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# Cyclic(alkyl)(amino)carbene ruthenium complexes for *Z*-stereoselective (asymmetric) olefin metathesis†‡

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The first *Z*-stereoselective catechodithiolate ruthenium complexes containing cyclic(alkyl)(amino)carbene ligands are reported. Isolated in nearly quantitative yields or *in situ* generated, these catalysts demonstrated remarkable *Z* selectivity (*Z*/*E* ratio up to >98/2) in ring-opening metathesis polymerization (ROMP), ring-opening-cross metathesis (ROCM) and cross-metathesis (CM). Thanks to the efficient chiral HPLC resolution of racemic CAAC-complex precursors, optically pure dithiolated complexes were also synthesized allowing to produce enantioenriched *Z*-ROCM products in >99/1 *Z*/*E* with good levels of enantioselectivity.

## Introduction

Discovered in the mid of last century, olefin metathesis[1] has become a practical and versatile synthetic tool to efficiently produce carbon–carbon double bonds. Relevant applications were successfully disclosed in various fields such as natural product synthesis,[2] the transformation of renewable feedstocks[3] or the production of innovative materials (polymers).[4] This resounding success stems from the elaboration of well-defined, air stable and easy to handle ruthenium-benzylidene complexes that proved to be highly tolerant towards many organic functionalities.[1] Obviously, the asymmetric version of this reaction was also intensively studied with either optically pure ruthenium or molybdenum catalysts, offering a straightforward access to highly valuable chiral building blocks with high enantiopurity.[5] As the *Z*-alkene moiety is ubiquitous in numerous relevant chiral molecules, special attention has been given to the design of catalysts which can control both the enantioselectivity and the *Z*-selectivity[6,7] of metathesis transformations. Nevertheless, as depicted in Fig. 1, examples remain scarce.[8] For instance, chiral Mo-complexes **Mo-1** bearing a monodentate BINOL-type ligand demonstrated a high enantioinduction in asymmetric ring-opening cross-metathesis (AROCM) combined with a remarkable degree of *Z*-selectivity (Fig. 1, eqn (1)).[8a,b] Stereogenic-at-ruthenium complex **Ru-1** featuring a chiral bidentate N-heterocyclic carbene (NHC) ligand furnished tetrahydropyran products in high ees and good to excellent *Z*:*E* ratio (Fig. 1, eqn (2)).[8c] Optically pure cyclometalated Ru-catalyst **Ru-2** has proved to be highly efficient in AROCM, affording various *Z*-alkenes with high ees (Fig. 1, eqn (3)).[8d] Noticeable, **Ru-2** also promoted the first *Z*-asymmetric cross-metathesis (ACM), albeit a moderate 50% ee was observed (Fig. 1, eqn (4)).[8e]

Despite these significant breakthroughs, the development of new chiral *Z*-selective metathesis catalysts remains a challenging objective. Recently, our groups reported an expedient access to the first optically pure **Ru-3** complexes[9] containing cyclic(alkyl)(amino)carbene (CAAC)[10,11] ligands (Fig. 1B). These new chiral complexes demonstrated excellent catalytic performances in asymmetric olefin metathesis with good enantioselectivities (up to 92%).[9] In light of these promising results, we wished to investigate the development of their *Z*-enantioselective congeners (Fig. 1B). Herein, we focused our attention on catechodithiolate Ru-complexes,[7e,f] a class of catalysts which combine easy accessibility (one step from commercially

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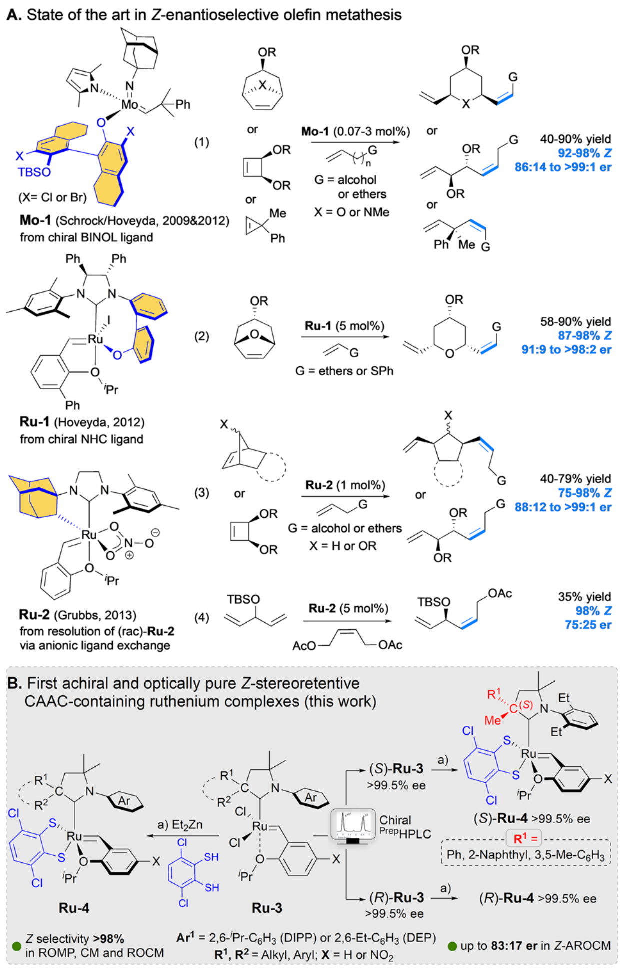
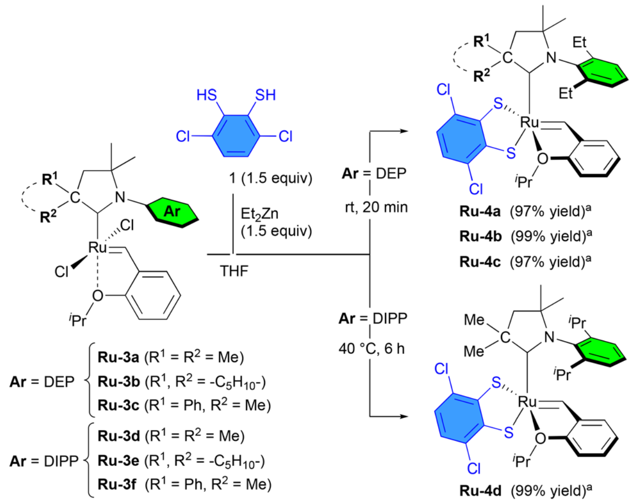



Fig. 1 (A) Previously described *Z*-enantioselective olefin metathesis catalysed by Mo- or Ru-complexes. (B) Development of achiral and optically pure *Z*-stereoretentive CAAC–Ru complexes (this work).

available 2nd generation Hoveyda-type complexes)[12] and remarkable efficiency towards a wide range of *Z*-alkenes in high purity (>98% *Z*). Since, their asymmetric version has not yet been reported, *we investigated both achiral and chiral CAAC ligands and their use in Z-stereoselective ROMP, ROCM, CM and also in asymmetric ROCM.*

## Results and discussion

We initiated our study by the synthesis of catechodithiolate Ru-catalysts starting from previously reported CAAC-containing Hoveyda type complexes **Ru-3** (Scheme 1).[13] Even in the presence of the sterically congested chiral quaternary center (*i.e.* **Ru-4c**), complexes **Ru-3a–c** featuring a *N*-2,6-diethylphenyl (DEP) group afforded the expected dithiolate **Ru-4a–c** in nearly quantitative isolated yields (97–99%, within 20 min at ambient temperature). In marked contrast, **Ru-3d–f** complexes containing the bulkier *N*-2,6-diisopropylphenyl (DIPP) group appeared more challenging. In this case, **Ru-3d** required a prolonged reaction time (6 h, 40 °C) to afford the corresponding dithiolate **Ru-4d** in




Scheme 1 Synthesis of catechodithiolate CAAC **Ru-4a–d**. [a]Isolated yield.

99% isolated yield, whereas rapid decomposition of the corresponding dithiolate Ru-species was observed for **Ru-3e–3f**.

The latter, likely results from a severe steric clash between the catechol dithiolate and the DIPP moiety of the CAAC ligand (also observed when comparing $\%V_{bur}$ of **Ru-3a–3b** to that of **Ru-3e–3f**)[14] leading to extremely short-lived **Ru-4e–4f** complexes. According to the dissymmetry of the CAAC unit, 2 rotamers could be expected for **Ru-4** complexes.[15] However, $^{1}$H and $^{13}$C NMR analysis showed that only one rotamer is observed in solution for **Ru-4a–d** (see ESI‡ for details). Nuclear Overhauser effects (nOe) between the prominent benzylidene proton and the aryl alkyl groups were observed in NOESY experiments performed in Tol-$d_8$ at 0 °C which features the *N*-aryl above the styrenyl-ether moiety. While we were not able to obtain suitable crystals from $^{DEP}$CAAC **Ru-4a–c**, we could perform an X-ray diffraction analysis of **Ru-4d** (Fig. 2), which confirms the structure of the rotamer observed in solution.[16]

Catalytic performances of catechodithiolate CAAC **Ru-4a–d** were initially evaluated in the ROMP of norbornene **2a** (Table 1).[17] All complexes demonstrated good reactivity at 0.1 mol%, allowing full conversion within 30 min and affording the expected polymer **3a** in 89–98% isolated yield. While an excellent >95% syndiotacticity was observed in each case,[18] a

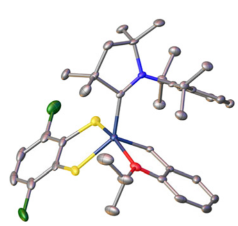
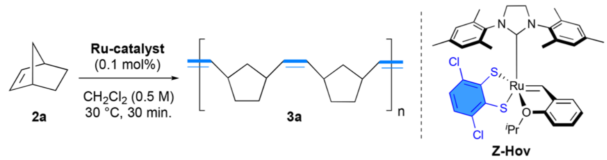


Fig. 2 Solid-state structure of complex **Ru-4d** from single crystal X-ray diffraction. Displacement ellipsoids are drawn at 30% probability. Hydrogen atoms have been omitted for clarity.

Table 1 Catalytic performances of catechodithiolate CAAC **Ru-4a–d** in ring-opening metathesis polymerization of norbornene **2a**




| Entry | Catalyst | Yield[a] (%) | $Z:E$[b] ratio | Syndiotacticity[c] (%) | $M_w$[d] (kg mol$^{-1}$) | $Đ$[d] |
|---|---|---|---|---|---|---|
| 1 | **Ru-4a** | 93 | 97 : 3 | >95 | 5478 | 4.3 |
| 2 | **Ru-4b** | 91 | 96 : 4 | >95 | 5351 | 3.9 |
| 3 | **Ru-4c** | 98 | 92 : 8 | >95 | 2452 | 5.0 |
| 4 | **Ru-4d** | **89** | **>98 : 2** | **>95** | **563** | **1.9** |
| 5 | **Z-Hov** | 92 | >98 : 2 | Atactic | 731 | 2.8 |

[a] Isolated yield. [b] Molar ratio of $E$ and $Z$ isomers were obtained by $^1$H NMR analysis ($CDCl_3$). [c] Determined by $^{13}$C NMR spectroscopy at 55 °C ($CDCl_3$) after hydrogenation of the polymers (see ESI†). [d] Determined by SEC in THF at 40 °C.



slight difference of $Z:E$ ratio occurred ranging from 92 : 8 (entry 3; **Ru-4c**) to >98 : 2 (entry 4; **Ru-4d**). Interestingly, **Ru-4d** significantly differs from its $^{DEP}$CAAC–Ru congeners as well as the NHC-containing **Z-Hov** by producing **3a** with the lowest dispersity (1.9) and molar mass (563 kg mol$^{-1}$; entry 4).[17c]

It is also worth noting that **Z-Hov** afforded **3a** as an atactic polymer despite similar high *Z*-selectivity (entry 5). The ROMP of norbornadiene[17a,c] or *exo*-norbornene derivatives **2b–g**[19] were next studied with $^{DEP}$CAAC **Ru-4b** and $^{DIPP}$CAAC **Ru-4d** catalysts (Scheme 2a). Here also, excellent *Z*-selectivities (>98 : 2) and yields (94–98%) were reached, except for substrates **2e–g** which gave no or low conversion even under more drastic conditions (see ESI‡ for details).

Of note, a prolonged reaction time (1–3 h *vs.* 10–30 min) was required for diol **3c**, but without any alteration of the *Z*-selectivity.[20] Interestingly, polymer **3b** was formed in up to 75% syndiotacticity with $^{DEP}$CAAC **Ru-4b**, surpassing the **Z-Hov** catalyst (55%).[21] The lower 50% syndioselectivity observed with $^{DIPP}$CAAC **Ru-4d** could result from steric clash with the bulkier DIPP substituent.[18] On the other hand, only atactic polymers **3c**, **d** were obtained from ROMP of functionalized norbornenes **2c** and **2d** independent of the catalyst used, also suggesting that a significant steric clash occurred between the CAAC units and the substrates.[22]

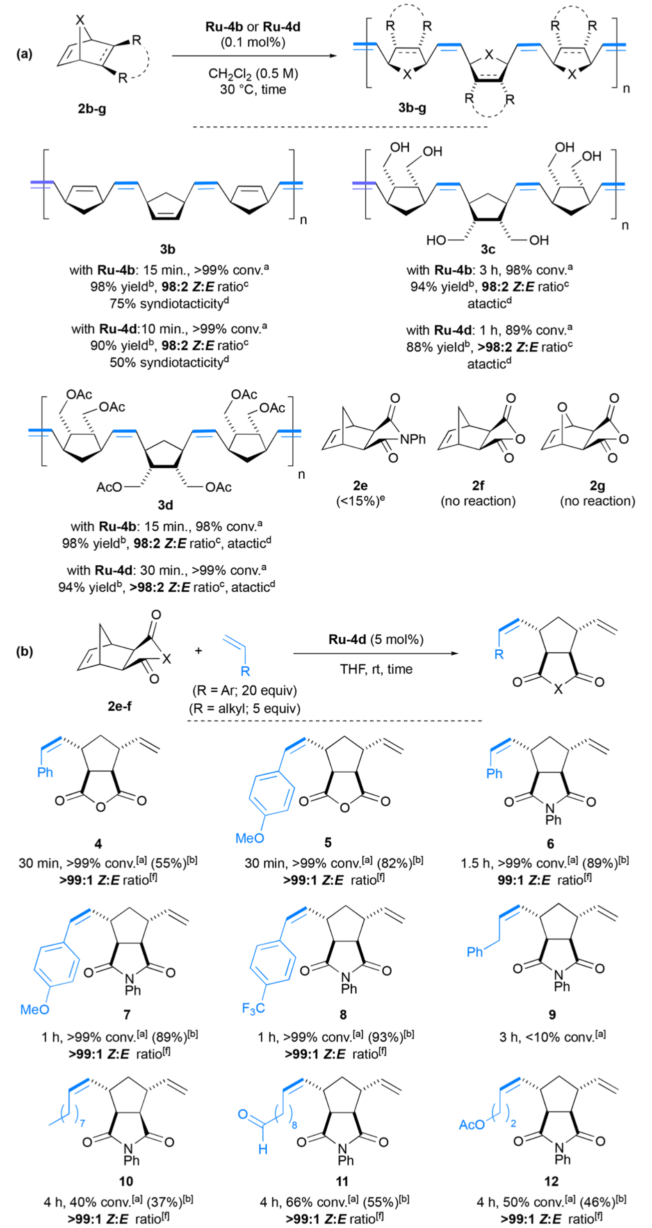
We next turned our investigation to ROCM transformation involving norbornenes **2e** and **2f** and various cross-olefin partners (Scheme 2b). Here also, **Ru-4d** proved to be highly efficient with functionalized styrenes, furnishing internal alkenes in moderate to high yield (55–93%) and excellent *Z*-selectivity (>98%). The reaction with aliphatic olefins[7g] also led to a remarkable *Z*-selectivity albeit lower conversions and yields were observed, and only traces of **9** were detected in the case of allylbenzene.

The catechodithiolate CAAC–Ru complexes were also investigated in cross-metathesis between 1-decene **13** and *cis*-butenediol **14a** (Table 2). We observed excellent $Z:E$ ratios (98 : 2) across of our range of catalysts, with **Ru-4d** also appearing to be the most efficient, furnishing the expected *Z*-product **15** in a moderate 48% isolated yield (entry 4). Performing the reaction at higher or lower temperature did not improve the conversion (entries 6 and 7). Since higher catalyst loading (10 mol%) or sequential addition of catalyst (4 × 1.25 mol%) were also unsuccessful to improve the conversion (17%, see ESIError! Bookmark not defined. for details), we suspect self-poisoning of the active catalytic species.[11e,f] Next, we studied the performance of **Ru-4d** in various CM reactions. As depicted in Scheme 3, high levels of *Z*-selectivity were obtained, ranging from 95% to >98%.

Nevertheless, the conversion remained moderate furnishing the corresponding *Z*-products in 18–43% isolated yield. Furthermore, only traces of **22** was observed in the case of styrene as olefin partner.

Having showed the high *Z*-selectivity in ROMP, ROCM and CM, we next investigated the performance in *Z*-enantioselective ROCM of optically pure catechodithiolate $^{DEP}$CAAC–Ru complexes featuring various groups at the chiral quaternary center (*i.e.* Ph, 2-naphthyl, 3,5-dimethylphenyl). We also considered their nitro-Grela variant with a $-NO_2$ activating group on the styrenylether fragment. First, we performed the preparative HPLC resolution of $^{DEP}$CAAC **Ru-3c–g**, **i** on a Chiralpak IE phase (Scheme 3, see ESI‡ for details),[23] affording each enantiomer in nearly quantitative yield and excellent optical purity (>98.5% ee). Note that the chiroptical properties of these optically pure Ru-complexes were obtained through electronic circular dichroism (ECD) (see ESI‡ for details). We unambiguously confirmed the absolute configuration of second eluted **Ru-3g**, **i** complexes by X-ray diffraction study (*S*, Fig. 3)[16] and attributed by analogy the same (*S*) configuration to second eluted **Ru-3c**, **h**. Optically pure complexes (−)-(*S*)-**Ru-3c** and (+)-(*R*)-**Ru-3c** were then converted into corresponding catechodithiolated counterparts (−)-(*S*)-**Ru-4c** and (+)-(*R*)-**Ru-4c** in 99% isolated yield (Scheme 4).

The latter was then evaluated in *Z*-enantioselective ROCM between *exo*-norbornene **2c** and styrene to furnish enantioenriched cyclopentane **23** with 99% *Z*-selectivity and 78 : 22 enantiomeric ratio (Table 3,

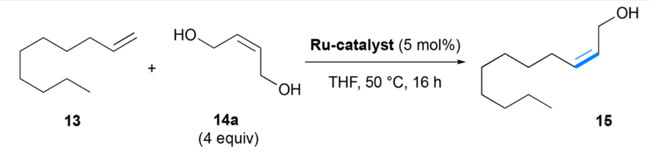



**Scheme 2** Scope of ROMP (a) and ROCM (b) catalysed by catechodithiolate $^{DEP}$CAAC **Ru-4b** or $^{DIPP}$CAAC **Ru-4d**. $^a$Conversions were determined by $^1$H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. $^b$Isolated yield. $^c$Molar ratio of *E* and *Z* isomers were monitored by $^1$H NMR analysis ($CDCl_3$ or DMSO-$d_6$). $^d$Determined by $^{13}$C NMR spectroscopy. $^e$Catalysts **Ru-4b, d** were used. $^f$Determined by GC analysis.

entry 2). This catalytic performance is quite similar to that of (*R*)-**Ru-3c** affording **23** in 29% isolated yield[24] and 76 : 24 er (entry 1).

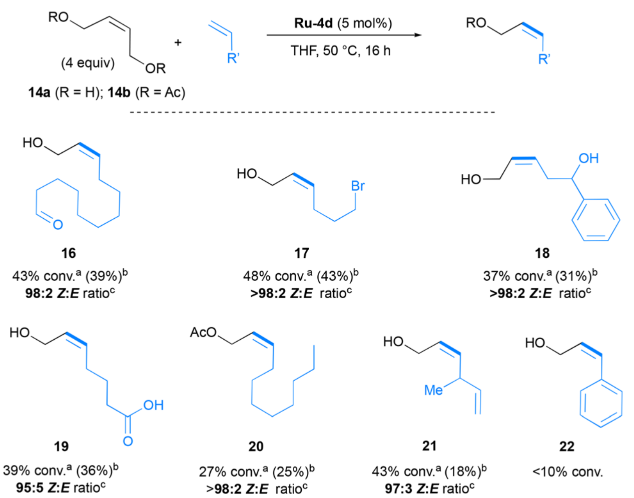
While the selectivity remained moderate, it is worth mentioning that previous AROCM involving *exo*-norbonenes are scarce and have been obtained in even lower enantioselectivities (up to 67 : 33 er for **23**).[25] We next turned our attention to optically pure nitro-Grela type pre-catalysts $^{DEP}$-CAAC–**Ru-3g–i**. Unexpectedly, the corresponding dithiolated

**Table 2** Catalytic performances of catechodithiolate CAAC–Ru-complexes **Ru-4a–d** in cross-metathesis between 1-decene **13** and *cis*-butenediol **14a**




| Entry | Catalyst | Conv.$^a$ (%) yield$^b$ (%) | $Z:E$ ratio$^c$ (%) |
|---|---|---|---|
| 1 | **Ru-4a** | 36 (32) | >98 : 2 |
| 2 | **Ru-4b** | 35 (26) | 98 : 2 |
| 3 | **Ru-4c** | 40 (31) | 98 : 2 |
| 4 | **Ru-4d** | **50 (48)** | **98 : 2** |
| 5$^d$ | **Ru-4d** | 42 (36) | >98 : 2 |
| 6$^e$ | **Ru-4d** | 50 (48) | 98 : 2 |

$^a$ Conversions were determined by $^1$H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. $^b$ Isolated yield. $^c$ Molar ratio of *E* and *Z* isomers were monitored by $^1$H NMR analysis ($CDCl_3$). $^d$ Reaction performed at 20 °C. $^e$ Reaction performed at 80 °C in 2-Me-THF.




**Scheme 3** Scope of cross-metathesis catalysed by catechodithiolate $^{DIPP}$CAAC **Ru-4d**. $^a$Conversions were determined by $^1$H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. $^b$Isolated yield. $^c$Determined by $^1$H NMR spectroscopy.

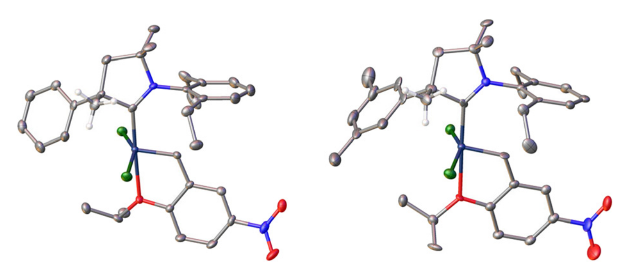
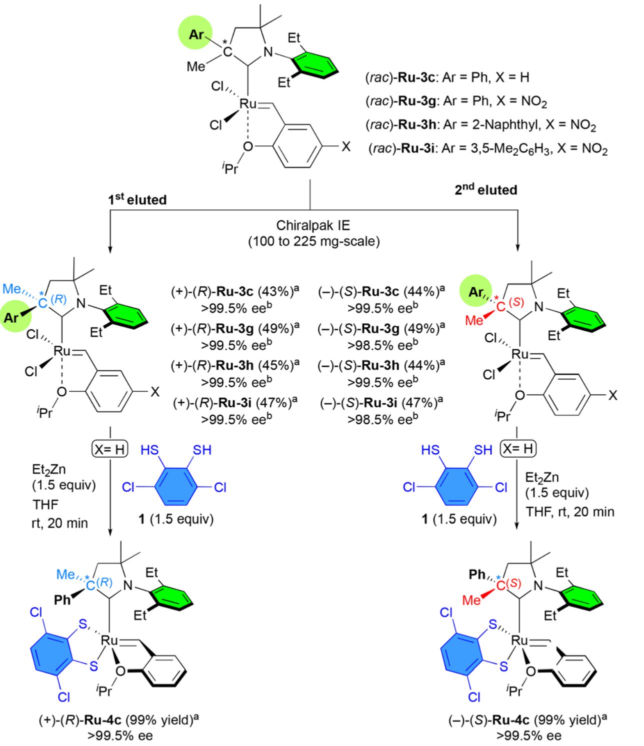


**Fig. 3** Solid-state structure of optically pure (−)-(*S*)-**Ru-3g** (left) and (−)-(*S*)-**Ru-3i** (right) from single crystal X-ray diffraction. Displacement ellipsoids are drawn at 50% probability. Most hydrogen atoms have been omitted for clarity.




**Scheme 4** Scope of optically pure $^{DEP}$CAAC–Ru complexes **Ru-3c**, **g–i** and catechodithiolate **Ru-4c**. [a]Isolated yield after preparative chiral resolution. [b]Determined by chiral-stationary phase HPLC analysis.

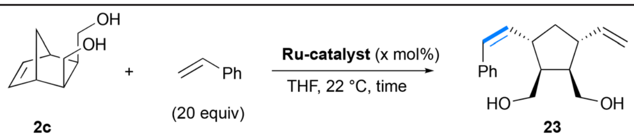
complexes proved to be too unstable in solution to be isolated.[7h] Gratifyingly by capitalizing on recent results from our lab,[9] we confirmed that (*R*)-**Ru-4c** can be generated *in situ* (IS) promoting the AROCM with the same efficiency (entry 3 *vs.* 2). Under similar conditions, we observed faster reactivity with nitro-Grela IS (+)-(*R*)-**Ru-4g–i** affording full conversion within 30 min. In all cases, (*Z*)-**23** was exclusively formed with similar levels of enantioselectivity, meanwhile the highest isolated yield (44%, entry 5) was obtained with IS (+)-(*R*)-**Ru-4h** featuring a 2-napthyl at the chiral quaternary center.

Having identified *in situ* generated (+)-(*R*)-**Ru-4h** as the most efficient *Z*-enantioselective CAAC–Ru catalyst, we evaluated its scope across a broad range of substrates (Scheme 5). AROCM products **4–8** and **24–26** were formed in excellent *Z*-selectivity ranging from 95 : 5 to 99 : 1 *Z*/*E* ratio, except for **27** and **28** for which the starting-material was recovered despite a higher catalyst loading and/or a prolongated reaction time. The highest enantioselectivities (82 : 18 to 83 : 17 er) were reached with *exo*-norbornenes featuring an anhydride or a succinimide function, leading respectively to *trans* cyclopentanes **4–5** and **6–7** with 56–83% isolated yield. A drop in enantioselectivity was observed with protected diols reacting with styrene (**24–26**; 64.5 : 35.5 to 75 : 25 er), although these ers remain higher than in previous reports.[22] Finally, a similar level of enantioselectivity was also observed with 1-decene as cross-olefin partner (**10**; 72.5 : 27.5 er).

## Conclusions

In summary, we have developed the first *Z*-stereoselective catechodithiolate ruthenium complexes containing cyclic(alkyl)(amino)carbene ligands. Amongst a selection of CAAC Ru-complexes, $^{DEP}$CAAC **Ru-4b** and $^{DIPP}$CAAC **Ru-4d** have proven to be efficient toward the formation of *Z*-internal olefins. Moderate to good yields and remarkable *Z*-selectivity (>98%) were obtained in various ROMP, CM and ROCM transformations. Notably, the resulting polymers from norbornene **2a** and norbornadiene **2b** were formed with good to excellent syndiotacticity (75 to >95%), surpassing that of NHC-based catechodithiolate Ru-catalysts. Additionally, thanks to the efficient and rapid access to optically pure CAAC Ru-complexes (>98.5% ee), the first synthesis of enantiopure catechodithiolate $^{DEP}$CAAC–Ru complexes was also achieved. Isolated or formed *in situ*, those new chiral *Z*-selective catalysts demonstrated good catalytic performances in *Z*-enantioselective ROCMs involving reluctant *exo*-norbornene derivatives (up to 99 : 1 *Z* : *E* ratio; and up to 83 : 17 er). Further works dealing with the

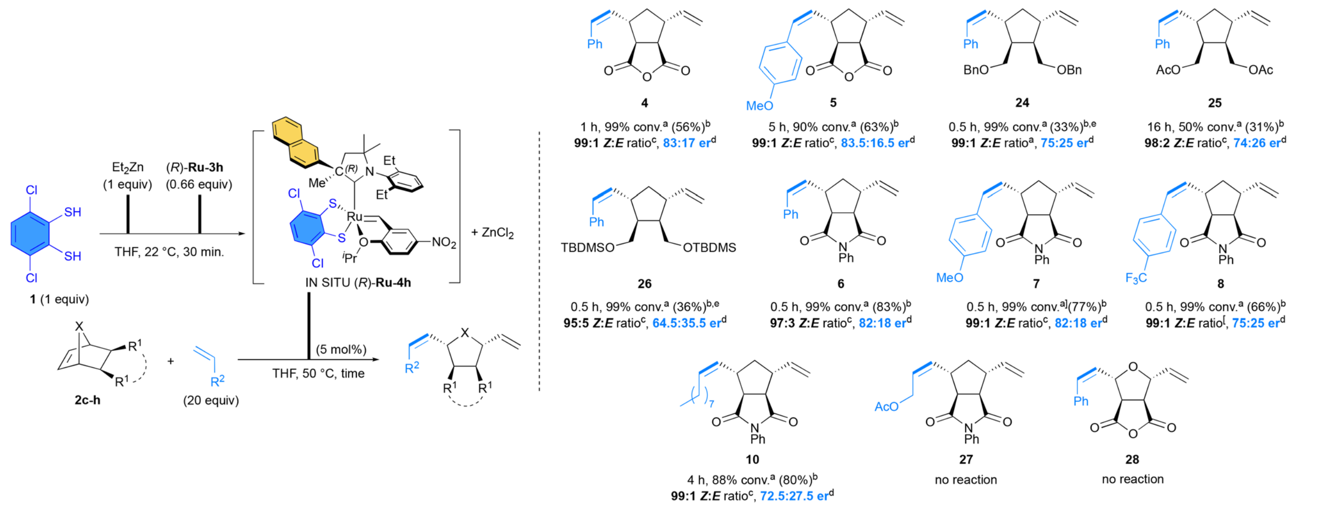
**Table 3** Evaluation of optically pure $^{DEP}$CAAC Ru-complexes **Ru-3c** and catechodithiolate **Ru-4c**, **g–f** in *Z*-enantioselective ROCM of norbornene **2c**




**2c** **23**

| Entry | Catalyst (mol%) | Time (h) | Conv.[a] (%) (yield)[b] | *Z* : *E* ratio[c] | er (*Z*)-**23**[d] |
|---|---|---|---|---|---|
| 1 | (*R*)-**Ru-3c** (1) | 2 | 99 (29) | 65 : 35 | 76 : 24[e] |
| 2 | (*R*)-**Ru-4c** (5) | 2 | 99 (26) | 99 : 1 | 78 : 22 |
| 3[f] | IS (*R*)-**Ru-4c** (5) | 2 | 99 (26) | 99 : 1 | 77.5 : 22.5 |
| 4[f] | IS (*R*)-**Ru-4g** (5) | 0.5 | 99 (20) | 99 : 1 | 77.5 : 22.5 |
| 5[f] | IS (*R*)-**Ru-4h** (5) | 0.5 | **99 (44)** | **99 : 1** | **78.5 : 21.5** |
| 6[f] | IS (*R*)-**Ru-4i** (5) | 0.5 | 99 (31) | 99 : 1 | 78 : 22 |

[a] Conversions were determined by $^{1}$H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. [b] Isolated yield. [c] Determined by GC analysis. [d] Determined by HPLC analysis on chiral phase. [e] er for (*E*)-**23**: 69.5 : 30.5. [f] The catechodithiolate catalyst was generated *in situ* by reacting **1** with $Et_2Zn$ followed by the addition of respective (*R*)-**Ru-3** (see Scheme 5 and ESI† for details).



Scheme 5 Scope of $Z$-enantioselective ROCM catalysed by *in situ* (IS) generated optically pure catechodithiolate $^{DEP}$CAAC–**Ru-4h**. [a]Determined by $^1$H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. [b]Isolated yield. [c]Determined by GC analysis. [d]Determined by HPLC analysis on chiral phase. [e]The corresponding polymer was also formed as by-product.

modification of the catechodithiolate ligand[17a] for improving the catalyst efficiency toward ACM reactions as well as the continuous flow synthesis of enantioenriched $Z$-alkenes are underway and will be reported soon.[26]

## Data availability

All experimental and crystallographic data associated with this work are available in the ESI.‡

## Author contributions

G. B., R. J. and M. M. conceived, designed and directed the project. J. M., F. V., J. L. and J. T. conducted all the experiments. N. V. performed the chiral resolution of complexes. T. V. developed GC analysis methods while T. R. accomplished of X-ray diffraction analysis. The manuscript was written and reviewed by R. J. and M. M. The ESI‡ was written by J. M.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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with CAAC–**Ru-4** complexes could result from a lower steric repulsion between the catechodithiolate fragment and CAAC ligands.

19 *Endo*-Norbornene derivatives were also investigated but only starting materials were recovered. We suspected an important steric clash occurred avoiding the approach of CAAC–**Ru-4** to the substrate.

20 Prolonged reaction times could be detrimental to the *Z*-selectivity with cyclometalated Ru-catalyst **Ru-2** but never with catechodithiolate Ru-complexes, see: A. Dumas, R. Tarrieu, T. Vives, T. Roisnel, V. Dorcet, O. Baslé and M. Mauduit, *ACS Catal.*, 2018, **8**, 3257.

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