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The Intermolecular Pauson–Khand Reaction of *meso*-Substituted Porphyrins

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The intermolecular Pauson–Khand reaction is often limited by the poor reactivity and selectivity of simple alkenes. Here we expanded the range of reagents to simple alkenyl- and alkynyl-substituted porphyrins. The two expected regioisomers could be obtained in a combined yield of up to 72 %. In addition, use of the Pauson–Khand reaction provides a simple and novel pathway for the preparation of porphyrin dimers in a nearly quantitative yield.

Introduction

The range of applications for porphyrins continues to grow, and the development of new synthetic routes presents a crucial step in several application areas. While design pathways using total synthesis of novel porphyrins continue to be developed, they often require numerous steps. Therefore, the functionalisation of simple porphyrin substituents offers a complementary and perhaps more wide-ranging approach that may be applied to various substitution patterns of different tetrapyrroles. Ideally, these new synthetic methods involve simple starting materials, one reaction step and high yields without the formation of any by-products.

The Pauson–Khand reaction has these features and has to the best of our knowledge not been used with porphyrins previously. Since its discovery by Pauson and Khand in 1971[1] this reaction has remained the most flexible and atom-economical method for the synthesis of five-membered rings.[2] It involves the reaction of an alkene, an alkyne and a carbon monoxide molecule in a transition-metal-mediated coupling to form a cyclopentenone system. The reaction mechanism proposed by Magnus and co-workers[3,4] has been widely accepted, and many five-membered carbocycles thus prepared have been shown to exhibit biological activity.[5,6]

Although the first intramolecular version of the Pauson–Khand reaction was reported by Schore[7] only ten years after the initial discovery, it has received most attention.[8] This variation is thermodynamically more favored, and the formation of regioisomers can be excluded. On the other hand, the intermolecular version appears to be synthetically more demanding as has been limited by the poor reactivity and selectivity of simple alkenes. Sterically hindered alkenes are disfavored, and in many cases yields are only moderate. Hence, the intermolecular Pauson–Khand reaction has been restricted to strained alkenes, such as norbornene and norbornadiene, and there is a continuing need to widen the scope of this reaction. As part of our ongoing studies on the development of new reactions for the functionalisation of porphyrins[9] we have undertaken an initial study of the Pauson–Khand reaction of porphyrins.

The most common pathways for cyclisation reactions at the porphyrin ring system involve Diels–Alder and 1,3-dipolar cycloaddition reactions. These synthetic methods have mostly been applied to the β-position of the aromatic system.[10] Just recently, the Huisgen 1,3-dipolar cycloaddition for the formation of heterocyclic five-membered rings has been carried out at substituents located at the *meso*-position.[11] Herein, we report an alternative pathway for cyclisation reactions involving *meso*-substituents. We describe the extension of the intermolecular Pauson–Khand reaction to simple alkene- as well as alkyne-substituted porphyrins and illustrate its utility for the preparation of porphyrin dimers in high yields.

Results and Discussion

For studies in analogy to the investigations of Pauson and co-workers on the reactivity of styrene[12] we prepared [5,10,15-tris(4-methylphenyl)-20-vinylporphyrinato]nickel(II) (**4**). The synthesis of this compound involved Suzuki cross-coupling[9b] of 5-bromo-10,15,20-tris(4-methylphenyl)porphyrin (**2**), obtained by bromination[13] of **1** with vinylboronic acid pinacol ester to afford **3**, followed by metallation with nickel(II) acetate.[14] The vinylporphyrin **4** was treated with phenylacetylene and $Co_2(CO)_8$ in THF under heating at reflux for 4 d. Unfortunately, the only product that could be isolated was the formyl-substituted porphyrin analogue **5** in 11% yield. Most likely the double bond of compound **4** was too close to the porphyrin macrocycle and consequently sterically too hindered to take part in the reaction. Therefore, the allyl-substituted porphyrin **6**[9b] with

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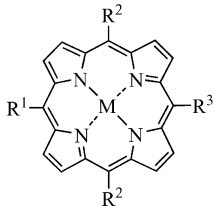
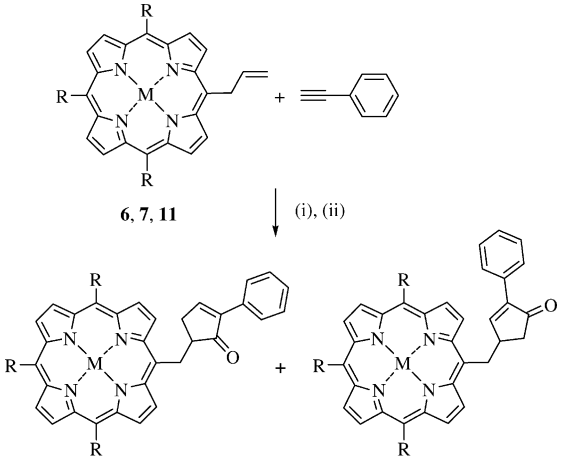


1–**21**

1 $R^1 = R^2 = 4\text{-MeC}_6H_4$, $R^3 = H$, M = 2 H
2 $R^1 = R^2 = 4\text{-MeC}_6H_4$, $R^3 = Br$, M = 2 H
3 $R^1 = R^2 = 4\text{-MeC}_6H_4$, $R^3 = vinyl$, M = 2 H
4 $R^1 = R^2 = 4\text{-MeC}_6H_4$, $R^3 = vinyl$, M = Ni
5 $R^1 = R^2 = 4\text{-MeC}_6H_4$, $R^3 = formyl$, M = Ni
6 $R^1 = R^2 = 4\text{-MeC}_6H_4$, $R^3 = allyl$, M = Ni
7 $R^1 = R^2 = 4\text{-MeC}_6H_4$, $R^3 = allyl$, M = Zn
8 $R^1 = R^2 = n\text{-}C_6H_{13}$, $R^3 = H$, M = 2 H
9 $R^1 = R^2 = n\text{-}C_6H_{13}$, $R^3 = Br$, M = 2 H
10 $R^1 = R^2 = n\text{-}C_6H_{13}$, $R^3 = allyl$, M = 2 H
11 $R^1 = R^2 = n\text{-}C_6H_{13}$, $R^3 = allyl$, M = Ni
12 $R^1 = R^2 = 4\text{-MeC}_6H_4$, $R^3 = TMSethynyl$, M = 2 H
13 $R^1 = R^2 = 4\text{-MeC}_6H_4$, $R^3 = TMSethynyl$, M = Ni
14 $R^1 = R^2 = 4\text{-MeC}_6H_4$, $R^3 = ethynyl$, M = Ni
15 $R^1 = R^2 = 4\text{-MeC}_6H_4$, $R^3 = ethynyl$, M = Zn
16 $R^1 = R^2 = n\text{-}C_6H_{13}$, $R^3 = TMSethynyl$, M = 2 H
17 $R^1 = R^2 = n\text{-}C_6H_{13}$, $R^3 = TMSethynyl$, M = Ni
18 $R^1 = R^2 = n\text{-}C_6H_{13}$, $R^3 = ethynyl$, M = Ni
19 $R^1 = H$, $R^2 = 4\text{-MeC}_6H_4$, $R^3 = 4\text{-ethynylC}_6H_4$, M = 2 H
20 $R^1 = H$, $R^2 = 4\text{-MeC}_6H_4$, $R^3 = 4\text{-ethynylC}_6H_4$, M = Ni
21 $R^1 = H$, $R^2 = 4\text{-MeC}_6H_4$, $R^3 = 4\text{-ethynylC}_6H_4$, M = Zn

an extra carbon atom between the porphyrin moiety and the double bond was chosen as starting material. Indeed, the Pauson–Khand reaction of **6** with phenylacetylene proceeded cleanly, and the two products **22** and **23** could be obtained in 19 and 34% yield, respectively (Scheme 1). The reaction could also be carried out with the (porphyrinato)-zinc(II) complex **7** to afford compounds **24** and **25** in lower yields.



6, **7**, **11** (i), (ii)

22, **24**, **26** **23**, **25**, **27**

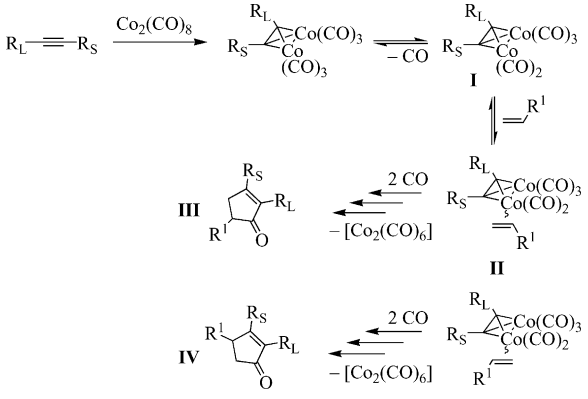
Starting compound	R	M	Product	Yield [%]
6	4-MeC_6H_4	Ni	**22**, **23**	19, 34
7	4-MeC_6H_4	Zn	**24**, **25**	8, 15
11	n-C_6H_{13}	Ni	**26**, **27**	14, 19

[a] 39; 33

Scheme 1. Pauson–Khand reaction of allylporphyrins. Reaction conditions: (i) $Co_2(CO)_8$, THF, Δ, overnight; (ii) $Co_2(CO)_8$, THF, Schlenk tube, 3 d. [a] Reaction carried out under condition (ii).

Next, we examined whether the reaction is also applicable to alkyl-substituted porphyrins by using (5-allyl-10,15,20-trihexylporphyrinato)nickel(II) (**11**) as test compound. Its synthesis involved the nucleophilic substitution of 5,15-dihexylporphyrin with *n*-hexyllithium to obtain the 5,10,15-trihexylporphyrin (**8**), bromination[13] of **8** to afford **9** followed by reaction with allylboronic acid pinacol ester under Suzuki cross-coupling conditions[12] to afford **10** and subsequent metallation to the nickel(II) complex **11**.[14] The Pauson–Khand reaction of **11** led to the formation of products **26** and **27**, albeit in lower yields (14 and 19%, respectively) compared to the *meso*-arylporphyrins.

Various possibilities have been reported to improve the yield of the Pauson–Khand reaction;[15] notably replacement of Co by a different transition metal or use of additives. Hence, $Mo(CO)_6$ was used instead of $Co_2(CO)_8$ in the reaction of **6** with phenylacetylene.[16] However, no reaction was observed, and only starting material was recovered. Use of *N*-methylmorpholine *N*-oxide as an additive gave the same result.[17] Addition of molecular sieves (4 Å) resulted in the formation of compounds **22** and **23** without improvement of the yield.[18] As no starting material could be recovered or detected by TLC in the initial Pauson–Khand reaction of **6**, we assumed that the remaining equivalents of allylporphyrin were inserted in the (alkyne)$Co_2(CO)_6$ complex **I**, as shown in the reaction mechanism (Scheme 2).



Scheme 2. Postulated mechanism for the Pauson–Khand reaction. R_L = larger group, R_S = smaller group.

However, the (alkyne)$Co_2(CO)_5$(alkenylporphyrin) complex **II** could not be isolated.[19] In an attempt to "force" this intermediate to proceed in the reaction, the reaction of compound **6** with phenylacetylene and $Co_2(CO)_8$ was again carried out in THF, however, this time in a Schlenk tube. The solution was degassed, and the reaction mixture was heated to 80 °C until no change was observed by TLC. Indeed, the yield could be improved, and products **22** and **23** were obtained after 3 d in 39% and 33%, respectively.

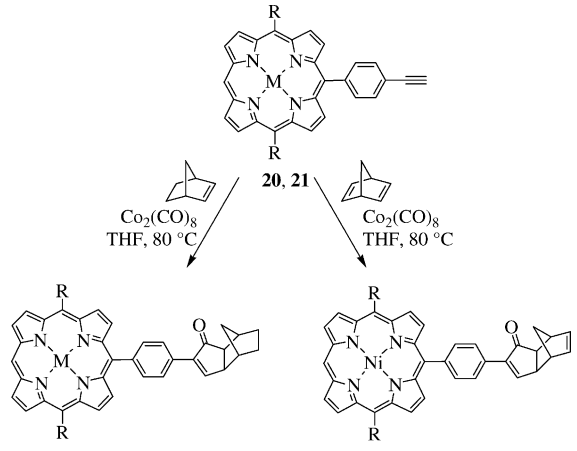
Compounds **22** and **23** are the two regioisomers expected from the reaction mechanism, in analogy to compounds **III** and **IV** in Scheme 2 with the larger residue R_L of the alkyne partner in 2-position of the cyclopentenone. As the smaller alkyne residue is R_S = H, complex **II** is non-selective and the residue originating from the alkene partner can add to the 4-position or, alternatively, the 5-position of the cyclopentenone. The ratio of the two regioisomers from this reaction is approximately 1:1, which is typical for reactions of terminal alkynes with monosubstituted alkenes.[20] However, it is also known that the regioselectivity can be quite random. When the reaction was stopped after 1 d, the main isomer obtained was the one according to **IV**, whereas after 3 d the isomer according to **III** was obtained in a slightly higher yield. This kind of reversal of regioselectivity has previously been described for promoters,[21] different solvents[22] and thermolyses, but the reason for this unexpected selectivity remains unclear.[23]

Other alkyne partners were also treated with **6**, namely ethynyltrimethylsilane, hexyne, dimethyl ethylacetylenedicarboxylate and propargyl toluene-4-sulfonate. Unfortunately, these attempts were unsuccessful.

Next, we investigated the reaction with the porphyrin bearing the alkyne group by using porphyrin **14** and allylbenzene.[24] Preparation of compound **14** involved the synthesis of **12** from **2** by Sonogashira reaction with ethynyltrimethylsilane, followed by deprotection to afford **13**, and metallation. However, no product was formed by using the standard Pauson–Khand conditions. This can be related to the poor reactivity of the alkene partner mentioned above, as it was found that terminal alkenes usually result in low yields. It has been shown that insertion of the alkene into the Co–C bond is the rate-determining reaction step and is related to the back-donation of electrons from the d-orbitals of the cobalt atom to the π*-orbitals of the alkene;[24] de Bruin et al. showed that the lower the LUMO of the alkene, the higher the reactivity and suggested the following order of reactivity for the thermal version of the Pauson–Khand reaction: cyclohexene < cyclopentene < norbornene.

Hence, cyclohexene, norbornene and compound **6** were treated with **14**; again unsuccessfully. To create a more electron-rich alkyne, the zinc(II) compound **15** and the trialkyl-substituted porphyrin **18** were synthesised. Compound **18** was prepared by Sonogashira reaction of **9** with ethynyltrimethylsilane to afford **16**, followed by deprotection of the ethynyl group to give **17** and metallation to **18**. Alkyl substituents on the porphyrin increase the electron density of the macrocycle due to the electron-donating effect, and zinc(II) belongs to one of the metals that induce the highest negative charge in the porphyrin periphery.[25] Again, no product was obtained when compounds **15** and **18** were treated with norbornene under Pauson–Khand conditions. Attempts to isolate the presumed complex **I** failed. Possibly, the alkyne group is sterically too hindered by the macrocycle for the reaction to proceed, similar to the situation found with the vinylporphyrins. It appears that the mechanism of the Pauson–Khand reaction seems to be sterically quite demanding, which is conceivable when imagining complexes **I** and **II** 3-dimensionally.

Consequently, a spacer was introduced between the porphyrin macrocycle and the terminal alkyne. The most straightforward procedure to synthesise such a compound was the introduction of a 4-ethynylphenyl substituent by nucleophilic reaction of 5,15-bis(4-methylphenyl)porphyrin with the organolithium analogue[26] to afford the 4-ethynylphenyl-substituted porphyrin **19**. Thus, compounds **20** and **21** were prepared through metallation and treated with norbornene to obtain the Pauson–Khand products **28** and **29** in very good yields (Scheme 3).



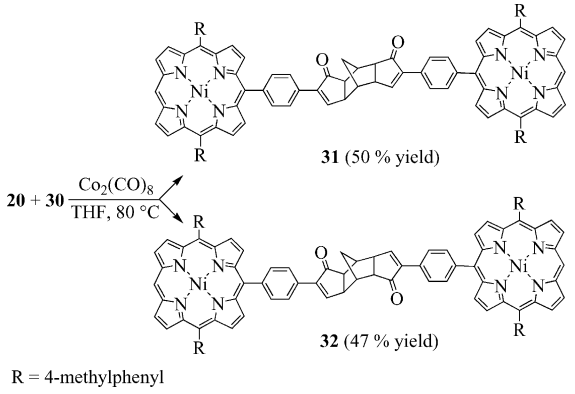
Starting compound	R	M	Product	Yield [%]
20	4-MeC_6H_4	Ni	**28**	85
21	4-MeC_6H_4	Zn	**29**	78
20	4-MeC_6H_4	Ni	**30**	38

Scheme 3. Pauson–Khand reaction of (ethynylphenyl)porphyrins.

The regioselectivity of the products with regard to the cyclopentenone is in agreement with the theoretical expectation. The larger group of the alkyne partner is located in the 2-position of the cyclopentenone, and several studies have shown the reaction of norbornene to be completely *exo*-face-selective.[27] The yield of the reaction of **20** with norbornadiene for the formation of **30** was only moderate. Possibly the product **30** reacted further with the starting material **20** by a double Pauson–Khand reaction,[28] but the product mixture could not be analysed.

Based on these observations, compound **20** was directly treated with **30** in an attempt to prepare a porphyrin dimer by the Pauson–Khand reaction. Indeed, the two fractions obtained were identified as the dimers **31** and **32** in excellent

yields of 50% and 47%, respectively (Scheme 4).[28] Compounds **31** and **32** are the two expected regioisomers of the double Pauson–Khand reaction. The stereochemistry of the second addition is also known to be *exo*-selective. The tetracyclic linker unit has been detected previously when the reaction was carried out with an excess of alkyne.[28] Accordingly, norbornadiene was treated with a two-fold excess of porphyrin **20**. The main product obtained was compound **30**; however, the amount of the other fractions was again too small for analysis. Hence, the two-step strategy for producing the dimers **31** and **32** is the more promising pathway and affords the combined products nearly quantitatively.



Scheme 4. Synthesis of porphyrin dimers by double Pauson–Khand reaction.

Conclusions

We have shown that the Pauson–Khand reaction offers an alternative pathway for cyclisation reactions with porphyrin substituents in the *meso*-position. The intermolecular Pauson–Khand reaction is applicable to alkene- as well as alkyne-substituted porphyrins. Steric considerations require the reaction centre to be in a certain distance to the macrocycle, and the reaction is somewhat limited with regard to the non-porphyrin reactants; e. g., allylporphyrins could serve as the alkene partner to obtain the expected two regioisomers in a combined yield of up to 72%. Likewise, (ethynylphenyl)porphyrins were treated with norbornene and norbornadiene in moderate to high yields. In addition to expanding the scope of the Pauson–Khand reaction to technically and medicinally relevant complex heterocycles, the simple formation of porphyrin dimers through a sequential double Pauson–Khand reaction in quantitative (combined) yield indicates the potential of this method for the coupling of porphyrin-based units.

Experimental Section

General Methods: ^{1}H and ^{13}C NMR spectra were recorded with a Bruker DPX 400 MHz (400.13 MHz for ^{1}H NMR; 100.61 MHz for ^{13}C NMR) and/or a Bruker AV 600 MHz (600.13 MHz for ^{1}H NMR; 150.90 MHz for ^{13}C NMR) NMR spectrometer. Chemical shifts are reported in ppm. Data are reported as follows: chemical shift, multiplicity (s: singlet, d: doublet, dd: doubledoublet, t: triplet, m: multiplet, br: broad), coupling constants (*J* in Hz), integration and assignment. High resolution mass spectrometry was carried out with a Micromass/Waters Corp., USA liquid chromatography time-of-flight spectrometer equipped with an electrospray source or a MALDI Q TOF Premier MS system. Melting points were acquired with a Stuart SMP10 melting point apparatus and are uncorrected. Thin layer chromatography (TLC) was performed on silica gel 60 F_{254} (Merck) precoated aluminum sheets. Chromatography on silica gel was carried out by using a forced flow of the indicated solvent system on Fluka Silica Gel 60 (230–400 mesh). Tetrahydrofuran (THF) and diethyl ether were distilled from sodium/benzophenone under nitrogen. All commercial chemicals were supplied and used without further purification. Compounds **8**[29a] and **15**[29b] were prepared as reported previously.

Synthesis of Starting Materials

5,10,15-Tris(4-methylphenyl)porphyrin (1): A 1-L 3-necked round-bottom flask was charged with *p*-bromotoluene (5 g, 29.25 mmol, 14 equiv.) in dry diethyl ether (100 mL) under Ar. *n*-Butyllithium (14 mL, 35.1 mmol, 17.2 equiv.) was added dropwise at –70 °C over 30 min. After the addition was complete, the reaction mixture was warmed to room temp. and was stirred for 1 h (colour change to white). Next, 5,15-bis(4-methylphenyl)porphyrin (1 g, 2.04 mmol, 1 equiv.) dissolved in THF (500 mL) under Ar and cooled to –20 °C was added. The combined reaction mixture was stirred at room temp. for 1 h (colour change to brown), then water (5 mL, colour change to emerald green) and DDQ (2.1 g, 9.25 mmol, 4 equiv.) were added (colour change to red). After 1 h, the crude product was filtered through a layer of silica gel and recrystallised from CH_2Cl_2/MeOH. The product was obtained as purple crystals in 1.08 g (1.86 mmol, 91%) yield. Analytical data were as reported by Lindsey et al.[30]

5,10,15-Tris(4-methylphenyl)-20-vinylporphyrin (3): A 50-mL Schlenk-tube was filled with Ar and charged with 5-bromo-10,15,20-tris(4-methylphenyl)porphyrin (300 mg, 0.455 mmol, 1 equiv.) in dry THF (50 mL). K_3PO_4 (2.0 g, 9.1 mmol, 20 equiv.) was added, and the solution was degassed by three freeze-pump-thaw cycles and put under Ar again. Vinylboronic acid pinacol ester (0.8 mL, 4.55 mmol, 10 equiv.) and $Pd(PPh_3)_4$ (53 mg, 0.0455 mmol, 0.1 equiv.) were added, and the reaction mixture was heated to 80 °C overnight. Then the solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2. The crude product was washed with a saturated solution of $NaHCO_3$, water and brine and dried with Na_2SO_4. Purification was carried out by dry-loaded column chromatography on silica gel (CH_2Cl_2/C_6H_{14}, 1:2, v/v). The product was obtained after recrystallisation from CH_2Cl_2/MeOH as purple crystals in 144 mg (0.24 mmol, 52%) yield. M.p. > 300 °C. R_f = 0.43 (CH_2Cl_2/C_6H_{14}, 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = –2.67 (br., 2 H, N*H*), 2.73 (s, 3 H, $C_6H_4CH_3$), 2.73 (s, 6 H, $C_6H_4CH_3$), 6.15 (dd, $^3J_{H,H}$ = 17.5, $^2J_{H,H}$ = 1.8 Hz, 1 H, CH=CH_2), 6.59 (dd, $^3J_{H,H}$ = 11.7, ^2J = 1.8 Hz, 1 H, CH=CH_2), 7.57 (d, $^3J_{H,H}$ = 8.2 Hz, 4 H, H_{Ar}), 7.59 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H, H_{Ar}), 8.09 (d, $^3J_{H,H}$ = 7.6 Hz, 4 H, H_{Ar}), 8.12 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H, H_{Ar}), 8.84 (s, 4 H, β-*H*), 8.95 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 9.26 (dd, $^3J_{H,H}$ = 17.0, $^3J_{H,H}$ = 11.1 Hz, 1 H, C*H*=CH$_2$), 9.50 (d, $^3J_{H,H}$ = 5.3 Hz, 2 H, β-*H*) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 21.6, 117.0, 120.1, 120.2, 127.3, 127.4, 127.6, 131.1 (br.), 134.5, 137.4, 137.5, 139.2 ppm. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 421 (6.0), 521 (5.0), 556 (4.9), 596 (4.87), 653 (4.86) nm. HRMS (ES+): calcd. for $C_{43}H_{34}N_4$ [M + H]$^+$ 607.2862, found 607.2861.

[5,10,15-Tris(4-methylphenyl)-20-vinylporphyrinato]nickel(II) (4): A 50-mL 2-necked round-bottomed flask was charged with 5,10,15-

tris(4-methylphenyl)-20-vinylporphyrin (**3**, 70 mg, 0.116 mmol, 1 equiv.) and $Ni(acac)_2$ (45 mg, 0.174 mmol, 1.5 equiv.) in toluene (30 mL). The reaction mixture was heated to reflux until completion (ca. 30 min, TLC control). The solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2. The crude product was filtered through a layer of silica gel and washed with CH_2Cl_2. After recrystallisation from CH_2Cl_2/MeOH, the product was obtained as dark red needles in 54.6 mg (0.08 mmol, 71%) yield. M.p. 212 °C. R_f = 0.85 (CH_2Cl_2/C_6H_{14}, 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.65 (s, 3 H, $C_6H_4CH_3$), 2.66 (s, 6 H, $C_6H_4CH_3$), 5.64 (dd, $^3J_{H,H}$ = 17.5, $^2J_{H,H}$ = 1.8 Hz, 1 H, CH=CH_2), 5.68 (dd, $^3J_{H,H}$ = 17.5, $^2J_{H,H}$ = 1.8 Hz, 1 H, CH=CH_2), 7.48 (d, $^3J_{H,H}$ = 7.6 Hz, 4 H, H_{Ar}), 7.50 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H, H_{Ar}), 7.88 (d, $^3J_{H,H}$ = 5.9 Hz, 4 H, H_{Ar}), 7.89 (d, $^3J_{H,H}$ = 5.9 Hz, 2 H, H_{Ar}), 8.71 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 8.72 (d, $^3J_{H,H}$ = 5.3 Hz, 2 H, β-*H*), 8.84 (d, $^3J_{H,H}$ = 5.3 Hz, 2 H, β-*H*), 8.96 (dd, $^3J_{H,H}$ = 17.0, $^3J_{H,H}$ = 11.0 Hz, 1 H, C*H*=CH$_2$), 9.35 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 21.0, 114.5, 118.2, 127.2, 127.6, 130.9, 131.6, 131.7, 132.1, 133.0, 133.1, 135.4, 136.9, 137.3, 140.8, 141.5, 141.9 ppm. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 420 (5.5), 535 (4.7) nm. HRMS (ES+): calcd. for $C_{43}H_{32}N_4Ni$ [M + H]$^+$ 663.2059, found 663.2031.

5,10,15-Trihexylporphyrin (8): A 1-L 3-necked round-bottom flask was filled with Ar and charged with 5,15-dihexylporphyrin (940 mg, 1.967 mmol, 1 equiv.) in dry THF (500 mL). The solution was cooled to –78 °C, and *n*-hexyllithium (5.13 mL, 11.8 mmol, 6 equiv.) was added dropwise over 20 min. After complete addition, the reaction mixture was stirred at –78 °C for 15 min, before it was warmed to room temp. (colour change to brown). After 1 h, water (4 mL, colour change to emerald green) and DDQ (2.7 g, 11.8 mmol, 6 equiv.) were added (colour change to red). Triethylamine (3 mL) was added after an additional 1 h of stirring, and the crude product was filtered through a layer of silica. After recrystallisation from CH_2Cl_2/MeOH, the product was obtained in 290 mg (0.516 mmol, 26%) yield as purple needles. M.p. 142 °C. R_f = 0.22 (CH_2Cl_2/C_6H_{14}, 1:2, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = –2.84 (br. s, 2 H, N*H*), 0.97 (t, $^3J_{H,H}$ = 7.3 Hz, 6 H, $C_5H_{10}CH_3$), 0.99 (t, $^3J_{H,H}$ = 7.6 Hz, 3 H, $C_5H_{10}CH_3$), 1.44 (m, 6 H, $C_4H_8CH_2CH_3$), 1.56 (m, 6 H, $C_3H_6CH_2CH_2CH_3$), 1.84 (m, 6 H, $C_2H_4CH_2C_2H_4CH_3$), 2.56 (m, 6 H, $CH_2CH_2C_3H_6CH_3$), 4.99 (t, $^3J_{H,H}$ = 8.2 Hz, 4 H, $CH_2C_4H_8CH_3$), 5.08 (t, $^3J_{H,H}$ = 8.2 Hz, 2 H, $CH_2C_4H_8CH_3$), 9.31 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 9.52 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 9.55 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 9.62 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$, 25 °C): δ = 13.9, 22.6, 30.1, 30.2, 31.7, 31.8, 34.9, 35.3, 36.1, 38.5, 38.7, 38.9, 102.8, 118.5, 119.8, 119.9, 120.2, 127.7, 128.1, 128.5, 131.1, 145.1 (br.), 146.6 (br.) ppm. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 412 (5.5), 512 (4.6), 545 (4.5), 591 (4.4), 647 (4.4) nm. HRMS (ES+): calcd. for $C_{38}H_{50}N_4$ [M + H]$^+$ 563.4114, found 563.4124.

5-Bromo-10,15,20-trihexylporphyrin (9): A 250-mL round-bottom flask was charged with 5,10,15-trihexylporphyrin (**8**, 222 mg, 0.39 mmol, 1 equiv.) in chloroform (100 mL). *N*-Bromosuccinimide (NBS, 83 mg, 0.468 mmol, 1.2 equiv.) and pyridine (0.2 mL) were added, and the reaction mixture was stirred at room temp. until completion (ca. 30 min, TLC control). The solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2. The crude product was filtered through a layer of silica gel and washed with CH_2Cl_2. After recrystallisation from CH_2Cl_2/MeOH, the product was obtained in 220 mg (0.34 mmol, 88%) yield as brown needles. M.p. 133 °C; R_f = 0.41 (CH_2Cl_2/C_6H_{14}, 1:2, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = –2.66 (br. s, 2 H, N*H*), 0.97 (t, $^3J_{H,H}$ = 7.3 Hz, 6 H, $C_5H_{10}CH_3$), 0.99 (t, $^3J_{H,H}$ = 7.6 Hz, 3 H, $C_5H_{10}CH_3$), 1.43 (m, 6 H, $C_4H_8CH_2CH_3$), 1.54 (m, 6 H, $C_3H_6CH_2CH_2CH_3$), 1.82 (m, 6 H, $C_2H_4CH_2C_2H_4CH_3$), 2.51 (m, 6 H, $CH_2CH_2C_3H_6CH_3$), 4.91 (m, 6 H, $CH_2C_4H_8CH_3$), 9.45 (d, $^3J_{H,H}$ = 5.2 Hz, 2 H, β-*H*), 9.46 (d, $^3J_{H,H}$ = 5.8 Hz, 2 H, β-*H*), 9.50 (d, $^3J_{H,H}$ = 5.2 Hz, 2 H, β-*H*), 9.67 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 14.2, 22.8, 30.2, 30.3, 31.9, 35.4, 35.8, 38.7, 38.8, 101.1, 119.9, 120.4, 128.7 (br.), 131.9 (br.) ppm. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 420 (6.3), 521 (5.2); 557 (5.2), 602 (5.1), 661 (5.1) nm. HRMS (ES+): calcd. for $C_{38}H_{49}BrN_4$ [M + H]$^+$ 641.3219, found 641.3227.

5-Allyl-10,15,20-trihexylporphyrin (10): A 50-mL Schlenk-tube was filled with Ar and charged with 5-bromo-10,15,20-trihexylporphyrin (**9**, 300 mg, 0.468 mmol, 1 equiv.) in dry THF (50 mL). K_3PO_4 (2.0 g, 9.36 mmol, 20 equiv.) was added, and the solution was degassed by three freeze-pump-thaw cycles and put under Ar again. Allylboronic acid pinacol ester (0.9 mL, 4.68 mmol, 10 equiv.) and $Pd(PPh_3)_4$ (54 mg, 0.0468 mmol, 0.1 equiv.) were added, and the reaction mixture was heated to 80 °C overnight. Then the solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2. The crude product was washed with a saturated solution of $NaHCO_3$, water and brine and dried with Na_2SO_4. Purification was carried out by dry-loaded column chromatography on silica gel (CH_2Cl_2/C_6H_{14}, 1:2, v/v). After recrystallisation from CH_2Cl_2/MeOH, the product was obtained in 170 mg (0.28 mmol, 60%) yield as purple crystals. M.p. 114 °C; R_f = 0.49 (CH_2Cl_2/C_6H_{14}, 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = –2.59 (br. s, 2 H, N*H*), 0.97 (t, $^3J_{H,H}$ = 7.3 Hz, 6 H, $C_5H_{10}CH_3$), 0.99 (t, $^3J_{H,H}$ = 7.6 Hz, 3 H, $C_5H_{10}CH_3$), 1.43 (m, 6 H, $C_4H_8CH_2CH_3$), 1.54 (m, 6 H, $C_3H_6CH_2CH_2CH_3$), 1.85 (m, 6 H, $C_2H_4CH_2C_2H_4$-CH_3), 2.54 (m, 6 H, $CH_2CH_2C_3H_6CH_3$), 4.95 (m, 6 H, $CH_2C_4H_8CH_3$), 5.18 (d, $^3J_{H,H}$ = 17.0 Hz, 1 H, CH_2CH=CH_2), 5.25 (d, $^3J_{H,H}$ = 9.9 Hz, 1 H, CH_2CH=CH_2), 5.74 (d, $^3J_{H,H}$ = 5.3 Hz, 2 H, CH_2CH=CH$_2$), 6.88 (m, 1 H, CH_2CH=CH$_2$), 9.48 (d, $^3J_{H,H}$ = 4.8 Hz, 4 H, β-*H*), 9.50 (d, $^3J_{H,H}$ = 5.2 Hz, 4 H, β-*H*) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 14.2, 22.8, 30.4, 31.9, 35.5, 35.6, 38.8, 39.0, 113.9, 115.9, 118.6, 118.9, 126.6 (br.), 128.2 (br.), 141.7 ppm. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 419 (5.6), 520 (4.6), 555 (4.5), 600 (4.5), 659 (4.5) nm. HRMS (ES+): calcd. for $C_{41}H_{54}N_4$ [M + H]$^+$ 603.4427, found 603.4423.

[5-Allyl-10,15,20-trihexylporphyrinato]nickel(II) (11): A 50-mL 2-necked round-bottom flask was charged with 5-allyl-10,15,20-trihexylporphyrin (**10**, 170 mg, 0.28 mmol, 1 equiv.) and $Ni(acac)_2$ (108 mg, 0.42 mmol, 1.5 equiv.) in toluene (50 mL). The reaction mixture was heated to reflux until completion (ca. 30 min, TLC control). The solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2. The crude product was filtered through a layer of silica gel and washed with CH_2Cl_2. The product was obtained in 132 mg (0.20 mmol, 71%) yield as a red low-melting solid. R_f = 0.67 (CH_2Cl_2/C_6H_{14}, 1:2, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.93 (t, $^3J_{H,H}$ = 7.3 Hz, 6 H, $C_5H_{10}CH_3$), 0.95 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, $C_5H_{10}CH_3$), 1.34 (m, 6 H, $C_4H_8CH_2CH_3$), 1.43 (m, 6 H, $C_3H_6CH_2CH_2CH_3$), 1.59 (m, 6 H, $C_2H_4CH_2C_2H_4CH_3$), 2.26 (m, 6 H, $CH_2CH_2C_3H_6CH_3$), 4.48 (m, 6 H, $CH_2C_4H_8CH_3$), 5.18 (d, $^3J_{H,H}$ = 5.9 Hz, 2 H, CH_2CH=CH$_2$), 5.23 (d, $^3J_{H,H}$ = 10.0 Hz, 1 H, CH_2CH=CH_2), 5.31 (d, $^3J_{H,H}$ = 17.5 Hz, 1 H, CH_2CH=CH_2), 6.71 (m, 1 H, CH_2CH=CH$_2$), 9.25 (d, $^3J_{H,H}$ = 4.8 Hz, 4 H, β-*H*), 9.26 (d, $^3J_{H,H}$ = 5.2 Hz, 4 H, β-*H*) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 14.2, 22.7, 30.1, 31.8, 33.9, 37.3, 37.9, 112.6, 115.6, 117.1, 117.3, 129.7, 129.8, 129.9, 141.0, 141.1, 141.2 ppm. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 420 (5.4), 539 (4.5), 570 (4.3) nm. HRMS (ES+): calcd. for $C_{41}H_{52}N_4Ni$ [M + H]$^+$ 659.3624, found 659.3593.

5,10,15-Tris(4-methylphenyl)-20-[(trimethylsilyl)ethynyl]porphyrin (12): A 100-mL Schlenk-tube was filled with Ar and charged with

5-bromo-10,15,20-tris(4-methylphenyl)porphyrin (200 mg, 0.30 mmol; 1 equiv.) in dry THF/triethylamine (60 mL, 1:3, v/v). The solution was degassed by five freeze-pump-thaw cycles and put under Ar again. Ethynyltrimethylsilane (0.4 mL, 3.0 mmol, 10 equiv.), copper(I) iodide (14 mg, 0.075 mmol, 0.25 equiv.) and $Pd(PPh_3)_2Cl_2$ (25 mg, 0.036 mmol, 0.12 equiv.) were added, and the reaction mixture was stirred at room temp. overnight. Then CH_2Cl_2 (60 mL) was added, and the solution was washed with water and dried with Na_2SO_4. After purification by dry-loaded column chromatography on silica gel (CH_2Cl_2/C_6H_{14}, 1:2, v/v), the product was obtained in 146 mg (0.216 mmol, 72%) yield as purple crystals. M.p. > 300 °C. R_f = 0.41 (CH_2Cl_2/C_6H_{14}, 1:2, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = –2.40 (br. s, 2 H, N*H*), 0.63 (s, 9 H, SiCH_3), 2.72 (s, 3 H, $C_6H_4CH_3$), 2.74 (s, 6 H, $C_6H_4CH_3$), 7.56 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, H_{Ar}), 7.59 (d, $^3J_{H,H}$ = 8.2 Hz, 4 H, H_{Ar}), 8.07 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, H_{Ar}), 8.10 (d, $^3J_{H,H}$ = 8.2 Hz, 4 H, H_{Ar}), 8.80 (s, 4 H, β-*H*), 8.93 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 9.66 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 0.4, 21.6, 29.7, 98.7, 101.7, 107.2, 121.1, 121.2, 127.4, 127.5, 130.6 (br.), 131.9 (br.), 134.4, 134.5, 137.5 ppm. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 429 (5.7), 529 (4.6), 568 (4.6), 604 (4.4), 657 (4.5) nm. HRMS (ES+): calcd. for $C_{46}H_{40}N_4Si$ [M + H]$^+$ 677.3101, found 677.3095.

{5,10,15-Tris(4-methylphenyl)-20-[(trimethylsilyl)ethynyl]-porphyrinato}nickel(II) (13): A 50-mL 2-necked round-bottomed flask was charged with 5,10,15-tris(4-methylphenyl)-20-[(trimethylsilyl)ethynyl]porphyrin (**12**, 100 mg, 0.148 mmol; 1 eqiv.) and Ni(acac)$_2$ (57 mg, 0.222 mmol, 1.5 equiv.) in toluene (30 mL). The reaction mixture was heated to reflux until completion (ca. 30 min, TLC control). The solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2. The crude product was filtered through a layer of silica gel and washed with CH_2Cl_2. After the solvent was removed under reduced pressure, the product was obtained in a quantitative yield (107 mg, 0.146 mmol, 99%) as purple crystals. M.p. > 300 °C. R_f = 0.86 (CH_2Cl_2/C_6H_{14}, 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.56 (s, 9 H, SiCH_3), 2.65 (s, 3 H, $C_6H_4CH_3$), 2.68 (s, 6 H, $C_6H_4CH_3$), 7.49 (d, $^3J_{H,H}$ = 8.0 Hz, 4 H, H_{Ar}), 7.51 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, H_{Ar}), 7.88 (d, $^3J_{H,H}$ = 4.8 Hz, 4 H, H_{Ar}), 7.90 (d, $^3J_{H,H}$ = 5.2 Hz, 2 H, H_{Ar}), 8.69 (d, $^3J_{H,H}$ = 5.3 Hz, 2 H, β-*H*), 8.71 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 8.83 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 9.51 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 1.1, 29.7, 102.2, 119.5, 119.6, 126.9, 127.1, 127.8, 127.9, 132.5, 132.6, 133.2, 133.4, 133.5, 133.6, 133.7, 140.4, 140.5, 142.4, 142.8, 143.0, 143.1 ppm. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 417 (5.2), 533 (4.5) nm.

[5-Ethynyl-10,15,20-tris(4-methylphenyl)porphyrinato]nickel(II) (14): A 100-mL round-bottom flask was charged with {10,15,20-tris(4-methylphenyl)-5-[(trimethylsilyl)ethynyl]porphyrinato}-nickel(II) **13** (108 mg, 0.146 mmol, 1 equiv.) and tetrabutylammonium fluoride (61 mg, 0.234 mmol, 1.6 equiv.) in CH_2Cl_2 (50 mL). The reaction mixture was stirred at room temp. until completion (ca. 30 min, TLC control). The crude product was filtered through a short layer of silica and washed with CH_2Cl_2. After the solvent was removed under reduced pressure, the product was obtained in a quantitative yield (97 mg, 0.146 mmol, 100%) as dark red crystals. M.p. > 300 °C. R_f = 0.63 (CH_2Cl_2/C_6H_{14}, 1:2, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.66 (s, 3 H, $C_6H_4CH_3$), 2.68 (s, 6 H, $C_6H_4CH_3$), 4.08 (s, 1 H, C≡C*H*), 7.49 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, H_{Ar}), 7.52 (d, $^3J_{H,H}$ = 8.2 Hz, 4 H, H_{Ar}), 7.88 (d, $^3J_{H,H}$ = 6.5 Hz, 2 H, H_{Ar}), 7.90 (d, $^3J_{H,H}$ = 7.6 Hz, 4 H, H_{Ar}), 8.71 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 8.73 (d, $^3J_{H,H}$ = 5.3 Hz, 2 H, β-*H*), 8.85 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 9.54 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 21.5, 29.8, 84.1, 84.2, 96.9, 119.8, 120.8, 127.6, 127.7, 131.4, 132.1, 132.5, 133.3, 133.5, 133.6, 137.5, 137.6, 137.7, 142.5, 142.6, 143.4, 145.1 ppm. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 423 (5.5), 537 (4.7), 571 (4.6) nm. HRMS (ES+): calcd. for $C_{43}H_{30}N_4Ni$ [M + H]$^+$ 661.1902, found 661.1870.

10,15,20-Trihexyl-5-[(trimethylsilyl)ethynyl]porphyrin (16): A 50-mL Schlenk-tube was filled with Ar and charged with 5-bromo-10,15,20-trihexylporphyrin (**9**, 100 mg, 0.156 mmol, 1 equiv.) in dry THF/triethylamine (40 mL, 3:1, v/v). The solution was degassed by five freeze-pump-thaw cycles and put under Ar again. Ethynyltrimethylsilane (0.2 mL, 1.56 mmol, 10 equiv.), copper(I) iodide (8 mg, 0.039 mmol, 0.25 equiv.) and $Pd(PPh_3)_2Cl_2$ (13 mg, 0.019 mmol, 0.12 equiv.) were added, and the reaction mixture was stirred at room temp. overnight. Then CH_2Cl_2 (30 mL) was added, and the solution was washed with water and dried with Na_2SO_4. The product was obtained as purple crystals in 69 mg (0.10 mmol, 67%) yield. M.p. 119 °C. R_f = 0.71 (CH_2Cl_2/C_6H_{14}, 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = –2.40 (br. s, 2 H, N*H*), 0.68 (s, 9 H, SiCH_3), 0.97 (t, $^3J_{H,H}$ = 7.3 Hz, 6 H, $C_5H_{10}CH_3$), 0.99 (t, $^3J_{H,H}$ = 7.6 Hz, 3 H, $C_5H_{10}CH_3$), 1.43 (m, 6 H, $C_4H_8CH_2CH_3$), 1.53 (m, 6 H, $C_3H_6CH_2CH_2CH_3$), 1.79 (m, 6 H, $C_2H_4CH_2C_2H_4CH_3$), 2.47 (m, 6 H, $CH_2CH_2C_3H_6CH_3$), 4.81 (t, $^3J_{H,H}$ = 8.1 Hz, 4 H, $CH_2C_4H_8CH_3$), 4.86 (t, $^3J_{H,H}$ = 8.1 Hz, 2 H, $CH_2C_4H_8CH_3$), 9.33 (d, $^3J_{H,H}$ = 5.1 Hz, 2 H, β-*H*), 9.38 (d, $^3J_{H,H}$ = 4.2 Hz, 2 H, β-*H*), 9.40 (d, $^3J_{H,H}$ = 4.2 Hz, 2 H, β-*H*), 9.65 (d, $^3J_{H,H}$ = 4.8 Hz, 2 H, β-*H*) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 0.5, 14.2, 22.8, 30.3, 30.4, 31.9, 36.3, 37.0, 38.6, 38.9, 96.8, 100.7, 107.6, 120.3, 121.8, 128.6 (br.), 130.7 (br.) ppm. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 428 (5.8), 532 (4.7), 571 (4.8), 611 (4.6), 669 (4.7) nm. HRMS (ES+): calcd. for $C_{43}H_{58}N_4Si$ [M + H]$^+$ 659.4509, found 659.4494.

{10,15,20-Trihexyl-5-[(trimethylsilyl)ethynyl]porphyrinato}nickel(II) (17): A 50-mL 2-necked round-bottom flask was charged with 10,15,20-trihexyl-5-[(trimethylsilyl)ethynyl]porphyrin (**16**, 44 mg, 0.066 mmol, 1 equiv.) and Ni(acac)$_2$ (25 mg, 0.1 mmol, 1.5 equiv.) in toluene (20 mL). The reaction mixture was heated to reflux until completion (ca. 2 h, TLC control). The solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2. The crude product was filtered through a layer of silica gel and washed with CH_2Cl_2. After the solvent was removed under reduced pressure, the product was obtained in 46 mg (0.064 mmol, 98%) yield of a red low-melting solid. R_f = 0.95 (CH_2Cl_2/C_6H_{14}, 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.59 (s, 9 H, SiCH_3), 0.92 (t, $^3J_{H,H}$ = 7.2 Hz, 6 H, $C_5H_{10}CH_3$), 0.94 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, $C_5H_{10}CH_3$), 1.34 (m, 6 H, $C_4H_8CH_2CH_3$), 1.43 (m, 6 H, $C_3H_6CH_2CH_2CH_3$), 1.60 (m, 6 H, $C_2H_4CH_2C_2H_4CH_3$), 2.26 (m, 6 H, $CH_2CH_2C_3H_6CH_3$), 4.42 (m, 6 H, $CH_2C_4H_8CH_3$), 9.18 (d, $^3J_{H,H}$ = 5.0 Hz, 2 H, β-*H*), 9.20 (d, $^3J_{H,H}$ = 2.1 Hz, 2 H, β-*H*), 9.22 (d, $^3J_{H,H}$ = 2.0 Hz, 2 H, β-*H*), 9.42 (d, $^3J_{H,H}$ = 5.0 Hz, 2 H, β-*H*) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 0.4, 14.2, 22.7, 29.8, 30.1, 30.2, 31.8, 34.0, 34.2, 37.4, 37.5, 96.4, 101.2, 105.5, 118.4, 119.6, 129.3, 129.8, 130.2, 131.7, 140.9, 141.4, 142.2, 143.9 ppm. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 428 (5.3), 548 (4.4), 585 (4.3) nm. HRMS (ES+): calcd. for $C_{43}H_{56}N_4NiSi$ [M + H]$^+$ 715.3706, found 715.3718.

(5-Ethynyl-10,15,20-trihexylporphyrinato)nickel(II) (18): A 50-mL round-bottomed flask was charged with {10,15,20-trihexyl-5-[(trimethylsilyl)ethynyl]porphyrinato}nickel(II) (**17**, 46 mg, 0.064 mmol, 1 equiv.) and tetrabutylammonium fluoride (25 mg, 0.1 mmol, 1.6 equiv.) in CH_2Cl_2 (20 mL). The reaction mixture was stirred at room temp. until completion (ca. 30 min, TLC control). The crude product was filtered through a short layer of silica gel and washed with CH_2Cl_2. After the solvent was removed under

reduced pressure, the product was obtained in 41 mg (0.06 mmol, 99%) yield of a red low-melting solid. R_f = 0.89 (CH_2Cl_2/C_6H_{14}, 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.94 (t, $^3J_{H,H}$ = 7.2 Hz, 6 H, $C_5H_{10}CH_3$), 0.96 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, $C_5H_{10}CH_3$), 1.37 (m, 6 H, $C_4H_8CH_2CH_3$), 1.43 (m, 6 H, $C_3H_6CH_2CH_2CH_3$), 1.59 (m, 6 H, $C_2H_4CH_2C_2H_4CH_3$), 2.25 (m, 6 H, $CH_2CH_2C_3H_6CH_3$), 4.04 (s, 1 H, C≡C*H*), 4.32 (t, $^3J_{H,H}$ = 8.1 Hz, 2 H, $CH_2C_4H_8CH_3$), 4.37 (t, $^3J_{H,H}$ = 8.0 Hz, 4 H, $CH_2C_4H_8CH_3$), 9.12 (d, $^3J_{H,H}$ = 5.0 Hz, 2 H, β-pyrrole-*H*), 9.14 (d, $^3J_{H,H}$ = 5.0 Hz, 2 H, β-*H*), 9.19 (d, $^3J_{H,H}$ = 4.8 Hz, 2 H, β-*H*), 9.42 (d, $^3J_{H,H}$ = 4.8 Hz, 2 H, β-*H*) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 14.2, 22.7, 29.8, 30.0, 30.1, 31.8, 33.9, 34.2, 37.4, 37.6, 83.6, 84.2, 94.9, 118.4, 119.7, 129.3, 129.8, 130.3, 131.4, 140.8, 141.4, 142.2, 143.9 ppm. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 425 (5.6), 545 (4.6), 581 (4.5) nm. HRMS (ES+): calcd. for $C_{40}H_{48}N_4Ni$ $[M + H]^+$ 643.3311, found 643.3282.

5-(4-Ethynylphenyl)-10,20-bis(4-methylphenyl)porphyrin (19): A 250-mL 3-necked round-bottom flask was filled with Ar and charged with *p*-bromobenzene (1.113 g, 6.15 mmol, 15 equiv.) in dry diethyl ether (3 mL). *n*-Butyllithium (4.9 mL, 12.3 mmol, 30 equiv.) was added dropwise at –78 °C over 1 h. After the addition was complete, the reaction mixture was warmed to –45 °C (by addition of cooling solvent to the cooling bath), and dry THF (2 mL) was added until a white solid was formed. 5,15-Bis(4-methylphenyl)porphyrin (**1**, 200 mg, 0.41 mmol, 1 equiv.) dissolved in dry THF (150 mL) was added quickly, and the reaction mixture was stirred at room temp. overnight (colour change to brown). Then water (2 mL, colour change to emerald green) and DDQ (1.4 g, 6.15 mmol, 15 equiv.) were added (colour change to red). After 1 h, the crude product was filtered through a layer of silica gel and recrystallised from CH_2Cl_2/MeOH. The product was obtained in 95 mg (0.16 mmol, 39%) yield as purple crystals. M.p. > 300 °C. R_f = 0.24 (CH_2Cl_2/C_6H_{14}, 1:4, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = –2.99 (br. s, 2 H, N*H*), 2.75 (s, 6 H, $C_6H_4CH_3$), 3.35 (s, 1 H, C≡C*H*), 7.01 (d, $^3J_{H,H}$ = 7.6 Hz, 4 H, H_{Ar}), 7.91 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, H_{Ar}), 8.15 (d, $^3J_{H,H}$ = 7.6 Hz, 4 H, H_{Ar}), 8.21 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H, H_{Ar}), 8.86 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 8.97 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 9.08 (d, $^3J_{H,H}$ = 4.1 Hz, 2 H, β-*H*), 9.37 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 10.25 (s, 1 H, *meso*-*H*) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.1, 77.8, 83.3, 104.5, 118.8, 119.4, 121.1, 127.2, 129.9, 130.5, 133.9, 134.2, 137.0, 138.3, 142.9, 145.3 (br.), 146.7 (br.) ppm. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 414 (5.7), 509 (4.6), 543 (4.4), 582 (4.4), 639 (4.4) nm. HRMS (ES+): calcd. for $C_{42}H_{30}N_4$ $[M + H]^+$ 591.2549, found 591.2524.

[5-(4-Ethynylphenyl)-10,20-bis(4-methylphenyl)porphyrinato]nickel-(II) (20): A 100-mL 2-necked round-bottom flask was charged with 5-(4-ethynylphenyl)-10,20-bis(4-methylphenyl)porphyrin (**19**, 176 mg, 0.3 mmol, 1 equiv.) and $Ni(acac)_2$ (116 mg, 0.45 mmol, 1.5 equiv.) in toluene (50 mL). The reaction mixture was heated to reflux until completion (ca. 4 h, TLC control). The solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2 and filtered through a layer of silica gel. After recrystallisation from CH_2Cl_2/MeOH, the product was obtained as red needles in 166 mg (0.257 mmol, 86%) yield. M.p. > 300 °C. R_f = 0.77 (CH_2Cl_2/C_6H_{14}, 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.69 (s, 6 H, $C_6H_4CH_3$), 3.30 (s, 1 H, C≡C*H*), 7.53 (d, $^3J_{H,H}$ = 7.6 Hz, 4 H, H_{Ar}), 7.84 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, H_{Ar}), 7.94 (d, $^3J_{H,H}$ = 7.6 Hz, 4 H, H_{Ar}), 8.01 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H, H_{Ar}), 8.76 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 8.84 (d, $^3J_{H,H}$ = 5.3 Hz, 2 H, β-*H*), 8.95 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 9.16 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 9.86 (s, 1 H, *meso*-*H*) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 21.5, 78.2, 83.6, 104.7, 118.2, 118.9, 121.6, 127.6, 130.6, 131.6, 132.2, 132.3, 132.7, 133.6, 133.7, 137.9, 141.8, 141.9, 142.8, 142.9, 143.0 ppm. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 409 (5.4), 523 (4.6), 550 (4.4) nm. HRMS (ES+): calcd. for $C_{42}H_{28}N_4Ni$ $[M + H]^+$ 647.1746, found 647.1755.

[5-(4-Ethynylphenyl)-10,20-bis(4-methylphenyl)porphyrinato]zinc(II) (21): A 100-mL round-bottomed flask was charged with 5-(4-ethynylphenyl)-10,20-bis(4-methylphenyl)porphyrin (**19**, 76 mg, 0.03 mmol, 1 equiv.) in CH_2Cl_2 (50 mL). $Zn(OAc)_2$ (10 mg, 0.045 mmol, 1.5 equiv.) dissolved in MeOH (5 mL) was added, and the reaction mixture was stirred at room temp. until completion (ca. 1 h, TLC control). The crude product was filtered through a layer of silica gel. After the solvent was removed under reduced pressure, the product was obtained quantitatively (84 mg, 0.03 mmol, 99%) as pink crystals. M.p. > 300 °C. R_f = 0.46 (CH_2Cl_2/C_6H_{14}, 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.76 (s, 6 H, $C_6H_4CH_3$), 3.34 (s, 1 H, C≡C*H*), 7.61 (d, $^3J_{H,H}$ = 7.6 Hz, 4 H, H_{Ar}), 7.92 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H, H_{Ar}), 8.14 (d, $^3J_{H,H}$ = 8.2 Hz, 4 H, H_{Ar}), 8.21 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, H_{Ar}), 8.97 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 9.06 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 9.13 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 9.38 (d, $^3J_{H,H}$ = 4.1 Hz, 2 H, β-*H*), 10.23 (s, 1 H, *meso*-*H*) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 21.6, 83.8, 105.9, 120.2, 120.8, 121.3, 127.4, 130.3, 131.5, 131.7, 132.1, 132.7, 134.4, 134.5, 137.2, 139.6, 143.7, 149.3, 149.7, 150.3 ppm. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 415 (5.7), 542 (4.8) nm. HRMS (ES+): calcd. for $C_{42}H_{30}N_4$ $[M]^+$ 652.1605, found 652.1588.

Pauson–Khand Reaction of Allylporphyrins

General Procedure: Phenylacetylene (10 equiv.) was placed into a round-bottom flask under Ar in dry THF (20 mL). $Co_2(CO)_8$ (10 equiv.) was added, and the reaction mixture was stirred at room temp. until formation of the complex (ca. 1 h, monitored by TLC). Then the allylporphyrin (**6**, **7**, **11**) (40–45.5 mg; 1 equiv.) was added, and the reaction mixture was heated at reflux for 12 h. The crude products were purified by dry-loaded column chromatography on silica gel (CH_2Cl_2/C_6H_{14}, 1:1, v/v). The first fraction of the column was assumed to be the remaining (phenylacetylene)(porphyrin)Co complex. Recrystallisation was carried out from CH_2Cl_2/MeOH.

[5-Formyl-10,15,20-tris(4-methylphenyl)porphyrinato]nickel(II) (5): The product was obtained from the Pauson–Khand reaction of [5,10,15-tris(4-methylphenyl)-20-vinylporphyrinato]nickel(II) (**20**, 55 mg, 0.08 mmol, 1 equiv.) and phenylacetylene in 6 mg (9 μmol, 11%) yield as bright green crystals. M.p. 81 °C. R_f = 0.66 (CH_2Cl_2/C_6H_{14}, 1:2, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.65 (s, 3 H, $C_6H_4CH_3$), 2.67 (s, 6 H, $C_6H_4CH_3$), 7.50 (t, $^3J_{H,H}$ = 8.0 Hz, 6 H, H_{Ar}), 7.85 (d, $^3J_{H,H}$ = 8.0 Hz, 6 H, H_{Ar}), 8.60 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 8.68 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 8.88 (d, $^3J_{H,H}$ = 5.2 Hz, 2 H, β-*H*), 9.80 (d, $^3J_{H,H}$ = 5.2 Hz, 2 H, β-*H*), 12.0 (s, 1 H, C*H*O) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 21.0, 120.6, 127.3, 130.1, 131.4, 132.9, 135.0, 136.5, 137.3, 140.5, 141.5, 143.9, 192.3 ppm. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 426 (4.8), 552 (3.8), 593 (3.9) nm.

{5,10,15-Tris(4-methylphenyl)-20-[(2-oxo-3-phenylcyclopent-3-en-1-yl)methyl]porphyrinato}nickel(II) (22): By using [5-allyl-10,15,20-tris(4-methylphenyl)porphyrinato]nickel(II) (**6**, 40 mg, 0.059 mmol, 1 equiv.) as starting material, the reaction was carried out in a Schlenk-tube, and the solution was degassed by three freeze-pump-thaw cycles and refilled with Ar. The product was obtained as the second fraction by column chromatography followed by recrystallisation as red crystals in 18.8 mg (0.023 mmol, 39%) yield. M.p. 146 °C. R_f = 0.21 (CH_2Cl_2/C_6H_{14}, 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.97 (m, 1 H, C=CHCH_2CHCH$_2$), 2.25 (m, 1 H, C=CHCH_2CHCH$_2$), 2.66 (s, 3 H, $C_6H_4CH_3$), 2.67 (s, 6 H, $C_6H_4CH_3$), 3.24 (m, 1 H, C=CHCH$_2$C*H*CH$_2$), 4.55 (dd, $^3J_{H,H}$ =

14.0, $^2J_{H,H}$ = 11.1 Hz, 1 H, C=CHCH$_2$CHCH_2), 5.69 (dd, $^3J_{H,H}$ = 14.6, $^2J_{H,H}$ = 4.1 Hz, 1 H, C=CHCH$_2$CHCH_2), 7.39 (d, $^3J_{H,H}$ = 5.9 Hz, 1 H, H_{Ar}), 7.43 (m, 2 H, H_{Ar}), 7.49 (d, $^3J_{H,H}$ = 7.0 Hz, 4 H, H_{Ar}), 7.49 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H, H_{Ar}), 7.55 (dd, $^3J_{H,H}$ = 2.9, $^3J_{H,H}$ = 1.8 Hz, 1 H, C=C*H*CH$_2$CHCH$_2$), 7.73 (d, $^3J_{H,H}$ = 6.4 Hz, 2 H, H_{Ar}), 7.88 (d, $^3J_{H,H}$ = 3.5 Hz, 4 H, H_{Ar}), 7.89 (d, $^3J_{H,H}$ = 3.5 Hz, 2 H, H_{Ar}), 8.74 (d, $^3J_{H,H}$ = 4.1 Hz, 2 H, β-*H*), 8.74 (d, $^3J_{H,H}$ = 4.6 Hz, 2 H, β-*H*), 8.88 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 9.44 (d, $^3J_{H,H}$ = 5.3 Hz, 2 H, β-*H*) ppm. ^{13}C NMR (150.9 MHz, CDCl$_3$, 25 °C): δ = 14.1, 21.5, 22.7, 29.4, 29.7, 31.9, 32.8, 35.0, 52.3, 114.5, 118.6, 127.0, 127.6, 128.4, 129.7, 131.6, 132.3, 133.1, 133.6, 137.4, 142.2, 142.4, 142.8, 157.3, 207.8 ppm. UV/Vis (CH$_2$Cl$_2$): λ_{max} (lg ε) = 419 (5.4), 523 (4.7) nm. HRMS (ES+): calcd. for $C_{53}H_{40}N_4NiO$ [M + H]$^+$ 807.2634, found 807.2648.

{5,10,15-Tris(4-methylphenyl)-20-[(4-oxo-3-phenylcyclopent-2-en-1-yl)methyl]porphyrinato}nickel(II) (23): The product was obtained as the third fraction by column chromatography of the reaction above. Recrystallisation gave 15.7 mg (0.019 mmol, 33%) yield of red crystals. M.p. 182 °C. R_f = 0.16 (CH$_2$Cl$_2$/C$_6$H$_{14}$, 1:1, v/v). ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 2.63 (m, 1 H, COCH_2CH), 2.66 (s, 3 H, C$_6$H$_4$CH_3), 2.68 (s, 6 H, C$_6$H$_4$CH_3), 2.77 (dd, $^3J_{H,H}$ = 18.7, $^2J_{H,H}$ = 6.4 Hz, 1 H, COCH_2CH), 3.70 (m, 1 H, COCH$_2$C*H*), 4.80 (dd, $^3J_{H,H}$ = 14.0, $^2J_{H,H}$ = 9.4 Hz, 1 H, COCH$_2$CHCH_2), 5.10 (dd, $^3J_{H,H}$ = 14.0, $^2J_{H,H}$ = 7.0 Hz, 1 H, COCH$_2$CHCH_2), 7.28 (m, 5 H, H_{Ar}), 7.49 (s, 1 H, C*H*=CCO), 7.50 (d, $^3J_{H,H}$ = 4.7 Hz, 4 H, H_{Ar}), 7.51 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H, H_{Ar}), 7.89 (d, $^3J_{H,H}$ = 5.3 Hz, 4 H, H_{Ar}), 7.91 (d, $^3J_{H,H}$ = 7.0 Hz, 2 H, H_{Ar}), 8.76 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 8.76 (d, $^3J_{H,H}$ = 5.3 Hz, 2 H, β-*H*), 8.88 (d, $^3J_{H,H}$ = 5.3 Hz, 2 H, β-*H*), 9.28 (d, $^3J_{H,H}$ = 5.3 Hz, 2 H, β-*H*) ppm. ^{13}C NMR (150.9 MHz, CDCl$_3$, 25 °C): δ = 13.9, 21.3, 22.5, 29.5, 30.8, 31.8, 43.1, 43.5, 113.3, 118.6, 118.7, 127.0, 127.5, 128.2, 128.3, 129.0, 131.0, 132.2, 132.22, 132.9, 133.4, 133.5, 137.3, 137.6, 137.63, 142.0, 142.2, 142.4, 142.5, 142.8, 160.9, 206.1 ppm. UV/Vis (CH$_2$Cl$_2$): λ_{max} (lg ε) = 419 (5.6), 531 (4.6) nm. HRMS (ES+): calcd. for $C_{53}H_{40}N_4NiO$ [M + H]$^+$ 807.2634, found 807.2663.

{5,10,15-Tris(4-methylphenyl)-20-[(2-oxo-3-phenylcyclopent-3-en-1-yl)methyl]porphyrinato}zinc(II) (24): By using [5-allyl-10,15,20-bis(4-methylphenyl)porphyrinato]zinc(II) (**7**, 40 mg, 0.059 mmol, 1 equiv.) as starting material, the product was obtained as the second fraction by column chromatography followed by recrystallisation as purple crystals in 3.8 mg (4 μmol, 8%) yield. M.p. > 300 °C. R_f = 0.19 (CH$_2$Cl$_2$/C$_6$H$_{14}$, 1:1, v/v). ^{1}H NMR (600 MHz, CDCl$_3$, 25 °C): δ = 2.31 (m, 1 H, C=CHCH_2CHCH$_2$), 2.73 (s, 3 H, C$_6$H$_4$CH_3), 2.76 (s, 6 H, C$_6$H$_4$CH_3), 2.95 (m, 1 H, C=CHCH_2CHCH$_2$), 3.83 (m, 1 H, C=CHCH$_2$C*H*CH$_2$), 4.94 (dd, $^3J_{H,H}$ = 14.7, $^2J_{H,H}$ = 11.0 Hz, 1 H, C=CHCH$_2$CHCH_2), 5.98 (dd, $^3J_{H,H}$ = 14.7, $^2J_{H,H}$ = 4.4 Hz, 1 H, C=CHCH$_2$CHCH_2), 7.41 (t, $^3J_{H,H}$ = 7.3 Hz, 1 H, H_{Ar}), 7.48 (dd, $^3J_{H,H}$ = 7.3, $^3J_{H,H}$ = 7.3 Hz, 2 H, H_{Ar}), 7.58 (d, $^3J_{H,H}$ = 7.3 Hz, 2 H, H_{Ar}), 7.58 (d, $^3J_{H,H}$ = 5.9 Hz, 2 H, H_{Ar}), 7.60 (d, $^3J_{H,H}$ = 5.1 Hz, 2 H, H_{Ar}), 7.75 (dd, $^3J_{H,H}$ = 2.8, $^3J_{H,H}$ = 2.4 Hz, 1 H, C=C*H*CH$_2$CHCH$_2$), 7.86 (d, $^3J_{H,H}$ = 7.4 Hz, 2 H, H_{Ar}), 8.10 (d, $^3J_{H,H}$ = 7.3 Hz, 2 H, H_{Ar}), 8.11 (d, $^3J_{H,H}$ = 5.9 Hz, 2 H, H_{Ar}), 8.13 (d, $^3J_{H,H}$ = 7.3 Hz, 2 H, H_{Ar}), 8.95 (d, $^3J_{H,H}$ = 5.2 Hz, 2 H, β-*H*), 8.95 (d, $^3J_{H,H}$ = 5.2 Hz, 2 H, β-*H*), 8.88 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 9.69 (d, $^3J_{H,H}$ = 4.4 Hz, 2 H, β-*H*) ppm. ^{13}C NMR (150.9 MHz, CDCl$_3$, 25 °C): δ = 13.9, 21.4, 22.5, 29.2, 29.5, 30.7, 33.0, 36.3, 54.6, 117.3, 120.7, 127.0, 127.1, 128.4, 128.8, 131.6, 131.8, 131.9, 132.6, 134.2, 136.9, 139.7, 142.2, 149.8, 149.9, 150.1, 150.4, 157.1, 207.9 ppm. UV/Vis (CH$_2$Cl$_2$): λ_{max} (lg ε) = 422 (5.9), 551 (4.8), 589 (4.6) nm. HRMS (ES+): calcd. for $C_{53}H_{40}N_4OZn$ [M + H]$^+$ 813.2572, found 813.2590.

{5,10,15-Tris(4-methylphenyl)-20-[(4-oxo-3-phenylcyclopent-2-en-1-yl)methyl]porphyrinato}zinc(II) (25): The product was obtained as the third fraction of the reaction above by column chromatography followed by recrystallisation as purple crystals in 7.3 mg (9 μmol, 15%) yield. M.p. > 300 °C. R_f = 0.12 (CH$_2$Cl$_2$/C$_6$H$_{14}$, 1:1, v/v). ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 2.74 (s, 3 H, C$_6$H$_4$CH_3), 2.75 (s, 6 H, C$_6$H$_4$CH_3), 2.88 (m, 2 H, COCH_2CH), 4.14 (m, 1 H, COCH$_2$C*H*), 5.07 (dd, $^3J_{H,H}$ = 14.7, $^2J_{H,H}$ = 9.8 Hz, 1 H, COCH$_2$CHCH_2), 5.35 (dd, $^3J_{H,H}$ = 14.7, $^2J_{H,H}$ = 6.9 Hz, 1 H, COCH$_2$CHCH_2), 7.29 (s, 2 H, H_{Ar}), 7.50 (m, 3 H, H_{Ar}), 7.56 (s, 1 H, C*H*=CCO), 7.59 (d, $^3J_{H,H}$ = 3.9 Hz, 4 H, H_{Ar}), 7.60 (d, $^3J_{H,H}$ = 1.9 Hz, 4 H, H_{Ar}), 8.10 (d, $^3J_{H,H}$ = 7.9 Hz, 4 H, H_{Ar}), 8.13 (d, $^3J_{H,H}$ = 2.9 Hz, 2 H, H_{Ar}), 8.96 (d, $^3J_{H,H}$ = 3.9 Hz, 2 H, β-*H*), 8.96 (d, $^3J_{H,H}$ = 3.9 Hz, 2 H, β-*H*), 9.04 (d, $^3J_{H,H}$ = 3.9 Hz, 2 H, β-*H*), 9.44 (d, $^3J_{H,H}$ = 4.9 Hz, 2 H, β-*H*) ppm. ^{13}C NMR (150.9 MHz, CDCl$_3$, 25 °C): δ = 13.9, 21.4, 22.5, 29.2, 29.5, 31.8, 40.5, 43.3, 45.4, 53.2, 115.9, 120.9, 121.1, 127.1, 127.2, 128.2, 128.3, 128.4, 131.2, 131.9, 132.0, 132.6, 134.2, 134.3, 136.9, 137.0, 139.6, 139.7, 142.2, 149.8, 150.2, 150.5, 161.6, 206.5 ppm. UV/Vis (CH$_2$Cl$_2$): λ_{max} (lg ε) = 422 (5.6), 552 (4.5), 588 (4.4) nm. HRMS (ES+): calcd. for $C_{53}H_{40}N_4OZn$ [M + H]$^+$ 813.2572, found 813.2585.

{5,10,15-Trihexyl-20-[(2-oxo-3-phenylcyclopent-3-en-1-yl)-methyl]porphyrinato}nickel(II) (26): By using [5-allyl-10,15,20-trihexylporphyrinato]nickel(II) (**11**, 45.5 mg, 0.069 mmol, 1 equiv.) as starting material, the product was obtained as the second fraction by column chromatography followed by recrystallisation as red crystals in 7.4 mg (9 μmol, 14%) yield. M.p. 102 °C. R_f = 0.15 (CH$_2$Cl$_2$/C$_6$H$_{14}$, 1:1, v/v). ^{1}H NMR (600 MHz, CDCl$_3$, 25 °C): δ = 0.92 (t, $^3J_{H,H}$ = 7.2 Hz, 6 H, C$_5$H$_{10}$CH_3), 0.92 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, C$_5$H$_{10}$CH_3), 1.35 (m, 6 H, C$_4$H$_8$CH_2CH$_3$), 1.43 (m, 6 H, C$_3$H$_6$CH_2CH$_2$CH$_3$), 1.58 (m, 6 H, C$_2$H$_4$CH_2C$_2$H$_4$CH$_3$), 1.89 (m, 1 H, C=CHCH_2CHCH$_2$), 2.12 (m, 1 H, C=CHCH_2CHCH$_2$), 2.26 (m, 6 H, CH$_2$CH_2C$_3$H$_6$CH$_3$), 3.12 (m, 1 H, C=CHCH$_2$C*H*CH$_2$), 4.42 (dd, $^3J_{H,H}$ = 14.3, $^2J_{H,H}$ = 11.3 Hz, 1 H, C=CHCH$_2$CHCH_2), 4.51 (m, 6 H, CH_2C$_4$H$_8$CH$_3$), 5.61 (dd, $^3J_{H,H}$ = 14.7, $^2J_{H,H}$ = 4.1 Hz, 1 H, C=CHCH$_2$CHCH_2), 7.37 (t, $^3J_{H,H}$ = 7.2 Hz, 1 H, H_{Ar}), 7.42 (dd, $^3J_{H,H}$ = 7.5, $^3J_{H,H}$ = 7.2 Hz, 2 H, H_{Ar}), 7.52 (m, 1 H, C=C*H*CH$_2$CHCH$_2$), 7.73 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, H_{Ar}), 9.28 (d, $^3J_{H,H}$ = 5.3 Hz, 2 H, β-*H*), 9.28 (d, $^3J_{H,H}$ = 6.4 Hz, 2 H, β-*H*), 9.30 (d, $^3J_{H,H}$ = 5.3 Hz, 2 H, β-*H*), 9.37 (d, $^3J_{H,H}$ = 4.9 Hz, 2 H, β-*H*) ppm. ^{13}C NMR (150.9 MHz, CDCl$_3$, 25 °C): δ = 13.9, 22.5, 29.9, 31.6, 32.6, 33.8, 34.6, 37.0, 37.1, 51.8, 112.6, 117.0, 117.2, 126.9, 128.3, 129.7, 129.8, 130.1, 131.5, 140.9, 141.0, 141.1, 142.1, 157.2, 207.7 ppm. UV/Vis (CH$_2$Cl$_2$): λ_{max} (lg ε) = 421 (5.3), 540 (4.5), 574 (4.3) nm. HRMS (ES+): calcd. for $C_{50}H_{58}N_4NiO$ [M + H]$^+$ 789.4042, found 789.4028.

{5,10,15-Trihexyl-20-[(4-oxo-3-phenylcyclopent-2-en-1-yl)methyl]-porphyrinato}nickel(II) (27): The product was obtained as the third fraction of the reaction above by column chromatography followed by recrystallisation as red crystals in 10.3 mg (0.013 mmol, 19%) yield. M.p. 136 °C. R_f = 0.23 (CH$_2$Cl$_2$/C$_6$H$_{14}$, 1:1, v/v). ^{1}H NMR (600 MHz, CDCl$_3$, 25 °C): δ = 0.92 (t, ^3J = 7.3 Hz, 6 H, C$_5$H$_{10}$CH_3), 0.92 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, C$_5$H$_{10}$CH_3), 1.35 (m, 6 H, C$_4$H$_8$CH_2CH$_3$), 1.44 (m, 6 H, C$_3$H$_6$CH_2CH$_2$CH$_3$), 1.59 (m, 6 H, C$_2$H$_4$CH_2C$_2$H$_4$CH$_3$), 2.28 (m, 6 H, CH$_2$CH_2C$_3$H$_6$CH$_3$), 2.60 (m, 1 H, COCH_2CH), 2.74 (m, 1 H, COCH_2CH), 3.59 (m, 1 H, COCH$_2$C*H*), 4.51 (m, 6 H, CH_2C$_4$H$_8$CH$_3$), 4.71 (dd, $^3J_{H,H}$ = 13.9, $^2J_{H,H}$ = 9.4 Hz, 1 H, COCH$_2$CHCH_2), 4.99 (dd, $^3J_{H,H}$ = 14.3, $^2J_{H,H}$ = 7.2 Hz, 1 H, COCH$_2$CHCH_2), 7.26 (s, 1 H, C*H*=CCO), 7.26 (d, $^3J_{H,H}$ = 1.9 Hz, 2 H, H_{Ar}), 7.27 (d, $^3J_{H,H}$ = 1.5 Hz, 1 H, H_{Ar}), 7.51 (m, 2 H, H_{Ar}), 9.23 (d, $^3J_{H,H}$ = 5.3 Hz, 2 H, β-*H*), 9.29 (d, $^3J_{H,H}$ = 4.9 Hz, 2 H, β-*H*), 9.30 (d, $^3J_{H,H}$ = 5.7 Hz, 4 H, β-*H*) ppm. ^{13}C NMR (150.9 MHz, CDCl$_3$, 25 °C): δ = 13.9, 22.5, 29.5, 29.9, 31.6,

33.9, 37.2, 38.8, 43.1, 43.2, 111.6, 117.2, 117.4, 127.0, 128.1, 128.2, 129.3, 129.8, 129.9, 131.1, 131.1, 140.9, 141.2, 141.3, 142.3, 161.1, 206.2 ppm. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 421 (5.5), 538 (4.8), 570 (4.6) nm. HRMS (ES+): calcd. for $C_{50}H_{58}N_4NiO$ $[M + H]^+$ 789.4042, found 789.4020.

Pauson–Khand Reaction of (4-Ethynylphenyl)porphyrins

General Procedure: The (4-ethynylphenyl)porphyrin (**20**, **21**) (26–50 mg; 1 equiv.) was placed into a Schlenk tube under Ar in dry THF (20 mL). The solution was degassed by three freeze-pump-thaw cycles and refilled with Ar. Next $Co_2(CO)_8$ (10 equiv.) was added, and the reaction mixture was stirred at room temp. until formation of the complex (ca. 1 h, monitored by TLC). Then norbornene or norbornadiene (2 equiv.) was added, and the reaction mixture was heated at 80 °C for 12 h. The crude products were purified by dry-loaded column chromatography on silica gel (CH_2Cl_2/C_6H_{14}, 1:1, v/v). The first fraction of the column was assumed to be the remaining (norbornene/norbornadiene)(porphyrin)Co complex, and the product was obtained as the second fraction. Recrystallisation was carried out from CH_2Cl_2/MeOH.

{5,15-Bis(4-methylphenyl)-10-[4-(3-oxotricyclo[5.2.1.0^{2,6}]dec-4-en-4-yl)phenyl]porphyrinato}nickel(II) (28): By using [5-(4-ethynylphenyl)-10,20-bis(4-methylphenyl)porphyrinato]nickel(II) (**20**, 40 mg, 0.062 mmol, 1 equiv.) and norbornene (2 equiv.) as starting materials, the product was obtained after recrystallisation as purple crystals in 40.4 mg (0.053 mmol, 85%) yield. M.p. > 300 °C. R_f = 0.24 (CH_2Cl_2/C_6H_{14}, 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.14 (d, $^3J_{H,H}$ = 10.5 Hz, 1 H, CHCH_2CH), 1.31 (dd, $^3J_{H,H}$ = 11.7, $^3J_{H,H}$ = 10.5 Hz, 1 H, CHCH_2CH), 1.46 [m, 2 H, C=CH(CH)$_2$-CH_2], 1.77 [m, 2 H, CO(CH)$_2$CH_2], 2.42 (s, 1 H, COCHC*H*CH$_2$), 2.54 (d, $^3J_{H,H}$ = 5.3 Hz, 1 H, COC*H*CHCH$_2$), 2.64 (s, 1 H, C=CHCHC*H*CH$_2$), 2.69 (s, 6 H, $C_6H_4CH_3$), 2.87 (d, $^3J_{H,H}$ = 2.9 Hz, 1 H, C=CHC*H*CHCH$_2$), 7.53 (d, $^3J_{H,H}$ = 7.0 Hz, 4 H, H_{Ar}), 7.94 (d, $^3J_{H,H}$ = 5.9 Hz, 4 H, H_{Ar}), 7.96 (s, 1 H, C=C*H*), 8.06 (s, 4 H, H_{Ar}), 8.81 (d, $^3J_{H,H}$ = 5.9 Hz, 2 H, β-*H*), 8.83 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 8.95 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 9.16 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 9.86 (s, 1 H, *meso*-*H*) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 21.1, 28.0, 28.8, 31.0, 28.1, 39.2, 45.5, 54.7, 104.1, 118.3, 118.4, 125.0, 127.2, 130.5, 131.5, 131.6, 131.7, 137.2, 133.2, 136.9, 137.5, 140.9, 141.8, 142.3, 142.5, 145.5, 160.4, 208.9 ppm. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 409 (5.8), 522 (4.9), 550 (4.7) nm. HRMS (ES+): calcd. for $C_{50}H_{38}N_4NiO$ $[M + H]^+$ 769.2477, found 769.2479.

{5,15-Bis(4-methylphenyl)-10-[4-(3-oxotricyclo[5.2.1.0^{2,6}]dec-4-en-4-yl)phenyl]porphyrinato}zinc(II) (29): By using [5-(4-ethynylphenyl)-10,20-bis(4-methylphenyl)porphyrinato]zinc(II) (**21**, 40 mg, 0.061 mmol) and norbornene as starting materials, after recrystallisation the product was obtained as pink crystals in 36.7 mg (0.047 mmol, 78%) yield. M.p. > 300 °C. R_f = 0.31 (CH_2Cl_2/C_6H_{14}, 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.99 (d, $^3J_{H,H}$ = 6.4 Hz, 1 H, CHCH_2CH), 1.14 (d, $^3J_{H,H}$ = 11.1 Hz, 1 H, CHCH_2CH), 1.46 [m, 2 H, C=CH(CH)$_2$CH_2], 1.78 [m, 2 H, CO(CH)$_2$CH_2], 2.44 (d, $^3J_{H,H}$ = 2.3 Hz, 1 H, COCHC*H*CH$_2$), 2.48 (d, $^3J_{H,H}$ = 5.3 Hz, 1 H, COC*H*CHCH$_2$), 2.58 (s, 1 H, C=CHCHC*H*CH$_2$), 2.76 (s, 6 H, $C_6H_4CH_3$), 2.88 (s, 1 H, C=CHC*H*CHCH$_2$), 7.61 (d, $^3J_{H,H}$ = 7.6 Hz, 4 H, H_{Ar}), 7.98 (d, $^3J_{H,H}$ = 2.9 Hz, 1 H, C=C*H*), 8.07 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, H_{Ar}), 8.15 (d, $^3J_{H,H}$ = 7.6 Hz, 4 H, H_{Ar}), 8.25 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H, H_{Ar}), 9.01 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 9.04 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 9.15 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 9.43 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 10.29 (s, 1 H, *meso*-*H*) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$, 25 °C): δ = 21.0, 21.4, 22.5, 23.7, 26.9, 28.4, 34.7, 38.4, 39.5, 47.9, 54.9, 105.7, 120.6, 120.7, 124.9, 125.4, 127.2, 128.1, 130.5, 131.5, 131.7, 131.8, 132.4, 132.5, 134.3, 134.4, 135.6, 136.9, 139.6, 139.7, 142.9, 134.1, 145.3, 145.9, 148.7, 149.5, 149.8, 150.2, 150.3, 1501.4, 160.6, 186.0, 209.2 ppm. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 415 (6.2), 543 (5.1), 582 (4.9) nm. HRMS (ES+): calcd. for $C_{50}H_{38}N_4OZn$ $[M]^+$ 774.2337, found 774.2338.

{5,15-Bis(4-methylphenyl)-10-[4-(3-oxotricyclo[5.2.1.0^{2,6}]dec-4,8-dien-4-yl)phenyl]porphyrinato}nickel(II) (30): By using [5-(4-ethynylphenyl)-10,20-bis(4-methylphenyl)porphyrinato]nickel(II) (**20**, 50 mg, 0.077 mmol) and norbornadiene as starting materials, after recrystallisation the product was obtained as red crystals in 22.2 mg (0.028 mmol, 38%) yield. M.p. > 300 °C. R_f = 0.21 (CH_2Cl_2/C_6H_{14}, 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.56 (d, $^3J_{H,H}$ = 1.2 Hz, 2 H, CHCH_2CH), 2.64 (d, $^3J_{H,H}$ = 5.3 Hz, 2 H, COC*H*CH), 2.69 (s, 6 H, $C_6H_4CH_3$), 2.94 (s, 1 H, C=CHCHC*H*), 3.01 (m, 1 H, C=CHC*H*CH), 3.17 (d, $^3J_{H,H}$ = 1.2 Hz, 1 H, COCHC*H*), 6.35 (dd, $^3J_{H,H}$ = 5.3, $^3J_{H,H}$ = 2.9 Hz, 1 H, C*H*=CH), 6.43 (dd, $^3J_{H,H}$ = 5.3, $^3J_{H,H}$ = 2.9 Hz, 1 H, C*H*=CH), 7.53 (d, $^3J_{H,H}$ = 7.6 Hz, 4 H, H_{Ar}), 7.94 (d, $^3J_{H,H}$ = 8.2 Hz, 4 H, H_{Ar}), 7.99 (d, $^3J_{H,H}$ = 2.9 Hz, 1 H, C=C*H*), 8.06 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, H_{Ar}), 8.06 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, H_{Ar}), 8.80 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 8.83 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 8.94 (d, $^3J_{H,H}$ = 5.3 Hz, 2 H, β-*H*), 9.16 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-*H*), 9.86 (s, 1 H, *meso*-*H*) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$, 25 °C): δ = 21.3, 41.4, 43.4, 44.2, 49.3, 53.6, 104.4, 118.6, 125.3, 127.5, 130.9, 131.7, 131.8, 131.9, 132.5, 133.5, 133.7, 137.1, 137.3, 137.9, 138.5, 141.3, 142.1, 142.6, 142.7, 142.8, 146.9, 160.2, 207.8 ppm. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 409 (5.7), 523 (4.7), 548 (4.5) nm. HRMS (MALDI LD+): calcd. for $C_{50}H_{36}N_4NiO$ $[M]^+$ 766.2243, found 766.2251.

10,10′-[(3,11-Dioxotetracyclo[5.2.1.0^{2,6}.0^{8,12}]trideca-4,9-dien-4,10-diyl)bis(4,1-phenylene)]bis{[5,15-bis(4-methylphenyl)porphyrinato]-nickel(II)} (31): By using [5-(4-ethynylphenyl)-10,20-bis(4-methylphenyl)porphyrinato]nickel(II) (**20**, 26 mg, 0.039 mmol) and {5,15-Bis(4-methylphenyl)-10-[4-(3-oxotricyclo[5.2.1.0^{2,6}]dec-4,8-dien-4-yl)phenyl]porphyrinato}nickel(II) (**30**, 30 mg, 0.039 mmol) as starting materials, the product was obtained as the second fraction of the column chromatography after recrystallisation in 28 mg (0.019 mmol, 50%) yield as red crystals. M.p. > 300 °C. R_f = 0.69 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.31 (s, 2 H, CHCH_2CH), 2.69 (s, 12 H, $C_6H_4CH_3$), 2.84 (m, 4 H, C=CHC*H*C*H*C*H*C*H*C=C, CH_2C*H*), 3.16 (m, 2 H, COC*H*CHC*H*CO), 7.54 (d, $^3J_{H,H}$ = 7.6 Hz, 8 H, H_{Ar}), 7.95 (d, $^3J_{H,H}$ = 8.2 Hz, 8 H, H_{Ar}), 8.02 (d, $^3J_{H,H}$ = 2.34 Hz, 2 H, C=C*H*), 8.09 (s, 8 H, H_{Ar}), 8.81 (d, $^3J_{H,H}$ = 5.3 Hz, 4 H, β-*H*), 8.84 (d, $^3J_{H,H}$ = 4.7 Hz, 4 H, β-*H*), 8.95 (d, $^3J_{H,H}$ = 4.7 Hz, 4 H, β-*H*), 9.17 (d, $^3J_{H,H}$ = 4.7 Hz, 4 H, β-*H*), 9.86 (s, 2 H, *meso*-*H*) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 21.5, 29.7, 41.3, 47.2, 55.1, 104.6, 118.6, 118.8, 125.6, 127.6, 130.4, 131.9, 132.1, 132.2, 132.7, 133.7, 133.9, 137.5, 141.8, 142.2, 142.8, 142.9, 143.0, 146.6, 159.2, 207.8 ppm. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 410 (5.6), 521 (4.9), 551 (4.7) nm. HRMS (MALDI LD+): calcd. for $C_{93}H_{64}N_8O_2Ni_2$ $[M]^+$ 1440.3859, found 1440.3795.

10,10′-[(3,9-Dioxotetracyclo[5.2.1.0^{2,6}.0^{8,12}]trideca-4,10-dien-4,10-diyl)bis(4,1-phenylene)]bis{[5,15-bis(4-methylphenyl)porphyrinato]-nickel(II)} (32): The product was obtained as the third fraction of the reaction above after recrystallisation in 26.5 mg (0.018 mmol, 47%) yield as red crystals. M.p. > 300 °C. R_f = 0.19 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.22 (s, 2 H, CHCH_2CH), 2.69 (s, 12 H, $C_6H_4CH_3$), 2.72 (d, $^3J_{H,H}$ = 5.3 Hz, 2 H, C*H*CH$_2$C*H*), 3.06 (m, 4 H, COC*H*C*H*), 7.53 (d, $^3J_{H,H}$ = 7.6 Hz, 8 H, H_{Ar}), 7.89 (d, $^3J_{H,H}$ = 1.8 Hz, 2 H, C=C*H*), 7.95 (d, $^3J_{H,H}$ = 8.2 Hz, 8 H, H_{Ar}), 8.06 (d, $^3J_{H,H}$ = 8.8 Hz, 4 H, H_{Ar}), 8.09 (d, $^3J_{H,H}$ = 8.2 Hz, 4 H, H_{Ar}), 8.81 (d, $^3J_{H,H}$ = 5.3 Hz, 4 H, β-*H*), 8.85 (d,

$^3J_{H,H}$ = 5.3 Hz, 4 H, β-*H*), 8.95 (d, $^3J_{H,H}$ = 4.7 Hz, 4 H, β-*H*), 9.17 (d, $^3J_{H,H}$ = 4.7 Hz, 4 H, β-*H*), 9.86 (s, 2 H, *meso*-*H*) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 21.1, 29.3, 40.5, 41.2, 47.7, 53.5, 104.2, 118.2, 118.3, 125.1, 127.2, 129.9, 131.4, 131.6, 131.8, 132.2, 133.3, 133.5, 137.0, 137.5, 141.3, 141.7, 142.3, 142.4, 142.5, 145.9, 158.4, 206.7 ppm. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 410 (5.7), 521 (4.9), 548 (4.7) nm. HRMS (MALDI LD+): calcd. for $C_{93}H_{64}N_8O_2Ni_2$ $[M]^+$ 1440.3859, found 1440.3929.

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