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Synthesis, Transformations, And Comparative Studies of Porphyryl Acrylic Acids and Their Homologues

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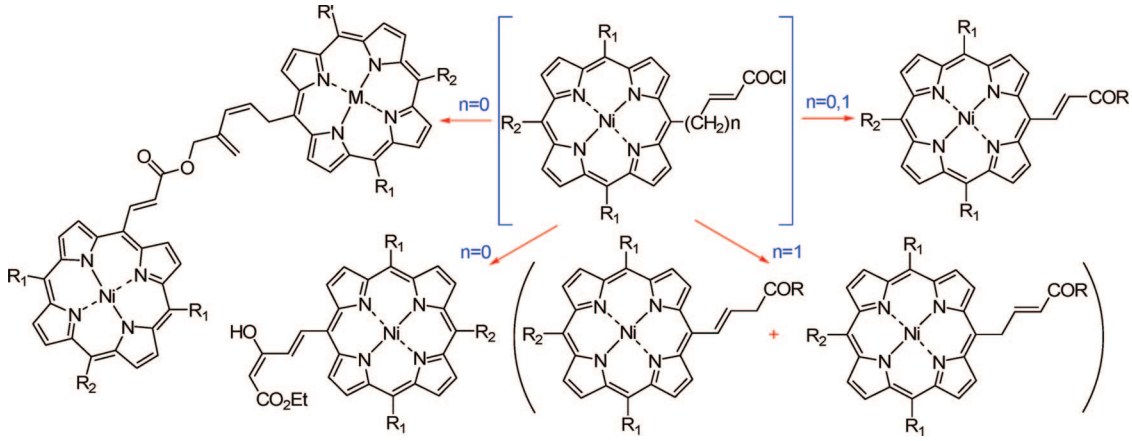

The reactivity of porphyryl acrylates and their homologues was studied systematically and to establish their potential as building blocks for the synthesis of novel tetrapyrroles. A new synthetic approach for multifunctional porphyrins was developed using α,β-unsaturated acyl porphyrins as versatile building blocks with yields of 44−95%. The reaction of acyl chlorides generated in situ with ethyl diazoacetate in the presence of PPh_3 led to the corresponding phosphazine, which was quickly self-transformed into a novel porphyrin β-keto ester system in up to 78% yield. Comparative studies of the next homologue of acrylic porphyrins, i.e., those bearing an additional CH_2 group next to the double bond of the α,β-unsaturated fragment, showed that these can undergo rearrangement reactions via vinylketenes to yield both regioisomers. Depending on the reaction conditions, this method gives regioselectively access to either a rearrangement product or the product of esterification reactions in yields of 81% or 57%, respectively. Enyne metathesis of novel propargyl esters with allyl porphyrins provided an easy access to 1,3-disubstituted butadienes in up to 76% yield.

Introduction

The chemistry of acyl compounds has a long history that can be traced back to the early part of the last century.[1] Acyl building blocks derived from carboxylic acids are some of the best known and most valuable synthons and are widely used in the synthesis of organic fine chemicals. A variety of synthetic methodologies has been developed to access these reactive molecules. α,β-Unsaturated acyl compounds are a subclass of these derivatives and constituents of numerous natural and synthetic products which display a wide range of biological activities. As multimodal groups they possess two reactively reverse sites (e.g., COX and C═C) suitable for C−C and C−X bond (trans)formations. The carbonyl unit is a versatile electrophile, while the double bond can react as a nucleophile. Thus, depending on the conditions and reagents used, these reactive sites can either be activated or deactivated at the same time in a favorable manner. Therefore, their chemistry offers significant synthetic prospects based on different types of possible reactions (e.g., Claisen condensation and related acylations, substitutions, (1,2-

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1,4- or cyclo)additions, to name a few) that can be carried out to afford novel tetrapyrrole-based materials.

Porphyrins and their derivatives are one of the most important classes of heterocycles with unique properties. The practical utilization of these macrocycles is expanding rapidly in emerging areas such as cancer therapy, artificial photosynthesis, sensors, nonlinear optics, nanomaterials, and use as pigments and oxidation catalysts.[2−4] These and many other possible applications of porphyrins require the development of new and more efficient reactions to introduce functional groups into the macrocycle. Broadly speaking, at present the chemistry available for porphyrin modification is based on metal-catalyzed[5] and organolithium[6] approaches that sometimes require special conditions which leaves room for alternative synthetic methodologies. Surprisingly, acyl chemistry has not been used much for the modification of porphyrins. Several reports described the utilization of porphyrin−benzoic acids[7] as building blocks for porphyrin thin films,[7,8] and surface porphyrin monolayers for use as sensor materials.[8−12] Remarkably, functionalization of these compounds involved mostly carbodiimide chemistry.[7,13] Only a few reports have been published using porphyrin benzoyl acyl chlorides[11,12,14] to leave the chemistry almost untouched. Similarly, while the synthesis of acrylic porphyrins is well-known,[15] their chemistry remains relatively unexplored.

In the context of a program aimed at the development of novel porphyrin bioconjugates suitable for cell targeting, we have systematically studied the reactivity of porphyryl acyl acrylates and their homologues. Here we present results on the synthesis, transformation, and comparative studies of a series of porphyryl acrylic derivatives.

Results and Discussion

1. Generation of Acyl Chlorides and Their Reactivity toward Simple Nucleophiles. For our initial studies, we chose **3** and **4** with either one or two acroleinyl groups as model compounds. Porphyrins **3** and **4** were synthesized via Heck reaction from a bromoporphyrin **1** or **2** and methyl acrylate in 80−95% yields. They were easily hydrolyzed in KOH−EtOH to the acrylic acids **5** and **6** in 80−95% yields (Scheme 1).The corresponding acyl chlorides **7** and **8** were easily generated upon treatment of **5** and **6** with $SOCl_2$−THF in situ. Light heating (35 °C) is essential to accelerate the formation of these green-purple materials. Moreover, the acyl chlorides are moisture sensitive, hydrolyzing back into the corresponding acids **5** and **6**. Hence, they were used immediately in further transformations. To evaluate the reactivity of these intermediates, we simply used the nucleophiles such as ROH and R_2NH. These studies have shown that the acyl chlorides **7** and **8** in situ generated can be easily converted into the novel porphyrin adducts **3b** and **9**−**12** in good yields (Scheme 1).

This methodology can also be applied for the preparation of dimeric porphyrins. For example, the reaction of **7** with 5-(4-hydroxyphenyl)-10,20-bis(3-methoxyphenyl)porphyrin **13** resulted in the formation of dimer **14**. Noteworthy, the first attempt to carry out this reaction in THF shown to be successful for the synthesis of **3b** and **9**−**12** resulted in a very low yield of **14**. However, replacement of THF by dichloromethane provided dimer **14** in 51% (Scheme 2).

2. Reactivity. Next, we turned our attention to the respective β-keto ester systems. Indeed, porphyrins bearing β-keto esters

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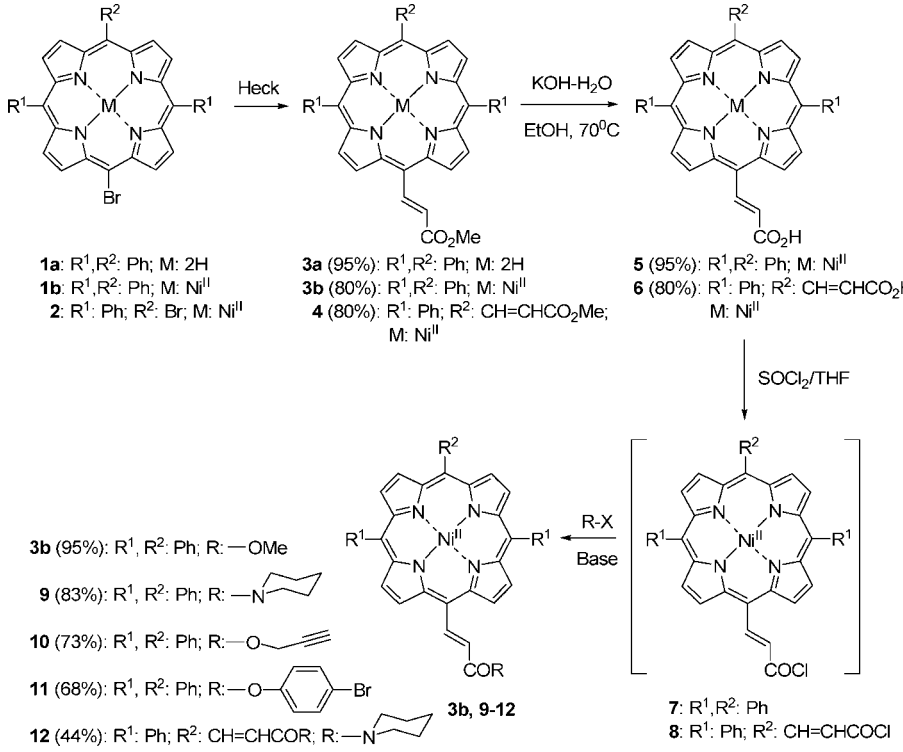
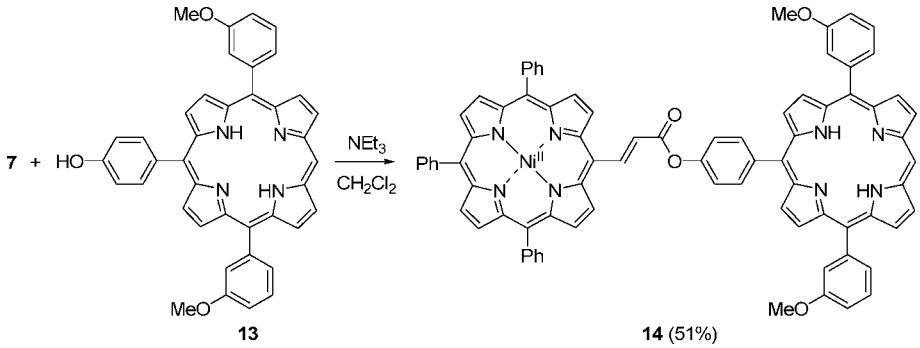
SCHEME 1. Generation of Acyl Chlorides 7 and 8 and Synthesis of the Porphyrins 3b and 9−12



SCHEME 2. Synthesis of Porphyrin Dimer 14



as β-substituents can be converted into biologically active phaeoporphyrins via photoinduced cyclization.[16] While diazo compounds are widely used as versatile precursors in synthetic chemistry,[17] surprisingly, only one strategy was applied for the synthesis of diazo β-keto esters using acrylic acid halides in the reaction of the latter with mercuryl diazoacetate reported by Padwa et al.[17] In this context, the reaction of acyl chloride **7** with ethyl diazoacetate in the presence of PPh_3 offers an entry into the important and unexplored class of porphyryl β-keto esters. Acyl chloride **7** generated in situ was treated with a mixture of ethyl diazoacetate and PPh_3 in dichloromethane at 35 °C for several hours to give the phosphazine **15** in 70% yield (Scheme 3). Some structural diversity was observed in solutions of $CDCl_3$ where slow conversion of **15** and formation of **16** was detected over the course of 7 days. Compound **16** trapped in $CDCl_3$ appears to be a product of partial hydrolysis of phosphazine **15**. However, compound **15** proved to be quite unstable in dichloromethane and autotransformed (24 h) into the stable β-keto ester **17** in 78% (Scheme 3). According to ^{1}H NMR data, porphyrin **17** exists only in the enol form in a solution of either $CDCl_3$ or CD_2Cl_2. More detailed NMR analyses showed that compound **17** consists of only one stereoisomer. Importantly, no response between either H_x and H_z or in the pair of H_y with H_z were observed in 1D NOE experiments. Strong NOE were detected for the CH_2-group of CO_2Et and H_z, and also between H_x and H_y with β-Hs. These results confirm that **17** has a 2*E*,4*E*-configuration as shown in Scheme 3. Noteworthy, the synthesis of the β-keto esters are generally requiring the hydrolysis of the phosphazines formed in the reaction of the nonacrylic acid chlorides with diazoacetate and further elimination of an NNH_2 group.[18] In our case, this reaction offers a versatile approach to yield porphyryl hydroxydienoates in just one step.

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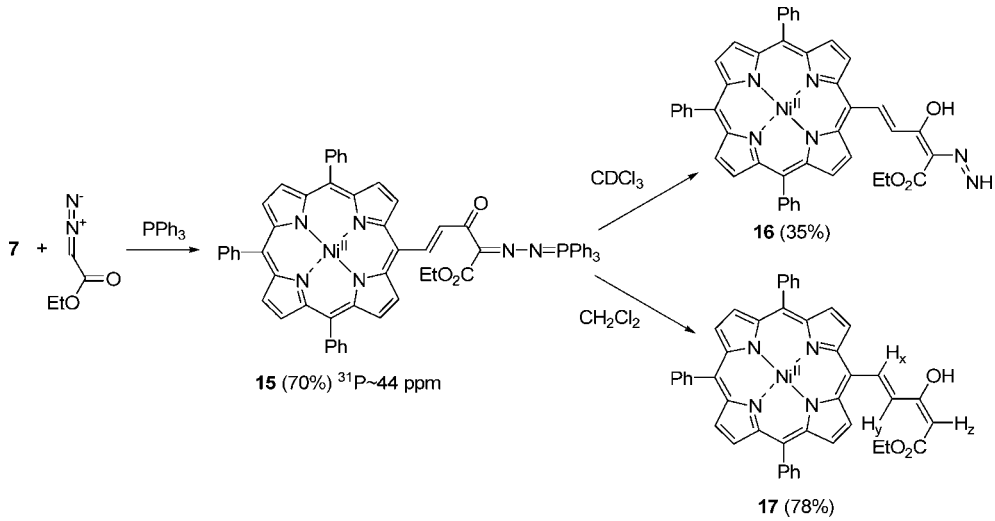
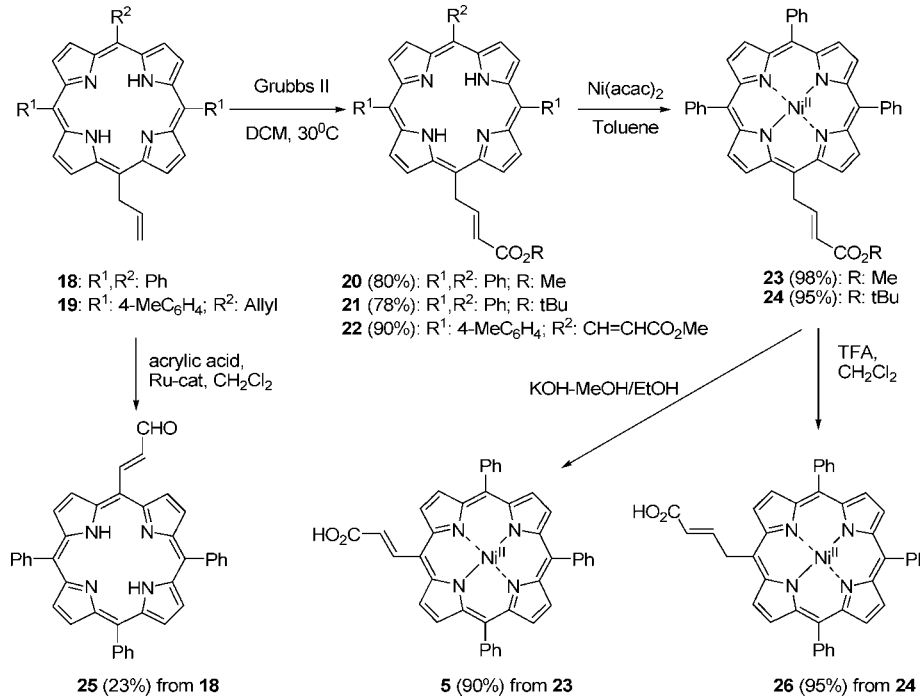
SCHEME 3. Reaction of 7 with Ethyl Diazoacetate via Formation of Phosphazine 15 and Conversion to 16 and 17



SCHEME 4. Synthesis and Transformations of Acrylic Esters 20−24



3. Homologues. The reactions of acyl chlorides bearing α-Hs with tertiary amines is an old and common method for the synthesis of ketenes and is often used for in situ generation, e.g., in cycloadditions and other reactions typical for ketenes.[19] Our investigations were further inspired by the fact that substituted vinyl ketenes can be formed in situ by dehydrohalogenation of α,β-unsaturated acyl chlorides, and as unstable species, they can be activated and trapped.[19,20]Strategically, the series of the next homologues of the acrylates **3** and **4** bearing CH_2 groups accessible for double-bond migration were prepared using the metathesis approach for the synthesis of α,β-unsaturated ketones reported by us earlier,[21] followed by ester hydrolysis. Metathesis of the allyl porphyrins **18**, **19** and corresponding acrylate esters in the presence of Grubbs II catalyst in dichloromethane provided an easy access to the corresponding esters **20**−**22** in about 80−90% yield (Scheme 4).

Unexpectedly, a first attempt to hydrolyze the methyl ester **23** in KOH−EtOH resulted in formation of a very polar compound, which when treated with HCl (1 N) yielded **5** in 90%. The analytical data obtained were in accordance with the structure of a product prepared through an alternative approach via Heck reaction. In order to avoid basic conditions, we considered an alternative approach for the synthesis of a

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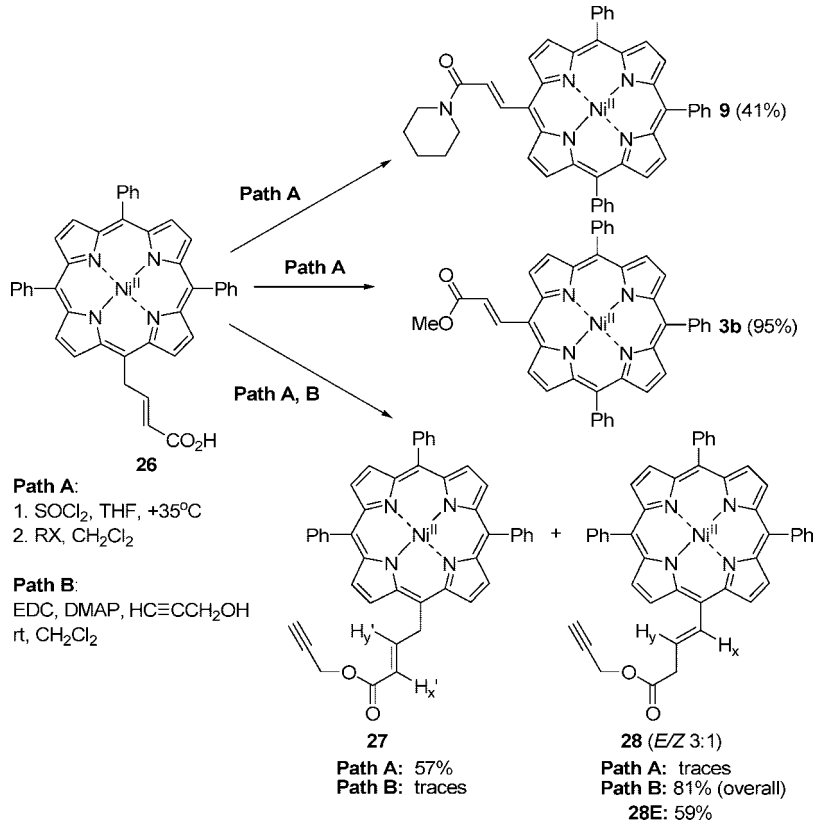
SCHEME 5. Transformations of 26. Synthesis of 3b, 9, 27, and 28



porphyrin acrylic acid involving allyl porphyrin **18** and the acrylic acid in the presence of Grubbs II catalyst. However, test reactions gave the acroleinyl porphyrin **25** in 23% yield. Similar transformations of (allyl porphyrinato)nickel(II) complexes into porphyryl acroleins—albeit catalyzed by $Ni(OAc)_2$—were recently reported by us.[15] Finally, the *tert*-butyl ester **24** was successfully converted into the free acid **26** in the presence of trifluoroacetic acid in dichloromethane in 95% (Scheme 4).

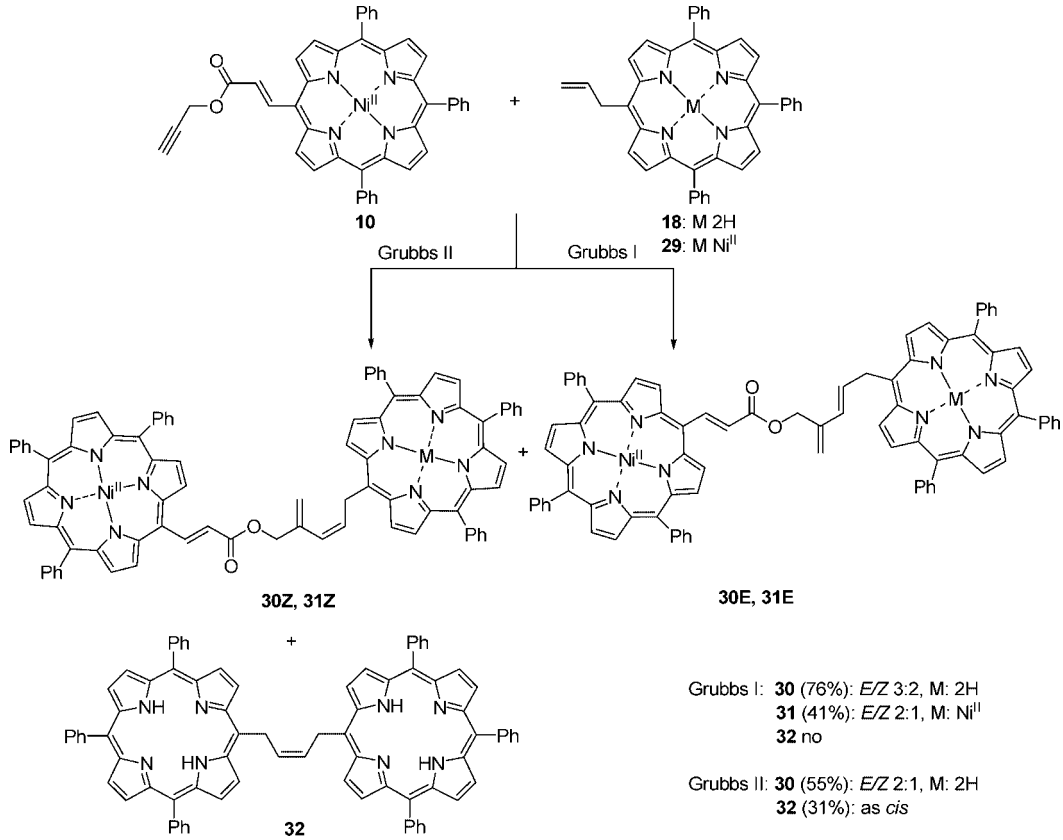
The corresponding acyl chloride generated from porphyrin **26** by treatment with $SOCl_2$ in THF reacted with piperidine in the absence of NEt_3 to give the compound **9** in 41% yield (Scheme 5). Reaction of acyl chloride of **26** with MeOH and $N(i\text{-}Pr)_2Et$ (4 equiv) led to the porphyrin **3b** in almost quantitative yield (95%). Analytical data for the compounds **3b** and **9** prepared via these routes were the same as those derived for the compounds prepared using the alternative approach outlined in Scheme 1. The reaction pathway (mechanism) of **26** into **3b** and **9** seems to be similar to the one for the hydrolytic conversion of **23** to **5**, where "elimination" of a CH_2 fragment was observed, too. Assuming, that a vinyl ketene might be an intermediate of these transformations; we slightly changed the synthetic approach and used a bulky soft base (DMAP) and a reactive propargyl alcohol. Indeed, the reaction of **26** with propargyl alcohol provided only the esterification product **27** in 57% yield. However, traces of the rearrangement product **28** could be detected as well. In order to improve the yield of **28** and to confirm its structure, porphyrin **26** was alternatively treated with a mixture of DMAP−EDAC (*N*-ethyl-*N*′-(3-dimethylaminopropyl)carbodiimide) in dichloromethane, followed by addition of propargyl alcohol. Surprisingly, two regioisomeric products (**27** and **28**) were detected, with the regioisomer **28** being the major product. Moreover, compound **28** presented a mixture of stereomers in a ratio of 3:1, with an overall yield for the two stereomers of 81% (Scheme 5).

^1H NMR analysis confirmed the differences between **27** and **28** (here, data for the major stereoisomer **28E** are given). The signal for a double bond hydrogen atom H_x in **28E** was shifted to 8.76 ppm (d) compared to 5.83 ppm (d) for H_x' in **27**. Likewise, the signals for the methylene hydrogen atoms (5.48 ppm, d) and a double-bond hydrogen atom H_y' (7.92 ppm, dt) in **27** were shifted toward higher field (3.79 ppm, d and 6.17 ppm, dt, respectively) in **28E**. This confirms compound **28** to be a rearrangement product. An analysis of the ^1H NMR ^3J coupling constants of the CH═CH fragment in the stereomeric mixture **28** (J for E 15.2 Hz and for Z 11.3. Hz) revealed the stereochemistry of the major product to be E. This major stereoisomer **28E** was isolated in 59% yield. The formation of both regioisomers **27** and **28** under different reaction conditions suggests a competition[20] of the two reaction pathways involving substitution and elimination processes. The vinyl ketene is the result of an elimination reaction causing a migration of the double bond and formation of **28**. The observation of the *E*/*Z* mixture **28** suggests a pathway via a vinyl ketene intermediate where the original stereochemistry is lost. In contrast, the intermediate of the substitution reaction leading to the esterification product **27** is most likely a zwitterionic dienolate.

4. C−C Coupling Reactions. Enyne metathesis is a unique and interesting transformation involving the reaction between an alkene and an alkyne partner.[22] We used enyne metathesis starting from the propargyl ester **10** and the allyl porphyrins **18** and **29** to prepare the synthetically useful 1,3-disubstituted

(22) Blechert, S.; Connon, S. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 1900–1923, and references cited therein. (b) For the first report of enyne metathesis, see: Katz, T. J.; Sivavec, T. M. *J. Am. Chem. Soc.* **1985**, *107*, 737–738.

SCHEME 6. Enyne Metathesis of 10 and Allyl Porphyrins 18 and 29. Synthesis of 1,3-Disubstituted Butadienes 30 and 31



butadiene derivatives **30** and **31** (Scheme 6). Such compounds offer themselves toward structural elaboration via Diels−Alder and other cycloaddition reactions. We next compared the reactivity and chemoselectivity of both generations of Grubbs catalysts. Enyne metathesis of porphyrin **10** and the allyl porphyrin **18** resulted only in formation of **30**, with *E*/*Z* = 3:2 in a good yield of 76%. Although stereochemistry of the reaction of allyl porphyrinatonickel **29** and **10** using the same catalyst was slightly improved to give *E*/*Z* = 2:1, compounds **31** were isolated in 41% yield. In the case of Grubbs II catalyst, a competing CM homodimerization of the allyl porphyrin **18** took place, resulting in a mixture of alkene **32** (31%, *cis* isomer) and the 1,3-disubstituted butadiene derivatives **30** (55%) (Scheme 6).

The assignment of the stereochemistry of the 1,3-disubstituted butadienes **30** and **31** was based on NMR analyses involving 1D NOE, 2D-ROESY, HSQC, and HMBC experiments. For the major stereomer in the **31E/Z** mixture, ROESY experiments showed a reliable correlation between H_x and H_b and between H_y and H_z. A strong response was found for each of the H_x-H_b and H_y-H_z pairs in 1D NOE as well. ROESY analysis of the minor isomer of **31** showed the appropriate correlations between H_a and H_z and between H_y and H_b. The stereochemistry of the minor product in **31** could be assigned as *Z* and the major one as the *E*-isomer as illustrated in Figure 1. Similar results were obtained for the porphyrin **30**. Thus, based on these analytical data, the major stereomer has *E* stereochemistry in both mixtures of **30** and **31**.

Conclusions

Based on acrylic porphyrins and some homologues, a new synthetic approach has been developed for multifunctional porphyrins. Our studies show that the acyl chlorides **7** and **8** generated in situ can easily be converted using simple nucleophiles into the corresponding acyl derivatives. The reaction of **7** with ethyl diazoacetate via the instable phosphazine **15** represents a convenient entry into the important class of β-keto esters **17**. We could show that the phosphazine **15** was self-converted into the β-keto ester, possibly via intermediate **16**. Interestingly, compound **17** exists only as the enol form in halogenated solvents, and its stereochemistry was assigned as the 2*E*,4*E*-configuration. The next homologues **23** and **26** of the acrylic porphyrins (**3** and **4**), can undergo rearrangement via vinyl ketenes under basic conditions to yield both regioisomers **27** and **28**. Variation of the reaction conditions regioselectively provides access to either a rearrangement (**28**, 81%) or an esterification product (**27**, 57%). Finally, enyne metathesis

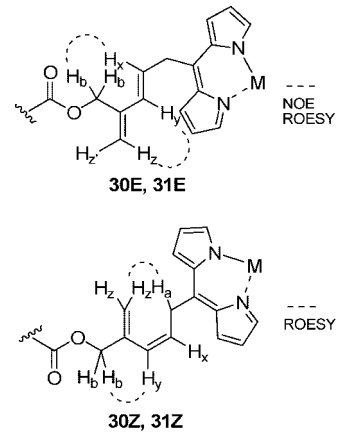


FIGURE 1. Assignments of the stereochemistry for the 1,3-disubstituted butadienes **30** and **31**.

of the novel propargyl esters with allyl porphyrins provided an easy access to 1,3-disubstituted butadienes **30** and **31** in up to 76% yield. Porphyrin arrays can be constructed using cycloaddition reactions based on the dimeric porphyrins **30**−**32** presented. The syntheses described provide access to the novel porphyrins and expand the repertoire of the porphyrin based reagents to be utilized for the further functionalization of the porphyrin periphery. They can serve as versatile building blocks for the facile transformation into porphyrin bioconjugates, e.g., amino and hydroxy acid derivatives, especially, for medicinal applications.

Experimental Section

All solvents were distilled prior to use. All reagents were purchased from Sigma-Aldrich and were used without any further purification. Allyl porphyrins (**18**, **19**, and **29**) and bromoporphyrins **1** and **2** were synthesized according to the procedures previously reported.[15,21] General experimental and analytical techniques used were as described previously.[15]

Synthesis of the Compounds 3. A heterogeneous solution of a bromoporphyrin **1** (0.32 mmol), methyl acrylate (0.29 mL, 3.2 mmol), PPh_3 (252 mg, 0.96 mmol), $Pd(OAc)_2$ (14.4 mg, 0.064 mmol), and K_2CO_3 (442 mg, 3.2 mmol) in toluene (120 mL) was heated under argon at 110 °C for 36−48 h (TLC control). The reaction mixture was filtered through a plug of silica and washed with ethyl acetate. After removal of the solvents under reduced pressure, the residue was recrystallized from CH_2Cl_2−MeOH to give **3** in 80−95%. The analytical data for **3** were in accordance with the data previously reported.[15]

(2*E*,2′*E*)-Dimethyl 3,3′-[(5,15-Diphenylporphyrinato-10,20-diyl)-nickel(II)]diacrylate 4. A heterogeneous solution of (5,15-dibromo-10,20-diphenylporphyrinato)nickel(II) **2** (200 mg, 0.32 mmol), methyl acrylate (0.58 mL, 6.4 mmol), PPh_3 (420 mg, 1.6 mmol), $Pd(OAc)_2$ (14.4 mg, 0.064 mmol), and K_2CO_3 (885 mg, 6.4 mmol) in toluene (120 mL) was heated under argon at 110 °C for 72 h (TLC control). The reaction mixture was filtered through a plug of silica and washed with ethyl acetate. After removal of the solvents under reduced pressure, the residue was recrystallized from CH_2Cl_2−MeOH to give **4** (200 mg, 91%) as a green-violet solid: mp >300 °C; R_f 0.7 (ethyl acetate/hexane, 1:2 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.97 (s, 6H), 6.28 (d, J = 15.6 Hz, 2H), 7.71 (m, 6H), 7.95 (m, 4H), 8.75 (d, J = 4.9 Hz, 4H), 9.31 (d, J = 4.9 Hz, 4H), 9.81 (d, J = 15.6 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 51.6, 110.5, 119.5, 126.7, 127.6, 131.3, 131.5, 133.0, 133.2, 139.3, 140.6, 141.3, 143.0, 166.2; UV−vis (CH_2Cl_2) λ_{max} (log ε) 438 (5.3), 568 (4.2), 610 (4.3); TOF MS LD+ ($C_{40}H_{28}N_4NiO_4$) calcd for [M + Na] 709.1362, found 709.1369.

General Procedure for the Synthesis of 5 and 6 via Hydrolysis with EtOH−KOH. To porphyrins **3** and **4** (0.3 mmol) in EtOH (30 mL) was added an aqueous solution (2 mL) of KOH (400 mg). The reaction was heated at 70 °C for 24−72 h (TLC control) resulting in complete dissolution of the porphyrin. Ethanol was removed under reduced pressure, and the violet solid left was treated with HCl (1 N). The crystals formed were filtered off and washed with HCl (1 N) (10 mL) and distilled H_2O (20 mL). The free acid was dried in vacuo to yield the products **5** and **6** (91−95%).

(*E*)-3-[(5,10,15-Triphenylporphyrinato-20-yl)nickel(II)]acrylic acid 5: purple solid (189 mg, 95%); mp >300 °C; R_f 0.2 (ethyl acetate/hexane, 1:2 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.39 (d, J = 15.4 Hz, 1H), 7.72 (m, 9H), 8.00 (m, 6H), 8.69 (m, 4H), 8.87 (d, J = 4.8 Hz, 2H), 9.42 (d, J = 4.8 Hz, 2H), 10.03 (d, J = 15.4 Hz, 1H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 108.4, 119.6, 120.7, 126.8, 126.9, 127.8, 129.0, 131.0, 132.2, 132.7, 133.3, 133.4, 133.8, 140.0, 141.4, 142.1, 142.9, 146.7, 159.4, 169.9; UV−vis (CH_2Cl_2) λ_{max} (log ε) 429 (5.3), 546 (4.3), 585 (4.2) nm; TOF MS LD+ ($C_{41}H_{26}N_4NiO_2$) calcd for [M] 664.14, found 664.11.

(2*E*,2′*E*)-3,3′-[(5,15-Diphenylporphyrinato-10,20-diyl)nickel(II)]-diacrylic acid 6: violet solid (180 mg, 91%); mp >300 °C; R_f 0.1 (ethyl acetate/hexane, 1:2 v/v); ^{1}H NMR (400 MHz, THF-d_8) δ 6.24 (d, J = 15.8 Hz, 2H), 7.71 (m, 6H), 7.97 (m, 4H), 8.72 (d, J = 4.7 Hz, 4H), 9.40 (d, J = 4.7 Hz, 4H), 9.80 (d, J = 15.8 Hz, 2H), 11.28 (br, 2H); ^{13}C NMR (100.6 MHz, THF-d_8) δ 112.6, 120.6, 128.2, 129.1, 133.0, 134.2, 134.4, 134.5, 141.2, 142.3, 142.9, 143.5, 167.0; UV−vis (THF) λ_{max} (log ε) 435 (4.2), 561 (3.2), 607 (3.2) nm; TOF MS LD+ ($C_{38}H_{24}N_4NiO_4$) calcd for [M] 658.1151, found 658.1132.

General Procedure for Synthesis of 9−12: Generation of Acyl Chloride 7 and Its Reactions with Nucleophiles. To a solution of acid **5** (30 mg, 0.045 mmol) in anhydrous THF (4 mL) were added $SOCl_2$ (0.025 mL, 0.225 mmol) in 1 mL of THF and DMF (2−3 drops) under argon. The mixture was warmed to 35 °C and stirred for 60 min (color change from red to green). The volatiles were removed under reduced pressure, and the remaining acyl chloride **7** (purple-greenish solid) was dissolved in anhydrous CH_2Cl_2 (ca. 5 mL). The respective nucleophile (0.09−0.225 mmol) dissolved in CH_2Cl_2 (ca. 2−5 mL) followed by NEt_3 (0.013 mL, 0.09 mmol) in CH_2Cl_2 (0.5 mL) were added, and the reaction was stirred for several hours (TLC control) at 35 °C under argon. The reaction mixture was filtered through a plug of silica and washed with CH_2Cl_2, and the solvents were removed in vacuo. The crude products were purified by flash chromatography on silica with CH_2Cl_2/hexane or ethyl acetate/hexane to give the corresponding porphyrins **9**−**11** (68−95%).

(*E*)-1-(Piperidin-1-yl)-3-[(5,10,15-triphenylporphyrinato-20-yl)nickel(II)]prop-2-en-1-one 9. To a solution of the acyl chloride **7** generated from **5** (30 mg, 0.045 mmol) in anhydrous CH_2Cl_2 (5 mL) were added piperidine (0.015 mL, 0.15 mmol) in CH_2Cl_2 (1 mL) and NEt_3 (0.008 mL, 0.06 mmol) in CH_2Cl_2 (0.5 mL). The reaction was stirred for 1 h (TLC control) at 35 °C under argon, and the resulting mixture was worked up as described above. The crude product was purified by flash chromatography on silica (hexane/CH_2Cl_2, 2:1 v/v) to give **9** (18.2 mg, 83%) as a violet solid.

9 via **26**: To a solution of acid **26** (30 mg, 0.044 mmol) in anhydrous THF (5 mL) were added $SOCl_2$ (0.016 mL, 0.22 mmol) in 1 mL of THF and DMF (2−3 drops) under argon. The mixture was stirred at 35 °C for 1 h. The volatiles were removed under reduced pressure, and the remained acyl chloride was dissolved in anhydrous CH_2Cl_2 (5 mL). Piperidine (0.031 mL, 0.309 mmol) in CH_2Cl_2 (1 mL) was added to the reaction mixture, which was stirred for 18 h (TLC control) at 35 °C under argon. The reaction mixture was filtered through a plug of silica and washed with CH_2Cl_2, and the solvents were removed in vacuo. The crude products were purified by flash chromatography on silica (hexane/CH_2Cl_2, 1:1 v/v) to give **9** (13.8 mg, 42%) as a violet solid: mp >300 °C; R_f 0.5 (ethyl acetate/hexane, 1:3 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.68 (m, 6H), 3.50 (m, 2H), 3.77 (m, 2H), 6.79 (d, J = 15.8 Hz, 1H), 7.66 (m, 9H), 7.93 (m, 6H), 8.60 (m, 4H), 8.79 (d, 2H, J = 4.4 Hz), 9.33 (d, 2H, J = 4.4 Hz), 9.82 (d, J = 15.8 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 24.5, 25.7, 26.5, 29.7, 42.6, 47.3, 108.3, 109.7, 114.3, 120.1, 121.4, 127.1, 128.1, 131.2, 132.4, 133.0, 133.5, 134.2, 136.5, 140.0, 141.5, 141.8, 142.2, 143.2, 147.0, 165.9; UV−vis (CH_2Cl_2) λ_{max} (log ε) 423 (4.3), 538 (3.1) nm; TOF MS LD+ ($C_{46}H_{35}N_5ONi$) calcd for [M] 731.2195, found 731.2225.

(*E*)-Propargyl 3-[(5,10,15-Triphenylporphyrinato-20-yl)nickel(II)]acrylate 10. To a solution of acyl chloride **7** generated from **5** (30 mg, 0.045 mmol) in anhydrous CH_2Cl_2 (5 mL) were added propargyl alcohol (0.013 mL, 0.225 mmol) in CH_2Cl_2 (1 mL) and NEt_3 (0.013 mL, 0.09 mmol) in CH_2Cl_2 (0.5 mL). The reaction was stirred for several hours (TLC control) at 35 °C under argon, and the resulting mixture was worked up as described above. The crude product was purified by flash chromatography on silica (CH_2Cl_2/hexane = 1/1) to give **10** (31.7 mg, 73%) as a purple solid: mp 143−158 °C dec; R_f 0.6 (CH_2Cl_2/hexane = 1/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.62 (br, 1H), 5.01 (br, 2H), 6.37 (d, J = 15.8 Hz, 1H), 7.71 (m, 9H), 7.99 (m, 6H), 8.68 (dd, J = 4.7, 4.7

Hz, 4H), 8.85 (d, J = 4.7 Hz, 2H), 9.39 (d, J = 4.7, 2H), 9.97 (d, J = 15.8 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 51.9, 74.7, 108.6, 119.1, 120.1, 126.5, 126.6, 127.47, 127.5, 129.5, 130.9, 131.9, 132.4, 133.06, 133.1, 133.2, 133.3, 139.7, 141.0, 141.1, 141.7, 142.4, 144.7, 165.0; UV−vis (CH_2Cl_2) λ_{max} (log ε) 429 (5.4), 547 (4.3), 587 (4.2) nm; TOF MS LD+ ($C_{44}H_{28}N_4NiO_2$) calcd for [M] 702.1566, found 702.1531.

(*E*)-4-Bromophenyl 3-[(5,10,15-Triphenylporphyrinato-20-yl)-nickel(II)]acrylate 11. To a solution of acyl chloride **7** generated from **5** (30 mg, 0.045 mmol) in anhydrous CH_2Cl_2 (5 mL) were added 4-bromophenol (15.6 mg, 0.09 mmol) in CH_2Cl_2 (1 mL) and NEt_3 (0.013 mL, 0.09 mmol) in CH_2Cl_2 (0.5 mL). The reaction was stirred for several hours (TLC control) at 35 °C under argon, and the resulting mixture was worked up as described above. The crude product was purified by flash chromatography on silica (CH_2Cl_2/hexane, 1:1 v/v) to give **11** (25.1 mg, 68%) as a violet solid: mp 173 °C; R_f 0.25 (CH_2Cl_2/hexane = 1/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.50 (d, J = 15.2 Hz, 1H), 7.24 (d, J = 8.8 Hz, 2H), 7.61 (d, J = 8.8 Hz, 2H), 7.71 (m, 9H), 7.99 (m, 6H), 8.66 (d, J = 5.2 Hz, 2H), 8.70 (d, J = 5.2 Hz, 2H), 8.87 (d, J = 5.2 Hz, 2H), 9.44 (d, J = 5.2 Hz, 2H), 10.08 (d, J = 15.2 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 108.3, 118.5, 119.3, 120.4, 123.1, 123.6, 125.1, 126.5, 126.6, 127.5, 127.6, 129.2, 130.8, 132.0, 132.1, 132.5, 132.6, 133.05, 133.1, 133.5, 139.7, 141.1, 141.8, 142.5, 145.7, 149.5, 163.9; UV−vis (CH_2Cl_2) λ_{max} (log ε) 430 (5.3), 547 (4.3), 592 (4.3) nm; TOF MS LD+ ($C_{47}H_{29}BrN_4NiO_2$) calcd for [M] 818.0827, found 818.0826.

(2*E*,2′*E*)-3,3′-[(5,15-Diphenylporphyrinato-10,20-diyl)nickel(II)]-bis(1-(piperidin-1-yl)prop-2-en-1-one) 12. To a solution of acid **6** (30 mg, 0.045 mmol) in anhydrous THF (5 mL) were added $SOCl_2$ (0.013 mL, 0.18 mmol) in 1 mL of THF and DMF (2−3 drops) under argon, and the mixture was stirred for 2 h. The volatiles were removed under reduced pressure, and the remaining purple-greenish acyl chloride **8** was dissolved in anhydrous THF (5 mL). NEt_3 (0.013 mL, 0.09 mmol) in THF (1 mL) was added, and stirring was continued for 15 min. Piperidine (0.09−0.225 mmol) dissolved in THF (1 mL) was added, and the reaction was stirred for 30 min (TLC control) at rt under argon. The mixture was filtered through a plug of silica and washed with ethyl acetate, followed by removal of the solvents in vacuo. The residue was purified by flash chromatography on silica with ethyl acetate/hexane = 1:2 to give **12** (16 mg, 44%) as a green-purple solid: mp 282 °C; R_f 0.15 (ethyl acetate/hexane = 1/2, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.67 (m, 12H), 3.54 (m, 4H), 3.82 (m, 4H), 6.67 (d, J = 15.2 Hz, 2H), 7.70 (m, 6H), 7.96 (m, 4H), 8.74 (d, J = 4.7 Hz, 4H), 9.32 (d, J = 4.7 Hz, 4H), 9.80 (d, J = 15.2 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 24.2, 25.2, 26.3, 43.1, 46.6, 112.1, 119.0, 126.7, 127.6, 131.5, 132.7, 132.9, 133.0, 139.5, 140.6, 141.1, 164.0; UV−vis (CH_2Cl_2) λ_{max} (log ε) 436 (5.5), 557 (4.6), 604 (4.6) nm; TOF MS LD+ ($C_{48}H_{42}N_6NiO_2$) calcd for [M] 792.2723, found 792.2720.

(*E*)-4-[5,15-Bis(3-methoxyphenyl)porphyrin-10-yl]phenyl 3-[(5,10,15-Triphenylporphyrinato-20-yl)nickel(II)]acrylate 14. To a solution of acyl chloride **7** generated from **5** (30 mg, 0.045 mmol) in anhydrous CH_2Cl_2 (5 mL) were added 5-(4-hydroxyphenyl)-10,20-bis(3-methoxyphenyl)porphyrin **13** (26.3 mg, 0.43 mmol) in CH_2Cl_2 (1 mL) and NEt_3 (0.013 mL, 0.09 mmol) in CH_2Cl_2 (0.5 mL). The reaction was stirred for 24 h (TLC control) at 35 °C under argon, and the resulting mixture was worked up as described above. Purification by flash chromatography on silica (ethyl acetate/hexane, 1:2 v/v) afforded **14** (27.6 mg, 51%) as a purple solid: mp 247 °C; R_f 0.8 (ethyl acetate/hexane, 1:2 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ −2.97 (s, 2H), 4.05 (s, 6H), 6.73 (d, J = 15.8 Hz, 1H), 7.40 (m, 2H), 7.74 (m, 13H), 7.89 (m, 4H), 8.04 (m, 6H), 8.35 (m, 2H), 8.72 (dd, J = 4.7, 4.7 Hz, 4H), 8.94 (d, J = 4.7 Hz, 2H), 9.02 (dd, J = 4.7, 4.7 Hz, 4H), 9.12 (d, J = 4.7 Hz, 2H), 9.37 (d, J = 4.7 Hz, 2H), 9.58 (d, J = 4.7 Hz, 2H), 10.28 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 55.1, 104.5, 108.3, 113.1, 119.0, 119.3, 119.5, 120.2, 120.3, 126.6, 126.7, 127.3, 127.4, 127.5, 127.6, 129.8, 130.5, 131.0, 131.1 (br), 132.0, 132.5, 133.1, 133.2, 133.5, 134.9, 139.7, 139.8, 141.2, 141.8, 142.5, 142.6, 145.6, 146.2 (br), 150.4, 157.6, 164.4; UV−vis (CH_2Cl_2) λ_{max} (log ε) 413 (5.5), 432 (5.2), 508 (4.4), 543 (4.3), 585 (4.3), 635 (4.0) nm; TOF MS LD+ ($C_{81}H_{54}N_8NiO_4$) calcd for [M + H] 1261.3700, found 1261.366.

Reaction of 7 with Ethyl Diazoacetate. Synthesis of 15−17. Ethyl 2-(Triphenylphosphoranylidene)-5-[(5,10,15-triphenylporphyrinato-20-yl)nickel(II)]azino-3-oxopent-4-enoate 15. Ethyl diazoacetate (20.6 mg, 0.18 mmol) in CH_2Cl_2 (1 mL), PPh_3 (47.3 mg, 0.18 mmol), and NEt_3 (0.013 mL, 0.09 mmol) in CH_2Cl_2 (0.5 mL) were added to a solution of acyl chloride **7** generated from **5** (30 mg, 0.045 mmol) in anhydrous CH_2Cl_2 (5 mL). The reaction was stirred for 2 h (TLC control) at 35 °C under argon, and the resulting mixture was diluted with hexane and quickly filtered through a short column of silica. The volatiles were removed in vacuo, and the solid residue was washed with hexane (3 × 5 mL) and dried under vacuum to give **15** (32.2 mg, 70%) as a pale purple solid: R_f 0.4 (CH_2Cl_2/hexane, 1:1 v/v); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 1.45 (t, J = 7.0 Hz, 3H), 4.44 (q, J = 7.0 Hz, 2H), 6.84 (d, J = 15.4 Hz, 1H), 7.54 (m, 9H), 7.74 (m, 15H), 8.00 (m, 6H), 8.68 (dd, J = 5.0 Hz, 5.0 Hz, 4H), 8.83 (d, J = 5.0 Hz, 2H), 9.38 (d, J = 5.0, 2H), 9.80 (d, J = 15.4 Hz, 1H); ^{31}P NMR (162 MHz, CD_2Cl_2) 44.26; ^{13}C NMR (150.9 MHz, CD_2Cl_2) δ 14.2, 62.5, 110.2, 120.0, 120.8, 127.2, 127.3, 128.2, 128.7, 128.8, 131.2, 131.8, 131.9, 132.4, 132.5 (m), 132.9, 133.1, 133.6, 133.7, 133.8, 133.9, 136.0, 140.4, 140.5, 141.6, 141.7, 141.9, 142.6, 143.2, 145.8, 148.6, 162.6; TOF MS LD+ ($C_{63}H_{45}N_6NiO_3P$) calcd for [M + 2H − O] 1008.2852, found 1008.2845; calcd for [M − H_2O − PPh_3] 745.1862, found 745.1868.

Ethyl 2-Diazenyl-5-[(5,10,15-triphenylporphyrinato-20-yl)nickel(II)]-3-hydroxypenta-2,4-dienoate 16. yield 12 mg (35%); R_f 0.6 (ethyl acetate/hexane, 2:1 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38 (t, J = 7.0 Hz, 3H), 4.32 (q, J = 7.0 Hz, 2H), 6.75 (br, 1H), 7.35 (d, J = 15.8 Hz, 1H), 7.71 (m, 9H), 7.99 (m, 6H), 8.67 (dd, J = 5.3 Hz, 5.0 Hz, 4H), 8.85 (d, J = 5.3 Hz, 2H), 9.44 (d, J = 5.3, 2H), 10.06 (d, J = 15.8 Hz, 1H), 12.46 (br, 1H); UV−vis (CH_2Cl_2) λ_{max}(A) 433 (1.0), 547 (0.1), 592 (0.09) nm; TOF MS LD+ ($C_{45}H_{32}N_6NiO_3$) calcd for [M + Na] 785.1787, found 785.1779.

(2*E*,4*E*)-Ethyl 3-Hydroxy-5-[(5,10,15-triphenylporphyrinato-20-yl)nickel(II)]penta-2,4-dienoate 17. Phosphazine **15** (32 mg, 0.31 mmol) was dissolved in dichloromethane and allowed to stand for 24 h. The solvent was removed under reduced pressure, and the residue was recrystallized from CH_2Cl_2−MeOH to give **17** (18 mg, 78%) as a violet solid: mp >300 °C; R_f 0.0 (ethyl acetate/hexane, 1:2 v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.46 (t, J = 7.0 Hz, 3H), 4.47 (q, J = 7.0 Hz, 2H), 6.84 (d, J = 15.2 Hz, 1H), 7.59 (s, 1H), 7.71 (m, 9H), 7.99 (m, 6H), 8.67 (dd, J = 4.7, 4.7 Hz, 4H), 8.85 (d, J = 5.2 Hz, 2H), 9.37 (d, J = 5.2, 2H), 9.79 (d, J = 15.2 Hz, 1H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 14.2, 62.2, 109.7, 119.7, 120.6, 126.9, 127.0, 127.9, 128.0, 131.1, 132.4, 132.8, 133.5, 133.6, 133.7, 135.7, 140.2, 141.4, 141.6, 142.3, 142.9, 145.6, 147.8, 162.5; UV−vis (CH_2Cl_2) λ_{max} (log ε) 435 (5.8), 547 (4.8), 597 (4.8) nm; TOF MS LD+ ($C_{45}H_{32}N_4NiO_3$) calcd for [M + 2H + 2Na] 782.1780, found 782.1621.

General Procedure: Synthesis of 20−22 via Cross-Metathesis. A mixture of allyl porphyrin (0.3 mmol), acrylate (1.5−3.0 mmol), and Grubbs II catalyst (25.5 mg, 0.03 mmol) in dry CH_2Cl_2 (25 mL) was stirred at 35 °C under argon for 12 h (TLC control). The solution was filtered through a plug of silica and washed with CH_2Cl_2. The solvent was removed under reduced pressure followed by recrystallization of the solid residue from CH_2Cl_2−MeOH to give **20**−**22** (78−90%).

(*E*)-Methyl 4-[(5,10,15-Triphenylporphyrinato-20-yl)nickel(II)]-but-2-enoate 20. Porphyrin **18** (174 mg, 0.3 mmol), methyl acrylate (129 mg, 1.5 mmol), and Grubbs II catalyst (25.5 mg, 0.03 mmol) gave **20** (153 mg, 80%) a violet solid: mp >300 °C; R_f 0.45 (ethyl acetate/hexane, 1:5 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ −2.74 (s, 2H), 3.55 (s, 3H), 5.72 (d, J = 15.8 Hz, 1H), 5.87 (d, J = 5.9 Hz, 2H), 7.76 (m, 9H), 7.94 (m, 1H), 7.99 (m, 6H), 8.81 (br, 4H), 8.91 (d, J = 4.8 Hz, 2H), 9.34 (d, J = 4.8 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 37.4, 51.4, 113.2, 120.0, 120.3, 123.0, 126.6, 127.8,

134.5, 142.0, 142.6, 150.7, 166.9; UV−vis (CH_2Cl_2) λ_{max} (log ε) 419 (4.3), 517 (3.1), 553 (2.8), 657 (2.8) nm; HRMS (ES+) [$C_{43}H_{32}N_4O_2$] calcd for [M + H] 637.2604, found 637.2596.

(*E*)-*tert*-Butyl 4-(5,10,15-Triphenylporphyrin-20-yl)but-2-enoate 21. Porphyrin **18** (174 mg, 0.3 mmol), *tert*-butyl acrylate (192 mg, 1.5 mmol), and Grubbs II catalyst (25.5 mg, 0.03 mmol) gave **21** (159 mg, 78%) as a violet solid: mp >300 °C; R_f 0.4 (ethyl acetate/hexane=1/5, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ −2.70, 1.34 (s, 9H), 5.66 (d, J = 15.8 Hz, 1H), 5.91 (d, J = 5.8 Hz, 2H), 7.80 (m, 9H), 7.90 (dt, J = 15.8, 5.8 Hz, 1H), 8.25 (m, 6H), 8.86 (br, 4H), 8.97 (d, J = 4.7 Hz, 2H), 9.42 (d, J = 4.7 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 27.5, 36.8, 79.8, 113.2, 119.5, 119.8, 124.8, 126.2, 126.3, 127.3, 127.6 (br), 130.6 (br), 134.1, 141.5, 141.7, 148.8, 165.5; UV−vis (CH_2Cl_2) λ_{max} (log ε) 418 (4.0), 444 (3.6), 516 (2.6), 550 (2.3), 594 (2.3), 654 (2.7) nm; HRMS (ES+) [$C_{46}H_{38}N_4O_2$] calcd for [M + H] 679.3073, found 679.3085.

(2*E*,2′*E*)-Dimethyl 4,4′-[5,15-Triphenylporphyrin-10,20-diyl]dibut-2-enoate 22. Porphyrin **19** (171 mg, 0.3 mmol), methyl acrylate (258 mg, 3.0 mmol), and Grubbs II catalyst (25.5 mg, 0.03 mmol) gave **22** (186 mg, 90%) as a violet solid: mp >300 °C; R_f 0.4 (ethyl acetate/hexane, 1:2 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ −2.68 (s, 2H), 2.75 (s, 6H), 3.56 (s, 6H), 5.74 (d, J = 15.8 Hz, 2H), 5.91 (d, J = 5.3 Hz, 4H), 7.59 (m, 4H), 7.96 (dt, J = 15.8, 5.3 Hz, 1H), 8.09 (m, 4H), 8.93 (d, J = 4.7 Hz, 4H), 9.35 (d, J = 4.7 Hz, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 22.3, 36.8, 51.0, 112.7, 119.5, 122.5, 127.0, 134.0, 137.0, 138.7, 150.3, 166.5; UV−vis (CH_2Cl_2) λ_{max} (log ε) 516 (4.1), 552 (4.0), 592 (3.0) nm; HRMS (ES+) [$C_{44}H_{38}N_4O_4$] calcd for [M + H] 687.2971, found 687.2972.

(*E*)-Methyl 4-[(5,10,15-Triphenylporphyrinato-20-yl)nickel]but-2-enoate 23. A mixture of porphyrin **20** (191 mg, 0.3 mmol) and Ni(II)(acac)$_2$ (308 mg, 1.2 mmol) in toluene (100 mL) was stirred at 110 °C for 2 h (TLC control). The reaction mixture was filtered through a plug of silica and washed with CH_2Cl_2. The solvents were removed under reduced pressure, and the residue was recrystallized from CH_2Cl_2−MeOH to give **23** (204 mg, 98%) as a purple solid: mp >300 °C; R_f 0.33 (ethyl acetate/hexane, 1:5 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.60 (s, 3H), 5.36 (d, J = 4.4 Hz, 2H), 5.81 (d, J = 15.6 Hz, 1H), 7.67 (m, 9H), 7.82 (m, 1H), 7.98 (m, 6H), 8.71 (br, 4H), 8.77 (d, J = 4.8 Hz, 2H), 9.13 (d, J = 4.4 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 36.5, 51.5, 111.9, 118.8, 122.8, 126.9, 127.8, 129.2, 132.4, 133.1, 133.7, 140.7, 142.2, 142.3, 142.5, 142.7, 150.3, 166.9; UV−vis (CH_2Cl_2) λ_{max} (lg ε) 416 (4.3), 530 (3.0) nm; TOF MS LD+ [$C_{43}H_{30}N_4O_2Ni$] calcd for [M + Na] 715.1620, found 715.1596.

(*E*)-*tert*-Butyl 4-[(5,10,15-Triphenylporphyrinato-20-yl)nickel-(II)]but-2-enoate 24. Compound **24** was prepared from **21** (203 mg, 0.3 mmol) using the same procedure as for the synthesis of **23**. Recrystallization from CH_2Cl_2−MeOH gave **24** (210 mg, 95%) as a purple solid: mp >300 °C; R_f 0.75 (ethyl acetate/hexane, 1:5 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 (s, 9H), 5.26 (d, J = 4.9 Hz, 2H), 5.73 (d, J = 15.6 Hz, 1H), 7.70 (m, 10H), 8.03 (m, 6H), 8.78 (br, 4H), 8.81 (d, J = 4.9 Hz, 2H), 9.13 (d, J = 4.9 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 28.1, 36.3, 80.4, 112.3, 118.8, 119.0, 124.9, 127.0, 127.9, 129.4, 132.4, 133.1, 133.8, 140.8, 142.2, 142.4, 142.5, 142.8, 148.8, 166.0; UV−vis (CH_2Cl_2) λ_{max} (log ε) 416 (4.4), 530 (3.2) nm; TOF MS LD+ [$C_{46}H_{36}N_4O_2Ni$] calcd for [M] 734.2219, found 734.2192.

(*E*)-5-Acroleinyl-10,15,20-triphenylporphyrin 25. Grubbs II catalyst (8.5 mg, 0.01 mmol) and acrylic acid (0.03 mL, 0.43 mmol) were added to a solution of porphyrin **18** (51 mg, 0.09 mmol) in dry CH_2Cl_2 (20 mL). The mixture was stirred for 18 h and then filtered through a plug of silica eluting with CH_2Cl_2. Purification by column chromatography (hexane/CH_2Cl_2, 2:1 v/v) gave **25** (12 mg, 0.02 mmol, 23%) as a purple solid: mp >300 °C; R_f 0.48 (ethyl acetate/hexane, 1:3 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ −2.40 (s, 2H), 7.16 (d, J = 7.8 Hz, 15.6 Hz, 1H), 7.76 (m, 9H), 8.17 (m, 6H), 8.77 (dd, J = 4.8, 4.8 Hz, 4H), 8.91 (d, J = 4.8 Hz, 2H), 9.39 (d, J = 4.8 Hz, 2H), 10.02 (d, J = 15.6 Hz, 1H), 10.23 (d, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.7, 32.0, 110.8, 121.7, 122.7, 126.8, 128.0, 134.4, 141.2, 141.8, 154.0, 192.4; UV−vis (CH_2Cl_2) λ_{max} (log ε) 429 (4.3), 523 (2.9), 570 (3.0), 660 (2.7), 666 (2.6) nm; HRMS (ES+) [$C_{41}H_{28}N_4O$] calcd for [M + H] 593.2341, found 593.2357.

(*E*)-4-[(5,10,15-Triphenylporphyrinato-20-yl)nickel(II)]but-2-enoic Acid 26. A solution of porphyrin **24** (100 mg, 0.136 mmol) and TFA (0.85 mL) in CH_2Cl_2 (20 mL) was stirred at 35 °C for 12 h (TLC control). The solvents were removed under reduced pressure, and the solid residue was dried in vacuo to give **26** (88 mg, 95%) as red solid: mp >300 °C; R_f 0.1 (CH_2Cl_2/hexane, 2:1 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40 (d, J = 4.8 Hz, 2H), 5.80 (d, J = 15.6 Hz, 1H), 7.66 (m, 9H), 7.95 (m, 7H), 8.69 (br, 4H), 8.77 (d, J = 5.0 Hz, 2H), 9.10 (d, J = 5.0 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 25.1, 31.0, 36.6, 111.9, 118.9, 119.2, 126.9, 127.8, 129.0, 132.4, 132.4, 133.2, 133.8, 140.7, 142.2, 142.5, 142.8, 154.0; UV−vis (CH_2Cl_2) λ_{max} (lg ε) 415 (5.3), 529 (4.2) nm; TOF MS LD+ ($C_{42}H_{28}N_4NiO_2$) calcd for [M] 678.1566, found 678.1564.

(*E*)-Propargyl 4-[(5,10,15-Triphenylporphyrinato-20-yl)nickel-(II)]but-2-enoate 27. DMAP (15 mg, 0.124 mmol) in CH_2Cl_2 (1 mL) was added to a solution of the acyl chloride generated from **26** (42 mg, 0.062 mmol) in anhydrous CH_2Cl_2 (5 mL). The reaction mixture was stirred for 10 min, and propargyl alcohol (0.036 mL, 0.62 mmol) in CH_2Cl_2 (0.5 mL) was added. Stirring was continued for 1 h (TLC control) at 35 °C under argon. The resulting mixture was filtered through a plug of silica and washed with CH_2Cl_2. Purification using silica TLC plates (CH_2Cl_2/hexane, 1:2 v/v) afforded **27** (25 mg, 57%) as a purple solid: mp >300 °C; R_f 0.4 (CH_2Cl_2/hexane, 1:1 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (t, J = 2.3 Hz, 1H), 4.61 (d, J = 2.3 Hz, 2H), 5.48 (d, J = 5.8 Hz, 2H), 5.83 (d, J = 15.6 Hz, 1H), 7.68 (m, 9H), 7.92 (dt, J = 5.8 Hz, 15.6 Hz, 1H), 7.98 (m, 6H), 8.70 (s, 4H), 8.79 (d, J = 5.0 Hz, 2H), 9.18 (d, J = 5.0 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 36.6, 51.9, 74.8, 111.5, 118.8, 119.1, 122.3, 126.9, 127.78, 127.8, 129.2, 132.4, 133.2, 133.7, 140.7, 142.2, 142.3, 142.5, 142.7, 151.6, 165.6; UV−vis (CH_2Cl_2) λ_{max} (log ε) 415 (4.7), 530 (3.7) nm; TOF MS ($C_{45}H_{30}N_4NiO_2$) calcd for [M − H] 717.1598, found 717.1612.

(*E*)-Propargyl 4-[(5,10,15-Triphenylporphyrinato-20-yl)nickel-(II)]but-3-enoate 28E. *N*-Ethyl-*N*′-(3-dimethylaminopropyl)carbodiimide hydrochloride (23.7 mg, 0.124 mmol) and propargyl alcohol (0.036 mL, 0.62 mmol) were added to a solution of **26** (42 mg, 0.062 mmol) in anhydrous CH_2Cl_2 (5 mL) and DMAP (15 mg, 0.124 mmol). The reaction mixture was stirred for 12 h (TLC control) at rt. The resulting mixture was filtered through a plug of silica and washed with CH_2Cl_2. Purification by column chromatography (CH_2Cl_2/hexane, 1:2 v/v) afforded **28-E/Z** (ratio *E*/*Z* = 3:1, 36 mg, 81%) as a purple solid. Additional purification on silica TLC plates (ethyl acetate/hexane = 1/10) gave **28E** (26.2 mg, 59%): mp >300 °C; R_f 0.45 (CH_2Cl_2/hexane, 1:1 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.57 (t, J = 2.0 Hz, 1H), 3.79 (d, J = 7.8 Hz, 2H), 4.88 (d, J = 2.0 Hz, 2H), 6.17 (dt, J = 7.8 Hz, 15.2 Hz, 1H), 7.71 (m, 9H), 8.00 (m, 6H), 8.71 (dd, J = 4.9 Hz, 4.9 Hz, 4H), 8.76 (d, J = 15.2 Hz, 1H), 8.82 (d, J = 4.9 Hz, 2H), 9.38 (d, J = 4.9 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 38.7, 52.1, 74.8, 113.4, 118.3, 118.5, 126.5, 127.3, 131.1, 131.76, 131.8, 132.2, 133.17, 133.2, 135.0, 140.2, 141.0, 141.4, 141.86, 141.9, 170.3; UV−vis (CH_2Cl_2) λ_{max} (log ε) 419 (5.2), 534 (4.1) nm; TOF MS LD+ ($C_{45}H_{30}N_4NiO_2$) calcd for [M] 716.1722, found 716.1746.

2-Methylene-5-[(5,10,15-triphenylporphyrin-20-yl)pent-3-enyl 3-[(5,10,15-Triphenylporphyrinato-20-yl)nickel(II)]acrylate 30. The allyl porphyrin **18** (8.2 mg, 0.014 mmol) in dry CH_2Cl_2 (10 mL) was added dropwise under argon to a solution of porphyrin propargyl ester **10** (10 mg, 0.014 mmol) and Grubbs I catalyst (2.34 mg, 0.003 mmol) in dry CH_2Cl_2 (10 mL). The reaction mixture was stirred for 18 h at 35 °C and then filtered through a plug of silica and washed with CH_2Cl_2. The volatiles were removed in vacuo, and the remaining solid was purified by flash chromatography on silica (hexane/CH_2Cl_2, 1:1 v/v) to yield **30** (13.9 mg, 76%, *E*/*Z* 3:2) as a purple solid: mp >300 °C; R_f 0.3 (ethyl acetate/hexane, 1:5 v/v); UV−vis (CH_2Cl_2) λ_{max} (log ε) 420 (4.0), 519 (3.0), 550

(3.0), 596 (3.0), 656 (3.2) nm; TOF MS LD+ ($C_{85}H_{58}N_8O_2Ni$) calcd for [M] 1280.4036, found 1280.4056; NMR key data (**30*E***) ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.01 (m, 3H, CH_2OCO, *C*═CH*H*), 5.24 (s, 1H, *C*═CH*H*), 5.93 (d, J = 5.6 Hz, 2H, CH_2CH═), 6.29 (d, J = 15.8 Hz, 1H, C*H*═CHCH$_2$) 6.30 (d, J = 15.4 Hz, 1H, CH═C*H*CO), 6.95 (dt, J = 5.6 Hz, 15.8 Hz, 1H, CH═C*H*CH$_2$), 9.83 (d, J = 15.4 Hz, 1H, C*H*═CHCO); ^{13}C NMR (150 MHz, $CDCl_3$) δ 38.0 (*C*H$_2$CH═), 64.2 (*C*H$_2$OCO), 116.8 (*C*═*C*H$_2$), 130.9 (CH═*C*HCO), 134.2 (CH═*C*HCH$_2$), 133.9 (*C*H═CHCH$_2$), 144.2 (*C*H═CHCO), 165.3 (*C*O$_2$); (**30*Z***) ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.30 (s, 2H, CH_2OCO), 5.97 (s, 1H, *C*═CH*H*), 6.04 (s, 1H, *C*═CH*H*), 6.16 (m, 3H, CH_2CH═, C*H*═CHCH$_2$), 6.48 (d, J = 15.4 Hz, 1H, CH═C*H*CO), 6.83 (dt, J = 6.8 Hz, 11.3 Hz, 1H, CH═C*H*CH$_2$), 10.03 (d, J = 15.4 Hz, 1H, C*H*═CHCO); ^{13}C NMR (150 MHz, $CDCl_3$) δ 35.1 (*C*H$_2$CH═), 68.0 (*C*H$_2$OCO), 118.2 (*C*═*C*H$_2$), 124.2 (*C*H═CHCH$_2$), 130.9 (CH═*C*HCO), 137.5 (CH═*C*HCH$_2$), 144.5 (*C*H═CHCO), 165.6 (*C*O$_2$).

2-Methylene-5-[(5,10,15-triphenylporphyrinato-20-yl)nickel(II)]-pent-3-enyl 3-[(5,10,15-Triphenylporphyrinato-20-yl)nickel(II)]-acrylate 31. The synthesis of **31** was carried out as described above for **30** using the porphyrin propargyl ester **10** (10 mg, 0.014 mmol), Grubbs I catalyst (2.34 mg, 0.003 mmol), and allyl porphyrin **29** (9.0 mg, 0.014 mmol). The mixture of **31** (7.8 mg, 41%, *E*/*Z* 2:1) was obtained as as a purple solid: mp >300 °C; R_f 0.49 (ethyl acetate/hexane, 1:5 v/v); UV−vis (CH_2Cl_2) λ_{max} (log ε) 418 (4.0), 533 (2.9) 590 (2.0) nm; TOF MS LD+ ($C_{85}H_{56}N_8O_2Ni_2$) calcd for [M + H] 1337.3311, found 1337.3322; NMR key data (**31*E***) ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.02 (s, 2H, CH_2OCO), 5.16 (s, 1H, *C*═CH*H*), 5.31 (s, 1H, *C*═CH*H*), 5.46 (d, J = 5.6 Hz, 2H, CH_2CH═), 6.29 (d, J = 15.8 Hz, 1H, CH═C*H*CO), 6.43 (d, J = 16.2 Hz, 1H, C*H*═CHCH$_2$), 6.84 (dt, J = 5.6 Hz, 16.2 Hz, 1H, CH═C*H*CH$_2$), 9.82 (d, J = 15.8 Hz, 1H, C*H*═CHCO); ^{13}C NMR (150 MHz, $CDCl_3$) δ 36.8 (*C*H$_2$CH═), 64.0 (*C*H$_2$OCO), 117.0 (*C*═*C*H$_2$), 130.4 (*C*H═CHCH$_2$), 130.9 (CH═*C*HCO), 133.7 (CH═*C*HCH$_2$), 144.0 (*C*H═CHCO), 165.3 (*C*O$_2$); (**31*Z***) ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.24 (s, 2H, CH_2OCO), 5.68 (d, J = 6.4 Hz, 2H, CH_2CH═), 5.83 (s, 1H, *C*═CH*H*), 5.94 (s, 1H, *C*═CH*H*), 6.18 (d, J = 11.7 Hz, 1H, C*H*═CHCH$_2$), 6.44 (d, J = 15.4 Hz, 1H, CH═C*H*CO), 6.77 (dt, J = 6.4 Hz, 11.7 Hz, 1H, CH═C*H*CH$_2$), 10.01 (d, J = 15.4 Hz, 1H, C*H*═CHCO); ^{13}C NMR (150 MHz, $CDCl_3$) δ 33.7 (*C*H$_2$CH═), 67.4 (*C*H$_2$OCO), 118.0 (*C*═*C*H$_2$), 124.7 (*C*H═CHCH$_2$), 130.8 (CH═*C*HCO), 136.9 (CH═*C*HCH$_2$), 144.4 (*C*H═CHCO), 165.4 (*C*O$_2$).

Synthesis of 30 and 32 Using Grubbs II Catalyst. The allyl porphyrin **18** (8.2 mg, 0.014 mmol in 10 mL dry CH_2Cl_2) was added dropwise under argon to a solution of the porphyrin propargyl ester **10** (10 mg, 0.014 mmol) and Grubbs II catalyst (2.41 mg, 0.003 mmol) in dry CH_2Cl_2 (10 mL). The reaction mixture was stirred for 18 h at 35 °C and then filtered through a plug of silica. Flash column chromatography on silica (hexane/CH_2Cl_2, 1:1 v/v) gave **30** (10 mg, 55%, *E*/*Z* 3:2) as the first fraction and **32** (18.2 mg, 31%) as the second fraction.

(*Z*)-1,4-Bis[5,10,15-triphenylporphyrin-20-yl]but-2-ene 32: yield 18.2 mg (31%); mp >300 °C; R_f 0.54 (ethyl acetate/hexane, 1:3 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ −2.73 (s, 4H), 5.70 (br, 4H), 6.67 (br, 2H), 7.75 (m, 20H), 8.19 (m, 12H), 8.81 (br, 12H), 9.40 (d, 4H, J = 5.2 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 29.27, 116.26, 119.18, 126.13, 126.26, 127.17, 128.36, 134.01, 134.07, 135.09, 141.80; UV−vis (CH_2Cl_2) λ_{max} (lg ε) 420 (4.2), 517 (3.0), 551 (2.6), 593 (2.5), 650 (2.5) nm; HRMS (ES+) [$C_{41}H_{28}N_4O$] calcd for [M + H] 1129.4710, found 1129.4679.

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Supporting Information Available: Characterization data including 1D and 2D NMR spectra of compounds **4**−**6**, **9**−**12**, **14**−**17**, **20**−**28**, and **30**−**32**. This material is available free of charge via the Internet at http://pubs.acs.org.

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