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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.

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## Introduction

Grubbs (**1a** & **1b**) and Hoveyda–Grubbs (**2a** & **2b**) rutheniumbased 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).<sup>1,2</sup>

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.<sup>3-10</sup> 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.<sup>4</sup> 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. -NO2 and -SO<sub>2</sub>NMe<sub>2</sub>, 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  $\pi$ 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(n)-catalysts, a number of oxygen chelated Ru(n)-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.<sup>11–13</sup>

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 Rucarbenoids, Grubbs (II) and Hoveyda–Grubbs (II) catalysts.

The target structures (7**a**-7**c**) 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 7**a** and 7**b** 



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

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#### Table 1 Examples of modified Hoveyda-Grubbs (II) catalysts



Entry	Cat.	R <sub>1</sub>	$R_2$	$R_3$	$R_4$	$R_5$
1	2a (ref. 2)	TT	Dh			
1	3a (lel. 3)	п	P11	—	—	
2	<b>3b</b> (ref. 5–7)	$NO_2$	Н	—	—	—
3	<b>3c</b> (ref. 8)	SO <sub>2</sub> NMe <sub>2</sub>	Ph	_	—	—
4	<b>4a</b> (ref. 3)	_	—	Н	Н	Me, Et
5	<b>4b</b> (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)	—	—	Н	Me	NMe <sub>2</sub>



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( $\pi$ ) 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 graycarbon; 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 <sup>1</sup>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.<sup>14</sup> 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 1propenyls 6a-6c were then reacted with Grubbs (II) catalyst 1b in the presence of dry Amberlyst-15 hydrogen form in refluxing dichloromethane to afford  $Ru(\pi)$ -complexes 7a-7c in good yields (ESI<sup>†</sup>).

#### 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  $Ru(\pi)$  ion for 7a and 7b (ESI<sup> $\dagger$ </sup>). Similarly, an additional coordination is possible through the nitrogen atom



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

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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-4methylbenzenesulfonamide **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 <sup>1</sup>H NMR, by monitoring the allyloxy  $-OCH_2CH=CH_2-$  protons (H<sub>3</sub>)

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<sub>2</sub>Cl<sub>2</sub> 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 7**b** 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-1H-pyrrole derivatives 9b and 9c



Entry	Prod.	Solvent	Temp. (°C)	Time	Yield <sup>c</sup> (%)
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	$70^b$

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



Fig. 7 Time profile of the RCM reaction of diene 8a catalyzed by (A) 7b and (B) 2b as monitored by <sup>1</sup>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<sup>†</sup>).

Table 3	Synthesis of (un)substituted $N,N$ -diallylanilines $(8d-8s)^a$						
	R <sub>4</sub> R <sub>3</sub> R <sub>2</sub>	NH <sub>2</sub> Br K <sub>2</sub> C R <sub>1</sub> ref	CO <sub>3</sub> , CH <sub>3</sub> CN lux, 2 days	R <sub>4</sub> R <sub>3</sub> R <sub>2</sub>	R <sub>1</sub> 8d-8s	*	
Entry	Product	R <sub>1</sub>	$R_2$	R <sub>3</sub>	$R_4$	Yield <sup>b</sup> (%)	
1	8d	Н	Н	Н	н	70	
2	8e	OMe	Н	Н	Н	50	
3	8f	Н	OMe	Н	н	64	
4	8g	Н	Н	OMe	н	44	
5	8ĥ	Н	Н	Ме	н	86	
6	8i	Ме	Ме	Н	н	50	
7	8j	Н	Ме	Н	Me	65	
8	8k	F	Н	Н	н	45	
9	81	Н	Br	Н	н	55	
10	8m	Cl	Н	Н	н	63	
11	8n	Н	Н	Cl	н	40	
12	80	F	Н	F	н	63	
13	8p	Н	F	F	н	40	
14	8q	F	Н	Cl	Н	46	

<sup>*a*</sup> 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. <sup>*b*</sup> Isolated yield by chromatography.

Cl

н

н

NO<sub>2</sub>

Η

Н

54

40

#### 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<sup>†</sup>).

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–80**) 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<sub>2</sub>) 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.<sup>16</sup> Hence, from our published



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

Me

н

15

16

8r

88



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-

Catalyst (mol%), yields and $E/Z$ ratios of macrocycles <b>11a–c</b> $^{\circ}$					
Product	Cat./(mol%)	$\operatorname{Yield}^{b}(\%)$	Product $E: Z$ ratio <sup>1</sup>		
11a	<b>1a</b> , 2.5 mol%	92	78:22		
11a	7 <b>b</b> , 1.0 mol%	98	100:0		
11b	1a, 2.5 mol%	91	75:25		
11b	7 <b>b</b> , 1.0 mol%	98	100:0		
11c	1a, 5.0 mol%	97	75:25		
11 <b>c</b>	7 <b>b</b> , 1.0 mol%	70	92:8		
	Catalyst ( Product 11a 11b 11b 11b 11c 11c	Catalyst (mol%), yields and         Product       Cat./(mol%)         11a       1a, 2.5 mol%         11a       7b, 1.0 mol%         11b       1a, 2.5 mol%         11b       7b, 1.0 mol%         11c       1a, 5.0 mol%         11c       7b, 1.0 mol%	Catalyst (mol%), yields and <i>E/Z</i> ratios of         Product       Cat./(mol%)       Yield <sup>b</sup> (%)         11a       1a, 2.5 mol%       92         11a       7b, 1.0 mol%       98         11b       1a, 2.5 mol%       91         11b       7b, 1.0 mol%       98         11b       7b, 1.0 mol%       98         11c       1a, 5.0 mol%       97         11c       7b, 1.0 mol%       70		

<sup>a</sup> Reaction condition: acyclic macrodienes (0.2 mmol), DCM (25 mL), 40 °C. <sup>b</sup> Determined by <sup>1</sup>H NMR.

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 <sup>1</sup>H NMR spectra (400 MHz, CDCl<sub>3</sub>, 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<sub>2</sub>CH=CH<sub>2</sub>, H<sub>1</sub> in 10a-10c & H<sub>1</sub>/H<sub>7</sub> in 10a), *i.e.* the disappearance of: [H1 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<sub>1</sub> in 10b, Fig. 8C; two sets of doublet of a doublet at 4.96-4.98 ppm (dd, I = 1.3, 10.5 Hz, 2H) and at 5.08–5.13 ppm (dd, I = 1.3, 10.5 Hz, 2H)17.3 Hz, 2H); H1 in 10c, Fig. 8E; two sets of doublet of a doublet



Fig. 8 <sup>1</sup>H NMR (400 MHz, 600 MHz, CDCl<sub>3</sub>) spectra of **10a**, **10b** and 10c (a) before RCM and (b) after RCM.



Chemical Shift (ppm) Fig. 9 Full <sup>1</sup>H NMR of (A) **10a**; (B) **11a**; (C) **10b**; (D) **11b**; (E) **10c** and (F)

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<sub>2</sub>CH=CHCH<sub>2</sub>O-, H<sub>2</sub> in 11a–11c & H<sub>6</sub> in 11c), *i.e.* 

[**H**<sub>2</sub> 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), **H**<sub>6</sub> 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), **H**<sub>2</sub> in **11b**, Fig. 8D; a triplet at 5.99 ppm (t, J = 3.0 Hz, 2H), **H**<sub>2</sub> 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( $\pi$ ) complexes have been established as efficient catalysts for ringclosing 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. <sup>1</sup>H and <sup>13</sup>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); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 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); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 19.2, 29.5, 68.6, 112.8, 121.7, 125.6, 126.8,

(0)

11c

127.1, 127.9, 127.91, 154.9; m/z (EI) 240 (M<sup>+</sup>, 75%), 242 (M<sup>+2</sup>, 74%); m/z (EI) 240.0145 (M<sup>+</sup>, C<sub>11</sub>H<sub>13</sub><sup>79</sup>BrO requires 240.0144).<sup>14</sup>

#### 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; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  = 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); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$  = 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<sup>+</sup>); *m/z* (EI) 311.1515 (M<sup>+</sup>, C<sub>19</sub>H<sub>21</sub>NO<sub>3</sub> 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 2-[2-(2-propenylphenoxy)-ethoxy]colorless solid, i.e. 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; <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ )  $\delta = 1.89$  (dd, J = 6.8, 1.6 Hz, 3H, 2.29 (s, 3H), 4.20 (d, I = 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); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 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<sup>+</sup>); m/z (EI) 423.1499 (M<sup>+</sup>, C<sub>24</sub>H<sub>25</sub>NO<sub>4</sub>S 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; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 1.92$ 

 $(dd, J = 5.4, 1.2 \text{ Hz}, 3\text{H}), 2.43 \text{ (s}, 3\text{H}), 3.40 \text{ (m}, 2\text{H}), 4.00 \text{ (t}, J = 5.1 \text{ Hz}, 2\text{H}), 4.94 \text{ (bs}, 1\text{H}), 6.19-6.22 \text{ (m}, 1\text{H}), 6.59 \text{ (dd}, J = 15.6, 1.8 \text{ Hz}, 1\text{H}), 6.70 \text{ (d}, J = 8.4 \text{ Hz}, 1\text{H}), 6.94 \text{ (t}, J = 7.8 \text{ Hz}, 1\text{H}), 7.13 \text{ (dt}, J = 1.2, 7.2 \text{ Hz}, 1\text{H}), 7.30 \text{ (d}, J = 8.4 \text{ Hz}, 1\text{H}), 7.39 \text{ (dd}, J = 7.8, 1.2 \text{ Hz}, 1\text{H}), 7.77 \text{ (d}, J = 7.8 \text{ Hz}, 2\text{H}); {}^{13}\text{C} \text{ NMR} (100 \text{ MHz}, \text{CDCl}_3) \\ \delta = 19.2, 21.7, 42.9, 67.0, 112.5, 121.8, 125.4, 126.8, 127.18, 127.24, 127.5, 128.0, 130.0, 137.0, 143.8, 154.8;$ *m/z*(EI) 331 (M<sup>+</sup>);*m/z*(EI) 331.1238 (M<sup>+</sup>, C<sub>18</sub>H<sub>21</sub>NO<sub>3</sub>S 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; <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  = 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); <sup>13</sup>C NMR (150 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  = 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<sup>+</sup>, 0.2%), 763 (M<sup>+2</sup>, 0.17%); *m/z* (EI) 761.1719 (M<sup>+</sup>, C<sub>38</sub>H<sub>43</sub><sup>35</sup>Cl<sub>2</sub>N<sub>3</sub>-O<sub>3</sub><sup>102</sup>Ru requires 761.1719).

#### Ru(II) complex 7b

Green crystals in 0.019 g (96% yield); mp 206–207 °C; <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  = 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); <sup>13</sup>C NMR (150 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  = 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<sub>43</sub>H<sub>47</sub><sup>35-</sup>Cl<sub>2</sub>N<sub>3</sub>O<sub>4</sub><sup>102</sup>RuS requires 873.1702).

#### Ru(II) complex 7c

Green crystals in 0.022 g (95% yield); mp 214–215 °C; <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  = 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); <sup>13</sup>C NMR (150 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta = 19.6$ , 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<sup>+</sup>, C<sub>37</sub>H<sub>43</sub><sup>35</sup>Cl<sub>2</sub>N<sub>3</sub>O<sub>3</sub><sup>102</sup>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.<sup>18–24</sup>

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

Colorless oil in 0.9 g (44% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 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); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  = 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<sup>+</sup>); m/z (EI) 201.1515 (M<sup>+</sup>, C<sub>14</sub>H<sub>19</sub>N requires 201.1512).

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

Colorless oil in 0.95 g (50% yield); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  = 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); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  = 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<sup>+</sup>); *m/z* (EI) 191.1102 (M<sup>+</sup>, C<sub>12</sub>H<sub>14</sub>NF requires 191.1105).

#### N,N-Diallyl-2,4-difluoroaniline (80)

Colorless oil in 0.84 g (40% yield) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 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); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 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<sup>+</sup>); m/z (EI) 209.1011 (M<sup>+</sup>, C<sub>12</sub>H<sub>13</sub>F<sub>2</sub>N requires 209.1011).

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

Colorless oil in 1.41 g (63% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 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); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  = 54.6, 117.0, 117.2, 117.7, 121.4, 124.3, 134.5, 154.2, 155.8; m/z (EI) 225 (M<sup>+</sup>); m/z (EI) 225.0718 (M<sup>+</sup>, C<sub>12</sub>H<sub>13</sub>FCIN 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.<sup>25,26</sup>

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

Colorless oil in 0.008 g (47% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 3.84$  (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); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta = 55.7$ , 63.2, 107.0, 113.1, 119.6, 130.5, 142.2, 160.7; m/z (EI) 175 (M<sup>+</sup>); m/z (EI) 175.0993 (M<sup>+</sup>, C<sub>11</sub>H<sub>13</sub>NO requires 175.0992).

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

Colorless oil in 0.0046 g (27% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 2.31$  (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); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta =$  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<sup>+</sup>); m/z (EI) 173.1198 (M<sup>+</sup>, C<sub>12</sub>H<sub>15</sub>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; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 2.42 (s, 6H), 4.20 (s, 4H), 6.04 (s, 2H), 6.30 (s, 2H), 6.49 (s, 1H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  = 21.9, 54.6, 109.4, 118.0, 126.5, 139.0, 147.5. *m/z* (EI) 173 (M<sup>+</sup>); *m/z* (EI) 173.1198 (M<sup>+</sup>, C<sub>12</sub>H<sub>15</sub>N requires 173.1199).

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

Colorless oil in 0.015 g (85% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 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); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  = 54.8, 110.2, 114.3, 118.8, 123.7, 126.4, 130.7, 148.3; *m*/*z* (EI) 223 (M<sup>+</sup>); *m*/*z* (EI) 222.9991 (M<sup>+</sup>, C<sub>10</sub>H<sub>10</sub>NBr requires 222.9991).

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

Colorless oil in 0.017 g (98% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 4.41$  (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); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta = 57.4$ , 117.1, 119.5, 122.3, 126.3, 127.6, 132.1, 145.5; m/z (EI) 179 (M<sup>+</sup>); m/z (EI) 179.0497 (M<sup>+</sup>, C<sub>10</sub>H<sub>10</sub>NCl requires 179.0496).

#### 2,4-Difluorophenyl-2,5-dihydro-1H-pyrrole (90)

Colorless oil in 0.016 g (90% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 4.32$  (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); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta = 56.7$ , 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<sup>+</sup>); m/z (EI) 181.0699 (M<sup>+</sup>, C<sub>10</sub>H<sub>9</sub>NF<sub>2</sub> requires 181.0698).

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

Colorless oil in 0.018 g (90% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 4.30$  (d, J = 2.9 Hz, 4H), 5.93 (s, 2H), 6.78 (t, J = 8.8 Hz, 1H), 7.01–7.08 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta = 56.7$ , 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<sup>+</sup>); m/z (EI) 197.0400 (M<sup>+</sup>, C<sub>10</sub>H<sub>9</sub>NFCl requires 197.0402).

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

Colorless oil in 0.01 g (57% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 2.46$  (s, 3H), 4.16 (s, 4H), 5.96 (s, 2H), 6.98 (d, 1H, J = 7.8), 7.05–7.12 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta = 17.3$ , 58.0, 109.3, 116.1, 122.2, 126.8, 128.1, 136.3, 150.9. m/z (EI) 193 (M<sup>+</sup>); m/z (EI) 193.0654 (M<sup>+</sup>, C<sub>11</sub>H<sub>12</sub>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.<sup>17</sup>

## Conflicts of interest

There are no conflicts to declare.

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## Notes and references

1 T. M. Trnka and R. H. Grubbs, The development of L2X2Ru=CHR olefin metathesis catalysts: an organometallic success story, *Acc. Chem. Res.*, 2001, **34**, 18–29.

- 2 A. H. Hoveyda and A. R. Zhugralin, The remarkable metalcatalysed olefin metathesis reaction, *Nature*, 2007, **450**, 243–251.
- 3 A. M. Dunne, S. Mix and S. Blechert, A highly efficient olefin metathesis initiator: improved synthesis and reactivity studies, *Tetrahedron Lett.*, 2003, 44(13), 2733–2736.
- 4 H. Wakamatsu and S. Blechert, A Highly Active and Air-Stable Ruthenium Complex for Olefin Metathesis, *Angew. Chem., Int. Ed.*, 2002a, 41(5), 794–796; H. Wakamatsu and S. Blechert, A New Highly Efficient Ruthenium Metathesis Catalyst, *Angew. Chem., Int. Ed.*, 2002b, 41(13), 2403–2405; K. P. Wang, S. Y. Yun, D. Lee and D. J. Wink, Structure and Reactivity of Alkyne-Chelated Ruthenium Alkylidene Complexes, *J. Am. Chem. Soc.*, 2009, 131(42), 15114–15115.
- 5 K. Grela, S. Harutyunyan and A. Michrowska, A Highly Efficient Ruthenium Catalyst for Metathesis Reactions, *Angew. Chem., Int. Ed.*, 2002, **41**(21), 4038–4040.
- 6 S. Harutyunyan, A. Michrowska and K. Grela, *Catalysts for Fine Chemical Synthesis, Metal Catalysed Carbon-Carbon Bond-Forming Reactions*, ed. S. J. Connon, A. M. Dunne, S. Blechert, G. Bhaskar and B. Venkateswara Rao, John Wiley & Sons, Ltd, 2004, vol. 3, pp. 169–173.
- 7 A. Michrowska, R. Bujok, S. Harutyunyan, V. Sashuk, G. Dolgonos and K. Grela, Nitro-Substituted Hoveyda-Grubbs Ruthenium Carbenes: Enhancement of Catalyst Activity through Electronic Activation, *J. Am. Chem. Soc.*, 2004, **126**(30), 9318–9325.
- 8 Z.-Y. Zhan, Preparation of ruthenium complex ligand, ruthenium complexes, supported ruthenium complex catalysts for olefin metathesis, *WO Patent*, 2007003135, 2007.
- 9 Y. Zhang, M. Shao, H. Zhang, Y. Li, D. Liu, y. Cheng, G. Liu and J. Wang, Synthesis and reactivity of oxygen chelated ruthenium carbene metathesis catalysts, *J. Organomet. Chem.*, 2014, **756**, 1–9.
- 10 L. Cavallo, Mechanism of Ruthenium-Catalyzed Olefin Metathesis Reactions from a Theoretical Perspective, *J. Am. Chem. Soc.*, 2002, **124**(30), 8965–8973.
- 11 M. Bieniek, R. Bujok, M. Cabaj, N. Lugan, G. Lavigne, D. Arlt and K. Grela, Advanced Fine-Tuning of Grubbs/Hoveyda Olefin Metathesis Catalysts:A Further Step toward an Optimum Balance between Antinomic Properties, *J. Am. Chem. Soc.*, 2006, **128**(42), 13652–13653.
- 12 S.-X. Luo, K. M. Engle, X. Dong, A. Hejl, M. K. Takase, L. M. Henling, P. Liu, K. N. Houk and R. H. Grubbs, An Initiation Kinetics Prediction Model Enables Rational Design of Ruthenium Olefin Metathesis Catalysts Bearing Modified Chelating Benzylidenes, ACS Catal., 2018, 8(5), 4600–4611.
- 13 E. Merino, E. Poli, U. Díaz and D. Brunel, Synthesis and characterization of new ruthenium N-heterocyclic carbene Hoveyda II-type complexes. Study of reactivity in ring closing metathesis reactions, *Dalton Trans.*, 2012, **41**, 10913–10918.
- 14 N. L. Bauld, D. Gao and J. T. Alpin, Cation radical chain cycloaddition polymerization: a fundamentally new polymerization mechanism, *J. Phys. Org. Chem.*, 1999, 12(11), 808–818.

- 15 Crystallographic data of compounds 7a, 7b and 7c have been deposited with the Cambridge Data Center as supplementary publication # CCDC 2105379, 1481883, 2105381 respectively, Copies of the data can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail deposit@ccdc.cam.uk.
- 16 (a) Y. A. Ibrahim, H. Behbehani and M. R. Ibrahim, Efficient atom economic approaches towards macrocyclic crownamides via ring closure metathesis, *Tetrahedron Lett.*, 2002, 43, 4207–4210; (b) H. Behbehani, M. R. Ibrahim and Y. A. Ibrahim, Efficient atom economic approaches towards macrocyclic crown diamides via ring-closing metathesis, *Tetrahedron Lett.*, 2002, 43, 6421–6426; (c) Y. A. Ibrahim, H. Behbehani and N. S. Khalil, Efficient route to 20–32 membered macrocyclic crown diamides via ring closing metathesis, *Tetrahedron*, 2004, 60, 8429–8436.
- 17 Y. A. Ibrahim and E. John, Efficient synthesis of 18–40 membered macrocyclic polyoxadiamides and polyoxatetraamides *via* ring closing metathesis, *Tetrahedron*, 2006, **62**, 1001–1014.
- 18 W. Chen and J. Wang, Synthesis of Pyrrole Derivatives from Diallylamines by One-Pot Tandem Ring-Closing Metathesis and Metal-Catalyzed Oxidative Dehydrogenation, Organometallics, 2013, 32(6), 1958–1963.
- 19 N. Scalacci, G. W. Black, G. Mattedi, N. L. Brown, N. J. Turner and D. Castagnolo, Unveiling the Biocatalytic Aromatizing

Activity of Monoamine Oxidases MAO-N and 6-HDNO: Development of Chemoenzymatic Cascades for the Synthesis of Pyrroles, *ACS Catal.*, 2017, 7(2), 1295–1300.

- 20 B. Schmidt, S. Krehl and E. Jablowski, Assisted tandem catalytic RCM-aromatization in the synthesis of pyrroles and furans, *Org. Biomol. Chem.*, 2012, **10**, 5119–5130.
- 21 S. J. Lia, L. Hana and S. K. Tian, 1,2-Aminohalogenation of arynes with amines and organohalides, *Chem. Commun.*, 2019, 55, 11255–11258.
- 22 K. H. Kang, K. Il Choi, H. Y. Koh, Y. Kim, B. Y. Chung and Y. S. Cho, *Synth. Commun.*, 2006, **31**(15), 2277–2286.
- 23 T. Saitoh, S. Yoshida and J. Ichikawa, Naphthalene-1,8diylbis(diphenylmethylium) as an Organic Two-Electron Oxidant:Benzidine Synthesis *via* Oxidative Self -Couplingof *N*,*N*-Dialkylanilines, *J. Org. Chem.*, 2006, 71(17), 6414–6419.
- 24 C. Chiappe, P. Piccioli and D. Pieraccini, Selective Nalkylation of anilines in ionic liquids, *Green Chem.*, 2006, **8**(3), 277–281.
- 25 L. A. Gharat, 3-Azabicyclo[3.1.0]hexane derivatives as vanilloid receptor ligands, pharmaceutical compositions containing them and process for their preparation, PCT Int. Appl., WO2008/010061A2, 2008.
- 26 M. Fuji, J. Chiwata, M. Ozaki, S. Aratani and Y. Obora, In Situ-Generated Niobium-Catalyzed Synthesis of 3-Pyrroline Derivatives via Ring-Closing Metathesis Reactions, ACS Omega, 2018, 3(8), 8865–8873.