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Highly efficient Ru(II)–alkylidene based Hoveyda–Grubbs catalysts for ring-closing metathesis reactions†

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Three novel phosphine-free Ru-alkylidenes (**7a–7c**) have been synthesized and utilized as efficient catalysts for ring closing metathesis (RCM) reaction. Spectroscopic data, *i.e.* NMR and HRMS, along with single crystal X-ray diffraction analysis, were used to confirm their chemical structures. The tosylated carbenoid **7b** showed the highest efficiency in cyclizing different acyclic diene substrates. RCM of various (un) substituted *N*,*N*-diallylaniline derivatives and stereoselective RCM of different macromolecular dienes were well tolerated using only a catalytic amount (0.5–2.0 mol%) of the additive catalyst (**7b**) as compared to the well-known Grubbs (II) and Hoveyda–Grubbs (II) catalysts.

Introduction

Grubbs (**1a** & **1b**) and Hoveyda–Grubbs (**2a** & **2b**) ruthenium-based carbenoids (Fig. 1) have been established as efficient catalysts for carbon–carbon double bond formation with unparallel openings for synthetic chemists to explore their utility in the synthesis of medium to large ring systems *via* the remarkable olefin reaction, ring-closing metathesis (RCM).[1,2]

Chemical modifications of these organometallics upon varying the type and number of the legating sites around the Ru(II) center have many beneficial aspects that are crucial for developing more efficient catalysts with high activity and stability along with excellent tolerance behavior toward other functionalities.[3–10] For example, Ru-complex **3a** (ref. 3) (Table 1, entry 1), with a bulky phenyl substituent on the *ortho*-position, showed an increase initiation rate for different olefin reactions.[4] Also an enhanced reactivity has been attained in case of electron withdrawing groups containing catalysts, *i.e.* **3b** (ref. 5–7) and **3c** (ref. 8) (Table 1, entries 2 & 3), were subjected. The presence of a bulky *o*-phenyl or electron withdrawing groups, *e.g.* $-NO_2$ and $-SO_2NMe_2$, about the Ru(II) ion, has considerable effect in destabilizing the so-called oxygen–ruthenium interaction, leading to an increase in the catalytic activity toward C–C π-bonds, that enhanced formation of 14-electron Ru-carbene species.[9,10]

In an attempt to improve the initiation rate, as well as the stability of Hoveyda–Grubbs Ru(II)-catalysts, a number of oxygen chelated Ru(II)-alkylidenes bearing extra carbonyl groups such as ketonic **4a** (ref. 3), ester **4b–4d** (ref. 3, 6, 11 and 12) and amide **4e** (ref. 6) functionalities, have been made (Table 1, entries 4–8). Most of these complexes, which have been verified by X-ray single crystal, shows an extra coordination with the carbonyl oxygen which result in an additional protection of the metal site, and hence, exhibiting a higher activity and stability than those achieved earlier.[11–13]

In this work, we describe the synthesis with full structural characterization by NMR and HRMS spectral data along with single X-ray diffraction analysis of three novel phosphine-free Ru-alkylidene complexes (**7a–7c**) (Fig. 2). Complete data are included in the ESI section.† Also, the catalytic activity of the new catalysts toward ring-closing metathesis (RCM) reaction has been examined in which various (un)substituted *N*,*N*-diallylanilines and stereoselective RCM of different macromolecular dienes were well tolerated using only 0.5–2.0 mol% of the additive catalyst, *i.e.* **7b**, as compared to the well-known Ru-carbenoids, Grubbs (II) and Hoveyda–Grubbs (II) catalysts.

The target structures (**7a–7c**) were obtained from the reaction of freshly prepared vinylbenzene substrates (**6a–6c**) with Grubbs (II) catalyst **1b** as shown in Fig. 2. While Ru(II) ions in **7a** and **7b**

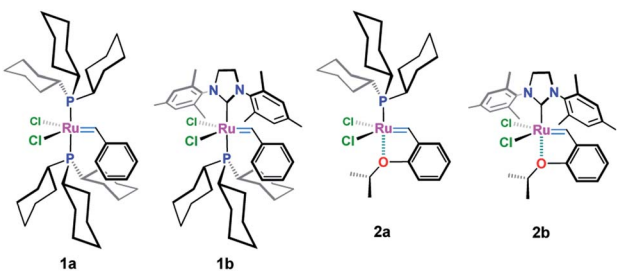

Fig. 1 Grubbs' (**1a** & **2a**) and Hoveyda–Grubbs' (**1b** & **2b**) catalysts.

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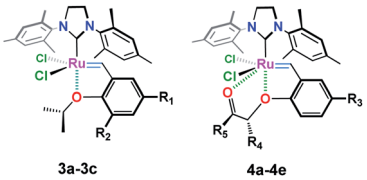
† Electronic supplementary information (ESI) available. CCDC 2105379, 1481883 and 2105381. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1ra07428h

Table 1 Examples of modified Hoveyda–Grubbs (II) catalysts



Entry	Cat.	R_1	R_2	R_3	R_4	R_5
1	**3a** (ref. 3)	H	Ph	—	—	—
2	**3b** (ref. 5–7)	NO_2	H	—	—	—
3	**3c** (ref. 8)	SO_2NMe_2	Ph	—	—	—
4	**4a** (ref. 3)	—	—	H	H	Me, Et
5	**4b** (ref. 3)	—	—	COMe	H, Me	OMe
6	**4c** (ref. 6)	—	—	H, NO_2	Me	OMe
7	**4d** (ref. 11 and 12)	—	—	H, Me, OMe, NO_2	Me	OEt
8	**4e** (ref. 6)	—	—	H	Me	NMe_2

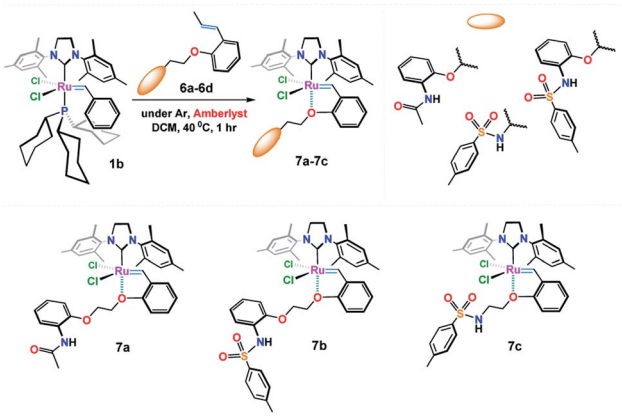
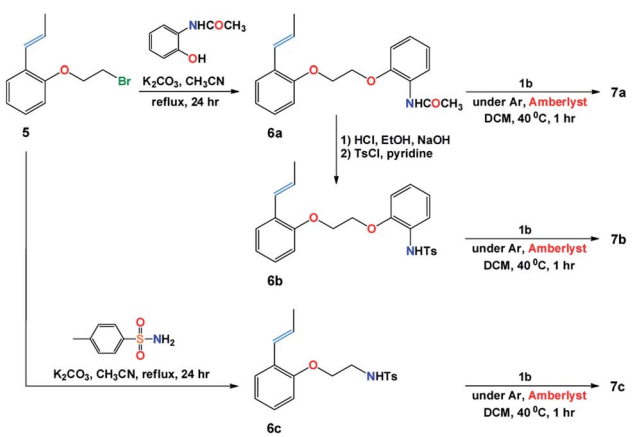


Fig. 2 The structure of the novel Ru-alkylidene catalysts **7a–7c**.

complexes are surrounded by 2-(*N*-acetamide) and 2-(*N*-4-methylbenzenesulfonamide) based phenoxy substituents, catalyst **7c** composes of 4-methylbenzenesulfonamide moiety around the Ru(II) central core.



Scheme 1 Synthesis of Ru(II)-alkylidene complexes **7a–7c**.

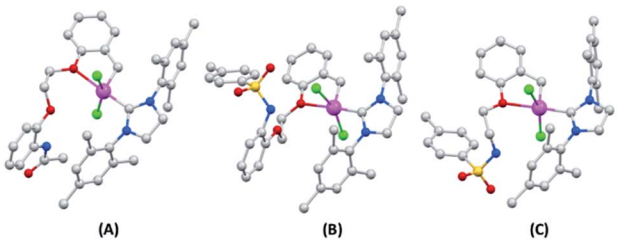


Fig. 3 Crystal structure of (A) **7a**; (B) **7b** and (C) **7c**; color code gray-carbon; red-oxygen; blue-nitrogen; green-chlorine; yellow-sulfur; pink-ruthenium. Hydrogen atoms are hided for clarity.

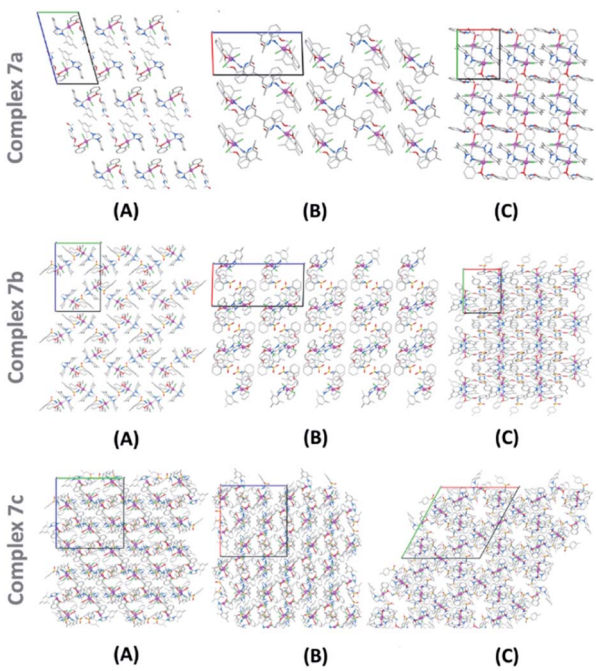


Fig. 4 Packing pattern of complexes **7a–7c** in their crystal network; view along the (A) *a*-direction; (B) *b*-direction and (C) *c*-direction; colour code: red-oxygen; blue-nitrogen; grey-carbon; and pink-zinc (hydrogens has been hided for clarity).

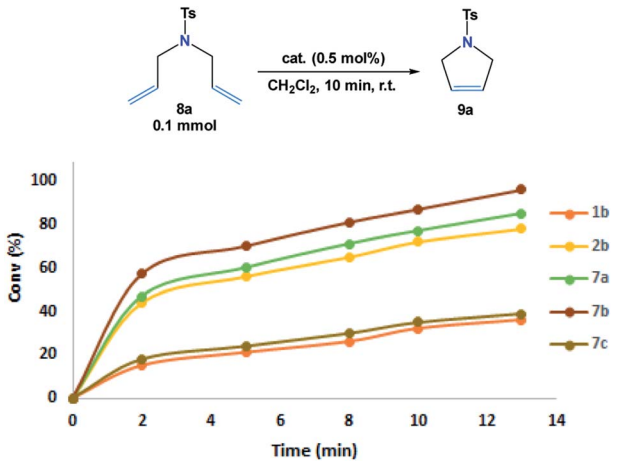


Fig. 5 Conversion (%) of cyclic alkene **8a** in 10 min at 25 °C with the additive catalysts (0.5 mol%). Determined by ^{1}H NMR.

Result and discussion

Synthesis of Ru-based catalysts 7a–7c

Scheme 1 illustrates the synthetic procedure for the synthesis of the Ru-alkylidenes **7a–7c** starting from the appropriate vinylbenzene derivatives **6a–c**. Compound **5** was prepared following the synthetic procedure described in literature.[14] Substitution reaction of compound **5** with 2-acetamidophenol and *p*-toluenesulfonamide in the presence of potassium carbonate in refluxing acetonitrile, resulted in the formation of vinylbenzenes **6a**, and **6c**, respectively, whereas vinyl derivative **6b** was prepared upon deprotecting the amino acetyl group of **6a** in acidic media, followed by treating the resulted compound with tosyl chloride in presence of pyridine. The complementary 1-propenyls **6a–6c** were then reacted with Grubbs (II) catalyst **1b** in the presence of dry Amberlyst-15 hydrogen form in refluxing dichloromethane to afford Ru(II)-complexes **7a–7c** in good yields (ESI†).

Single crystal X-ray diffraction study of the complexes 7a–7c

Single crystals of **7a–7c** structures were successfully grown by solvent diffusion method and their corresponding structural details were investigated by X-ray diffraction analysis (Fig. 3).[15] Strong non-bonding interactions among the adjacent atoms in these complexes making them pack efficiently to form stable crystal networks (Fig. 4). These novel structures consistent of a coordination number 5 around the Ru(II) center. The 5-coordination geometry is providing a distorted trigonal bipyramid shape to all complexes at the Ru(II) site. However, for both **7a** and **7b**, there is an oxygen atom available in the flexible spacer fragment of the structure which are positioned at a suitable distance (about 3.5 A) to engage a coordination bond with the Ru(II) metal ion through its lone pair of electrons. As a result, a distorted octahedral geometry could also be possible with hexa-coordinated Ru(II) ion for **7a** and **7b** (ESI†). Similarly, an additional coordination is possible through the nitrogen atom

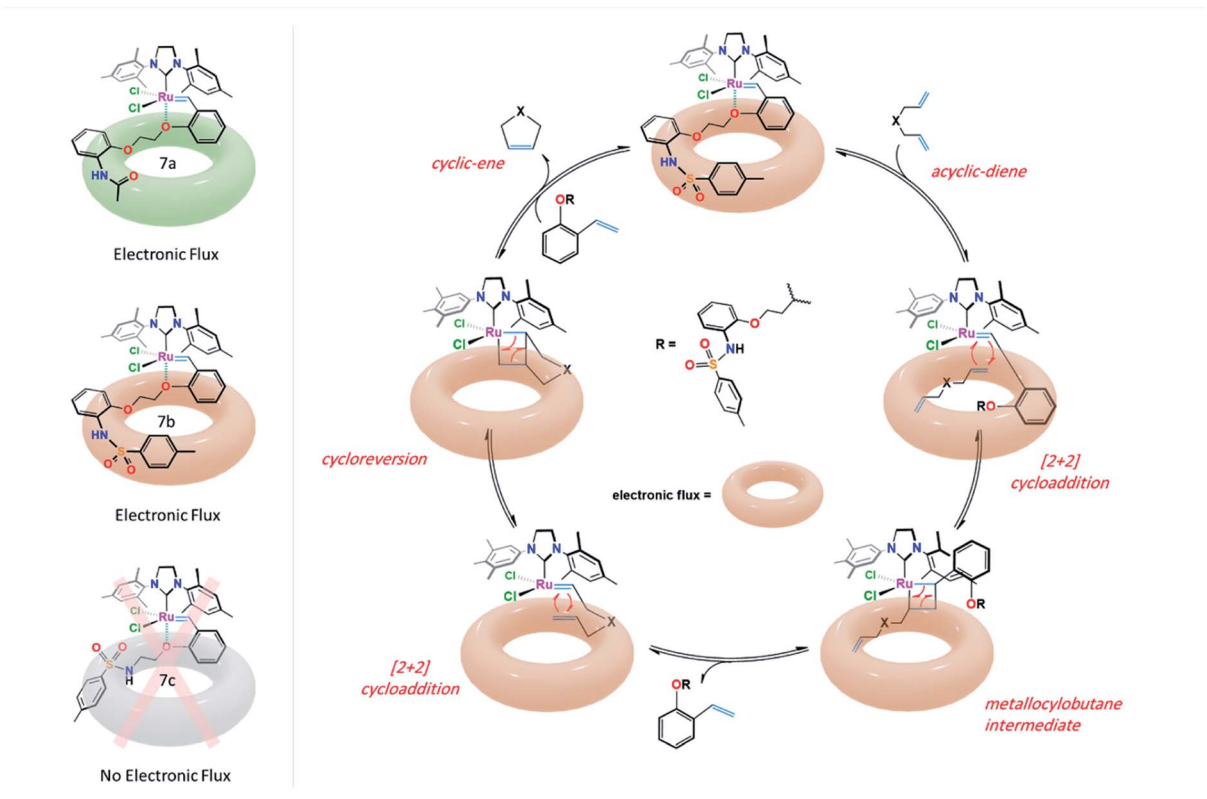


Fig. 6 Electronic flux in complexes **7a** & **7b** and proposed ring-closing metathesis (RCM) reaction mechanism catalyzed by catalyst **7b**.

in complex **7c**, though, the orientation of its N–H bond might inhibit the possibility of such a N–Ru coordination.

Optimizing ring-closing metathesis catalysed by Ru(II)-complexes (7a–7c), Grubbs (1b) and Hoveyda–Grubbs (2b) catalysts

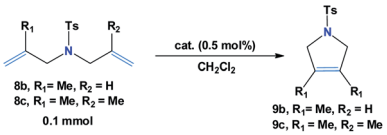
The ring-closing metathesis (RCM) was investigated to evaluate the catalytic activity of the novel complexes (**7a–7c**) as compared to both Grubbs **1b** and Hoveyda–Grubbs **2b** catalysts. For optimization, RCM reactions of *N*,*N*-diallyl-4-methylbenzenesulfonamide **8a** (ref. 9) (0.1 mmol) with the additive catalysts (0.5 mol%) were carried out only in 10 min in 1 mL dichloromethane at 25 °C (Fig. 5).

From the results shown in Fig. 5, it was observed that the RCM reactions of the studied diene **8a** were poorly progressed in the presence of **7c** and Grubbs **1b** catalysts (<40% conv.), whereas, the cyclization of **8a** was enhanced to 78% conv. when Hoveyda–Grubbs **2b** was subjected. Remarkably, in the reactions catalyzed by **7a** and **7b**, conversion yields of 84% and 96% were obtained. Such results can be possibly explained from the crystal structure demonstrated in Fig. 3. The crystal structures of **7a** and **7b** shows an open area in between the dichloro ruthenium fraction and two parallelly oriented flexible aromatic substituents. These aromatic substituents could provide a delocalized electronic flux in this open area to accommodate the approaching diene guest during the catalytic reaction (Fig. 6).

Moreover, **7b** complex, amongst the catalysts, was used for further investigations. The catalytic efficiency along with the initiation rate of **7b** as compared to Hoveyda–Grubbs **2b** toward the olefination reaction of diene **8b** was determined by ^{1}H NMR, by monitoring the allyloxy –OC**H**$_2$CH=CH$_2$– protons (**H**$_3$) before and after the pyrrole **9a** formation, at different reaction time, of 2, 4, 6, 8 and 10 min (Fig. 7). Both reactions were performed in a 600 MHz NMR instrument under the following reaction condition; diene **8a** (0.1 mmol) with the additive catalysts (0.5 mol%) in 1 mL CD_2Cl_2 at 25 °C. Notably, it was determined from the time profile introduced in Fig. 7A that the cyclization process of **8a** was effectively proceeded by **7b** catalyst in which ~80% conversion was obtained only in 2 min as compared to <80% conversion achieved in 10 min when Hoveyda–Grubbs **1b** was subjected (Fig. 7B).

Next, the capability of catalyst **7b** in catalyzing acyclic diene moieties was examined toward *N*-allyl-4-methyl-*N*-(2-methylallyl) **8b** and 4-methyl-*N*,*N*-bis(2-methylallyl) **8c** benzenesulfonamides and results are tubulated in Table 2. These

Table 2 Synthesis of 3-methyl and 3,4-dimethyl-1-tosyl-2,5-dihydro-1*H*-pyrrole derivatives **9b** and **9c**



Entry	Prod.	Solvent	Temp. (°C)	Time	Yield[c] (%)
1	**9b**	DCM	25	30 min	100[a]
2	**9c**	DCM	25	24 h	N/A[a]
3	**9c**	DCM	40	24 h	14[a]
4	**9c**	Toluene	80	24 h	70[b]

[a] Reaction condition: **8b**/**8c** (0.1 mmol), cat. **7b** (0.5 mol%), DCM or toluene (1 mL). [b] 1.0 mol% of the additive cat. [c] Determined by ^{1}H NMR.

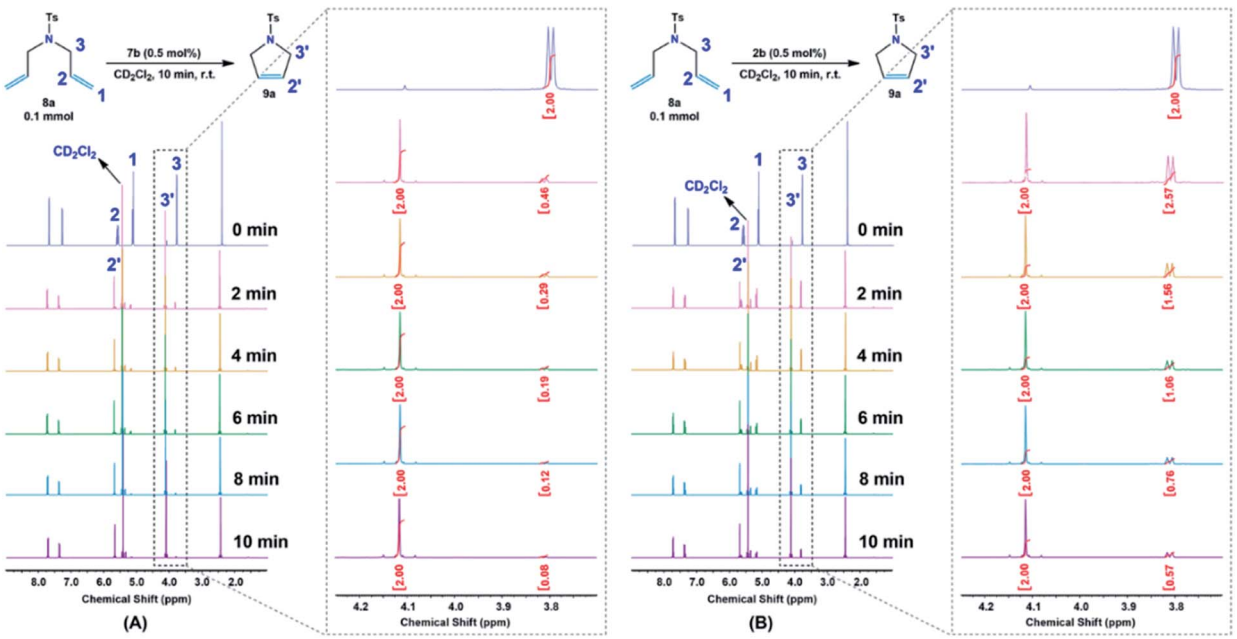


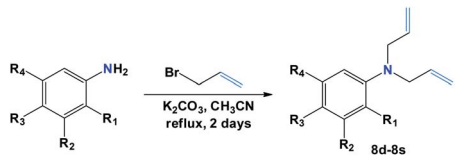
Fig. 7 Time profile of the RCM reaction of diene **8a** catalyzed by (A) **7b** and (B) **2b** as monitored by ^{1}H NMR at different reaction time.

results indicate that the reaction of diene **8b** in dichloromethane was well tolerated in the presence of catalyst **7b** (0.5 mol%) in which a stoichiometric quantity of **9b** was obtained in 30 min at 25 °C (Table 2, entry 1). However, no reaction took place in case of diene **8c** under similar reaction condition (Table 2, entry 2). Likewise, an insignificant improvement in pyrrole **9c** formation was observed when the RCM reaction was performed at a higher reaction temperature (40 °C, 14% yield), though, elevating the temperature to 80 °C by replacing dichloromethane with toluene as a solvent media, resulted in the desired pyrrole product **9c** in good yield (70%) within 24 h.

Synthesis of (un)substituted *N*,*N*-diallyl aniline derivatives (8d–8s)

To further scope the ability of **7b** in catalyzing RCM reactions, a series of (un)substituted *N*,*N*-diallylaniline derivatives (**8d–8s**) have been prepared. All allyl containing anilines were attained in good to high yields from the substitution reaction of (un) substituted aniline substrates (1.0 mmol) with allyl bromide (3.0 mmol and additional 1.0 mmol was added every 12 h) in the presence of potassium carbonate. All reactions were carried out in refluxing acetonitrile for 2 days and results are presented in Table 3. The structure of all novel dienes (**8f**, **8i–8m**, **8p–8r**) were confirmed from their respective NMR and HRMS spectral data (ESI†).

Table 3 Synthesis of (un)substituted *N*,*N*-diallylanilines (8d–8s)[a]



Entry	Product	R_1	R_2	R_3	R_4	Yield[b] (%)
1	**8d**	H	H	H	H	70
2	**8e**	OMe	H	H	H	50
3	**8f**	H	OMe	H	H	64
4	**8g**	H	H	OMe	H	44
5	**8h**	H	H	Me	H	86
6	**8i**	Me	Me	H	H	50
7	**8j**	H	Me	H	Me	65
8	**8k**	F	H	H	H	45
9	**8l**	H	Br	H	H	55
10	**8m**	Cl	H	H	H	63
11	**8n**	H	H	Cl	H	40
12	**8o**	F	H	F	H	63
13	**8p**	H	F	F	H	40
14	**8q**	F	H	Cl	H	46
15	**8r**	Me	Cl	H	H	54
16	**8s**	H	H	NO_2	H	40

[a] Reaction condition: aniline substrates (1.0 mmol), allyl bromide (3.0 mmol), potassium carbonate (4.0 mmol), acetonitrile (20 mL), reflux, 2 days, an additional allyl bromide (1.0 mmol) was added to the reaction mixture every 12 h. [b] Isolated yield by chromatography.

Scoping the RCM reaction of (un)substituted *N*,*N*-diallylanilines (8d–8s) using catalyst 7b

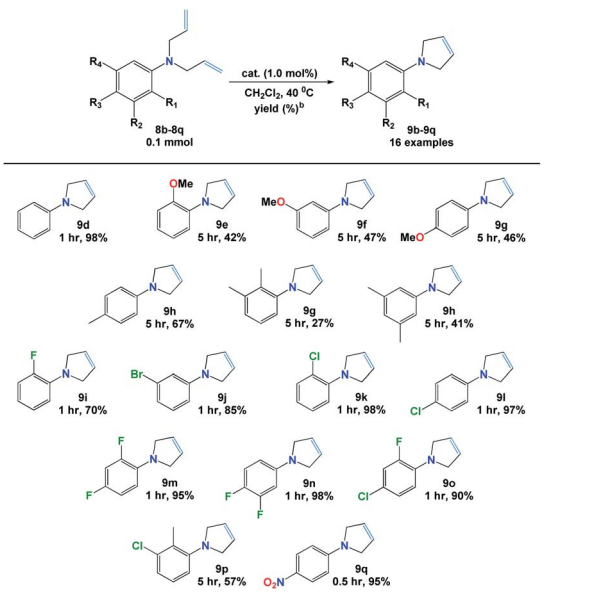
Next, we explored the RCM reaction of the obtained dienes (**8d–8s**) catalyzed by complex **7b**. It was found that the reactions were not competent using 0.5 mol% of additive catalyst in dichloromethane at 25 °C. However, better results were efficiently obtained by increasing the catalytic amount of **7b** to 1.0 mol% in refluxing dichloromethane and results are presented in Table 4. The structures of all new dienes (**8i**, **8k**, **8o** & **8q**) were confirmed using NMR and HRMS spectroscopic techniques (ESI†).

From the results, it was observed that the reaction of diene **8d** was efficiently proceeded in only 1 h to give pyrrole **9d** in excellent yield (98%). However, lower yields (27–67%) along with longer reactions time, *i.e.* 5 h, were attained when electron-donor groups containing dienes (**8e–8h**) were used. Further, the cyclization process occurred with ease (>90% yields) in 1 h when halogenated dienes (**8j–8o**) were applied with an exception of 2-fluoro *N*,*N*-diallylaniline (**8i**) which was gained in 70% yield. Similarly, the strongly electron withdrawing group ($-NO_2$) presented in **8q** was found to be the most reactive diene toward RCM in which 95% of pyrrole **9q** was achieved only in 30 min. Still, the presence of both electron donor (–Me) and electron with drawing (–Cl) groups, on **8p** core, resulted in **9p** in 57% in 5 h. All novel pyrroles (**9f**, **9i**, **9j**, **9l**, **9m**, **9o**, **9q** & **9r**) were fully utilized from their respective NMR and HRMS spectral data (ESI†).

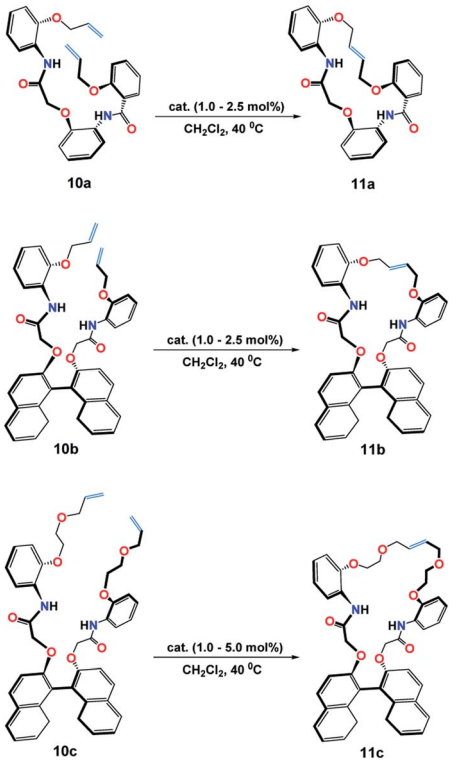
Synthesis of unsaturated macrocyclic structures *via* RCM reaction using catalyst 7b

RCM reaction has been applied as a key step synthetic process for macrocyclization reactions.[16] Hence, from our published

Table 4 Scoping the RCM reaction using catalyst 7b [a]



[a] Reaction condition: *N*,*N*-diallylanilines (0.1 mmol), cat. **7b** (1.0 mol%), DCM (1 mL), 40 °C. [b] Isolated yield by chromatography.



Scheme 2 RCM of dienes **10a–10c** catalysed by complex **7b** and Grubbs (I) **1a** in the synthesis of macrocycles **11a–11c**.

data based on the construction of macrocycles **11a–11c** catalyzed by Grubbs (I) **1a**, complex **7b** has been used for comparison (Scheme 2).[17]

Following the typical procedure reported: macrocyclic dienes (0.2 mmol), DCM (25 mL), 40 °C in 24 h (Table 5), it was found that the macrocyclization of diene **10a** catalyzed by complex **7b** (1.0 mol%) in the formation of crown **11a** was achieved in 98% yield as compared to 92% yield when Grubbs **1a** (2.5 mol%) was used (Table 5, entries 1 & 2), whereas, 1.0 mol% of catalyst **7b** was capable to catalyze the RCM reaction of dienes **10b** and **10c** to yield macrocycles **11b** and **11c** in 98%.and 70%, respectively (Table 5, entries 3–6).

Interestingly, a control of the stereoselectivity, that Grubbs (I) lacks, was feasibly obtained when catalyst **7b** was applied in which both **10a** and **10b** products were attained in their *E*-configurations, while macrocyclic crown **10c** was afforded, mainly, in its *E*-configuration, *i.e.* *E* (92%) : *Z* (8%). These results were determined upon comparing the ^{1}H NMR spectra (400 MHz, $CDCl_3$, at 25 °C) of the macrocyclic crowns (**11a–11c**) and their corresponding macrodienes (**10a–10c**) before and after the RCM reactions (Fig. 8).

The disappearance of the terminal allyloxy protons (–$OCH_2CH{=}CH_2$, H_1 in **10a–10c** & H_1/H_7 in **10a**), *i.e.* the disappearance of: [H_1 in **10a**, Fig. 8A; two sets of doublet of a doublet at 4.94–4.97 ppm (dd, J = 1.3, 10.5 Hz, 1H) and at 5.27–529 ppm (dd, J = 1.3, 10.5 Hz, 1H), H_7 in **10a**, Fig. 8A; two sets of doublet of a doublet at 5.03–5.07 ppm (dd, J = 1.5, 17.3 Hz, 1H) and at 5.36–5.40 ppm (dd, J = 1.3, 17.3 Hz, 1H); H_1 in **10b**, Fig. 8C; two sets of doublet of a doublet at 4.96–4.98 ppm (dd, J = 1.3, 10.5 Hz, 2H) and at 5.08–5.13 ppm (dd, J = 1.3, 17.3 Hz, 2H); H_1 in **10c**, Fig. 8E; two sets of doublet of a doublet

Table 5 Catalyst (mol%), yields and *E*/*Z* ratios of macrocycles **11a–c** [a]

Entry	Product	Cat./(mol%)	Yield[b] (%)	Product *E* : *Z* ratio[b]
1	**11a**	**1a**, 2.5 mol%	92	78 : 22
2	**11a**	**7b**, 1.0 mol%	98	100 : 0
3	**11b**	**1a**, 2.5 mol%	91	75 : 25
4	**11b**	**7b**, 1.0 mol%	98	100 : 0
5	**11c**	**1a**, 5.0 mol%	97	75 : 25
6	**11c**	**7b**, 1.0 mol%	70	92 : 8

[a] Reaction condition: acyclic macrodienes (0.2 mmol), DCM (25 mL), 40 °C. [b] Determined by ^{1}H NMR.

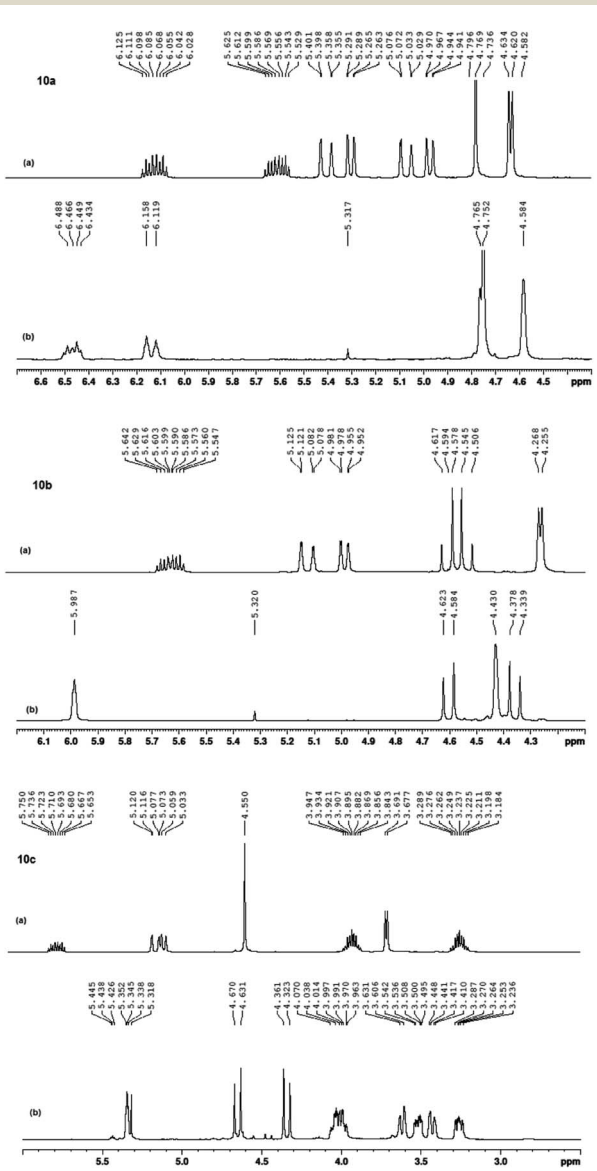


Fig. 8 ^{1}H NMR (400 MHz, 600 MHz, $CDCl_3$) spectra of **10a**, **10b** and **10c** (a) before RCM and (b) after RCM.

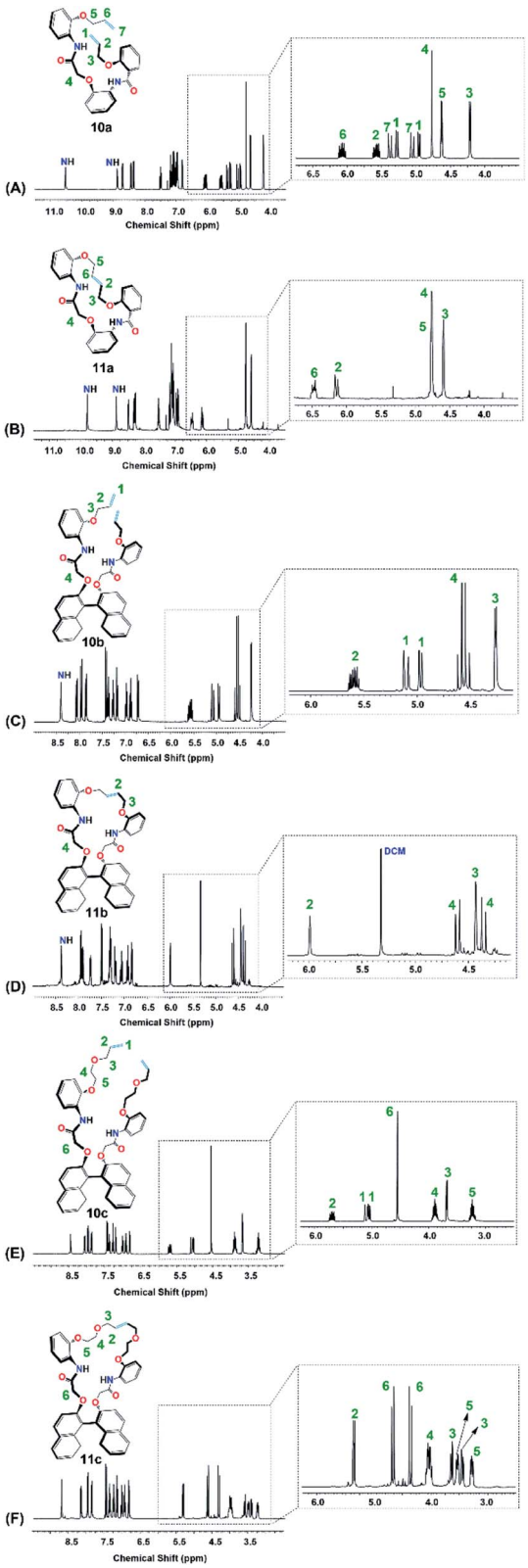


Fig. 9 Full ^{1}H NMR of (A) **10a**; (B) **11a**; (C) **10b**; (D) **11b**; (E) **10c** and (F) **11c**.

at 5.03–5.06 ppm (dd, $J = 0.8$, 10.5 Hz, 2H) and at 5.08–5.12 ppm (dd, $J = 1.5$, 17.3 Hz, 2H)] and the shift of the internal allyl protons (–OCH$_2$C**H**=C**H**CH$_2$O–, $\mathbf{H_2}$ in **11a–11c** & $\mathbf{H_6}$ in **11c**), *i.e.* [$\mathbf{H_2}$ in **11a**, Fig. 8B; two sets of triplets at 6.12 ppm (t, $J = 4.5$ Hz, 1H) and at 6.16 ppm (t, $J = 4.5$ Hz, 1H), $\mathbf{H_6}$ in **11a**, Fig. 8B; two sets of triplets at 6.45 ppm (t, $J = 6.5$ Hz, 1H) and at 6.49 ppm (t, $J = 4.5$ Hz, 1H), $\mathbf{H_2}$ in **11b**, Fig. 8D; a triplet at 5.99 ppm (t, $J = 3.0$ Hz, 2H), $\mathbf{H_2}$ in **11c**, Fig. 8F; a triplet at 5.35 ppm for the *E*-configuration (t, $J = 3.0$ Hz, 2H, 92%) and a triplet at 5.44 ppm for the *Z*-configuration (t, $J = 3.0$ Hz, 2H, 8%)] were used to confirm the formation of the products (Fig. 9).

Conclusion

In conclusion, three catalytic systems (**7a–7c**) based on Hoveyda–Grubbs complex have been successfully prepared and characterized from their respective NMR and HRMS spectral data and X-ray single structure. The synthesized Ru(II) complexes have been established as efficient catalysts for ring-closing metathesis (RCM). Complex **7b**, among the other catalytic structures prepared, was found to have the highest efficiency in catalyzing different (un)substituted *N*,*N*-diallylanilines for 1*H*-pyrroles formation. Also, a control of the stereoselectivity, *i.e.* *E*-configuration, of macrocyclic crowns have been obtained using complex **7b**.

Experimental

General

All reactions were carried out under nitrogen atmosphere unless otherwise noted, all analyses determined in Research Sector Projects Unit (RSPU) at Kuwait, TLC was performed using Polygram sil G/UV 254 TLC plates and visualization was carried out by ultraviolet lights at 254 nm and 350 nm. Column chromatography was performed using Merck silica gel 60 of mesh size 0.040–0.063 mm. ^{1}H and ^{13}C NMR spectra were recorded using Bruker NEO 400 MHz, Bruker Avance II 600 MHz superconducting NMR spectrometers. Mass spectra were recorded with a GCMS-DFS-Thermo, High Resolution spectrometer and Bruker, ultraflextreme mass spectrometer MALDI-ToF MS with Smartbeam-II laser. The single crystal X-ray analysis was carried out on Rigaku Rapid II and Bruker X8 prospector diffractometers respectively. Melting points were determined *via* differential scanning calorimetry (DSC) analyses on Shimadzu DSC-50.

1-(2-Bromoethoxy)-2-propenylbenzene (5)

A catalytic amount of palladium chloride (0.02 g, 0.2 mol%) was added to 50 mL DCM and 30 drops of acetonitrile. The mixture was stirred for 5 min at room temperature followed by the addition of 1-allyl-2-(2-bromoethoxy)-benzene (14 g, 58 mmol) allowing the reaction mixture to stir for 40 h at room temperature. The mixture was washed with water, extracted with DCM and passed through a short column using hexane as an eluent to give compound **5** as colorless oil in 12.6 g (90% yield); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.90$ (d, $J = 6.5$ Hz, 3H), 3.68 (t, $J = 6.3$ Hz, 2H), 4.30 (t, $J = 6.3$ Hz, 2H), 6.21–6.30 (m, 1H), 6.74 (d, $J = 16.0$ Hz, 1H), 6.82 (d, $J = 8.2$ Hz, 1H), 6.94 (t, $J = 7.4$ Hz, 1H), 7.16 (t, $J = 7.6$ Hz, 1H), 7.41 (d, $J = 7.6$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 19.2, 29.5, 68.6, 112.8, 121.7, 125.6, 126.8,

127.1, 127.9, 127.91, 154.9; *m*/*z* (EI) 240 (M^+, 75%), 242 (M^{+2}, 74%); *m*/*z* (EI) 240.0145 (M^+, $C_{11}H_{13}{}^{79}BrO$ requires 240.0144).[14]

N-{2-[2-(2-Propenyl-phenoxy)-ethoxy]-phenyl}-acetamide (6a)

A mixture of compound **5** (6.0 g, 2.5 mmol), *o*-acetamidophenol (4.9 g, 3.2 mmol) and anhydrous potassium carbonate (4.3 g, 3.1 mmol) in dry acetonitrile (50 mL) was heated under reflux overnight. The residue was filtered off and the solvent was evaporated. The remaining crude product was recrystallized from ethanol to give compound **6a** as colorless crystals in 6.6 g (85% yield); mp 143–144 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 1.79 (dd, J = 6.6 Hz, 3H), 2.03 (s, 3H), 4.38–4.43 (m, 4H), 6.21–6.31 (m, 1H), 6.62 (dd, J = 1.2, 14.5 Hz, 1H), 6.90–6.95 (m, 2H), 7.04–7.07 (m, 2H), 7.15–7.22 (m, 2H), 7.43 (d, J = 7.6 Hz, 1H), 7.97 (d, J = 7.6 Hz, 1H), 8.90 (bs, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 18.7, 23.9, 66.9, 67.7, 112.7, 113.2, 120.8, 120.9, 121.9, 124.1, 125.3, 125.9, 126.1, 126.3, 127.95, 128.0, 148.6, 155.0, 168.3; *m*/*z* (EI) 311 (M^+); *m*/*z* (EI) 311.1515 (M^+, $C_{19}H_{21}NO_3$ requires 311.1516).

4-Methyl-*N*-{2-[2-(2-propenyl-phenoxy)-ethoxy]-phenyl}-benzenesulfonamide (6b)

A mixture of compound **6a** (4 g, 1.3 mmol), and conc. HCl (4 mL) in ethanol (40 mL) was heated under reflux for 2 h. Ethanol was evaporated, ether was added to this mixture and the precipitated solid material was collected and crystallized from ethanol. The obtained phenylamine salt was stirred in NaOH solution for 10 min which was then extracted with DCM and dried over anhydrous sodium sulfate and evaporated. The obtained colorless solid, *i.e.* 2-[2-(2-propenylphenoxy)-ethoxy]-phenylamine (0.28 g, 1 mmol), was dissolved in dry pyridine (1.8 mL) followed by the addition of *p*-toluenesulfonyl chloride (0.25 g, 1.2 mmol). The mixture was stirred at 0 °C for 1 h and then kept overnight in the fridge. The precipitate obtained after addition of cold water was collected and recrystallized from ethanol to give compound **6b** as colorless crystals in 0.31 g (70% yield); mp 136–137 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.89 (dd, J = 6.8, 1.6 Hz, 3H), 2.29 (s, 3H), 4.20 (d, J = 3.4 Hz, 4H), 6.21–6.30 (m, 1H), 6.67 (d, J = 16.0 Hz, 1H), 6.86 (dd, J = 8.0, 2.4 Hz, 2H), 6.94 (t, J = 7.6 Hz, 1H), 7.00 (t, J = 7.6 Hz, 1H), 7.05–7.11 (m, 4H), 7.23 (t, J = 7.2 Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.59 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 19.1, 21.6, 66.9, 67.5, 112.1, 112.6, 121.8, 121.9, 125.49, 125.50, 126.6, 126.9, 127.1, 127.4, 127.8, 128.0, 129.5, 136.5, 143.7, 148.8, 155.2; *m*/*z* (EI) 423 (M^+); *m*/*z* (EI) 423.1499 (M^+, $C_{24}H_{25}NO_4S$ requires 423.1499).

p-Methyl-*N*-[2-(2-propenyl-phenoxy)-ethyl]-benzenesulphonamide (6c)

A mixture of compound **5** (2.4 g, 1.0 mmol), *p*-toluenesulphonamide (5.1 g, 3.0 mmol), and anhydrous potassium carbonate (2.0 g, 1.5 mmol) in dry acetonitrile (75 mL) was heated under reflux overnight. The residue was filtered off and the solvent was evaporated *in vacuo*. The remaining product was purified by column chromatography using eluent pet. ether/EtOAc in the ratio of 2 : 1 to give compound **6c** as colorless crystals in 0.83 g (25% yield); mp 102–103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.92 (dd, J = 5.4, 1.2 Hz, 3H), 2.43 (s, 3H), 3.40 (m, 2H), 4.00 (t, J = 5.1 Hz, 2H), 4.94 (bs, 1H), 6.19–6.22 (m, 1H), 6.59 (dd, J = 15.6, 1.8 Hz, 1H), 6.70 (d, J = 8.4 Hz, 1H), 6.94 (t, J = 7.8 Hz, 1H), 7.13 (dt, J = 1.2, 7.2 Hz, 1H), 7.30 (d, J = 8.4 Hz, 1H), 7.39 (dd, J = 7.8, 1.2 Hz, 1H), 7.77 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 19.2, 21.7, 42.9, 67.0, 112.5, 121.8, 125.4, 126.8, 127.18, 127.24, 127.5, 128.0, 130.0, 137.0, 143.8, 154.8; *m*/*z* (EI) 331 (M^+); *m*/*z* (EI) 331.1238 (M^+, $C_{18}H_{21}NO_3S$ requires 331.1237).

General procedure for the synthesis of the novel Ru(II)-catalysts (7a–c)

To a flame-dried Schlenk flask equipped with a Teflon-coated magnetic stir bar under argon, was charged with each of compounds **6a–c** (0.03 mmol), dry Amberlyst-15 hydrogen form (0.025 g), **1b** (0.035 mmol) in 2 mL DCM. The resulting mixture was stirred at 40 °C for 3–4 h till the reaction color changes from maroon to brown or green. The reaction vessel was cooled to room temperature, and the reaction mixture was filtered through a pad of cotton in a glass pipette to remove the Amberlyst-15 resin. The filtrate was then concentrated *in vacuo* and the crude product was precipitated by dilution with cold petroleum ether (40–60 mL) which then dried under high vacuum to obtain the desired product.

Ru(II) complex 7a

Green solid in 0.021 g, (90% yield); mp 105–106 °C; ^{1}H NMR (600 MHz, CD_2Cl_2) δ = 1.90 (s, 3H), 2.22 (s, 6H), 2.31 (s, 12H), 4.04 (s, 4H), 4.13 (t, J = 4.2 Hz, 2H), 4.35 (t, J = 4.2 Hz, 2H), 6.73 (dd, J = 8.4, 1.2 Hz, 1H), 6.83–6.85 (m, 5H), 6.91–6.96 (m, 3H), 7.00 (dt, J = 7.8, 1.8 Hz, 1H), 7.51 (dt, J = 8.4, 2.4 Hz, 1H), 8.23 (dd, J = 8.4, 1.8 Hz, 1H), 8.31 (s, 1H), 16.60 (s, 1H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ = 19.0, 20.8, 24.4, 51.8, 65.7, 68.5, 112.3, 112.8, 120.6, 121.4, 122.1, 123.3, 123.8, 129.2, 129.4, 129.8, 138.6, 138.9, 144.6, 147.0, 153.1, 168.8, 209.2, 294.2; *m*/*z* (EI) 761 (M^+, 0.2%), 763 (M^{+2}, 0.17%); *m*/*z* (EI) 761.1719 (M^+, $C_{38}H_{43}{}^{35}Cl_2N_3O_3{}^{102}Ru$ requires 761.1719).

Ru(II) complex 7b

Green crystals in 0.019 g (96% yield); mp 206–207 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 2.30 (s, 6H), 2.39 (s, 3H), 2.42 (s, 12H), 3.97 (t, J = 4.4 Hz, 2H), 4.05 (t, J = 4.4 Hz, 2H), 4.16 (s, 4H), 6.67 (d, J = 8.0 Hz, 1H), 6.86 (d, J = 8.4 Hz, 2H), 6.92 (s, 2H), 7.05–7.10 (m, 6H), 7.19 (t, J = 6.8 Hz, 1H), 7.51 (d, J = 7.6 Hz, 2H), 7.59 (d, J = 8.0 Hz, 1H), 7.70 (t, J = 8.4 Hz, 1H), 7.90 (s, 1H), 16.69 (s, 1H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ = 19.6, 21.4, 21.8, 52.3, 65.0, 68.5, 112.2, 112.9, 121.8, 122.9, 124.5, 124.7, 126.4, 126.9, 127.8, 129.6, 130.0, 130.3, 137.9, 139.2, 139.4, 143.7, 145.0, 150.0, 153.5, 209.5, 294.9; *m*/*z* (MALDI-MS) 874.958 (M + 1, $C_{43}H_{47}{}^{35}Cl_2N_3O_4{}^{102}RuS$ requires 873.1702).

Ru(II) complex 7c

Green crystals in 0.022 g (95% yield); mp 214–215 °C; ^{1}H NMR (600 MHz, CD_2Cl_2) δ = 2.40 (s, 6H), 2.43 (s, 15H), 3.09 (m, 2H), 3.95 (t, J = 4.5 Hz, 2H), 4.21 (s, 4H), 6.42 (d, J = 8.4 Hz, 1H), 6.44 (t, J = 6.0 Hz, 1H), 6.99 (m, 2H), 7.05 (s, 4H), 7.25 (d, J = 8.4 Hz,

2H), 7.84 (m, 1H), 7.69 (d, J = 8.4 Hz, 2H), 16.55 (s, 1H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ = 19.6, 21.4, 21.8, 41.2, 52.2, 69.1, 113.1, 112.6, 124.3, 127.1, 130.0, 130.26, 130.3, 139.4, 139.8, 140.1, 143.6, 145.2, 153.4, 209.6, 296.1; m/z (FAB-MS) 781 (M^+, $C_{37}H_{43}{}^{35}Cl_2N_3O_3{}^{102}RuS$ requires 781.1440).

General procedure for the synthesis of *N,N*-diallylanilines (8d–8s)

A mixture of (un)substituted anilines (10.0 mmol), allyl bromide (30.0 mmol) and anhydrous K_2CO_3 (40.0 mmol) in acetonitrile (20 mL) was heated under reflux for 48 h. An additional allyl bromide (10.0 mmol) was added to the reaction mixture every 12 h. The solvent was removed *in vacuo* and the remaining material was purified by chromatography on silica gel using pet. ether/EtOAc (4 : 1) as eluent to give the desired products as colorless oil. The spectroscopic data for compounds **8d–h**, **8j**, **8l–n**, **8p**, **8r** and **8s** are coherent with those reported in literature.[18–24]

N,N-Diallyl-2,3-dimethylaniline (8i)

Colorless oil in 0.9 g (44% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.30 (s, 3H), 2.31 (s, 3H), 3.59 (d, J = 5.6 Hz, 4H), 5.13 (d, J = 10.0 Hz, 2H), 5.20 (d, J = 17.2 Hz, 2H), 5.79–5.89 (m, 2H), 6.92–6.95 (m, 2H), 7.07 (t, J = 7.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 14.3, 20.9, 56.3, 117.1, 120.0, 125.2, 132.9, 135.7, 138.0, 150.1; m/z (EI) 201 (M^+); m/z (EI) 201.1515 (M^+, $C_{14}H_{19}N$ requires 201.1512).

N,N-Diallyl-2-fluoroaniline (8k)

Colorless oil in 0.95 g (50% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 3.84 (d, J = 3.8 Hz, 4H), 5.19 (d, J = 6.8 Hz, 2H), 5.23 (d, J = 11.4 Hz, 2H), 5.86–5.93 (m, 2H), 6.88 (s, 1H), 6.97 (s, 1H), 6.97–7.05 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 54.3, 116.2–116.3, 117.1, 120.6, 121.1–121.0, 124.0, 134.7, 138.4, 154.5–156.1; m/z (EI) 191 (M^+); m/z (EI) 191.1102 (M^+, $C_{12}H_{14}NF$ requires 191.1105).

N,N-Diallyl-2,4-difluoroaniline (8o)

Colorless oil in 0.84 g (40% yield) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.76 (d, J = 5.6 Hz, 4H), 5.17–5.24 (m, 4H), 5.81–5.91 (m, 2H), 6.75–6.85 (m, 2H), 6.90–6.96 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 55.0, 104.4–104.9, 110.3–110.6, 117.6, 122.2–122.3, 134.7, 134.9–135.0, 154.6–156.4, 157.1–158.8; m/z (EI) 209 (M^+); m/z (EI) 209.1011 (M^+, $C_{12}H_{13}F_2N$ requires 209.1011).

N,N-Diallyl-4-chloro-2-fluoroaniline (8q)

Colorless oil in 1.41 g (63% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.79 (d, J = 5.9 Hz, 4H), 5.17–5.23 (m, 4H), 5.80–5.89 (m, 2H), 6.89 (s, 1H), 6.99–7.06 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 54.6, 117.0, 117.2, 117.7, 121.4, 124.3, 134.5, 154.2, 155.8; m/z (EI) 225 (M^+); m/z (EI) 225.0718 (M^+, $C_{12}H_{13}FClN$ requires 225.0715).

General procedure for the ring-closing metathesis in the synthesis of 1-phenyl-2,5-dihydro-1*H*-pyrrole derivatives (9d–9s)

Into a solution of each of the dienes **8d–s** (0.1 mmol) in CH_2Cl_2 (1 mL), catalyst **7b** (1 mg, 1.0 mol%) was added and the reaction mixture heated at 40 °C and completion of reaction was monitored by TLC. The solvent was removed *in vacuo* and the remaining material was purified by chromatography on silica gel using pet. ether/EtOAc (4 : 1) as eluent to give the desired products. The spectroscopic data for compounds **9d**, **9e**, **9g**, **9h**, **9k**, **9n**, **9p** and **9s** are coherent with those reported in literature.[25,26]

1-(3-Methoxyphenyl)-2,5-dihydro-1*H*-pyrrole (9f)

Colorless oil in 0.008 g (47% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.84 (s, 3H), 4.17 (s, 4H), 5.96 (s, 2H), 6.24 (s, 1H), 6.30 (d, J = 8.4 Hz, 1H), 6.37 (dd, J = 8.4, 2.0 Hz, 1H), 7.21 (t, J = 8.0H, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 55.7, 63.2, 107.0, 113.1, 119.6, 130.5, 142.2, 160.7; m/z (EI) 175 (M^+); m/z (EI) 175.0993 (M^+, $C_{11}H_{13}NO$ requires 175.0992).

1-(2,3-Dimethylphenyl)-2,5-dihydro-1*H*-pyrrole (9i)

Colorless oil in 0.0046 g (27% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.31 (s, 3H), 2.35 (s, 3H), 4.13 (s, 4H), 5.96 (s, 2H), 6.89 (d, J = 7.2 Hz, 1H), 7.02 (d, J = 8.0 Hz, 1H), 7.11 (t, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 15.9, 21.0, 58.3, 116.2, 123.7, 125.9, 127.2, 129.9, 138.3, 149.5; m/z (EI) 173 (M^+); m/z (EI) 173.1198 (M^+, $C_{12}H_{15}N$ requires 173.1199).

1-(3,5-Dimethylphenyl)-2,5-dihydro-1*H*-pyrrole (9j)

Colorless solid in 0.070 g (41% yield); mp 48–49 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.42 (s, 6H), 4.20 (s, 4H), 6.04 (s, 2H), 6.30 (s, 2H), 6.49 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 21.9, 54.6, 109.4, 118.0, 126.5, 139.0, 147.5. m/z (EI) 173 (M^+); m/z (EI) 173.1198 (M^+, $C_{12}H_{15}N$ requires 173.1199).

1-(3-Bromophenyl)-2,5-dihydro-1*H*-pyrrole (9l)

Colorless oil in 0.015 g (85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.11 (s, 4H), 5.97 (s, 2H), 6.47 (dd, J = 2.0,8.0 Hz, 1H), 6.69 (s, 1H), 6.82 (d, J = 7.6 Hz, 1H), 7.11 (t, J = 8.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 54.8, 110.2, 114.3, 118.8, 123.7, 126.4, 130.7, 148.3; m/z (EI) 223 (M^+); m/z (EI) 222.9991 (M^+, $C_{10}H_{10}NBr$ requires 222.9991).

2-Chlorophenyl-2,5-dihydro-1*H*-pyrrole (9m)

Colorless oil in 0.017 g (98% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.41 (s, 4H), 5.93 (s, 2H), 6.77 (t, J = 7.4 Hz, 1H), 6.90 (s, 1H), 7.18 (dt, J = 1.2, 7.2 Hz, 1H), 7.32 (dd, J = 1.2, 8.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 57.4, 117.1, 119.5, 122.3, 126.3, 127.6, 132.1, 145.5; m/z (EI) 179 (M^+); m/z (EI) 179.0497 (M^+, $C_{10}H_{10}NCl$ requires 179.0496).

2,4-Difluorophenyl-2,5-dihydro-1H-pyrrole (9o)

Colorless oil in 0.016 g (90% yield); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 4.32$ (d, $J = 2.7$ Hz, 4H), 5.94 (s, 2H), 6.57 (s, 1H), 6.76–6.86 (m, 1H), 6.97–7.01 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 56.7$, 104.6–105.1, 110.8–111.1, 114.7–114.8, 126.3, 133.0–133.1, 149.7–152.3, 153.2–155.7; *m*/*z* (EI) 181 (M^+); *m*/*z* (EI) 181.0699 (M^+, $C_{10}H_9NF_2$ requires 181.0698).

1-(4-Chloro-2-fluorophenyl)-2,5-dihydro-1*H*-pyrrole (9q)

Colorless oil in 0.018 g (90% yield); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 4.30$ (d, $J = 2.9$ Hz, 4H), 5.93 (s, 2H), 6.78 (t, $J = 8.8$ Hz, 1H), 7.01–7.08 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 56.7$, 115.4, 116.8–117.0, 120.6–120.7, 124.0, 126.1, 134.9–135.0, 149.8–152.2; *m*/*z* (EI) 197 (M^+); *m*/*z* (EI) 197.0400 (M^+, $C_{10}H_9NFCl$ requires 197.0402).

3-Chloro-2-methylphenyl-2,5-dihydro-1*H*-pyrrole (9r)

Colorless oil in 0.01 g (57% yield); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 2.46$ (s, 3H), 4.16 (s, 4H), 5.96 (s, 2H), 6.98 (d, 1H, $J = 7.8$), 7.05–7.12 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) $\delta = 17.3$, 58.0, 109.3, 116.1, 122.2, 126.8, 128.1, 136.3, 150.9. *m*/*z* (EI) 193 (M^+); *m*/*z* (EI) 193.0654 (M^+, $C_{11}H_{12}NCl$ requires 193.0653).

General procedure for the ring-closing metathesis in the synthesis of macrocycles (9d–9s)

Into a solution of each of the dienes **10a–c** (0.2 mmol) in CH_2Cl_2 (25 mL), catalyst **7b** (1.0 mol%) was added and the reaction mixture heated at 40 °C and completion of reaction was monitored by TLC. The reaction mixture was mixed with silica gel (100–200 mm, 0.1 g), stirred for 30 min, filtered and the silica was washed with DCM (15 mL) to obtain the desired products as colorless solids. The spectroscopic data for compounds **11a–c** are coherent with those reported in literature.[17]

Conflicts of interest

There are no conflicts to declare.

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