Organic & Biomolecular Chemistry

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Org. Biomol. Chem.*, 2023, **21**, 69

Received 11th October 2022,
Accepted 22nd November 2022

DOI: 10.1039/d2ob01861f

rsc.li/obc

Substitution pattern in ruthenium octa-n-butoxyphthalocyanine complexes influence their reactivity in N–H carbene insertions†

Andrey P. Kroitor,[a,b] Alexander A. Dmitrienko,[c] Alexander G. Martynov,[*b] Yulia G. Gorbunova[*b,c,d] and Alexander B. Sorokin[*a]

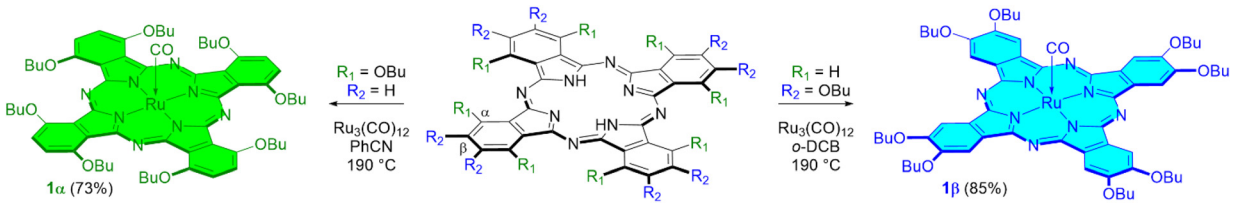
Ruthenium phthalocyanine complexes bearing *n*-OBu substituents in the peripheral or non-peripheral positions are efficient catalysts for the selective double or single carbene insertion to the amine N–H bonds. This complementary reactivity of two Ru complexes can be used for the synthesis of asymmetric tertiary amines and diamines bearing different substituents and has been demonstrated by two examples of readily available primary amines using different carbene precursors in successive reactions.

Catalytic X–H (X = N, C, O, S...) insertion of carbenes represents a powerful strategy for the construction of C–X bonds.[1] In particular, porphyrin complexes[2] and engineered hemoproteins[3] are remarkably efficient in cyclopropanation and C–X carbene insertion reactions. However, it should be noted that carbene insertion into amine N–H bonds is more demanding compared to other C–X bonds because of the catalyst poisoning due to amine coordination to the metal sites. The selectivity to single N–H insertion products is also often limited. In recent years, a variety of transition metal complexes[4] and engineered hemoproteins[5] have been reported for the insertion of carbenes to the N–H bonds of amines. Along with Rh, Ir, Fe and Co complexes, considerable attention has been devoted to Ru compounds.[6] Among them, Ru porphyrins have been extensively studied as efficient catalysts for carbene transfer reactions,[7] principally in cyclopropanation of olefins.[8] Noteworthily, other tetrapyrrolic complexes, *e.g.* Ru phthalocyanines, have been rarely studied in these reactions.[9] In general, the nature of the substituents of the phthalocyanine ligand determines the electronic properties of the corresponding complexes and hence their catalytic activity.[10] Our previous study showed that peripherally substituted Ru(II) octa-*n*-butoxyphthalocyaninate β-$(BuO)_8$PcRu(CO) (**1β**) was an efficient catalyst for the carbene insertion into amine N–H bonds under practical reaction conditions.[11] A large variety of structurally divergent amines were selectively converted into mono-substituted glycine derivatives using a 0.05 mol% catalyst loading, a high amine concentration (1 M) and 1.1 equiv. of ethyl diazoacetate (EDA) with up to quantitative yields and turnover numbers reaching 2000. In the course of our studies, we have found that the catalytic properties of the Ru(II) octa-*n*-butoxyphthalocyanine complex depend on the position of the substituents. Therein, we report that peripherally and non-peripherally substituted complexes β-$(BuO)_8$PcRu(CO) and α-$(BuO)_8$PcRu(CO) (**1α**) exhibit different properties in carbene insertion to amine N–H bonds, providing selectively either double or single N–H insertion products, respectively. We demonstrate how the complementary catalytic properties of **1α** and **1β** can in principle be used for the synthesis of elaborated amine derivatives with various substitution patterns.

The peripherally substituted complex **1β** was prepared by refluxing the metal-free phthalocyanine H_2[β-$(BuO)_8$Pc] with $Ru_3(CO)_{12}$ in *o*-dichlorobenzene (*o*-DCB) according to an optimized published procedure[9b] with an 85% yield (Scheme 1). Our attempts to synthesize **1α** from non-peripherally substituted phthalocyanine H_2[α-$(BuO)_8$Pc] and $Ru_3(CO)_{12}$ using the same protocol led to a mixture of unidentified products, as was indicated by MALDI-TOF MS analyses. The replacement of *o*-DCB with pure PhCN distilled in a vacuum over P_2O_5 and then over K_2CO_3 led to a high yield of the target **1α** complex (Scheme 1). The PhCN purity plays a crucial role since even the traces of benzamide in the solvent result in a very low yield of **1α**. Contrary to the preparation of peripherally substituted Ru

[a]*Institut de recherches sur la catalyse et l'environnement de Lyon (IRCELYON), UMR 5256, CNRS – Université Lyon 1, 2 av. A. Einstein, 69626 Villeurbanne, France. E-mail: alexander.sorokin@ircelyon.univ-lyon1.fr*
[b]*Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninskii pr., 31, bldg. 4, 119071 Moscow, Russia. E-mail: martynov@phyche.ac.ru*
[c]*Lomonosov Moscow State University, Leninskie Gory, 1-3, Moscow, 119991, Russia*
[d]*Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii pr., 31, 119991 Moscow, Russia. E-mail: yulia@igic.ras.ru*

†Electronic supplementary information (ESI) available: Synthetic procedures and compound characterization data. See DOI: https://doi.org/10.1039/d2ob01861f



Scheme 1 Synthesis of the peripherally and non-peripherally substituted ruthenium octa-*n*-butoxyphthalocyanines **1β** and **1α**.

phthalocyanines by the treatment with $Ru_3(CO)_{12}$ in *o*-DCB accompanied by the formation of μ-carbido dimers,[9b] no corresponding μ-carbido dimer was formed during the synthesis of **1α** in PhCN. The ^{1}H NMR spectrum of **1α** confirmed its diamagnetic nature. The presence of the axial carbonyl ligand was evidenced by the strong CO stretching band at 1948 cm^{-1} in the IR spectrum. The comparison of the UV-vis spectra of the solutions of both Ru phthalocyanines shows the significant red-shift of the Q band from 655 nm for the peripheral **1β** complex to 717 nm for the non-peripherally substituted species **1α** (Fig. S4†). This means a difference in their electronic structures, which, in turn, can induce a difference in the catalytic properties.

The catalytic properties of the complexes were evaluated in the reaction of 2.1 equiv. of EDA with aromatic amines **2a–2j** (1 M) in CH_2Cl_2 at 40 °C using 0.05 mol% catalyst loading (Table 1). It is worth noting that carbene transfer reactions catalyzed by metal complexes are typically carried out under an inert atmosphere.[1–3] Importantly, the carbene insertion to amines catalyzed by **1β** and **1α** can be performed under air without decreasing the product yields, which represents a significant practical advantage. Aniline derivatives bearing electron-donating (Table 1, entries 1–3 and 8) or electron-withdrawing groups (Table 1, entries 4 and 5) were converted into the N–H double insertion products **4** with almost quantitative yields. Two strong electron-withdrawing groups of 3,5-ditrifluoromethylaniline **2f** decrease its nucleophilic properties, resulting in a 1 : 1 ratio of the products of double and single N–H insertions – d- and s-products: **4f** and **3f**, respectively (Table 1, entry 6). The presence of methyl and isopropyl substituents in the *ortho*-positions is well tolerated and the corresponding d-products **4g** and **4h** were obtained in 89 and 97% yields, respectively (Table 1, entries 7 and 8). However, the bulky *tert*-butyl *o*-substituent prevents the second N–H insertion (Table 1, entry 9). The **1β** – EDA system shows a clear preference for N–H insertion compared to the cyclopropanation of the double bond. The products of single and double carbene insertions to *p*-aminostyrenes **3j** and **4j** as well as the cyclopropanation product of **4j** were obtained in 10, 62 and 18% yields, respectively (Table 1, entry 10).

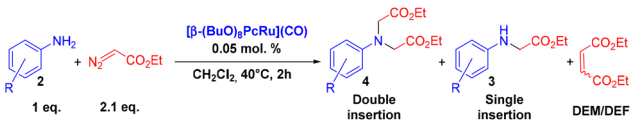
The **1α** complex exhibited a lower catalytic activity in the reaction of aniline with EDA under conditions used for **1β**, providing a 35% conversion into the s-product **3a**. We optimized the protocol towards a quantitative substrate conversion (Table S1†). The replacement of CH_2Cl_2 with MeCN did not improve the aniline conversion. A slow addition of an EDA/aniline mixture to the solution of **1α** in CH_2Cl_2 resulted in a sharp drop of the conversion. However, increasing of the catalyst amount to 0.1 and 0.15 mol% allowed for the improvement of aniline conversion into 71 and 96%, respectively (Table S1†). Importantly, only the s-product **3a** was selectively formed. Thus, the substrate scope was explored using 0.15 mol% of the catalyst and 2.1 equiv. of EDA in CH_2Cl_2 at 40 °C (Table 2). Although the s-products can be obtained with 1.1 equiv. of EDA, we used excess EDA in order to compare the catalytic properties of the two complexes under the same conditions except the catalyst loading.

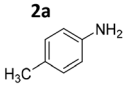
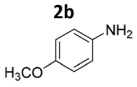
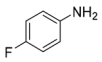
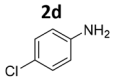
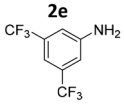
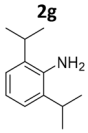
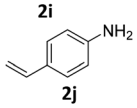
In sharp contrast to **1β** selectively providing d-products, **1α** shows a very high selectivity to s-products even in the presence of 2.1 equiv. of EDA. Quasi-quantitative yields of monosubstituted glycine derivatives were obtained from aniline with electron-donating (Table 2, entries 1–3 and 8) and electron-withdrawing (Table 2, entries 4 and 5) substituents. While 2,6-diisopropylaniline **2h** afforded a 97% yield of **3h**, less hindered highly nucleophilic 2,6-dimethylaniline afforded an 80 : 20 ratio of the s- and d-products **3g** and **4g**, respectively (Table 2, entries 7 and 8). Noteworthily, a highly selective single N–H insertion was observed in the reaction with *p*-aminostyrene, and no double insertion and no cyclopropanation of the double bond were observed in this case (Table 2, entry 10).

The synthetic utility of Ru(II) octa-*n*-butoxyphthalocyaninates **1α** and **1β** due to their different catalytic properties was demonstrated in the derivatization of three aromatic diamines with different electronic properties and substitution patterns (Scheme 2). The carbene insertion to diamines leads to the formation of four products: single insertion (s), single–single insertion (ss), single–double insertion (sd) and double–double insertion (dd). Thus, a selective preparation of the desired product is more challenging compared to the synthesis of simple amines. Using 0.05 mol% of **1β** and 4.1 equiv. of EDA, *p*-phenylenediamine **5** was converted into the dd-product **5dd** in a quantitative yield (TON = 8000) (Scheme 2a).

During its isolation by column chromatography with SiO_2, **5dd** underwent partial elimination of one CH_2COOEt group, affording a double insertion-imine product **5s′d** identified by GC-MS and ^{1}H NMR. Purification using neutral Al_2O_3 prevented degradation and **5dd** was obtained in a 92% isolated

Table 1 Selective double carbene N–H insertion into aromatic amines mediated by the peripheral **1β** complex[a]



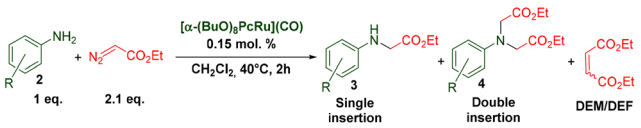
Entry	Substrate	Conversion, %	Double N–H insertion, yields of **4**,[b] %	Single N–H insertion, yields of **3**, %	Yield of DEM (DEF),[e] %
1	 **2a**	98	97 (92)	1	9 (1)
2	 **2b**	99	98 (97)	1	9 (<0.5)
3	 **2c**	100	97 (97)	3	10 (0.5)
4	 **2d**	100	99 (96)	1	8 (0.5)
5	 **2e**	100	94 (94)	6	12 (1)
6	 **2f**	100	51 (43)	49	28 (5)
7	 **2g**	97	89 (89)	8	10 (1)
8	 **2h**	100	97 (97)	3	25 (2)
9	 **2i**	88	0	88[c]	50 (5)
10	 **2j**	90[d]	62 (55)	10	9 (0.5)

[a] Conditions: 0.5 mmol of amine, 1.05 mmol of EDA, 0.05 mol% of the catalyst, 0.5 mL of CH_2Cl_2, air, 40 °C. [b] Yields determined by ^{1}H NMR (isolated yields). [c] The product of the single N–H insertion was isolated in a 51% yield. [d] The cyclopropanation product of the double N–H carbene insertion was obtained in an 18% isolated yield. [e] Yields of diethylmaleate (DEM) and diethylfumarate (DEF) determined by ^{1}H NMR are based on the initial amount of EDA.

yield. As expected, the **1α** complex was selective to the formation of the ss-product **5ss** from *p*-phenylenediamine. In the presence of 0.15 mol% of **1α**, **5ss** was formed in 50% yield (Scheme 2b). Under the standard conditions with 0.3 mol% of **1α** (0.15 mol% per NH_2 group), **5ss** and **5sd** were obtained in 85% and 4% yields, respectively. Upon chromatographic purification either with SiO_2 or Al_2O_3, these compounds underwent a partial transformation to imine derivatives, which could not be separated from the target product **5ss**.

The 2 h reaction of 2,6-dichloro-1,4-diaminobenzene **6** with 4.1 equiv. of EDA mediated by **1α** led to the formation of **6s**, **6ss**, **6sd** and **6dd** products in 5%, 45%, 47% and 3% yields, respectively (Scheme 2d). Owing to their similar polarity, this mixture was difficult to separate and **6ss** could be isolated in a 9% yield. When the reaction was performed for 3 h, the product **6sd** was formed in a 75% yield and was isolated in a 50% yield. In the presence of **1β**, the products **6s**, **6ss**, **6sd** and **6dd** were formed in 9%, 5%, 13% and 66% yields, respectively (Scheme 2c). The target product **6dd** was isolated in a 61% yield. This example indicates that the optimization of the reaction conditions depending on the properties of diamine can afford the desired product in a good yield.

Table 2 Selective single carbene N–H insertion into aromatic amines mediated by the non-peripheral **1α** complex[a]



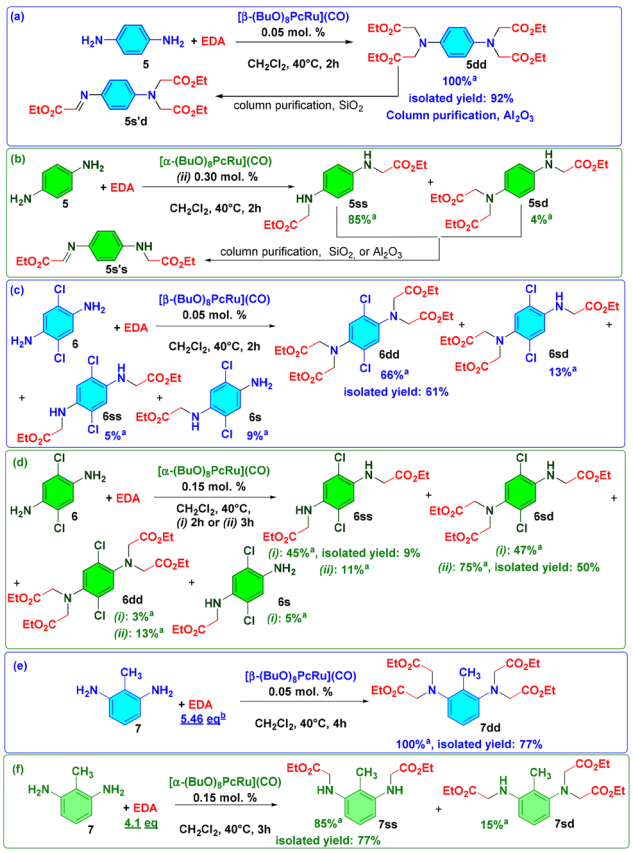
Entry	Substrate	Conversion, %	Single N–H insertion, yields,[b] %	Double N–H insertion, yields, %	Yield of DEM (DEF),[c] %
1	**2a**	96	96 (96)	0	0.5 (tr.)
2	**2b**	99	96 (93)	3	2 (0)
3	**2c**	93	93 (93)	0	tr. (0)
4	**2d**	100	97 (97)	3	2 (0)
5	**2e**	98	98 (85)	0	2 (0)
6	**2f**	40	40 (n.d.)	0	1 (0)
7	**2g**	100	80 (29)	20	9 (tr.)
8	**2h**	100	97 (97)	3	9 (0)
9	**2i**	55	55 (40)	0	3 (0)
10	**2j**	95	95 (95)	0	tr. (0)

[a] Conditions: 0.5 mmol of amine, 1.05 mmol of EDA, 0.15 mol% of the catalyst, 0.5 mL of CH_2Cl_2, air, 40 °C. [b] Yields determined by ^{1}H NMR (isolated yields). [c] Yields of diethylmaleate (DEM) and diethylfumarate (DEF) determined by ^{1}H NMR are based on the initial amount of EDA.

Indeed, under standard conditions, **1β** catalyzed the reaction of 2,6-diaminotoluene **7** with 4.1 equiv. of EDA, forming a mixture of **7dd** (57%) and **7sd** products (42%), which could not be completely separated. When 5.46 equiv. of EDA were added in 4 portions during 3 h, a quantitative formation of **7dd** was observed and the target product was isolated in 82% yield (Scheme 2e). In a complementary manner, **1α** provided 85% yield of **7ss**, accompanied by 15% yield of **7sd** (Scheme 2f). The desired **7ss** was isolated in a 77% yield.

Such a different reactivity of two Ru phthalocyanines opens up new opportunities for the synthesis of elaborated amine derivatives, *e.g.*, unsymmetrical tertiary amines bearing three different groups. In the first step, readily available primary amines and diamines can be converted into s- or ss-products using the **1α** catalyst. Next, **1β** can catalyze the N–H insertion of another carbene to an s-product to afford an unsymmetrical $NR_1R_2R_3$ amine. The feasibility of this strategy was first evaluated using diazoacetonitrile as a carbene precursor and *N*-methylaniline **8** as a model substrate. N_2CHCN is a particularly useful compound to introduce nitrile groups into organic molecules.[8c,12]

Compared to EDA, the use of N_2CHCN as a carbene precursor has still been rather limited[13] because of the explosion propensity of a neat compound.[12] Recently, the safe generation of N_2CHCN *in situ* or the use of diluted solutions has been proposed.[12] The high yields of the tertiary amine **9** were obtained from *N*-methylaniline using both protocols (Fig. S131†). Among the organic solvents tested, the highest yield of **9** (83%) was obtained using 1,2-dichloroethane. The use of 0.57 M

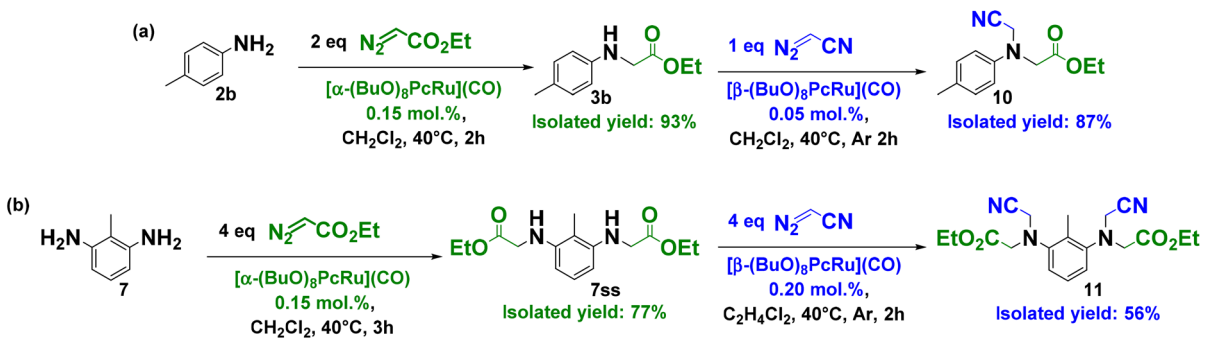


Scheme 2 Functionalization of the aromatic diamines – (a, b) *p*-phenylenediamine, (c, d) 2,6-dichloro-1,4,-diaminobenzene and (e, f) 2,6-diaminotoluene with EDA in the presence of **1α** and **1β**. [a] Yields were determined from the ^{1}H NMR spectra.

N_2CHCN solution in DCE (1.1 equiv.) afforded the target unsymmetrical tertiary amine in 97% yield in the presence of 0.05 mol% of **1β** instead of 0.1 mol% of the catalyst charge applied for the *in situ* protocol (Fig. S131†).

Upon applying the efficient protocols for the selective single carbene insertion from EDA to primary amines catalyzed by **1α** and for the efficient functionalization of secondary amines using N_2CHCN in combination with **1β**, we have prepared unsymmetrical tertiary amines, starting from the simple aromatic amine and diamine (Scheme 3). First, ethyl *p*-tolylglycinate **3b** was obtained from *p*-toluidine and EDA in the presence of **1α** in 93% isolated yield (Scheme 3a). The subsequent treatment of **3b** with N_2CHCN and **1β** afforded the target unsymmetrical tertiary amine **10** in 87% isolated yield. This approach was further extended to primary diamine exemplified by 2,6-diaminotoluene **7** converted into **7ss** in 77% yield through the reaction with EDA and **1α** (Scheme 3b). The second step was accomplished using N_2CHCN and 0.2 mol% of **1β**, providing 56% isolated yield of the asymmetric tertiary diamine **11**. Asymmetric tertiary diamines can in principle be prepared in two steps using the same peripheral complex, but the product yields will be lower because of the formation of the side single–double insertion product and lower substrate conversion. Furthermore, the isolation of the target product is much more difficult in this case. Thus, the two-step strategy involving two catalysts is particularly useful to access the asymmetric tertiary amines.

In conclusion, the Ru(II) octa-*n*-butoxyphthalocyanine complexes are efficient catalysts for the carbene insertion to amine N–H bonds under practical reaction conditions. Using a low loading of these air-tolerant catalysts and a near-equivalent substrate/carbene precursor ratio, a wide range of simple amines and diamines were converted into different products in high yields. Importantly, the position of the substituents in the Ru(II) octa-*n*-butoxyphthalocyanine complexes controls their catalytic properties: the non-peripherally and peripherally substituted complexes **1α** and **1β** afford single and double N–H insertion products, respectively. Due to the complementary catalytic properties of the two Ru complexes, a novel synthetic strategy was proposed, which can provide access to asymmetric tertiary amines and diamines, starting from simple readily available compounds. This approach was validated using *p*-toluidine and 2,6-diaminotoluene as model substrates. Since *N*-aryl amines are important building blocks in natural products and synthetic compounds, this approach might be useful to access elaborated functionalized amines with interesting biological and pharmacological properties.[14]



Scheme 3 Preparation of unsymmetrical tertiary amines from primary amines – (a) *p*-toluidine and (b) 2,6-diaminotoluene by successive carbene transfer reactions catalyzed by **1α** and **1β**.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

This work was supported by the CNRS and RFBR through the International Emerging Action 2021 and the research project 21-53-15004.

References

1 (*a*) C. Damiano, P. Sonzini and E. Gallo, *Chem. Soc. Rev.*, 2020, **49**, 4867–4905; (*b*) A. Ford, H. Miel, A. Ring, C. N. Slattery, A. R. Maguire and M. A. McKervey, *Chem. Rev.*, 2015, **115**, 9981–10080; (*c*) M. J. Weissenborn and R. M. Koenigs, *ChemCatChem*, 2020, **12**, 2171–2179; (*d*) V. Carreras, N. Tanbouza and T. Ollevier, *Synthesis*, 2021, **53**, 79–94; (*e*) D. Intrieri, D. M. Carminati and E. Gallo, *Dalton Trans.*, 2016, **45**, 15746–15761; (*f*) I. Aviv and Z. Gross, *Chem. – Eur. J.*, 2008, **14**, 3995–4005; (*g*) R. F. J. Epping, M. M. Hoeksma, E. O. Bobylev, S. Mathew and B. de Bruin, *Nat. Chem.*, 2022, **14**, 550–557.

2 D. Intrieri, D. M. Carminati and E. Gallo, in *Handbook of Porphyrin Science*, ed. K. M. Kadish, K. M. Smith and R. Guilard, World Scientific, Singapore, 2016, vol. 38, pp. 1–99.

3 (*a*) Y. Yang and F. H. Arnold, *Acc. Chem. Res.*, 2021, **54**, 1209–1225; (*b*) D. M. Carminati and R. Fasan, *ACS Catal.*, 2019, **9**, 9683–9697; (*c*) B. J. Wittmann, A. M. Knight, J. L. Hofstra, S. E. Reisman, S. B. J. Kan and F. H. Arnold, *ACS Catal.*, 2020, **10**, 7112–7116; (*d*) K. Chen and F. H. Arnold, *J. Am. Chem. Soc.*, 2020, **142**, 6891–6895.

4 (*a*) I. Aviv and Z. Gross, *Chem. Commun.*, 2006, 4477–4479; (*b*) C. J. Moody, *Angew. Chem., Int. Ed.*, 2007, **46**, 9148–9150; (*c*) B. Liu, S.-F. Zhu, W. Zhang, C. Chen and Q.-L. Zhou, *J. Am. Chem. Soc.*, 2007, **129**, 5834–5835; (*d*) B. Xu, S.-F. Zhu, X.-L. Xie, J.-J. Shen and Q.-L. Zhou, *Angew. Chem., Int. Ed.*, 2011, **50**, 11483–11486.

5 (*a*) Z. J. Wang, N. E. Peck, H. Renata and F. H. Arnold, *Chem. Sci.*, 2014, **5**, 598–601; (*b*) G. Sreenilayam and R. Fasan, *Chem. Commun.*, 2015, **51**, 1532–1534; (*c*) V. Steck, G. Sreenilayam and R. Fasan, *Synlett*, 2020, **31**, 224–229; (*d*) V. Steck, D. M. Carminati, N. R. Johnson and R. Fasan, *ACS Catal.*, 2020, **10**, 10967–10977; (*e*) D. Nam, A. Tinoco, Z. Shen, R. D. Adukure, G. Sreenilayam, S. D. Khare and R. Fasan, *J. Am. Chem. Soc.*, 2022, **144**, 2590–2602.

6 G. Maas, *Chem. Soc. Rev.*, 2004, **33**, 183–190.

7 (*a*) E. Galardon, P. Le Maux and G. Simonneaux, *J. Chem. Soc., Perkin Trans. 1*, 1997, 2455–2456; (*b*) C.-M. Ho, J.-L. Zhang, C.-Y. Zhou, O.-Y. Chan, J. J. Yan, F.-Y. Zhang, J.-S. Huang and C.-M. Che, *J. Am. Chem. Soc.*, 2010, **132**, 1886–1894; (*c*) K.-H. Chan, X. Guan, V. K.-Y. Lo and C.-M. Che, *Angew. Chem., Int. Ed.*, 2014, **53**, 2982–2987; D. Carrié, T. Roisnel and G. Simonneaux, *Polyhedron*, 2021, **205**, 115294.

8 (*a*) Y. Ferrand, P. Le Maux and G. Simonneaux, *Org. Lett.*, 2004, **6**, 3211–3214; (*b*) C.-Y. Zhou, J.-S. Huang and C.-M. Che, *Synlett*, 2010, 2681–2700; (*c*) Y. Ferrand, P. Le Maux and G. Simonneaux, *Tetrahedron: Asymmetry*, 2005, **16**, 3829–3836; (*d*) E. Galardon, P. Le Maux and G. Simonneaux, *Tetrahedron*, 2000, **56**, 615–621; (*e*) H.-X. Wang, Q. Wan, K. Wu, K.-H. Low, C. Yang, C.-Y. Zhou, J.-S. Huang and C.-M. Che, *J. Am. Chem. Soc.*, 2019, **141**, 9027–9046; (*f*) E. Galardon, P. Le Maux and G. Simonneaux, *Chem. Commun.*, 1997, 927–928; (*g*) H. F. Srour, P. Le Maux, S. Chevance, D. Carrié, N. Le Yondre and G. Simonneaux, *J. Mol. Catal. A: Chem.*, 2015, **407**, 194–203.

9 (*a*) H.-H. Liu, Y. Wang, Y.-J. Shu, X.-G. Zhou, J. Wu and S.-Y. Yan, *J. Mol. Catal. A: Chem.*, 2006, **246**, 49–52; (*b*) A. P. Kroitor, L. P. Cailler, A. G. Martynov, Yu. G. Gorbunova, A. Yu. Tsivadze and A. B. Sorokin, *Dalton Trans.*, 2017, **46**, 15651–15655.

10 (*a*) A. B. Sorokin, *Chem. Rev.*, 2013, **113**, 8152–8191; (*b*) E. A. Lukyanets and V. N. Nemykin, *J. Porphyrins Phthalocyanines*, 2010, **14**, 1–40; (*c*) V. N. Nemykin and E. A. Lukyanets, *ARKIVOC*, 2010, 136–208.

11 L. P. Cailler, A. P. Kroitor, A. G. Martynov, Y. G. Gorbunova and A. B. Sorokin, *Dalton Trans.*, 2021, **50**, 2023–2031.

12 P. K. Mykhailiuk and R. M. Koenigs, *Chem. – Eur. J.*, 2020, **26**, 89–101.

13 (*a*) K. Hock, R. Spitzner and R. M. Koenigs, *Green Chem.*, 2017, **19**, 2118–2122; (*b*) A. L. Chandgude and R. Fasan, *Angew. Chem., Int. Ed.*, 2018, **57**, 15852–15856; (*c*) C. Empel, K. J. Hock and R. M. Koenigs, *Org. Biomol. Chem.*, 2018, **16**, 7129–7133; (*d*) C. Empel, K. J. Hock and R. M. Koenigs, *Chem. Commun.*, 2019, **55**, 338–341.

14 (*a*) O. I. Afanasyev, E. A. Kuchuk, K. M. Muratov, G. L. Denisov and D. Chusov, *Eur. J. Org. Chem.*, 2021, 543–586; (*b*) P. Ruiz-Castillo and S. L. Buchwald, *Chem. Rev.*, 2016, **116**, 12564–12649.

