrast to the RCM synthesis of crown ethers, azacrowns and crowndiamides where the *trans* geometry competes considerably and is even more favoured in many cases [10,20,21]. Moreover, the present investigation presents interesting examples of stereoselective *Z* macrocyclic olefin formation most probably controlled largely by the rigidity and planarity of the diarylformazan moiety that becomes, at the end, a part of the macrocyclic crown-formazan.

5. Conclusion

The present review describes our recent contribution to the utility of RCM technique as an efficient route to a large number of highly functionalized macrocyclic compounds. These products are of high interest in the fields of supramolecular chemistry, molecular recognition and organic synthesis. Macrocyclic compounds presented in this article constitute polyoxa-monoamides, diamides and tetraamides and dioxatetraaza-macrocycles with ring sizes extending from 8 to 40 membered rings and were mainly prepared in good to excellent yields using Grubbs' Ru catalyst (**I**). Moreover, examples of RCM presented here offer one of the best known, highly stereoselective, synthesis of crown-formazans containing *cis*-double bonds. It also, expands the utility of RCM methodology and its application to the synthesis of cyclic olefins of large ring sizes with the good tolerance of Grubbs' catalyst (**I**) to additional functional groups.

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