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Synthesis of a novel class of chiral *N*,*N*,*N*-tridentate pyridinebisimidazoline ligands and their application in Ru-catalyzed asymmetric epoxidations

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Abstract—A new class of easily tunable *N*,*N*,*N*-pyridinebisimidazoline (pybim) ligands have been synthesized. The synthesis and tunability of these chiral tridentate ligands are much easier and flexible compared to the popular pyboxes, making the former a suitable ligand tool box for various asymmetric transformations. Ruthenium complexes of the new ligands were synthesized and applied in the asymmetric epoxidation of olefins using hydrogen peroxide as the oxidant. Excellent yields and moderate to good enantioselectivities were achieved in the epoxidation of aromatic olefins.

1. Introduction

Asymmetric synthesis continues to be an important area of research in organic chemistry due to the special properties of enantiomerically pure compounds, which are the focus of modern pharmaceutical industry.[1] Among the different methods available, transition metal-catalyzed asymmetric reactions offer an efficient and elegant way for the synthesis of pure enantiomers.[2] Generally, the design and synthesis of a chiral controller ligand is the most critical step in the development of a new catalyst for asymmetric reactions. A wide variety of chiral mono-, bi- and multidentate ligands with *P*, *N*, *O* and other coordinating atoms are now available and used extensively for all kinds of catalytic reactions. Prominent examples of the so-called privileged ligand classes include salens,[3] bisoxazolines,[4] phosphinooxazolines,[5] tartrate derivatives[6] and cinchona alkaloids.[7] However, there is still an increasing demand for new and improved ligands. State-of-the-art chiral ligands[8] should offer the user a series of advantages: obviously it should give a highly selective, active and productive catalyst. Moreover, the ligand should be prepared conveniently and economically from a mg- to kg-scale. Unfortunately, each catalytic reaction needs its own optimized ligand. To find a suitable optimal catalyst for a specific reaction, a library of ligands having a basic core skeleton amenable for easy functionalization should be conceivable without much difficulty. However, the systematic modification of a structure of new ligands is often difficult and time consuming.

In this context, we designed a new chiral ligand scaffold, which could be efficiently synthesized and easily functionalized.[9] Herein, we report the synthesis of a library of a new class of chiral ligands by easy functionalization of a basic skeleton, along with the application of these ligands in the Ru-catalyzed asymmetric epoxidation of olefins. The effect of acids as additives in these reactions is also demonstrated.

The starting point of this work was our studies on ruthenium-catalyzed epoxidation of olefins with C_2-symmetric pyridinebisoxazolines (pybox) as the chiral ligand.[10] During the study of the pybox ligands, we came to realize that the synthesis of a library of pybox ligands is limited and time consuming, due to the difficulty of functionalization of the ligand backbone and step-wise formation of the oxazoline moiety.[11]

To circumvent this problem, we thought of replacing the oxygen atoms in pybox by nitrogens, which gives the

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advantage of functionalization at nitrogen in an easy manner; thus allowing the synthesis of a library of ligands from a basic skeleton by N-alkylation, N-arylation, N-acylation, etc. to vary the reactivity as well as the selectivity in catalytic asymmetric reactions (Fig. 1). Although pyboxes are extensively used in stereoselective reactions,[12] to the best of our knowledge, analogous chiral pyridinebisimidazoline ligands, here abbreviated as pybim, have not been synthesized and applied in asymmetric catalysis prior to our work.[9]

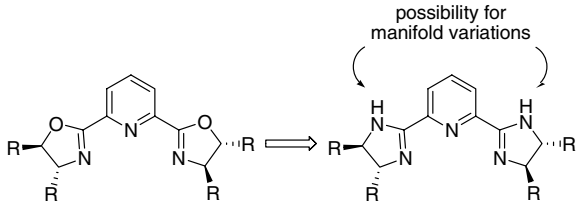


Figure 1. Design of pybim from pybox ligands.

2. Results and discussion

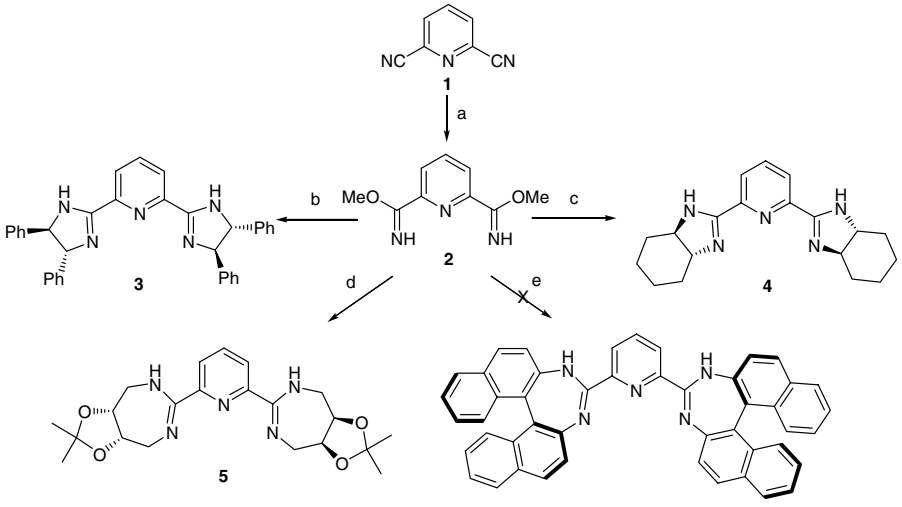
Bisimidate **2** was easily prepared by stirring the commercially available 2,6-pyridinedinitrile **1** with a catalytic amount of sodium in anhydrous methanol at room temperature, followed by neutralization with acetic acid and subsequent removal of the solvent (Scheme 1).[13] Reaction of bisimidate **2** with diamines should give the cyclic diimine derivatives. Thus, treatment of **2** with (*R*,*R*)-1,2-diphenylethylenediamine or (*R*,*R*)-1,2-diaminocyclohexane smoothly afforded the corresponding pyridine–bisimidazoline derivatives (pybims) **3** and **4** in 84% and 95% yield, respectively, by refluxing in dichloromethane.

Interestingly, the related pyridinebisdiazepine **5** could be also synthesized by reaction of **2** with (4*S*,5*R*)-4,5-di-(aminomethyl)-2,2-dimethyl dioxolane. To the best of our knowledge, this is the first example of a chiral pyridinebisdiazepine. However, the preparation of the corresponding bisbinaphthyl derivative failed, presumably due to the greater strain in forming this benzoanellated seven-membered ring (see Scheme 1).

Next, pybims **3** and **4** were taken for further studies due to their stability in air and moisture, efficient formation and scope for easy derivatization. Notably, the synthesis of **3**, has been performed on 10 g scale without any problems and purification is possible by crystallization.[9,14] The presence of two secondary amino groups on the pybims, which are amenable for easy functionalization, allows for the formation of a library of compounds easily from a single basic skeleton, which is not possible in the popular pybox ligands. Thus, 29 ligands were prepared by coupling pybims **3** and **4** with a variety of reagents, such as acid chlorides, chloroformates and sulfonyl chlorides, etc.

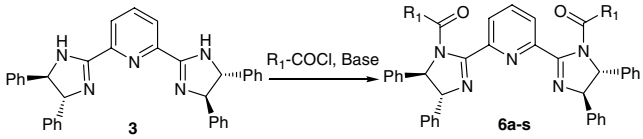
Initially, we prepared a series of amide derivatives of **3** by reaction with acid chlorides in the presence of a base in dichloromethane at room temperature (Table 1). After screening bases, such as NaH, KO^{t}Bu, triethylamine, pyridine, 4-dimethylaminopyridine (DMAP), etc., we found that DMAP was the most suitable for this reaction.

Hence, reaction of tetraphenyl pybim **3** with benzoyl chloride in the presence of DMAP in dichloromethane at room temperature furnished, after column chromatography, dibenzoyl pybim **6a** as a white solid in 96% yield. The ^{1}H NMR spectrum of **6a** showed doublets at δ 5.15 and 5.19 with a coupling constant of 3.40 Hz corresponding to the two pairs of mutually coupled vicinal protons on the imidazoline rings. The aromatic protons of the phenyl groups were observed at δ 7.02–7.43 as multiplets and those of the pyridine rings were observed at δ 7.73 as doublet of a doublet and at δ 7.83 as doublet.



Scheme 1. Reagents and conditions: (a) Na (10 mol %), MeOH, rt; (b) (1*R*,2*R*)-diphenylethylenediamine, CH_2Cl_2, 50 °C; (c) (1*R*,2*R*)-diaminocyclohexane, CH_2Cl_2, 50 °C; (d) (4*S*,5*S*)-4,5-diaminomethyl-2,2-dimethyldioxolane, CH_2Cl_2, 50 °C; (e) (*R*)-2,2-diamino-1,1-binaphthyl, CH_2Cl_2, 50 °C.

Table 1. Synthesis of *N*-acyl-protected pybims from acid chlorides



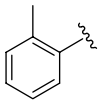
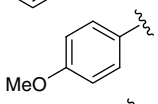
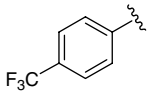
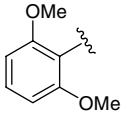
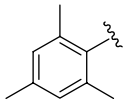
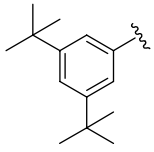
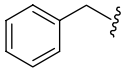
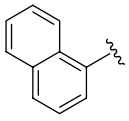
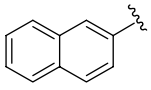
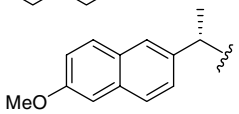
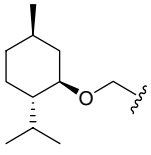
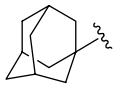
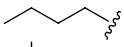
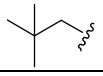
Entry	R_1	Ligand	Yield (%)[a]
1		**6a**	96
2		**6b**	99
3		**6c**	87
4		**6d**	97
5		**6e**	47
6		**6f**	45[b]
7		**6g**	32
8		**6h**	87
9		**6i**	100
10		**6j**	94
11		**6k**	76
12		**6l**	62
13		**6m**	92
14		**6n**	96
15		**6o**	86

Table 1 (*continued*)

Entry	R_1	Ligand	Yield (%)[a]
16		**6p**	93
17		**6q**	92
18		**6r**	93
19		**6s**	83

Reagents and conditions:
[a] DMAP (3 equiv), CH_2Cl_2, rt, 1–5 h.
[b] NaH (3 equiv), PhCl, reflux, 45 h.

The ^{13}C NMR spectra showed two peaks at δ 60.4 and 71.9, corresponding to the two pairs of symmetrical benzylic carbons on the imidazoline rings. The aromatic carbons and the imino carbon on the imidazoline were distributed from δ 125.5–139.4, while the amide carbon was observed at δ 169.3. The IR spectrum showed the characteristics of an amide carbonyl stretching vibration with an absorption at 1670 cm^{-1}. EI-MS showed a molecular mass peak at 728 (M^+), which was further supported by HRMS.

Using the above reaction conditions, ligands **6b**–**s** were prepared with a variety of substitution pattern, such as mono-, di- and tri-substituted aryls, 1- and 2-naphthyls, adamantyl and various alkyl groups (see Table 1). In the case of the trimethylbenzoyl derivative **6f**, reacting the trimethylbenzoyl chloride with **3** in refluxing chlorobenzene in the presence of NaH was necessary to furnish the product in good yield (Table 1, entry 6). For the (*S*)-methoxy-α-methyl-2-naphthalene acetyl derivative **6l**, the chloride required for the reaction was prepared in situ from the corresponding acid with excess of thionyl chloride in refluxing chloroform (Table 1, entry 12).

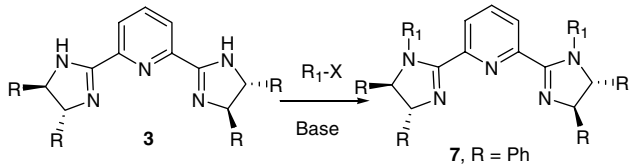
Next, we tried acylation with aliphatic carboxylic acid derivatives. Menthyl- and adamantyl-derived pybims **6m** and **6n** were formed in excellent yields. Less bulky aliphatic carboxylic acids formed the corresponding *N*-acyl pybims also in excellent yields (Table 1, entries 15–18). Protecting the –NH groups of **3** with trimethylacetyl chloride met with defeat obviously due to steric reasons. However, *tert*-butylacetyl chloride reacted smoothly, affording **6s** in 83% yield (Table 1, entry 19).

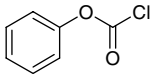
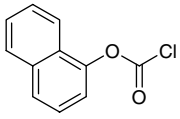
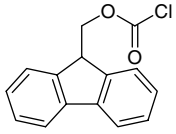
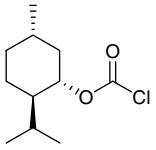
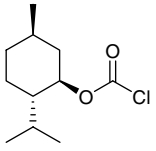
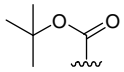
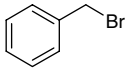
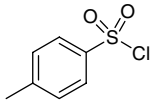
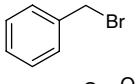
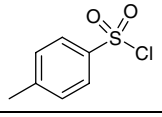
We then reacted **3** with chloroformates. Thus, by following the above procedure, a series of carbamates **7a**–**f** was prepared in excellent yields (Table 2). The reaction was found to be fast compared to that of acid chlorides. In addition, **7f** was prepared by reaction of **3** with di-*tert*-butyldicarbonate in the presence of DMAP at room temperature (Table 2, entry 6). To vary the substituent pattern of the pybim scaffold further, we reacted benzyl bromide and tosyl chloride with **3**, which afforded **7g** and **7h** in 65% and 85% yield, respectively (Table 2, entries 7 and 8).

Similar to **3**, reaction of dicyclohexyl pybim **4** with benzyl bromide and *p*-tosyl chloride gave products **8a** and

8b in good yield (Table 2, entries 9 and 10). However, reactions of **4** with benzoyl chloride, *p*-methoxy benzoyl chloride and (−)-menthyl chloroformate were unsuccessful due to the instability of the products during column chromatography. The reason for this is not clear.

Table 2. Synthesis of N-protected pybims from chloroformates and other halides



Entry	R_1-X	Ligand	Yield (%)[a]
1		**7a**	98
2		**7b**	84
3		**7c**	94
4		**7d**	90
5		**7e**	94
6		**7f**	91[b]
7		**7g**	65[c]
8		**7h**	85
9		**8a**	68[c]
10		**8b**	93

Reagents and conditions:
[a] DMAP (3 equiv), CH_2Cl_2, rt, 1 h.
[b] $(Boc)_2O$ (3 equiv), DMAP, (3 equiv), CH_2Cl_2, rt, 12 h.
[c] NaH (2.5 equiv), THF, rt, 4 h.

Attempts were also made to prepare urea derivatives of the pybim by reaction of **3** with phenylisocyanate in the presence of various bases and also using dibutyltindilaurate,[15] which resulted only in the trimerization of phenylisocyanate.

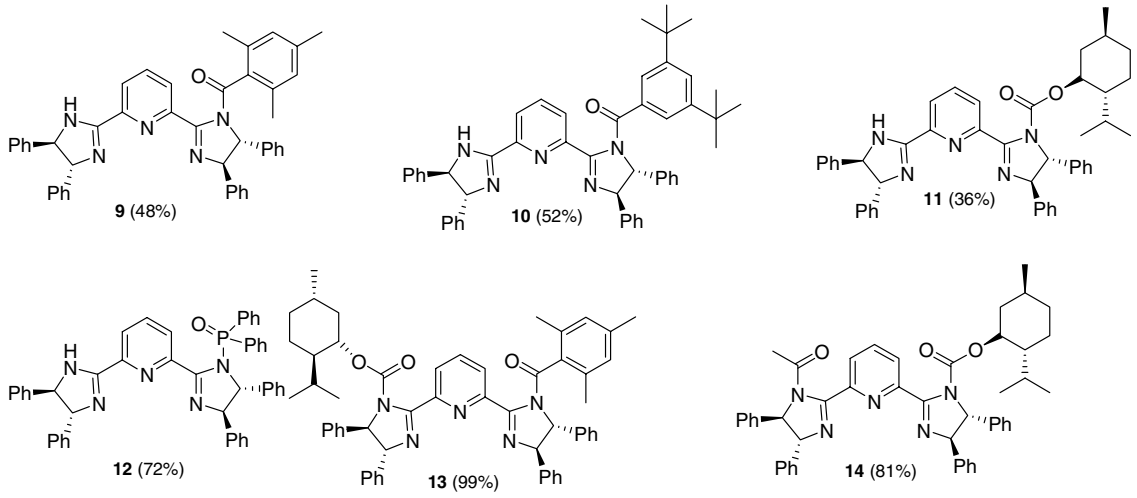
All new compounds shown were fully characterized (NMR, IR, MS and HRMS or EA) and gave satisfactory analytical data.

During the synthesis of trimethylbenzoyl pybim **6f**, we isolated a considerable amount of the mono-protected pybim **9** (Scheme 2). This prompted us to synthesize a few more mono-protected pybims **10**–**12** by reaction of **3** with 1 equiv of a suitable acid chloride or chloroformate compound. The idea behind this was to also synthesize asymmetrically substituted pybims by reacting the free –NH– of the mono-protected pybim with a second different protecting group.

We presumed that an unsymmetrical complex prepared from such a ligand would direct the substrate (e.g., olefin in epoxidation) to occupy a specific orientation in the transition state and thereby induce selectivity during catalysis. With this in mind, compounds **13** and **14** were synthesized from the mono-protected pybims **9** and **11** with (+)-menthyl chloroformate and acetyl chloride, respectively. Unfortunately, an attempted one-pot sequential protection of the two amino groups of **3** by different protecting groups was unsuccessful since it produced an inseparable mixture of products.

With a library of pybims in hand, we searched for a suitable reaction to test the usefulness of these ligands in catalysis. Clearly, it was an objective to demonstrate that the substitution of an imidazoline –NH group had a significant impact on catalysis. Due to the structural analogy of the pybim ligands to the pyboxes, it was reasonable to believe that any reaction that is catalyzed by metal pybox complexes should also be suitable for pybims as well. Hence, pybims should act as suitable ligands for aziridination, epoxidation, carbene reactions, addition of nucleophiles to carbonyl groups, etc.[12] Amongst the many catalytic reactions known for pyboxes, we selected asymmetric epoxidation using hydrogen peroxide for our studies since we were recently involved in investigating this type of reaction.[10d,16]

Consequently, we decided to investigate the behaviour of the new ligands in the Ru-catalyzed asymmetric epoxidation[9,17] of styrene and *trans*-stilbene with H_2O_2. For this purpose, ligand **6a** was reacted with $[Ru(p\text{-cymene})Cl_2]_2$ and disodium pyridine-2,6-dicarboxylate (pydic) in MeOH–H_2O mixture at 65 °C to afford, after purification by column chromatography, the dark brown solid **15a** in good yield (Table 3, entry 1).[18] The ^1H NMR of **15a** showed two doublets at δ 4.42 and 5.15 for two protons each corresponding to the mutually coupled protons of the imidazoline rings. The aromatic protons of the four phenyl groups and those from the pyridine dicarboxylate ring were distributed from δ 6.56–7.65. The three mutually coupled protons of the pyridine ring of the pybim moiety resonated at δ 7.73 as a triplet and at δ 8.22 as a doublet ($J = 8.10$ Hz).



Scheme 2. Unsymmetrical pybim ligands.

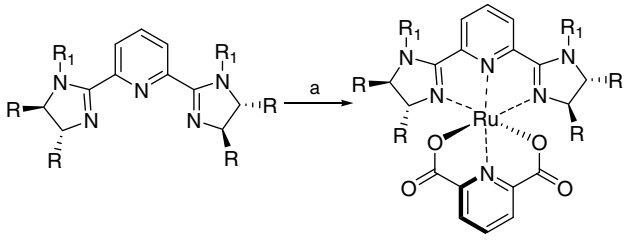
In the ^{13}C NMR, the two symmetrical benzylic carbon atoms on the imidazoline rings were seen at δ 74.1 and 77.5 while the two carbonyls were observed at δ 170.2 and 170.4. Mass spectrum and elemental analysis were in agreement with the structure assigned.

In a similar manner, Ru (pybim)(pydic) complexes **15b**–**s**, **16a**–**h** and **17a**,**b** were prepared in good to excellent yields (Table 3). All compounds were fully characterized and gave satisfactory spectral and analytical data. Due to the presence of a large hydrocarbon skeleton, the di-*tert*-butylbenzoyl ligand **6g** and the Fmoc-derived ligand **7c** were sparingly soluble in MeOH and therefore modification of the general reaction condition was needed to prepare the corresponding ruthenium complexes **15g** and **16c**. Thus, in the case of **6g**, the complexation was performed in a mixture of 12:5:1 *tert*-amyl-OH/MeOH/H_2O, which afforded complex **15g** in acceptable yields (Table 3, entry 7). Formation of **16c** was achieved in 59% yield by using a mixture of 4:4:1 *n*-BuOH/MeOH/H_2O as the solvent system. Unsymmetrical ligands **12**–**14** were also transformed into their respective ruthenium complexes **18**–**20** by following the general complexation procedure in good yields without any difficulty (Scheme 3).

We mentioned earlier that the synthesis of pybim ligands **4** is sometimes difficult due to their unstable nature during purification by silica gel and alumina column chromatography. We circumvented this problem by reacting **4** with the appropriate acid chlorides or chloroformates and subjecting the crude product directly to complexation with a ruthenium source and Na_2pydic. In this way, we were able to prepare ruthenium complexes **21**–**23** (Scheme 4).

With a number of Ru(pybim)(pydic) complexes in hand, we tested the asymmetric epoxidation of styrene and *trans*-stilbene using H_2O_2 as the oxidant. For the catalysis experiments, we chose the reaction conditions, which we developed earlier for the epoxidation of olefins using pybox ligands (rt, 3 equiv of H_2O_2 (30% in water) were slowly dosed into the reaction mixture by a syringe pump).[10d]

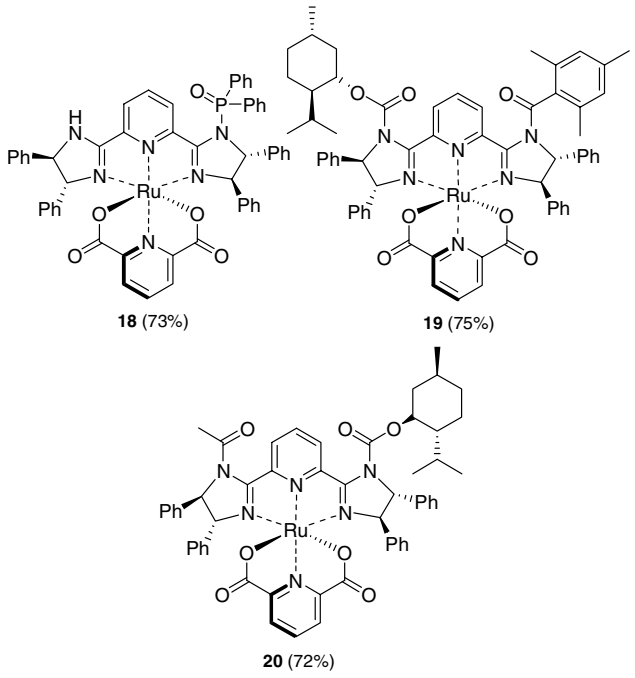
Table 3. Synthesis of Ru(pybim)(pydic) complexes



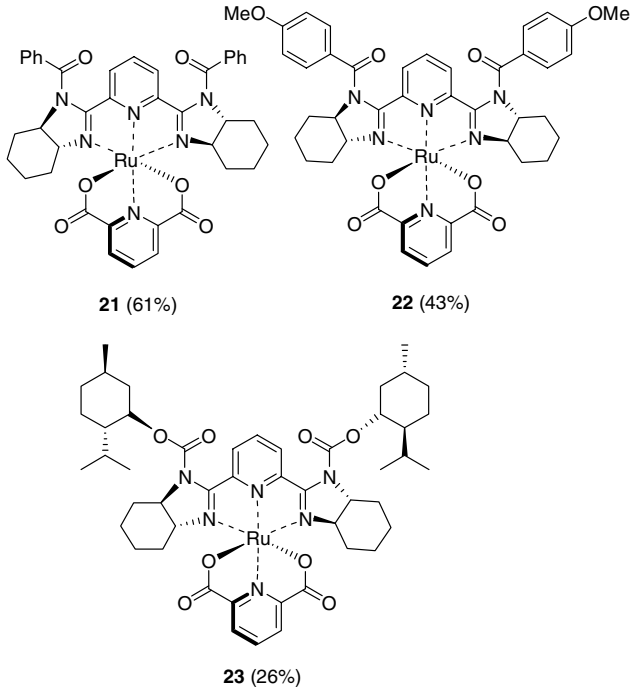
6a-s: R = Ph, For R_1 seeTable 1 — **15a-s**
7a-h: R = Ph, For R_1 seeTable 2 — **16a-h**
8a, b: R = -$(CH_2)_4$-, For R_1 seeTable 2 — **17a, b**

Reagents and conditions: (a) [Ru(*p*-cymene)$Cl_2]_2$, Na_2pydic, MeOH, H_2O, 65 °C, 1 h.

Entry	Ligand	Complex	Yield (%)
1	**6a**	**15a**	56
2	**6b**	**15b**	93
3	**6c**	**15c**	75
4	**6d**	**15d**	71
5	**6e**	**15e**	42
6	**6f**	**15f**	59
7	**6g**	**15g**	43
8	**6h**	**15h**	30
9	**6i**	**15i**	49
10	**6j**	**15j**	40
11	**6k**	**15k**	64
12	**6l**	**15l**	78
13	**6m**	**15m**	46
14	**6n**	**15n**	66
15	**6o**	**15o**	68
16	**6p**	**15p**	75
17	**6q**	**15q**	98
18	**6r**	**15r**	77
19	**6s**	**15s**	77
20	**7a**	**16a**	52
21	**7b**	**16b**	33
22	**7c**	**16c**	60
23	**7d**	**16d**	52
24	**7e**	**16e**	58
25	**7f**	**16f**	77
26	**7g**	**16g**	45
27	**7h**	**16h**	50
28	**8a**	**17a**	55
29	**8b**	**17b**	55



Scheme 3. Unsymmetrical Ru(pybim)(pydic) complexes.



Scheme 4. In situ generation of ruthenium complexes **21**–**23**.

To find the optimum catalyst concentration, the epoxidation of styrene was performed using **16d** with varying catalyst loading. It was observed that full conversion and best yield were obtained in the presence of 5 mol % of catalyst (Fig. 2). This catalyst loading was used throughout our studies.

Next, all the complexes prepared were screened for the asymmetric epoxidation of styrene and *trans*-stilbene

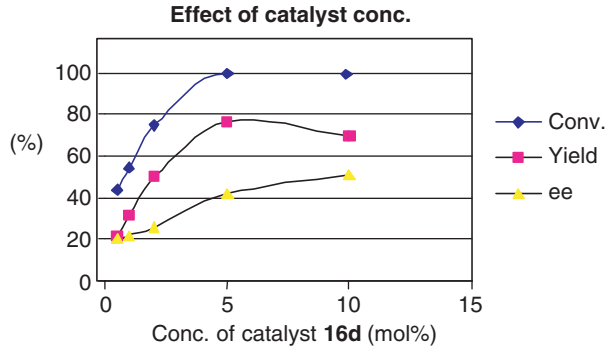


Figure 2. Effect of concentration of catalyst **16d** on the epoxidation of styrene.

and the results are shown in Table 4. Almost all complexes studied gave full conversion. However, it is important to note that the chemo- and enantioselectivity of the catalyst are dependent on the respective substituent on the nitrogen of the imidazoline ring (remote functionality) of the Ru(pybim)(pydic) complex. Although a rationalization on the electronic and/or steric influence of the substituent at the nitrogen of the imidazoline ring is difficult on the basis of the catalysis results depicted in Table 4, certain groups such as the 2-naphthyl, menthyl, etc. can be identified as potential substituents for the control of enantioselectivity.

In the case of styrene epoxidation, the yield of the product varied from 65% to 75% for benzoyl-protected pybims **15a**–**l**, while that for aliphatic *N*-acyl-protected pybims **15n**–**s** showed a small increment (80–85%) (Table 4, entries 1–12 and 14–19). The carbamate complexes **16a**–**f** showed similar reactivities towards styrene (70–80%) and *trans*-stilbene (87–100%); but the enantioselectivities varied. To our delight, the dimethoxybenzoyl pybim complex **15e** and the menthyl carbamate complex **16d** showed the highest enantioselectivities (45% and 43%) for styrene (Table 4, entries 5 and 23), which is one of the most difficult substrates for epoxidation using H_2O_2 and often found in the literature with low yields and enantioselectivities.[19]

Due to the better reactivity of *trans*-stilbene, most of the complexes gave excellent yields with this substrate. Moreover, the enantioselectivities observed were also good. Notable are the performances of **15e**, **15i** and **15j** in the category of benzoyl-derived pybims and **16b**, **16d** and **16e** in the category of carbamate-functionalized pybims (Table 4, entries 5, 9, 10, 21, 23 and 24). In general, the carbamate-derived complexes gave better enantioselectivities both in styrene and *trans*-stilbene epoxidation.

All the complexes derived from **4** showed poor performances in both reactivity and enantioselectivity (Table 4, entries 28, 29, and 31–35). The unsymmetrical pybim complex **19**, which had a menthyl group on one side of the pybim and a trimethylbenzoyl group at the other, showed enantioselectivities comparable to those observed for complex **16d** (Table 4, entry 31 vs 23). The enantioselectivities observed for **15e** for styrene (45%)

Table 4. Ru(pybim)(pydic)-catalyzed asymmetric epoxidation of styrene and *trans*-stilbene using H_2O_2 as the oxidant[a]

Entry	Catalyst	Ph				Ph Ph			
		Time (h)	Conv. (%)	Yield (%)	ee (%)	Time (h)	Conv. (%)	Yield (%)	ee (%)
1	**15a**	12	100	64	15	12	100	90	34
2	**15b**	12	100	75	25	12	100	99	52
3	**15c**	12	100	78	1	12	100	99	38
4	**15d**	12	100	63	7	12	100	78	33
5	**15e**	12	100	77	**45**	16	92	84	46
6	**15f**	16	84	63	22	16	46	32	45
7	**15g**	12	100	67	18	12	100	96	40
8	**15h**	12	100	74	16	16	88	87	34
9	**15i**	12	100	70	32	12	100	95	70
10	**15j**	16	100	67	21	12	100	91	56
11	**15k**	12	100	76	6	12	100	99	43
12	**15l**	16	100	71	29	12	100	94	69
13	**15m**	12	100	67	23	12	100	90	39
14	**15n**	12	100	83	8	12	100	97	28
15	**15o**	12	100	84	20	12	100	97	51
16	**15p**	12	100	80	26	12	100	100	54
17	**15q**	12	100	85	28	12	100	100	52
18	**15r**	16	96	80	31	12	100	90	61
19	**15s**	12	100	80	30	12	100	100	66
20	**16a**	12	100	71	15	12	100	95	60
21	**16b**	12	100	77	26	12	100	99	**71**
22	**16c**	12	100	78	34	12	100	97	59
23	**16d**	12	100	72	**43**	12	100	97	**71**
24	**16e**	12	92	78	37	12	100	97	69
25	**16f**	12	100	77	13	16	94	87	59
26	**16g**	—	—	—	—	16	90	79	11
27	**16h**	12	100	73	17	16	77	63	21
28	**17a**	12	81	55	2	16	85	79	1
29	**17b**	12	100	63	31	12	100	93	8
30	**18**	12	100	70	6	12	100	93	39
31	**19**	12	100	68	**42**	12	100	93	**71**
32	**20**	12	100	86	34	12	100	100	57
33	**21**	16	87	67	3	16	98	93	5
34	**22**	16	88	64	3	12	100	93	7
35	**23**	16	94	61	9	16	94	90	7

[a] Reaction conditions: 0.5 mmol of olefin in *tert*-amyl alcohol (9 mL) was oxidized in the presence of 5 mol % Ru-catalyst using 1.5 mmol (170 μL) of H_2O_2 (30% in water) in *tert*-amyl alcohol (830 μL) by a syringe pump over a period of 12 h.

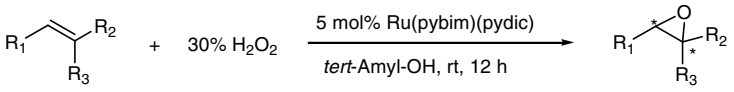
and **16d** for *trans*-stilbene (71%) are comparable to the highest values reported so far in the literature for the asymmetric epoxidation using H_2O_2 as oxidant.[10d] In addition, the reactivities of pybim complexes are comparable to that of pyboxes in the epoxidation of styrene and *trans*-stilbene. Interestingly, the sterically bulky and flexible (*S*)-methoxy-α-methyl-2-naphthalene acetyl complex **15l** gave 69% ee for *trans*-stilbene epoxide (Table 4, entry 12).

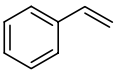
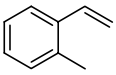
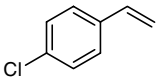
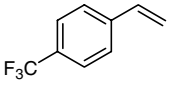
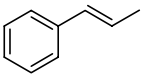
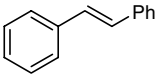
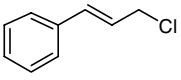
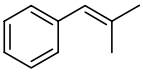
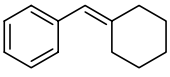
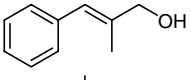
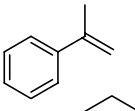
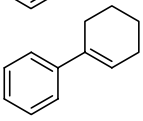
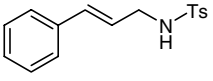
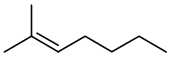
Next, we tested the scope of the catalysts in the epoxidation of other olefins. For this purpose, we selected complexes **16b** and **16d**, and applied them in the epoxidation of a variety of substrates. The results are shown in Table 5. To our delight, mono-, di- and tri-substituted aromatic olefins gave excellent yields (up to 100%) and moderate to good enantioselectivities (see Table 5). Electron donating/withdrawing groups on the aromatic ring of styrene did not influence much either the reactivity or enantioselectivity (Table 5, entries 1–4). Excellent reactivities and enantioselectivities were obtained with both complexes **16b** and **16d** when β-substituted styrenes were used as the substrates (Table 5, entries 5, 6, 8 and 9). However, α-substituted styrenes gave poor enantioselectivities (entries 11 and 12). Epoxidation of *N*-tosylcinnamylamine (Table 5, entry 13) using catalysts **16b** and **16d** gave very low ee (1–3%) and the epoxide was found to be unstable in the GC column and thus a reliable data on yield and selectivity could not be obtained.

Finally, we studied the epoxidation of styrene with **16d** in the presence of varying concentrations of acetic acid as the additive. The use of acids for the enhancement of efficiency of metal-catalyzed reactions is known in the literature and the reason for such enhancements can be attributed to the stabilization of the complex under the reaction conditions.[20] However, the results revealed that acetic acid had no significant influence on the conversion, yield or ee of the epoxidation of styrene (Table 6).

Other carboxylic acids, such as trifluoroacetic acid, benzoic acid, *p*-methoxy- and *p*-chloro-benzoic acids, were also tested. Trifluoroacetic acid showed a marginal

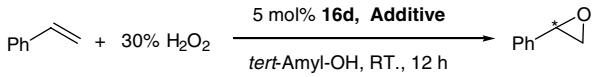
Table 5. Scope and limitations of the Ru(pybim)(pydic) catalysts in asymmetric epoxidation



Entry	Substrate	16b				16d			
		Conv. (%)	Yield (%)	Selec.[a] (%)	ee (%)	Conv. (%)	Yield (%)	Selec.[a] (%)	ee (%)
1		100	77	77	26	100	76	76	42
2		100	68	68	23	100	88	88	43
3		100	72	72	31	100	68	68	50
4		78	50	64	28	68	60	88	42
5		100	100	100	56	100	100	100	65
6		100	100	100	71	100	97	97	71
7		70	52	74	23	90	71	79	23
8		100	79	79	62	100	82	82	68
9		100	100	100	58	100	100	100	54
10		100	47	47	11	100	47	47	7
11		100	69	69	2	100	55	55	1
12		100	73	73	3	100	72	72	0
13		100	—	—	5	100	—	—	2
14		—	—	—	—	100	76	76	n.d.

[a] Selectivity refers to the ratio of yield to conversion in percentage.

Table 6. Effect of additives on the epoxidation of styrene



HOAc (mol%)	Conv. (%)	Yield (%)	ee (%)	Additive (20 mol %)	Conv. (%)	Yield (%)	ee (%)
0	100	76	42	CH_3COOH	100	76	42
2.5	100	71	45	CF_3COOH	100	54	32
5.0	100	72	43	PhCOOH	100	72	43
10.0	100	72	44	4-MeO-$C_6H_4CO_2H$	100	71	44
20.0	100	73	42	4-Cl-$C_6H_4CO_2H$	100	75	42

decrease in yield and ee while all other acids showed no appreciable influence.

Considering the parallels between pyboxes and pybims in their structure, reactivity and enantioselectivity in epoxidation reactions, a mechanistic pathway similar to that proposed for Ru(pybox)(pydic) involving a ruthenium dioxocomplex[10d] as the active species was envisaged for the pybim-catalyzed epoxidation.

3. Conclusion

We have designed and synthesized a new class of easily tunable pyridinebisimidazoline ligands (pybim). The tunability of these ligands is much higher compared to that of the structurally related pybox ligands. The ligands were easily transformed into Ru(pybim)(pydic) complexes and applied in the catalytic asymmetric epoxidation of styrene and *trans*-stilbene. The newly developed pybim complexes showed comparable reactivities and enantioselectivities to those obtained by using pybox complexes. The scope and limitations of the complexes were investigated on the asymmetric epoxidation of a variety of olefins.

The facile synthesis of the pybim ligands together with their easy tunability makes them a suitable toolbox for application to numerous other catalytic asymmetric reactions.

4. Experimental

4.1. General

All reagents were used as purchased from commercial suppliers without further purification. Solvents were dried and purified by conventional methods prior to use. Melting points were determined on a Leica galen III melting point apparatus and were uncorrected. Optical rotations were measured with a Perkin–Elmer (model 241MC) polarimeter. Column chromatography was carried out using silica gel from Fluka. TLC was performed on Merck 60 F_{254} silica gel plates. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX-400 spectrometer using the solvent as the internal reference. Data are reported as follows: chemical shifts (δ) in parts per million, coupling constants (J) in hertz. Mass spectra were recorded with an AMD 402/3 mass spectrometer. GC analyses were performed with a Hewlett Packard HP 6890 model spectrometer and UV–vis spectra were recorded with a Shimadzu (model UV-1601) spectrophotometer. HPLC analyses were performed with a Hewlett Packard HP 1090 instrument using Chiralcel AD, Chiralcel OB–H, Chiralcel OD, Chiralcel OD-H or Whelk chiral column. Elemental analyses were performed on a CHNS 932 analyzer from Leo company.

4.2. Pyridine-2,6-dicarboximidic acid dimethyl ester 2

To pyridine-2,6-carbodinitrile **1** (5.35 g, 41.5 mmol) in anhydrous MeOH (100 mL), was added metallic Na (120 mg, 5.20 mmol). After stirring for 40 h at room temperature, AcOH (300 μL, 5.25 mmol) was added and the solvent removed under reduced pressure to give **2** as a pale yellow powder (8.50 g, 100 %), which was used without further purification.

4.3. 2,6-Bis-([4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine 3

In a 50 mL oven dried pressure tube, **2** (455 mg, 7.06 mmol) and (*R*,*R*)-1,2-diphenylethylene diamine (1.00 g, 4.70 mmol) were dissolved in dichloromethane (30 mL). The resulting mixture was stirred at refluxing temperature for two days. Then, water (20 mL) was added, the phases separated and the aqueous phase extracted with dichloromethane (2×20 mL). The combined organic layer was dried over Na_2SO_4 and the solvent removed in vacuo to give a light yellow solid, which was purified by silica gel column chromatography to give **3** as a white solid (1.15 g, 95%). $R_f = 0.52$ (CH_2Cl_2/MeOH 10:1); mp = 123–126 °C; $[\alpha]_D^{20} = +112.4$ (c 0.52, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.90 (br s, 4H), 7.22–7.31 (m, 20H), 7.89 (t, $J = 7.8$, 1H), 8.46 (d, $J = 7.8$, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 74.9, 125.5, 127.1, 128.3, 129.2, 136.1, 138.2, 142.9, 162.1; EI-MS: m/z 519 (M^+); Anal. Calcd (%) for $C_{35}H_{29}N_5$: C, 78.19; H, 5.81; N, 13.03. Found: C, 78.20; H, 5.58; N, 13.20.

4.4. 2,6-Bis-([4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine 3

A 100 mL pressure tube was charged with **2** (4.55 g, 23.6 mmol), (*R*,*R*)-1,2-diphenylethylenediamine (10.0 g, 47.1 mmol) and 75 mL of dichloromethane. The resulting mixture was stirred at reflux for two days. To the reaction mixture, 50 mL of water was added and the phases separated; the aqueous phase was extracted with dichloromethane (2×50 mL). The combined organic layers were dried over $MgSO_4$ and the solvent removed in vacuo to give a light yellow solid, which was purified by crystallization (ether/ethyl acetate) to give **3** (7.62 g, 62%).

4.5. 2,6-Bis-([3*aR*,7*aR*]-3a,4,5,6,7,7a-hexahydro-1*H*-benzoimidazol-2-yl)-pyridine 4

A 50 mL oven dried pressure tube was charged with **2** (804 mg, 4.17 mmol), (*R*,*R*)-1,2-diaminocyclohexane (1.00 g, 8.75 mmol) and dichloromethane (40 mL). After the resulting mixture was stirred at refluxing temperature for two days, water (20 mL) was added and the phases separated. The aqueous phase was extracted with dichloromethane (2×20 mL). The combined organic layer was dried over Na_2SO_4 and the solvent removed in vacuo to give a light yellow solid, which was purified by crystallization (ethyl acetate) to give **4** as a white solid (1.12 g, 84%). mp = 320–322 °C; $[\alpha]_D^{20} = +242.4$ (c 0.52, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ (1.34m, 4H), 1.55 (m, 4H), 1.83 (m, 4H), 2.28 (m, 4H), 3.36 (m, 4H) 7.81 (t, $J = 7.3$, 1H), 7.21 (d, $J = 7.3$, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 21.6, 22.9, 30.7, 23.5, 137.3, 147.8, 164.6;

EI-MS: m/z 323 (M^+); Anal. Calcd (%) for $C_{19}H_{25}N_5$: C, 70.76; H, 7.79; N, 21.65. Found: C, 70.32; H, 7.81; N, 21.59.

4.6. (3*aR*,6*Z*,8*aS*)-4,5,8,8a-tetrahydro-6-(6-((*Z*,3*aR*,8*aS*)-4,5,8,8a-tetrahydro-2,2-dimethyl-3a*H*-[1,3]dioxolo[4,5-*e*]-[1,3]diazepin-6-yl)pyridin-2-yl)-2,2-dimethyl-3a*H*-[1,3]dioxolo[4,5-e][1,3]diazepine 5

Compound **5** was prepared as described for the synthesis of **3** using **2** (292 mg, 1.50 mmol), (4*S*,5*R*)-4,5-di-(aminomethyl)-2,2-dimethyl dioxolane (500 mg, 3.10 mmol) and 15 mL of dichloromethane in a pressure tube at 50 °C. After 2 days, the solvents were removed in vacuo to give a light yellow oil, which was purified by column chromatography on neutral alumina to give a white solid (100 mg, 16%). $R_f = 0.75$ (CH_2Cl_2/MeOH 10:1, neutral alumina); mp = 232–234 °C; $[\alpha]_D^{20} = +32.7$ (c 0.21, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.43 (s, 12H), 3.18 (br s, 4H), 3.68 (m, 4H), 3.85 (br s, 4H), 7.77 (t, $J = 7.9$, 1H), 8.29 (d, $J = 7.9$, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.8, 78.8, 80.4, 111.1, 122.4, 137.7, 151.3, 151.9; EI-MS: m/z 415 (M^+); HRMS (ESI+): calcd for $C_{21}H_{29}N_5O_4$: 415.2219. Found: 415.2213.

4.7. General procedure for the synthesis of *N*-acyl-protected pybim ligands (procedure A)

A 50 mL oven dried one necked round bottom flask fitted with a magnetic stirring bar was charged with **3** (208 mg, 0.4 mmol) and DMAP (147 mg, 1.2 mmol) in anhydrous CH_2Cl_2 (15 mL). The mixture was cooled to 0 °C and then acid chloride or chloroformate (1.2 mmol) added dropwise. The cooling bath was removed and the reaction mixture stirred at rt and the progress of the reaction was monitored by TLC. The reaction mixture was then washed with water (2×20 mL), dried over Na_2SO_4, concentrated and purified by column chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent.

4.8. 2,6-Bis-(1-benzoyl-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine 6a

Prepared according to general procedure A using **3** (200 mg, 0.38 mmol), DMAP (140 mg, 1.15 mmol), benzoyl chloride (134 μL, 1.15 mmol) and dichloromethane (8 mL). The residue was purified by silica gel column chromatography to give **6a** as a white solid (270 mg, 96%). $R_f = 0.27$ (CH_2Cl_2/MeOH 100:5); mp = 110–113 °C; $[\alpha]_D^{20} = -68.1$ (c 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.15 (d, $J = 3.4$, 2H), 5.19 (d, $J = 3.4$, 2H), 7. 02–7.06 (m, 4H), 7.11–7.13 (m, 6H), 7.25–7.29 (m, 6H), 7.33–7.36 (m, 6H), 7.39–7.43 (m, 8H), 7.73 (dd, $J = 6.7$, 8.7, 1H), 7.83 (d, $J = 7.1$, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 60.4, 71.9, 125.5, 126.3, 126.7, 126.9, 127.3, 127.4, 127.4, 128.0, 128.1, 128.3, 128.4, 129.1, 131.9, 134.6, 137.7, 139.4, 169.3; IR (KBr): $\nu = 3060$, 1670, 1358 cm^{-1}; EI-MS: m/z 728 (M^+); HRMS (ESI+): calcd for $C_{49}H_{38}N_5O_2$: 728.3025. Found: 728.3016.

4.9. 2,6-Bis-(1-(2-methyl-benzoyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine 6b

Prepared according to general procedure A using **3** (208 mg, 0.4 mmol), DMAP (147 mg, 1.2 mmol) and *o*-toluoyl chloride (160 μL, 1.2 mmol) in anhydrous CH_2Cl_2 (15 mL) for 12 h followed by column chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent to give pale yellow crystals (304 mg, 100%). $R_f = 0.80$ (CH_2Cl_2/MeOH 100:5); mp = 116–118 °C; $[\alpha]_D^{20} = -115.7$ (c 0.67, $CHCl_3$); ^{1}H NMR (300 MHz, CD_2Cl_2): δ 2.08 (s, 6H), 5.22 (br d, $J = 2.43$, 4H), 6.77 (t, $J = 7.53$, 2H), 6.89–6.96 (m, 4H), 7.03 (t, $J = 7.92$, 2H), 7.02–7.29 (m, 6H), 7.37–7.58 (m, 17H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ 19.4, 70.6, 78.4, 124.3, 124.9, 125.3, 126.3, 127.1, 127.8, 128.1, 129.1, 129.2, 129.9, 130.5, 135.0, 137.1, 140.7, 141.8, 149.9, 168.8; IR (KBr): $\nu = 3061$, 3027, 1675, 1625, 1331 cm^{-1}; HRMS: calcd for $C_{51}H_{41}N_5O_2{\cdot}H^+$: 756.3339. Found: 756.3326; Anal. Calcd (%) for $C_{51}H_{41}N_5O_2{\cdot}2H_2O$: C, 77.35; H, 5.73; N, 8.84. Found: C, 78.02; H, 5.44; N, 8.68.

4.10. 2,6-Bis-(1-(4-methoxy-benzoyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine 6c

Prepared according to general procedure A using **3** (400 mg, 0.77 mmol), DMAP (206 mg, 1.69 mmol), 4-methoxybenzoyl chloride (260 μL, 1.92 mmol) and dichloromethane (10 mL). The residue was purified by silica gel column chromatography using MeOH–CH_2Cl_2 as the gradient eluent to give **6c** as a white solid (527 mg, 87%). $R_f = 0.48$ (CH_2Cl_2/MeOH 100:5); mp = 191–193 °C; $[\alpha]_D^{20} = -86.4$ (c 0.41, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 3.66 (s, 6H), 5.08 (d, 2H), 5.10 (d, 2H), 6.53 (d, $J = 8.9$, 4H), 7.04–7.12 (m, 6H), 7.26–7.40 (m, 18H), 7.81 (dd, $J = 6.9$, 8.3, 1H), 7.92 (d, $J = 7.5$, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 56.1, 72.6, 79.9, 113.9, 125.2, 126.1, 127.2, 128.1, 128.3, 128.7, 129.7, 131.3, 138.1, 141.1, 142.5, 150.2, 161.6, 163.1, 169.9, 193.6; EI-MS: m/z 787 (M^+); HRMS: calcd for $C_{51}H_{42}N_5O_4{\cdot}H^+$: 788.3238. Found: 788.3240.

4.11. 2,6-Bis-(1-(4-trifluoromethyl-benzoyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine 6d

Prepared according to general procedure A using **3** (400 mg, 0.77 mmol), DMAP (281 mg, 2.31 mmol), 4-trifluoromethylbenzoyl chloride (286 μL, 1.92 mmol) and dichloromethane (10 mL). The residue was purified by silica gel column chromatography using MeOH–CH_2Cl_2 as the gradient eluent to give **6d** as a white solid (600 mg, 97%). $R_f = 0.55$ (CH_2Cl_2/MeOH 100:5); mp = 114–117 °C; $[\alpha]_D^{20} = -41.9$ (c 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.13 (d, $J = 3.5$, 2H), 5.22 (d, $J = 3.5$, 2H), 7.09–7.18 (m, 6H), 7.30–7.38 (m, 20H), 7.15–7.38 (m, 20H), 7.41–7.45 (m, 4H), 7.85 (dd, $J = 6.7$, 8.5, 1H), 7.94 (d, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 72.4, 79.9, 125.6, 125.7, 125.8, 126.1, 127.0, 128.7, 128.9, 129.3, 129.8, 138.6, 139.2, 140.7, 141.8, 149.8, 160.3, 168.7; EI-MS: m/z 864 (M^+); Anal. Calcd (%) for $C_{51}H_{35}N_5F_6O_2$: C, 70.91; H, 4.08; N, 8.11. Found: C, 70.77; H, 3.85; N, 8.05.

4.12. 2,6-Bis-(1-(2,6-dimethoxy-benzoyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine 6e

Prepared according to general procedure A using **3** (208 mg, 0.4 mmol), DMAP (147 mg, 1.2 mmol) and 2,6-dimethoxybenzoyl chloride (245 mg, 1.2 mmol) in refluxing 1,2-dichloroethane (15 mL) for 24 h followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent afforded pale yellow crystals (167 mg, 47%). $R_f = 0.25$ (CH_2Cl_2/MeOH 100:5); mp = 135–138 °C; $[\alpha]_D^{20} = -86.1$ (*c* 0.37, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.72 (s, 6H), 3.83 (s, 6H), 5.02 (d, $J = 2.82$, 2H), 5.65 (d, $J = 2.56$, 2H), 6.04 (d, $J = 8.52$, 2H), 6.16 (d, $J = 8.52$, 2H), 6.57 (d, $J = 8.52$, 2H), 6.85 (t, $J = 8.32$, 2H), 7.05 (d, $J = 7.72$, 2H), 7.33–7.55 (m, 15H), 7.56 (d, $J = 7.12$, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.9, 58.4, 59.2, 104.5, 124.7, 125.5, 127.2, 127.5, 128.1, 128.5, 128.7, 129.3, 129.9, 130.9, 139.2, 148.9, 157.9, 164.1, 167.1; IR (KBr): $\nu = 2934$, 1674, 1628, 1596, 1112 cm^{-1}; FAB-MS: *m*/*z* 848 (M^+); HRMS: calcd for $C_{53}H_{46}N_5O_6$: 848.3448. Found: 848.3437.

4.13. 2,6-Bis-(1-(2,4,6-trimethoxy-benzoyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine 6f

Prepared according to general procedure A using **3** (415 mg, 0.8 mmol), NaH (64 mg, 2.4 mmol) and 2,4,6-trimethylbenzoyl chloride (448 mg, 2.4 mmol) in refluxing chlorobenzene (20 mL) for 45 h followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent afforded pale yellow crystals (296 mg, 45%). $R_f = 0.30$ (CH_2Cl_2/MeOH 100:5); mp = 96–98 °C; $[\alpha]_D^{20} = -49.2$ (*c* 0.43, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.13 (br s, 18H), 4.82 (d, $J = 8.52$, 2H), 5.13 (d, $J = 8.52$, 2H), 7.30–7.44 (m, 27H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 18.5, 19.2, 19.9, 69.1, 77.8, 122.9, 125.3, 126.1, 126.3, 126.5, 126.6, 127.6, 127.9, 128.2, 128.9, 129.4, 138.8, 141.5, 142.8; IR (KBr): $\nu = 2921$, 1673, 1629, 1330 cm^{-1}; HRMS: calcd for $C_{55}H_{50}N_5O_2$: 812.3964. Found: 812.3965.

4.14. 2,6-Bis-(1-(3,5-di-*tert*-butylbenzoyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine 6g

Prepared according to general procedure A using **3** (363 mg, 0.7 mmol), DMAP (244 mg, 2.0 mmol) and 3,5-di-*tert*-butylbenzoyl chloride (524 mg, 2.0 mmol) in dichloromethane (20 mL) for 12 h followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent afforded pale yellow crystals (216 mg, 32%). $R_f = 0.30$ (CH_2Cl_2/MeOH 100:5); $[\alpha]_D^{20} = -93.3$ (*c* 0.45, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.00 (s, 36H), 5.18 (br s, 2H), 5.44 (d, $J = 4.96$, 2H), 7.12–7.30 (m, 10H), 7.38 (t, $J = 7.12$, 4H), 7.43–7.50 (m, 12H), 7.72–7.75 (m, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 30.7, 34.6, 71.0, 78.8, 124.3, 125.0, 126.3, 127.8, 128.1, 129.1, 129.3, 134.9, 135.8, 137.4, 141.9, 169.6; IR (KBr): $\nu = 2963$, 1673, 1364 cm^{-1}; HRMS: calcd for $C_{65}H_{69}N_5O_2{\cdot}H^+$: 952.5529. Found: 952.5536; Anal. Calcd (%) for $C_{65}H_{69}N_5O_2{\cdot}3H_2O$: C, 77.58; H, 7.51; N, 6.95. Found: C, 77.72; H, 7.04; N, 6.67.

4.15. 2,6-Bis-(1-phenylacetyl-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine 6h

Prepared according to general procedure A using **3** (208 mg, 0.4 mmol), DMAP (147 mg, 1.2 mmol) and phenylacetyl chloride (159 μL, 1.5 mmol) in dichloromethane (15 mL) for 1.5 h at rt followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent afforded pale yellow crystals (246 mg, 87%). $R_f = 0.30$ (CH_2Cl_2/MeOH 100:5); mp = 83–84 °C; $[\alpha]_D^{20} = +27.4$ (*c* 0.23, $CHCl_3$); ^{1}H NMR (300 MHz, CD_2Cl_2): δ 3.57 (s, 4H), 5.15 (d, $J = 2.64$, 2H), 5.39 (d, $J = 2.82$, 2H), 6.84–6.89 (m, 4H), 7.13–7.44 (m, 22H), 7.54–7.59 (m, 4H), 7.92–8.04 (m, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ 43.3, 70.1, 78.1, 124.9, 125.1, 126.3, 127.0, 128.1, 128.5, 129.0, 129.4, 133.8, 138.2, 140.7, 141.7, 150.5, 158.6, 169.0; HRMS: calcd for $C_{51}H_{41}N_5O_2{\cdot}H^+$: 756.3338. Found: 756.3333; Anal. Calcd (%) for $C_{51}H_{41}N_5O_2{\cdot}H_2O$: C, 79.15; H, 5.60; N, 9.05. Found: C, 79.15; H, 5.85; N, 8.37.

4.16. 2,6-Bis-(1-(diphenylacetyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine 6i

Prepared according to general procedure A **3** (208 mg, 0.4 mmol), DMAP (147 mg, 1.2 mmol) and diphenylacetyl chloride (310 μL, 1.4 mmol) in 1,2-dichloromethane (20 mL) for 2 h followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent afforded pale yellow crystals (366 mg, 100%). $R_f = 0.50$ (CH_2Cl_2/MeOH 100:5); mp = 108–109 °C; $[\alpha]_D^{20} = -29.6$ (*c* 0.13, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.00 (br s, 2H), 5.10 (d, $J = 2.80$, 2H), 5.37 (br s, 2H), 6.80 (d, $J = 7.32$, 4H), 6.99–7.33 (m, 32H), 7.57 (dd, $J = 3.96$, 7.36, 4H), 7.74 (d, $J = 7.76$, 2H), 7.93 (t, $J = 7.72$, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 40.1, 57.1, 116.5, 125.1, 126.3, 127.1, 127.3, 127.9, 128.1, 128.5, 128.6, 128.7, 128.8, 128.9, 129.0, 129.4, 135.8, 138.3, 140.7, 154.8, 169.7; IR (KBr): $\nu = 1686$, 1366, 1152 cm^{-1}; FAB-MS: *m*/*z* 908 (M^+); HRMS: calcd for $C_{63}H_{49}N_5O_2{\cdot}H^+$: 908.3964. Found: 908.4009; Anal. Calcd (%) for $C_{63}H_{49}N_5O_2{\cdot}2H_2O$: C, 80.15; H, 5.65; N, 7.42. Found: C, 80.57; H, 5.01; N, 6.98.

4.17. 2,6-Bis-(1-naphthoyl-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine 6j

Prepared according to general procedure A using **3** (400 mg, 0.77 mmol), DMAP (281 mg, 2.31 mmol) and 1-naphthoyl chloride (255 μL, 1.69 mmol) in dichloromethane (16 mL). The residue was purified by silica gel column chromatography using MeOH–CH_2Cl_2 as the gradient eluent to give **6j** as a white solid (600 mg, 94%). $R_f = 0.37$ (CH_2Cl_2/MeOH 100:5); mp = 130–132 °C; $[\alpha]_D^{20} = -104.3$ (*c* 0.20, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.17 (unresolved d, 2H), 5.51 (unresolved d, 2H), 6.98 (m, 4H), 7.15 (m, 2H), 7.34–7.70 (m, 31H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 70.2, 77.7, 116.6, 123.6, 123.6, 125.2, 126.2, 126.4, 126.9, 128.0, 128.1, 129.1, 129.2, 130.4, 132,8, 132.9, 135.6, 135,8, 137.5, 137.5, 140.8, 141.9, 149.2, 149.3, 156.2; EI-MS: *m*/*z* 828 (M^++1), 827 (M^+); HRMS: calcd for $C_{57}H_{42}N_5O_2{\cdot}H^+$: 828.3338. Found: 828.3355.

4.18. 2,6-Bis-(2-naphthoyl-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine 6k

Prepared according to general procedure A using **3** (260 mg, 0.5 mmol), DMAP (180 mg, 1.5 mmol) and 2-naphthoyl chloride (294 mg, 1.5 mmol) in 1,2-dichloroethane (15 mL) for 2 h at rt followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent afforded pale yellow crystals (326 mg, 76%). $R_f = 0.60$ (CH_2Cl_2/MeOH 100:5); mp = 129–130 °C; $[\alpha]_D^{20} = +39.1$ (*c* 0.39, $CHCl_3$); ^{1}H NMR (300 MHz, CD_2Cl_2): δ 5.16 (br s, 4H), 6.99–7.05 (m, 6H), 7.22–7.58 (m, 24H), 7.68–7.75 (m, 5H) 7.87 (d, $J = 7.71$, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ 72.1, 79.0, 124.3, 124.8, 125.4, 126.4, 126.6, 127.5, 127.6, 127.8, 127.9, 128.0, 128.7, 129.0, 129.1, 131.7, 132.2, 134.5, 137.3, 140.2, 141.7, 149.2, 160.5, 169.6; IR (KBr): $\nu = 1669$, 1358, 1321, 1136 cm^{-1}; HRMS: calcd for $C_{57}H_{41}N_5O_2{\cdot}H^+$: 828.3338. Found: 828.3340; Anal. Calcd (%) for $C_{57}H_{41}N_5O_2{\cdot}H_2O$: C, 80.92; H, 5.12; N, 8.27. Found: C, 80.72; H, 4.29; N, 7.90.

4.19. 2,6-Bis-(1-[(2*S*)-2-(6-methoxy-naphthalen-2-yl)-propionyl]-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine 6l

Prepared according to general procedure A using **3** (400 mg, 0.77 mmol), DMAP (281 mg, 2.31 mmol), (*S*)-2-(6-methoxy-naphthaten-2-yl)-propionyl chloride (574 mg, 2.31 mmol) and dichloromethane (10 mL). The residue was purified by silica gel column chromatography using MeOH–CH_2Cl_2 as the gradient eluent to give **6l** as a white solid (450 mg, 62%). $R_f = 0.75$ (CH_2Cl_2/EtOAc 8:2); mp = 115–118 °C; $[\alpha]_D^{20} = -46.6$ (*c* 0.25, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.31 (d, 6H), 3.73 (q, 2H), 3.91 (s, 6H), 4.95 (d, $J = 4.8$, 2H), 5.18 (d, $J = 4.8$, 2H), 6.93–7.17 (m, 16H), 7.33–7.35 (m, 6H), 7.44 (m, 2H), 7.52–7.54 (m, 4H), 7.57–7.60 (m, 4H) 7.83 (d, $J = 7.6$, 2H), 7.98 (t, $J = 7.6$, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 20.5, 45.6, 55.3, 68.4, 78.9, 105.5, 116.7, 118.7, 123.7, 125.3, 125.5, 126.0, 126.1, 127.6, 127.7, 128.1, 128.9, 129.3, 129.4, 133.7, 135.2, 137.5, 140.6, 141.7, 151.1, 157.8, 159.2, 171.3; EI-MS: *m*/*z* 944 (M^+); HRMS: calcd for $C_{63}H_{53}N_5O_4$: 944.4176. Found: 944.4167.

4.20. 2,6-Bis-(1-(2-(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyloxy-acetyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine 6m

Prepared according to general procedure A using **3** (416 mg, 0.8 mmol), DMAP (294 mg, 2.4 mmol) and (−)-menthoxyacetyl chloride (540 μL, 2.4 mmol) in dichloromethane (20 mL) for 1 h followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent afforded pale yellow crystals (673 mg, 92%). $R_f = 0.75$ (CH_2Cl_2/MeOH 100:5); mp = 60–61 °C; $[\alpha]_D^{20} = -21.8$ (*c* 0.16, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.54 (d, $J = 6.92$, 6H), 0.72 (d, $J = 6.52$, 6H), 0.79 (d, $J = 7.12$, 6H), 0.80–1.23 (m, 8H), 1.49–1.68 (m, 10H), 2.87 (dt, $J = 4.16$, 10.68, 2H), 3.85 (d, $J = 14.64$, 2H), 4.03 (d, $J = 14.68$, 2H), 5.15 (d, $J = 2.56$, 2H), 5.42 (d, $J = 2.56$, 2H), 7.24–7.49 (m, 20H), 8.03–8.12 (m, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 15.6, 20.8, 21.8, 22.9, 25.2, 31.5, 34.3, 39.9, 48.1, 69.5, 70.1, 77.7, 80.8, 124.8, 125.0, 126.5, 127.8, 128.0, 129.0, 129.2, 137.8, 140.8, 141.7, 150.1, 158.6, 169.5; IR (KBr): $\nu = 2954$, 2924, 1680, 1617, 1383 cm^{-1}; HRMS: calcd for $C_{59}H_{69}N_5O_4{\cdot}H^+$: 912.5428. Found: 912.5410; Anal. Calcd (%) for $C_{59}H_{69}N_5O_4{\cdot}H_2O$: C, 76.18; H, 7.69; N, 7.53. Found: C, 76.18; H, 8.21; N, 6.46.

4.21. 2,6-Bis-(1-adamantoyl-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine 6n

Prepared according to general procedure A using **3** (200 mg, 0.38 mmol), DMAP (206 mg, 1.69 mmol) and adamantoyl chloride (260 μL, 1.92 mmol) in dichloromethane (10 mL). The residue was purified by silica gel column chromatography using MeOH–CH_2Cl_2 as the gradient eluent afforded **6n** as a white solid (310 mg, 96%). $R_f = 0.53$ (CH_2Cl_2/MeOH 100:5); mp = 132–135 °C; $[\alpha]_D^{20} = -22.0$ (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.43–1.46 (m, 6H), 1.52–1.60 (m, 14H), 1.77–1.80 (m, 12H), 5.16 (d, $J = 4.2$, 2H), 5.29 (d, $J = 4.2$, 2H), 7.24–7.26 (m, 4H), 7.32–7.42 (m, 16H), 7.95 (dd, $J = 6.8$, 8.6, 1H), 8.03 (d, $J = 6.8$, 1H), 8.03 (d, $J = 8.6$, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 28.1, 36.2, 39.0, 43.7, 71.3, 81.6, 124.2, 126.1, 126.5, 127.9, 127.9, 128.9, 129.2, 137.1, 141.1, 142.2, 150.7, 163.7, 181.3; EI-MS: *m*/*z* 844 (M^+); HRMS: calcd for $C_{57}H_{58}N_5O_2$: 844.4590. Found: 844.4574.

4.22. 2,6-Bis-(1-acetyl-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine 6o

Prepared according to general procedure A using **3** (420 mg, 0.81 mmol), DMAP (296 mg, 2.42 mmol) and acetyl chloride (178 μL, 2.42 mmol) in dichloromethane (20 mL) for 2 h followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent afforded a pale yellow solid (419 mg, 86%). $R_f = 0.45$ (CH_2Cl_2/MeOH 100:5); mp = 108–109 °C; $[\alpha]_D^{20} = -24.5$ (*c* 0.35, $CHCl_3$); ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.93 (s, 6H), 5.14 (d, $J = 2.64$, 2H), 5.34 (d, $J = 2.64$, 2H), 7.29–7.55 (m, 20H), 8.07–8.09 (m, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ 24.5, 70.0, 78.0, 78.1, 124.7, 125.0, 126.3, 128.0, 128.1, 129.1, 129.3, 138.3, 140.8, 141.8, 150.4, 158.8, 168.0; IR (KBr): $\nu = 2929$, 1727, 1405, 1210 cm^{-1}; EI-MS: *m*/*z* 603 (M^+); HRMS: calcd for $C_{39}H_{33}N_5O_2{\cdot}H^+$: 604.2707. Found: 604.2704.

4.23. 2,6-Bis-(1-pentanoyl-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine 6p

Prepared according to general procedure A using **3** (520 mg, 1.00 mmol), DMAP (367 mg, 3.00 mmol) and valeryl chloride (358 μL, 3.00 mmol) in dichloromethane (25 mL) for 2 h followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent afforded a pale yellow solid (637 mg, 93%). $R_f = 0.30$ (CH_2Cl_2/MeOH 100:5); mp = 50–51 °C; $[\alpha]_D^{20} = -9.6$ (*c* 0.24, $CHCl_3$); ^{1}H NMR (300 MHz, CD_2Cl_2): δ 0.68 (t, $J = 7.35$, 6H), 0.89–1.12 (m, 4H), 1.29–1.59 (m, 4H), 1.98–2.29 (m, 4H), 5.15 (d, $J = 2.82$, 2H), 5.32

(unresolved d, 2H), 7.29–7.56 (m, 20H), 8.02–8.09 (m, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ 13.4, 22.1, 26.7, 36.0, 69.9, 78.1, 124.4, 125.1, 126.2, 127.9, 128.1, 129.1, 129.3, 138.1, 141.0, 142.0, 150.8, 159.1, 171.1; IR (KBr): $\nu = 2957$, 2931, 1685 (br), 1453, 1380 cm^{-1}; EI-MS: m/z 687 (M^+); HRMS: calcd for $C_{45}H_{45}N_5O_2$: 687.3568. Found: 687.3593; Anal. Calcd (%) for $C_{45}H_{45}N_5O_2{\cdot}H_2O$: C, 76.57; H, 6.71; N, 9.92. Found: C, 76.79; H, 6.76; N, 9.36.

4.24. 2,6-Bis-(1-(2-methyl propanoyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine 6q

Prepared according to general procedure A using **3** (520 mg, 1.00 mmol), DMAP (367 mg, 3.00 mmol) and isobutyryl chloride (315 μL, 3.00 mmol) in dichloromethane (25 mL) for 2 h followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent afforded a pale yellow solid (607 mg, 92%). $R_f = 0.45$ (CH_2Cl_2/MeOH 100:5); mp = 86–87 °C; $[\alpha]_D^{20} = -34.8$ (*c* 0.22, $CHCl_3$); ^{1}H NMR (300 MHz, CD_2Cl_2): δ 0.87 (d, $J = 6.78$, 6H), 0.93 (d, $J = 6.78$, 6H), 2.37–2.45 (m, 2H), 5.14 (d, $J = 2.82$, 2H), 5.27 (d, $J = 2.82$, 2H), 7.30–7.54 (m, 20H), 7.99–8.10 (m, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ 18.6, 19.8, 33.9, 70.1, 78.4, 124.3, 125.2, 126.2, 127.9, 128.1, 129.1, 129.3, 137.9, 141.1, 142.2, 151.1, 159.4, 175.8; IR (KBr): $\nu = 2973$, 1691 (br), 1618, 1466, 1388 cm^{-1}; EI-MS: m/z 659 (M^+); HRMS: calcd for $C_{43}H_{41}N_5O_2$: 659.3255. Found: 659.3263; Anal. Calcd (%) for $C_{43}H_{41}N_5O_2{\cdot}H_2O$: C, 76.19; H, 6.39; N, 10.33. Found: C, 76.19; H, 6.18; N, 9.96.

4.25. 2,6-Bis-(1-(3-methyl butanoyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine 6r

Prepared according to general procedure A using **3** (520 mg, 1.00 mmol), DMAP (367 mg, 3.00 mmol) and isovaleryl chloride (367 μL, 3.00 mmol) in dichloromethane (25 mL) for 2 h followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent afforded a pale yellow solid (638 mg, 93%). $R_f = 0.35$ (CH_2Cl_2/MeOH 100:5); mp = 59–60 °C; $[\alpha]_D^{20} = -21.7$ (*c* 0.21, $CHCl_3$); ^{1}H NMR (300 MHz, CD_2Cl_2): δ 0.68 (d, $J = 6.39$, 6H), 0.71 (d, $J = 6.39$, 6H), 1.89–2.00 (m, 2H), 2.05–2.16 (m, 4H), 5.15 (d, $J = 2.82$, 2H), 5.30 (d, $J = 2.82$, 2H), 7.31–7.55 (m, 20H), 8.01–8.10 (m, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ 22.1, 25.5, 45.0, 70.0, 68.2, 124.4, 125.1, 126.2, 127.9, 128.1, 129.1, 129.3, 138.0, 141.0, 142.0, 150.9, 159.2, 170.6; IR (KBr): $\nu = 2958$, 1691 (br), 1466, 1375 cm^{-1}; EI-MS: m/z 687 (M^+); HRMS: calcd for $C_{45}H_{45}N_5O_2$: 687.3568. Found: 687.3553; Anal. Calcd (%) for $C_{45}H_{45}N_5O_2{\cdot}H_2O$: C, 76.57; H, 6.71; N, 9.92. Found: C, 76.51; H, 6.54; N, 9.33.

4.26. 2,6-Bis-(1-(3,3-dimethyl butanoyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine 6s

Prepared according to general procedure A using **3** (520 mg, 1.00 mmol), DMAP (367 mg, 3.00 mmol) and *tert*-butylacetyl chloride (417 μL, 3.00 mmol) in dichloromethane (25 mL) for 2 h followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent afforded a pale yellow solid (595 mg, 83%). $R_f = 0.25$ (CH_2Cl_2/MeOH 100:5); mp = 74–75 °C; $[\alpha]_D^{20} = -35.4$ (*c* 0.21, $CHCl_3$); ^{1}H NMR (300 MHz, CD_2Cl_2): δ 0.81 (s, 18H), 1.93 (d, $J = 15.24$, 2H), 2.08 (d, $J = 15.24$, 2H), 5.15 (d, $J = 2.82$, 2H), 5.28 (d, $J = 2.82$, 2H), 7.30–7.56 (m, 20H), 7.99–8.12 (m, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ 29.3, 31.3, 47.9, 70.1, 78.1, 124.2, 125.2, 126.3, 127.9, 128.0, 129.0, 129.3, 138.0, 141.1, 142.1, 151.2, 159.4, 170.0; IR (KBr): $\nu = 2954$, 1691 (br), 1466, 1361 cm^{-1}; EI-MS: m/z 715 (M^+); HRMS: calcd for $C_{47}H_{49}N_5O_2$: 715.3881. Found: 715.3872; Anal. Calcd (%) for $C_{47}H_{49}N_5O_2{\cdot}H_2O$: C, 76.91; H, 7.00; N, 9.54. Found: C, 76.98; H, 6.61; N, 8.96.

4.27. 2,6-Bis-(1-(phenoxycarbonyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine 7a

Prepared according to general procedure A using **3** (260 mg, 0.5 mmol), DMAP (184 mg, 1.5 mmol) and phenyl chloroformate (190 μL, 1.5 mmol) in dichloromethane (20 mL) for 1 h followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent afforded pale yellow crystals (387 mg, 98%). $R_f = 0.65$ (CH_2Cl_2/MeOH 100:5); mp = 90–91 °C; $[\alpha]_D^{20} = +8.4$ (*c* 0.38, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.52 (d, $J = 3.96$, 2H), 5.63 (d, $J = 3.76$, 2H), 6.96–6.99 (m, 4H), 7.24–7.34 (m, 6H), 7.46–7.52 (m, 6H), 7.60–7.72 (m, 10H), 7.76–7.79 (m 4H), 8.19–8.29 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 70.5, 78.3, 121.0, 124.6, 125.3, 126.2, 127.9, 128.1, 129.0, 129.1, 129.2, 137.3, 140.7, 141.4, 149.6, 150.2, 158.4; IR (KBr): $\nu = 1744$, 1631, 1493, 1355, 1201, 1328 cm^{-1}; FAB-MS: m/z 759 (M^+); HRMS: calcd for $C_{49}H_{37}N_5O_4{\cdot}H^+$: 760.2924. Found: 760.2927.

4.28. 2,6-Bis-(1-(1-naphthyloxycarbonyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine 7b

Prepared according to general procedure A using **3** (260 mg, 0.5 mmol), DMAP (184 mg, 1.5 mmol) and 1-naphthyl chloroformate (240 μL, 1.5 mmol) in dichloromethane (20 mL) for 1 h followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent afforded pale yellow crystals (369 mg, 84%). $R_f = 0.60$ (CH_2Cl_2/MeOH 100:5); mp = 104–106 °C; $[\alpha]_D^{20} = -7.2$ (*c* 0.34, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.52 (d, $J = 3.76$, 2H), 5.70 (d, $J = 3.76$, 2H), 7.07 (dd, $J = 1.00$, 7.72, 2H), 7.18–7.31 (m, 6H), 7.38–7.43 (m, 6H), 7.50 (m, 3H), 7.58–7.67 (m, 9H), 7.73 (d, $J = 8.12$, 2H), 7.79–7.81 (m, 4H), 7.87 (d, $J = 8.32$, 2H), 8.10 (m, 1H), 8.21 (d, $J = 7.56$, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 70.7, 78.3, 117.8, 120.8, 124.8, 125.1, 125.5, 125.8, 126.1, 126.2, 126.5, 127.6, 128.0, 128.2, 129.2, 129.4, 134.3, 137.2, 140.9, 141.6, 145.9, 149.5, 149.7, 158.7; IR (KBr): $\nu = 1749$, 1335, 1224, 1153 cm^{-1}; FAB-MS: m/z 860 (M^+); Anal. Calcd (%) for $C_{57}H_{41}N_5O_4{\cdot}H_2O$: C, 77.97; H, 4.94; N, 7.98. Found: C, 77.88; H, 4.93; N, 7.54.

4.29. 2,6-Bis-(1-(9-fluorenylmethyloxycarbonyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine 7c

Prepared according to general procedure A using **3** (208 mg, 0.4 mmol), DMAP (147 mg, 1.2 mmol) and

9-fluorenylmethyl chloroformate (315 mg, 1.2 mmol) in dichloromethane (20 mL) for 1 h followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent afforded pale yellow crystals (367 mg, 94%). $R_f = 0.40$ (CH_2Cl_2/MeOH 100:5); mp = 115–116 °C; $[\alpha]_D^{20} = +21.7$ (*c* 0.12, $CHCl_3$); ^1H NMR (400 MHz, CD_2Cl_2): δ 3.87 (t, $J = 6.12$, 2H), 4.07 (dd, $J = 7.92$, 10.48, 2H), 4.33 (dd, $J = 5.68$, 10.52, 2H), 5.08 (d, $J = 3.36$, 2H), 5.15 (d, $J = 3.16$, 2H), 6.88 (dd, $J = 1.00$, 7.52, 2H), 7.00 (dt, $J = 1.20$, 7.52, 2H), 7.04 (d, $J = 7.36$, 2H), 7.09–7.19 (m, 8H), 7.27–7.35 (m, 8H), 7.38–7.49 (m, 10H), 7.67 (t, $J = 6.76$, 4H), 7.89–7.96 (m, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 46.7, 68.1, 69.7, 78.6, 119.8, 119.9, 124.0, 124.7, 125.0, 125.1, 126.3, 127.1, 127.6, 127.7, 127.9, 128.0, 129.1, 129.2, 137.4, 141.0, 141.1, 141.2, 142.1, 143.1, 143.9, 149.9, 151.6, 158.5; IR (KBr): $\nu = 1731$, 1395, 1327, 1135 cm^{-1}; HRMS: calcd for $C_{65}H_{49}N_5O_4 \cdot H^+$: 964.3857. Found: 964.3869; Anal. Calcd (%) for $C_{65}H_{49}N_5O_4 \cdot 2H_2O$: C, 78.06; H, 5.34; N, 7.00. Found: C, 78.69; H, 5.06; N, 6.91.

4.30. 2,6-Bis-(1-((1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyloxy carbonyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine 7d

Prepared according to general procedure A using **3** (400 mg, 0.77 mmol), DMAP (281 mg, 2.31 mmol) and (+)-menthyl chloroformate (364 μL, 1.69 mmol) in dichloromethane (10 mL). The residue was purified by silica gel column chromatography using MeOH–CH_2Cl_2 as the gradient eluent to give a white solid (610 mg, 90%). $R_f = 0.34$ (CH_2Cl_2/MeOH 100:2); mp = 88–90 °C; $[\alpha]_D^{20} = -1.1$ (*c* 0.50, $CHCl_3$); ^1H NMR (400 MHz, CD_2Cl_2): δ 0.37 (d, 6H), 0.55 (d, 6H), 0.53–0.59 (m, 6H), 0.63 (d, $J = 8.12$, 6H), 0.74–0.88 (m, 2H), 1.05 (m, 2H), 1.34–1.41 (m, 6H), 1.75 (m, 2H), 4.22 (unresolved ddd, $J = 4.36$, 2H), 5.04 (d, $J = 3.16$, 2H) 5.24 (d, $J = 3.16$, 2H), 7.24–7.37 (m, 12H), 7.41–7.45 (m, 4H), 7.56–7.58 (m, 4H), 7.84 (d, $J = 7.16$, 1H), 7.84 (d, $J = 8.12$, 1H), 7.96 (dd, $J = 7.12$, 8.12, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 16.9, 21.0, 22.0, 24.1, 26.8, 31.8, 34.6, 40.8, 47.2, 69.9, 77.7, 79.1, 124.1, 125.8, 126.9, 128.4, 128.7, 129.7, 129.8, 137.8, 142.2, 143.1, 151.6, 151.8, 159.1; EI-MS: *m*/*z* 884 (M^+); Anal. Calcd (%) for $C_{57}H_{65}N_5O_4$: C, 77.43; H, 7.41; N, 7.92. Found: C, 77.04; H, 7.63; N, 7.85.

4.31. 2,6-Bis-(1-((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyloxy carbonyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine 7e

Prepared according to general procedure A using **3** (400 mg, 0.77 mmol), DMAP (281 mg, 2.31 mmol) and (−)-menthyl chloroformate (364 μL, 1.69 mmol) in dichloromethane (10 mL). The residue was purified by silica gel column chromatography using MeOH–CH_2Cl_2 as the gradient eluent to give a white solid (640 mg, 94%). $R_f = 0.34$ (CH_2Cl_2/MeOH 100:2); mp = 88–90 °C; $[\alpha]_D^{20} = -48.7$ (*c* 0.25, $CHCl_3$); ^1H NMR (400 MHz, CD_2Cl_2): δ 0.67 (d, 6H), 0.76 (d, 6H), 0.70–0.79 (m, 2H), 0.95–1.13 (m, 6H), 1.39–1.46 (m, 2H), 1.60–1.69 (m, 6H), 1.86–1.90 (m, 2H), 4.58 (unresolved ddd, $J = 4.36$, 2H), 5.28 (d, $J = 3.48$, 1H), 5.40 (d, $J = 3.48$, 1H), 7.43–7.62 (m, 12H), 7.58–7.62 (m, 4H), 7.71–7.73 (m, 4H), 8.03 (d, $J = 6.93$, 1H), 8.03 (d, $J = 8.32$, 1H), 8.14 (dd, $J = 6.95$, 8.32, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 16.3, 21.2, 22.3, 23.6, 26.7, 31.9, 34.7, 41.3, 47.6, 70.5, 77.3, 79.3, 124.4, 125.9, 127.0, 128.3, 128.7, 129.7, 129.8, 137.6, 142.1, 143.2, 151.5, 152.3, 159.6; EI-MS: *m*/*z* 884 (M^+); Anal. Calcd (%) for $C_{57}H_{65}N_5O_4$: C, 77.43; H, 7.41; N, 7.92. Found: C, 77.50; H, 7.65; N, 7.79.

4.32. 2,6-Bis-(1-(1,1-dimethylethyloxy carbonyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1-*H*-imidazol-2-yl)-pyridine 7f

Prepared according to general procedure A using **3** (260 mg, 0.5 mmol), DMAP (184 mg, 1.5 mmol) and di-*tert*-butyldicarbonate (760 μL, 1.5 mmol) in dichloromethane (20 mL) for 12 h followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent afforded pale yellow crystals (337 mg, 91%). $R_f = 0.40$ (CH_2Cl_2/MeOH 100:5); mp = 84–85 °C; $[\alpha]_D^{20} = -17.1$ (*c* 0.19, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 1.35 (s, 18H), 5.39 (d, $J = 3.60$, 2H), 5.54 (d, $J = 3.36$, 2H), 7.48–7.57 (m, 6H), 7.64–7.76 (m, 10H), 7.86 (m, 4H), 8.21 (m, 2H), 8.27 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.6, 69.4, 77.9, 82.4, 123.4, 124.9, 126.2, 127.6, 128.0, 129.0, 129.2, 137.3, 141.1, 142.2, 150.0, 151.0, 158.9; IR (KBr): $\nu = 2976$, 1718, 1630, 1368, 1138 cm^{-1}; HRMS: calcd for $C_{45}H_{45}N_5O_4 \cdot H^+$: 720.3550. Found: 720.3530.

4.33. 2,6-Bis-(1-benzyl-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine 7g

To a solution of **3** (434 mg, 0.83 mmol) in anhydrous THF (15 mL) was added sodium hydride (80.2 mg, 3.34 mmol) at 0 °C. After 15 min, benzyl bromide (298 μL, 1.85 mmol) was slowly added and the reaction mixture stirred at room temperature for 4 h. Then, the reaction mixture was quenched with water and the aqueous phase extracted with dichloromethane (2 × 20 mL). The organic layer was dried over Na_2SO_4 and the solvents removed in vacuo to give pale yellow oil, which was further purified by column chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent to afford **7g** as a white solid (380 mg, 65%). $R_f = 0.57$ (CH_2Cl_2/MeOH 100:5); mp = 75–78 °C; $[\alpha]_D^{20} = +33.7$ (*c* 0.14 $CHCl_3$); ^1H NMR (400 MHz, CD_2Cl_2): δ 4.02 (d, $J = 15.5$, 2H), 4.38 (d, $J = 9.1$, 2H), 4.92 (d, $J = 9.1$, 2H), 5.60 (d, $J = 15.5$, 2H), 7.02 (m, 4H), 7.11 (m, 4H), 7.19–7.29 (m, 22H), 8.04 (dd, $J = 7.5$, 8.1, 1H), 8.31 (d, $J = 7.9$, 2H); ^{13}C NMR (400 MHz, CD_2Cl_2): δ 50.0, 74.4, 78.5, 126.9, 127.6, 127.9, 127.9, 128.4, 128.9, 129.1, 129.2, 129.6, 136.5, 138.1, 138.6, 142.4, 144.6, 150.7, 163.2; EI-MS: *m*/*z* 699 (M^+); Anal. Calcd (%) for $C_{49}H_{41}N_5 \cdot 0.5H_2O$: C, 83.02; H, 5.97; N, 9.88. Found: C, 82.68; H, 5.49; N, 9.62.

4.34. 2,6-Bis-(1-[toluene-4-sulfonyl]-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine 7h

A 50 mL Schlenk tube was charged with **3** (400 mg, 0.77 mmol), DMAP (281 mg, 2.31 mmol) and dichloromethane

(15 mL). The resulting mixture was cooled to 0 °C, and tosyl chloride (323 mg, 1.69 mmol) added neat at once. The ice bath was removed, and the reaction mixture was stirred at room temperature for 5 h. The solvent was removed under vacuo, the residue partitioned between saturated NH_4Cl (25 mL) and ethyl acetate (25 mL), and the aqueous phase re-extracted with ethyl acetate (2×25 mL). The combined organic layer was dried over $MgSO_4$, and the solvent removed in vacuo. The residue was crystallized from ethyl acetate/hexane to give **7h** as a white solid (635 mg, 99%). $R_f = 0.50$ (CH_2Cl_2/MeOH 100:1); mp = 105–107 °C; $[\alpha]_D^{20} = -29.6$ (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.11 (s, 6H), 5.18 (d, 2H), 5.37 (d, 2H), 7.85 (d, $J = 8.1$, 4H), 7.15–7.38 (m, 20H), 7.47 (d, $J = 8.1$, 4H), 8.12 (dd, $J = 6.5$, 8.6, 1H), 8.18 (d, $J = 6.5$, 1H), 8.18 (d, $J = 8.6$, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 20.7, 71.0, 78.8, 125.5, 125.8, 125.9, 127.4, 127.5, 127.6, 128.3, 128.5, 129.2, 134.5, 136.4, 140.8, 140.9, 143.9, 149.4, 156.9; EI-MS: *m*/*z* 827 (M^+); Anal. Calcd (%) for $C_{49}H_{41}N_5O_4S_2 \cdot (C_2H_5)_2O \cdot H_2O$: C, 69.18; H, 5.81; N, 7.61; S, 6.97. Found: C, 69.36; H, 5.53; N, 7.37; S, 7.28.

4.35. 2,6-Bis-(1-benzyl-[3*aR*,7*aR*]-3a,4,5,6,7,7a-hexahydro-1*H*-benzoimidazol-2-yl)-pyridine 8a

To a solution of **4** (200 mg, 0.62 mmol) in anhydrous THF (15 mL) was added sodium hydride (59 mg, 2.47 mmol) at 0 °C. After 15 min, benzyl bromide (220 μL, 1.85 mmol) was slowly added and the reaction mixture stirred at room temperature for 4 h. Then, the reaction mixture was quenched with water and the aqueous phase extracted with dichloromethane (2×20 mL). The organic layer was dried over Na_2SO_4 and the solvents were removed in vacuo to give a light yellow solid, which was purified by column chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent to give **8a** as a white solid (213 mg, 68%). $R_f = 0.50$ (CH_2Cl_2/MeOH 9:1); mp = 183–185 °C; $[\alpha]_D^{20} = +191.2$ (*c* 0.37, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.07–1.18 (m, 2H), 1.24–1.41 (m, 6H), 1.67–1.85 (m, 6H), 2.25–2.29 (m, 2H), 2.66 (ddd, $J = 3.3$, 11.4, 14.7, 2H), 3.05 (ddd, $J = 3.3$, 11.4, 14.7, 2H), 4.54 (d, $J = 15.6$, 2H), 4.64 (d, J=15.6, 2H), 7.05 (m, 4H), 7.18 (m, 6H), 7.80 (dd, $J = 7.3$, 8.4, 1H), 7.93 (d, $J = 7.3$, 1H), 7.93 (d, $J = 8.4$, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 25.2, 26.3, 30.5, 31.9, 51.3, 71.2, 71.4, 125.7, 127.6, 128.7, 138.1, 139.1, 151.1, 165.9; EI-MS: *m*/*z* 503 (M^+); Anal. Calcd (%) for $C_{33}H_{37}N_5 \cdot H_2O$: C, 75.97; H, 7.53; N, 13.42. Found: C, 76.07; H, 7.26; N, 13.21.

4.36. 2,6-Bis-(1-[toluene-4-sulfonyl]-[3*aR*,7*aR*]-3a,4,5,-6,7,7a-hexahydro-1*H*-benzoimidazol-2-yl)-pyridine 8b

A 50 mL Schlenk tube was charged with **4** (323 mg, 1.00 mmol), DMAP (366 mg, 3.00 mmol) and dichloromethane (15 mL). The resulting mixture was cooled to 0 °C, and tosyl chloride (476 mg, 2.50 mmol) added neat at once. The ice bath was removed, and the reaction mixture stirred at room temperature for 5 h. The solvent was removed under vacuo, the residue partitioned between saturated NH_4Cl (25 mL) and ethyl acetate (25 mL), and the aqueous phase re-extracted with ethyl acetate (2×25 mL). The combined organic layer was dried over $MgSO_4$, and the solvent was removed in vacuo. The residue was crystallized from ethyl acetate/hexane to give **8b** as a white solid (585 mg, 93%). $R_f = 0.45$ (CH_2Cl_2/MeOH 100:6); mp = 254–255 °C; $[\alpha]_D^{20} = +60.4$ (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): δ (1.59–1.76m, 6H), 1.9–2.1 (m, 2H), 2.13–2.21 (m, 4H), 2.60 (s, 6H), 2.66 (m, 2H), 2.90 (m, 2H), 3.50 (ddd, $J = 3.0$, 10.9, 13.7, 2H), 3.58 (ddd, $J = 3.0$, 10.9, 13.7, 2H), 7.38 (d, $J = 8.4$, 4H), 7.82 (d, $J = 8.4$, 4H), 7.88 (d, $J = 7.9$, 2H), 8.12 (dd, $J = 7.5$, 8.1, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 22.1, 25.4, 26.0, 31.5, 31.7, 70.1, 72.7, 125.5, 128.6, 130.2, 136.2, 137.1, 144.8, 151.0, 158.9; EI-MS: *m*/*z* 631 (M^+); Anal. Calcd (%) for $C_{33}H_{37}N_5O_4S_2$: C, 62.73; H, 5.90; N, 11.08; S, 10.15. Found: C, 62.77; H, 5.94; N, 10.99; S, 10.24.

4.37. 1-((4*R*,5*R*)-4,5-dihydro-2-(6-((4*R*,5*R*)-4,5-dihydro-4,5-diphenyl-1*H*-imidazol-2-yl)pyridin-2-yl)-4,5-diphenylimidazol-1-yl)(mesityl)methanone 9

Prepared according to general procedure A using **3** (415 mg, 0.8 mmol), NaH (64 mg, 2.4 mmol) and 2,4,6-trimethyl benzoyl chloride (448 mg, 2.4 mmol) in refluxing chlorobenzene (20 mL) for 45 h followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent to afford pale yellow crystals (255 mg, 48%). $R_f = 0.20$ (CH_2Cl_2/MeOH 100:5); mp = 96–98 °C; $[\alpha]_D^{20} = +47.8$ (*c* 0.16, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.96 (s, 3H), 2.01 (s, 6H), 4.43 (m, 1H), 5.25 (d, $J = 4.16$, 2H), 5.62 (m, 2H), 6.35 (s, 1H), 6.37 (s, 1H); 6.97–7.18 (m 3H), 7.26–7.58 (m, 18H), 7.69 (d, $J = 7.32$, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 19.2, 20.6, 69.1, 77.8, 116.7, 122.9, 125.3, 126.2, 126.5, 126.6, 127.2, 127.9, 128.5, 128.8, 129.0, 129.3, 129.4, 142.9, 149.2, 168.7; IR (KBr): $\nu = 3423$, 2921, 1679, 1430, 1328 cm^{-1}; FAB-MS: *m*/*z* 664 (M^+); Anal. Calcd (%) for $C_{45}H_{38}N_5O_1 \cdot H_2O$: C, 79.15; H, 5.90; N, 10.25. Found: C, 79.78; H, 6.29; N, 9.69.

4.38. 1-(3,5-Di-*tert*-butylphenyl)((4*R*,5*R*)-4,5-dihydro-2-(6-((4*R*,5*R*)-4,5-dihydro-4,5-diphenyl-1*H*-imidazol-2-yl)-pyridin-2-yl)-4,5-diphenylimidazol-1-yl)methanone 10

Prepared according to general procedure A using **3** (363 mg, 0.7 mmol), DMAP (244 mg, 2.0 mmol) and 3,5-di-*tert*-butyl benzoyl chloride (524 mg, 2.0 mmol) in dichloromethane (20 mL) for 12 h followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent to afford pale yellow crystals (335 mg, 52%). $R_f = 0.20$ (CH_2Cl_2/MeOH 100:5); mp = 97–99 °C; $[\alpha]_D^{20} = -2.9$ (*c* 0.19, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.13 (s, 18H), 4.77 (d, $J = 8.52$, 1H), 5.06 (d, $J = 9.32$, 1H), 5.26 (d, $J = 4.56$, 1H), 5.31 (unresolved d, 1H), 7.23–7.45 (m, 23H), 7.81 (t, $J = 7.92$, 1H), 7.93 (dd, $J = 1.16$, 7.72, 1H), 8.19 (dd, $J = 1.20$, 7.92, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 30.9, 34.6, 70.3, 72.6, 78.8, 81.1, 122.4, 123.5, 125.5, 125.9, 126.2, 126.5, 126.6, 127.2, 128.0, 128.5, 128.7, 128.9, 129.2, 134.9, 137.2, 140.8, 141.6, 147.9, 149.6, 150.8, 160.3, 161.7, 170.6; IR (KBr): $\nu = 3414$, 2962, 1673, 1332 cm^{-1}; HRMS: calcd for $C_{50}H_{49}N_5O \cdot H^+$: 736.4015. Found:

736.3992; Anal. Calcd (%) for $C_{50}H_{49}N_5O_1{\cdot}H_2O$: C, 79.65; H, 6.82; N, 9.29. Found: C, 80.10; H, 6.71; N, 8.88.

4.39. 1-((1*R*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyloxycarbonyl)(4*R*,5*R*)-4,5-dihydro-2-(6-((4*R*,5*R*)-4,5-dihydro-4,5-diphenyl-1*H*-imidazol-2-yl)pyridin-2-yl)-4,5-di-phenylimidazole-1-carboxylate 11

Prepared according to general procedure A using **3** (260 mg, 0.50 mmol), DMAP (61 mg, 0.5 mmol) and (+)-menthyl chloroformate (90 μL, 0.42 mmol) in dichloromethane (20 mL) for 2 h followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent to afford pale yellow crystals (126 mg, 36%); $R_f = 0.20$ (CH_2Cl_2/MeOH 100:5); mp = 72–73 °C; $[\alpha]_D^{20} = +60.6$ (*c* 0.23, $CHCl_3$). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.43 (d, $J = 6.94$, 3H), 0.56 (d, $J = 6.98$, 3H), 0.71–0.83 (m, 4H), 0.84 (d, $J = 6.52$, 3H), 1.46–1.68 (m, 5H), 1.94 (br d, 1H), 4.33 (dt, $J = 4.16$, 10.68, 1H), 4.85 (br d, $J = 7.92$, 1H), 5.11–5.17 (m, 3H), 7.31–7.44 (m, 20H), 7.87 (dd, $J = 1.2$, 7.76, 1H), 7.99 (t, $J = 7.72$, 1H), 8.42 (dd, $J = 1.2$, 7.92, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 15.4, 20.6, 21.8, 22.8, 25.4, 31.3, 34.0, 40.8, 46.8, 70.2, 76.8, 78.4, 123.4, 125.1, 125.7, 126.3, 127.9, 128.9, 129.1, 137.0, 141.7, 142.6, 147.9, 158.6, 162.1; IR (KBr): $\nu = 3421$ (br), 2955, 1726, 1433 cm^{-1}; EI-MS: *m*/*z* 701 (M^+); HRMS: calcd for $C_{46}H_{47}N_5O_2{\cdot}H^+$: 702.3777. Found: 702.3808.

4.40. 1-((4*R*,5*R*)-4,5-Dihydro-2-(6-((4*R*,5*R*)-4,5-dihydro-4,5-diphenyl-1*H*-imidazol-2-yl)pyridin-2-yl)-4,5-diphenylimidazol-1-yl)(diphenyl)phosphine oxide 12

Prepared according to general procedure A using **3** (208 mg, 0.4 mmol), DMAP (147 mg, 1.2 mmol) and diphenylphosphinyl chloride (230 μL, 1.2 mmol) in 1,2-dichloromethane (20 mL) for 8 h followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent to afford pale yellow crystals (218 mg, 72%). $R_f = 0.20$ (CH_2Cl_2/MeOH 100:5); mp = 121–122 °C; $[\alpha]_D^{20} = +53.1$ (*c* 0.72, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.59 (t, $J = 2.76$, 1H), 4.89 (d, $J = 8.32$, 1H), 5.11 (d, $J = 8.52$, 1H), 5.16 (d, $J = 2.16$, 1H), 7.08–7.13 (m, 6H), 7.21–7.34 (m, 13H), 7.39–7.50 (m, 1H), 7.79 (t, $J = 7.72$, 1H), 8.12 (dd, $J = 1.00$, 7.72, 1H), 8.26 (dd, $J = 1.20$, 7.92, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 70.0, 74.8, 78.2, 78.8, 124.1, 125.3, 125.8, 126.2, 126.9, 127.1, 127.8, 127.9, 128.1, 128.2, 128.3, 128.8, 129.0, 131.2, 131.6, 131.8, 131.9, 135.8, 137.4, 142.2, 142.7, 147.3, 147.9, 154.8, 160.9, 161.7; IR (KBr): $\nu = 3422$ (br), 1605, 1451, 1209 (P=O), 1122 cm^{-1}; HRMS: calcd for $C_{47}H_{38}N_5PO{\cdot}H^+$: 720.2852. Found: 720.2868; Anal. Calcd (%) for $C_{47}H_{38}N_5PO{\cdot}H_2O$: C, 76.50; H, 5.46; N, 9.49. Found: C, 76.05; H, 4.96; N, 9.13.

4.41. 2-(1-(2,4,6-Trimethyl-benzoyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-6-(1-((1*R*,2*R*,5*S*)-2-iso-propyl-5-methylcyclohexyl-3-oxycarbonyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)pyridine 13

Prepared according to general procedure A using **9** (193 mg, 0.28 mmol), DMAP (70 mg, 0.57 mmol) and (+)-menthyl chloroformate (130 μL, 0.57 mmol) in dichloromethane (10 mL) for 6 h followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent to afford pale yellow crystals (247 mg, 99%). $R_f = 0.80$ (CH_2Cl_2/MeOH 100:5); mp = 94–96 °C; $[\alpha]_D^{20} = -23.9$ (*c* 0.13, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.44 (d, $J = 6.52$, 3H), 0.51 (d, $J = 6.92$, 3H), 0.57 (d, $J = 7.12$, 3H), 0.59–0.95 (m, 5H), 1.16–1.46 (m, 4H), 2.02 (s, 6H), 2.08 (s, 3H), 4.21 (dt, $J = 4.36$, 10.68, 1H), 5.15 (d, $J = 3.16$, 1H), 5.20 (d, $J = 4.52$, 1H), 5.24 (d, $J = 4.36$, 1H), 5.72 (d, $J = 3.20$, 1H), 6.38 (s, 1H), 6.47 (s, 1H), 7.31–7.58 (m, 21H), 7.74 (d, $J = 7.12$, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 15.9, 19.4, 19.9, 20.3, 20.6, 21.4, 23.0, 25.8, 31.1, 33.8, 40.0, 46.1, 68.5, 69.7, 77.0, 77.5, 78.4, 122.7, 123.5, 125.2, 125.3, 125.4, 126.3, 126.4, 127.3, 127.8, 127.9, 128.0, 128.3, 128.9, 129.1, 129.4, 132.8, 135.8, 136.6, 139.1, 141.1, 142.5, 142.7, 149.8, 151.2, 157.8, 168.5; IR (KBr): $\nu = 2954$, 2926, 1716, 1673, 1334 cm^{-1}; HRMS: calcd for $C_{56}H_{57}N_5O_3{\cdot}H^+$: 848.4540. Found: 848.4515; Anal. Calcd (%) for $C_{56}H_{57}N_5O_3{\cdot}H_2O$: C, 77.66; H, 6.67; N, 8.08. Found: C, 77.22; H, 7.15; N, 7.58.

4.42. 2-(1-((4*R*,5*R*)-(1*R*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyl-3-oxycarbonyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-6-(1-(acetyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)pyridine 14

Prepared according to general procedure A using **11** (220 mg, 0.31 mmol), DMAP (116 mg, 0.94 mmol) and acetyl chloride (69 μL, 0.94 mmol) in dichloromethane (10 mL) for 2 h followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent to afford a pale yellow solid (189 mg, 81%). $R_f = 0.50$ (CH_2Cl_2/MeOH 100:5); mp = 73–74 °C; $[\alpha]_D^{20} = -11.1$ (*c* 0.23, $CHCl_3$); ^{1}H NMR (300 MHz, CD_2Cl_2): δ 0.42 (d, $J = 6.57$, 3H), 0.55 (d, $J = 6.99$, 3H), 0.67 (d, $J = 7.14$, 3H), 0.61–0.96 (m, 4H), 1.39–1.46 (m, 2H), 1.61–1.73 (m, 3H), 1.90 (s, 3H), 4.28 (dt, $J = 4.35$, 10.74, 1H), 5.08 (d, $J = 2.64$, 1H), 5.14 (d, $J = 3.39$, 1H), 5.25 (d, $J = 3.39$, 1H), 5.36 (d, $J = 2.64$, 1H), 7.28–7.47 (m, 17H), 7.56–7.58 (m, 3H), 7.90 (dd, $J = 1.86$, 6.78, 1H), 8.03 (d, $J = 2.07$, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ 16.0, 20.4, 21.3, 23.1, 24.5, 25.9, 31.1, 33.9, 40.3, 46.6, 69.5, 69.8, 76.9, 78.1, 78.4, 124.0, 124.1, 125.1, 126.3, 127.8, 128.0, 129.1, 129.3, 137.8, 141.0, 141.4, 141.7, 142.5, 150.5, 151.2, 158.4, 158.7, 167.9; IR (KBr): $\nu = 2955$, 1717, 1627, 1453, 1373 cm^{-1}; EI-MS: *m*/*z* 743 (M^+); HRMS: calcd for $C_{48}H_{49}N_5O_3{\cdot}H^+$: 744.3908. Found: 744.3897.

4.43. General procedure for the preparation of Ru(pybim)(pydic) complexes (procedure B)

A 25 mL oven dried Schlenk tube was charged with $[Ru(p\text{-cymene})Cl_2]_2$ (306 mg, 0.5 mmol) and pybim (1 mmol) in 10 mL methanol. In another 25 mL Schlenk tube 2,6-pyridinedicarboxylate disodium salt (211 mg, 1 mmol) was dissolved in a mixture of water (5 mL) and methanol (5 mL). The solution was purged with argon for ca. 10 min and then transferred via a cannula into the Schlenk tube containing the ruthenium source

at rt. The mixture was then heated at 65 °C for 1 h, cooled to rt and then diluted with CH_2Cl_2 (30 mL). The mixture was washed with water (2 × 20 mL), dried over Na_2SO_4, concentrated and purified by column chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent to give the Ru(pybim)(pydic) complex as a dark brown solid after crystallization from CH_2Cl_2–hexane.

4.44. Ruthenium{2,6-bis-(1-benzoyl-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine}{pyridine-2,6-dicarboxylate} 15a

Prepared according to general procedure B using **6a** (100 mg, 0.14 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (42 mg, 0.070 mmol) and Na_2pydic (29 mg, 0.140 mmol) to give **15a** as a dark brown solid (78 mg, 56%). $R_f = 0.37$ (CH_2Cl_2/MeOH 100:5); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.42 (d, $J = 4.1$, 2H), 5.16 (d, $J = 4.6$, 2H), 6.56 (d, $J = 7.7$, 4H), 6.92 (d, $J = 7.3$, 4H), 7.03–7.06 (m, 4H), 7.17 (t, $J = 7.5$, 4H), 7.23–7.29 (m, 10H), 7.42–7.50 (m, 8H), 7.61–7.65 (m, 1H), 7.73 (t, $J = 8.1$, 1H), 8.22 (d, $J = 8.1$, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 74.1, 77.5, 125.9, 126.2, 126.3, 126.4, 128.5, 128.7, 128.7, 128.8, 129.2, 129.4, 132.7, 133.6, 134.9, 135.8, 136.3, 140.3, 149.0, 150.3, 163.1, 170.2, 170.4; UV–vis (CH_2Cl_2: λ_{max}/nm, log ε): 374 (4.00), 493 (4.26); FAB-MS: *m*/*z* 994 (M^+); Anal. Calcd (%) for $C_{56}H_{40}N_6O_6$-Ru·0.5H_2O: C, 65.47; H, 3.99; N, 8.11. Found: C, 65.60; H, 4.09; N, 8.06.

4.45. Ruthenium{2,6-bis-(1-(2-methylbenzoyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine}-{pyridine-2,6-dicarboxylate} 15b

Prepared according to general procedure B using [Ru(*p*-cymene)Cl_2]$_2$ (80 mg, 0.13 mmol), pybim **6b** (206 g, 0.26 mmol) and disodium 2,6-pyridinedicarboxylate (55 mg, 0.26 mmol) in MeOH/H_2O (15:5 mL) at 65 °C for 1 h followed by chromatography on silica gel using 3% MeOH–CH_2Cl_2 to afford **15b** as a dark brown powder (258 mg, 93%). $R_f = 0.25$ (CH_2Cl_2/MeOH 100:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.32 (s, 6H), 4.69 (d, $J = 4.36$, 2H), 5.08 (d, $J = 3.96$, 2H), 6.84 (d, $J = 6.92$, 4H), 6.89 (d, $J = 7.16$, 4H), 7.15–7.23 (m, 3H), 7.31–7.51 (m, 19H), 7.74–7.83 (m, 3H), 8.02 (t, $J = 8.12$, 1H), 8.80 (d, $J = 8.12$, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.1, 31.5, 73.6, 125.3, 125.9, 126.1, 126.9, 127.0, 127.3, 128.8, 128.9, 129.2, 129.3, 130.8, 130.9, 133.6, 134.3, 136.4, 139.7, 148.6, 150.6, 162.6, 169.4, 170.5; UV–vis (CH_2Cl_2: λ_{max}/nm, log ε): 491 (4.30), 365 (3.98); FAB-MS: *m*/*z* 1023 (M^++1); HRMS: calcd for $C_{58}H_{44}N_6O_6Ru{\cdot}H^+$: 1023.2444. Found: 1023.2422. Anal. Calcd (%) for $C_{58}H_{44}N_6O_6Ru{\cdot}H_2O$: C, 66.98; H, 4.46; N, 8.08. Found: C, 66.50; H, 4.01; N, 7.67.

4.46. Ruthenium{2,6-bis-(1-(4-methoxy-benzoyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine}-{pyridine-2,6-dicarboxylate} 15c

Prepared according to general procedure B using **6c** (200 mg, 0.25 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (78 mg, 0.13 mmol) and Na_2pydic (54 mg, 0.25 mmol) to give **15c** as a dark brown solid (200 mg, 75%). $R_f = 0.34$ (CH_2Cl_2/MeOH 20:1); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 3.97 (s, 6H), 4.40 (d, $J = 4.0$, 2H), 5.20 (d, $J = 4.0$, 2H), 6.56 (dd, $J = 8.1$, 1.2 Hz, 4H), 6.77 (unresolved dd, 4H), 7.98 (m, 4H), 7.17 (tt, $J = 1.0$, 7.4, 2H), 7.25–7.31 (m, 6H), 7.45–7.50 (m, 6H), 7.62 (dd, $J = 7.1$, 8.1, 1H), 7.70 (d, $J = 8.1$, 1H), 8.12 (d, $J = 8.1$, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 55.6, 74.4, 77.5, 113.8, 125.5, 125.9, 125.9, 125.9, 126.3, 126.3, 128.6, 128.8, 129.1, 129.4, 131.2, 134.7, 136.4, 140.6, 149.1, 150.3, 163.5, 163.5, 170.1, 170.2; UV–vis (CH_2Cl_2: λ_{max}/nm, log ε): 372 (3.99), 491 (4.23); FAB-MS: *m*/*z* 1055 (M^++1); Anal. Calcd (%) for $C_{58}H_{44}N_6O_8Ru{\cdot}2H_2O$: C, 63.90; H, 4.44; N, 7.71. Found: C, 63.96; H, 4.39; N, 7.52.

4.47. Ruthenium{2,6-bis-(1-(4-trifluoromethyl-benzoyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine}{pyridine-2,6-dicarboxylate} 15d

Prepared according to general procedure B using **6d** (200 mg, 0.25 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (76 mg, 0.12 mmol) and Na_2pydic (53 mg, 0.25 mmol) to give **15d** as a dark brown solid (200 mg, 71%). $R_f = 0.40$ (CH_2Cl_2/MeOH 100:6); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.45 (d, $J = 4.2$, 2H), 5.10 (d, $J = 4.2$, 2H), 6.55 (dd, $J = 8.1$, 0.9, 4H), 6.88 (unresolved dd, 4H), 7.04 (unresolved dd, 4H), 7.18 (unresolved tt, 2H), 7.24–7.33 (m, 6H), 7.48 (d, $J = 7.5$, 2H), 7.51–7.55 (m, 8H), 7.63 (dd, $J = 7.8$, 7.6, 1H), 7.82 (t, $J = 8.1$, 1H), 8.35 (d, $J = 8.1$, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 74.1, 77.7, 125.5, 126.5, 125.9, 126.0, 126.3, 126.4, 126.5, 128.8, 128.9, 129.1, 129.3, 129.6, 133.9, 135.1, 136.0, 137.0, 139.8, 148.8, 150.1, 162.5, 169.0, 170.1; UV–vis (CH_2Cl_2: λ_{max}/nm, log ε): 376 (4.00), 494 (4.25); FAB-MS: *m*/*z* 1130 (M^+); Anal. Calcd (%) for $C_{58}H_{38}N_6O_6$-$F_6Ru{\cdot}H_2O$: C, 60.68; H, 3.51; N, 7.32. Found: C, 60.51; H, 3.38; N, 7.12.

4.48. Ruthenium{2,6-bis-(1-(2,6-dimethoxybenzoyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine}{pyridine-2,6-dicarboxylate} 15e

Prepared according to general procedure B using [Ru(*p*-cymene)Cl_2]$_2$ (55 mg, 0.09 mmol), **6e** (156 mg, 0.17 mmol) and disodium 2,6-pyridinedicarboxylate (36 mg, 0.17 mmol) in MeOH/H_2O (15:5 mL) at 65 °C for 1 h followed by chromatography on silica gel using 2.5% MeOH–CH_2Cl_2 to give **15e** as a dark brown powder (84 mg, 42%). $R_f = 0.25$ (CH_2Cl_2/MeOH 100:5); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 3.15 (s, 6H), 3.60 (s, 6H), 4.26 (d, $J = 3.56$, 2H), 4.91 (br s, 2H), 6.24 (d, $J = 6.76$, 2H), 6.47–6.64 (m, 10H), 7.03–7.26 (m, 14H), 7.48 (d, $J = 7.52$, 2H), 7.62 (t, $J = 7.36$, 1H), 7.86 (br s, 1H), 9.03 (br s, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 55.6, 72.2, 78.5, 103.3, 103.8, 113.9, 125.8, 126.0, 126.5, 128.3, 128.5, 128.7, 128.9, 131.5, 133.8, 137.2, 140.1, 148.6, 150.7, 164.5; UV–vis (CH_2Cl_2: λ_{max}/nm, log ε): 488 (4.65); FAB-MS: *m*/*z* 1116 (M^++2); HRMS: calcd for $C_{60}H_{48}N_6O_{10}Ru{\cdot}H^+$: 1115.2554. Found: 1115.2559. Anal. Calcd (%) for $C_{60}H_{48}N_6O_{10}Ru{\cdot}2H_2O$: C, 62.66; H, 4.56; N, 7.31. Found: C, 62.79; H, 4.94; N, 7.01.

4.49. Ruthenium{2,6-bis-(1-(2,4,6-trimethylbenzoyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine}{pyridine-2,6-dicarboxylate} 15f

Prepared according to general procedure B using $[Ru(p\text{-cymene})Cl_2]_2$ (98 mg, 0.16 mmol), **6f** (266 mg, 0.33 mmol) and disodium 2,6-pyridinedicarboxylate (70 mg, 0.33 mmol) in $MeOH/H_2O$ (15:5 mL) at 65 °C for 1 h followed by chromatography on silica gel using $MeOH–CH_2Cl_2$ as the gradient eluent to afford **15f** as a dark brown powder (217 mg, 59%). $R_f = 0.40$ (CH_2Cl_2/MeOH 100:5); ^1H NMR (400 MHz, CD_2Cl_2): δ 1.56 (s, 6H), 1.99 (s, 6H), 2.25 (s, 6H), 4.50 (d, $J = 3.16$, 2H), 4.62 (unresolved d, 2H), 6.46 (d, $J = 7.52$, 4H), 6.61 (m, 6H), 6.80 (s, 2H), 7.05–7.26 (m, 12H), 7.44 (d, $J = 7.52$, 2H), 7.55 (t, $J = 7.76$, 1H), 7.91 (t, $J = 8.12$, 1H), 8.92 (d, $J = 7.72$, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 18.3, 19.0, 20.9, 72.9, 76.0, 125.8, 126.1, 126.4, 127.7, 128.2, 128.4, 128.6, 128.9, 129.1, 132.2, 132.9, 135.0, 135.4, 135.8, 136.6, 139.8, 148.7, 150.8, 162.6, 169.2, 170.3; UV–vis (CH_2Cl_2: λ_{max}/nm, $\log\varepsilon$): 763 (3.28), 489 (4.32), 356 (4.03); HRMS: calcd for $C_{62}H_{52}N_6O_6Ru{\cdot}H^+$: 1079.3070. Found: 1079.3099. Anal. Calcd (%) for $C_{62}H_{52}N_6O_6Ru{\cdot}H_2O$: C, 67.19; H, 4.91; N, 7.58. Found: C, 67.25; H, 4.96; N, 7.28.

4.50. Ruthenium{2,6-bis-(1-(3,5-bis-(1,1-dimethylethyl)-benzoyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine}{pyridine-2,6-dicarboxylate} 15g

Prepared according to general procedure B using $[Ru(p\text{-cymene})Cl_2]_2$ (49 mg, 0.08 mmol), **6g** (164 mg, 0.17 mmol) and disodium 2,6-pyridinedicarboxylate (36 mg, 0.17 mmol) in a mixture of *tert*-amylalcohol/$MeOH/H_2O$ (12:5:1 mL) at 65 °C for 2 h followed by chromatography on silica gel using $MeOH–CH_2Cl_2$ as the gradient eluent to afford **15g** as a dark brown powder (96 mg, 43%). $R_f = 0.35$ (CH_2Cl_2/MeOH 100:5); ^1H NMR (400 MHz, CD_2Cl_2): δ 1.12 (s, 36H), 4.33 (d, $J = 3.96$, 2H), 5.19 (d, $J = 3.96$, 2H), 6.56 (d, $J = 7.16$, 4H), 6.97 (m, 4H), 7.04 (t, $J = 7.92$, 4H), 7.14–7.19 (m, 2H), 7.26–7.30 (m, 10H), 7.47–7.52 (m, 4H), 7.62 (t, $J = 7.92$, 1H), 7.77 (t, $J = 8.12$, 1H), 8.28 (d, $J = 8.32$, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 30.8, 34.7, 73.9, 77.8, 122.7, 125.6, 125.9, 126.1, 126.3, 126.4, 127.2, 128.7, 129.2, 129.6, 132.9, 134.8, 136.3, 140.4, 149.0, 150.4, 151.5, 163.3, 170.1, 171.5; UV–vis (CH_2Cl_2: λ_{max}/nm, $\log\varepsilon$): 595 (3.64), 491 (4.32), 371 (4.02); HRMS: calcd for $C_{72}H_{72}N_6O_6Ru{\cdot}H^+$: 1219.4635. Found: 1219.4702. Anal. Calcd (%) for $C_{72}H_{72}N_6O_6Ru{\cdot}H_2O$: C, 69.94; H, 6.03; N, 6.80. Found: C, 69.96; H, 5.75; N, 6.64.

4.51. Ruthenium{2,6-bis-(1-(2-phenylacetyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine}{pyridine-2,6-dicarboxylate} 15h

Prepared according to general procedure B using $[Ru(p\text{-cymene})Cl_2]_2$ (107 mg, 0.17 mmol), **6h** (264 mg, 0.35 mmol) and disodium 2,6-pyridinedicarboxylate (74 mg, 0.35 mmol) in $MeOH/H_2O$ (15:5 mL) at 65 °C for 1 h followed by chromatography on silica gel using $MeOH–CH_2Cl_2$ as the gradient eluent to afford **15h** as a dark brown powder (54 mg, 30%). $R_f = 0.25$ (CH_2Cl_2/MeOH 100:5); ^1H NMR (400 MHz, CD_2Cl_2): δ 3.68 (s, 4H), 4.28 (d, $J = 3.76$, 2H), 5.28 (d, $J = 3.76$, 2H), 6.44 (d, $J = 7.32$, 4H), 6.96–7.02 (m, 6H), 7.07–7.15 (m, 8H), 7.21–7.25 (m, 6H), 7.31–7.44 (m, 6H), 7.56–7.66 (m, 3H), 7.76 (t, $J = 8.32$, 1H), 8.65 (d, $J = 8.32$, H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 42.3, 71.2, 76.8, 125.4, 125.9, 126.1, 127.4, 127.8, 128.6, 128.8, 129.1, 129.2, 129.9, 132.9, 134.8, 135.8, 136.6, 140.0, 140.4, 152.5, 161.7, 170.1, 172.5; UV–vis (CH_2Cl_2: λ_{max}/nm, $\log\varepsilon$): 488 (4.32); HRMS: calcd for $C_{58}H_{44}N_6O_6Ru{\cdot}H^+$: 1023.2442. Found: 1023.2456.

4.52. Ruthenium{2,6-bis-(1-(2,2-diphenylacetyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine}-{pyridine-2,6-dicarboxylate} 15i

Prepared according to general procedure B using $[Ru(p\text{-cymene})Cl_2]_2$ (73 mg, 0.12 mmol), **6i** (215 mg, 0.23 mmol) and disodium 2,6-pyridinedicarboxylate (49 mg, 0.23 mmol) in $MeOH/H_2O$ (15:5 mL) at 65 °C for 1 h followed by chromatography on silica gel using $MeOH–CH_2Cl_2$ as the gradient eluent to afford **15i** as a dark brown powder (137 mg, 49%). $R_f = 0.45$ (CH_2Cl_2/MeOH 100:5); ^1H NMR (400 MHz, CD_2Cl_2): δ 4.21 (d, $J = 3.56$, 2H), 5.01 (s, 2H), 5.18 (d, $J = 3.60$, 2H), 6.28 (d, $J = 7.92$, 4H), 6.87 (t, $J = 7.72$, 4H), 6.93–6.95 (m, 4H); 7.05–7.27 (m, 22H), 7.39–7.42 (m, 8H), 7.58 (t, $J = 7.32$, 1H), 7.72 (t, $J = 8.32$, 1H), 8.61 (d, $J = 8.32$, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 56.7, 70.7, 76.7, 125.1, 125.9, 126.7, 127.5, 127.8, 127.9, 128.3, 128.4, 128.9, 129.1, 129.3, 129.4, 130.0, 134.9, 136.0, 136.5, 138.8, 140.1, 148.6, 150.3, 161.9, 170.0, 170.3; UV–vis (CH_2Cl_2: λ_{max}/nm, $\log\varepsilon$): 488 (4.32), 356 (4.04); HRMS: calcd for $C_{70}H_{52}N_6O_6Ru$: 1175.3118. Found: 1175.3105. Anal. Calcd (%) for $C_{70}H_{52}N_6O_6Ru{\cdot}2H_2O$: C, 69.47; H, 4.66; N, 6.94. Found: C, 69.12; H, 4.40; N, 6.73.

4.53. Ruthenium{2,6-bis-(1-naphthoyl-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine}{pyridine-2,6-dicarboxylate} 15j

Prepared according to general procedure B using **6j** (500 mg, 0.60 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (184 mg, 0.30 mmol) and Na_2pydic (126 mg, 0.60 mmol) to afford **15j** as a dark brown solid (262 mg, 40%). $R_f = 0.31$ (CH_2Cl_2/MeOH 100:6); ^1H NMR (400 MHz, CD_2Cl_2): δ 4.43 (d, $J = 3.9$, 2H), 4.90 (d, $J = 3.9$, 2H), 6.61 (m, 8H), 7.02–7.24 (m, 16H), 7.39–7.42 (m, 2H), 7.45–49 (m, 4H), 7.60 (dd, $J = 7.1$, 8.1, 1H), 7.82–7.90 (m, 7H), 7.95 (d, $J = 8.1$, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 73.8, 76.9, 116.7, 124.2, 124.5, 125.9, 125.9, 126.2, 126.6, 126.6, 126.7, 127.1, 127.6, 128.4, 128.7, 129.1, 129.1, 129.6, 131.2, 130.7, 133.5, 135.0, 136.3, 140.0, 148.8, 150.5, 162.7, 169.1, 170.2; UV–vis (CH_2Cl_2: λ_{max}/nm, $\log\varepsilon$): 492 (4.26); FAB-MS: m/z 1094 (M^+); Anal. Calcd (%) for $C_{64}H_{44}N_6O_6Ru{\cdot}2H_2O$: C, 68.01; H, 4.28; N, 7.44. Found: C, 67.94; H, 4.00; N, 7.22.

4.54. Ruthenium{2,6-bis-(2-naphthoyl-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine}{pyridine-2,6-dicarboxylate} 15k

Prepared according to general procedure B using $[Ru(p\text{-cymene})Cl_2]_2$ (104 mg, 0.17 mmol), **6k** (286 mg, 0.34 mmol) and disodium 2,6-pyridinedicarboxylate (72 mg, 0.34 mmol) in MeOH/H_2O (15:5 mL) at 65 °C for 1 h followed by chromatography on silica gel using 2% MeOH–CH_2Cl_2 to afford **15k** as a dark brown powder (247 mg, 64%). $R_f = 0.30$ (CH_2Cl_2/MeOH 100:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.79 (d, $J = 4.16$, 2H), 5.40 (d, $J = 4.16$, 2H), 6.88 (d, $J = 7.16$, 4H), 7.16 (d, $J = 6.96$, 4H), 7.37 (t, $J = 7.72$, 4H), 7.47–7.59 (m, 10H), 7.76–7.86 (m, 10H), 8.55 (d, $J = 8.12$, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.83, 74.35, 124.6, 125.9, 126.1, 126.7, 127.0, 127.7, 128.4, 128.5, 128.8, 128.9, 129.3, 129.6, 130.2, 131.7, 134.2, 135.0, 136.2, 140.6, 148.8, 150.5, 163.4, 170.5, 170.7; UV–vis (CH_2Cl_2: λ_{max}/nm, log ε): 495 (4.37), 378 (4.05); FAB-MS: m/z 1095 (M^++1); HRMS: calcd for $C_{64}H_{44}N_6O_6Ru$: 1094.2366. Found: 1094.2395. Anal. Calcd (%) for $C_{64}H_{44}N_6O_6Ru{\cdot}2H_2O$: C, 68.02; H, 4.28; N, 7.44. Found: C, 68.20; H, 4.88; N, 7.01.

4.55. Ruthenium{2,6-bis-(1-[(2*S*)-2-(6-methoxy-naphthalen-2-yl)-propionyl]-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine}{pyridine-2,6-dicarboxylate} 15l

Prepared according to general procedure B using **6l** (150 mg, 0.16 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (49 mg, 0.080 mmol) and Na_2pydic (34.0 mg, 0.16 mmol) to afford **15l** as a dark brown solid (150 mg, 78%). $R_f = 0.45$ (CH_2Cl_2/MeOH 100:6); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.50 (d, $J = 6.5$, 6H), 3.80 (q, $J = 6.5$, 2H), 3.86 (s, 6H), 4.05 (d, $J = 3.1$, 2H), 5.18 (d, $J = 3.1$, 2H), 6.02 (d, $J = 7.7$, 2H), 6.46 (t, $J = 7.6$, 4H), 6.72 (t, $J = 7.4$, 2H), 7.01 (unresolved d, 2H), 7.07–7.10 (m, 6H), 7.24 (unresolved dd, 2H), 7.33 (d, $J = 7.8$, 2H), 7.37 (m, 6H), 7.50 (t, $J = 7.8$, 1H), 7.59 (t, 6H), 7.93 (*t*, $J = 8.3$ Hz, 1H), 8.86 (d, $J = 8.3$, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 20.8, 45.6, 55.3, 69.9, 76.5, 78.8, 105.5, 116.9, 119.2, 125.2, 125.4, 125.5, 125.6, 125.8, 127.9, 127.9, 128.1, 128.5, 129.0, 129.1, 129.3, 129.9, 133.8, 134.1, 136.1, 140.2, 148.6, 150.6, 158.0, 162.3, 169.9, 171.9; UV–vis (CH_2Cl_2: λ_{max}/nm, log ε): 333 (3.65), 488 (4.27); FAB-MS: m/z 1211 (M^+); Anal. Calcd (%) for $C_{70}H_{56}N_6O_8Ru$: C, 69.47; H, 4.66; N, 6.94. Found: C, 69.96; H, 4.49; N, 6.64.

4.56. Ruthenium{2,6-bis-(1-(2-(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl-3-oxy-acetyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine}{pyridine-2,6-dicarboxylate} 15m

Prepared according to general procedure B using $[Ru(p\text{-cymene})Cl_2]_2$ (168 mg, 0.27 mmol), **6m** (500 mg, 0.55 mmol) and disodium 2,6-pyridinedicarboxylate (116 mg, 0.55 mmol) in MeOH/H_2O (15:5 mL) at 65 °C for 1 h followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent to afford **15m** as a dark brown powder (297 mg, 46%). $R_f = 0.30$ (CH_2Cl_2/MeOH 100:5); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.69 (d, $J = 6.92$, 6H), 0.81 (d, $J = 6.92$, 6H), 0.84 (d, $J = 6.56$, 6H), 0.87–0.95 (m, 4H), 1.00–1.07 (m, 2H), 1.21–1.31 (m, 4H), 1.52–1.60 (m, 4H), 1.81–1.84 (m, 2H), 2.03–2.09 (m, 2H), 3.08 (dt, $J = 3.96$, 10.52, 2H), 3.95 (d, $J = 14.68$, 2H), 4.17 (d, $J = 14.68$, 2H), 4.32 (d, $J = 3.96$, 2H), 5.42 (d, $J = 3.96$, 2H), 6.54 (d, $J = 7.12$, 4H), 7.02–7.10 (m, 8H), 7.17–7.21 (m, 2H), 7.32–7.34 (m, 6H), 7.45 (d, $J = 7.52$, 2H), 7.61 (t, $J = 8.32$, 1H), 7.83 (t, $J = 8.32$, 1H), 8.73 (d, $J = 8.36$, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 15.9, 20.7, 21.9, 23.1, 25.5, 31.4, 34.3, 39.8, 47.9, 68.2, 70.6, 77.2, 80.8, 125.4, 125.9, 126.2, 127.7, 128.7, 129.1, 129.2, 129.7, 136.7, 140.1, 148.8, 150.4, 162.0, 168.6, 170.1; UV–vis (CH_2Cl_2: λ_{max}/nm, log ε): 352 (3.92), 488 (4.28); HRMS: calcd for $C_{66}H_{72}N_6O_8Ru$: 1178.4456. Found: 1178.4506. Anal. Calcd (%) for $C_{66}H_{72}N_6O_8Ru{\cdot}H_2O$: C, 66.26; H, 6.23; N, 7.02. Found: C, 66.57; H, 6.36; N, 6.78.

4.57. Ruthenium{2,6-bis-(1-adamantoyl-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine}{pyridine-2,6-dicarboxylate} 15n

Prepared according to general procedure B using **6n** (150 mg, 0.18 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (54 mg, 0.09 mmol) and Na_2pydic (37 mg, 0.18 mmol) to afford **15n** as a dark brown solid (130 mg, 66%). $R_f = 0.35$ (CH_2Cl_2/MeOH 100:5); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.56 (m, 6H), 1.65 (m, 8H), 1.82–1.85 (m, 6H), 1.90–1.96 (m, 12H), 4.26 (d, $J = 2.7$, 2H), 5.53 (d, $J = 2.7$, 2H), 6.52 (m, 4H), 7.04–7.08 (m, 8H), 7.19 (m, 2H), 7.29–7.33 (m, 6H), 7.48 (d, $J = 7.5$, 2H), 7.64 (dd, $J = 8.1$, 7.3, 1H), 7.83 (dd, $J = 8.7$, 7.5, 1H) 7.96 (d, $J = 7.7$, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 28.1, 36.1, 39.4, 44.2, 71.5, 78.8, 125.1, 125.2, 125.8, 126.2, 126.6, 128.6, 128.7, 129.2, 129.5, 134.6, 136.1, 140.6, 149.1, 150.7, 165.1, 170.0, 181.1; UV–vis (CH_2Cl_2: λ_{max}/nm, log ε): 458 (3.96), 487 (4.22); FAB-MS: m/z 1111 (M^++1); Anal. Calcd (%) for $C_{64}H_{60}N_6O_6Ru{\cdot}H_2O$: C, 68.13; H, 5.54; N, 7.45. Found: C, 67.65; H, 5.59; N, 7.14.

4.58. Ruthenium{2,6-bis-(1-acetyl-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine}{pyridine-2,6-dicarboxylate} 15o

Prepared according to general procedure B using $[Ru(p\text{-cymene})Cl_2]_2$ (152 mg, 0.25 mmol), **6o** (300 mg, 0.50 mmol) and disodium 2,6-pyridinedicarboxylate (105 mg, 0.50 mmol) in MeOH/H_2O (15:5 mL) at 65 °C for 1 h followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent to afford **15o** as a dark brown powder (292 mg, 68%). $R_f = 0.35$ (CH_2Cl_2/MeOH 100:5); ^{1}H NMR (300 MHz, CD_2Cl_2): δ 2.15 (s, 6H), 4.31 (d, $J = 3.75$, 2H), 5.22 (d, $J = 3.78$, 2H), 6.56 (d, $J = 7.17$, 4H), 7.03–7.23 (m, 10H), 7.36 (t, $J = 3.75$, 6H), 7.44 (d, $J = 7.53$, 2H), 7.60 (t, $J = 7.14$, 1H), 7.83 (t, $J = 8.10$, 1H), 8.74 (d, $J = 8.28$, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ 23.7, 72.0, 76.6, 125.4, 125.8, 126.1, 126.5, 127.8, 128.6, 129.1, 129.2, 129.7, 134.7, 136.8, 140.1, 148.7, 150.4, 162.2, 168.7, 170.2; UV–vis (CH_2Cl_2: λ_{max}/nm, log ε): 487 (4.29); HRMS: calcd for $C_{46}H_{36}N_6O_6Ru$: 870.1740, Found:

870.1730. Anal. Calcd (%) for $C_{46}H_{36}N_6O_6Ru{\cdot}4H_2O$: C, 58.65; H, 4.71; N, 8.92. Found: C, 59.08; H, 4.25; N, 8.82.

4.59. Ruthenium{2,6-bis-(1-pentanoyl-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine}{pyridine-2,6-dicarboxylate} 15p

Prepared according to general procedure B using [Ru(*p*-cymene)Cl_2]$_2$ (133 mg, 0.22 mmol), **6p** (300 mg, 0.44 mmol) and disodium 2,6-pyridinedicarboxylate (92 mg, 0.44 mmol) in MeOH/H_2O (15:5 mL) at 65 °C for 1 h followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent to afford **15p** as a dark brown powder (310 mg, 75%). $R_f = 0.10$ (CH_2Cl_2/MeOH 100:5); ^{1}H NMR (300 MHz, CD_2Cl_2): δ 0.80 (t, $J = 7.35$, 6H), 1.21–1.32 (m, 4H), 1.56–1.64 (m, 4H), 2.20–2.31 (m, 2H), 2.37–2.47 (m, 2H), 4.31 (d, $J = 3.78$, 2H), 5.23 (d, $J = 3.78$, 2H), 6.56 (d, $J = 7.17$, 4H), 7.03–7.22 (m, 10H), 7.34 (t, $J = 3.00$, 6H), 7.45 (d, $J = 7.56$, 2H), 7.60 (t, $J = 7.17$, 1H), 7.83 (t, $J = 8.28$, 1H), 8.68 (d, $J = 8.28$, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ 13.5, 22.1, 26.7, 35.2, 71.5, 76.7, 125.3, 125.8, 126.1, 126.5, 127.6, 128.6, 129.0, 129.2, 129.7, 134.7, 136.9, 140.3, 148.7, 150.5, 162.4, 170.2, 171.8; UV–vis (CH_2Cl_2: λ_{max}/nm, log ε): 487 (4.35); HRMS: calcd for $C_{52}H_{48}N_6O_6Ru$: 954.2679. Found: 954. 2654. Anal. Calcd (%) for $C_{52}H_{48}N_6O_6Ru{\cdot}H_2O$: C, 64.25; H, 5.18; N, 8.65. Found: C, 64.43; H, 5.23; N, 8.34.

4.60. Ruthenium{2,6-bis-(1-(2-methyl propanoyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine}{pyridine-2,6-dicarboxylate} 15q

Prepared according to general procedure B using [Ru(*p*-cymene)Cl_2]$_2$ (139 mg, 0.23 mmol), **6q** (300 mg, 0.45 mmol) and disodium 2,6-pyridinedicarboxylate (95 mg, 0.45 mmol) in MeOH/H_2O (15:5 mL) at 65 °C for 1 h followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent to afford **15q** as a dark brown powder (406 mg, 98%). $R_f = 0.15$ (CH_2Cl_2/MeOH 100:5); ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.00 (d, $J = 6.78$, 6H), 1.12 (d, $J = 6.78$, 6H), 2.59–2.68 (m, 2H), 4.33 (d, $J = 3.78$, 2H), 5.27 (d, $J = 3.75$, 2H), 6.56 (d, $J = 6.96$, 4H), 7.03–7.23 (m, 10H), 7.32–7.35 (m, 6H), 7.45 (d, $J = 7.35$, 2H), 7.61 (t, $J = 6.96$, 1H), 7.82 (t, $J = 8.28$, 1H), 8.52 (d, $J = 8.31$, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ 18.8, 19.8, 33.8, 71.4, 76.9, 125.3, 125.8, 126.1, 126.5, 127.2, 128.7, 129.0, 129.3, 129.7, 134.7, 136.7, 140.3, 148.8, 150.5, 162.6, 170.2, 176.6; UV–vis (CH_2Cl_2: λ_{max}/nm, log ε): 352 (3.92), 488 (4.30); HRMS: calcd for $C_{50}H_{44}N_6O_6Ru{\cdot}H^+$: 927.2444. Found: 927.2419. Anal. Calcd (%) for $C_{50}H_{44}N_6O_6Ru{\cdot}H_2O$: C, 63.61; H, 4.91; N, 8.90. Found: C, 63.49; H, 4.74; N, 8.52.

4.61. Ruthenium{2,6-bis-(1-(3-methyl butanoyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine}-{pyridine-2,6-dicarboxylate} 15r

Prepared according to general procedure B using [Ru(*p*-cymene)Cl_2]$_2$ (133 mg, 0.22 mmol), **6r** (300 mg, 0.44 mmol) and disodium 2,6-pyridinedicarboxylate (92 mg, 0.44 mmol) in MeOH/H_2O (15:5 mL) at 65 °C for 1 h followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent to afford **15r** as a dark brown powder (320 mg, 77%). $R_f = 0.10$ (CH_2Cl_2/MeOH 100:5); ^{1}H NMR (300 MHz, CD_2Cl_2): δ 0.84 (d, $J = 6.39$, 6H), 0.90 (d, $J = 6.42$, 6H), 2.09–2.19 (m, 4H), 2.28–2.34 (m, 2H), 4.31 (d, $J = 3.57$, 2H), 5.24 (d, $J = 3.57$, 2H), 6.56 (d, $J = 7.17$, 4H), 7.03–7.23 (m, 10H), 7.35 (t, $J = 3.21$, 6H), 7.45 (d, $J = 7.32$, 2H), 7.61 (t, $J = 7.14$, 1H), 7.85 (t, $J = 8.28$, 1H), 8.65 (d, $J = 8.28$, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ 21.9, 22.3, 25.6, 44.1, 71.4, 76.8, 125.3, 125.8, 126.1, 126.6, 127.5, 128.6, 129.0, 129.2, 129.7, 134.7, 136.8, 140.3, 148.7, 150.5, 162.5, 170.2, 171.3; UV–vis (CH_2Cl_2: λ_{max}/nm, log ε): 350 (3.92), 487 (4.30); HRMS: calcd for $C_{52}H_{48}N_6O_6Ru$: 954.2679. Found: 954.2660. Anal. Calcd (%) for $C_{52}H_{48}N_6O_6Ru{\cdot}H_2O$: C, 64.25; H, 5.18; N, 8.65. Found: C, 64.62; H, 5.31; N, 8.33.

4.62. Ruthenium{2,6-bis-(1-(3,3-dimethylbutanoyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine}{pyridine-2,6-dicarboxylate} 15s

Prepared according to general procedure B using [Ru(*p*-cymene)Cl_2]$_2$ (128 mg, 0.21 mmol), **6s** (300 mg, 0.42 mmol) and disodium 2,6-pyridinedicarboxylate (88 mg, 0.42 mmol) in MeOH/H_2O (15:5 mL) at 65 °C for 1 h followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent to afford **15s** as a dark brown powder (315 mg, 77%). $R_f = 0.10$ (CH_2Cl_2/MeOH 100:5); ^{1}H NMR (300 MHz, CD_2Cl_2): δ 0.96 (s, 18H), 2.26 (d, $J = 7.35$, 4H), 4.33 (d, $J = 3.60$, 2H), 5.22 (d, $J = 3.57$, 2H), 6.56 (d, $J = 7.14$, 4H), 7.03–7.24 (m, 10H), 7.35 (t, $J = 3.03$, 6H), 7.45 (d, $J = 7.32$, 2H), 7.60 (t, $J = 7.17$, 1H), 7.85 (t, $J = 8.28$, 1H), 8.58 (d, $J = 8.28$, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ 29.4, 31.8, 47.1, 71.8, 76.7, 125.5, 125.8, 126.1, 126.6, 127.2, 128.6, 129.0, 129.2, 129.7, 134.7, 136.8, 140.4, 148.7, 150.6, 162.7, 170.2, 171.0; UV–vis (CH_2Cl_2: λ_{max}/nm, log ε): 354 (3.97), 488 (4.34); HRMS: calcd for $C_{54}H_{52}N_6O_6Ru$: 982.2992. Found: 982.2984. Anal. Calcd (%) for $C_{54}H_{52}N_6O_6Ru{\cdot}H_2O$: C, 64.85; H, 5.44; N, 8.40. Found: C, 64.69; H, 5.64; N, 8.01.

4.63. Ruthenium{2,6-bis-(1-(benzyloxycarbonyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine}-{pyridine-2,6-dicarboxylate} 16a

Prepared according to general procedure B using [Ru(*p*-cymene)Cl_2]$_2$ (80 mg, 0.13 mmol), **7a** (206 mg, 0.26 mmol) and disodium 2,6-pyridinedicarboxylate (55 mg, 0.26 mmol) in MeOH/H_2O (15:5 mL) at 65 °C for 1 h followed by chromatography on silica gel using 2.5% MeOH–CH_2Cl_2 to afford **16a** as a dark brown powder (147 mg, 52%). $R_f = 0.10$ (CH_2Cl_2/MeOH 100:5); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.48 (d, $J = 4.96$, 2H), 5.58 (d, $J = 5.16$, 2H), 6.65 (d, $J = 8.32$, 4H), 7.02 (m, 4H), 7.11 (m, 4H), 7.20–7.41 (m, 18H), 7.51 (d, $J = 8.12$, 2H), 7.65 (t, $J = 7.32$, 1H) 7.75 (t, $J = 8.32$, 1H), 9.01 (d, $J = 8.32$, 2H); ^{13}C NMR

(100 MHz, CD_2Cl_2): δ 72.6, 75.9, 121.2, 126.0, 126.1, 126.3, 126.4, 126.5, 127.7, 128.7, 128.9, 129.3, 129.4, 134.9, 136.8, 140.4, 148.7, 150.1, 150.2, 160.3, 170.4; UV–vis (CH_2Cl_2: λ_{max}/nm, log ε): 486 (4.32); FAB-MS: m/z 1026 (M^+); HRMS: calcd for $C_{56}H_{40}N_6O_8Ru$: 1026.1951. Found: 1026.1991. Anal. Calcd (%) for $C_{56}H_{40}N_6O_8Ru{\cdot}2H_2O$: C, 63.33; H, 4.18; N, 7.91. Found: C, 63.45; H, 3.59; N, 7.65.

4.64. Ruthenium{2,6-bis-(1-(1-naphthyloxycarbonyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine}{pyridine-2,6-dicarboxylate} 16b

Prepared according to general procedure B using [Ru(*p*-cymene)Cl_2]$_2$ (86 mg, 0.14 mmol), **7b** (258 mg, 0.29 mmol) and disodium 2,6-pyridinedicarboxylate (61 mg, 0.29 mmol) in MeOH/H_2O (15:5 mL) at 65 °C for 1 h followed by chromatography on silica gel using 2% MeOH–CH_2Cl_2 to afford **16b** as a dark brown powder (118 mg, 33%). $R_f = 0.10$ (CH_2Cl_2/MeOH 100:5); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.53 (d, $J = 4.92$, 2H), 5.75 (d, $J = 4.96$, 2H), 6.71 (d, $J = 3.00$, 4H), 7.12–7.17 (m, 6H), 7.20 (dd, $J = 1.00$, 7.72, 2H), 7.24–7.33 (m, 8H), 7.35–7.40 (m, 6H), 7.44–7.53 (m, 6H), 7.64 (t, $J = 6.96$, 1H) 7.65 (t, $J = 7.16$, 1H), 7.77 (d, $J = 8.32$, 2H), 7.86 (d, $J = 8.32$, 2H), 9.03 (d, $J = 8.32$, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 72.7, 76.0, 118.1, 120.6, 125.3, 126.1, 126.2, 126.3, 126.4, 126.7, 126.8, 127.9, 128.0, 128.8, 129.3, 129.5, 134.6, 135.1, 136.9, 140.5, 145.9, 148.7, 150.1, 150.2, 160.3, 170.4; FAB-MS: m/z 1128 (M^++2); HRMS calcd for $C_{64}H_{44}N_6O_8Ru{\cdot}H^+$: 1127.2342. Found: 1127.2326. Anal. Calcd (%) for $C_{64}H_{44}N_6O_8Ru$: C, 66.14; H, 4.16; N, 7.23. Found: C, 66.64; H, 4.71; N, 6.85.

4.65. Ruthenium{2,6-bis-(1-(9-fluorenylmethyl-oxycarbonyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine}{pyridine-2,6-dicarboxylate} 16c

Prepared according to general procedure B using [Ru(*p*-cymene)Cl_2]$_2$ (80 mg, 0.13 mmol), **7c** (264 mg, 0.27 mmol) and disodium 2,6-pyridinedicarboxylate (57 mg, 0.27 mmol) in a mixture of *n*-BuOH/MeOH/H_2O (16:8:4 mL) at 65 °C for 2 h followed by chromatography on silica gel using EtOAc–hexane as the gradient eluent to afford **16c** as a dark brown powder (195 mg, 60%). $R_f = 0.40$ (EtOAc); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.16 (d, $J = 4.36$, 4H), 4.57 (dd, $J = 5.36$, 10.92, 2H), 4.76 (d, $J = 4.36$, 2H), 4.88 (dd, $J = 5.16$, 10.92, 2H), 6.37 (dd, $J = 1.00$, 7.92, 4H), 6.71 (d, $J = 6.92$, 4H), 7.01–7.08 (m, 6H), 7.14–7.27 (m, 14H), 7.31–7.38 (m, 4H), 7.42 (d, $J = 7.52$, 2H), 7.54–7.58 (m, 3H), 7.64 (d, $J = 7.56$, 2H), 7.69 (t, $J = 8.32$, 1H), 8.78 (d, $J = 8.32$, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 42.0, 68.1, 71.8, 75.7, 119.9, 120.1, 124.5, 125.7, 125.8, 126.1, 127.2, 127.5, 127.9, 128.4, 128.6, 129.1, 135.8, 136.9, 140.7, 141.1, 141.4, 142.9, 143.3, 148.7, 150.1, 160.6, 170.3; UV–vis (CH_2Cl_2: λ_{max}/nm, log ε): 486 (4.35); FAB-MS: m/z 1230 (M^+); HRMS: calcd for $C_{72}H_{52}N_6O_8Ru{\cdot}H^+$: 1231.3028. Found: 1231.3035. Anal. Calcd (%) for $C_{72}H_{52}N_6O_8Ru{\cdot}3H_2O$: C, 67.33; H, 4.55; N, 6.54. Found: C, 67.14; H, 4.30; N, 6.35.

4.66. Ruthenium{2,6-bis-(1-((1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl-3-oxycarbonyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine}{pyridine-2,6-dicarboxylate} 16d

Prepared according to general procedure B using [Ru(*p*-cymene)Cl_2]$_2$ (416 mg, 0.68 mmol), **7d** (1200 mg, 1.36 mmol) and disodium 2,6-pyridinedicarboxylate (287 mg, 1.36 mmol) in MeOH/H_2O (35:10 mL) at 65 °C for 1 h followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent to afford **16d** as a dark brown powder (814 mg, 52%). $R_f = 0.40$ (CH_2Cl_2/MeOH 100:5); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.57 (d, $J = 6.92$, 6H), 0.60 (d, $J = 6.76$, 6H), 0.73–0.87 (m, 4H), 0.89 (d, $J = 6.52$, 6H), 0.92–1.16 (m, 10H), 1.43–1.52 (m, 4H), 4.27 (d, $J = 5.12$, 2H), 4.68 (dt, $J = 4.36$, 10.88, 2H), 5.28 (d, $J = 5.16$, 2H), 6.54 (dd, $J = 1.00$, 8.12, 4H), 7.01–7.09 (m, 8H), 7.17 (t, $J = 7.52$, 2H), 7.25–7.29 (m, 6H), 7.42 (d, $J = 7.52$, 2H), 7.56 (t, $J = 7.16$, 1H), 7.76 (t, $J = 8.32$, 1H), 9.08 (d, $J = 8.32$, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 20.6, 21.7, 22.9, 25.3, 31.5, 34.0, 41.0, 47.0, 72.2, 75.7, 78.2, 125.8, 125.9, 126.4, 127.9, 128.4, 128.5, 129.1, 134.5, 135.8, 137.4, 141.1, 148.8, 150.4, 151.5, 160.9, 170.4; HRMS: calcd for $C_{64}H_{68}N_6O_8Ru{\cdot}H^+$: 1151.4220. Found: 1151.4206.

4.67. Ruthenium{2,6-bis-(1-((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl-3-oxycarbonyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine}{pyridine-2,6-dicarboxylate} 16e

Prepared according to general procedure B using [Ru(*p*-cymene)Cl_2]$_2$ (69 mg, 0.11 mmol), **7e** (200 mg, 0.23 mmol) and disodium 2,6-pyridinedicarboxylate (48 mg, 0.23 mmol) in MeOH/H_2O (35:10 mL) at 65 °C for 1 h followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent to afford **16e** as a dark brown powder (214 mg, 81%). $R_f = 0.22$ (CH_2Cl_2/MeOH 100:5); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.68 (m, 2H), 0.75 (d, $J = 6.9$, 6H), 0.78 (d, $J = 6.9$, 6H), 0.85 (d, $J = 6.5$, 6H), 0.99–1.08 (m, 2H), 1.24–1.31 (m, 4 H), 1.40–1.49 (m, 2H), 1.64–1.77 (m, 6 H), 1.85–1.88 (m, 2H), 4.34 (d, $J = 4.8$, 2H), 4.74 (unresolved ddd, $J = 4.4$, 2 H), 5.33 (d, $J = 4.8$, 2H), 6.55 (dd, $J = 8.2$, 1.1, 4H), 7.03–7.10 (m, 8H), 7.10 (*tt*, $J = 7.4$, 1.1, 2H), 7.27–7.31 (m, 6H), 7.50 (d, $J = 8.3$, 1H), 7.50 (d, $J = 7.1$, 1H), 7.63 (dd, $J = 8.3$, 7.1, 1H), 7.75 (t, $J = 8.2$, 1H), 8.94 (d, $J = 8.3$, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 15.9, 20.5, 21.7, 23.1, 26.5, 31.4, 33.9, 40.3, 47.2, 72.2, 75.4, 78.1, 125.9, 126.1, 126.2, 127.7, 128.5, 128.6, 129.1, 129.1, 134.5, 135.8, 137.2, 140.7, 148.9, 150.3, 151.4, 161.1, 170.3; UV–vis (CH_2Cl_2: λ_{max}/nm, log ε): 371 (3.58), 486 (4.26); FAB-MS: m/z 1151 (M^++1); Anal. Calcd (%) for $C_{64}H_{68}N_6O_8Ru{\cdot}H_2O$: C, 65.79; H, 6.04; N, 7.19. Found: C, 66.02; H, 6.28; N, 6.96.

4.68. Ruthenium{2,6-bis-(1-(1,1-dimethylethyloxy carbonyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine}{pyridine-2,6-dicarboxylate} 16f

Prepared according to general procedure B using [Ru(*p*-cymene)Cl_2]$_2$ (92 mg, 0.15 mmol), **7f** (227 mg,

0.30 mmol) and disodium 2,6-pyridinedicarboxylate (63 mg, 0.30 mmol) in MeOH/H_2O (15:5 mL) at 65 °C for 1 h followed by chromatography on silica gel using 2.5% MeOH–CH_2Cl_2 to afford **16f** as a dark brown powder (208 mg 77%). $R_f = 0.25$ (CH_2Cl_2/MeOH 100:5); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.39 (s, 18H), 4.27 (d, $J = 5.16$, 2H), 5.26 (d, $J = 5.36$, 2H), 6.54 (dd, $J = 1.43$, 7.92, 4H), 7.01–7.08 (m, 8H), 7.15–7.19 (m, 2H), 7.27–7.28 (m, 6H), 7.43 (d, $J = 7.52$, 2H), 7.56 (t, $J = 7.16$, 1H), 7.75 (t, $J = 8.32$, 1H), 8.89 (d, $J = 8.12$, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.7, 72.6, 75.7, 84.3, 125.7, 125.9, 126.0, 126.4, 127.6, 128.4, 128.5, 129.1, 134.4, 137.4, 141.2, 148.8, 150.5, 150.6, 161.2, 170.4; UV–vis (CH_2Cl_2: λ_{max}/nm, log ε): 486 (4.27), 373 (3.71); HRMS: calcd for $C_{52}H_{48}N_6O_8Ru{\cdot}H^+$: 987.2575. Found: 987.2581. Anal. Calcd (%) for $C_{52}H_{48}N_6O_8Ru{\cdot}H_2O$: C, 62.20; H, 5.02; N, 8.37. Found: C, 62.12; H, 5.36; N, 8.12.

4.69. Synthesis of ruthenium{2,6-bis-(1-benzyl-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine}-{pyridine-2,6-dicarboxylate} 16g

Prepared according to general procedure B using **7g** (61 mg, 0.09 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (27 mg, 0.04 mmol) and Na_2pydic (18 mg, 0.09 mmol) to afford **16g** as a dark brown solid (46 mg, 55%). $R_f = 0.29$ (CH_2Cl_2/MeOH 100:5); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.45 (br, 2H), 4.82 (br, 2H), 5.10 (br, 2H), 5.36 (br, 2H), 6.48 (d, $J = 7.3$, 4H), 6.89 (m, 4H), 7.03 (t, $J = 7.2$, 2H), 7.10–7.12 (m, 4H), 7.20–7.40 (m, 22H), 7.86 (br, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 50.4, 75.9, 77.3, 116.6, 125.4, 126.9, 127.3, 127.7, 127.8, 127.9, 128.6, 128.7, 129.0, 129.1, 132.9, 135.8, 138.3, 138.9, 148.7, 166.1; UV–vis (CH_2Cl_2: λ_{max}/nm, log ε): 386 (sh) (3.52), 499 (4.33); FAB-MS: *m*/*z* 966 (M^+); HRMS (ESI+): calcd for $C_{56}H_{44}N_6O_4{}^{102}Ru$: 966.2434. Found: 966.2468.

4.70. Ruthenium{2,6-bis-(1-[toluene-4-sulfonyl]-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine}-{pyridine-2,6-dicarboxylate} 16h

Prepared according to general procedure B using **7h** (54 mg, 0.06 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (20 mg, 0.03 mmol) and Na_2pydic (14 mg, 0.06 mmol) to afford **16h** as a dark brown solid (39 mg, 55%). $R_f = 0.39$ (CH_2Cl_2/MeOH 100:5); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.45 (s, 6H), 4.12 (d, $J = 5.7$, 2H), 4.98 (d, $J = 5.7$, 2H), 5.66 (d, $J = 7.5$, 4H), 6.67 (m, 4H), 6.95 (t, $J = 7.4$, 2H), 7.12 (d, $J = 7.9$, 2H), 7.17–7.19 (m, 4H), 7.27–7.31 (m, 5H), 7.34–7.38 (m, 6H), 7.55 (d, $J = 8.3$, 4H), 8.00 (t, $J = 8.3$, 1H), 9.41 (d, $J = 8.3$, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 21.5$, 73.6, 76.1, 125.5, 126.0, 126.1, 127.0, 127.5, 128.3, 128.8, 129.3, 130.8, 132.0, 135.1, 135.8, 136.7, 140.6, 146.6, 148.1, 150.5, 156.1, 159.7, 170.2; UV–vis (CH_2Cl_2: λ_{max}/nm, log ε): 352 (sh) (3.90), 490 (4.22), 587 (sh) (3.55); FAB-MS: *m*/*z* 1094 (M^+); HRMS (ESI+): calcd for $C_{56}H_{44}N_6O_8{}^{102}RuS_2$: 1094.2122. Found: 1094.1705.

4.71. Ruthenium {2,6-bis-(1-benzyl-[3*aR*,7*aR*]-3a,4,5,6,7,7a-hexahydro-1*H*-benzoimidazol-2-yl)-pyridine}{pyridine-2,6-dicarboxylate} 17a

Prepared according to general procedure B using **8a** (100 mg, 0.20 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (61 mg, 0.10 mmol) and disodium pyridine-2,6-dicarboxylate (42 mg, 0.20 mmol) in MeOH/H_2O (15:5 mL) at 65 °C for 1 h followed by chromatography on silica gel using 2.5% MeOH–CH_2Cl_2 to afford **17a** as a dark brown powder (70 mg, 45%). $R_f = 0.17$ (CH_2Cl_2/MeOH 100:5); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.92–0.94 (m, 2H), 1.05–1.11 (m, 6H), 1.38–1.43 (m, 2H), 1.53–1.55 (m, 2H), 1.68–1.70 (m, 4H), 1.94–1.97 (m, 2H), 3.70 (br, 4H), 4.72 (br, 2H), 5.47 (br, 2H), 7.16 (t, $J = 7.9$, 1H), 7.30–7.34 (m, 2H), 7.39–7.45 (m, 10H), 8.04–8.07 (m, 1H), 8.14 (d, $J = 7.4$, 4H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 23.9, 24.7, 28.9, 50.8, 70.1, 72.9, 78.8, 116.6, 126.4, 126.6, 127.6, 129.0, 133.7, 135.8, 150.4, 168.8; UV–vis (CH_2Cl_2: λ_{max}/nm, log ε): 321 (3.72), 394 (3.48), 498 (4.30); FAB-MS: *m*/*z* 770 (M^+); Anal. Calcd (%) for $C_{40}H_{40}N_6O_4Ru{\cdot}H_2O$: C, 60.98; H, 5.37; N, 10.67. Found: C, 60.95; H, 5.30; N, 10.79.

4.72. Ruthenium {2,6-bis-(1-[toluene-4-sulfonyl]-[3*aR*,7*aR*]-3a,4,5,6,7,7a-hexahydro-1*H*-benzoimidazol-2-yl)-pyridine}{pyridine-2,6-dicarboxylate} 17b

Prepared according to general procedure B using **8b** (100 mg, 0.16 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (48 mg, 0.08 mmol) and Na_2pydic (33 mg, 0.16 mmol) to afford **17b** as a brown solid (72 mg, 50%). $R_f = 0.24$ (CH_2Cl_2/MeOH 100:5); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.67–0.70 (m, 2H), 0.82–0.88 (m, 2H), 1.05–1.14 (m, 2H), 1.26 (m, 2H), 1.45–1.48 (m, 2H), 1.69–1.71 (m, 4H), 2.39 (s, 6H), 2.47–2.50 (m, 4H), 3.67–3.73 (m, 2H), 7.30 (d, $J = 8.2$, 4H), 7.44 (d, $J = 8.2$, 4H), 7.77 (t, $J = 8.1$, 1H), 8.02 (d, $J = 7.7$, 1H), 8.19 (d, $J = 7.7$, 2H), 8.77 (d, $J = 8.1$, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 21.7, 24.3, 24.4, 27.4, 27.8, 29.6, 69.1, 71.8, 126.7, 127.2, 127.3, 127.9, 130.6, 135.8, 136.8, 145.6, 150.0, 151.2, 164.1, 170.9; UV–vis (CH_2Cl_2: λ_{max}/nm, log ε): 307 (sh) (4.01), 368 (sh) (3.65), 491 (4.17); FAB-MS: *m*/*z* 898 (M^+); Anal. Calcd (%) for $C_{40}H_{40}N_6O_8RuS_2$: C, 53.50; H, 4.49; N, 9.36; S, 7.14. Found: C, 53.16; H, 4.86; N, 8.94; S, 6.70.

4.73. Ruthenium{(2-(1-(diphenylphosphinyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl))-6-([4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-imidazol-2-yl)-pyridine}{pyridine-2,6-dicarboxylate} 18

Prepared according to general procedure B using [Ru(*p*-cymene)Cl_2]$_2$ (43 mg, 0.07 mmol), **12** (127 mg, 0.17 mmol) and disodium 2,6-pyridinedicarboxylate (30 mg, 0.14 mmol) in MeOH/H_2O (15:5 mL) at 65 °C for 1 h followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent to afford **18** as a dark brown powder (96 mg, 73%). $R_f = 0.10$ (CH_2Cl_2/MeOH 100:5); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.20 (d, $J = 3.56$, 2H), 5.01 (br s, 2H), 5.18 (d, $J = 3.60$, 2H), 6.28 (d, $J = 7.92$, 4H), 6.87 (t, $J = 7.72$, 4H), 6.93–6.95 (m, 4H); 7.05–7.13 (m, 8H), 7.16–7.27 (m,

6H), 7.57 (t, $J = 7.32$, 1H), 7.72 (t, $J = 8.32$, 1H), 8.61 (d, $J = 8.32$, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 56.6, 70.7, 76.7, 125.1, 125.9, 126.7, 127.5, 127.8, 127.9, 128.3, 128.4, 128.9, 129.1, 129.3, 129.4, 130.0, 134.9, 136.0, 136.5, 138.8, 140.1, 148.6, 150.3, 161.9, 170.1, 170.3; UV–vis (CH_2Cl_2: λ_{max}/nm, $\log\varepsilon$): 489 (4.17); HRMS: calcd for $C_{54}H_{41}N_6PO_5Ru{\cdot}H^+$: 986.2008. Found: 986.2004.

4.74. Ruthenium{(2-(1-(2,4,6-trimethyl-benzoyl))-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-6-(1-((1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl-3-oxycarbonyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine}{pyridine-2,6-dicarboxylate} 19

Prepared according to general procedure B using [Ru(*p*-cymene)Cl_2]$_2$ (67 mg, 0.11 mmol), **13** (195 mg, 0.22 mmol) and disodium 2,6-pyridinedicarboxylate (46 mg, 0.22 mmol) in MeOH/H_2O (15:5 mL) at 65 °C for 1 h followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent to afford **19** as a dark brown powder (185 mg, 75%). $R_f = 0.40$ (CH_2Cl_2/MeOH 100:5); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.57 (d, $J = 6.92$, 3H), 0.61 (d, $J = 6.92$, 3H), 0.91 (d, $J = 6.56$, 3H), 0.74–1.69 (m, 5H), 1.21–1.34 (m, 2H), 1.42–1.55 (m, 2H), 1.94 (s, 6H), 2.24 (s, 3H), 4.38 (d, $J = 2.96$, 1H), 4.40 (d, $J = 5.36$, 1H), 4.55 (br s, 1H), 4.70 (dt, $J = 4.36$, 10.72, 1H), 5.35 (d, $J = 5.56$, 1H), 6.40 (d, $J = 7.52$, 2H), 6.54–6.63 (m, 5H), 6.77 (s, 1H), 7.02–7.13 (m, 8H), 7.15–7.31 (m, 6H), 7.41 (dd, $J = 1.20$, 7.56, 1H), 7.44 (dd, $J = 1.20$, 7.92, 1H), 7.56 (t, $J = 7.72$, 1H), 7.84 (t, $J = 8.12$, 1H), 8.83 (d, $J = 7.92$, 1H), 9.19 (d, $J = 8.32$, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 15.5, 18.3, 18.9, 20.6, 20.9, 21.7, 22.8, 25.3, 31.5, 34.0, 41.0, 47.0, 72.3, 72.9, 75.7, 75.9, 78.3, 125.7, 125.8, 126.0, 126.3, 126.5, 127.8, 128.2, 128.5, 128.9, 129.0, 129.1, 129.2, 132.3, 132.9, 134.7, 135.3, 136.4, 137.5, 139.7, 141.1, 148.7, 150.3, 151.5, 154.7, 161.1, 169.0, 170.4; UV–vis (CH_2Cl_2: λ_{max}/nm, $\log\varepsilon$): 487 (4.30); HRMS: calcd for $C_{63}H_{60}N_6O_7Ru{\cdot}H^+$: 1115.3645. Found: 1115.3668. Anal. Calcd (%) for $C_{63}H_{60}N_6O_7Ru{\cdot}H_2O$: C, 66.83; H, 5.52; N, 7.42. Found: C, 66.63; H, 5.95; N, 7.03.

4.75. Ruthenium{(2-(1-((1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl-3-oxycarbonyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-6-(1-acetyl)-[4*R*,5*R*]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-pyridine}{pyridine-2,6-dicarboxylate} 20

Prepared according to general procedure B using [Ru(*p*-cymene)Cl_2]$_2$ (72 mg, 0.12 mmol), **14** (175 mg, 0.24 mmol) and disodium 2,6-pyridinedicarboxylate (50 mg, 0.24 mmol) in MeOH/H_2O (15:5 mL) at 65 °C for 1 h followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent to afford **20** as a dark brown powder (171 mg, 72%). $R_f = 0.20$ (CH_2Cl_2/MeOH 100:5); ^{1}H NMR (300 MHz, CD_2Cl_2): δ 0.57 (d, $J = 6.96$, 3H), 0.60 (d, $J = 6.96$, 3H), 0.85–1.12 (m, 5H), 1.25–1.27 (m, 2H), 1.54–1.61 (m, 2H), 2.14 (s, 3H), 4.26 (d, $J = 3.78$, 1H), 4.31 (d, $J = 5.28$, 1H), 4.69 (dt, $J = 4.35$, 10.74, 1H), 5.19 (d, $J = 3.78$, 1H), 5.30 (d, $J = 5.28$, 1H), 6.53–6.57 (m, 4H), 7.00–7.44 (m, 16H), 7.58 (t, $J = 7.35$, 1H), 7.79 (t, $J = 8.28$, 1H), 8.71 (d, $J = 7.89$, 1H), 9.12 (d, $J = 7.89$, 1H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ 15.4, 20.6, 21.7, 22.8, 23.7, 25.3, 31.5, 34.0, 41.0, 46.9, 72.0, 72.2, 75.7, 76.6, 78.2, 125.4, 125.7, 125.8, 125.9, 126.1, 126.2, 126.4, 127.7, 128.0, 128.4, 128.5, 128.6, 129.1, 129.2, 129.3, 129.7, 134.6, 136.8, 137.4, 140.1, 141.1, 148.7, 148.8, 150.2, 150.7, 151.4, 161.0, 162.1, 168.6, 170.3; UV–vis (CH_2Cl_2: λ_{max}/nm, $\log\varepsilon$): 486 (4.30); HRMS: calcd for $C_{55}H_{52}N_6O_7Ru$: 1010.2941. Found: 1010.2927; Anal. Calcd (%) for $C_{55}H_{52}N_6O_7Ru{\cdot}H_2O$: C, 64.25; H, 5.29; N, 8.17. Found: C, 64.22; H, 5.71; N, 7.96.

4.76. General procedure for the preparation of Ru(dicyclohexylpybim)(pydic) complexes via in situ generation (procedure C)

In a 50 mL oven dried one necked round bottom flask fitted with a magnetic stirring bar under argon, **4** (130 mg, 0.4 mmol) and DMAP (147 mg, 1.2 mmol) were dissolved in anhydrous CH_2Cl_2 (15 mL). The mixture was cooled to 0 °C and then the corresponding acid chloride or chloroformate (1.2 mmol) added dropwise. The cooling bath was removed and the reaction mixture was stirred at rt and the progress of the reaction monitored by TLC. After full conversion, the reaction mixture was washed with water (2 × 20 mL), dried over Na_2SO_4, concentrated and transferred into a 25 mL Schlenk tube and dried in vacuum. To the remaining product methanol (10 mL) and [Ru(*p*-cymene)Cl_2]$_2$ (306 mg, 0.5 mmol) were added. Another 25 mL Schlenk tube was charged with disodium 2,6-pyridinedicarboxylate (211 mg, 1 mmol) and dissolved in a mixture of water (5 mL) and methanol (5 mL). The solution was purged with argon for ca. 10 min and then transferred via a cannula into the Schlenk tube containing the ruthenium source at rt. The mixture was then heated at 65 °C for 1 h, cooled to rt and diluted with CH_2Cl_2 (30 mL). The mixture was washed with water (2 × 20 mL), dried over Na_2SO_4, concentrated and purified by column chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent to give the Ru(dicyclohexylpybim)(pydic) complex as a dark brown solid after crystallization from CH_2Cl_2–hexane.

4.77. Ruthenium{2,6-bis-(1-benzoyl-[3*aR*,7*aR*]-3a,4,5,6,7,7a-hexahydro-1*H*-benzoimidazol-2-yl)-pyridine}{pyridine-2,6-dicarboxylate} 21

Prepared according to general procedure C using **4** (320 mg, 1 mmol), DMAP (269 mg, 2.2 mmol), benzoyl chloride (0.29 mL, 2.5 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (306 mg, 0.5 mmol) and disodium 2,6-pyridinedicarboxylate (211 mg, 1 mmol) followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent to afford **21** as a dark brown crystalline product (484 mg, 61%). $R_f = 0.25$ (CH_2Cl_2/MeOH 100:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.83–1.32 (m, 10H), 1.51–1.59 (m, 6H), 3.52 (dt, $J = 3.56$, 12.48, 2H), 3.91 (dt, $J = 2.96$, 11.68, 2H), 7.35 (t, $J = 8.08$, 1H), 7.46 (t, $J = 7.96$, 4H), 7.56 (t, $J = 6.36$, 2 H), 7.66–7.68 (m, 4 H), 7.72 (d, $J = 8.12$, 2H), 8.08 (t, $J = 7.52$, 1H), 8.28 (d, $J = 7.72$, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.2, 24.9, 28.2, 30.0, 71.4, 73.5, 125.0, 127.5. 127.7,

129.3, 129.5, 133.6, 135.0, 135.7, 136.1, 150.6, 151.1, 164.6, 168.1, 172.2; UV–vis (CH_2Cl_2: λ_{max}/nm, log ε): 492 (4.33), 379 (3.95); FAB-MS: m/z 798 (M^+); Anal. Calcd (%) for $C_{40}H_{36}N_6O_6Ru{\cdot}3H_2O$: C, 56.40; H, 4.97; N, 9.86. Found: C, 56.49; H, 4.64; N 9.53.

4.78. Ruthenium{2,6-bis-(1-(4-methoxybenzoyl)-[3*aR*, 7*aR*]- 3a,4,5,6,7,7a-hexahydro-1*H*-benzoimidazol-2-yl)-pyridine}{pyridine-2,6-dicarboxylate} 22

Prepared according to general procedure C using **4** (323 mg, 1 mmol), DMAP (276 mg, 2.2 mmol), 4-methoxy benzoyl chloride (514 mg, 3 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (306 mg, 0.5 mmol) and disodium 2,6-pyridinedicarboxylate (211 mg, 1 mmol) followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent to afford **22** as a dark brown crystalline product (376 mg, 43%). $R_f = 0.40$ (CH_2Cl_2/MeOH 100:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.82–1.31 (m, 10H), 1.50–1.61 (m, 4H), 1.76–1.79 (m, 2H), 3.49 (dt, $J = 3.16$, 12.08, 2H), 3.83 (s, 6H), 3.96 (dt, $J = 2.96$, 11.48, 2H), 6.91 (d, $J = 8.72$, 4H), 7.28 (t, $J = 8.12$, 1H), 7.60 (d, $J = 8.12$, 2H), 7.64 (d, $J = 9.12$, 4H), 8.07 (t, $J = 7.52$, 1H), 8.27 (d, $J = 7.72$, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 22.6, 23.7, 24.5, 27.7, 29.4, 31.5, 55.5, 71.1, 72.9, 114.2, 124.3, 126.6, 127.1, 135.0, 150.1, 150.6, 163.5, 164.2, 167.1, 171.7; UV–vis (CH_2Cl_2: λ_{max}/nm, log ε): 492 (4.37), 380 (4.01); FAB-MS: m/z 858 (M^+); Anal. Calcd (%) for $C_{42}H_{40}N_6O_8Ru{\cdot}H_2O$: C, 57.59; H, 4.83; N, 9.59. Found: C, 57.82; H, 4.68; N, 9.08.

4.79. Ruthenium{2,6-bis-(1-((1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyloxy-carbonyl)-[3*aR*,7*aR*]-3a,4,5,6,7,7a-hexahydro-1*H*-benzoimidazol-2-yl)-pyridine}{pyridine-2,6-dicarboxylate} 23

Prepared according to general procedure C using **4** (320 mg, 1 mmol), DMAP (269 mg, 2.2 mmol), (−)-menthyl chloroformate (0.64 mL, 3 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (306 mg, 0.5 mmol) and disodium 2,6-pyridinedicarboxylate (211 mg, 1 mmol) followed by chromatography on silica gel using MeOH–CH_2Cl_2 as the gradient eluent to afford **23** as a dark brown crystalline product (246 mg, 26%). $R_f = 0.50$ (CH_2Cl_2/MeOH 100:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.65–0.94 (m, 18H), 0.95–1.26 (m, 10H), 1.37–1.98 (m, 18H), 2.13 (d, $J = 8.92$, 2H), 2.60 (dd, $J = 2.96$, 12.28, 2H), 3.28 (m, 2H), 3.64 (m, 2H), 4.81 (dt, $J = 4.36$, 10.92, 2H), 7.53 (t, $J = 8.32$, 1H), 8.05 (t, $J = 7.92$, 1H), 8.25 (d, $J = 7.72$, 2H), 8.45 (d, $J = 8.32$, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.6, 20.7, 21.9, 23.6, 24.1, 24.5, 26.5, 27.8, 30.3, 31.4, 31.5, 34.0, 40.8, 47.2, 69.1, 71.6, 126.3, 127.1, 135.7, 150.6, 150.8, 151.3, 162.9, 171.7; UV–vis (CH_2Cl_2: λ_{max}/nm, log ε): 485 (4.32), 381 (3.64); FAB-MS: m/z 954 (M^+); Anal. Calcd (%) for $C_{48}H_{64}N_6O_8Ru{\cdot}2H_2O$: C, 58.22; H, 6.92; N, 8.49. Found: C, 58.39; H, 6.63; N, 8.25.

4.80. General procedure for asymmetric epoxidation with hydrogen peroxide

In a 25 mL Schlenk tube, the ruthenium catalyst (0.025 mmol) was stirred at room temperature in *tert*-amyl alcohol (9 mL) for 10 min. Olefin (0.5 mmol) and dodecane (GC internal standard, 100 μL) were added. To this mixture, a solution of 30% hydrogen peroxide (170 μL, 1.5 mmol) in *tert*-amyl alcohol (830 μL) was added over a period of 12 h by syringe pump. After the addition, aliquots were taken from the reaction mixture and subjected to GC analysis for the determination of yield and conversion. Finally, the reaction mixture was quenched with saturated Na_2SO_3 solution (10 mL), extracted with dichloromethane (2 × 10 mL) and washed with water (20 mL). The combined organic layers were dried over Na_2SO_4 and evaporated to give the crude epoxides. A solution of the crude product in hexane was used for the determination of the ee by HPLC.

4.81. Phenyloxirane

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.72 (dd, $J = 5.6$, 2.6, 1H), 3.06 (dd, $J = 5.6$, 4.2, 1H), 3.78 (dd, $J = 4.2$, 2.6, 1H), 7.16–7.29 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.3, 52.5, 125.6, 128.3, 128.6, 137.7; EI-MS: m/z 120 (M^+, 41), 119 (65), 92 (37), 91 (100), 90 (64), 89 (79); HPLC (Chiralcel OD-H (02), hexane/EtOH 99.95:0.05, flow rate 0.5 mL/min): t_R 6.27 min, 7.13 min.

4.82. 2-Tolyloxirane

^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.14–7.22 (m, 4H), 3.98 (dd, $J = 3.97$, 2.58, 1H), 3.13 (dd, $J = 5.75$, 3.97, 1H), 2.65 (dd, $J = 5.75$, 2.58, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 136.4, 136.2, 129.8, 127.6, 126, 124, 50.3, 50.1; EI-MS: $m/z = 134$ (M^+, 53), 119 (44), 118 (42), 117 (64), 105 (100), 103 (48), 91 (52), 78 (33), 77 (35); HPLC (Chiralpak AD-H, hexane/EtOH, 99.95:0.05, flow rate 1.5 mL/min): t_R 16.70 min, 19.84 min.

4.83. 4-Chlorophenyloxirane

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.68 (dd, $J = 5.6$, 2.6, 1H), 3.07 (dd, $J = 5.6$, 4.0, 1H), 3.76 (dd, $J = 4.0$, 2.6, 1H), 7.12–7.26 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.4, 51.9, 127.0, 128.8, 134.1, 136.3; EI-MS: m/z 156 (M^++2, 9), 155 (M^++1, 10), 154 (M^+, 28), 153 (M^+-1, 23), 125 (53), 119 (74), 89 (106); HPLC (Chiralcel OB–H, hexane, flow rate 1.0 mL/min): t_R 14.47 min, 17.18 min.

4.84. 4-Trifluoromethylphenyloxirane

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.77 (dd, $J = 5.6$, 2.6, 1H), 3.19 (dd, $J = 5.6$, 4.0, 1H), 3.92 (dd, $J = 4.0$, 2.6, 1H), 7.4 (d, $J = 8.1$, 2H), 7.6 (d, $J = 8.1$, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.4, 51.6, 125.4 (q, $J = 3.8$), 125.9, 141.9; EI-MS: m/z 188 (M^+, 14), 187 (20), 159 (49), 158 (48), 119 (100), 91 (37); HPLC (Chiralcel AD-151, hexane, flow rate 0.5 mL/min): t_R 12.30 min, 13.40 min.

4.85. *trans*-2-Methyl-3-phenyloxirane

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.44 (d, $J = 5.2$, 3H), 3.03 (dq, $J = 2.0$, 5.2, 1H), 3.57 (d, $J = 2.0$, 1H), 7.23–7.4

(m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.0, 59.2, 59.6, 125.7, 128.1, 128.5, 137.9; EI-MS: 134 (M^+, 52), 133 (65), 105 (51), 91 (42), 90 (100), 89 (77), 77 (23); HPLC (Chiralcel OD-H (069), hexane/EtOH, 99.95:0.05, flow rate 1.0 mL/min): t_R 11.90 min (2*S*,3*S*), 13.48 min (2*R*,3*R*).

4.86. *trans*-2,3-Diphenyloxirane

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24–7.31 (m, 10H), 3.87 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.1, 128.6, 128.6, 125.5, 62.8; EI-MS: $m/z = 197$ (M^++1, 18), 196 (M^+, 100), 195 (72), 178 (28), 167 (85), 90 (66), 89 (65); HPLC (Chiralcel OD-H, hexane/EtOH, 98:2, flow rate 0.5 mL/min): t_R 14.10 min (2*S*,3*S*), 4.79 min (2*R*,3*R*).

4.87. *trans*-2-Chloromethyl-3-phenyloxirane

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.28 (ddd, $J = 5.8$, 4.8, 1.9, 1H), 3.66 (dd, $J = 11.8$, 5.8, 1H), 3.72 (dd, $J = 11.8$, 4.8, 1H), 3.82 (d, $J = 1.9$, 1H), 7.26–7.38 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.3, 58.5, 60.9, 116.6, 125.6, 128.6, 135.9; GC-MS: m/z 168 (M^+); HPLC (Chiralpak AD-H, hexane/EtOH, 95:5, flow rate 1.0 mL/min): t_R 7.62 min, 9.09 min.

4.88. 2,2-Dimethyl-3-phenyloxirane

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (s, 3H), 1.45 (s, 3H), 3.83 (s, 1H), 7.21–7.33 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.9, 24.7, 61.0, 64.5, 126.3, 127.3, 128, 136.6; EI-MS: m/z 148 (M^+); HPLC (Chiralcel OD-H, hexane/EtOH, 99.95:0.05, flow rate 0.5 mL/min): t_R 11.78 min (3*S*), 18.63 min (3*R*).

4.89. 2-Phenyl-1-oxaspiro[2.5]octane

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22–1.31 (m, 2H), 1.37–1.85 (m, 8H), 3.85 (s, 1H), 7.23–7.34 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.5, 25.3, 25.5, 28.4, 35.4, 64.5, 65.5, 126.3, 127.2, 127.9, 136.3; GC-MS: m/z 188 (M^+); HPLC (Chiralpak AD-H, hexane/EtOH, 90:10, flow rate 1.0 mL/min): t_R 4.34 min, 4.72 min.

4.90. (2-Methyl-3-phenyl-oxiranyl)-methanol

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.07$ (s, 3H), 2.17 (dd, $J = 8.7$, 4.3 Hz, 1H), 3.74 (dd, $J = 12.5$, 8.7 Hz, 1H), 3.84 (dd, $J = 12.5$, 4.3 Hz, 1H), 4.20 (s, 1H), 7.25–7.36 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 13.41$, 60.13, 63.66, 64.90, 126.36, 127.52, 128.06, 135.54; EI-MS: m/z 164 (M^+); HPLC (Chiralcel AD-H, hexane/EtOH, 99.5:0.5, flow rate 0.5 mL/min): t_R 12.24 min, 12.86 min.

4.91. 2-Methyl-2-phenyloxirane

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.65 (s, 3H), 2.73 (d, $J = 5.4$, 1H), 2.90 (d, $J = 5.4$, 1H), 7.17–7.31 (m, 5H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.9, 57.2, 125.4, 127.6, 128.5, 141.3; EI-MS: m/z 134 (M^+, 35), 133 (87), 105 (100), 104 (41), 103 (58), 91 (23), 79 (37), 78 (54), 77 (49); HPLC (Chiralcel OD-H, hexane/*iso*-propanol, 99.95:0.05, flow rate 1.0 mL/min): t_R 9.78 min, 12.77 min.

4.92. 1,2-Epoxy-1-phenylcyclohexane

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23–7.32 (m, 4H), 7.15–7.2 (m, 1H), 2.99 (m, 1H), 2.16–2.25 (m, 1H), 2.00–2.09 (m, 1H), 1.87–1.95 (m, 2H), 1.44–1.58 (m, 2H), 1.34–1.44 (m, 1H), 1.18–1.3 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.6, 128.4, 127.3, 125.4, 62.1, 60.3, 29, 24.8, 20.2, 19.9; EI-MS: $m/z = 175$ (M^++1, 10), 174 (M^+, 82), 173 (100), 159 (21), 145 (40), 129 (50), 117 (47), 115 (58), 105 (68), 91 (58), 77 (43). HPLC (Chiralcel AD-H, hexane/EtOH, 99.95:0.05, flow rate 1.0 mL/min): $t_R = 8.35$ min, 9.07 min.

4.93. 4-Methyl-*N*-(*trans*-3-phenyl-oxiranylmethyl)-benzenesulfonamide

Mp 128–131 °C; $R_f = 0.23$ (hexane/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H), 3.10 (ddd, $J = 2.0$, 3.4, 4.6, 1H), 3.23 (ddd, $J = 4.6$, 6.8, 14.1, 1H), 3.38 (ddd, $J = 3.4$, 6.0, 14.1, 1H), 3.74 (d, $J = 2.0$, 1H), 4.82 (unresolved dd, 1H), 7.14–7.17 (m, 2H), 7.28–7.31 (m, 5H), 7.74 (d, $J = 8.3$, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.51, 43.70, 55.55, 60.12, 125.66, 127.06, 128.51, 128.88, 129.84, 131.04, 135.69, 135.89, 136.71, 143.75; EI-MS: m/z 303 (M^+); HRMS: calcd for $C_{16}H_{17}NO_3S$: 303.0929. Found 303.0939; HPLC (Whelk01 [*R*,*R*], hexane/EtOH, 90:10, flow rate 1.0 mL/min): t_R 10.01 min, 11.38 min.

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